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Thermo-economic assessment of CO$_2$ separation technologies in the framework of synthetic natural gas (SNG) production

Master's Thesis

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ABSTRACT

Synthetic Natural Gas (SNG) is one of the alternative fuels that can be produced from biomass. Its potential advantages are the possibility of mixing with fossil Natural Gas in the existing distribution infrastructure, and a production process based on proven technologies. SNG production is a highly integrated energy conversion process. It is based on gasification of biomass and the SNG produced has to be upgraded to meet the quality standards of Natural Gas. The gas upgrading process leads to a considerable energy penalty for the system, mainly due to the high energy demand for the separation of carbon dioxide from the methane.

This thesis is part of a broader project that aims to identify synergies between sub-processes in SNG production, in order to achieve a fully optimized process and a realistic SNG production cost. The object of this thesis was to compare three different configurations for the gas upgrade section based on different CO_2 separation technologies. They were integrated within the framework of a SNG production where the syngas at the inlet of the gas upgrade section contained around 46 % of CH_4 and 46 % of CO_2. The technologies investigated are: Membrane separation, vacuum pressure swing adsorption (VPSA) and absorption with mono-ethanolamine (MEA). For each technology a model of the gas upgrade section has been developed, using process simulation software (Aspen Plus). In the SNG production process, captured CO_2 can be considered as a product, and in the future revenue resulting from CO_2 capture can be significant for the economic performance of the plant. The VPSA configuration was judged not to be relevant for CO_2 capture, given the major energy penalty associated with compression of the separated CO_2 stream. The results of the simulations were combined with data from an existing model of SNG production, and pinch analysis was used as a tool to estimate the potential electricity production resulting from harnessing heat flows within the plant.

The studied configurations were even compared for their upgrade performance, their energy consumption and their economic performance calculated as variations of the costs and the revenues of the plant. Four different possible future energy market scenarios were used. The configurations achieve a CH_4 recovery between 80% for MEA absorption and 91% for membrane separation, with a power consumption of 2,7 MW and 5,6 MW, respectively. The economic results show that the revenues from CO_2 recovery are extremely relevant for the revenues of the plant and, depending on the scenario they can vary from 1 M€/y to 15 M€/y. The membrane configuration results in the best difference between revenues and costs, but it involves the highest investment cost, while the MEA results in the possibility to produce SNG with a system independent from the electricity-market.

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Alberto Alamia

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1 Introduction

This thesis presents a thermo economical assessment of CO_2 separation processes in the production process of synthetic natural gas (SNG).

The proposed SNG production process is based on gasification technology and can be integrated with cogeneration of heat and power. The CO_2 separation section demands a large amount of energy and its performance is relevant on the efficiency of the whole production process. The main focus of this thesis is to evaluate more suitable solutions for CO_2 separation considering their process integration in the framework of SNG production in order to achieve a high energy efficiency and low cost.

1.1 Background

Increasing the supply of renewable energy is one of most important challengers for coming decades; particular to achieve a new direction in climate changing.

Biomass has a dominant position in this scenario being the largest global contributor of renewable energy, it represents the 10% of word primary energy mix (based on IEA, 2006; and IPCC, 2007), this is mostly traditional biomass used for cooking and heating; although maintaining a significant potential to expand power and heat production due to large volumes of unused residues and wastes.

Biomass energy currently represents one of the most suitable way to achieve a sustainable energy mix in developed countries as well as in those countries that wish to achieve economic growth through a sustainable development.

One of most interesting routes to convert biomass feedstock in a denser and more useful energy carrier is production of biofuels that currently are the main sustainable opportunity to replace fossil fuels in many applications. First generation biofuels (produced primarily from food crops) such as bioethanol or biodiesel, increased their market quickly but in last years they face both social and environmental barriers mainly because they use food crops which lead to food price increases and change land use. This limited capacity in oil-product substitution has increased interest in developing biofuels from non-food biomass (lingo-cellulosic materials such as forest residues, cereal straw and bagasse). These 2nd generation biofuels could maintain many advantages of first generation fuels and significantly decrease the potential pressure on land use and improve greenhouse emission reductions if compared with 1st generation biofuels.

Production of 2nd generation biofuels is based on existing technologies that have been in operation for a number of decades; basically the different processes involve gasification to create syngas and then numerous options for downstream fuel production, including methanol, Fischer-Tropsch diesel, hydrogen or SNG (synthetic natural gas).

Several studies have been conducted to compare the overall conversion efficiencies of different production processes. These studies indicate that SNG production based on indirect gasification achieves higher feedstock conversion efficiency to biofuels when the process is optimized for maximum fuel production; it is estimated between 60 % and 70 % (Martin Gassner, 2009). SNG presents also technical advantages because the resulting gas has a quality level that allows injecting it into the existing network and devices without adaptations, so it can be considered as a non-conventional source for natural gas.

1.2 Object of the thesis

SNG production implies a polygeneration system where SNG production is integrated with heat and power generation. This scheme represents an interesting option to make the system more flexible and is of particular interest for plants of small to medium size (up to 100 MW input). The optimum choice for process design depends on several factors such as fuel supply and energy policy.

The general layout of SNG production process consists of three major steps: gasification (endothermic), methanation (exothermic) and gas-upgrade where methane is separated from carbon dioxide and hydrogen to achieve the required specifications.

Figure 1.1 Main steps of SNG production process (Heyne, o.a., 2009)

This thesis is part of a broader project that aims to identify, through integration methods and tools, synergies between sub-process in SNG production in order to achieve a fully optimized process and a realistic SNG production cost.

The focus of this study is the gas-upgrade section where the gas mixture, with around 45% [vol] of CH_4 and 45% [vol] of CO_2, must be upgraded to achieve the specification for injection in the pipeline. The process mainly consists of separation of CO_2 from methane, so two final products are generated in the plant - the SNG and the captured carbon dioxide stream.

Included in the study are the treatments to upgrade the SNG to the grid specification (mainly compression and cooling) and the treatment of the captured carbon dioxide. Depending on the CO_2 capture technique they require different amounts of energy.

For a good comparison between the solutions proposed it is important to consider the captured carbon dioxide stream as a product as well as the SNG, because of costs associated with climate policy instruments that result in charges for releasing CO_2 emissions in the atmosphere. Avoided CO_2 emissions to the atmosphere are thus assumed to generate cash flows in future energy conversion plants. To manage the CO_2 produced we considered the possibility of using a pipeline for the transportation and the storage in a capture and storage system, as discussed in (Axelsson, et al., 2010).

All the different separation technologies investigated involve different energy consumption (heat/electricity) and different integration configurations with the rest of the SNG production process.

In order to evaluate the possibilities of heat integration between the different sections of the SNG production process, pinch analysis is used. Operating in this way, technologies for CO_2 separation are evaluated also for their influence on the Grand Composite Curve (GCC), as well as for resulting differences in electric power production potential of the plant based on the Carnot-based GCC curves.

The importance of the carbon dioxide stream depends on the economic scenario considered and the assumed charges on the CO_2 emissions.

To be able to perform a consistent analysis of plant operating costs and revenues in the medium and long term, we considered four different energy market scenarios including possible future combinations of SNG price, electricity prices and CO_2 emission charges (Axelsson, et al., 2010). Two such scenarios are considered for the medium term (year 2020), and two for the long term (year 2050).

1.3 Reference SNG production process

This thesis will cover a specific section of the SNG production process, to develop our study we selected as reference the framework of a high efficiency SNG process. The system studied is able to produce SNG and electricity to sell on the market and has a separated CO_2 stream as secondary product.

Figure (1.1) shows the basic steps of the production process. All operations will be described in further detail in following paragraphs.

1.3.1 Wood drying

A wood drying section is essential before the gasifier inlet, to remove the moisture content in the wood. This mainly because in the gasifier heat is consumed at high temperature, above the process pinch, for water desorption and evaporation. Hence to limit the heat consumption in this section is essential for good process energy efficiency.

For an integrated gasification combined cycle (IGCC) process it has been shown that reducing the water content of the feed stock from 40 % to 15 % results in a improvement in electrical efficiency of 2,5 % (Heyne Stefan, February 2009).

For these reasons a drying section before the gasification is necessary. The most common technologies are steam drying, hot air drying and flue gases drying.

1.3.2 Gasification (boiler)

Gasification is a thermal process where solid macromolecules are broken into mainly hydrogen, carbon monoxide, carbon dioxide, hydrocarbons, tars and ash. The aim of the process is to break down the chemical bonds in the fuel in order to produce an energy rich gas.

Gasification is an endothermic process which requires external heat and it is divided into two steps; pyrolysis, which is a low temperature process that operates without any oxidation and gasification that needs a gasification agent that contains oxygen such as steam or air (GmbH, 2005).

The choice of the gasifier and the gasification medium is critical for the efficiency of the whole process. Different types of gasifies have been developed but the optimum solution depends mainly on feedstock properties and the targeted application of the resulting product. The gasification medium can be air, steam or oxygen.

In order to satisfy the requirements for a final gas product with high heating value, we must use an adequate gasification technology which produces an nitrogen free syngas with high methane content.

For SNG production from woody biomass the most indicated gasification technology is the Fluidized Bed; an example of existing plant using this kind of gasifier is in Güssing (Austria). It is an 8 MW_{th} input demonstration plant that performs a first law global efficiency for the whole system of about 80% of the wood Lower Heating Value (LHV).

In this study the feedstock gasification is performed using a innovative indirectly heated biomass gasification unit that has been built recently at Chalmers University of Technology as an integrated extension of a standard circulating fluidized bed (CFB) boiler for heat and power production (Heyne, et al., 2007).

This reactor has several advantages:

- *The gasification medium can be varied between oxygen, steam flue gases and recirculated syngas*
- *The syngas produced has high purity (almost free of nitrogen)*
- *Possibility of cogeneration with production of heat and power*
- *Increasing in electricity production by combusting the non-reacted char from gasification in the boiler and extracting high temperature excess heat from the syngas to SNG conversion steps.*

Figure 1.1 shows a schematic flow sheet of a CFB boiler with an integrated gasification unit. The combustion fuel is fed to the riser part of the boiler and the heat transfer with the gasification side occurs by the hot bed material.

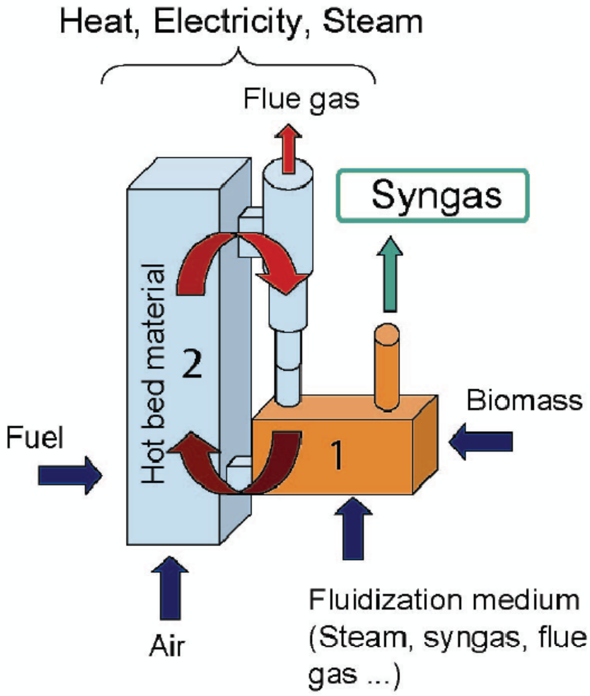
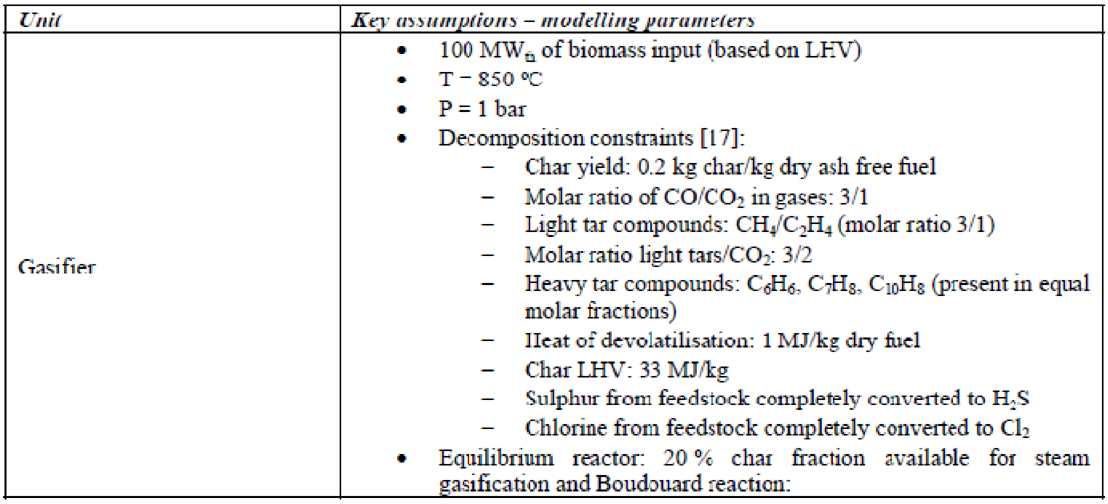


Figure 1.2 Schematic flow sheet of a biomass gasification unit integrated with a CFB Boiler (Heyne, et al., 2007)

Both sections are separated by a particle seal. Steam, air, oxygen, flue gases, or the syngas itself can be used as fluidization medium in the gasification reactor vessel. This unit works with an indirect gasification as well as the FICFB concept used in Güssing (Proll, 2007). But, instead of a single gasification reactor, a fluidized bed boiler is combined with a gasification reactor (Thunman H., 2007). The system has the advantage that if the gasification and syngas treatment line have to be stopped, it still is possible to run the power cycle by extracting all heat for the production of steam. The unit then operates as a standard CFB boiler.

In the reference process we used the following key assumptions.



Unit	*Key assumptions – modelling parameters*
Gasifier	• $100\ MW_{th}$ of biomass input (based on LHV) • $T - 850$ °C • $P = 1$ bar • Decomposition constraints [17]: – Char yield: 0.2 kg char/kg dry ash free fuel – Molar ratio of CO/CO_2 in gases: 3/1 – Light tar compounds: CH_4/C_2H_4 (molar ratio 3/1) – Molar ratio light tars/CO_2: 3/2 – Heavy tar compounds: C_6H_6, C_7H_8, $C_{10}H_8$ (present in equal molar fractions) – Heat of devolatilisation: 1 MJ/kg dry fuel – Char LHV: 33 MJ/kg – Sulphur from feedstock completely converted to H_2S – Chlorine from feedstock completely converted to Cl_2 • Equilibrium reactor: 20 % char fraction available for steam gasification and Boudouard reaction:

Figure 1.3 Key assumptions for the gasification unit in the reference process (Heyne, et al., 2007)

1.3.3 Gas cleaning

After the gasification the product gas contains contaminants as entrained ash and bed material, sulphur compounds (hydrogen sulphide, carbonyl sulphide), alkali compounds and tars or higher hydrocarbons. Those substances are always dangerous for pipes and plant equipment and they have to be removed, but in SNG production their removal is even more important. This because the methanation reaction uses catalyst that are highly sensitive to impurities in the gas, hence a gas cleaning section is essential.

Different techniques are used for gas cleaning, depending on the nature of the impurities.

For particulates the removal the system includes cyclones, filters and separators, it can also reduce the content of tar of the syngas. Cyclones are often used in series, where the first captures the largest particles and the following cyclones capture increasingly smaller particles. However, the cyclone cannot remove the finest particles, the limit depends on the design of the cyclone, but particles smaller than 5 μm cannot be captured by a cyclone.

Tar removal is one of the greatest technical challenges of gasification systems. The main reason for tar removal is that, when the temperature decreases in downstream processes, the tars condense and damage heat exchangers and other equipment.

Tar removal can be achieved with different techniques: by physical washing using organic solvents, wet electronic separators or catalytic reformers. The first option is not really feasible in this case because it requires syngas cooling that make heat recovery difficult in this step. Catalytic reforming is an option that allows keeping the carbon contained in the tars available for further conversion to fuel. Another technique to reduce the contents of tars in the syngas is to use a catalytic bed reactor during the gasification step. Pfeifer and Rauch (Pfeifer C., 2004) demonstrated that Oviline sand can reduce the tar content in syngas from steam gasification.

Sulphur compounds (mainly hydrogen sulphide), must to be removed from the syngas because they can be poisoning for the methanation catalyst. There are numerous processes for desulphurization, but there are two methods that are commonly used to remove sulphur from biosyngas. The first method uses regenerative sorbents (sulphur guards); they can be used to reduce the sulphur concentrations well below 1 ppm. A second option consists of washing techniques (such as chemical absorption) that can implemented making sulphur recover via Claus process. For example the Rectisol® process can separate hydrogen sulphide from the stream with concentrations high enough to allow the Claus process.

1.3.4 Methanation

In order to increase the methane content of the syngas from the gasification a methanation step is required. Methanation is a refining process where different components can convert to methane in the presence of a catalyst; the principal conversion is described by reaction (1)

$$CO + 3H_2 \leftrightharpoons CH_4 + H_2O \qquad (1)$$

There are two suitable options for the methanation process reactors: with fixed bed or with fluidized bed.

Fixed bed reactors achieve temperature control by recycling part of the product flow and usually operate in a temperature range between 250-500 °C. The temperature limitations are due to the risk of formation of carbon deposit on the catalyst surface at too low temperature and catalyst sintering at high temperature.

Alternatively, it is possible to use an internally cooled fluidized bed reactor that operates isothermally. A system with once-through methanation has been developed and successfully operated at pilot scale for gas produced by coal gasification (Martin Gassner, 2009).

Methane synthesis from a $H_2/CO/CO_2$ mixture is highly exothermic and reactor design is critical with regard to temperature control, and this reactor thus represents an important source of heat to consider when integrating the different sub-processes of SNG production.

1.3.5 Gas upgrade section

This section of the process needs to upgrade the syngas from the methanation to the quality specification required for the injection into the natural gas grid. This part of the production process is that investigated is this study and it includes the gas separation processes, pre-injection treatment of SNG (to obtain pressure and temperature required) and CO_2 removal.

The European Association for the Streamlining of Energy Exchange (EASEE-gas) recommends natural gas quality specifications including ranges for Wobbe index, relative density, water dew point and limits for sulphur compounds, oxygen and carbon dioxide concentrations.

To match all these specifications depending on the composition of the syngas from the methanation, different steps are required. The main step is the removal of carbon dioxide which represents a large fraction of the syngas coming from the methanation, but other treatments are also needed. The gas must be dried and traces of hydrogen must be removed if they exceed the concentration limit.

The framework of this section depends on the technology used for the CO_2 separation but all the solutions proposed perform the following steps

- *CO_2 separation*
- *Water separation*
- *H_2 separation*
- *SNG compression and cooling (to grid specification)*
- *Post-separation CO_2 treatment*

The main goal of this study is to identify an optimal solution for the gas upgrading section, that means mainly selection of the best solution for the carbon dioxide removal considering the effect on the whole plant. It is thus important to consider the power consumption not only for the separation process but also the consumption for the SNG compression and cooling to grid specifications and for the captured CO_2 treatment.

Carbon dioxide removal for gases containing CO_2 fractions above 40%, as in this case, is best achieved by chemical absorption, Pressure Swing Adsorption (PSA) and Membrane separation. Contrary to the chemical absorption process, the other two processes are almost neutral with regard to thermal energy, and require only mechanical power input.

Nowadays chemical absorption using amines is the most conventional and commercially best-proven option especially when CO_2 partial pressure is low, around 0,1 bar. It works by shifting chemical equilibrium with temperature rise or decrease, practically CO_2 binds to a chemical absorbent (amines) at lower temperature level and it is later released by increasing the temperature by hot steam.

The most common absorbents are primary amines applied in water solutions. In this study the selected unit operates with monoethanolamine (MEA). This technique has a heat consumption between 3.8 MJ/kg CO_2 (Suda et al. 1992) and 4.2 MJ/kg CO_2 (Ferla et al. 1995) by means of 2.3 bar/ 130-160 °C steam.

The cost of amine based capture systems are determined principally by the cost of installation and annual consumption of amines. It is however important to consider costs associated with effects on global plant balance such as cost of energy supplied for scrubbing which implies considerations about variations in the overall heat and power production; this influence will be common in all techniques.

The cost of removing CO_2 by heat regenerable solvents may be out of proportion if concentration of CO_2 is too high, in this context solutions that mainly uses power in place of heat are often more attractive.

Pressure Swing Adsorption process (PSA) is based on physical adsorption where CO_2 molecules are physically bound to a surface at high pressure, and released at low pressure. The system accomplishes a pressure swing cycle using two adsorption beds working alternately, one adsorbing while the other is being regenerated by purging. The high pressure level is typically between 1 bar and 6 bar and the lower between 200 millibars and 1 bar.

There are different PSA cycles available for CO_2 separation depending on the cycle steps and the material used to remove hydrogen excess. This system requires power for gas compression for each cycle that depends on pressure level, but is almost neutral in heat consumption.

Membrane separation has been proposed as a viable technology, since it is expected to be able to handle feed streams at high CO_2 concentrations and pressures. Typical pressure level for this technology is around 50 bar. This separation process is based on the difference in mobility of compounds through a surface; the driving force for component transport through the membrane is a difference in partial gas density of this component on the two sides of a membrane. Many kinds of membrane are available for CO_2 separation; both organic (such as cellulose acetate) or polymeric (such as polyamide) can be used to achieve high performance and limited cost; unfortunately a general trade-off exists between selectivity needed for a high purity product, and permeability desired to minimize membrane area and thus the capital cost.

2 Objectives

The overall objective of this thesis was to analyze different opportunities for carbon dioxide capture in the SNG production process. The selection of a specific technology for CO_2 removal results in a different upgrading performance and in different energy consumption. The integration of the section with the rest of the plant depends also on the technology used, while at the same time the heat consumption of the gas upgrade section modifies the overall process Grand Composite Curve (GCC), which in turn changes the opportunities for heat recovery within the process, and heat exchange with the heat and power steam cycle . In this study, it was assumed that heat released from the SNG plant is used to increase the power production in the steam CHP plant. The power produced by using the heat excess of the plant varies in the three cases and it was also analyzed.

Evaluating the opportunity for CO_2 separation was one of the main objectives of the study, it was realized where possible. Its influence will show up mainly in the economic evaluation.

2.1 Process flow-sheets definition

The first objective of the thesis has been to identify the framework of the whole gas upgrade section for each CO_2 separation technology. The focus of the study was the design of a flow-sheet with all the steps needed to upgrade the syngas to the SNG required specification. Since each separation technology is operating in a different way the resulting flow-sheets differ significantly considering the number of steps and processes involved. Once the SNG specifications were achieved we defined the treatments for the CO_2 rich stream resulting from the separation and the opportunity for storage.

The following Figure 2.1 shows the general flow-sheet of the gas upgrade section.

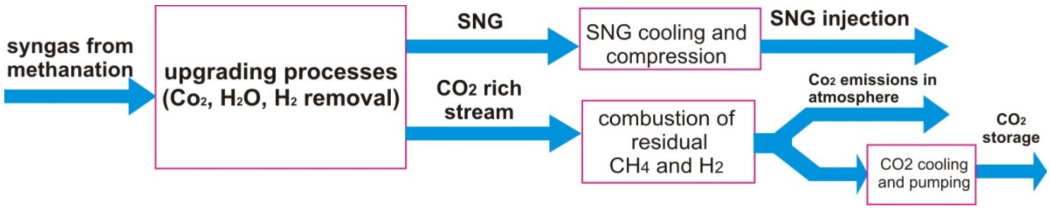


Figure 2.1 General flow-sheet of the gas upgrade section

2.2 Energetic evaluation

Since each solution needed different amounts of heat and/or power the second objective of the thesis was to evaluate the energy consumption of the section and the possibility of integration with the rest of the plant. Since the SNG production is a polygeneration process where SNG, electricity and CO_2 are produced (as main products) a different energy consumption of the gas upgrade section can result in a variation in the potential for electricity production. In order to evaluate the possibility of electricity production in the plant we used pinch analysis as a tool to calculate the potential power obtainable from the heat excess of the process. The Carnot GCCs (explained in a later section of this report) were calculated using the relevant streams of the whole plant and they were used as a basis for the electricity production calculation.

2.3 Economic evaluation

In order to facilitate the comparison between the different configurations studied, one of the objectives of the thesis was to evaluate the variation in costs and revenues of the SNG production process. They depend on the equipment needed in each configuration, on the power consumption and on the SNG and CO_2 produced. In this phase the importance of a CO_2 storage system will become evident. Of course an exact prediction of the future energy market is impossible to make, but with a set of energy market scenarios it should be possible to find a robust solution. Each solution has been evaluated against the background of four different scenarios, two on the short term (2020) and two on the long term (2050) with different CO_2 emission charges.

3 Methodology

The research focused on assessing CO_2 capture technologies, their performance and their energy consumption. A major share of work carried out involved the compilation of models for the carbon dioxide separation unit based on literature and industrial data. This was a critical issue to obtain reliable results from this study, to strengthen the validity of the results multiple data sources have been consulted when possible. During the definition of the models for the CO_2 separation unit and generally for the definition of the whole flow sheets of the gas upgrade section, several assumptions were made. They are discussed in more details in the following Chapters 4 and 5.

Figure 3.1 shows the working methodology used in this study. As it is shown the study has been divided into three main steps, a system definition of the gas upgrade section, an energetic analysis and an economic assessment.

Regarding the system definition it consists mainly in the design of different flow sheets of the gas upgrade section for each CO_2 removal process. This phase includes the creation of models for the CO_2 separation units and the definition of all the elements of the section necessary to achieve the SNG specification.

The flow-sheet of the gas upgrade section was simulated using Aspen® Plus software.

In this phase input data were considered for the composition, temperature and pressure of the syngas supply to the methanation section and the SNG specifications required, while literature data was used for each component of the section have been considered as technical assumptions.

In the Aspen flow-sheet all the components of the gas upgrade section were defined using data from literature, and the software provided the calculation of the whole section maintaining mass and energy balance. In order to achieve the SNG specification required, for composition and Wobbe index, it was necessary to optimize the value of some sensible parameters in the model of the CO_2 removal unit (particularly for the membrane units).

