POLITECNICO DI MILANO

Scuola di Ingegneria Industriale e dell'Informazione

Corso di Laurea in
Ingegneria Energetica

Post-combustion CO_2 Capture from a Natural Gas Combined Cycle with CO_2 membranes.

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Anno Accademico 2012 - 2013

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Sommario

Nuove soluzioni tecnologiche per applicazioni di cattura della CO_2 dai fumi di centrali elettriche sono in corso di ricerca oggigiorno.

Una di queste possibilità è quella di utilizzare i deep eutectic solvents, solventi di nuova generazione che sfruttati all'interno di una membrana supportata sembrano in grado di combinare buone proprietà tecniche per la separazione di CO_2 dai fumi, con un basso costo di realizzazione della membrana.

Soluzioni impiantistiche per la cattura di anidride carbonica che richiedono aree di membrana maggiori possono quindi essere prese in considerazione riducendo il consumo energetico necessario, fino ad oggi, in sistemi di questo tipo per la riduzione delle aree di membrana per il contenimento dei costi. Un netto miglioramento delle prestazione termodinamiche dell'impianto di cattura può essere quindi raggiunto riducendo la perdita di rendimento dovuta all'impianto di cattura.

L'applicazione a un NGCC di due differenti impianti di cattura della CO_2, basati su sistemi di separazioni a membrana, sono stati quindi analizzati in questo studio. Il primo utilizza un sistema di ricircolo selettivo, tramite una membrana selettiva alla CO_2 , in modo da aumentare la concentrazione di CO_2 nei gas combusti; nel secondo invece un semplice ricircolo di gas combusti (EGR) è utilizzato allo stesso scopo. I software GS e MATLAB sono stati utilizzati per la valutazione dell'impatto dell'applicazione di questi sistemi di cattura (comprensivi del sistema di compressione e purificazione della CO_2) sulle prestazioni termodinamiche del ciclo di potenza. Successivamente la metodologia usata dal gruppo di ricerca CO2CRC è stata applicata ai casi considerati per una valutazione di massima del costo della CO_2 evitata alla tonnellata ($\$/t_{evitata}$).

Per il solo secondo sistema considerato è stato creato un codice MATLAB che ne ottimizza automaticamente le variabili operative (pressioni e superfici) in modo da ottenere il minimo costo della CO_2 evitata.

Con entrambe le soluzioni un valore approssimativamente tra i 90 e i 95 $/t del costo della CO_2 evitata è stato stimato. In aggiunta sono state ottenute indicazioni di massima sulla configurazione dei due sistemi di cattura per minimizzarne il costo.

Parole chiave: NGCC, membrane per cattura di CO2, EGR, ricircolo selettivo, analisi economica

Abstract

New membrane technology for CO_2 capture application from power plants flue gas are nowadays under study. One of these is the possibility to use newly developed deep eutectic solvents in a supported membrane configuration that seems to be able to achieve at the same time a significant reduction of the specific cost of the membrane and good properties for CO_2 capture application.

This would allow to use larger membrane surface in CO_2 sequestration process reducing the energy required, in membrane systems like this, for the compression of flue gas used to enhance the driving force and reduce the total membrane area required for the separation. A sensible improvement of the thermodynamic performances of the capture system can be obtained reducing the reduction of efficiency that it causes to the power plant.

Two different membranes configuration to capture the CO_2 produced by an NGCC have been considered in this study. The first one uses a selective recirculation of CO_2 to enrich the flue gas of carbon dioxide, while the second one uses a simple EGR system. GS and MATLAB software have been used to evaluate the thermodynamic impact of the application of these two CCS system to the power plant (including the compression and purification unit), and the CO2CRC research group methodology have been used to have a first estimation of the cost of CO_2 avoided ($[\$/t_{avoided}]$) obtained.

For the second plant solution a MATALB code have been created to automatically optimize the operating variables of the capture unit to obtain the lowest CO_2 avoided cost.

With both solution a value of CO_2 avoidance cost approximately between 90 and 95$/t has been obtained, in addition first indications on the technical parameters to assume in the capture unit design have been obtained.

Keywords: NGCC, CO2 membranes, EGR, selective recirculation, economics

1 INTRODUCTION

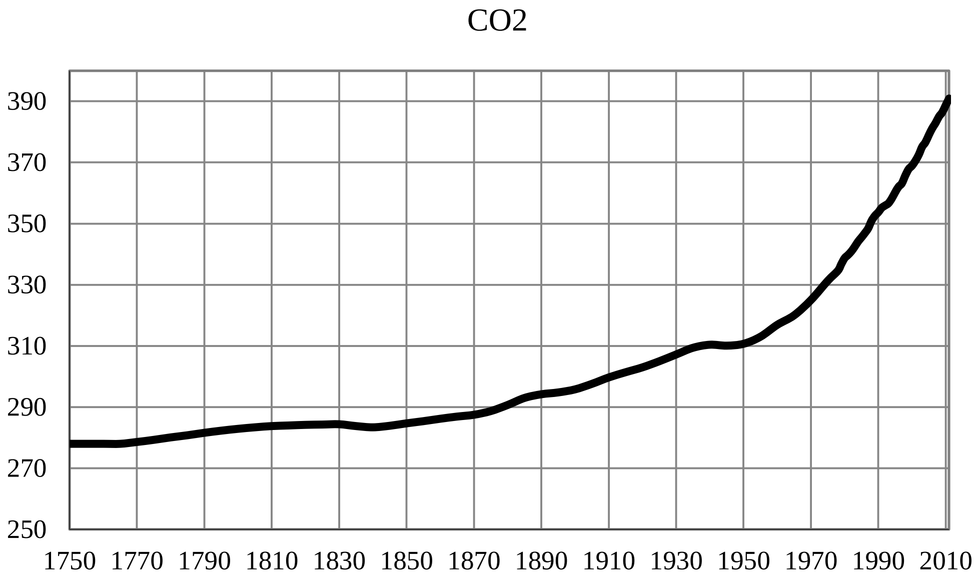
This chapter will first explain the importance of carbon capture and storage (CCS) from industrial sources of emission in the global strategy of CO2 anthropogenic emission reduction. Secondly an overview on the main index used to evaluate the performances of a CCS system will be highlighted.
The first part aims to explain the world context that makes scientific research about the implementation of CO_2 capture to existing power plant particularly important, justifying this study. The second part will explain which indices will be used to evaluate the impact of the CCS project analysed.

1.1 Carbon capture and storage for CO_2 reduction

1.1.1 CO2 Emissions in the world

In recent years many nations in the world started to put big technological and economic efforts in the field of greenhouse gas emission reduction. Different international agreements have been signed (such as the Kyoto Protocol and the Europe targets 20 20 20) with the objective of CO_2 emission reduction in order to decrease the impact of human activities on the environmental equilibrium.

According to Edenhofer et al. [1] the CO_2 concentration has nowadays rose to the value of 390 ppm starting from the preindustrial value of 280 ppm. This increase of approximately 40% in CO_2 concentration is thought to be caused by the huge increase in anthropogenic emissions, occurred with the industrial revolution, because of the huge amount of fossil fuel used to power industrial and transport machineries.



1.1 CO2 concentration trend in the last 250 years. [2]

The major source of CO_2 emission in the world is the combustion of fossil fuels which represents the 85% of total CO_2 emitted by humanity and can be divided in 3 main sector [3][4]: electricity generation, vehicle propulsion and direct use of fossil fuel for house and buildings heating purpose. Other sources exist, like emission due to industrial and chemical processes, waste treatment, etc., but are a minor fraction of the total.
In a developed nation like Italy the global fossil fuel consumption is almost equally divided among those 3 main sectors already listed.

An indiscriminate increase in greenhouse gas concentration is thought to cause, in the long term, an increase in the average temperature on earth, leading to dramatic change of the biological equilibrium and sea level. A clear technical solution to prevent global warming is not available nowadays and for this reason in every international agreement different routes of intervention have been taken in consideration.

The main paths highlighted are three. The first one is to increase the share of power and heat generated from renewable or low CO_2 sources such as wind, solar, hydro or nuclear in substitution of conventional systems powered by fossil fuel. The second one is to raise the energy efficiency in the final users of heat or electrical power in order to reduce the total primary energy supply (TPES). The last one is the implementation of carbon capture and storage (CCS) systems at greenhouse gas emission sources.

1.1.2 Possible application of Carbon Capture and Storage

CCS systems can be used to reduce the CO_2 emissions at stationary sources such as electricity power plants and large industrial heat utilities, such as still mills, because of the scale effect that affect the cost of these kind of plants.[3][4]

The emission due to house heating can be mitigated using CCS only when electricity is used as a thermal vector. This usually happens only when in a country there is large availability of low price electricity generated with renewable sources (such as hydropower in the Scandinavian peninsula) or nuclear power plants. Those are already low CO_2 emission technologies and so there is no need to use CCS.

Vehicle propulsion emissions could be effected by CCS systems only if there would be a mass switch to electrical and hydrogen propelled vehicle but this is not the case right now in the world.

These facts show that the electricity production is almost the only industry where CCS can be used for a substantial reduction of CO_2 emission at a reasonable cost. This means that CCS projects can affect approximately only 1/3 of the total world carbon dioxide emissions.

1.1.3 Reasons for Carbon Capture and Storage

CCS is one of the key ways available to meet the emission reduction targets set by different international agreements. In fact this technology would allow to continue to use fossil fuels for a longer period giving more time to governments to act a fuel switch towards renewable or less polluting sources and to achieve the emission reduction requested in the different agreements.
This is important as the only other option would be a sudden and quick increase of the electricity produced with renewable resources (or nuclear) that could give problem to the electric system for the uncertainty of the production.

CCS systems can be very important especially for those nations that produce a big share of their electricity using fossil fuels. Especially when dirty fossil fuels such as coal or oil are used. This happens because these fuels have a high carbon content, expressed as the ratio of kg of carbon burned per each unit of thermal energy obtained with the combustion (kg_C/MJ_{LVV}), that results in a higher specific emission of CO_2 per kWh of electricity produced.