The result of the calculation with Aspen provided the energy consumption (power and heat) of the section, the mass flow and the composition of the SNG stream and the CO_2 rich stream.

In the second phase a pinch analysis of the whole SNG process was performed, data from all the other streams involved in the process were available from a previous study. For the streams of gas upgrade section results from the Aspen calculation were used. The main goal of this phase was to calculate the specific energy consumption for the SNG process and the potential for electrical power production using excess heat from the process.

In the economic section the goal was to estimate the economic performance of the different solutions for four different economic scenarios. To estimate the investment costs of the gas upgrade section literature data were used, as well as for the SNG and electricity prices and CO_2 emissions charge.

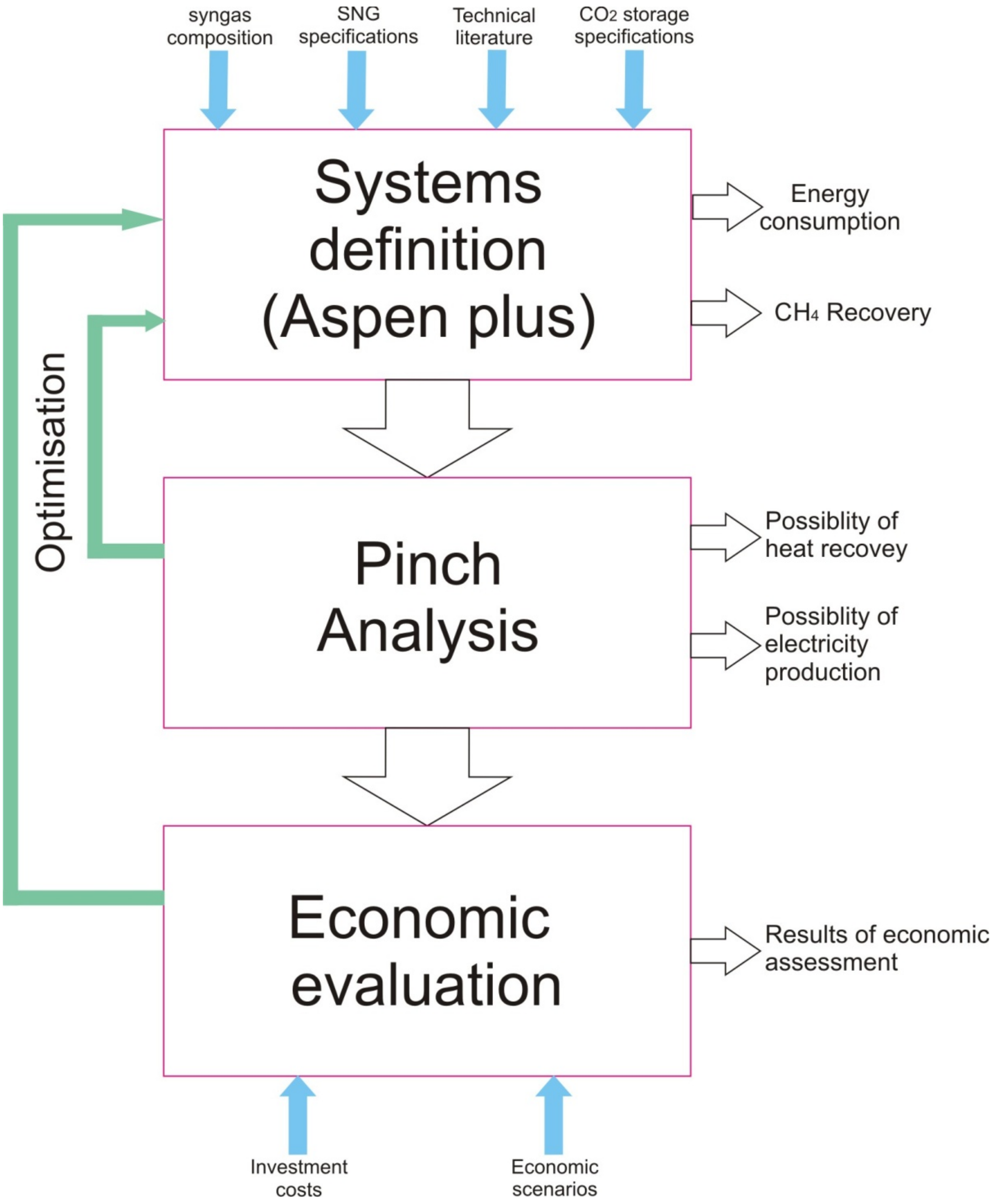


Figure 3.1 Overview for the flow-chart for the calculations

3.1 System definition

The SNG specification and the CO_2 storage specifications) are the process output conditions to be to satisfied, whereas the syngas composition from the gasifier unit is considered as an input.

To evaluate each process a number of performance indicators were identified.

3.1.1 Syngas composition

The syngas from the methanation has the composition shown in Table 3.1

Table 3.1 Syngas data at the inlet of the gas upgrade section

Total Flow [kg/h]	17095,9
Total Flow [kmol/h]	592,1
CH_4 [vol %]	46,1
CO_2 [vol %]	46,4
H_2O [vol %]	3,9
H_2 [vol %]	2,6
N_2 [vol %]	0,5
CO [vol %]	0,2
Pressure [bar]	0,9
Temperature [°C]	30

3.1.2 SNG grid specification

Currently there are no common specifications for the Natural Gas grid requirements in the European countries and each one has its own specifications. The only common gas quality specification set operating in Europe is provided by the Common Business Practice (CPB) that recommends specifications to streamline interoperability at cross border points in Europe and describes the recommended gas quality parameters, parameter ranges and the implementation plan. The European Association for the Streamlining of Energy Exchange (EASEE-gas) was created in the 2002 and its aim is to support the creation of an efficient European gas market through the promotion of common business practices (CBP’s). In order to achieve a common gas market in Europe the EASEE delivered some quality specification for the commerce of NG, this we used as reference for the study.

All the specification recommended from the EASEE are shown in appendix C.1, while the table 3.2 reports the most important limit values used in this study.

The calculation procedure for the Wobbe index is defined in the *ISO 6976:1995 Natural gas -- Calculation of calorific values, density, relative density and Wobbe index from composition.* Following the instruction of the EASEE (EASEE-gas, 2005) the Wobbe index (WI) was calculated with combustion reference temperature of 25 °C and a reference condition of 0°C and 1,01325 bar.

Table 3.2 EASEE gas quality specifications.

Parameter	Unit	Min	Max	Recommended implementation date
Wobbe index	kWh/m^3	13,60	15,81	1/10/2010
CO_2	mol%	-	2,5	1/10/2006
H_2O dew point	°C at 70 bar (a)	-	-8	1/10/2006

For injection into the high pressure gas grid other quality parameters must be satisfied, particularly the grid pressure and the temperature.

Table 3.3 SNG Pressure and temperature for grid injection

Pipeline pressure [bar]	60
Pipeline Temperature [°C]	20

3.1.3 CO_2 transportation and storage

There is increasing interest in implementing CO_2 capture in industrial processes. Widespread implementation of this technology requires development of a transportation and storage system for the carbon dioxide.

Nowadays CO_2 storage can be divided in three main groups: geological formations, mineralization and ocean storage. A brief introduction to them is provided below.

The storage in geological formations can be achieved in four ways. The first is pumping the CO_2 into depleted gas and oil fields. These fields have a proven storage potential. Another option is pumping the CO_2 into the oil field when they are still in operation, this practice can also enhance the oil recovery. Other possibilities are pumping the CO_2 inside geological formation filled with water or use it to recover methane that is bound in coal beds. The cost for the storage of CO_2 in this way is around 2-4 €/ton CO_2 on shore and 4-7 €/ton offshore (Elforsk, 2005).

Storage in minerals is now under research. It consists in using minerals as magnesium and calcium carbonates that react with the CO_2. However this method produces a quantity of carbonate that is four times as much as the amount of coal that is combusted. This solution is considered too costly.

Outside Europe, especially in Japan it is studied how to store the CO_2 in the oceans. This is possible because CO_2 has a higher density of water under 1500 m, and it will form a pool on the bottom of the ocean. This solution has been criticized a lot because of his high impact on the marine ecosystem (Elforsk, 2005).

The selection of a final storage is a critical issue. Elforsk (Elforsk, 2005) has performed a study to find a suitable storage alternative in Sweden and the findings from the Elforsk study were used as input data for this work. The selected site is an on-shore aquifer in southwest of Skåne in the south of Sweden. The storage cost is estimated at 3.3 €/ton CO_2.

The transportation of the CO_2 from the plant to the storage site is assumed to take place in a pipeline, which is the cheapest way for transporting of high quantities of CO_2. Hence it is assumed that the necessary infrastructure is ready to use. The cost of transportation is a function of the distance and it has been calculated with the following equation (Svensson R, 2008). Whereas the transportation cost is mainly due to the pressure losses in the pipeline, it will be updated with the electricity price, in the different scenarios.

$$0{,}1 + 0{,}008 \cdot distance = €/ton_{co2} \qquad (2)$$

For injection into the pipeline the CO_2 needs to be liquefied and compressed.

The quality of the CO_2 captured depends on the composition of the syngas and on the performance of the separation processes. Technically it is important to consider that the existing pipeline for CO_2 transportation are made of carbon steel. CO_2 must be injected without fractions of CH_4 or H_2S because they can format hydratate in presence of free water. Water should be removed to avoid problems with condensation (dew point limit).

Table 3.4 CO_2 pipeline injection specifications (Hektor, 2008)

Pipeline Pressure [bar]	120
Pipeline Temperature [°C]	30
CO_2 min fraction [% vol]	95

3.1.4 Performance indicators of the separation system

To compare the performance of the different CO_2 separation technologies we need some performance indicators besides the energy consumption.

Some of those parameters are defined from the SNG required specification (such as Wobbe Index (WI), content of CO_2 and water dew point). In the study has been considered also the CH_4 purity of the SNG and the CH_4 Recovery of the system.

The CH_4 purity is the mole fraction of the methane in the SNG. In order to reach the required WI must be at least 93%. The CH_4 recovery is defined as the percentage of the methane mole flow in the input syngas contained in the SNG produced. This indicator is influenced by the operating parameters of CO_2 separation units hence to optimize them we fixed a minimum value for the recovery of 60%.

The energy consumption for the upgrading of the SNG has been calculated as the power needed for the whole section including SNG compression and the CO_2 treatment divided for the incoming syngas mass flow. This is because the different CO_2 separation units work with different pressure levels, and we must consider if this final compression for the grid injection starts from a different pressure, because it will requires a different power.

3.2 Pinch analysis

The main goal of the pinch analysis was to estimate the possibility of integration and heat recovery of the gas upgrade section with the rest of the process.

Data about the relevant streams involved in the rest of the SNG production process were already available from a previous study. These data were combined with those of the gas upgrade section for each different case. The calculation made by Aspen flow sheet provided data about all the streams involved in the gas upgrade section included those for the cooling of compressors in each stage.

The pinch analyses of each system weren performed with Pro_Pi software (developed at Chalmers). For each case the Grand Composite Curve (GCC) of the system was calculated. The curves obtained for the Membrane and for the PSA case were relatively similar, while that for the MEA process was quite different. This is because the MEA technology requires mainly heat where as the other two are almost neutral in heat consumption.

Another objective of the Pinch analysis was to estimate the possibility of power production of the plant. The power is generated in a steam turbine and the steam is generated using the excess of heat from the process. In order to estimate it we used the Pro_Pi software to calculate the Carnot efficiency for each temperature level of the GCC, and by integration of the GCC values multiplied for the correspondent Carnot efficiency we calculate the Carnot based power generation potential (the theoretical maximum power obtainable form the process).

In order to estimate the real turbine power in the process we introduced the global Carnot efficiency defined as the ratio between the real produced power and the Carnot based power, which in case of a single heat source is defined as follow:

$$GCE = \frac{W_p}{Q_{in} \cdot \eta_{carnot}} \qquad (3)$$

Where GCE is the global Carnot efficiency, the W_p the power produced, Q_{in} the heat supplied to the system and η_{carnot} the Carnot efficiency.

A value of 0,73 was used in this study, based on detailed investigations conducted in previous studies.

Figures 3.2 and 3.3 show an example of GCC and Carnot GCC.

The PSA and the Membrane systems consume mainly electricity whereas the MEA technology consumes heat. The electricity is produced in a steam turbine using the steam generated with the heat excess of the system. Hence if we use more power for the gas upgrade section, it does not influence the electricity produced from the turbine but it results in a reduction of the electricity sold. While if we use more heat in the gas upgrade section it will result in a reduction of the steam generated and the power produced. In both the cases the revenues from the electricity are influenced by the energy consumption of the gas upgrade section.

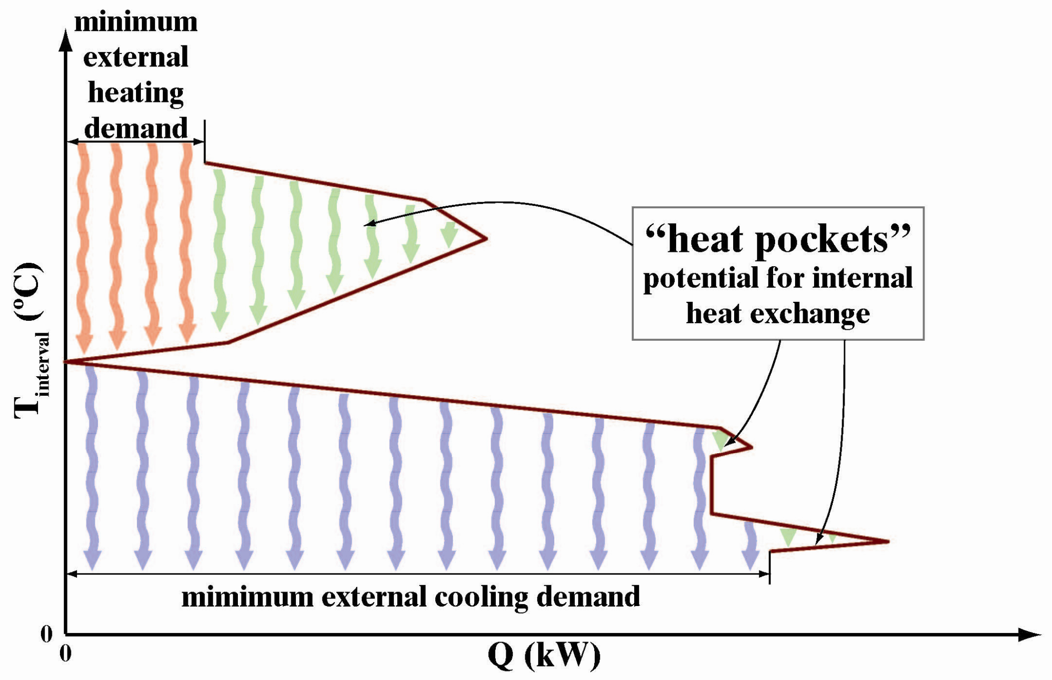


Figure 3.2 Example of GCC

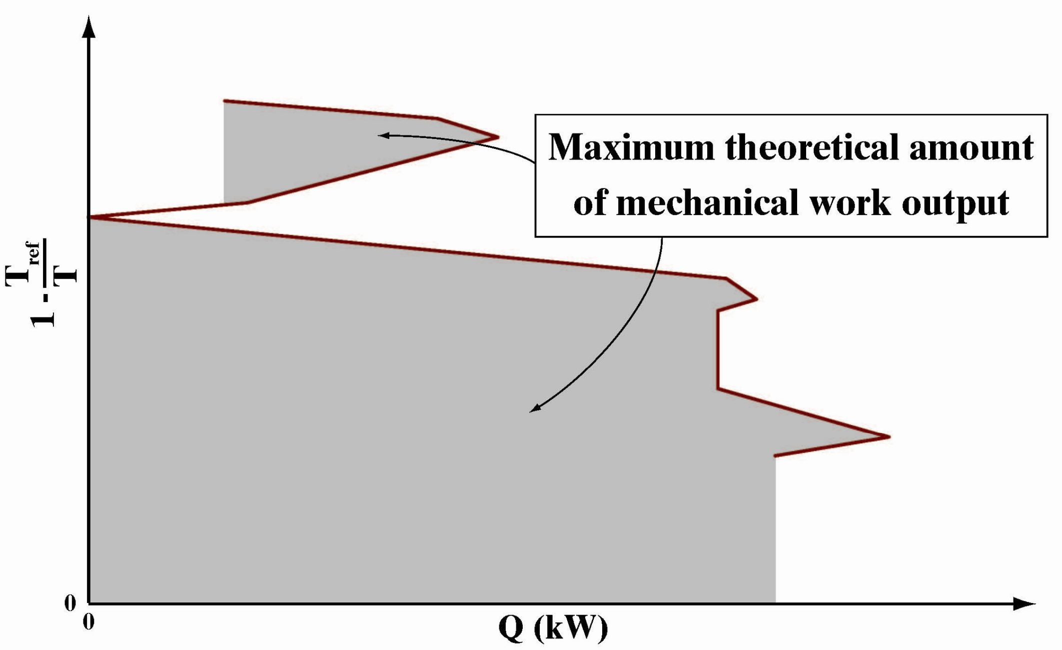


Figure 3.3 example of Carnot GCC

3.3 Economic assessment

In order to perform a comparison between the proposed solutions an economic assessment is necessary. It important to emphasize that this analysis is made to compare the different technologies, this means that some assumptions were made in the calculations.

The estimation of the capital investment was performed only for the gas upgrade section since the rest of the plant does not change in all the cases. Working capital as raw materials and supplies carried in stock or finished product stock were not considered, because they are supposed not to depend on the technology used in the gas upgrade section. Also manufacturing costs were excluded because they are supposed to be the same in each case.

Hence for the costs, the calculations were performed based on the fixed capital investment and energy consumption of the gas upgrade section.

The estimation of the capital investment was made at a study level, based on the knowledge of major items of equipment; it results in a probable accuracy of ± 30 %.

To evaluate the difference in the production of SNG, CO_2 and power the revenues for each product (SNG, CO_2 and electricity) were calculated, of course they concern the whole plant, hence all the difference between revenues and cost are valid only in this comparison but not for other considerations.

3.3.1 Estimation of capital investment

The estimation is based on knowledge of major items of equipment; the cost of these components was taken from different literature sources (presented in Chapter 7). Most cost data available for predesign estimate are valid only at the time they were published; because the price can change considerably with the time it is necessary to use a method to upgrade the cost data applicable at a past date to costs that are representative of conditions at later time. In this study cost index were used.

A cost index is an index value for a given time showing the cost at that time relative to a certain base time (Peters M., 2003). With this method the cost of equipment at the present time can be determined from the cost in a past time by multiplying the original cost for the ration of the indexes as in the following expression:

$$Present\ cost = original\ cost \cdot \left(\frac{index\ value\ at\ present}{index\ value\ at\ time\ of\ original\ cost}\right) \tag{4}$$

The index values used in the study are reported in the appendix C.2

In the calculation it is often necessary to estimate the cost of some equipment when cost data are not available for the particular size required. It is possible to estimate the equipment cost by scaling the cost from another equipment with different capacity, by using the so called *six-tenths factor rule*. According to this rule if the cost of a unit of a capacity b is known the cost of a similar unit with capacity a is $X^{0,6}$ times the cost of the first unit. Where X is the ratio between the capacities of the units (a divided b).

$$Cost\ of\ equipment\ a = (cost\ of\ equipment\ b) \cdot X^{0,6} \tag{5}$$

The application of this rule is for most equipment an oversimplification and the value of 0,6 is actually a generic one. For an higher precision the exponent of the equation can vary from 0,3 to 1 depending from the equipment as indicated in Peters and Timmerhaus (Peters M., 2003). The used values are specified for each equipment component in Chapter 7.

In order to estimate the total capital investment it is necessary to consider also all the other costs for the plant. They include direct costs (such as equipment installation instrumentations, piping, buildings, land etc...) and indirect costs (such as engineering and supervision, construction expenses and legal expenses etc...).

There are many methods to estimate the cost investment, in this study we used one based on the determination of the delivered-equipment cost. The other items included in the total cost are estimated with a proportion factor referred to the delivered-equipment cost. This is explained in the following equation cost (Peters M., 2003):

$$C_n = \sum(E + f_1 \cdot E + f_2 \cdot E + f_3 \cdot E + \dots + f_n \cdot E) \tag{6}$$

Where $f_1, f_2 \dots f_n$ are multiplying factors for installation, piping, indirect costs etc...and C_n is the total capital investment For each factor average values from literature have been used. From those values we can obtain each cost involved as a percentage of cost investment:

$$P_1 = \frac{f_1}{E \cdot \sum(1 + f_1 + f_2 + f_3 + \dots + f_n)} \tag{7}$$

The following appendix C.3 reports the percentages determined for each cost and used in the calculations. The expected accuracy on the cost investment is in the ± 20 to 30 percent range.

The annual cost for the maintenance was calculated as the 4% (Hektor, 2008) of the capital investment, while the annual cost of the initial capital investment we use a annuity factor of 0,1. Hence we consider an annual cost for the gas upgrade section of:

$$C_a = C_n \cdot 0{,}1 + C_n \cdot 0{,}04 \tag{8}$$

3.3.2 Energy cost of the gas upgrade section and revenues

The costs for the energy input flows of the section are the cost connected with the power consumption of the section since the heat necessary in the processes is recovered from other hot streams. The value of the power consumed is calculated using the selling price because it represents not-sold electricity. This cost is calculated only for the consumption of the gas upgrade section and they already include the CO_2 charge in the electricity price. The same price will be applied for the electricity produced and sold.

The SNG is assumed to be sold on the market with the Natural Gas price.

The captured CO_2 has a different cost depending if it is stored or not. In case the CO_2 is released in the atmosphere it will be necessary pay the CO_2 fee on the emissions. It varies considerably in the different scenarios and they have a strong influence in the economic performance. If the CO_2 is stored the only cost will be those for the transportation and storage, while the not-paid CO_2 fee can be considered as a revenue.

All the calculations were made on an annual base. Briefly the cost and revenues for the energy flows are calculated with the following equations:

$$\boldsymbol{El_{cost}}[€] = el_{consumption}\ [MWh] \cdot el_{price}\ [€/MWh] \qquad (9)$$

$$\boldsymbol{El_{rev}}[€] = el_{sold}\ [MWh] \cdot el_{price}\ [€/MWh] \qquad (10)$$

$$\boldsymbol{SNG_{rev}}[€] = SNG_{produced}[MWh] \cdot NG_{price}[€/MWh] \qquad (11)$$

$$\boldsymbol{CO_{2\,cost}}[€] = CO_{2\,captured}[ton] \cdot CO_{2\,charge}[€/ton] \qquad \textit{No } CO_2 \textit{ recovery} \qquad (12)$$

$$\boldsymbol{CO_{2\,rev}}[€] = CO_{2\,captured}[ton] \cdot (CO_{2\,charge}[€/ton] - CO_{2\,trasportation\ cost}[€/ton] - CO_{2\,storage\ cost}[€/ton]) \qquad CO_2 \textit{ recovery} \qquad (13)$$

Where *EL_{cost}* is the annual cost for electricity consumption, *EL_{rev}* is the annual cost and revenue from the sold electricity, *SNG_{rev}* and *CO_{2rev}* the revenues from the SNG and the CO_2 stored. The *CO_{2cost}* is the annual cost due to the CO_2 emission fee.

3.3.3 Energy market scenarios

The Energy market scenarios developed by Axelsson and Harvey (Axelsson, et al., 2010) were used as tools for the economic evaluation. In their work the authors developed a consistent set of energy market parameters and scenarios by estimating the effect on energy market prices if the external costs associated with the CO_2 emissions are internalized. Scenarios were defined assuming different target levels for CO_2 emissions and corresponding charges CO_2 sources. In this study we considered four scenarios, the first two represent the market in a near future, 2020, and they have the same fossil fuel price and a moderate or high level of CO_2 charges. The other two scenarios have a longer term (2050) with a new fossil fuel price and new CO_2 charges.

The scenarios include the possibility of CCS technology in the electricity production. All the data concerning the scenarios used in the study are reported in appendix C.4

In the scenarios a decreasing of CO_2 emission in the electric power sector is expected in 2050, but only with a high level of CO_2 charge can CCS technology become profitable in this sector. The prices for the energy flow for each scenario are shown in the following table.

Table 3.5 Prices data for each scenario

	Scenario 1	*Scenario 2*	*Scenario 3*	*Scenario 4*
Natural Gas price [€/MWh] including CO_2 charges	35	42	59	80
Whole sale electricity price [€/MWh]	51	74	71	84
CO_2 emissions charge [€/ton]	20	52	50	150

3.3.4 Economic comparison

In this study it is not possible to use common economic methods, such as breakeven point or Payback period, because we calculated costs for a section of the SNG process and revenues for the whole plant. Since the goal of this study is to compare the different technologies that are not really important. We conduct the comparison by calculating the difference between revenues and costs for each case and comparing them for each scenario. The values cannot be considered as the profit of the plant, however they are enough because all the other costs not considered are common in each case.

The following equations were used:

$$\boldsymbol{Tot\ cost}[€] = C_a[€] + El_{cost}[€]$$

$$\boldsymbol{Tot\ revenue}[€] = El_{revenue}[€] + SNG_{revenue}[€] - CO_{2\,cost}[€] \quad \textit{No } CO_2 \textit{ storage}$$

$$\boldsymbol{Tot\ revenue}[€] = El_{revenue}[€] + SNG_{revenue}[€] + CO_{2\,revenue}[€] \quad CO_2 \textit{ storage}$$

$$\Delta\,[€] = Tot\ revenue[€] - Tot\ cost[€] \qquad (14)$$

Where C_a is the annual cost due to the capital investment, El_{cost} is the annual cost for the electricity, $El_{revenue}$ and $SNG_{revenue}$ are the annual revenues from the electricity, and SNG while $CO_{2\,cost}$ is the annual cost for CO_2 emission and $CO_{2\,revenue}$ the annual revenue from CO_2 storage.

Hence in this way we can evaluate the best solution for each scenario.

3.3.5 General economic assumptions

The maintenance cost was assumed ase 4% of the capital investment. The assumed value for the annuity factor the working hours per year and the exchange rate between USD and Euro and SEK and Euro are listed in the next table.