1.1.4 CCS implementation problems

The implementation of capture and storage projects at large scale has three main problems that needs to be faced by designers.

First of all the cost of equipment and its operation to obtain a stream of CO_2 with the required characteristic for the transport and geological storage would increase the final cost of production of electricity.

The second problem is that, as it has already been said, CCS can be affectively applied only to huge source of emission as the cost of the equipment greatly profit of scale effect. This would make the application of CCS to smaller power plants even less economically interesting.

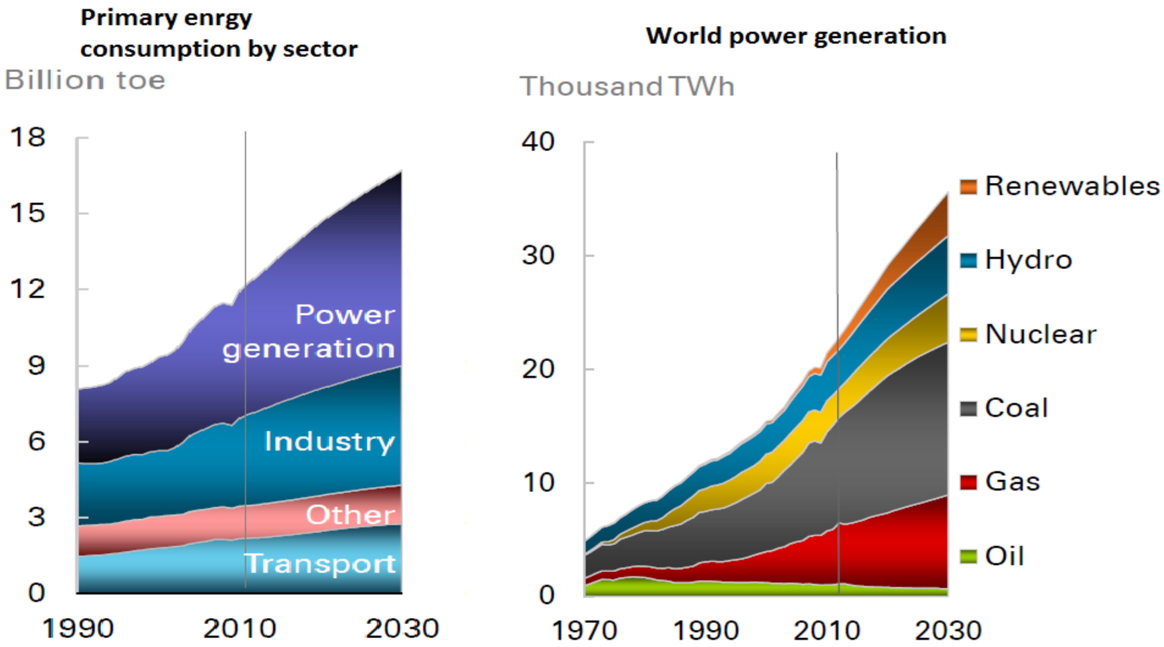
Another problem is the energy consumption to operate the capture system that reduces the amount of electricity produced by the power plant. This is also called the energy penalty of the capture system and is one of the most important parameter to be taken in consideration to evaluate the effectiveness of a specific capture technology.
The drop of efficiency of the power plant can be very significant (around a $\Delta\eta$=10%) and cause the increase of the price of electricity and the global consumption of fossil fuels at the same time.[5]
That also means that the actual total installed power could not be enough to meet the demand and that the building of new power plants could be needed to face the reduction of net power capacity.

Another problem that can be considered is that adding a carbon capture system, which is nothing different than a series of chemical reactors, to a power plant could affect its flexibility and capability to operate at partial load.

Last but not least we have to consider that often these capture system produce chemical wastes, such as exhausted amines for post-combustion capture. This rises the problem of their disposal and the problem of the production of chemical substances needed by the plant with additional costs and energy consumption. Another problem linked to these one is the still unknown pollutant potential of these substances and waste that can greatly affect the ecological of the whole process.

1.1.5 World and Italian power generation industries

Power generation industries represents the largest share of the total world primary energy consumption and its importance is foreseen to increase over time [6].

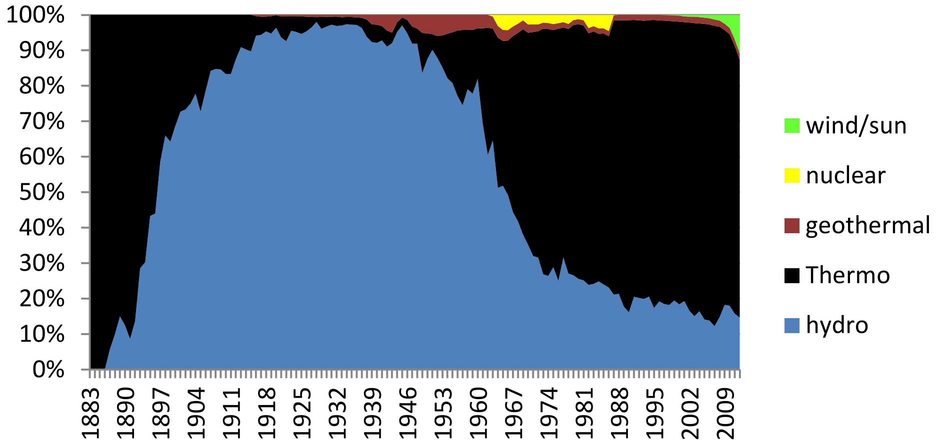


12 World primary energy consumption and power generation.[6]

In addition we can see from fig. 1.2 that it is predicted that most of the electricity will still be produced, in the near future, using conventional fossil fuels (coal, natural gas and oil) with great emission of CO_2 in the atmosphere.

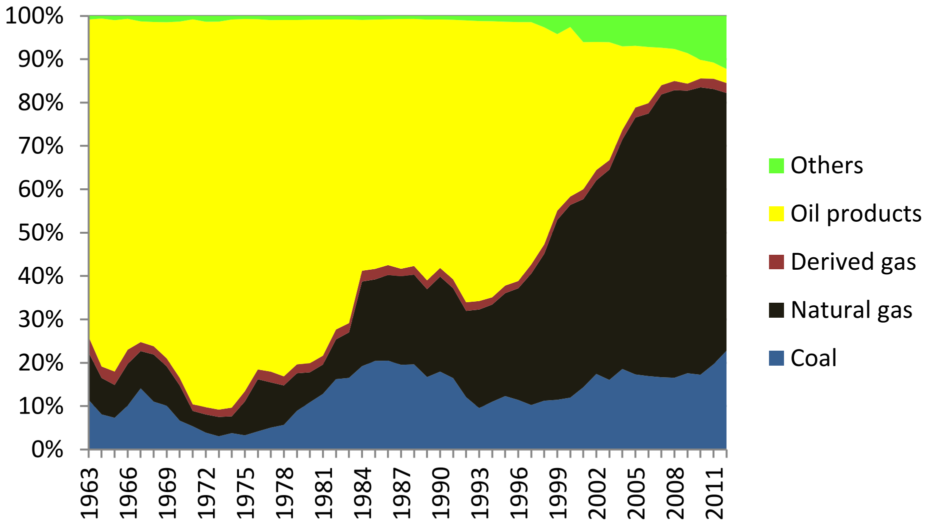
According to the statistics analyses done by TERNA company [7] it is easy to see how the Italian situation does not differ from the global one. Approximately the 73% of the electricity is produced with conventional thermodynamic power plants. Even if in the last years the share of electricity that uses renewable technologies is significantly increased (+200% from 2010 [7]) fossil fuels will play a key role in the generation of electricity for the next years.
A peculiarity of Italy is the total absence of generation through nuclear power plants since 1990, year in which was closed the last nuclear power plant in Italy, as a consequence of a 1987 popular referendum.

This caused an increase in the consumption of fossil fuels as the Italian hydropower was already very close to the maximum capacity as most of the suitable sites were already in use.



1.3 Electric energy sources in Italy since 1883.

The data at our disposal [7] tell us which fossil fuels have been used in the last 30 years in Italy in order to understand which plant may be more interesting to study.



1.4 Fuels used in thermodynamic power plant in Italy since 1963.

Natural gas represents almost 60% of the total fossil fuel consumption in the electricity industry. After 1990 it took pace a gradual fuel switching from oil products to less polluting and more efficient natural gas. Coal is used to produce less than 25% of the final electricity produced in the country. This large use of natural gas is an Italian peculiarity as in the rest of Europe, in nations such as Germany, Spain, United kingdom, coal represents usually more than 50% of the total fossil fuel consumption for electricity generation.

1.2 Parameters used to evaluate CO2 capture technologies

There are many parameters which need to be considered when evaluating a CCS technology, to fully understand its impact once applied to a power plant. Here the most important will be shown and explained.

1.2.1 Carbon capture ratio

The first thing to know is the fraction of $CO_{2,}$ emitted by a power plant, captured by the CCS systems. This parameter is usually fixed in a study because it is our main objective to achieve and a typical value used is 90%. This parameter is nothing more than the ratio (expressed in percentage) between the CO_2 separated from the main flue gas flow and the total amount of CO_2 produced by the power plant.

1.2.2 Energy penalty

Another important index is the so called "energy penalty" due to a CCS system. this parameter is defined as:[8]

$$EP = 1 - \frac{\eta_{ccs}}{\eta_{ref}} \qquad (1.1)$$

It synthesizes the effect of a CCS system on the global thermodynamic efficiency of a power plant.

Almost every CCS solution require a certain amount of power to be operated. This may be in the form of electrical power to supply the necessary auxiliary equipment, which reduces the net amount of energy available for the grid. It can also be in the form of heat obtained drawing steam out of the boiler (or an HRSG) before its expansion in the steam turbine, which decrease the thermic energy available to be converted into mechanical and electrical power by the turbine.

As result there is a drop in the thermal efficiency of the power plant; which means an increase of fuel burned to produce the same amount of electrical energy.

This parameter (if expressed as a percentage) is equal to the percentage loss of efficiency of the power plant due to the CCS system.

1.2.3 CO2 Avoided and CO2 captured

It is very important to understand the theoretical difference between the amount of CO_2 avoided and CO_2 captured by a capture system.

The amount of CO_2 avoided is the amount of CO2 that is not emitted compared with the reference case with no CCS; it is the difference between the global emission before and after the implementation of CCS on a power plant: [9]

$$CO_{2,avoided} = CO_{2,emitted\ by\ reference\ case} - CO_{2,emitted\ with\ CCS} \quad (1.2)$$

This definition is valid only if we are considering to produce the same amount of net electrical energy for the grid with the power plant before and after the CCS (when the energy required for the CCS is supposed to be produced by repowering the power plant).

In case we do not repower the base case power plant this comparison cannot be made with this formulation (because the power made available is reduced by the CCS needs) but we have to use a specific emission calculation.

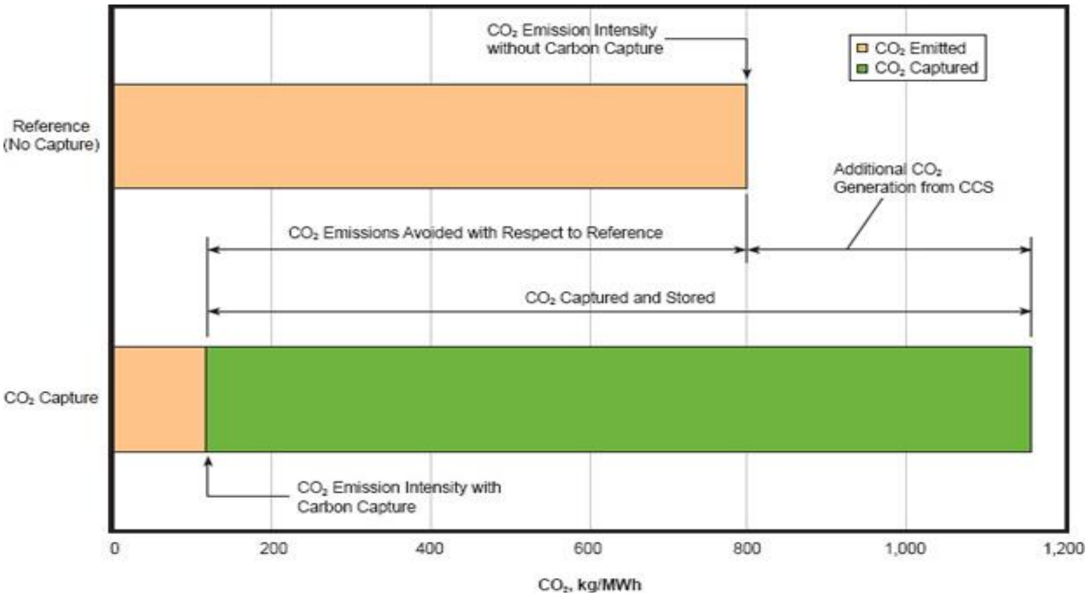
$$CO_{2,avoided} = (W_{ccs}) * (SE_{ref} - SE_{CCS}) \quad (1.3)$$

Where:

- W_{CCS} is equal to the electric power produced by the power plant when CCS is used. [MW]
- SE is the specific emission expressed as $[kg_{CO2}/MWh_{el}]$

The amount of CO_2 captured instead is just the total real amount of CO_2 that the capture system separates from the flue gas. Because of the energy penalty of the capture system the amount of carbon dioxide captured will always be larger than the amount of CO_2 avoided.

Fig. 1.5 gives a visual explanation of the differences of these two parameters.



1.5 Difference between CO2 avoided and captured by the CCS system.

1.2.4 SPECCA

Another important parameter that can be used to characterize a CCS system and to compare among them different solution is the SPECCA index (Specific Primary Energy Consumption for Carbon Avoided) defined as follow:[8]

$$SPECCA = \frac{HR_{CCS} - HR_{ref}}{E_{ref} - E_{CCS}} \quad \left[\frac{MJ}{kg_{CO2,avoided}}\right] \text{(1.4)}$$

$$SPECCA = \frac{3600 * \left(\frac{1}{\eta_{el,CCS}} - \frac{1}{\eta_{el,ref}}\right)}{SE_{ref} - SE_{CCS}} \quad \left[\frac{MJ}{kg_{CO2,avoided}}\right] \text{(1.5)}$$

where: HR = heat rate [MJ_{th}/MWh_{el}]
SE = specific emission of CO2 [kg_{CO2}/MWh_{el}]

With the heat rate that represents the thermal energy needed to generate one MWh of electric energy.

This index shortly express the energetic cost that needs to be sustained to capture CO2. This energy cost includes both the electrical and thermal power requirement for the CCS system.

1.2.5 Cost for CO2 avoided (CCA)

However capturing CO2 produce by a power plant a capture system do not only need an energy input, but requires also specific equipment that needs to be bought, transported to the location of the project and installed.
To evaluate the global impact on the economy of a system like this we also need to consider the engineering design, management and disposal of possible waste product costs.

We can summarize all this different influences in the avoidance cost index; this express the cost that is needed to avoid one tonne of CO2 from a specific power plant.

Once the LCOE (levelized cost of electricity) has been calculated for the reference case and the CCS case this index is easy to obtain:[10]

$$C.C.A\ (cost\ of CO2\ avoided) = \frac{LCOE_{CCS} - LCOE_{ref}}{E_{ref} - E_{CCS}} \left[\frac{\$}{t_{co2,avoided}}\right] \quad (1.6)$$

The LCOE [$\$/MWh_{el}$] (levelized cost of electricity) is the minimum price at which electricity needs to be sold, with the same nominal value over the operative life of the power plant, to cover the cost of the project during its life. The two terms used in eq. (1.6) are explained here:

$$LCOE_{with\ CCS} = \frac{NPV\ of\ power\ plant\ and\ CCS\ facility}{NPV\ of\ net\ power\ plant\ elecricity\ output} \quad (1.7)$$

$$LCOE_{without\ CCS} = \frac{NPV\ of\ projec\ costs\ for\ power\ plant}{NPV\ of\ net\ power\ plant\ electricity\ output} \quad (1.8)$$

1.3 Scope of the work

The present work will move from the idea of using the new Deep Eutectic Solvents (DES), under developing at the Eindhoven University of Technology (TU/e) in this last year, to create a capture system for natural gas combined cycle (NGCC).
This new class of solvents (it will be described in the next chapter) is under study in the context of the MEDUSAE project which aims to realize a supported liquid membrane (SLM) for CO_2 capture applications.

From a preliminary analysis it looks like that the specific cost of the membrane realized with this new technology will be strongly reduced compared with what available nowadays.
New system solutions, which requires larger membrane areas, can be then taken in consideration and this is the specific objective of the present work.

Two different system solutions (that will be described in chapter 3) will be applied to a natural gas combined cycle and their impact will be evaluated from both the thermodynamic and economic point of view.

It was decided to focus this study on natural gas fired power plants as they represents the most used technology for electricity generation in Italy. Another reason is that, because of the shale gas revolution, the overall consumption of natural gas for electricity generation is expected to significantly increase in future years.

The first objective of this work is to analyse the thermodynamic performances of the two capture systems chosen. The first one is a capture system with a selective recirculation of CO_2 implemented using a membrane. The second one is a capture system with non-selective recirculation of CO_2 with a simple EGR that can be done without using a dedicated membrane. (these system will be better described in chapter 3 and 6).

For the first capture system the objective is to understand the impact of different operating parameters on the system performances that will be analysed both from a thermodynamic and economic point of view. The cost of CO_2 avoided will be calculated in order to understand which configuration results to be more competitive.

The second capture system chosen is less complex as its configuration does not impact on the thermodynamic of the power section of the power plant because the recirculation of CO_2 is prior the capture system. For this reason a MATLAB code will be created to automatically optimize the technical parameters of the capture unite searching the configuration that gives the best economic performance in the form of the minimum cost of CO_2 avoided.

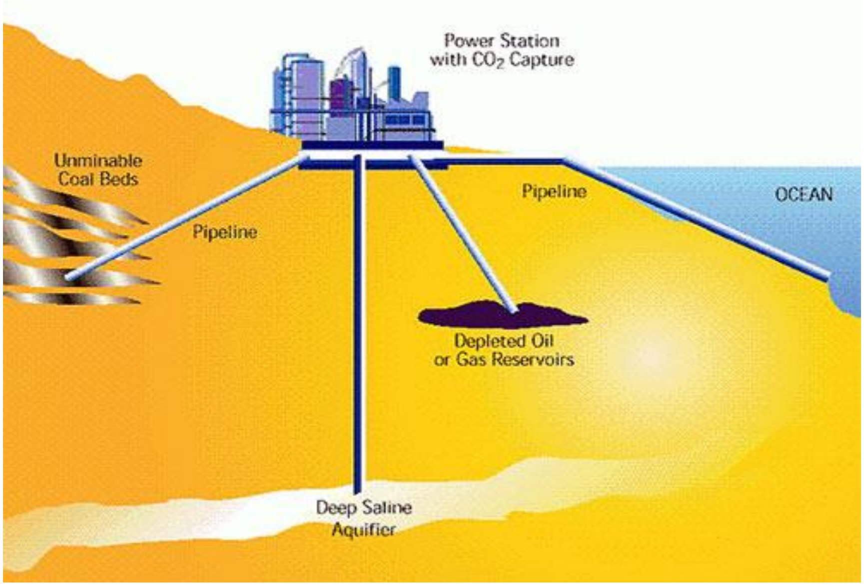
2 STATE OF ART

In this chapter will be first given an overview of the current technological state of art of CCS systems, with a particular interest on post-combustion capture systems as they include the solutions that will be analysed in this work.
Secondly an outlook over supported liquid membrane technologies for post-combustion capture will be given and will be better described the peculiarity of deep eutectic solvents.