Table 3.10 Economic assumptions

Annuity factor	0,1
Maintenance [%]	4%
Annual operating time [h/y]	8000
Exchange rate [USD/EUR]	1,42
Exchange rate [SEK/EUR]	10,1239

4 Literature review

In this section the three selected technologies for CO_2 removal are described, together with the other main steps of the upgrading process, dehydratation and captured CO_2 treatments.

4.1 Gas Drying

The water content increases the gas corrosivity, especially when acid gases, e.g. hydrogen sulfide and carbon dioxide are present. Another risk due to the presence of water is, in the case of gas cooling, the condensation of the water in the pipeline. The consequences of these phenomena are a higher corrosion and erosion rate and an increased pressure drop in the pipelines. These problems must be prevented by drying the gas.

Liquid desiccant dehydrators are simple to operate and maintain; and they represent the most common choice for natural gas dehydration. Glycols are typically used for applications where dew point reductiosn of the order of 15°C to 50°C are required.

Diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (TREG) are used as liquid desiccants, but TEG is the most common for natural gas dehydration.

Figure 4.1 shows the diagram of the optimized TEG dryer chosen in this application.

The drying process involves two main steps, the water absorption from the syngas by glycol at high pressure and low temperature and the reconcentration of the glycol at low pressure and high temperature.

In the diagram of the dryer are present also features needed to improve the energetic efficiency of the process such as an external gas-glycol heat exchanger, split lean/rich glycol heat exchange to control the temperature of the flash separator and filters, and stripping gas to improve glycol reconcentration.

4.1.1 Drying Process

In the inlet of the gas side a gas scrubber is present. Its purpose is to prevent accidental dumping of large quantities of water, hydrocarbons, treating chemicals or corrosion inhibitors into the glycol contactor. Even small quantities of these materials can result in excessive glycol losses due to foaming; the effect is a reduced efficiency, and an increased maintenance.

Following the process the syngas get inside the absorber where the regenerated Glycol is pumped to the top tray. The glycol absorbs water as it flows down through the contactor (absorber) countercurrent to the gas flow.

The gas outgoing from the top of the absorber is directed to a gas-glycol heat exchanger, it allows decreasing the temperature of the lean glycol from the boiler (around 200 °C) to 15°C warmer than effluent syngas. Otherwise, the top tray acts as a heat exchanger and the glycol's temperature on the top tray rises with a consequent increases of the effluent gas' water content.

After the absorber the gas is ready for the next step in the gas upgrading section. The others equipments of the dryer needed to restore the concentration of water in the glycol, by removing the water content from the rich glycol flow.

They mainly consist in a flash tank, a filtering section, the still column and the reboiler. The flash tank separates dissolved hydrocarbon gases from glycol, to reduce the subsequent vapor flow in the still column. The operating pressure range in tank is from 4.5 bar to 6 bar; while the separation temperature have to be controlled by using the rich glycol stream from the absorber, to keep it under the 90 °C, because the solubility of heavier hydrocarbons in the TEG increases with the temperature.

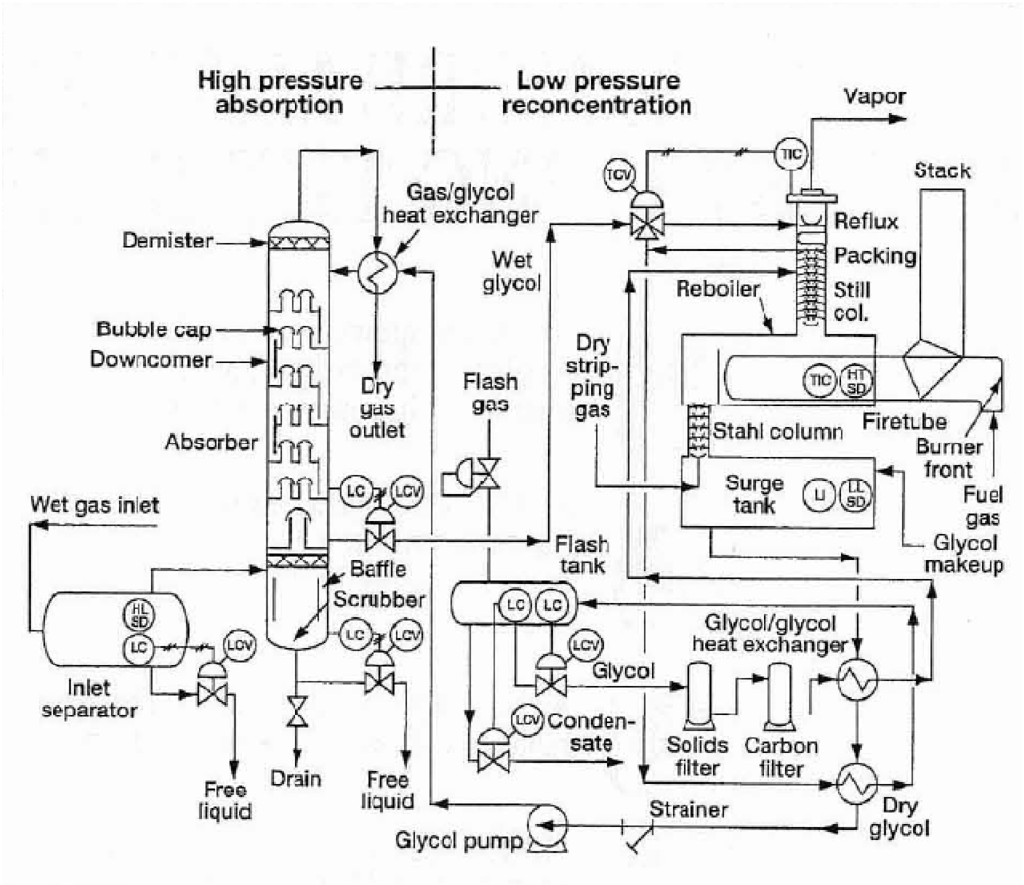


Figure 4.1 Process flowsheet for glycol dehydration (Manning, et al., 1993)

The regeneration of glycol occurs in the still column and in the reboiler, where the water is distilled from the glycol at near atmospheric pressure by application of heat from the reboiler. The operation is easy because the difference in boiling point of water and glycol is high; it allows covering a TEG purity up to 99.99 weigh percent.

The reboiler supplies heat to reconcentrate the glycol. This includes heating the glycol to the reboiler temperature (around 200 °C), vaporizing water in the still effluent, supplying the reflux duty and overcoming heat losses.

This component requires the main energy demand of the section; to evaluate it we used a empiric relation (Manning, et al., 1993) :

$$Q_r\ [btu/lb_{H20\,sep}] = 900 + 950 \cdot (gal\,TEG/lb_{\,H2O\,sep}) \qquad (15)$$

The ratio between the TEG and the water separated is a operating parameter of the plant; it usually included in the range between 2 and 5 [*gal/ lb*] (Manning, et al., 1993); we assumed to operate with 3.

The regenerated lean glycol outgoing from the surge drum is partly cooled in the lean-rich exchanger; pumped and cooled again in the glycol-gas heat exchanger before being recirculated to the contactor.

All the main data of the dryer are shown in Table 4.1. We assumed pressure drop on the gas side of 0.2 bar.

Table 4.1 Operating data for the dehydration section

Separation efficiency for H_2O	**99** %
Specific energy consumption	8,7225 $[MJ/kg_{H20\,sep}]$
Glycol/Water ratio	3 $[gal/lb]$

This solution for the drying section has been kept also all the studied cases, to allow an improved comparison between these solutions.

4.2 CO_2 removal by membrane

The CO_2 removal by membrane has become an established technology since its first use in the 1981. Now membranes are used both for bulk separation (as in this study) or in combination with other techniques such as chemical absorption.

In last decade membranes have been widely used in two main CO_2 removal applications: Natural Gas sweetening and Enhanced oil recovery (EOR). Hence a large literature about membranes for CO_2 separation is available.

4.2.1 Membrane process

According to H.P. HSIEH (HSIEH, 1996) definition a membrane is a "semi-permeable active or passive barrier, which under a certain driving force, permits preferential passage of one or more selected species or components (molecules, particles or polymers) of a gaseous and/or liquid mixture or solution"

The separation of a gas mixture occurs because the membrane has a selective permeation to the gas components. When the gas mixture at high pressure encounters a membrane, the difference of partial pressure between the two sides of the membrane drives the diffusion of the gas, but since the membrane has different permeation for each component some of them diffuse faster than the others. The membrane separates the gas mixture in two output streams, the permeate which has a high concentration in the most permeable components and the retenate which contains the least permeable components. In the case of CO_2 removal the permeate is rich in CO_2 while the retenate is rich in CH_4.

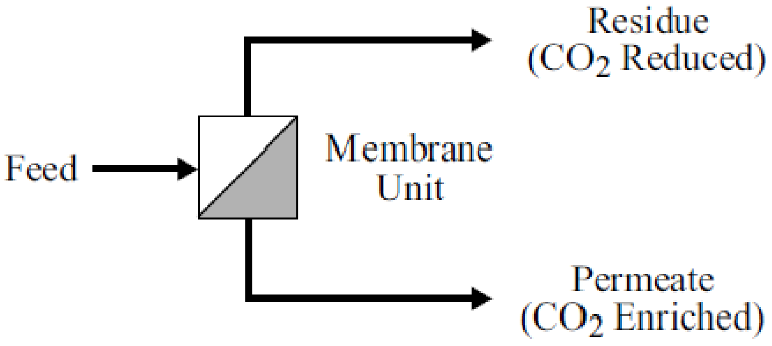


Figure 4.2 Single membrane scheme (Dortmundt D., 1999)

It is important to notice that the permeate flow has a strong pressure drop (the pressure ration is around 0,035) while the retenate has a smaller pressure drop (around 1 bar) due to the turbulence inside the membrane. That is important because the methane rich flow has to be compressed to 60 bar and a strong pressure drop in this phase would increase the energy consumption.

4.2.2 Membrane structure

Nowadays the most common solution to produce high performance membranes consists in an extremely thin non-porous layer mounted on a much thicker and highly porous layer of the same material. This structure is asymmetric and is in opposition with the old technology membranes called symmetric, having a homogenous structure. An example of an asymmetric membrane is shown in Figure 4.3

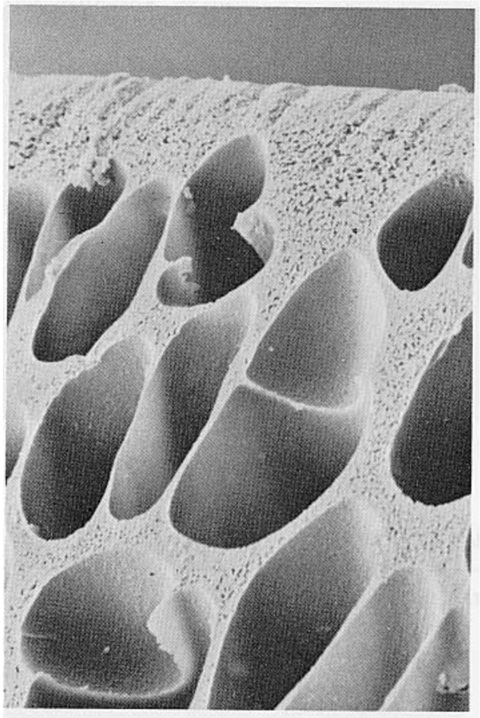


Figure 4.3 Asymmetric membrane structure (Dortmundt D., 1999)

The non-porous layer matches the requirement of the membrane, i.e. is highly selective and thin. The porous layer provides mechanical support and allows the gas flow to permeate through the non porous layer.

Nowadays the most commercially viable membranes used for CO_2 removal are polymer based, for example, cellulose acetate, polyamides, polyamides and polysulfone. The selected material for this study was the cellulose acetate, more specifications about the membrane are reported in Table 5.1.

4.2.3 Membrane modules and flow scheme

The membranes are produced in elements which can have two main forms: flat sheet or hollow fiber, the flat sheet elements are typically combined into a spiral-wound element and the hollow fibers are combined into a bundle similar to a shell and tube heat exchanger (Dortmundt D., 1999). A hollow fiber element is shown in figure 4.4

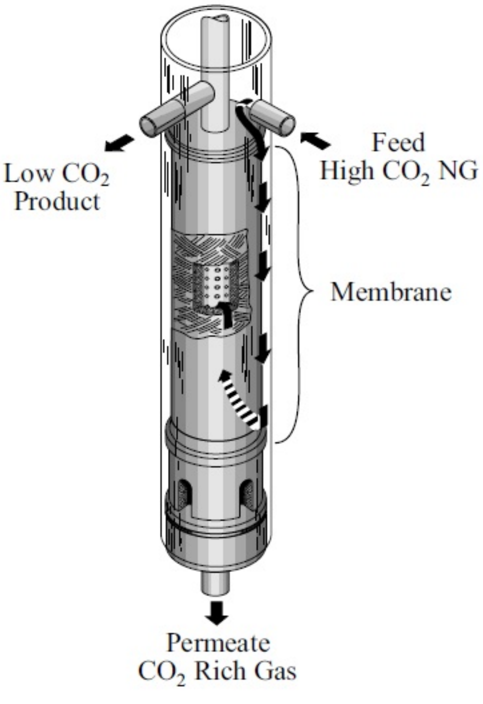


Figure 4.4 Hollow-fiber membrane element (Dortmundt D., 1999)

Once the membrane element are manufactured they are joined and inserted together into tubes. Many tubes are mounted on skids to accomplish a Membrane Separation unit. The simplest membrane processing scheme is a one stage process, where the inlet flow is separated in a single membrane separation unit. In some case a multi stage systems attempt to recover a higher portion of methane. In this study a two stage system has been used to achieve the required methane purity and recovery.

With this configuration a new compressor needs to recompress the permeate from the second stage to the inlet pressure in the first stage. The two stage flow scheme is shown in figure 4.5

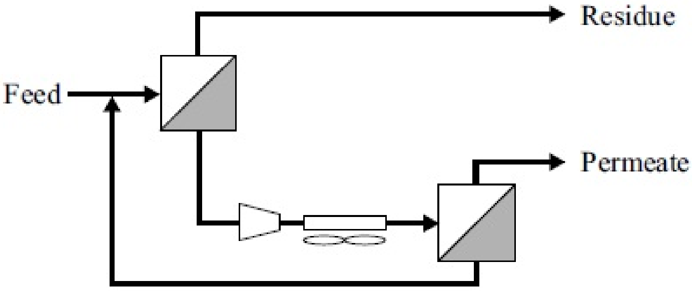


Figure 4.5 Two-stage membrane separation flow scheme (Dortmundt D., 1999)

4.3 CO_2 removal by Pressure Swing Adsorption

Separation of bulk gas mixtures by Pressure Swing Adsorption (PSA) processes has become a common industrial practice in the areas of air fractionation, gas separation, and hydrogen production.

Besides high separation efficiency and favorable economics provided by some of these processes, the key reason for such a phenomenal growth in the development of this technology is the design flexibility of these processes. Many combinations of the cyclic adsorption, desorption, and complementary steps and their operating conditions in conjunction with a variety of adsorbents (often multiple types used in the same process) can be utilized to obtain the desired separation goals.

4.3.1 Adsorption process

Physical adsorption involves reversible binding of molecules from the gaseous phase on surfaces of a highly porous adsorbent media. The reverse process is called desorption. In adsorption, the *adsorptive* accumulates on the *adsorbent* which is then loaded with *adsorbate.* During desorption, the adsorbate present in the condensed phase passes from the surface of the adsorbent into the gaseous phase.

It the adsorption separation three different principle mechanisms can be found: steric, kinetic, and equilibrium effects. The steric effect occurs with zeolite and carbon molecular sieves, which are the two most common adsorbents for CO_2 removal. These have a very narrow distribution of micropores. Only components with critical diameter smaller than the opening of the micropores will be adsorbed. In this way, mixtures can be separated by adsorption (Hans-Jörg Bart, 2005).

Three major types of processes have been established. Their names refer to the method of regeneration. The temperature swing process (TSA), the pressure swing process (PSA) or (VSA), and the concentration swing process (CSA) (Perry, et al., 1997).

PSA is nowadays considered a very suitable solution for CH_4/CO_2 gas mixture separation as many studies and experiments have demonstrated (Cavenati, et al., 2005), (Cavenati, et al., 2005). In this system the regeneration of the adsorption medium occurs because of a variation in the system pressure. The content equilibrium of adsorbate in the adsorbent depends on the pressure of the system; normally the adsorption takes place at elevate pressure and desorption at lower pressure, usually under atmospheric pressure. Those processes are usually called Vacuum Pressure Swing Adsorption (VPSA).

Separation by adsorption is not a continuous process, and it involves different phases besides adsorption and desorption, and each one has a different duration. Hence for a continuous production at least two beds are necessary.

The most commons adsorption mediums are Zeolite and Carbon Molecular Sieve, since they have different adsorption characteristics, they are sometimes used together in a single bed.

Since the adsorption phenomena is quite complex and many different equilibrium processes are involved, is difficult to develop an analytic model of the whole adsorption process. Other difficulties in the definition of an analytic model are due to the other parameters, as pressure levels and duration of different phases of the processes (adsorption, desorption etc…). Some studies (Cavenati, et al., 2005) (Cavenati, et al., 2005) (Delgado J., 2007), were conducted with an analytic-experimental approach, where a analytic model was combined with empiric results, but they are reliable only for that adsorption process and those adsorbents.

4.3.2 PSA separation process

In this study we used literature data to predict the performance of the chosen PSA unit, using data from a similar one. In this section the process steps are described for the selected PSA cycle.

By consulting literature about similar cases we decided to use a five step PSA cycle working on a four bed system coupled two by two. This kind of process is usually able to achieve a methane purity from 91 – 97 % and a recovery over 80%.

The cycle steps are:

1) *Feed*: in this step the inlet flow is injected in the bed. During the feed time the CO_2 is preferentially retained in the fixed-bed column, whereas CH_4 is released in the top at high pressure.
2) *Intermediate depressurization*: here the column inlet is closed and a fast depressurization to an intermediate pressure occurs. The exit stream in this phase is also considered to be a product, because it can be employed for pressure equalization to reduce the energy for pressurization in another bed. This has also a positive influence in the methane recovery of the system (Grande C., 2007).
3) *Counter-current blowdown:* the column is evacuated down to low pressure. In this step the CO_2 rich stream is produced and the adsorbent is partially regenerated.
4) *Counter-current purge with product*: in this step part of the product (CH_4 rich stream) is employed to displace the CO_2 to the feed end of the column; avoiding product contamination in the following cycle.
5) *Counter-current pressurization*: The column is pressurized from the low pressure to the high pressure employed in the feed with the product stream rich in CH_4 (Grande C., 2007).

The steps occur sequentially in the four beds, and the step duration is optimized to have high performance and continuous production. The PSA equipment scheme is shown in the following figure.

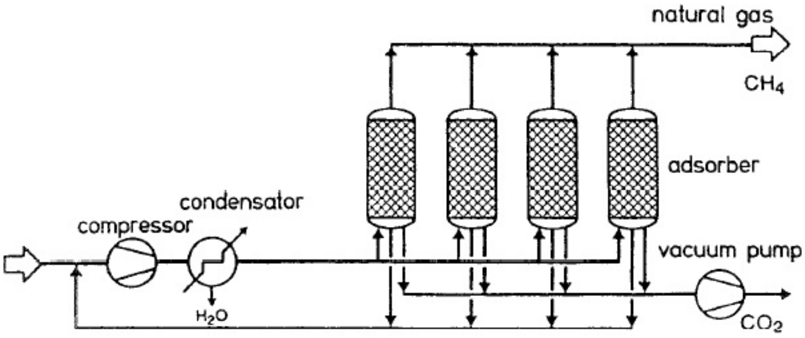


Figure 4.6 PSA separation flow scheme (Pilarczyk E., 1987)

4.4 CO_2 removal by MEA

Chemical absorption is nowadays the most common technique for CO_2 removal. It is very diffused both in the natural gas processes and in the flue gas process, and for many reasons amine based CO_2 absorption systems are the most suitable for combustion based power plants but they can also be used in NG upgrade.

The selected absorption processes uses mono-ethanol-amine (MEA), this is a thermally regenerable solvent, which has a strong affinity for CO_2. It is regenerated at elevated temperature hence the process requires thermal energy for the regeneration of the solvent.

Several researchers have modeled and studied the MEA absorption process (Rao, 2002), (Mariz, 1998) (Chapel D., 1999), most of their efforts focused on reducing the thermal energy requirement to increase the overall process efficiency and to reduce the expenses. In the modern plants the regeneration energy required is from 4,2 to 3,4 GJ/ton CO_2 depending on the plant (Abu-Zahara, et al., 2007).

4.4.1 MEA separation process

The MEA process considered in this study was designed based on a standard regenerative absorption-desorption cycle as shown in the simplified flow diagram figure 4.7

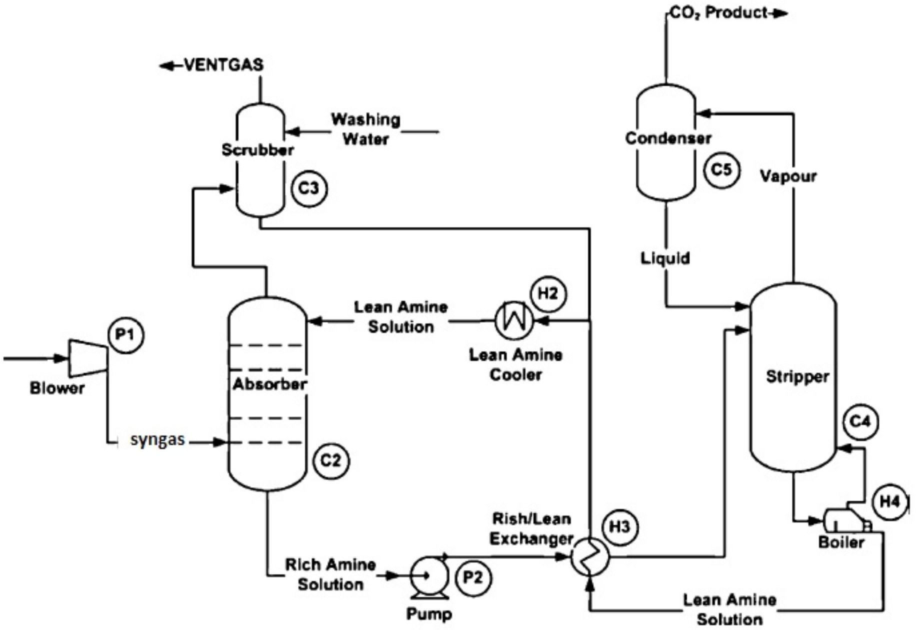


Figure 4.7 MEA process flow diagram (Abu-Zahara, et al., 2007)

The syngas passes from a gas blower to overcome the pressure drop in the MEA absorber. It enters the absorption column at the bottom and flows counter-current with the MEA solution. The MEA reacts with the CO_2 forming mainly carbonate ions as in equation 16

$$CO_2 + 2RNH_2 \rightleftarrows RNH_3^+ + RNHCOO^- \qquad (16)$$

From the reaction equation it is clear that at least two moles of MEA are needed for each mole of CO_2. The CO_2 lean gas enters a water wash scrubber where water and MEA vapour and droplets are recovered and recycled back into the absorber.

The rich solvent flow containing chemically the CO_2 is pumped to the top of a stripper passing through a lean/rich cross heat exchanger to heat the rich solvent to a temperature close to the stripper operating temperature (110–120 °C) while the CO_2 lean solution is cooled. In the stripper the chemical solvent is regenerated at higher temperatures (100–140°C) and at pressure close to atmospheric. The heat is supplied to the reboiler using steam (LP) to maintain regeneration conditions. This part has the main energy demand because the solvent has to be heated to provide both the required desorption heat for the removal of the chemically bound CO_2 and for the production of steam, which is used as stripping gas. Steam is recovered in the condenser and returned to the stripper. Then the produced CO_2 gas leaves the condenser. The lean solvent goes back to the absorber via the lean/rich heat exchanger and a cooler to cool its temperature down to the absorber level. Other energy demands occur in the condenser and in the amine cooler, they are two hot stream available for the pinch analysis.

4.5 H_2 removal by membrane

Hydrogen removal is needed in the gas upgrade process, because a high fraction of H_2 decreases the Wobbe index of the SNG. Hence in some case it was necessary to add a H_2 removal section. The H_2 separation occurs by a membrane system, it operates in a very similar way to the CO_2 membrane described in Section 4.2. The only difference is in the material and in the pressure level of the section, that change a little in the two cases where the H_2 membrane was used. The selected solution is a polymeric membrane that allows to have an high permeability and good selectivities.

5 Modelling of process

In this chapter all the details about the different technologies will be explained.

5.1 Framework of the gas-upgrade section with membrane separation

In order to investigate the impact of the separation system on the process integration we considered the possibility to have a multi-stage membrane separation. A single stage was not enough to achieve all the target requirements hence a two stage solution was studied.

Appendix A.1 shows the structure proposed for gas-upgrade section operating the CO_2 separation with two stage membrane technology.

The following description is referred to the scheme in Figure 1a.

The gas from the previous section of the plant must be upgraded by separation of CO_2, H_2O and H_2. The membrane technology allows performing a simultaneous bulk separation of CH_4 from CO_2 and H_2. To complete the upgrading process we need to add a drying section to remove the water contained in the syngas.

The drying is performed by a Glycol Dryer working with Triethylene glycol (TEG). This system was considered because is one of the most economical choices (Manning, et al., 1993). It has low equipment and operating costs, higher thermal stability and efficient regeneration with high reboiler temperature (concentration of TEG obtainable up to 99,9%). The dryer system performs a good absorption working with high pressure and low temperature. Hence operating conditions of the dryer are almost the same as for the membrane (30 bars and 40°C), and it was placed after the two membranes in order to reduce the size of this component. In fact after the separation unit it works only on the CH_4 rich stream that has a mass flow much smaller than the CO_2 rich stream. The system working under this operating condition achieves a separation efficiency for the H_2O of 99%.