2.1 State of art of carbon capture and storage

2.1.1 Introduction to carbon capture and storage

With carbon capture and storage we classify any technology that is used to produce energy vectors (such as heat, electricity, fuels) using fossil fuels but capturing the CO_2 that is commonly emitted in the process.
Different processes are used to separate carbon dioxide from the flue gas before they are released to the atmosphere. The CO_2 rich stream obtained is then compressed to high pressure value (100-150 bar), accordingly to the transport system used, and stored in safe and stable sites where it will be trapped forever.



2.1 Different CO2 storage system

Different storage system have been considered suitable to stock large amount of CO_2 for almost indeterminate time.

Geological storage seems to be the most suitable solution as many carbon deposits already exists in nature. To trap CO_2, can be both used natural formed CO_2 storage or depleted fossil fuel (such as oil and gas fields) deposits.
Another process that has shown to be economically successful is to inject CO_2 in active oil and gas fields in order to increase the pressure of the reservoir. This causes an increase in the availability of fossil fuel and the productivity of the extraction wells resulting in a profit increase. This operation is also known as enhanced oil recovery (EOR)

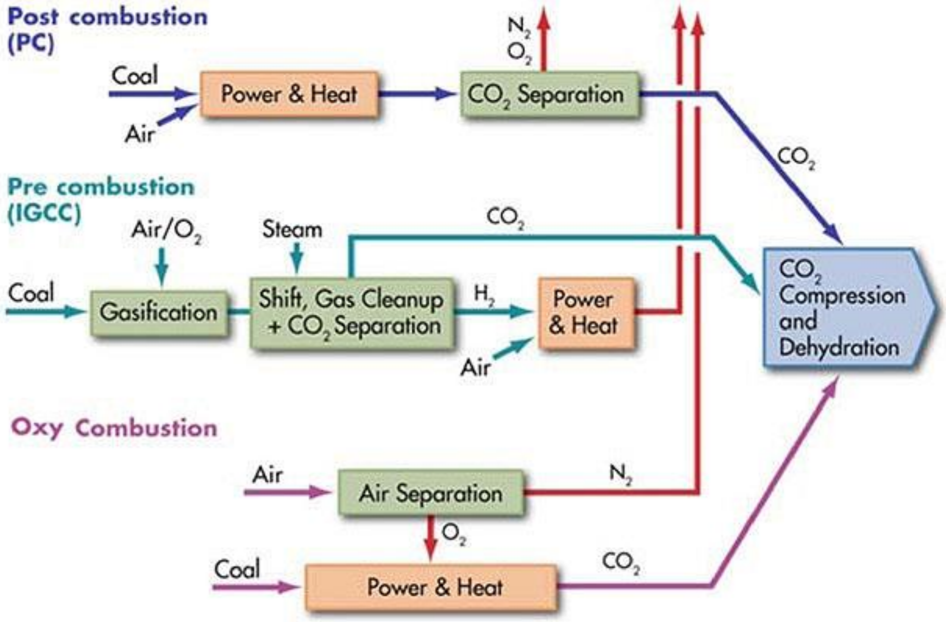
Oceanic trapping is another suitable option as at depth higher than 1500 m the combination of high pressure and absence of convective currents would avoid CO_2 to be vented back to the atmosphere. Some studies have anyway shown that considering longer time frame (thousands of years) the movement of CO_2 caused by diffusion process could not be neglected. This solution would also be very suitable as the storage capacity would be virtually infinite if compared with the amount of CO_2 produced by mankind.

Another option is to use inaccessible coal beds and deep saline aquifers that would allow to stock CO_2 in liquid phase at moderate pressures (around 80 bar) in porous rocks saturated by mineralized water where CO_2 would be chemically trapped. [12]

2.1.2 Carbon capture strategies

We have seen that many options exists for CO_2 storage, anyway the most expensive and complicated part of the process continue to be the capture system on which we will focus in this section.

All the different CCS systems studied in the past years can be classified in three main strategies according of when the separation of CO_2 is done as shown in Fig 2.2.



2.2 Main strategies for CO2 capture in a power station.

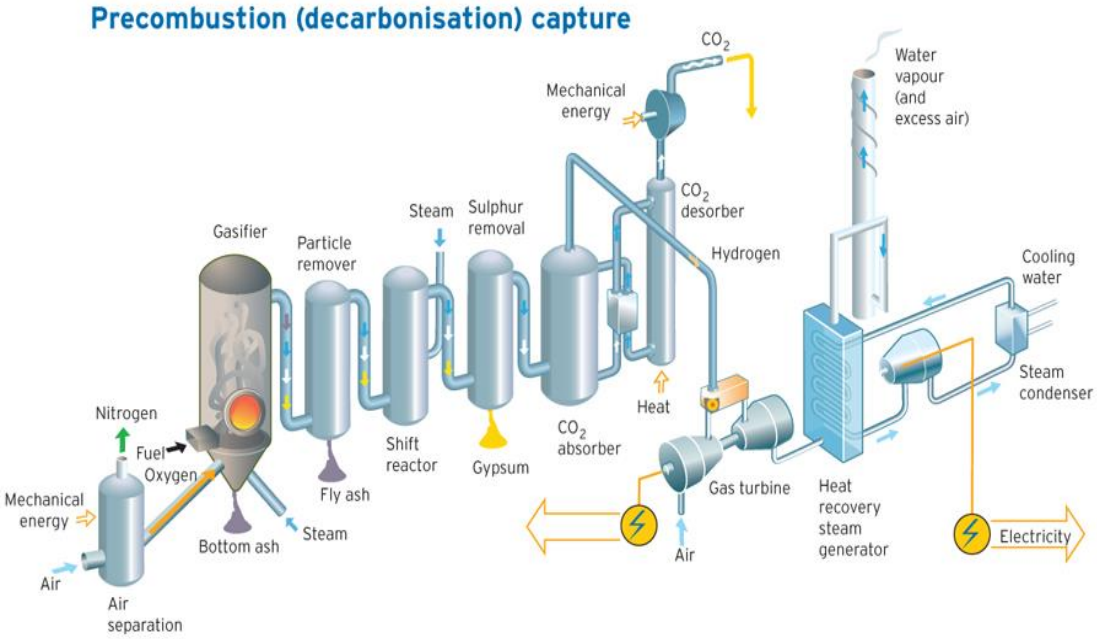
2.1.3 Pre-combustion systems

The first step of this strategy is to convert a fossil fuel such as coal or natural gas to a gas flow rich of H_2 and CO_2 in a series of chemical reactors reallocating the chemical energy of the starting fuel to a decarbonized one.
At this point with different technologies such as membranes, ammine adsorption, etc. CO_2 is separated from the fuel obtained in the previous gasification process.

The main advantage of this solution is that capturing carbon dioxide before the combustion of the fuel the CO_2 is not diluted by the combustion air. We both have a higher CO_2 concentration in the flow treated and a smaller flow to work with. This results in a much easier separation which requires smaller equipment and energy consumption.

The disadvantage of this solution is that in the chemical conversion of the fuel to H_2 before the combustion there is necessarily a loss of energy that reduce the overall net efficiency of the power station.
In addition the whole power plant, especially in NGCC, needs major modification as the combustion of hydrogen is strongly different than the combustion of the usual fuel used.[13][14]

This technology could be used very cost effectively in industrial plants for production of H_2 as the gasification process of the fuel is already existent. In this kind of plants CO_2 capture can be achieved just adding the separation section and the energy penalty resulting is very low (around 2-3%)[15]



2.3 Coal power plant with pre-combustion capture.

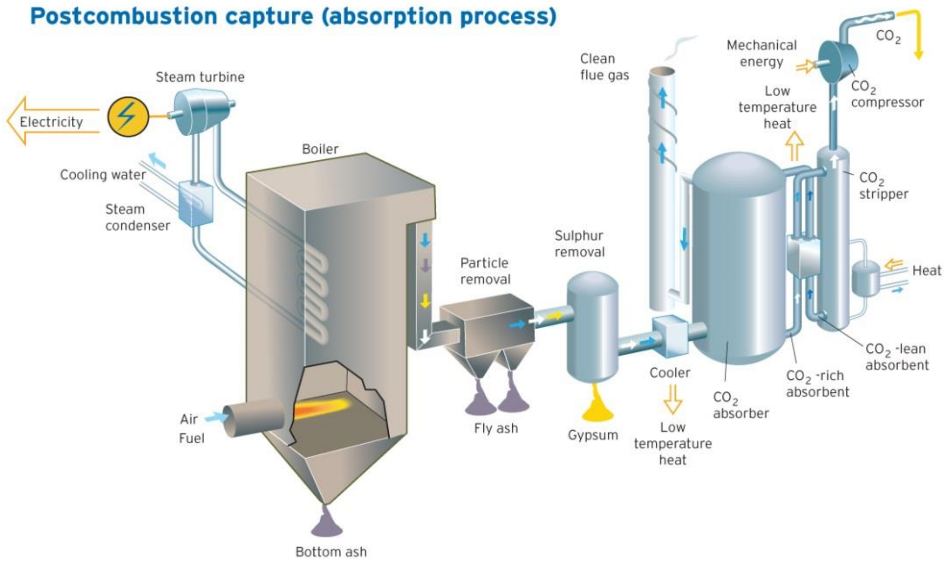
2.1.4 Post-combustion systems

With this kind of system we separate the CO_2 from the flue gas produced by a conventional combustion of a fossil fuel at the exit of the combustor. It can be applied to any kind of power plant as NGCC, USC, and IGCC with the appropriate modification.[11]

In this method, we use normal combustion equipment but the separation of CO_2 is more challenging than with pre-combustion systems because the volumetric flow of the flue gas is much larger. In addition the CO_2 concentration is lower as the combustion products are diluted by the oxidant, usually air, and it varies from approximately 4% of CO_2 in the flue gas for an NGCC to 10-15% in a USC .[13][14]

The main advantage of this solution is that an already existing power plant can be retrofitted to a solution with carbon capture with just minor changings. The modification of the boiler can be theoretically none and the equipment needed for capture can be simply added between the boiler and the chimney.

The disadvantage of this solution is that the concentration of CO_2 in the flue gas is much lower as is diluted by the presence of other combustion products and of the excess air needed in the combustor and the volumetric flow that has to be treated is much larger too. All of these results in larger equipment needed for capture (which is more expensive) and in higher energy consumption.



2.4 A coal power plant with post-combustion capture.

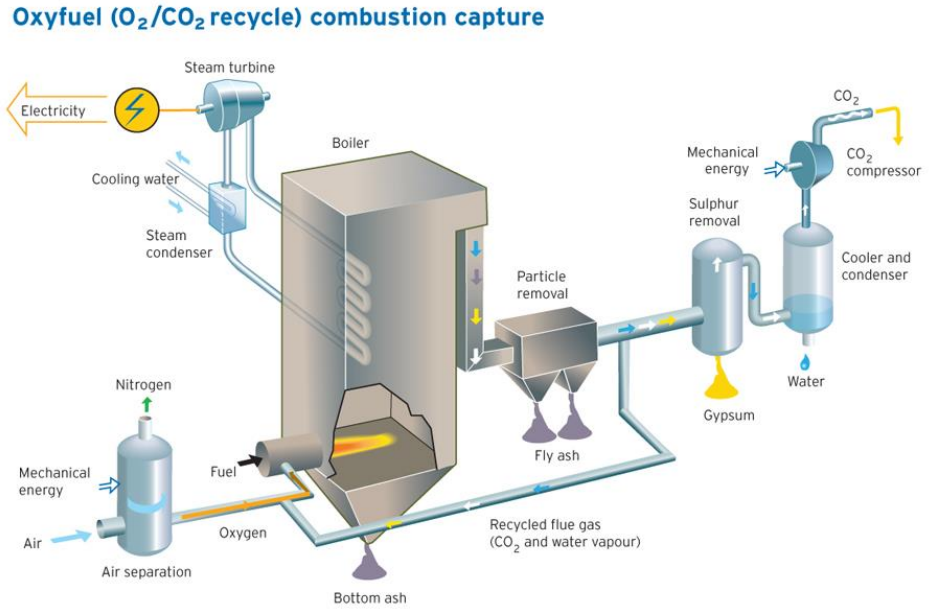
2.1.5 Oxy-combustion system

The concept at the base of oxy-combustion systems is that burning a fuel using pure oxygen instead of air the only two products of the reaction would be CO_2 and H_2O.
In this way the CO_2 reach stream can be obtained by just condensing the water vapour and a theoretical 100% of capture ratio could be achieved.

The problem of this technology is anyway just moved from the CO_2 separation system, that can be achieved relatively easily, to the problem of creating a pure stream of oxygen to burn the fuel.
An air separation unit (ASU) is, in fact, needed to create oxygen separating it from atmospheric air. This system can result to be both very expensive for the equipment required and for the electric consumption needed for its operation.

In addition, because combustion with pure oxygen is radically different than combustion with air, almost all the main equipment of the power plant (combustor ,boiler etc.) should be redesign with an additional increase in cost.

All of these factors results in a substantial increase of cost of the power plant and a drastic reduction of the overall efficiency of electric generation.[13][14]



2.5 A oxy-combustion system for CO2 capture from a coal power plant.

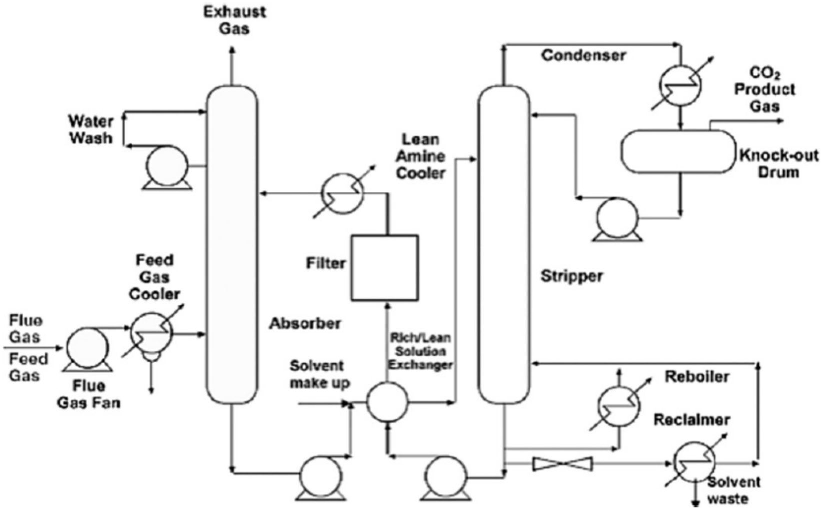
2.2 State of art of post-combustion capture systems

In this section an overview over the post-combustion capture technologies will be given as the system that will be analysed in this work falls into this category.

2.2.1 Absorption

Absorption technologies are based on the use of particular solvents that show high selectivity for CO_2. These solvents can be both chemical or physical but, as the CO_2 concentration is usually low for a post-combustion system, the most used is a mixture of monoethanolamine chemical solvents (MEA) and water, which shows a good absorption capacity for low CO_2 concentration. MEA based absorption technology is considered as reference for CO2 post-combustion separation.[16][9]

The solvent is used in a closed regenerative cycle in order to reduce at minimum solvent consumption. The system is formed by two different columns; in the first one low pressure flue gas gets in contact with clean solvent which absorbs CO_2, capturing it from the gas stream. Rich MEA solvent is then collected at the bottom of the column and sent to the second one. Hear enriched solvent is regenerated by heating it up by condensing steam taken from the boiler, while clean flue gas exits at the top of the column.[16][17]
Absorption is a chemical process favoured by low temperature and high pressure, and so when MEA is heated in the regeneration column it releases CO_2 that can be now collected, dried and compressed while clean solvent is resent in the first column to restart the cycle.



2.6 Chemical absorption unit for CO2 capture.

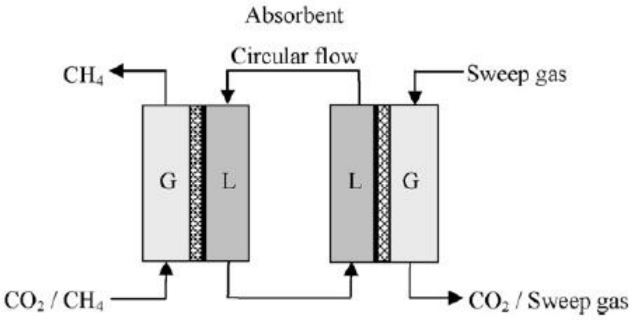
The main problem of this system is that the low CO_2 concentration in the flue gas treated force to use a large amount of solvents and to allow it to correctly flow the equipment have to be of big size. The energy cost, represented by the steam needed for the regeneration of the solvent that is subtracted to the turbine is substantial. In a coal fired power plant the flow needed can exceed the 50% of the total steam generated in the boiler due to the large amount of solvent (and mixed water) need to be heated.
High costs also arise due to the high corrosion power of a MEA solution that requires all equipment to be built using more expensive materials resistant to corrosion. Another problem is the presence of O_2 in the flue gas stream may degrade the MEA solvent. As a result the process will require periodic replacement increasing the operating costs coupled with the cost for disposal of the degraded solvent.[9]

The positive aspects of this system, on the other hand, are its capacity to reach high CO_2 capture ratio even from gas with low CO_2 concentration. Another positive aspect is the possibility to create a good purity CO_2 stream from any kind of source of CO_2 (chemical reactor, coal or natural gas power plant, etc.).

Physical absorption is based on absorption of CO_2 into a solvent based on Henry's law. The CO_2 is regenerated from the solvent through an increase in temperature or a decrease in pressure. Due to their behaviour physical absorption solvent are used effectively when the concentration of the pollutant that we need to separate is high. If the partial pressure of the pollutant is too low, a large amount of solvent would be needed and the regeneration step would require much more energy. For this reason physical absorption is not considered economic for CO_2 removal when concentration is lower than 15%. It is a method most used in pre-combustion systems (SelexolI or MDEA) rather than in post-combustion one.[11] [9][18]

Membrane absorption is another situation where the CO_2 is captured using an absorption solvent (it can be chemical and physical)[19]. However, in this case the contact between the solvent and the gas stream is promoted by the membrane that works as a contacting device. The membrane could or could not add additional selectivity to the system, and because the capacity of separation depends of the CO_2 concentration they are suitable to treat only high concentration CO_2 streams.[19][20]
The solvent anyway needs to be regenerated in a different reactor by heating it, as it is done in MEA absorption systems, or by reducing the pressure of the pollutant using a sweep stream in a different membrane system.

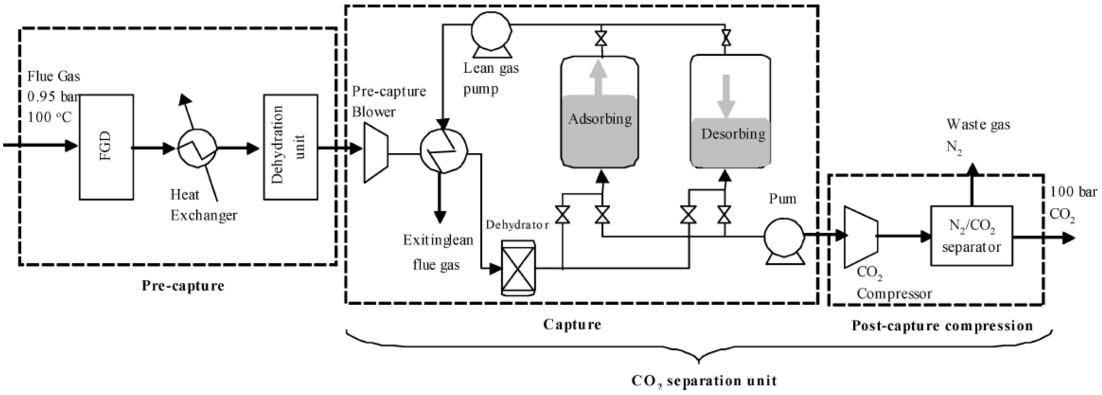
This technic could be used to capture CO_2 produced by a power plant, but only when the concentration of pollutant is particularly high. For this reason is not usually used and its application is mostly limited to natural gas purification for oil and gas industries application.