The gas upgrade shown in Figure 1a is performed in five main sections:

- *First compression*
- *Membrane separation units*
- *Dehydration*
- *Final SNG compression and cooling*
- *Captured CO_2 treatments*

The firsts compressor and cooler increase the pressure and cool down the temperature of the syngas to the operating conditions of the membrane of 30 [bar] and 40 [°C].

The permeate from the second stage of the CO_2 separation is recirculated to the feed of the first stage to increase the purity and the recovery. In this phase a compressor is required to increase the pressure of the permeate to the pressure of the fed syngas.

The dryer needs to remove the water content and the membrane performs the gas separation.

The final SNG compressor and cooler allows to achieve the pipeline condition of 60 bar and 20 °C.

The CO_2 treatments is needed to achieve the specification for injection in CO_2 pipeline

All the sections of the gas upgrade process are analyzed in the following paragraphs, and the complete results are in the appendix D.

5.1.1 First Compressor and cooler

The syngas from the previous section is at almost atmospheric pressure and must be compressed to ensure an operating pressure of the membrane of 30 bars. The compression is performed with a five-stage compressor with inter-cooling, each stage has the same compression ratio, maximum 4, such that the outlet temperature does not exceed 250 °C. The inter-stage cooling system is present in the first four stages from 40 °C to 120° C and no duty in the last stage

The compression process occurs with an isentropic efficiency of 76% and a mechanical efficiency of 99 %. It is important to notice that in this compression part of the water condenses and it is removed.

The following table reports the powers required form the compressor and the cooler.

The compression drives the syngas up to around 200°C, this temperature is too high for the dryer and the membrane. A cooling section is necessary to restore an operating temperature of 40°C.The pressure drop for the gas side was estimated at 2 % of incoming pressure [bar].

All the calculated operating data of these elements are shown in the appendix D.1

5.1.2 Final compressor and cooler

After the dehydratation the SNG reaches the required composition and only a final compression and the final cooling are necessary to reach the injection conditions in the national natural gas network; fixed at 60 bars and 20 °C.

To perform the compression we chose a double stage compressor with intermediate cooling, the inter-cooling decreases the temperature of gas coming from the first stage to the same value at the inlet of the compressor (around 40 °C). While the injection temperature is achieved with a following cooling to 20 °C.

The energy demands for this stage vary with the selected membranes, because of the variation of CH_4 recovery and consequently of the injected mass flow.

Appendix D.2 reports the energy demand and the other results obtained with the membranes chosen after the performed analysis on the whole section.

5.1.3 Second membrane permeate compressor

This compressor is needed to increase the pressure of the permeate of the second membrane to the pressure level of the feed of the first membrane. The unit has a compression ratio of around ten, realized by three compression stage with three intercoolers. The operating data of this compressor are shown in the appendix D.3

5.1.4 Capture CO_2 treatments

To bring the CO_2 to the injection conditions some treatment is necessary. First of all we need to burn the remaining methane and hydrogen contained in the CO_2 rich flow. The following steps are a cooling of the exhaust flow, a compression to 75 bar, cooling to condense the CO_2 to the liquid phase and a final pumping up to 120 bar.

CO_2 treatments:

- *CH_4 and H_2 combustion with O_2 flow*
- *Exhaust flow cooling*
- *Compression to 75,5 bar*
- *Cooling and CO_2 condensing*
- *CO_2 pumping to 120 bar and injection*

Since in the CO_2 rich stream fractions of hydrocarbons (CH_4 and H_2) are still present a combustion in a reactor is needed in this phase. This phase is complex because in order to keep an high CO_2 fraction in the exhaust flow the combustion must take place with only oxygen stream and not air. Otherwise the nitrogen content will be too high and it should be removed before the pipeline injection. The oxygen needed is provided from an integrated SOFC-SOEC system. This solution has been choice because the oxygen flow required is too small to justify a cryogenic system while a PSA equipment needs a too large equipment (Iora P., 2008).

Basically the SOFC (solid oxides fuel cell) is a high temperature (>650 ◦C) fuel cell that produces electric and thermal energy and steam from hydrogen and oxygen. The SOEC (solid oxide electrolyzer) (Udagawa J., 2004) is an electrolyzer that carries out inverse process of a SOFC, hence divides steam in hydrogen and oxygen molecules.

A detailed flow sheet of a SOFC-SOEC system (Iora P., 2008) is shown in Figure 5.1. The SOEC anode side is fed with a H_2O rich stream (stream 8) coming from the SOFC anode. Inside the SOEC, oxygen is separated and sent to storage (stream 14), in this case the oxygen produced under atmospheric pressure thus a multistage compressor is used. From the SOEC anode side outlet the steam rich in H_2 stream is brought to the SOFC anode for power generation (stream 7).

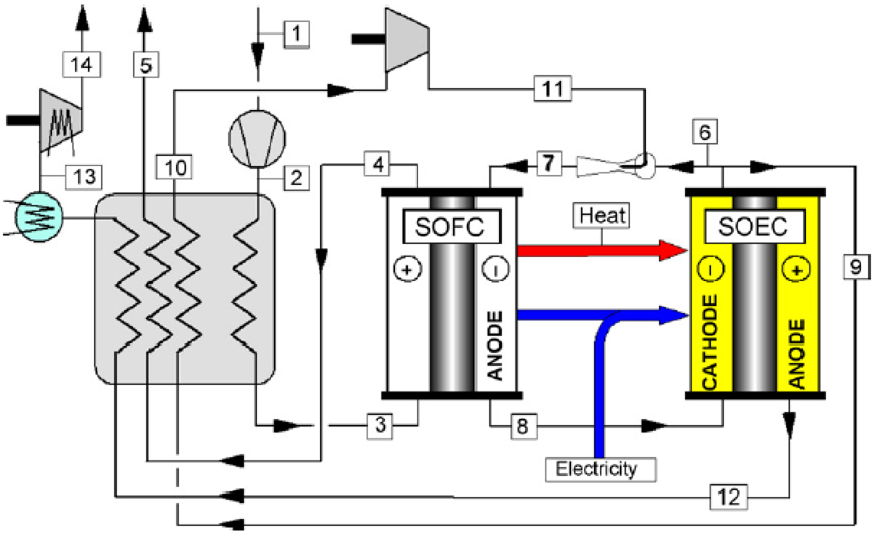


Figure 5.1 Flowsheet of an integrated SOFC–SOEC system for pure oxygen production. (Iora P., 2008)

Due to the high temperature of the SOFC heat exchangers are present to increase the efficiency of the system, and for pre-heating of the air inlet in the SOFC. Since the electricity produced in the fuel cell is not enough to cover the consumption of the SOEC, of course, other electricity is needed. This in the main energy consumption of this system together with that required for the compressors .According to Iora and Chiesa (Iora P., 2008) with a current density of 500 mA the energy consumption of the whole system requires 0,3 kWh/kg O_2 produced.

The combustion with oxygen occurs in the reactor at almost atmospheric pressure (the outlet stream from the membranes is at around 1 bar) and the temperature is kept at 600 °C. All the heat released in the combustion can be recovered and it will be considered in the pinch analysis. As well as the heat available from the following cooling of the outlet flow from the reactor. In this unit the CO_2 rich stream is cooled down before entering in the CO_2 compressor.

The compression takes place in a six stage compressor with six intercoolers steps, this unit bring the CO_2 flow to 75,5 bar with an outlet temperature around 100 °C. The CO_2 flow is now cooled down to 20 °C in a condenser and then pumped to 120 bar to be injected in the pipeline.

All the data about captured CO_2 treatments are available in the appendix D.4.

5.1.5 Model of the single stage membrane

In order to understand the behavior of the membrane section and their performance an analytic model was developed. The model was used to predict the performance of each single membrane unit, in particular it was used in the Aspen simulations to perform a sensitivity analysis on the whole section and find the optimal operating solution of the membranes.

To describe the behavior of a membrane separation unit different mathematical models are available; they are based on the solution-diffusion theory for gas separating membranes (Rautenbach R., 1989). According to the theory the local permeation of gas through a non-porous membrane can be described by Fick´s law:

$$d\dot{n}_{i,p} = \frac{dA \cdot P_i \cdot (p_{i,r} - p_{i,p})}{\delta}$$

Where $d\dot{n}_{i,p}$ is the molar flow of component i that permeates the membrane, A is the membrane area, δ is the thickness of the membrane, $p_{i,r}$ and $p_{i,p}$ are partial pressures of component i in the retenate and permeate sides of the membrane and P_i is the permeability of the membrane to the component i.

The permeability of a component through a membrane is often given in *barrer* [cm^2 s^{-1} cm Hg^{-1}] which corresponds to 7.5005 10^{-18} [m^2 s^{-1} Pa^{-1}] in SI units. This parameter is fundamental in gas separation but in calculations it is more useful to specify the selectivity $\alpha_{i,j}$ of i over j defined as the ratio between permeabilities of two species i and j.

Hence the permeation is described by a set of differential equations for each component of the mixture. To solve the problem different analytic models have been proposed for a binary mixture, for multi-components system no analytic solutions have been found in literature, but there are a number of algebraic model or numerical procedures available. Some of them. however, are impractical for flow sheet calculation because they lack numerical robustness.

In this study the Pettersen and Lient method (Pettersen T., 1993) has been used, a model developed for hollow-fiber modules in countercurrent operation. It uses an analogy with heat exchangers to achieve a simplified algebraic equation system but it gives validated result without requiring any long iterative calculations (Pettersen T., 1993), (Gassner M., 2009) .

The model of the hollow fiber is shown in Figure (5.3), and the assumptions of negligible pressure losses on the feed side and negligible axial diffusion in the feed and in the permeate were made.

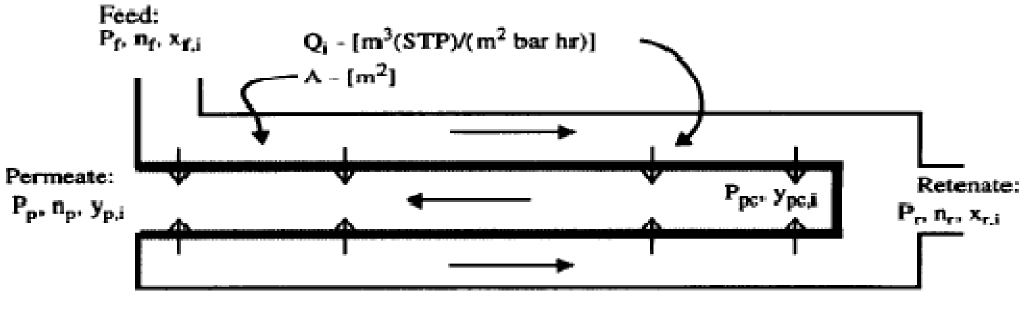


Figure 5.3 Simplified sketch of a hollow-fiber module (Pettersen T., 1993)

The model is based on the consideration that the membrane permeation is a rate-governed process where equilibrium is never reached, and it can be described by a relation between a driving force and a flux.

The permeation process through a membrane is described by Fick’s law, where the process driving force is the difference between the partial pressure between the retenate and the permeate sides and the flux is the molar flow of the component. It is evident the analogy with the well-know law of heat transfer ($Q = UA\Delta T$).

This model allows solving the problem with algebraic equations in place of differential ones, thus the permeate molar fraction $c_{i,p}$ of a substance i is calculated from design parameters:

- θ *, Molar stage cut*
- π , *Pressure Ratio*
- R , *Dimensionless permeation factor (interpreted also as dimensionless area of the membrane)*

They are defined as following:

$$\theta = \frac{n_p}{n_f}$$

$$\pi = \frac{P_f}{P_p}$$

$$R = \frac{A \cdot P_f \cdot Q_i}{n_f}$$

Where $n_p$and n_f are the mole flows in the permeate and feed side, P_f and P_p are the pressures on the feed and permeate side [bar], A is the membrane area [m^2], Q_i is the overall permeability constant [m^3 (STP)/(m^2 bar h)] and n_f id the flow rate [m^3 (STP)/h] of syngas.

In this study we selected a cellulose acetate membranes which are a well-established commercial solution for the removal of CO_2 from natural gas and in oil recovery. These membranes are available as a spiral wound or hollow fiber modules; typical proprieties of such membrane are shown in Table (5.1) these values have been used in our model (Gassner M., 2009).

Table 5.1 Properties of cellulose acetate membranes

Permeability CO_2	**9.00** [***barrer***]
Permeability H_2	2.63 [*barrer*]
Permeability CH_4, H_2O, N_2	0.426 [*barrer*]
Thickness	1000 [Å]

We performed a screening analysis with the Petterson model to understand the behavior of the membrane used in the study. We made the calculations by using the composition of the syngas at the inlet of the gas upgrade and a pressure ratio of 0.01. By solving the equations we found the R value for each molar stage cut. Results obtained are shown in next figures; they report the composition of the retenate and permeate flows and the dimensionless permeation factor.

As shown in Figure (5.5) the molar fraction of CH_4 and CO_2 in the retenate increase to an asymptotic value beyond a molar stage cut of 0.55. The concentration of CH_4 in the permeate increases and that of CO_2 decreases with the molar stage cut.

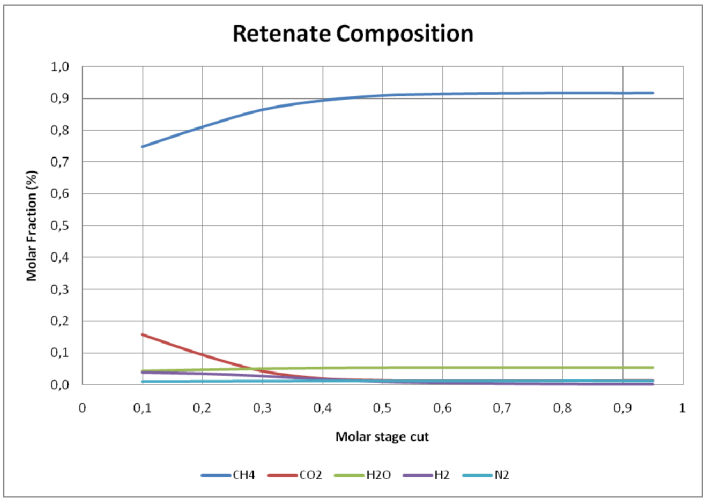


Figure 5.5 Retenate composition for different membrane unit models

The concentration in CO_2 in the retenate results are very low and almost negligible if we use a high molar stage cut. Presence of hydrogen is also reduced while concentration of nitrogen and water are not really modified by the membrane.

The water content is not really relevant in this calculation, because water has to be completely removed before the membrane to achieve the pipeline specifications. A special dryer will be located before the membrane, thus there will not be any water in the inlet of it.

The plot of the permeate composition, in Figure (5.6), shows that the ratio of CH_4 content in the permeate flow increases quickly with the stage cut. It is inversely proportional to the CH_4 recovery value.

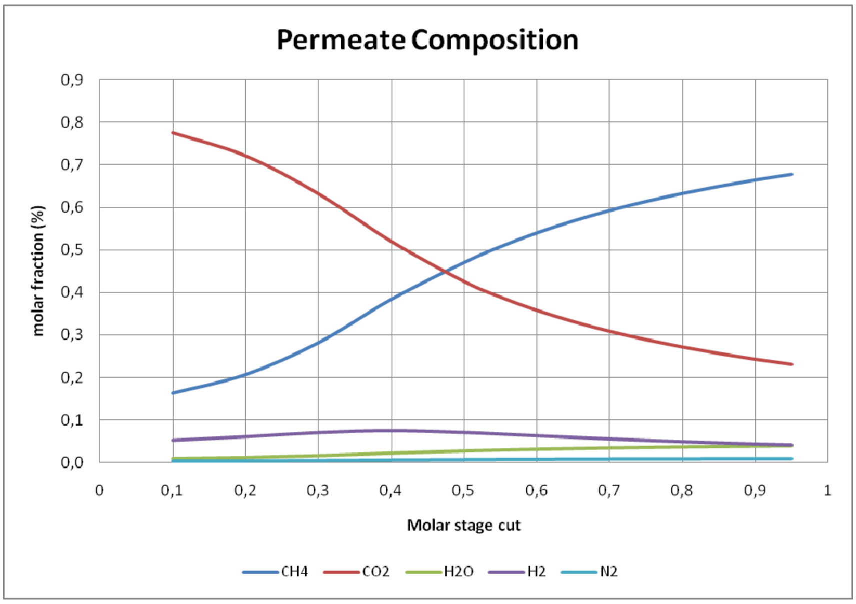


Figure 5.6 Permeate composition for different membrane unit models

It is evident that increasing the stage cut there is a tradeoff between the methane content in the retenate and the fraction of syngas resulting in the retenate flow.

From those plots it is possible to identify a suitable operation point for the system with a molar stage cut between 0.3 and 0.6.

Another interesting parameter of the process is the dimensionless permeation factor, which is directly connected with the membrane area. Figure (5.4) shows that the size of the membrane increases quickly with the molar stage cut to allow the passage of the increasing permeated flow through it. This will result in a higher initial cost for the equipment.

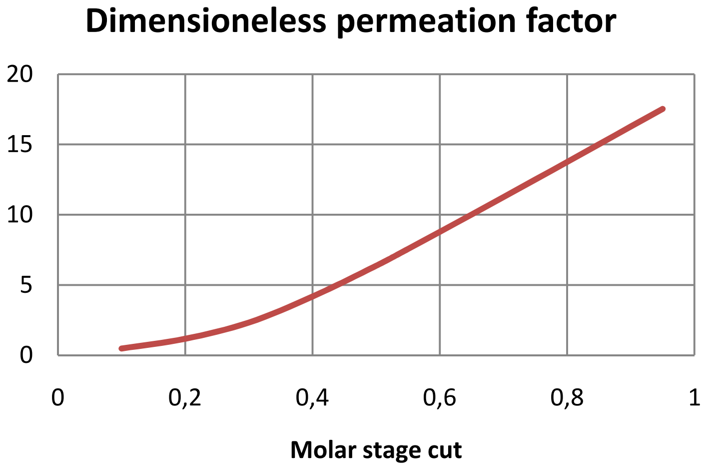


Figure 5.7 Dimensionless area for different membrane unit models

5.1.6 Analysis and results

Using the flowsheet simulation software, we performed an analysis of the gas upgrade section by changing two decision variables of the membrane. The decision variables are therefore chosen among the operating conditions of the membranes system and they include the stage cuts and the pressure ration of each membrane. Hence the influence of four values were investigated.

The main goal of the analysis was to find the optimal design for the membrane in order to produce the SNG with required specification and lower energy consumption.

In order to compare different possible designs we used a set of feasibility indicators such as CH_4 purity CH_4 recovery and the Wobbe index with a lower bound value to match; and a set of performance indicators to compare the different feasible solutions.

The performance indicators have been chosen on economic considerations; they are relative to energy consumption (operating costs) and to the size of the membrane (proportional to equipment costs).

The size of the membrane has been assessed by the dimensionless permeation factor defined in Section (5.1.5).

To select the optimal solution for the decision variables and the corresponding membrane we operated a sensitivity analysis on the pressure ratio and the two parameters for each membrane by using the Pettersen and Lien model. From the previous result on the model we considered suitable for the mole stage cut an interval between 0,3 and 0,8 while for the pressure ratio we used values between 0,035 and 0,06.

The flowsheet simulation programme was used to calculate the composition of the product gas and the energy consumption for each component of the section; it allows identifying the suitable solutions with a Wobbe index of least 13,6 kWh/m^3, a CO_2 content under 2,5 % vol and a minimum recovery of 60%. Increasing the recovery of CH_4 is important for the performance of the plant and also because it not possible send to the reactor a stream with a too high fraction of CH_4 (because the cooling system could not work properly). Hence the content of CH_4 in the permeate is considered as well.

For the first membrane we considered four levels of the pressure ratio 0,033 0,04 0,05 0,06 and five levels of the molar stage cut 0,3 0,4 0,5 0,6 0,7. For the second membrane the possible pressure levels were 0,04 0,05 0,06 and the molar stage cuts 0,3 0,4 0,5.

From the analysis it was evident that with a molar stage cut over 0,6 in the first membrane it is not possible to achieve a recovery value more than 60% .

It is also evident that the influence on CH_4 recovery of the molar stage cut values is stronger than that of pressure ratio values. In fact keeping the values of molar stage cut to 0,4 for both the membranes and changing the pressure ratio values the recovery of the system does not change so much (it is always around 90%). Table (5.2)

For all the cases the WI and the CO_2 content were inside the limits so the choice depends mainly on the recovery.

Table 5.2 Variation of the CH_4 recovery with the Pressure ratio

Press Ratio M1	Press Ratio M2	MSC M1	MSC M2	CH_4 Recovery [%]
0,033	0,04	0,4	0,4	90,78
0,033	0,06	0,4	0,4	90,28
0,04	0,04	0,4	0,4	90,72
0,04	0,06	0,4	0,4	90,20
0,06	0,04	0,4	0,4	90,58
0,06	0,06	0,4	0,4	90,04

Hence the factors with the main influence in on the recovery are the molar stage cut, but the best solution were found with the higher values of pressure ratio for both the membrane, 0,033 and 0,04. They were established to have retenate flows at atmospheric pressure.

The following graph (Figure 5.8) shows the dependence of the CH_4 recovery on the molar stage cut (MSC) values.

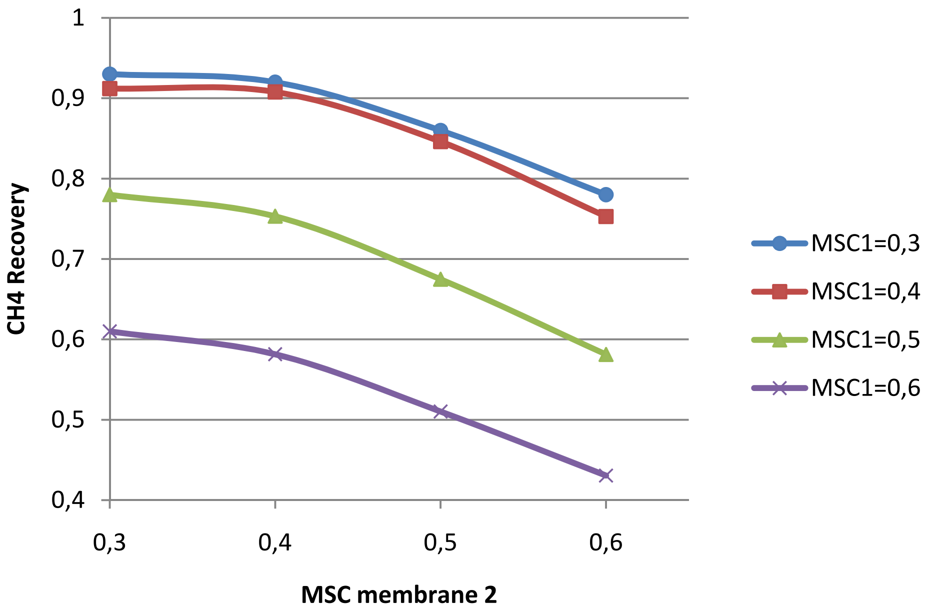


Figure 5.8 Variation of the CH_4 recovery with Molar stage cut (MSC) values

It is evident that the best recovery is obtained with a MSC of 0,3 in both the membranes, in this case the CH_4 recovery achieved is 92,9 %.

The following graphs in Figure (5.9) show that the Wobbe index of the product SNG depends strongly on the MSC values for both membranes. The required value of 13.6 kWh/m^3 is always satisfied in all cases with a MSC in the first membrane higher or equal to 0,4, and if it is 0,3 with at least a MSC in the second membrane of 0,5.

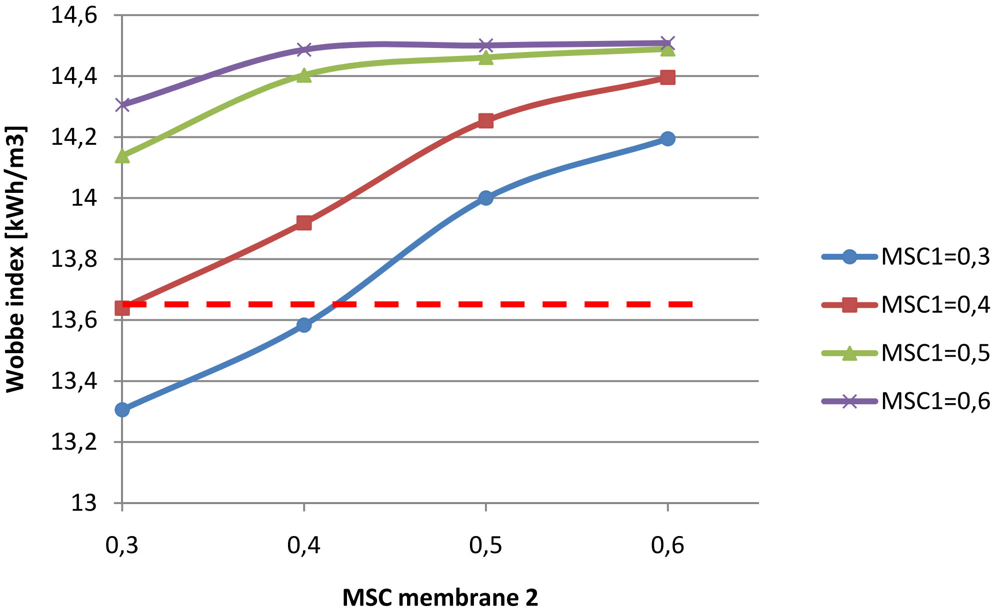


Figure 5.9 Variation of the Wobbe index with Molar stage cut values

The high value obtainable in this system is 14,6 with MSC1=0,5 and MSC2= 0,6 but in this case the recovery will result very low.

A higher stage cut means a better purity in the product flow because a larger part of the flow ratio is permeated from the membrane hence more CO_2 is removed. That will result in a lower flow ratio of gas produced, because a large part of the feed flow is present in the permeate.

The product flow contains mainly methane thus the CH_4 recovery depends strongly on the stage cut of the membrane, while the pressure ratio has a limited influence on it.

The molar stage cut is an important parameter to consider to choose the operating conditions because a small variation in the stage cut results in a relevant difference in recovery of CH_4 and of course in the production of SNG.

A third required specification is the CO_2 content in the SNG, which should be under 2,5% . Figure 5.10 reports the rates of CO_2 content in the SNG produced, it' easy to understand that they are in opposition with the WI, this because a high WI is mainly due to an high CH_4 fraction, that means a low CO_2 fraction. With high MSC values we can achieve a high WI and a low CO_2 content.