2.7 Membrane absorption system

2.2.2 Adsorption

Adsorption can be both a chemical of physical process where CO_2, in specific temperature and pressure conditions, creates bond with a solid surface and stays attached to it. As in the case of absorption, regeneration of the adsorbent is needed to ensure the process to be continuous and to create the CO_2 rich stream to compress and send to the storage system.
Regeneration can be achieved with an increase in temperature through heating, or a decrease in pressure, as both operations result in CO_2 to be released by the solid adsorption material. With different adsorbent bed connected in parallel it’s possible to operate a single reactor alternatively regenerating it without stopping the overall process.[21]



2.8 An example of adsorption system for CO2 capture applications

The weakness of this technology is the low adsorption capacity and selectivity of available adsorbent materials, that makes adsorption not easily applicable to a post-combustion capture systems, due to the low CO_2 concentration of flue gas.[22]

2.2.3 Membranes

With membrane based systems the selectivity is provided by the membrane itself that lets permeate CO_2 more easily than other gases. The driving force of the process is the difference in partial pressure of every chemical species at either sides of the membrane, for this reason these systems are suited to treat high concentration streams. There are many different solutions that use a different numbers of membranes in different configurations to achieve the CO_2 capture desired with good purity.

First of all we can distinguish two kind of membranes.[23] Membranes in the strict sense of the word where a solid structure (polymeric, metallic or zeolitic) separate selectively a chemical species according to different partial pressure. The leading process is diffusion in the membrane and the selectivity is caused by different molecules size and chemical affinity with the membrane.[23]

The second type of membranes is the supported liquid membrane[24]. In these membranes the solid structure does not have the objective of adding selectivity to the system but only to keep a solvent immobilized and still. The solvent can be blocked in the solid pores or be immobilized between two sheets of non-porous solid support. The active mean of transport of the chemical species desired is the solvent which absorb it from one side of the membrane and desorb it on the other side.

The main problem of these system is the large membranes area required to treat great volume of flue gas, that makes costs rise rapidly as there are no substantial scale effect on the membrane cost as bigger area are achieved just connecting more smaller modules.

Membrane systems have been successfully used in natural gas extraction industry to purify the natural gas produced by wells. Some gas fields in fact produce a natural gas with a strong presence of carbon dioxide (up to 40%) that needs to be purified to be able to transport and burn it. This shows how this technology could be used effectively if the CO_2 concentration in the flue gas produced by a power plant would be higher.

Flue gas produced by a boiler could be then enriched of CO_2 with a recirculation system that would allow to capture CO_2 with a very low operative cost. The energetic benefit comes from the fact that there is no need to heat the solvent to regenerate it which results in an enormous energy saving.

2.2.4 Cryogenic separation

As at atmospheric pressure CO_2 liquefies at -56.6°C, [25] we could think to cool all the flue gas produced by a fuel combustion and to separate CO_2 by condensing it. The energy costs that have to be sustained for the cooling however make this system not economically competitive for low concentration CO2 steams and is usually used just to additionally purify the CO_2 streams before sending it to the transportation system.[25]
The cost for cryogenic distillation has been predicted by lab-scale experiments to be approximately 32.7$/t CO2 separated [26]. This can be compared to the absorption cost of 13.9 $/t CO2 removed and adsorption's 27.8 $/t CO2 [25]

2.2.5 Hybrid cycle with MCFC

This solution, which is quite innovative, consists in feeding the CO_2 enriched flue gas to the cathode of a molten carbon fuel cell (MCFC) which is able to separate the CO_2 present from the N_2 diluent and to create a H_2O and CO_2 rich stream at the anode side of the fuel cell, making it easy to capture carbon dioxide.[27]
The benefit of this system is that there is little change needed to retrofit it to an existing power plant. On the other hand the short operative life and low reliability of MCFC makes this solution not economically competitive yet.

2.3 Membranes for CO2 separation

2.3.1 Membrane characteristics

As already said membrane systems have been successfully used in the last years in different application for gas separation and purification (as in the natural gas industry). Many different kind of membranes have been analysed and created to operate in different conditions and for different applications.

Despite this great variety of membrane types every membrane system can be described defining some of it technical characteristics that describes it ability to effectively separate gasses.

-Solubility: it express the amount of gas that can pass into solution in the membranes and it is a function of the chemical structure of the material with whole the membrane is built, the temperature and pressure.

Solubility is measured in $[mol/(m^3 * Pa^y)]$ where the exponent y depends on the diffusion mechanism that occurs in the considered membrane.

-Diffusivity: is represents the speed of diffusion of a specific gas into a material. It is a function of the kinetic energy of the moving molecules and the viscosity, the molecular size of the crossed material and temperature. This characteristic is measured in [m^2/s].

-Permeability: from a mathematic point of view it is the product between the diffusivity and the solubility of the considered gas. It represents how quickly a gas can flow through the considered material and it is measured in $[mol/(m * s * Pa^y)]$.

-Permeance: it represents the amount of gas that can permeate through a membrane per unit of surface and of partial pressure. It takes account of the membrane thickness also and it is characteristics of a specific combination of gas-membrane.

It is measured in $[mol/(m^2 * s * Pa^y)]$.

-Selectivity: It is the ratio of the permeability of different gas and it shows how a membrane is able to permeate one specific chemical special and not the others.

2.3.2 Description of the MATLAB model of the membrane

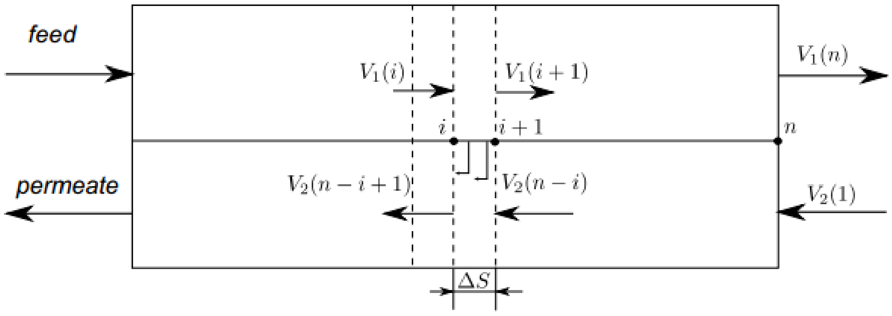
The simulations of the membranes that will be done for this work have been carried out using a MATLAB model developed by Marco Maran in the performance of his Master thesis. Here a short description of the simulation methodology will be given.

The assumptions at the base of the simulation code are the sequent:

-Permeation process follow Fick's law.
-Stationary condition.
-No membrane plasticization.
-No pressure loss.
-Temperature effect on membranes properties is negligible.
-No concentration boundary layer.

A numeric procedure is used to determine the amount of each of the chemical specie involved that permeates from the feed to the permeate side of the membrane. The Newton’s method is used for its quickness to reach the desired solution.

The surface is divided in a chosen number of smaller area and on each of it the Fick’s law is applied. On each section of the membrane the energy and mass balance is applied and the real trend of the concentration of each gas on both sides of the membranes is obtained. The calculation is iteratively repeated until, starting from the linear trend that is used as first try solution, correcting the concentration trend all the balances are verified.



2.9 Membrane schematization.

Being the membrane considered counter-flow the exit point the feed flow interacts with the input flow of the permeate side. This is why the calculation has to be iterative as the behaviour of each membrane section is influenced by both the following and the preceding ones.

2.4 State of art of deep eutectic solvents supported membranes

In this section an overview about the current state of art of this new class of solvents will be given as they will be used in the capture system analysed in this study.

2.4.1 Why deep eutectic solvents

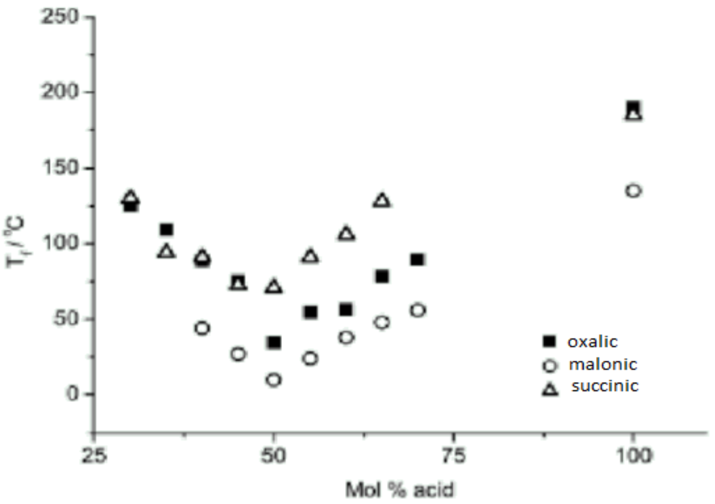
In most used CCS technology the CO_2 capture cost is high due to the high costs of the material used in the separation unit (e.g. palladium membranes for pre-combustion capture,
corrosion-resistant steels used in amine post-combustion absorption) or high operative costs (e.g. high pressure drops in multi-stages membrane

systems, solvent regeneration in pre and post-combustion absorption systems)[28].

Nowadays amine absorption of acid gasses seems the most advanced technology available and the one that can more easily approach the scale needed for power plants applications.
Main problems of this system are: high corrosion of the reactors where absorption and regeneration take place, solvent degradation due to contact with oxides and acid components present in the flue gas, high energy cost of the regeneration step of the solvent.

For these reasons big effort is concentrated on the research of new solvents to replace conventional ones in order to reduce the cost of CO_2 capture.
Ionic Liquids (IL) have been recently proposed as possible amine substitute as they exhibit some very interesting characteristics such as wide liquid range, non-flammability, thermal stability, good tunability, low corrosion power and easy recyclability.
Unfortunately difficult accessibility to some of their chemical components and low degree of recoverability are problems that limit their use in large scale.[29]

Recently a new type of solvent have been presented by Abbott et al. [30],realized with urea and choline chloride, materials with high melting point that, once mixed, they form an eutectic compound with large liquid range as shown in fig 2.10.