From the result must exclude the cases of MSC =0,3 in the first membrane if the value in the second is 0,3 or 0,4; and also the case of MSC=0,4 in the first and 0,3 in the second.

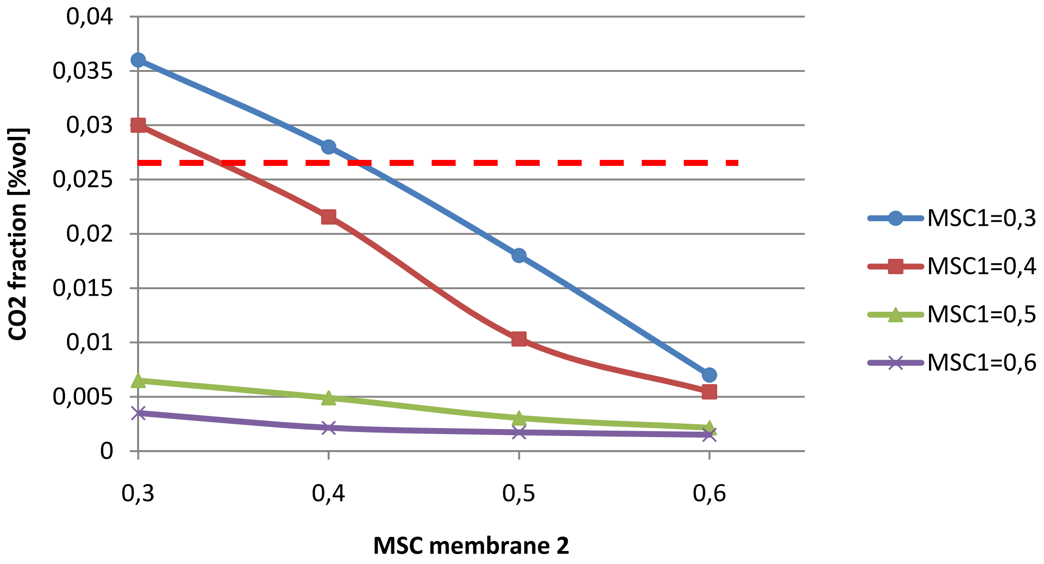


Figure 5.10 Variation of the CO_2 content with the Molar stage cut values

From the previous result we can select the optimal membranes for the system. We chose to use a molar stage cut of 0,4 in both the membranes and a pressure ratio of 0,033 in the first and 0,04 in the second. From the model equation the dimensionless permeation factor values have been calculated.

The appendix D.5 resume all the data for the membranes.

The performance of the gas upgrade section operating with the membrane system are shown in the following table.

Table 5.3 Overall data of the membrane units

CH_4 Recovery	**90,78** %
Wobbe index	13,92 $[kWh/m3]$
CO_2 fraction	2,16 %

5.1.7 Energy consumption of each elements

The appendix D.6 reports all the power and heat demand of the system, the total power demand for the gas upgrade section operating with membrane separation is:

Total power consumption: 5653 [kW]

5.2 Framework of the gas-upgrade section with PSA separation

The appendix A.2 shows the framework of the gas upgrade section working with the PSA separation unit. The following description refers to that scheme.

The gas upgrade is performed in six main sections:

- *First compression*
- *PSA separation unit*
- *Dehydration*
- *H_2 membrane separation*
- *Final SNG compression and cooling*
- *Captured CO_2 treatments*

Before the PSA unit the syngas is compressed to 9 bar as required by the PSA unit. After the CO_2 separation the water and H_2 have to be removed from the CH_4 rich flow. In this case as in the previous one the dryer is located after the separation to reduce the passing mass flow. For the H_2 removal a membrane is used, on this unit a sensitivity analysis on molar stage cut and pressure ratio was made with the same model as for the analysis of the CO_2 membrane case.

The final compression and cooling stages are needed to reach the pressure and temperature for the injection.

It is interesting to notice that in this case the total compression energy required to compress the methane from 1 bar to 60 bar is lower that in the membrane case. In both cases a double compression take place, from 1 bar to 30 bar and from 30 bar to 60 bar in the membrane case, and from 1 to 9 bar and from 8,5 to 60 bar in the PSA case. But in the membrane case the first compression that involves all the mass flow has a higher pressure ratio than in the PSA case (thus it requires more power). Another reason is that in the PSA case the pressure ratio for operation is more close to the ideal ratio (the square root of 60 bar) than in the case of membrane, hence this reduces more the required power.

The captured CO_2 treatments are different in this case. Since the CO_2 rich stream is removed at 0,1 bar the power needed to compress it to 75 bar is extremely high and technically very difficult. Hence is not really possible to implement CO_2 storage connected to a VPSA CO_2 separation system. The hydrocarbon content of the CO_2 rich stream is combusted in a reactor with air and the heat is recovered in the reactor and in the following cooler. After that the CO_2 is discharged to the atmosphere.

All the results for each element of the section are reported in the appendix E.

5.2.1 First Compressor

The syngas from the previous section is at almost atmospheric pressure and must be compressed to 8,5 bars. The compression is performed with a three-stage compressor with three intercoolers that keep the outlet temperature at 50°C. The compression process occurs with an isentropic efficiency of 76% and a mechanical efficiency of

99%. During this step part of the water content is removed. The following table reports the power demand for the compressor. The complete results are in appendix E.1

5.2.2 PSA unit

For a continuous SNG-production four absorbers are used, they work sequentially. They are filled with the carbon molecular sieve (CMS) because it results in an higher CH4 recovery than the silica gel or zeolite (Grande C., 2007) (Pilarczyk E., 1987) (Cavenati, et al., 2005). In order to obtain high performance this PSA cycle works between 9 bar and 0,1 bar (provided from the vacuum pump). In those systems the methane purity can be adjusted from 91% to 97% (Pilarczyk E., 1987). Thanks to the multi bed configuration it is possible to achieve a recovery around 95% (Hans-P. RIQUARTS, 1985), (Pilarczyk E., 1987).

Table 5.4 PSA unit performance

Adsorption medium	Carbon molecular sieve 3K (Tacheda)
higher pressure level	$9\ [bar]$
lower pressure level	$0{,}1\ [bar]$
CH_4 Recovery	$95\ \%$
CH_4 Purity (in the outlet stream)	$91\% \div 97\%$

5.2.3 Vacuum pump

To implement the adsorption cycle a blow pressure of 0,1 bar is necessary. The vacuum pump achieves this pressure level to take the CO_2 rich stream out from the PSA beds. It is a five stages unit with four intercoolers, it is a special equipment because of the high mass flow treated and the high pressure ratio needed.

The overall operating data of the vacuum pump are shown in the appendix E.3.

5.2.4 H_2 separation

This step is operated by a polymeric membrane, which is a common solution for H_2 separation. Also in this case an analysis was performed to find the better parameters for the membrane. It was an important optimization because a wrong choice of pressure ratio and molar stage cut of the membrane can compromise the performance of the whole system, particularly for the recovery.

The properties of the membrane are in the next table.

Table 5.5 H2 separation membrane properties

Thickness (Å)	*1000*
Permeability CO_2 [barrer]	*1120*
Permeability H_2 [barrer]	*2050*
Permeability CH_4, H_2O [barrer]	*160*
Permeability N_2,CO [barrer]	*240*

The H_2 stream separated from the SNG is recirculated to the methanation step of the process.

5.2.5 Final compressor and cooler

After the separation operations the SNG reaches the required composition and only a final compression and the final cooling are necessary to reach the pipeline injection conditions. The compression is effectuated in a three-stage compressor with two intercoolers, the SNG leaves the compressor at around 108 °C to be definitely cooled down to 20°C in the following cooler. The overall operating data are in appendix E.4

5.2.6 CO_2 captured treatments

In this case the CO_2 treatments consist only in the combustion of the remaining hydrocarbons and the recovery of the available heat. In this case we do not need combustion with pure oxygen and we can use normal air. The combustion occurs at 600 °C and atmospheric pressure and since the CH_4 content is not so high a catalytic reactor was used for the combustion. In the following heat exchangers the CO_2 rich stream is cooled down from 600 °C to around 70 °C before to be delivered in the atmosphere.

The appendix E.5 reports the available energies in the processes.

5.2.7 Analysis and results

In this case the analysis of the system was relatively straightforward and limited to the definition of the H_2 removal membrane parameters. The pressure ratio considered are from 0,15 to 0,2 in six steps. The molar stage cut varies from 0,1 to 0,2 in six steps too. All the proposed solution satisfy the WI , CO_2 content and CH_4 recovery specification, the selected one was that with the higher recovery. As in the previous case a low pressure ratio ensures good performance and since the H_2 fraction is already quite low a MSC of 0,1 represent the best solution (is difficult to realize a membrane with a lower MSC).

However also in this case the influence of the pressure ratio was limited hence a value from 0,17 to 0,15 does not give real difference in the performance.

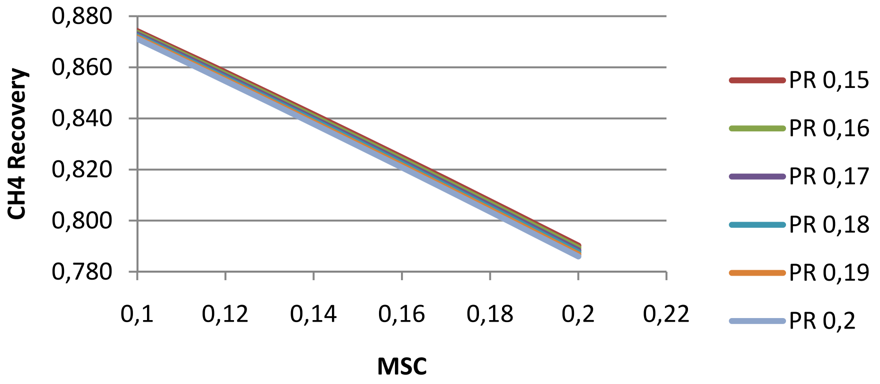


Figure 5.12 Variation of the CH_4 recovery (of the whole section) with the MSC and Pressure ratio

The following table resumes the performance of the gas upgrade section operating with PSA separation.

Table 5.6 Overall gas upgrade section performance

CH_4 Recovery	87,4 %
Wobbe index	13,83 $[kWh/m3]$
CO_2 fraction	2,21 %

The appendix E.6 contains the result of calculation for the H_2 membrane

5.2.8 Energy consumption of each elements

The appendix E.7 reports all the power and heat demand of the system, the total power demand for the gas upgrade section operating with membrane separation is:

Total power consumption: 2750 [kW]

5.3 Framework of the gas-upgrade section with MEA separation

The gas upgrade section in the MEA case in described in Figure 3a in Appendix A. The description is based on that scheme.

As shown in the scheme a blower is placed before the MEA unit to overcome the pressure drop in the separation unit, it is followed by a cooler needed to decrease the temperature to 40 °C before inlet in the MEA unit.

The separation unit is followed by the equipment for the water removal (the same dryer used in all the cases) and a membrane to remove the excess of H_2 and reach the required composition. A compression is needed before this section to provide the necessary pressure level to the membrane. The final stages with compression to 60 bar and cooling to 20 °C is present as for the other process configurations considered.

This separation technology is favourable for downstream storage of the separated CO_2, and it is also one of the easiest processes for CO_2 captured treatment investigated within the framework of this thesis. This is because the CO_2 separated is almost pure and there are no methane or hydrogen compounds that must be combusted. Hence the CO_2 flow can be directly compressed condensed and pumped to 120 bar.

The appendix F reports all the results.

5.3.1 Blower and first coolers

These equipment components are needed only to overcome the pressure drop in the MEA unit and restore the right temperature in the inlet of the separation unit. Their energy demands are reported in appendix F.1

5.3.2 MEA separation unit

This unit performs a separation of the 95% of the CO_2 in the stream but its major advantage is that almost all the methane is recovered in this phase, in fact it does not react with the amine and it is not removed from the main stream. The unit required heat for the reboiler, at around 115 °C. In addition, cooling is required in the condenser and in the amine cooler, whereas the power consumption is negligible.

The following table shows the performance of the MEA separation unit. The whole results are reported in the appendix F.2

Table 5.7 Key performance data for the MEA separation unit

CO_2 separation efficiency	*95%*
CH_4 Recovery	*99,99%*

5.3.3 Intermediate compression

This stage is needed to increase the pressure of the methane rich flow to the inlet pressure of the membrane, 9 bar. It is placed before the dryer because during the compression the condensate water is separated, this reduces the duty of the downstream dryer. The compressor data are shown in the appendix F.3.

5.3.4 H_2 separation membrane

Also in this case the H_2 separation is operated by a polymeric membrane, it is a common solution for H_2 separation. A sensitivity analysis on the MSC and pressure ration of the membrane was performed to study their influence on the performance of the whole section, mainly on the recovery value. Also in this case the membrane works with an inlet pressure of 9 bar as in the PSA case to limit the influence of this step in the comparison.

The properties of the membrane are listed in the next table.

Table 5.8 H_2 separation membrane properties

Thickness (Å)	*1000*
Permeability CO_2 [barrer]	*1120*
Permeability H_2 [barrer]	*2050*
Permeability CH_4, H_2O [barrer]	*160*
Permeability N_2,CO [barrer]	*240*

The H_2 stream separated from the SNG is recirculated to the methanation step of the process.

5.3.5 Final compressor and cooler

The last step of the upgrade process is again the SNG compression and cooling to the gas grid conditions. The compressor is a three-stage compressor with two intercoolers, the SNG leaves the compressor at around 107 °C to be definitely cooled down to 20°C in the aftercooler. Appendix F.4 reports the energy demand for the compressor and the cooler.

5.3.6 CO_2 treatments

In this case the CO_2 stream is almost pure and it does not contain any CH_4 or H_2, hence it is possible to inject the CO_2 into the pipeline without any combustion beforehand. The treatment steps are only the compression to 75,5 bar, the condensation and the pumping to 120 bar. The main power demand is required in the compressor while the pump has a limited power demand The appendix F.5 reports the data about the processes involved.

5.3.7 Analysis and results

The analysis of the MEA system as well as that for the PSA system was simpler than for the membrane based process and limited to the definition of the H_2 removal membrane parameters.

The pressure ratio considered are from 0,15 to 0,2 in six steps while the molar stage cut varies from 0,16 to 0,3 in eight steps. All the solutions found satisfied the WI value required (13,6 kWh/m^3) while the CO_2 content limitation was not always respected. Figure 5.14 shows the CO_2 content for different cases.

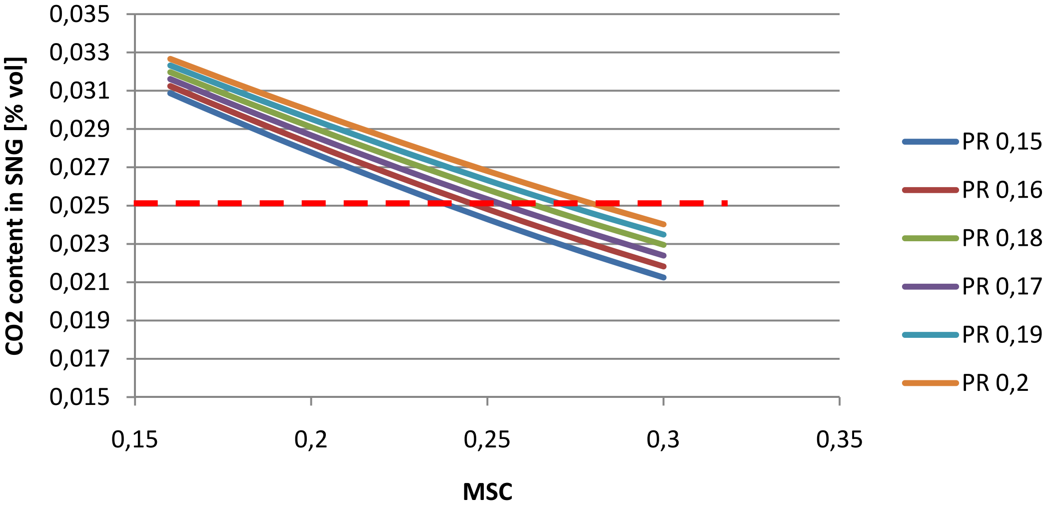


Figure 5.14 Variation of the CO_2 content in the SNG with the MSC and pressure ratio of the H_2 separation membrane

Not all the solutions respects the maximum required value of 2,5%, it is evident that a lower pressure ratio has a relevant influence on the CO_2 in the SNG gas, thus low pressure ratio will be preferred if possible.

In the CH_4 recovery the influence of the pressure ratio is not so pronounced but that of MSC is more clear, the next graph reports the recovery rates obtained from the analysis.

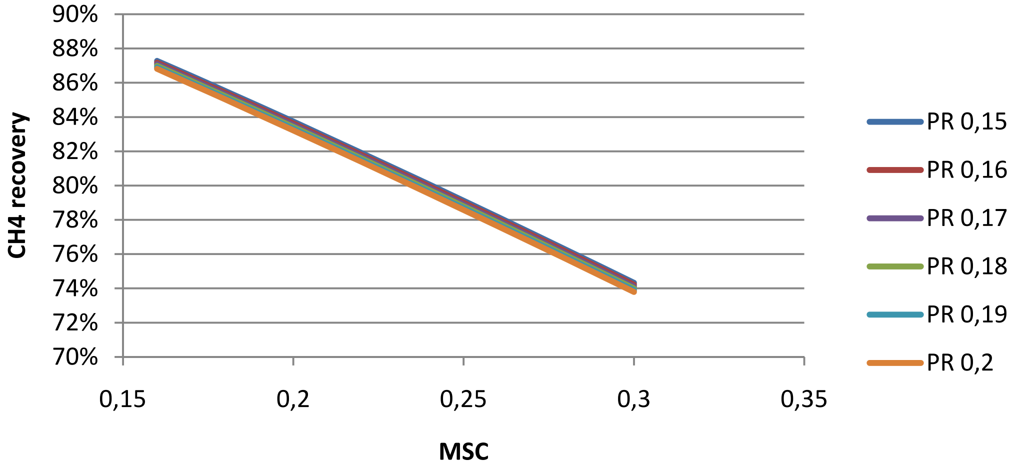


Figure 5.15 Variation of the CH_4 Recovery of the system with the MSC and pressure ratio of the H_2 separation membrane

The maximum recovery obtainable is 87% with a pressure ratio of 0,15 and a molar stage cut of 0,15 as well. But in this condition the CO_2 content in the SNG is too high hence the solution characterized in the following table was selected.

Table 5.9 Overall performance of gas upgrade section operating with MEA separation

CH_4 Recovery	80,04 %
Wobbe index	13,83 $[kWh/m3]$
CO_2 fraction	2,21 %

The appendix F.6 reports the whole results for the H_2 membrane.

This solution achieves more or less the same WI and CO_2 content as the PSA process (this means more or less the same SNG composition) but with a lower recovery. Furthermore, the MEA system offers the possibilities of CO_2 storage hence the choice of the best system cannot be made just on performance indicators.

5.3.8 Energy consumption of all process components

The appendix F.7 reports all the power and heat demand of the system, the total power demand for the gas upgrade section operating with membrane separation is:

Total power consumption: 2700 [kW]

5.4 Performance comparison

All the systems are able to perform the required gas upgrade, the first major difference between the process configurations considered is the degree of CH_4 recovery, the results were:

Table 5.10 Recovery comparison

Recovery Membrane system	*90,78 %*
Recovery PSA system	*87,4 %*
Recovery MEA system	*80,0 %*

The system that achieves the best recovery is the membrane, but it requires also the highest power to perform the separation, around 5 MW whereas the other two systems consume around 2,7 MW. The MEA system has also a high heat consumption, more than 11 MW at 200 °C in the reboiler, hence the PSA system results as the more efficient in energy consumption.

A negative aspect of the PSA system is that in not really possible to have a CO_2 storage, hence it will result in an high cost due to the CO_2 emissions fee.

6 Pinch Analysis

From previous process studies at the Division of Heat and Power Technology, data about all the relevant streams in the rest of the SNG production plant were known, hence it was possible to perform a pinch analysis of the whole system for each gas upgrade solution. To make the calculations the Pro_Pi software was used, it provided the GCC. Another objective of the pinch analysis was to estimate the potential for electric power production using excess heat from the process. The estimation was made by first estimating the theoretical potential by calculation of the graphical area delimited by the Carnot based GCC curve, and then correcting the number obtained using a Carnot global efficiency of 0,73. The potential for electricity that can be sold to the grid was calculated by subtracting the electricity consumption of the gas upgrade section and of the rest of the plant from the power production potential.

The electricity consumption of the rest of the plant was estimated at 2% of the thermal input of the gasifier 100 MW (Steinwall, 2002) thus the power consumption is 2 MW.

The following pages report for each technology the GCCs and a table with the electricity balance. The streams involved in the calculation are reported in the appendix B.1, B.2, B.3

6.1 Electricity production

The electricity produced was estimated with the method explained in the section (3.2), hence it mainly depends on the heat available from the SNG production. From the electricity produced value was possible to estimate the Turbine size and the steam condenser size. The electricity sold depends of course also on the electricity used inside the SNG production. For each case the results are presented in the following tables.

Table 6.1 Electricity production for the membrane case

Power available from the Carnot GCC	14667 [kW]
Carnot Global efficiency	0,73
Electricity produced	10707[kW]
Electricity required from gas upgrade section	5653 [kW]
Electricity required from the rest of the plant	2000 [kW]
Total electricity required from the plant	7653 [kW]
Electricity to sell	3054 [kW]
Turbine size	11000 [kW]

Table 6.2 Electricity production for the PSA case

Power available from the Carnot GCC	11940 [kW]
Carnot Global efficiency	0,73
Electricity produced	8716 [kW]
Electricity required from gas upgrade section	2750 [kW]
Electricity required from the rest of the plant	2000 [kW]
Total electricity required from the plant	4750 [kW]
Electricity to sell	3966 [kW]
Turbine size	9000 [kW]

Table 6.3 Electricity production for the MEA case

Power available from the Carnot GCC	*8078 [kW]*
Carnot Global efficiency	*0,73*
Electricity produced	*5897 [kW]*
Electricity required from gas upgrade section	*2700 [kW]*
Electricity required from the rest of the plant	*2000 [kW]*
Total electricity required from the plant	*4700 [kW]*
Electricity to sell	*1200 [kW]*
Turbine size	*6000 [kW]*

As expected the MEA case has the lowest Electricity production and potential for electricity export to the grid. The results of the PSA and the membrane cases are similar, the membrane needed more electricity for the gas upgrade section but it also has a higher electricity production potential in the turbine, hence the net electricity sales output results are similar.

Considering only the SNG produced (hence the CH_4 recovery) and the electricity produced the MEA system is the least competitive because it has a lower recovery and a lower electricity production, but it allows to store the CO_2 with a simpler (and cheaper) system compared with the membrane. The PSA has a number of benefits but it has the handicap of being essentially incompatible with CO_2 storage, and is unlikely to be competitive if high fee levels are levied on CO_2 emissions in the future.

6.2 Results

The streams involved in the pinch analysis of the SNG production are reported in the Appendix B Table 1b, 2b, and 3b for membrane, PSA and MEA case.

The Grand Composite curves obtained from the previous data are shown in the following figures. The GCC for the membrane and the PSA cases have similar shapes, because neither of the two processes require heat and the difference in the curves are due to the different hot streams of the compressors and the coolers. Otherwise in the GCC of the MEA it is possible to check the heat required for the separation process at around 115 °C.