Freezing points of choline chloride with oxalic, malonic, and succinic acids as a function of composition.

2.10 Freezing point of different deep eutectic solvents.

For the idea of creating a liquid solvent starting from solid components with high melting point these solvents have been called Deep Eutectic Solvents, and they present interesting properties which made them interesting as CO_2 capture solvents.

They seem to present most of the positive characteristics of IL but overtaking their main disadvantages. First of all DES can be easily prepared starting from renewable, non-toxic, natural chemicals which makes their preparation relatively cheap, and they can be tailored to specific use changing the amount and nature of starting materials of the mixture.

The low cost starting materials make them perfect for large scale application in chemical and power production industry.

The production process of DES is extremely easy as it is enough to mix the starting materials at moderate temperature. They can be easily recovered as no chemical reactions are involved in their formation significantly reducing the cost of disposal of degraded solvent.

2.4.2 Research on DES

The first article about DES was published in 2003 by Abbott et al [29] and since that moment the global interest about this new kind of solvents have grown progressively.

The background principle that makes possible to create a liquid solvent starting from solid components with high melting point is still not completely understood. Abbott et all. [29] suggested in their publication that the H-bonding formation between the starting materials can be the main reason for the drastic drop of the melting temperature of the compound. The eutectic behavior would be the result of the right combination of an hydrogen bond donor and an hydrogen bond acceptor.

In 2011 30 new possible combination have been discovered combining choline chloride, natural carboxylic acids, different sugars and water [30][31][32] which are called natural deep eutectic solvents (NDES) as they are formed by starting from natural and environmental friendly components.

The growing interest about these new solvents is mainly driven by the fact that they present most of the IL advantages but overcoming their limitation with the possibility to be prepared in an easy and cheap way and to be environmental friendly. [33]

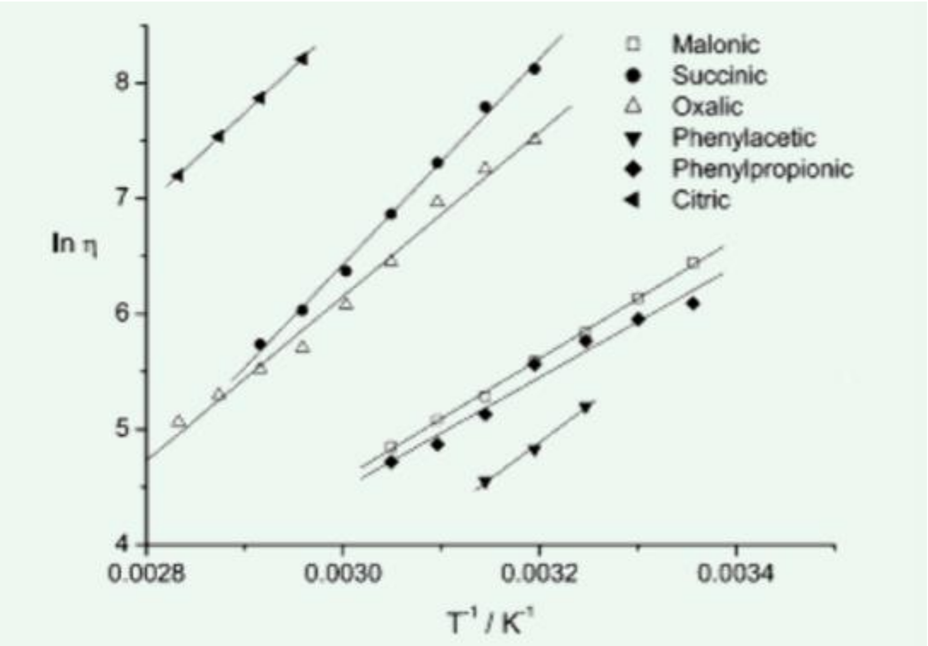
2.4.3 Use of DES in CO2 capture technology

As is has already been said DES can be a valid substitute of IL in CCS application, especially if used in a supported membrane system and they can be used in both pre and post-combustion CCS systems.

The use of DES in a supported liquid membranes provide many advantages compared with an absorption solution used with MEA solvent.

First of all there is no need for a thermal regeneration process which dramatically reduce the overall energy cost of capturing CO_2 and the efficiency loss due to capture system.

Secondly the solvent does not need to be moved and pumped which would cost a lot of energy because the DES viscosity is really high in the range of temperature of our interest (80°C – 100°C) as can be seen in fig. 2.11

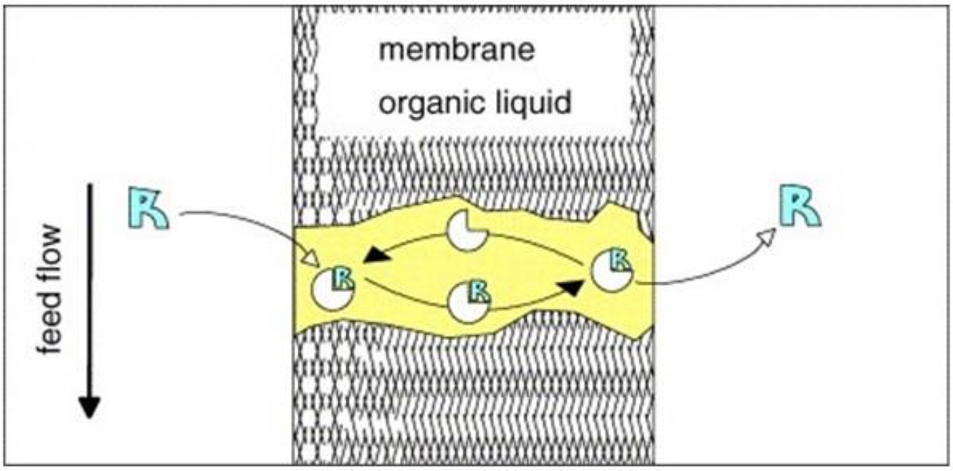


2.11 Viscosity of different deep eutectic solvents in function of temperature.

Last but not least, being the solvent immobilized into the membrane, it does not get in contact with any other equipment part reducing corrosion problems [33].

Two different configurations are usually used in supported liquid membranes[30][34].

In the first one it is used a porous support, usually a polymeric membrane, which can add or not selectivity to the system, in whose the solvent pores is placed and immobilized.



2.12 SLM principle of operation.

The other solution is to keep the solvent blocked between two non-porous membrane surfaces.(dense membranes)
The principles at the basis of these two solutions, however, is exactly the same: pollutant molecules diffuse or dissolve into the membrane or directly in the liquid solvent and is than desorbed at the opposite side usually due to a pressure difference, shown in fig. 2.12

We can find many different parameters that can have an effect on the membrane behaviour.
First of all temperature and pressure play a key role in the solvent permanence into the membrane. High operative temperature can cause evaporation and loss of solvent which then would have to be reintegrated, and removed from the flue gas streams before venting them to the atmosphere; low pressure can instead cause liquid solvent dispatch from the membrane pores.

DES seem ideal because they have characteristics that make them suitable to overcome these problems. Their low volatility, high viscosity (Cp>100 at room temperature for most of them) [35] and high chemical and thermal stability make them suitable for these applications [36].

Operative temperature is an important parameter for another reason too. The temperature range of an operating system is very important because it needs to be compatible with the freezing point of the DES solvent that need to be used.

Freezing temperature for many DES solvents have been obtained and the range goes from -66°C to 150°C but most of them are liquid at temperature below 100°C [35].

Currently a specific study about the use of DES supported liquid membranes does not exist yet. Although they are very similar to IL the number of papers about gas separation and liquid vapour equilibrium process using DES are scarce.

Some publications report examples of DES which present a high capacity towards CO_2 [37][38], but a regular analysis of CO_2 absorption capacity of all DES has not been realized.

The possibility to create a membrane for CO_2 capture application is under study right now at the TUE of Eindhoven where preliminary data obtained are listed here:

- Permeability: 500 [barrer] (167 [10^{-15} mol m m^{-2} s^{-1} Pa^{-1}])
- Selectivity CO_2/N_2: 50-80
- Membrane thickness: 50 [μm]

3 PLANTS DESCRIPTION

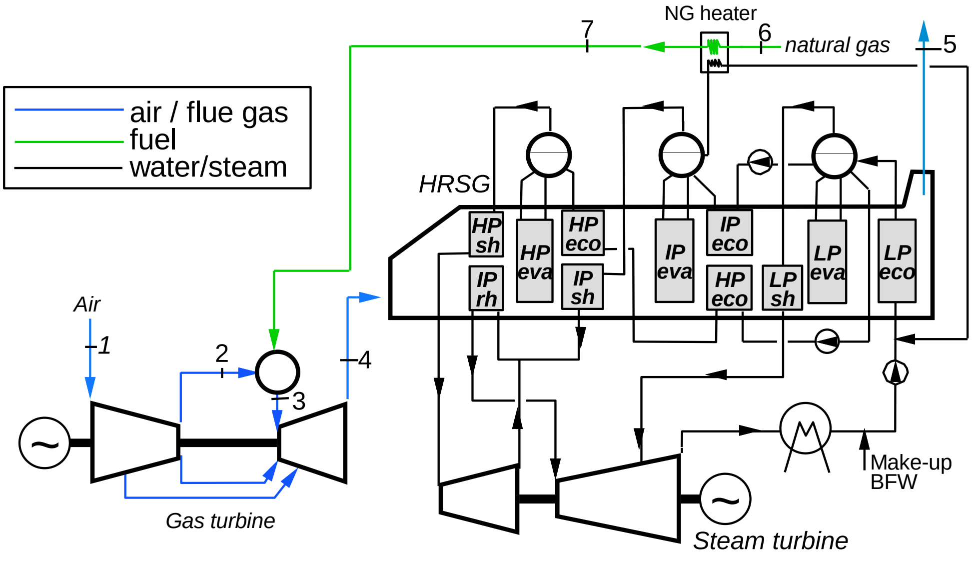
In this chapter a detailed description of the power plant studied will be given. First of all the base power station without the capture system will be described in detail and the assumptions for the simulation of the main equipment needed will be listed. In the second part will be described the modification of the power plant needed for the application of the two different capture system selected.