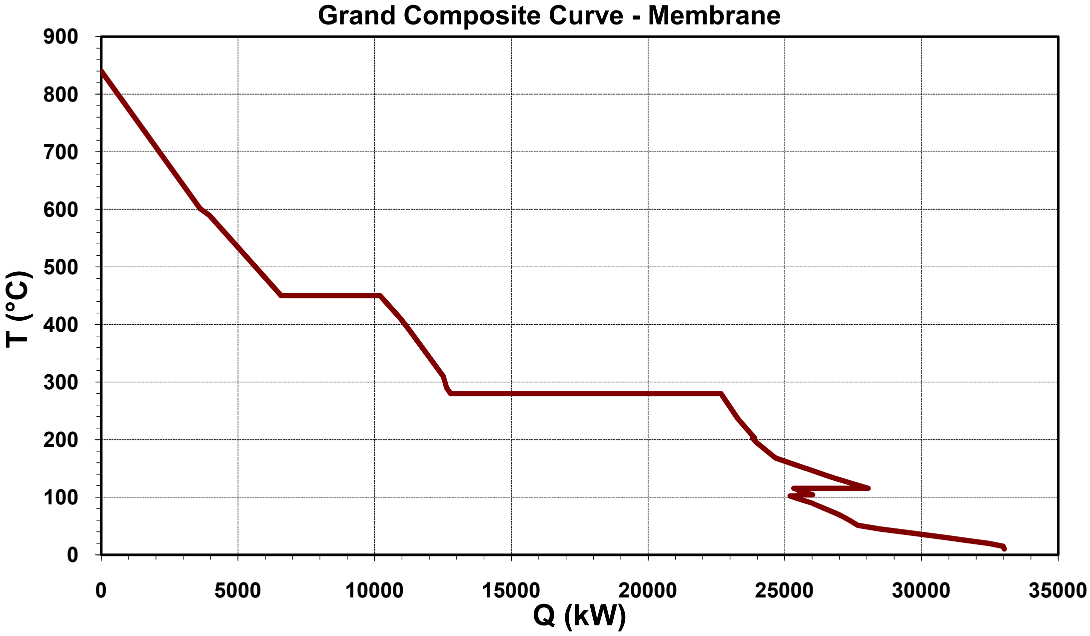


Figure 6.1 Grand Composite Curve for the SNG production process operating with CO_2 Membrane separation

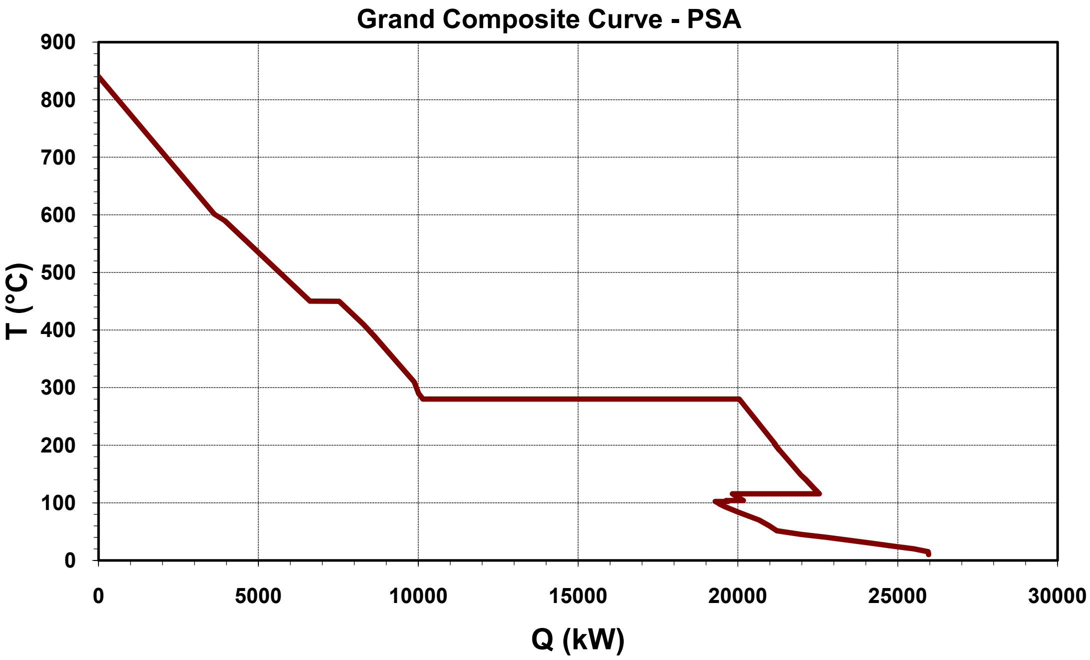


Figura 7.2 Grand Composite Curve for the SNG production process operating with PSA separation

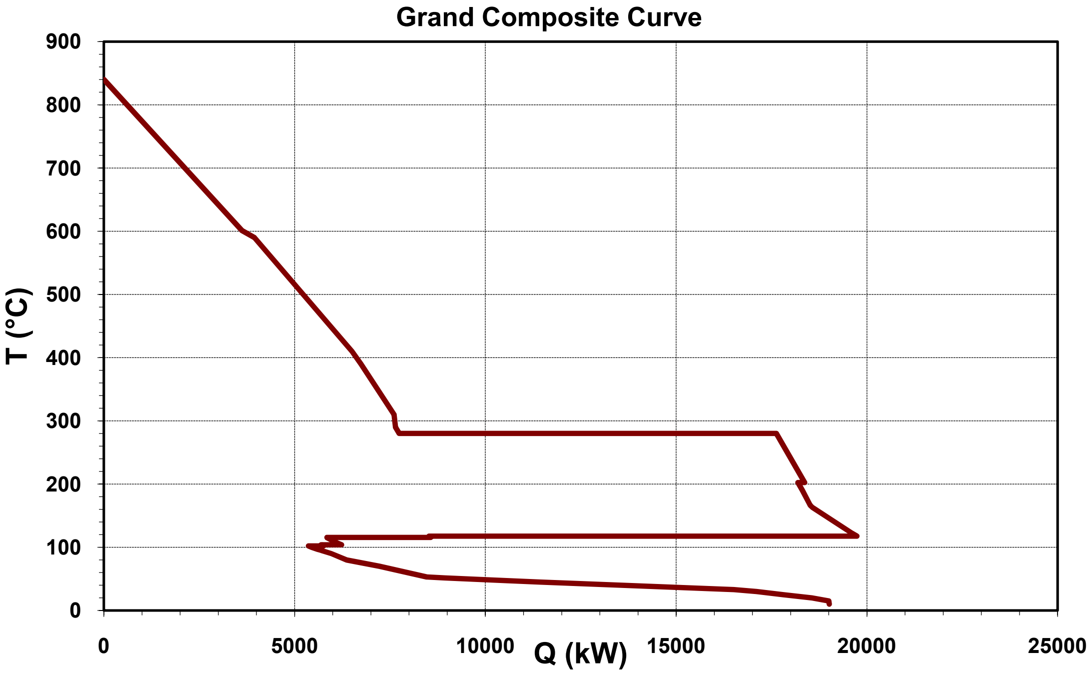


Figura 8.3 Grand Composite Curve for the SNG production process operating with MEA separation

The power produced in the plant was calculated from the Carnot Grand Composite Curve. They show the heat available in the process with the Carnot efficiency correspondent to the temperature at which the heat is available. By integration of this the potential power obtainable is known, and by using the Global Carnot Efficiency it possible to estimate a realistic potential for power export. The Carnot GCCs are shown in the following figures.

Figure 9.4 Carnot Grand Composite Curve for the Membrane case

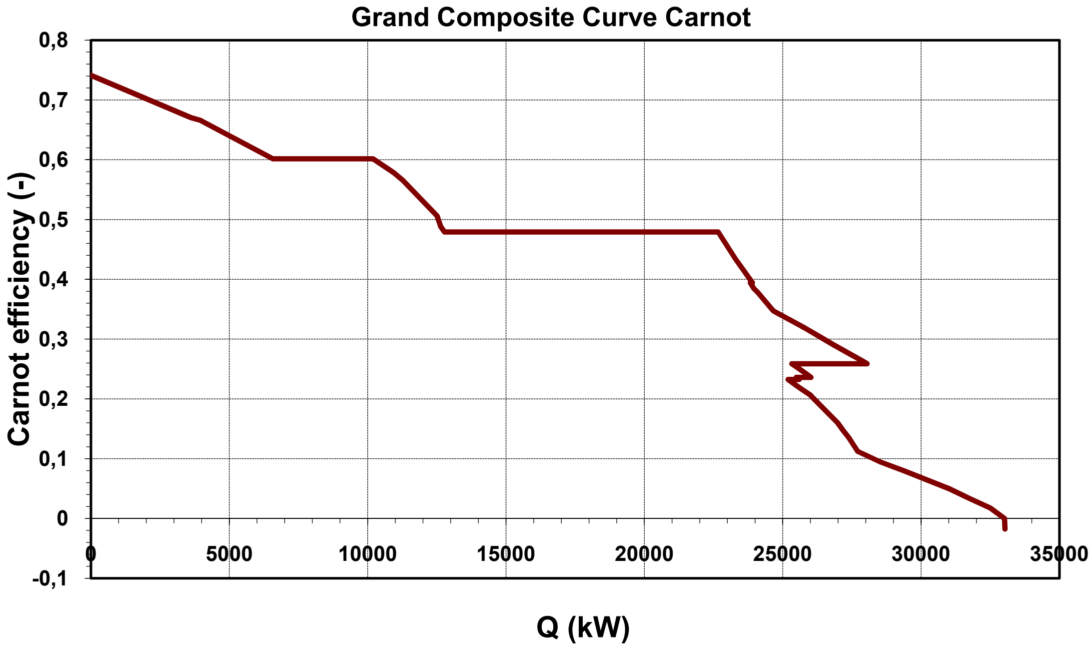


Figure 10.5 Carnot Grand Composite Curve for the PSA case

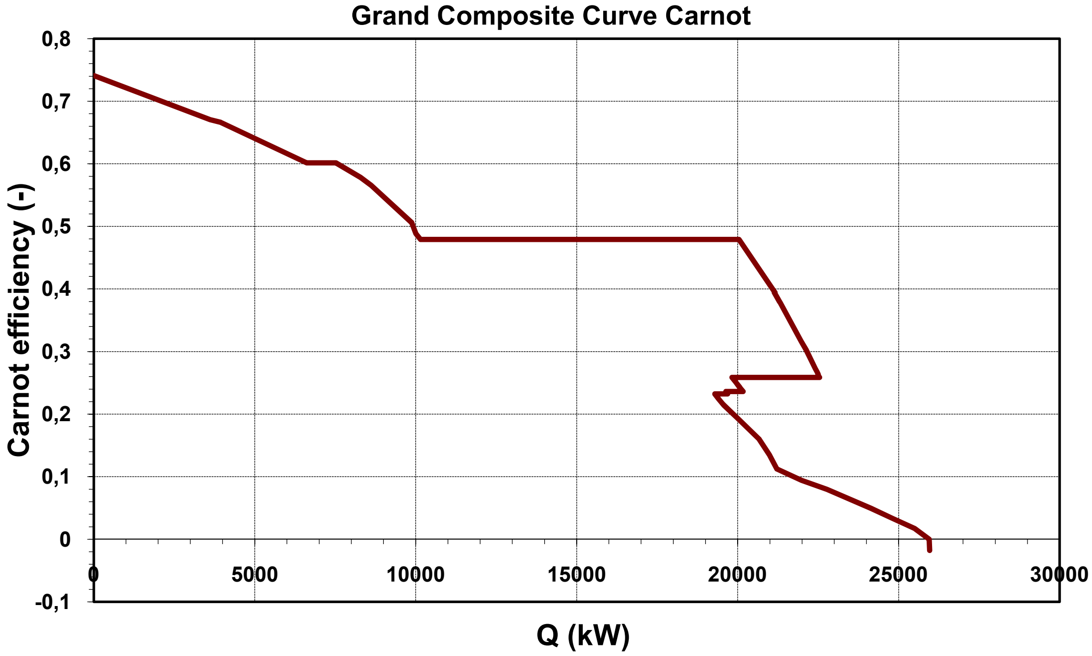
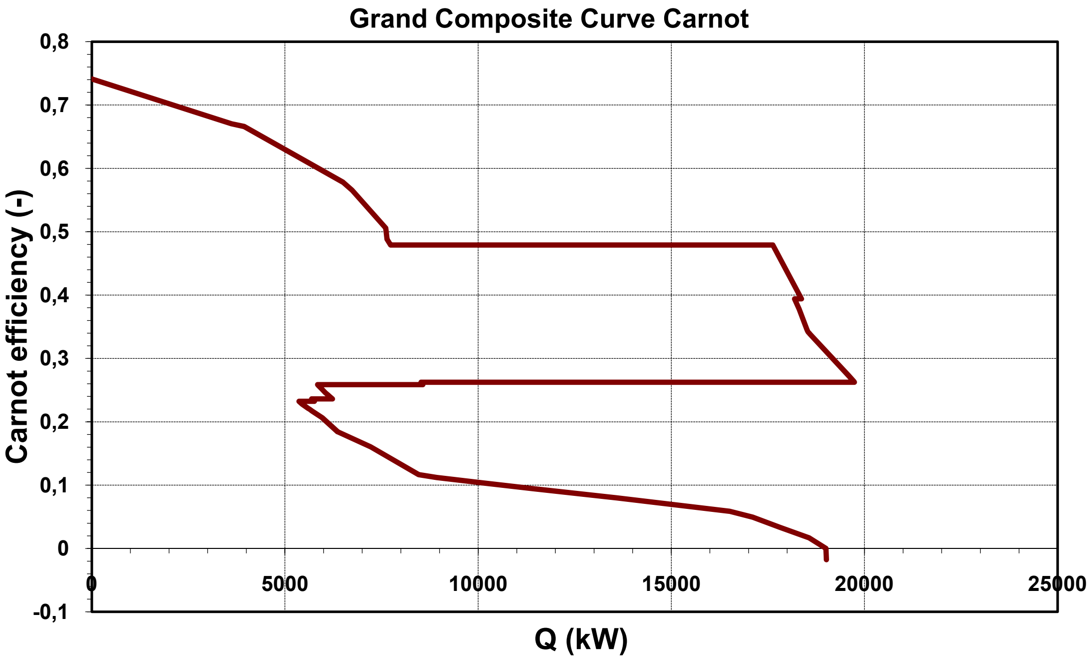


Figure 11.6 Carnot Grand Composite Curve for the MEA case



As the figures shown the MEA process has a completely different GCC. This is because of the heat required in the reboiler, more than 11 MW at 115 °C. This heat is represented by the horizontal line at 115 °C present in both the normal GCC and the Carnot GCC for the MEA case. The result of this is that the area of the Carnot GCC is smaller and it results in a lower potential power obtainable.

6.3 Electricity balance

By combining the power consumption data and the data from pinch analysis we can calculate the potential for power sale to the electricity grid, which will result in a revenue for the economic evaluation. Table 6.4 reports the electricity balance and the following figure shows a comparison between the three different cases.

Table 6.2 Electricity balance of the whole plant

	Membrane	*PSA*	*MEA*
Electricity consumption [MW]	*7,7*	*4,7*	*4,70*
Electricity production [MW]	*10,7*	*8,7*	*5,9*
Electricity sale [MW]	*3*	*4*	*1,2*

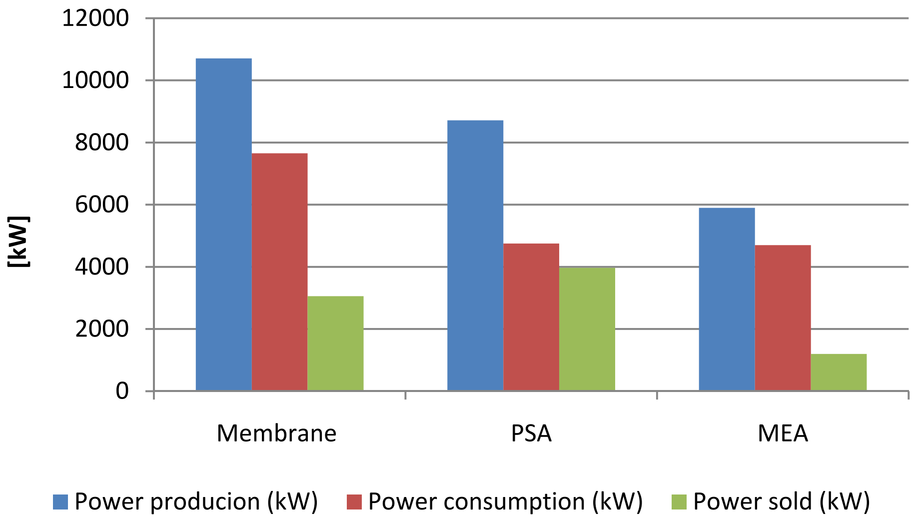


Figure 6.7 Comparison between the electricity balances of the three cases

As the graph show the PSA has the best performance in the in the electricity production.

7 Economic evaluation

The economic performance of the different configurations is evaluated here. To perform the calculations all the criteria discussed in Section 3.3 are used. The costs were calculated for the gas upgrade section and an annuity method was used to incorporate the investment cost and the process operating cost. Some assumption were made about manufacturing cost and other cost, because the aim of this assessment is compare the configuration and not give absolutes values about their economic performance. Hence costs that are common in all the configurations were not included in the calculations.

The annual cost was calculated including the annual capital cost, the annual maintenance cost and the annual energy cost of the section (electricity consumed in the gas upgrade section).

The revenues of the system were evaluated on the whole SNG production process, and include the revenues from sales of SNG and electricity as well as revenue from CO_2 storage (calculated as the cost of the CO_2 fee avoided minus the cost for the CO_2 storage). If is not possible to store the CO_2 the CO_2 fee was subtracted to the total revenues of the plant.

7.1 Capital investment

The investment costs were taken from different sources, indicated for each component. The cost were updated using the chemical engineering plant cost index the values used are shown in appendix C.3. We assumed that investment cost of each component is function of scale given by $C/C_0 = (S/S_0)^R$ (Hektor, 2008) where C is the investment cost, S the size and R a dimensionless factor depending on the type of equipment; for general equipment a value of 0,6 was used. In the next section the investment cost for the three cases was calculated.

The equipments evaluated in the capital investment of the section are that present in the flow-sheet schemes (Appendix A.1, A.2, A.3) but for each case the costs of the turbine and for the steam condenser used in the electricity generation were included.

The costs were evaluated for the purchased component including transportation cost but without installation, which was calculated as a percentage of the direct equipment cost.

7.1.1 Investment costs

In this section all the components of the gas upgrade section were evaluated, in the appendix G.1, G.2 and G.3 the costs of the purchased equipments are reported. In all the cases a considerable part of the equipment cost is due to the turbine and to compressors. In the PSA and MEA cases the compressors cost is lower than in the membranes one, because smaller compressors unit are used. The separation units are more expensive for the MEA and the PSA cases while the membranes are cheaper but this system requires more equipments for the CO_2 treatments and this increases its investment cost.

From the cost of the delivered equipment the cost of the total capital investmen has been calculated, with the method explained in the section 3.3.1

The results are reported in the following table and the whole calculation in the appendix G.1, G.2, G.3, G.4, G.5, G.6 for each case.

Table 7.1 Total capital investment and annual investment for the three cases

	Membrane	*PSA*	*MEA*
Total capital investment [M€/y]	*59,9361*	*50,1913*	*57,4404*
Annual capital investment [M€/y]	***5,9936***	***5,0191***	***5,7440***
Annual maintenance costs [M€/y]	***2,3974***	***2,0077***	***2,2976***

The PSA process has the lowest capital investment, with an annual capital investment of 5 M€/y while the other two solutions are slightly more expensive, around 5,8 M€/y.

7.1.2 Considerations about equipment costs

The next figure shows the equipment costs in the three configurations. It is representative of the difference between the different frameworks. The PSA achieved the lowest capital investment, only because it does not have a CO_2 treatment section. In fact the cost for the power production equipment and for the SNG upgrading are relevant. In a system based on PSA technology, which is compatible with CO_2 storage the total capital investment would most likely be similar to that of the membrane solution.

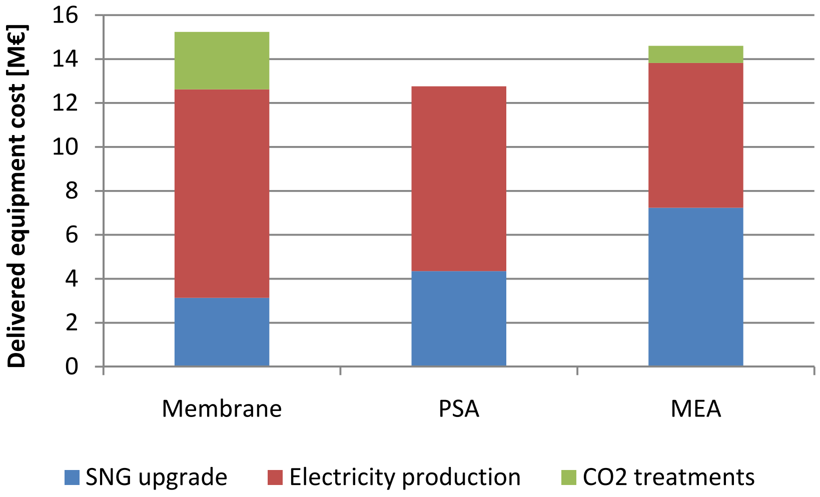


Figure 7.1 Investment costs divided by process section

7.2 Production costs

The production cost is mainly due to the energy needed in the processes. The cost depends on the electricity cost that it includes already the CO_2 emissions fee due to the power generation emissions. The appendixes G.7, G.8, G.9 report the calculation for the production costs in all the three configurations. The results are shown in the following table 7.2

Table 7.2 Electricity cost for the gas upgrade section in the three cases

Electricity cost [M€/y]	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
Membrane	*2,306*	*3,347*	*3,211*	*3,799*
PSA	*1,122*	*1,628*	*1,562*	*1,848*
MEA	*1,1016*	*1,598*	*1,534*	*1,814*

Between the Membrane and the PSA systems that requires only power the PSA achieves the specified separation at around half the cost of the other. The cost is comparable with that of the MEA, this because these two systems perform a compression of the gas, in two similar steps and it is more efficient than that of the membrane system.

7.3 Revenues

The revenues of the plant were calculated considering the whole production and the CO_2 stored.

The main product is the SNG and it generates the main revenue but depending on the scenario the revenue related to the CO_2 captured can have a great importance. Since the CO_2 emissions or storage cost concern the whole plant as the revenues from SNG and electricity they were considered in the revenues using equations 12 and 13.The revenues for the CO2 emission/storage are calculated as explained in the section.
The calculations are reported in the appendixes G.10, G.11, G.12, and a summary of the results in the following table 7.3

Table 7.3 Revenues of the whole plant in the three different cases

Total revenue	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
Membrane	*19,135*	*26,341*	*34,307*	*54,907*
PSA	*15,997*	*16,834*	*24,881*	*25,218*
MEA	*16,687*	*22,560*	*29,689*	*47,890*

Of the three product the revenue related to SNG if of course the most important. In all the three configurations the SNG revenue is almost the same since all of them perform good methane recovery, the membrane system performs the best recovery and thus an higher revenue, but also the other configuration achieve good results.

The revenues data show the importance of the CO_2 storage. In case of high charges on CO_2 emission, it is essential to adopt a process that enable CO_2 separation and storage since the cost due to fee on CO_2 delivered in the atmosphere would be too high. In fact in the scenarios 1 and 3 where the CO_2 charges are low the PSA configuration remains competitive, while with an higher CO_2 charges level (scenarios 2 and 4) the costs associated with CO_2 emissions are prohibitive.

On the other hand the membrane and the MEA system increase their revenues if the CO_2 emission charge increases. This because the not-payed CO_2 fee results in increasing revenues for this configurations.

7.4 Results of economic assessment

In order to compare the different solution a parameter was defined, it is the difference between the total revenue of the plant and the total annual cost of gas upgrade section.

This value called *delta* is a economic performance indicator for each configuration, because it considers the difference between all the revenues and costs that can vary by changing the gas upgrade section technology. By considering the values of *delta* the most attractive gas upgrade process configuration was identified for each scenario. The *delta* values are reported in the next tables for all the configurations and the scenarios.

Table 7.4 Economic performance of the membrane configuration in the different scenarios

Membrane	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
Annual cost [M€/y]	*10,697*	*11,738*	*11,602*	*12,190*
Annual revenue [M€/y]	*19,135*	*26,341*	*34,307*	*54,907*
Delta [M€/y]	*8,438*	*14,603*	*22,705*	*42,717*

Table 7.5 Economic performance of the PSA configuration in the different scenarios

PSA	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
Annual cost [M€/y]	*8,149*	*8,655*	*8,589*	*8,875*
Annual revenue [M€/y]	*15,997*	*16,834*	*24,881*	*25,218*

Delta [M€/y]	*7,848*	*8,179*	*16,292*	*16,343*

Table 7.6 Economic performance of the MEA configuration in the different scenarios

MEA	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
Annual cost [M€/y]	*9,143*	*9,639*	*9,575*	*9,855*
Annual revenue [M€/y]	*16,687*	*22,560*	*29,689*	*47,890*
Delta [M€/y]	*7,544*	*12,921*	*20,115*	*38,035*

The results for the membrane system show that this system provides good revenues from the SNG production because of the high recovery. But it has always an annual cost higher than others. The annual cost is influenced by the high power consumption of this system but it allows to sell a good amount of electricity that compensates for the other high energy costs. Since this system performs the CO_2 storage its economic performance is strongly influenced by the CO_2 emissions fee. In particular the with membrane separation the higher value of CO_2 (mainly because of CO_2 from the combustion of the methane residual) would be emitted in the atmosphere, hence the influence of the CO_2 fee is even stronger.

The PSA system has a different behaviour, it has the simplest equipment and hence the lower annual cost (and the most constant in the different scenarios) but the revenues are often too low to be competitive with the other solutions. It has good revenue due to the SNG production because of its high recovery and it is an intrinsically efficient process but since it is not compatible with CO_2 storage system its performance is inevitably extremely sensitive to the value of the CO_2 emissions fee. In fact in the first scenario, with very low CO_2 charges it is competitive with the others solutions but in the others scenarios it cannot compete. This is extremely indicative of the importance of CO_2 treatments in the next years.

The MEA system offers good economic performance in all the scenarios because of the CO_2 storage operated and the low energy consumption of the system. The revenues due to the SNG production are limited by the lower level of methane recovery achieved, but considering that the annual cost is always lower than in the membrane case (because of the lower power consumption and the cheaper equipment) part of the difference in the revenues is compensated.

The next figure reports the graphs for the annual cost, revenue and delta values.

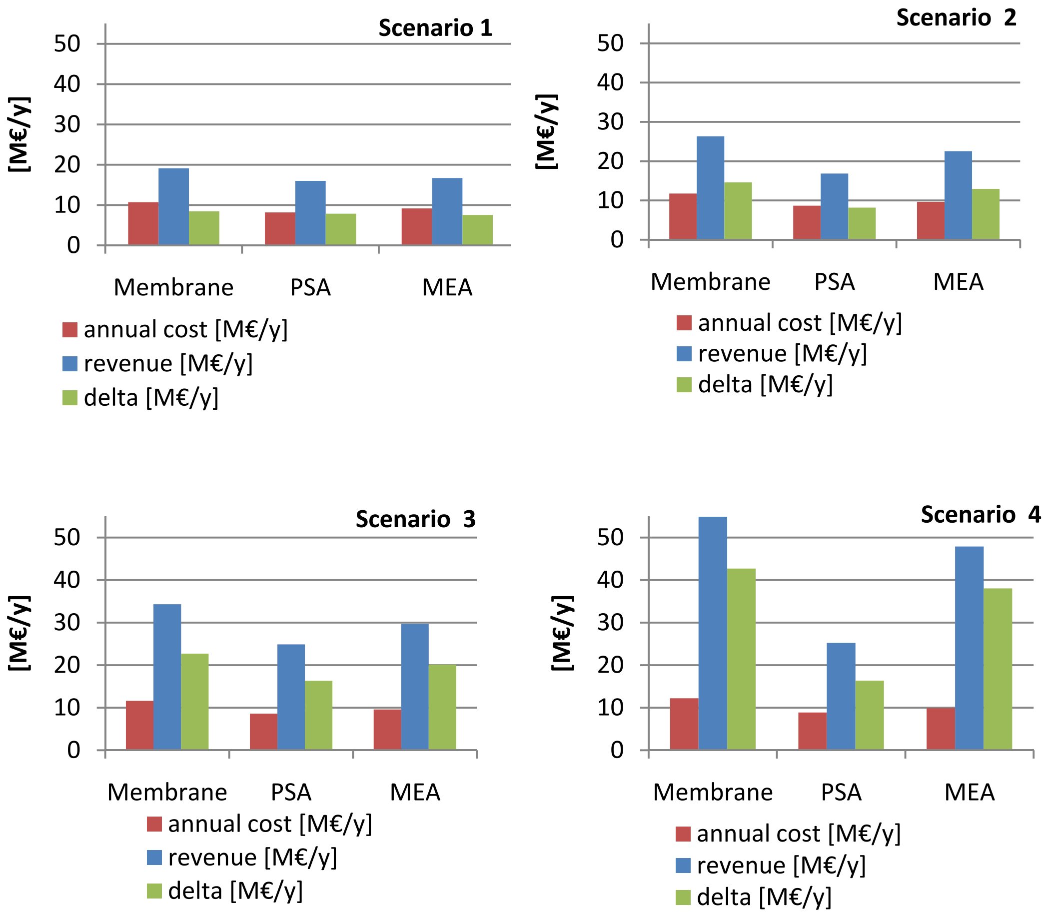


Figure 7.1 Annual cost, revenue and delta value of the three configuration in each scenario.

From these data, considering the *delta* value the solution with the membrane separation gave the highest economic performance in all the scenarios considered.

8 Conclusions

The results of this study include both the upgrade performance and energetic analysis, as well as the economic evaluation.

The energetic evaluation resulted in conclusions that are to some extent controversial to the results of the economic analysis. This is mainly the case for the PSA system, that achieved a high methane recovery, a low power consumption and the higher power production. Without considering the CO_2 storage it is the best solution. The other two solutions make some kind of trade-off between high recovery and high power consumption and low recovery and power consumption.

This indicates that the economic comparison is the best way to compare the different solutions.

The next table shows a brief summary of the performance and the energetic analysis for the three systems.

	Membrane	*PSA*	*MEA*
CH4 Recovery	*90,78 %*	*87,4 %*	*80 %*
SNG production [ton/y]	*34725*	*33650*	*30930*
Power consumption [MW]	*7,7*	*4,7*	*4,70*
Electricity production [MW]	*10,7*	*8,7*	*5,9*
Electricity sale [MW]	*3*	*4*	*1,2*

Table 8.1 SNG production, and electricity balance of the whole plant for each configuration

The results of this study show that the performance levels of each studied technology have a different sensibility to the parameter of the energy market scenarios. Thus the more suitable configuration will depend on the selected scenario and on technical considerations.

By analyzing the annual cost of each configuration, it is evident that there are two major parameters influencing the results. The first one is the framework of the section, thus all the equipments needed to perform the gas upgrade, and the second one is the efficiency of the process. The efficiency includes the power needed in the section and also considers the electricity that can be produced in the process, hence the PSA is more efficient than the MEA because this process has almost the same power consumption but the MEA system requires more heat, which results in a lower electricity production.

From an economic point of view we must consider that in a system that requires to produce more power a bigger equipment is necessary, and the cost for turbo-machines is predominant in the whole capital cost. The membrane requires the larger amount of energy, and it is also the most complex system, with the bigger number of components. The cost of the separation units is however not so high. The PSA process has the lowest equipment cost and is a much simpler process, but it is important to recall that this process does not include CO_2 recovery.

The resulting annual costs are shown in the previous tables. The membrane configuration was the most expensive solution for the overall costs, even though the CO2 separation technology itself is cheapest. This is though counteracted by the expensive aftertreatment costs for the CO_2-rich stream (combustion with pure oxygen)

In each cases the membrane system obtains the best revenues because the higher separation performance which allows an more elevated SNG production.

The electricity revenue resulted not really relevant in the comparison, when the CO_2 charge is high.

By analyzing the revenues of the plant the economic scenario used become determinant, because of the CO_2 emission charge value. This study demonstrate that if an high CO_2 emission charge is previewed a CO_2 storage system is necessary, also is the SNG price would be high. In the PSA case the defined economic evaluation parameter *delta* does not really change value between the scenario 3 and 4, because the high revenue due to the higher SNG price are balanced form the higher CO_2 emissions fee. Besides the MEA and the membrane systems had better revenues if the CO_2 fee increase.

Also if a high CO_2 emission fee is not expected the CO_2 storage system is already a convenient solution both in the short and in the long term as the results for scenarios 1 and 2 demonstrate.

Under these considerations we selected the membrane technology as the most economically robust choice. In the short term it is already competitive, and in the long term it should be the solution with higher performance. The only negative aspect is that it has the largest capital investment. However, if this technology becomes mainstream it can expected that the capital costs will decrease compared to other competing technologies.

If the capital investment is important in the choice of the CO_2 separation technology, the PSA system is a suitable solution in the short term scenarios.

The MEA system achieves consistently good results but it suffers from the low methane recovery performance and thus a lower SNG production level.

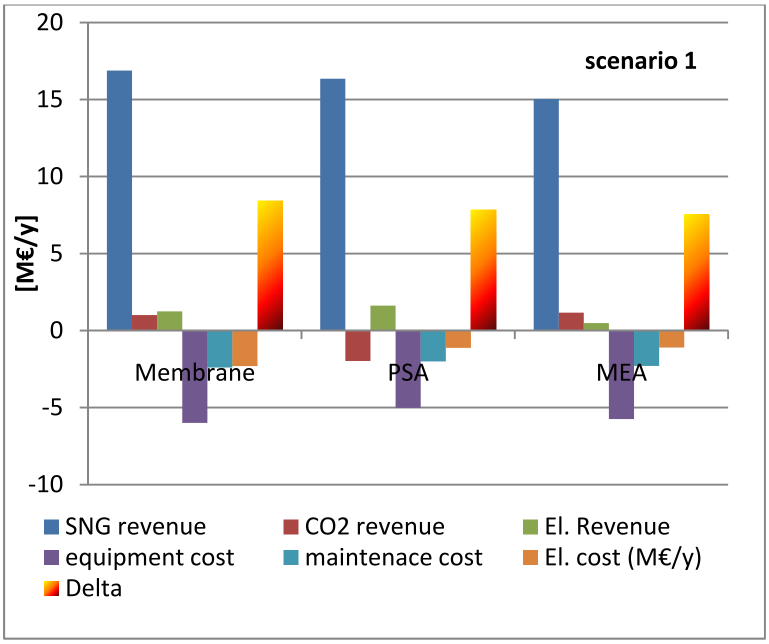


Figure 8.3 Economic performance of the three studied configuration in scenario 1

The result for the first scenario, shows that in the short term with low CO_2 emissions charge the all the three studied configurations are competitive.

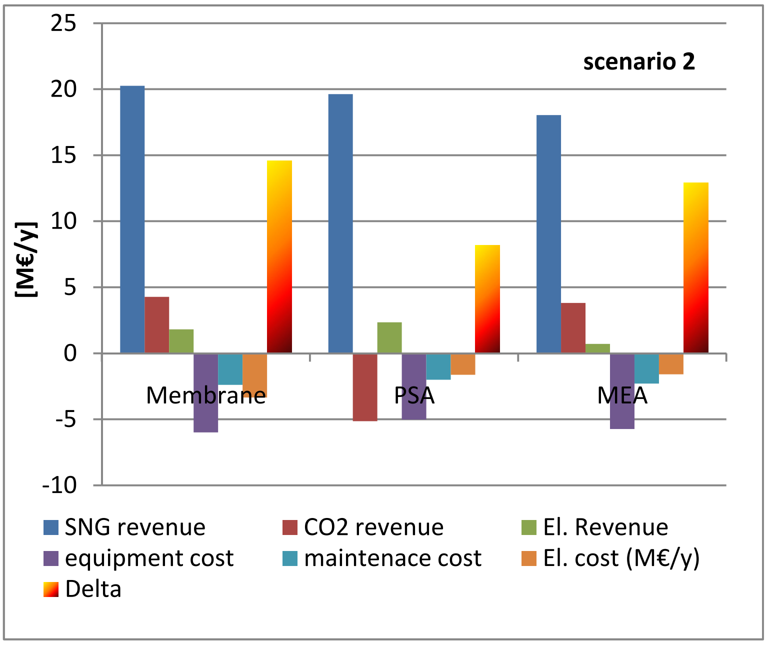


Figure 8.4 Economic performance of the three studied configurations in scenario 2

Increasing only the CO_2 emissions charge the PSA solution does not really improve its performance, and only the membrane and the MEA system are a good choice.

In the long term with higher SNG and electricity prices all the systems increase their revenues.

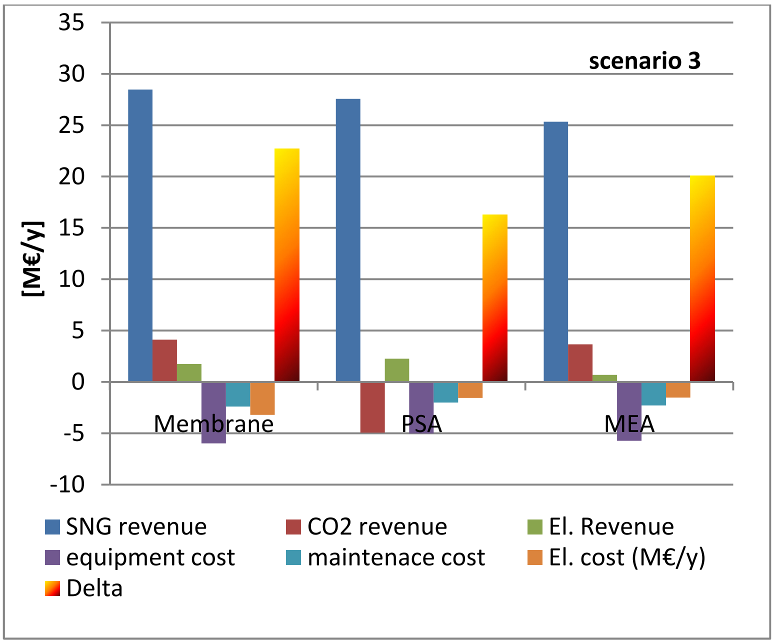


Figure 8.5 Economic performance of the three studied configuration in scenario 3

In the case with the higher level of CO_2 emissions charges and the higher SNG price the membrane technology achieves the best economic performance, and the MEA system can be also considered as a good solution. The configuration without the possibility of downstream CO_2 storage is not competitive at all, compared with the scenario 3 the *delta* value is almost the same also if the revenue increased.

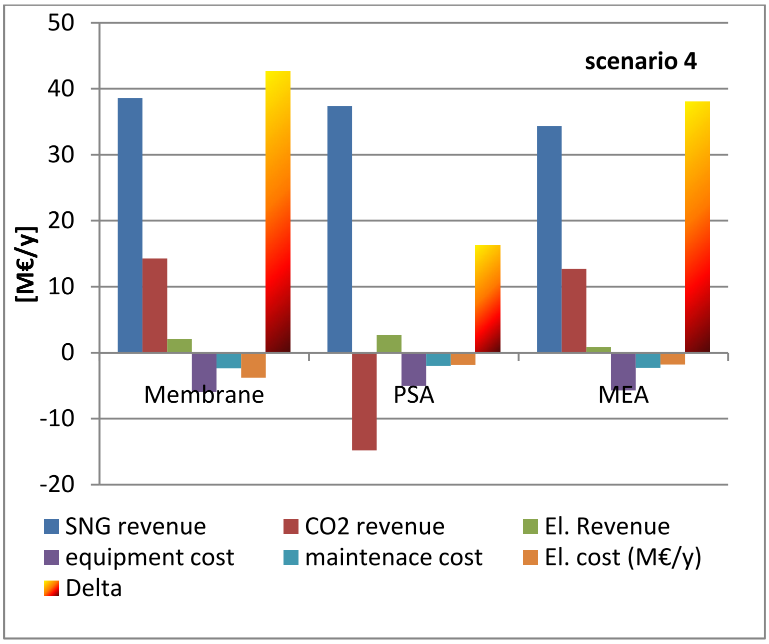


Figure 8.6 Economic performance of the three studied configuration in the scenario 4

For further works the suggestion is to investigate a way to realize a cheaper membrane system, since this technology is not fully developed. Another objective can be to study a PSA configuration operating with a discharge pressure for CO_2 at atmospheric level to enable a CO_2 storage system and make this technology competitive with the others (also if the separation efficiency would be lower).

9 Discussion

An important observation can be made about the MEA system, i.e. that it is less competitive than the membrane but its operating costs are essentially independent of the electricity market scenario. This is due to the fact that the revenues of electricity sale cover almost completely the cost for power consumption. This allows the MEA to be competitive also in scenarios with different electricity prices than that evaluated until now, while the membrane technology is very dependent on it because of its high consumption.

A second observation needs to be made about the assumption used in the study.

The results are valid under the assumptions made in the text, but some details needed to be specified. Particularly in the MEA and in the PSA cases the CH_4 recovery could actually be slightly higher, because the H_2 rich stream from the H_2 membrane, containing a high fraction of CH_4, is not wasted but recirculated to the methanation. Hence the methane contained in the stream is recovered and not wasted. This recirculation would result in a slightly difference in the composition of the input syngas. To evaluate this would require complex calculations and it could result in a not relevant variation of the known composition, hence we decided to neglected it. However this assumption could have introduced some uncertainty especially for the MEA case, where the H_2 membrane is the main cause of reduction of CH_4 recovery.

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APPENDIX A

A.1) Framework of the gas upgrade section operating with membrane separation technology

A.2) Framework of the gas upgrade section operating with PSA separation technology

A.3) Framework of the gas upgrade section operating with MEA separation technology

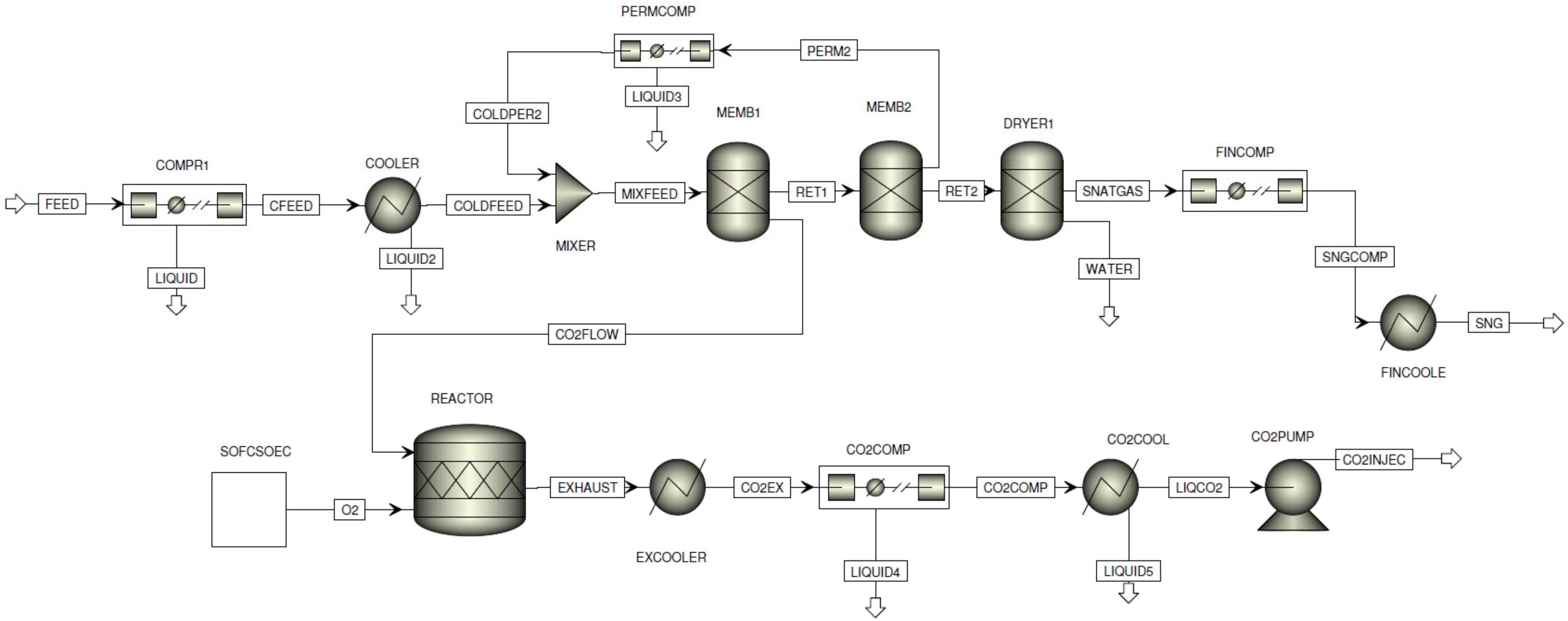

Figure A.1 Framework of the gas upgrade section operating with membrane separation technology

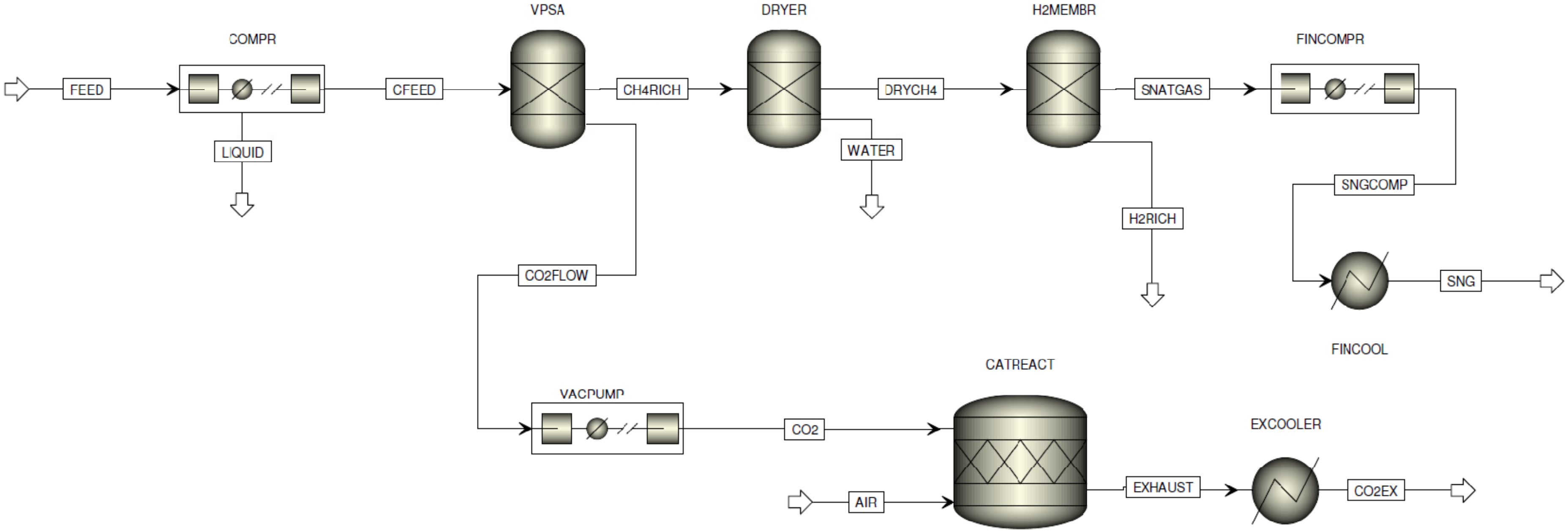

Figure A.2 Framework of the gas upgrade section operating with PSA separation technology

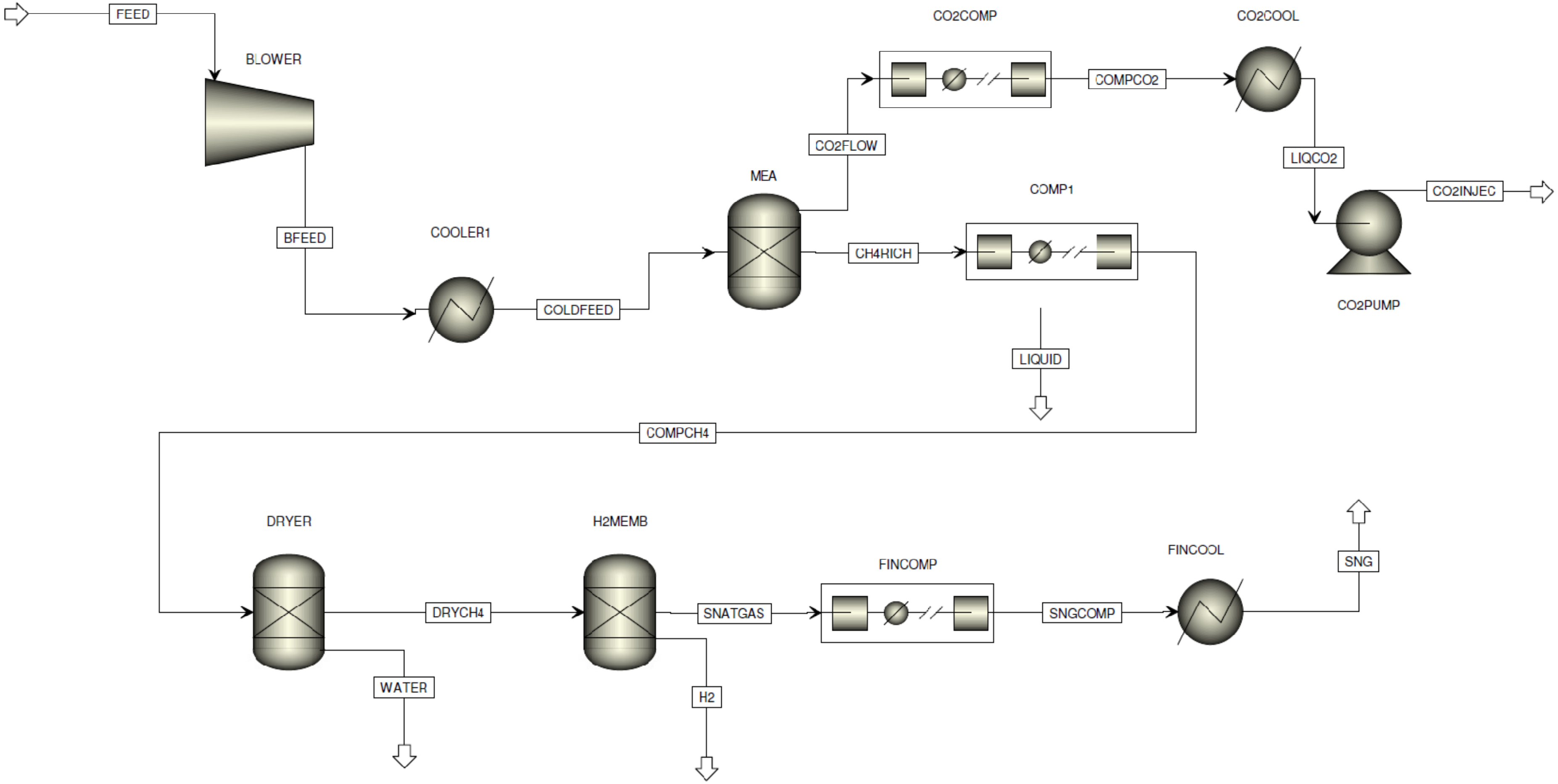

Figure A.3 Framework of the gas upgrade section operating with MEA separation technology

APPENDIX B

B.1)	Pinch analysis of SNG production with membrane CO_2 separation, table of streams
B.2)	Pinch analysis of SNG production with PSA CO_2 separation, table of streams
B.3)	Pinch analysis of SNG production with MEA CO_2 separation, table of streams

Table B.1 Streams involved in the pinch analysis of the SNG production with Membrane CO_2 separation technology

Type	Tstart [°C]	Ttarget [°C]	Q [kW]	ΔT [K]	Comments
Cold	10	113,06	553,7	5	Steam prep gasif - preheat
Cold	113,06	113,07	2722,1	2,5	Steam prep gasif - evap
Cold	113,06	400	672,5	10	Steam prep gasif - supheat
Hot	850	600	3787,1	10	Syngas cooling
Hot	611,22	400	3000	10	Syngas cooling
Hot	400	200	2636,8	10	Syngas cooling
Hot	200	80	1481,4	10	Syngas cooling
Hot	56,408	20	3349,5	5	Scrubbing water recycle cooling
Cold	99,753	99,76	397,2	2,5	Waste water stripper
Hot	99,753	25	314,9	5	Waster water cooling
Cold	15	300	2458,5	10	Syngas heat prior to methanation
Cold	10	101,54	95,3	5	Steam prep methanation - preheat
Cold	101,54	101,55	536,1	2,5	Steam prep methanation - evap
Cold	101,54	300	88,7	10	Steam prep methanation - supheat
Hot	300,01	300	9889,9	20	Methanation 1 heat
Hot	300	54,98	1907,9	10	Syngas cooling
Hot	54,98	30	1184,7	10	Syngas cooling - cond
Hot	97,7	40	384,5	10	Compressor cooling 1
Hot	109	70	250	10	Compressor cooling 2
Hot	143	100	286,7	10	Compressor cooling 3
Hot	177	125	360,5	10	Compressor cooling 4
Hot	205	40	1380	10	Cooler 1
Hot	148,11	50	209,8	10	Perm compress cooling 1
Hot	160,69	50	241,6	10	Perm compress cooling 2
Hot	161,75	40	277,4	10	Perm compress cooling 3
Cold	200	200,01	78	2,5	TEG dryer Rebolier
Hot	75,4	40	104	10	Final compressor cooling 1
Hot	40	20	170	10	Final cooler
Hot	600,01	600	3618	150	Reactor cooling
Hot	600	160	2018	10	Exhaust cooler
Hot	246,41	100	607,9	10	CO_2 compressor cooling 1
Hot	178,1	100	319,5	10	CO_2 compressor cooling 2
Hot	178,41	100	552,7	10	CO_2 compressor cooling 3
Hot	178,26	100	545,4	10	CO_2 compressor cooling 4
Hot	178,45	100	415,8	10	CO_2 compressor cooling 5
Hot	179,45	100	396,5	10	CO_2 compressor cooling 6
Hot	100	25	942,4	10	CO_2 cooler

Table B.2 Streams involved in the pinch analysis of the SNG production with PSA CO_2 separation technology

Type	**Tstart [°C]**	**Ttarget [°C]**	**Q [kW]**	**ΔT [K]**	**Comments**
Cold	10	113,06	553,7	5	Steam prep gasif - preheat
Cold	113,06	113,07	2722,1	2,5	Steam prep gasif - evap
Cold	113,06	400	672,5	10	Steam prep gasif - supheat
Hot	850	600	3787,1	10	Syngas cooling
Hot	611,22	400	3000	10	Syngas cooling
Hot	400	200	2636,8	10	Syngas cooling
Hot	200	80	1481,4	10	Syngas cooling
Hot	56,408	20	3349,5	5	Scrubbing water recycle cooling
Cold	99,753	99,76	397,2	2,5	Waste water stripper
Hot	99,753	25	314,89	5	Waster water cooling
Cold	15	300	2458,5	10	Syngas heat prior to methanation
Cold	10	101,54	95,3	5	Steam prep methanation - preheat
Cold	101,54	101,55	536,1	2,5	Steam prep methanation - evap
Cold	101,54	300	88,7	10	Steam prep methanation - supheat
Hot	300,01	300	9889,9	20	Methanation 1 heat
Hot	300	54,98	1907,9	10	Syngas cooling
Hot	54,98	30	1184,7	10	Syngas cooling - cond
Hot	103,6	50	338,6	10	Compressor cooling 1
Hot	126,5	50	580,3	10	Compressor cooling 2
Hot	126,7	50	596	10	Compressor cooling 3
Cold	200	200,01	18,5	2,5	TEG dryer reboiler
Hot	94	80	40,2	10	Vacuum pump cooling 1
Hot	126,1	110	51,6	10	Vacuum pump cooling 2
Hot	158,5	130	94,1	10	Vacuum pump cooling 3
Hot	201,8	150	101,1	10	Vacuum pump cooling 4
Hot	117,7	40	215,5	10	Final compressor cooling 1
Hot	107,7	40	192,1	10	Final compressor cooling 2
Hot	108,3	20	264,8	10	Final cooler
Hot	600,1	600	754,4	150	Cooling reactor
Hot	600	70	2570	10	Exhaust gas cooler

Table B.3 Streams involved in the pinch analysis of the SNG production with MEA CO_2 separation technology

Type	Tstart [°C]	Ttarget [°C]	Q [kW]	ΔT [K]	Comments
Cold	10	113,06	553,7	5	Steam prep gasif - preheat
Cold	113,06	113,07	2722,1	2,5	Steam prep gasif - evap
Cold	113,06	400	672,5	10	Steam prep gasif - supheat
Hot	850	600	3787,1	10	Syngas cooling
Hot	611,22	400	3000	10	Syngas cooling
Hot	400	200	2636,8	10	Syngas cooling
Hot	200	80	1481,4	10	Syngas cooling
Hot	56,408	20	3349,5	5	Scrubbing water recycle cooling
Cold	99,753	99,76	397,2	2,5	Waste water stripper
Hot	99,753	25	314,9	5	Waster water cooling
Cold	15	300	2458,5	10	Syngas heat prior to methanation
Cold	10	101,54	95,3	5	Steam prep methanation - preheat
Cold	101,54	101,55	536,1	2,5	Steam prep methanation - evap
Cold	101,54	300	88,7	10	Steam prep methanation - supheat
Hot	300,01	300	9889,9	20	Methanation 1 heat
Hot	300	54,98	1907,9	10	Syngas cooling
Hot	54,98	30	1184,7	10	Syngas cooling - cond
Hot	58,2	40	111,7	10	Cooler
Cold	115	115,01	11216,4	2,5	MEA reboiler
Hot	90	40	2243,3	10	MEA condenser
Hot	58	38	4422,5	5	MEA solvent condenser
Hot	119	50	309,6	10	Compressor cooling 1
Hot	124,7	50	368,1	10	Compressor cooling 2
Hot	124,6	50	302,8	10	Compressor cooling 3
Cold	200	200,01	177,2	2,5	TEG dryer reboiler
Hot	116,8	40	193,8	10	Final GN compressor cooling 1
Hot	106,1	40	170,8	10	Final GN compressor cooling 2
Hot	106,7	20	237,1	10	Final GN cooler
Hot	177,73	100	240,9	10	CO_2 compressor cooling 2
Hot	172,67	100	227,7	10	CO_2 compressor cooling 3
Hot	173,23	100	235,6	10	CO_2 compressor cooling 4
Hot	174,2	100	252,7	10	CO_2 compressor cooling 5
Hot	175,5	105	271,9	10	CO_2 compressor cooling 6
Hot	105	25	793,3	5	CO_2 cooler

APPENDIX C

C.1) EASEE gas quality specifications

C.2) Chemical engineering plant cost index (CEPCI) as published in Chemical Engineering Magazine, revision 11 may 2010

C.3) Percentages of each cost investment component

C.4) Energy market scenarios

Table C.1 EASEE gas quality specifications.

Parameter	Unit	Min	Max	Recommended implementation date
Wobbe index	kWh/m^3	13,60	15,81	1/10/2010
Relative density	m^3/m^3	0,555	0,700	1/10/2010
Total sulphur	mg/m^3	-	30	1/10/2006
H_2S + COS (as S)	mg/m^3	-	5	1/10/2006
RSH (as S)	mg/m^3	-	6	1/10/2006
O_2	mol%	-	0,01	1/10/2010
CO_2	mol%	-	2,5	1/10/2006
H_2O dew point	°C at 70 bar (a)	-	-8	1/10/2006
HC dew point	°C at 1-70 bar (a)	-	-2	1/10/2006

Table C.2 Chemical engineering plant cost index (CEPCI) as published in Chemical Engineering Magazine, revision 11 may 2010

Year	CEPCI	Year	CEPCI
1990	357,6	2001	394,3
1991	361,3	2002	395,6
1992	358,2	2003	401,7
1993	359,2	2004	444,2
1994	368,1	2005	468,2
1995	381,1	2006	499,6
1996	381,7	2007	525,4
1997	386,5	2008	575,4
1998	389,5	2009	521,9
1999	390,6	2010	532,9
2000	394,1		

Table C.3 Percentages of each cost investment component (Peters M., 2003)

Direct costs	Percentage	Indirect costs	Percentage
Purchased equipment cost	25,4 %	Engineering and supervision	6,8 %
installation equipment cost	8,5 %	Construction expense	8,5 %
Instrumentation installed	6,8 %	Legal expense	1,7 %
Piping	12,7 %	Contractor's fee	1,7 %
Electrical	4,2 %	Contingency	5,9 %
Buildings	4,2 %	Total	100%
Yard improvement	1,7 %		
Service facilities	11,0 %		
Land	0,8 %		

Table C.4 Input data for the energy market scenarios

	Scenario 1	*Scenario 2*	*Scenario 3*	*Scenario 4*
Year	2020	2020	2050	2050
Natural gas price [€/MWh]	27	27	44	44
Build margin power plant technology, electric power sector	Coal	Coal	Coal	Coal, CCS
CO_2 emissions associated with power production [kg/MWh]	722	722	619	120
CO_2 emissions charge [€/ton]	20	52	50	150
Natural Gas price [€/MWh] including CO_2 charges	35	42	59	80
Whole sale electricity price [€/MWh]	51	74	71	84

APPENDIX D – Framework of the Gas upgrade section with membrane separation

D.1) Overall data of first compressor and cooler

D.2) Overall data of final compressor and cooler

D.3) Overall data of permeate compressor

D.4) CO_2 aftertreatments data

D.5) Membrane units data

D.6) Power consumption

Table D.1 First Compressor and first cooler operating data

Mass flow	**4, 74** [**kg/s**]
Inlet pressure	0,9 [bar]
Inlet temperature	40 [°C]
Pressure ratio	31
Outlet Temperature	205 [°C]
Number of stages	5
Number of intercoolers	4
Isentropic efficiency	0.76
Power required	2370 [kW]
Total cooling duty	1282 [kW]
Inlet temperature cooler	**202** [°$\boldsymbol{C}$]
Outlet temperature cooler	40 [°C]
Cooling duty required	1381 [kW]

Table D.2 Final stage operating data

SNG Mass flow	**1, 206** [$\boldsymbol{kg/s}$]
Inlet pressure on the compressor	29 [bar]
Compression ratio	2.08
Isentropic efficiency	76 %
Power required	177[kW]
Cooling duty (compressor)	103 [kW]
Cooling duty (final cooler)	170 [kW]

Table D.3 Permeate compressor operating data

Mass flow	**$1,534\ [kg/s]$**
Pressure ratio	10
Power required	$700\ [kW]$
Cooling duty required	$730\ [kW]$

Table D.4 Overall data about CO_2 captured aftertreatments

O_2 mass flow	$1800\ [kg/h]$
Electricity for O_2 production	$0{,}3\ [kWh/kgO_2]$
CO_2 rich stream mass flow	$3{,}92\ [kg/s]$
Cooling duty Reactor	$3260\ [kW]$
Cooling duty Exhaust cooler	$2020\ [kW]$
Power CO_2 compressor	$1800\ [kW]$
Cooling duty CO_2 compressor	$2840\ [kW]$
Cooling duty CO_2 condenser	$942\ [kW]$
Power CO_2 pump	$37\ [kw]$

Table D.5 Overall data of the membrane units

Pressure Ratio memb.1	**$0,033$**
Mole stage cut memb.1	0,4
Dimensionless permeation factor memb.1	1,180
Pressure Ratio memb.2	0,04
Mole stage cut memb.2	0,4
Dimensionless permeation factor memb.2	1,198
CH_4 Recovery	90,78 %
Wobbe index	$13{,}92\ [kWh/m3]$
CO_2 fraction	2,16 %

Table D.6 Power consumption for each element of the gas upgrade section for membrane case

Power first compressor	*2369 [kW]*
Cold duty first compressor	*1282 [kW]*
Cold duty first cooler	*1381 [kW]*
Hot duty dryer	*78 [kW]*
Power final compressor	*177 [kW]*
Cold duty final compressor	*104 [kW]*
Cold duty final cooler	*170 [kW]*
Power permeate compressor	*730 [kW]*
Cold duty permeate compressor	*700 [kW]*
Cold duty reactor	*3620 [kW]*
Cold duty exhaust cooler	*2020 [kW]*
Power CO_2 *compressor*	*1800 [kW]*
Cold duty CO_2 *compressor*	*2840 [kW]*
Cold duty CO_2 *cooler*	*942 [kW]*
Power CO_2 *Pump*	*37 [kW]*
Electricity for oxygen production	*540 [kW]*
Total power consumption	*5653 [kW]*

APPENDIX E – Framework of the Gas upgrade section with PSA separation

Table E.1 First Compressor operating data

Mass flow	4,74 [kg/s]
Inlet pressure	1 [bar]
Inlet temperature	40 [°C]
Pressure ratio	9
Outlet Temperature	50 [°C]
Number of stages	3
Number of intercoolers	3
Isentropic efficiency	0.76
Power required	1482 [kW]
Total cooling duty	1515 [kW]

Table E.2 PSA unit performance

Adsorption medium	Carbon molecular sieve 3K (Tacheda)
higher pressure level	9 [bar]
lower pressure level	0,1 [bar]
CH_4 Recovery	95 %
CH_4 Purity (in the outlet stream)	91% ÷ 97%

Table E.3 Vacuum pump data

Mass flow	3,34 $[kg/s]$
Pressure ratio	10
Inlet pressure	0,1 $[bar]$
Power required	790 $[kW]$
Cooling duty required	290 $[kW]$

Table E.4 Final stage operating data

SNG Mass flow	$\mathbf{1,168\ [kg/s]}$
Inlet pressure on the compressor	8 [bar]
Compression ratio	7,54
Isentropic efficiency	76 %
Power required	534 $[kW]$
Cooling duty (compressor)	410 $[kW]$
Cooling duty (final cooler)	265 $[kW]$

Table E.5 Reactor and cooler data

CO_2 *rich mass flow*	3,92 $[kg/s]$
Cooling duty Reactor	910 $[kW]$
Cooling duty Exhaust cooler	3480 $[kW]$

Table E.6 H_2 removal membrane data and overall gas upgrade section performance

Molar stage cut	0,1
Pressure ratio	0,15
Dimensionless permeation factor	0,09
CH_4 Recovery	87,4 %
Wobbe index	13,83 $[kWh/m3]$
CO_2 fraction	2,21 %

Table E.7 Power consumption for each element of the gas upgrade section for PSA case

PW compressor 1	1428 [kW]
Cold duty compressor 1	1515 [kW]
PW vacuum pump	789 [kW]
Cold duty vacuum pump	287 [kW]
Hot duty dryer	18 [kW]
PW final compressor	534 [kW]
Cold duty final compressor	408 [kW]
Cold duty final cooler	265 [kW]
Cold duty reactor	909 [kW]
Cold duty Exhaust cooler	3479 [kW]
Total power consumption	2750 [kW]

APPENDIX F – Framework of the Gas upgrade section with MEA separation

F.1) Overall data of blower and first cooler
F.2) MEA unit data
F.3) Overall data of first compressor
F.4) Overall data of final compressor and cooler
F.5) Overall data of CO_2 aftertreatments
F.6) H_2 membrane unit data
F.7) Power consumption

Table F.1 Power consumption of the blower and the first cooler

Mass flow	*4,74 [kg/s]*
Outlet pressure	*1,2 [bar]*
Power required Blower	*172 [kW]*
Cooling duty Cooler 1	*112 [kW]*

Table F.2 Key performance data for the MEA separation unit

CO_2 *separation efficiency*	*95%*
CH_4 *Recovery*	*99,99%*
Hot duty reboiler	*11216 [kW]*
Cold duty condenser	*2243 [kW]*
Cold duty amine cooler	*4422 [kW]*

Table F.3 First compressor data

number of stages	*3*
intercoolers	*3*
inlet pressure	*1 [bar]*
pressure ratio	*9*
Power required	*760 [kW]*
Cold duty	*980 [kW]*

Table F.4 Final stage operating data

SNG Mass flow	**1,074 [kg/s]**
Inlet pressure on the compressor	8 [bar]
Compression ratio	7,54
Isentropic efficiency	76 %
Power required	472[kW]
Cooling duty (compressor)	365 [kW]
Cooling duty (final cooler)	237 [kW]

Table F.5 Overall data about CO_2 captured aftertreatments

CO_2 rich mass flow	3,34 [kg/s]
Power CO_2 compressor	1260 [kW]
Cooling duty CO_2 compressor	1230 [kW]
Cooling duty CO_2 cooler	795 [kW]
Power CO_2 pump	32 kW]

Table F.6 H_2 removal membrane data and overall gas upgrade section performance

Molar stage cut	0,1
Pressure ratio	0,15
Dimensionless permeation factor	0,09
CH_4 Recovery	87,4 %
Wobbe index	13,83 [kWh/m3]
CO_2 fraction	2,21 %

Table F.7 Power consumption for each component of the gas upgrade section for the MEA case

Power Blower	*172 [kW]*
Cold duty Cooler 1	*112 [kW]*
Hot duty MEA	*11216 [kW]*
Cold duty MEA condenser	*2243 [kW]*
Cold duty MEA (solvent cooler)	*4422 [kW]*
Power compressor 1	*760 [kW]*
Cold duty compressor 1	*980 [kW]*
Hot duty dryer	*177 [kW]*
Power final compressor	*472 [kW]*
Cold duty final compressor	*365 [kW]*
Cold duty final cooler	*237 [kW]*
Power CO_2 compressor	*1261 [kW]*
Cold duty CO_2 compressor	*1229 [kW]*
Cold duty CO_2 cooler	*793 [kW]*
Power CO_2 pump	*32 [kW]*
Total power consumption	*2700 [kW]*

APPENDIX G – Economic assessment data

G.1)	Cost of purchased equipment for the membrane case
G.2)	Cost of purchased equipment for the PSA case
G.3)	Cost of purchased equipment for the MEA case
G.4)	Capital cost for the membrane case
G.5)	Capital cost for the PSA case
G.6)	Capital cost for the MEA case
G.7)	Electricity cost for the membrane case
G.8)	Electricity cost for the PSA case
G.9)	Electricity cost for the MEA case
G.10)	Revenues for the membrane case
G.11)	Revenues for the PSA case
G.12)	Revenues for the MEA case

Table G.1 Cost of purchased equipment of the gas upgrade section for the membrane case

Component	*Details*	*Cost 2010 [M€]*	*Reference*
First compressor	*El.power: 2370 [kW]* *Cold duty: 1280 [kW]*	*1897500*	(Peters M., 2003)
Pipeline compressor	*El.power: 177 [kW]* *Cold duty: 1,28 [kW]*	*166000*	(Peters M., 2003)
Permeate compressor	*El.power: 700 [kW]* *Cold duty: 730 [kW]*	*522000*	(Peters M., 2003)
CO_2 compressor	*El.power: 1800 [kW]* *Cold duty: 2840 [kW]*	*1328000*	(Peters M., 2003)
CO_2 pump	*El. Power: 32 [kW]*	*57000*	(Peters M., 2003)
TEG dryer	*Vol. Flow: 4500 [Sm^3/h]*	*154500*	(Process group international, 2008)
First membrane	*Memb. Area: 13000 [m^2]*	*185000*	(Peters M., 2003)
Second membrane	*Memb. Area: 13100 [m^2]*	*186500*	(Peters M., 2003)
First Cooler	*Duty: 1380 [kW]*	*14500*	(Peters M., 2003)
Pipeline Cooler	*Duty: 170 [kW]*	*9500*	(Peters M., 2003)
Exhaust Cooler	*Duty: 2750 [kW] steam gen.*	*9500*	(Peters M., 2003)
CO_2 Cooler	*Duty: 945 [kW]*	*28500*	(Peters M., 2003)
Steam condenser	*Duty: 33000 [kW]*	*85500*	(Peters M., 2003)
Reactor	*Outlet mass flow: 7,18 [Sm^3/s]*	*680000*	(Peters M., 2003)
Turbine	*Electricity: 11 [MW]*	*9403000*	(Olsson, et al., 2006)
Oxygen generator	*O_2 mass flow: 0,25 [kg/s]*	*511000*	(Iora P., 2008)
Total equipment cost		***15238000***	

Table G.2 Cost of purchased equipment of the gas upgrade section for PSA case

Component	*Details*	*Cost 2010 [€]*	*Reference*
First compressor	*El.power: 1428 [kW]* *Cold duty: 1515[kW]*	*806500*	(Peters M., 2003)
Pipeline compressor	*El.power: 534 [kW]* *Cold duty: 408 [kW]*	*332000*	(Peters M., 2003)
Vacuum Pump	*El.power: 790 [kW]* *Cold duty: 290 [kW]*	*678500*	(Peters M., 2003)
TEG dryer	*Vol. Flow: 7052 [Sm^3/h]*	*202000*	(Process group international, 2008)
VPSA unit	*column h: 17,6 [m]; d:4,1 [m]*	*1470000*	(Peters M., 2003)
H_2 sep. membrane	*H_2 separated flow: 32,9 [kg/h]*	*167500*	(Hamelinck, et al., 2002)
Pipeline Cooler	*Duty: 265 [kW]*	*9500*	(Peters M., 2003)
CO_2 Cooler	*Duty: 2570 [kW]*	*28500*	(Peters M., 2003)
Steam condenser	*Duty: 27000 [kW]*	*76000*	(Peters M., 2003)
Reactor	*Outlet mass flow: 6,65 [Sm^3/s]*	*653000*	(Peters M., 2003)
Turbine	*Electricity: 9 [MW]*	*8337000*	(Olsson, et al., 2006)
Total equipment cost		***12760500***	

Table G.3 Cost of purchased equipment of the gas upgrade section for MEA case

Component	*Details*	*Cost 2010 [€]*	*Reference*
Blower	*Mass flow:*	*142500*	(Peters M., 2003)
First compressor	*El.power: 760 [kW]* *Cold duty: 980 [kW]*	*380000*	(Peters M., 2003)
Pipeline compressor	*El.power: 700 [kW]* *Cold duty: 730 [kW]*	*332000*	(Peters M., 2003)
CO_2 compressor	*El.power: 1260[kW]* *Cold duty: 1230 [kW]*	*711500*	(Peters M., 2003)
CO_2 pump	*El. Power: 32 [kW]*	*57000*	(Peters M., 2003)
TEG dryer	*Vol. Flow: 7052 [Sm^3/h]*	*202000*	(Process group international, 2008)
H_2 membrane	*H_2 separated flow: 15,9 [kg/h]*	*96000*	(Hamelinck, et al., 2002)
MEA unit	*CO2 sep. Mass flow: [3,2 kg/s]*	*6060500*	(Hektor, 2008)
First Cooler	*Duty: 112 [kW]*	*9500*	(Peters M., 2003)
Pipeline Cooler	*Duty: 237 [kW]*	*9500*	(Peters M., 2003)
CO_2 Cooler	*Duty: 795 [kW]*	*9000*	(Peters M., 2003)
Steam condenser	*Duty: 18000 [kW]*	*57000*	(Peters M., 2003)
Turbine	*Electricity: 6 [MW]*	*6537000*	(Olsson, et al., 2006)
Total equipment cost		***14603500***	

Table G.4 Capital cost for the membrane case

	cost [M€]
Purchased equipment cost	*15,2380*
Installation equipment cost	*5,0793*
Instrumentation installed	*4,0635*
Piping	*7,6190*
Electrical	*2,5397*
Buildings	*2,5397*
Yard improvement	*1,0159*
Service facilities	*6,6031*
Land	*0,5079*
Engineering and supervision	*4,0635*
Construction expense	*5,0793*
Legal expense	*1,0159*
Contractor's fee	*1,0159*
Contingency	*3,5555*
Total capital investment [M€/y]	*59,9361*
Annual capital investment [M€/y]	***5,9936***
Annual maintenance costs [M€/y]	***2,3974***

Table G.5 Capital cost for the PSA case

	cost [M€]
Purchased equipment cost	*12,7605*
Installation equipment cost	*4,2535*
Instrumentation installed	*3,4028*
Piping	*6,3803*
Electrical	*2,1268*
Buildings	*2,1268*
Yard improvement	*0,8507*
Service facilities	*5,5296*
Land	*0,4254*
Engineering and supervision	*3,4028*
Construction expense	*4,2535*
Legal expense	*0,8507*
Contractor's fee	*0,8507*
Contingency	*2,9775*
Total capital investment [M€/y]	*50,1913*
Annual capital investment [M€/y]	***5,0191***
Annual maintenance costs [M€/y]	***2,0077***

Table G.6 Capital cost for the MEA case

	cost [M€]
Purchased equipment cost	*14,6035*
Installation equipment cost	*4,8678*
Instrumentation installed	*3,8943*
Piping	*7,3018*
Electrical	*2,4339*
Buildings	*2,4339*
Yard improvement	*0,9736*
Service facilities	*6,3282*
Land	*0,4868*
Engineering and supervision	*3,8943*
Construction expense	*4,8678*
Legal expense	*0,9736*
Contractor's fee	*0,9736*
Contingency	*3,4075*
Total capital investment [M€/y]	*57,4404*
Annual capital investment [M€/y]	***5,7440***
Annual maintenance costs [M€/y]	***2,2976***

Table G.7 Electricity cost for the membrane configuration

Membrane system	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
CO_2 emissions [ton/y][1]	*32652*	*32652*	*32652*	*32652*
El. consumption [MWh/y]	*45224*	*45224*	*45224*	*45224*
Electricity cost [M€/y]	*2,306*	*3,347*	*3,211*	*3,799*

Table G.8 Electricity cost for the PSA configuration

PSA system	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
El. consumption [MWh/y]	*22000*	*22000*	*22000*	*22000*
CO_2 emissions [ton/y]	*15884*	*15884*	*15884*	*15884*
Electricity cost [M€/y]	*1,122*	*1,628*	*1,562*	*1,848*

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[1] emission due to the electricity production. The electricity price includes the CO_2 fee.

Table G.9 Electricity cost for the MEA configuration

MEA system	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
El. consumption [MWh/y]	*21600*	*21600*	*21600*	*21600*
CO_2 emissions [ton/y]	*15595*	*15595*	*15595*	*15595*
Electricity cost [M€/y]	*1,1016*	*1,598*	*1,534*	*1,814*

Table G.10 Revenues of the whole plant with the membrane configuration

Membrane system	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
SNG produced [MWh/y]	*482420*	*482420*	*482420*	*482420*
SNG revenue [M€/y]	*16,885*	*20,262*	*28,463*	*38,594*
Electricity sold [MWh/y]	*24456*	*24456*	*24456*	*24456*
Electricity revenue [M€/y]	*1,247*	*1,810*	*1,736*	*2,054*
CO_2 captured [ton/y]	*103467*	*103467*	*103467*	*103467*
CO_2 storage cost [M€/y]	*0,766*	*1,111*	*1,066*	*1,261*
CO_2 emission cost [M€/y]	*2,069*	*5,380*	*5,173*	*15,520*
Total revenue	*19,135*	*26,341*	*34,307*	*54,907*

Table G.11 Revenues of the whole plant with the PSA configuration

PSA system	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
SNG produced [MWh/y]	*467344*	*467344*	*467344*	*467344*
SNG revenue [M€/y]	*16,357*	*19,628*	*27,573*	*37,388*
Electricity sold [MWh/y]	*31728*	*31728*	*31728*	*31728*
Electricity revenue [M€/y]	*1,618*	*2,348*	*2,253*	*2,665*
CO_2 *emission [ton/y]*	*98899*	*98899*	*98899*	*98899*
CO_2 *emission cost [M€/y]*	*1,978*	*5,143*	*4,945*	*14,835*
Total revenue	*15,997*	*16,834*	*24,881*	*25,218*

Table G.12 Revenues of the whole plant with the MEA configuration

MEA system	*Scenario 1*	*Scenario 2*	*Scenario 3*	*Scenario 4*
SNG produced [MWh/y]	*429545*	*429545*	*429545*	*429545*
SNG revenue [M€/y]	*15,034*	*18,041*	*25,343*	*34,364*
Electricity sold [MWh/y]	*9607*	*9607*	*9607*	*9607*
Electricity revenue [M€/y]	*0,490*	*0,7109*	*0,682*	*0,807*
CO_2 *stored [ton/y]*	*92295*	*92295*	*92295*	*92295*
CO2 emission cost [M€/y]	*1,846*	*4,799*	*4,615*	*13,844*
CO_2 *stored cost [M€/y]*	*0,683*	*0,991*	*0,951*	*1,125*
Total revenue	*16,687*	*22,560*	*29,689*	*47,890*

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