3.1 Reference power plant

3.1.1 Plant configuration

The reference case that will be taken in consideration is a 400 MW size conventional natural gas combined cycle (NGCC) where the flue gas released by one gas turbine at high temperature are sent into a heat recovery steam generator (HRSG).

In Fig. 3.1 it is possible to see a simplified plant scheme that shows the main equipment and the flows of the power plant.



3.1 Reference case power plant scheme.

3.1.2 Fuel

The hypothesized fuel that will be used in the simulations is natural gas with the fixed composition showed in table 3.1.

Table 3.1 Natural gas composition

Chemical species	*Molar fraction [%]*
CH_4	89
C_2H_6	7
C_3H_8	1.1
CO_2	2
N_2	0.89

The fuel is hypothesized to be made available from the pipeline at a fixed temperature of 10 °C and a pressure of 70 bar. A dedicated compressor to take the fuel to the operative pressure of the combustor is not needed as the fuel is already pressurized.
Before being burned in the gas-turbine combustor, the fuel is heated to 160 °C using high temperature pressurized water taken from the HRSG.

All the simulations will be made using a fixed mass flow of fuel equal to the one used in the reference case (14.755 kg/s); the thermal input of the power plant will be the same in all the different cases that will be considered.

Knowing the composition of the natural gas burned the simulation programme used can easily calculate the LHV of this fuel which is equal to 46.77 kJ/kg.

In the HRSG the flue gas are cooled by generating steam at different pressure level that will be sent to a steam-turbine to generate extra electric power.

3.1.3 Main compressor of the gas turbine

The gas turbine operates using a simple joule cycle with no intercooled compression and post-combustion system. The turbine used is a single-shaft turbine with a compression ratio of 18 which gives the best thermodynamic performances.

The air taken by the compressor from the environment is at a fixed temperature of 15 °C and at a fixed pressure of 101325 Pa. The turbine uses air both for the burning process of the fuel, the cooling system in the turbine blades.

The compressor of the gas-turbine system brings the air from a pressure of 1,00.3 bar (lower than atmospheric pressure due to the pressure loss in the aspiration system) to a pressure of 18.16 bar causing the air to heat due to compression to 420 °C approximately.

Part of the air compressed is sent to the combustor where it is mixed with the natural gas and then burned. A part will be separated and used in the open cycle cooling system on the turbine blades and will be mixed with the flue gas produced by the combustion process during the expansion in the turbine. A little fraction of air (fixed at 0.75%) will be lost for leakages.

In table 3.2 are listed the main assumptions for the calculation of the compressor.

Table 3.1 List of assumptions for the compressor.

Parameter	***Value***	***Unit***
Compression ratio	18	[-]
polytropic efficiency	90	[%]
Organic efficiency	99.865	[%]
Leackage	0.75	[%]
$\Delta h_{is,max}$ per stage	2.3E04	[J/kg]

3.1.4 Combustor

In the combustor the hypothesis of complete combustion is made to calculate the composition of the flue gas. The production of NO_x is not taken into consideration by the simulation program but usually in a real gas-turbine the NO_x emissions are very low and controlled with a premixed combustion system that lowers the NO_x emission keeping the combustion temperature low. A selective catalytic reduction (SCR) system is usually not required to further reduce the nitrogen oxides concentration in the flue gas to respect the low limits.

Table 3.2 List of assumptions for the combustor

Parameter	***Value***	***Unit***
Efficiency of combustion	99.82	[%]
ΔP_{comb}	3	[%]

3.1.5 Gas-Turbine

Due to the pressure drop caused by the combustor and the HRSG the input pressure in the turbine is about 17 bar and the flue gas discharge in at 1.04 bar. To have a correct expansion of the flue gas 4 stages are requested and some of them will need a cooling system to resist at the high temperature of the flue gas.

The cooling system works in an open cycle solution and for this reason the flue gas produced in the combustor are mixed in every stages with the cooling streams resulting in a growing mas flow expanding in the turbine. The maximum turbine inlet temperature (TIT) allowable by material resistance is 1360 °C, for this reason the first three stages of expansion needs to be cooled with air taken from the compressor; in addition in the first two stages of the turbine a thermal barrier coating (TBC) is used to increase the material resistance at high temperature.

3.1.6 HRSG and steam cycle

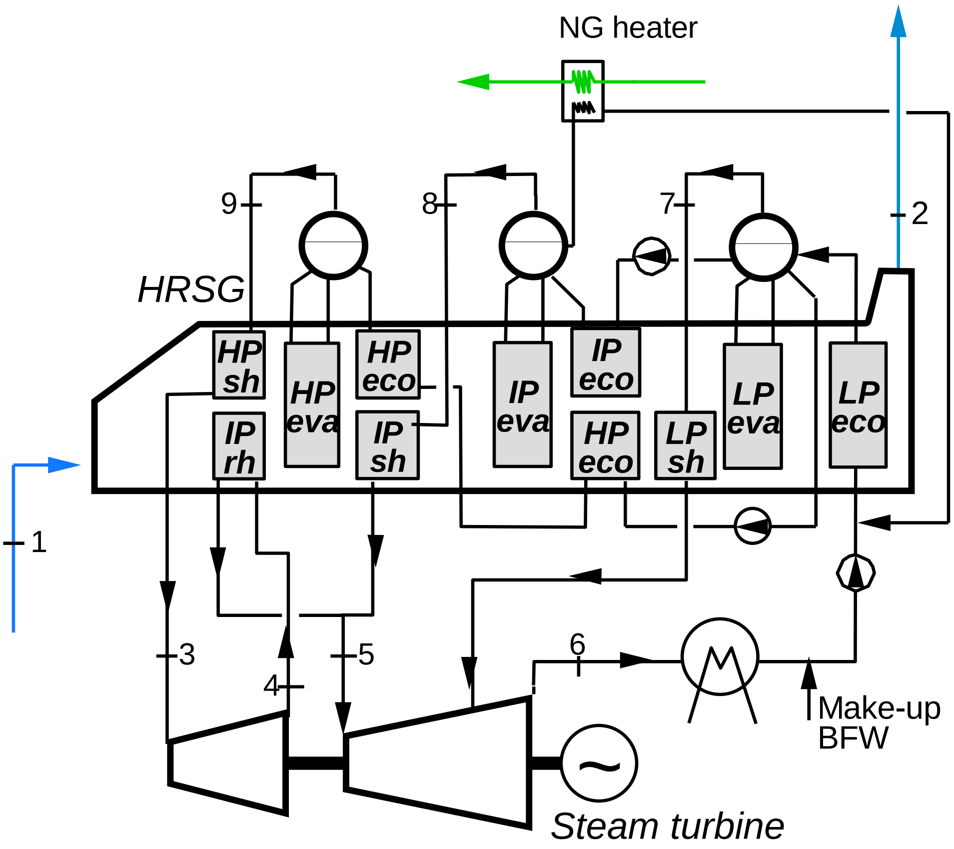
The gas obtained by mixing the combustion products with the cooling stream are still at high temperature at the end of the expansion (615 °C). A great part of the energy released by fuel combustion is still available as sensible heat; in the heat recovery steam generator the highest part possible of this energy is recovered generating stream at different pressure levels that will be used to power a steam turbine and generate additional electric power.

In our reference case steam is generated at three pressure levels (130 bar, 28 bar, 4 bar); the highest and lowest level are simple superheat section where steam is generated and then superheated. The middle pressure section also operate a reheat of the steam released by the high pressure turbine before resending it to the middle pressure stages.
Part of the water heated in the middle pressure economizer is taken out of the HRSG and used to heat the natural gas before sending it to the combustor.

Thanks to the HRSG and the bottoming cycle in general the global thermal efficiency of the power plant is greatly increased; it is possible to reach an efficiency of 58.59% while with the gas turbine only the efficiency would be 38.1%.

The final temperature of the flue gas in our reference case in approximately 80 °C. Lower temperature could be reached, if desired, cooling even more the flue gas, in this way the total heat recovered would increase but other problems may arise.

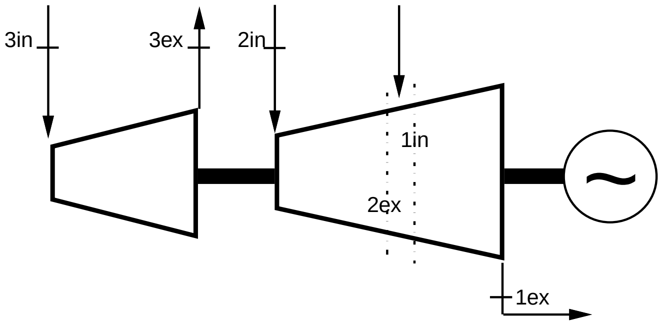
The condensation of the steam expanded in the turbine is done at a fixed temperature of 32.17 °C at which corresponds a pressure of 0.048 bar.



3.2 HRSG and steam cycle scheme.

Table 3.3 Steam cycle thermodynamic points.

	M [kg/s]	*P [bar]*	*T [°C]*	*h [kJ/kg]*
1	635.77	1.01	613.9	-618.45
2	635.77	1.01	81	-1213.21
3	75.329	120	559.51	3502.9
4	75.329	28	337.69	3093
5	89.8531	22.96	560.95	3599.2
6	99.5977	0.048	32.17	2376.9
7	9.7447	4	143.62	2737.6
8	14.6079	28	230.05	2802
9	75.329	130	320.83	2667



3.3 Steam turbine scheme.

Table 3.4 Expansion line of the steam turbine.

	M [kg/s]	*P [bar]*	*T [°C]*	*h [kJ/kg]*	*s [kJ/kgK]*	*x*
3in	75.329	120	559.51	3502.9	6.6784	1
3ex	75.329	28	337.69	3093	6.7375	1
2in	89.8531	22.96	560.95	3599.2	7.5338	1
2ex	89.8531	3.52	291.31	3050.6	7.5968	1
1in	99.5977	3.52	291.81	3051.6	7.5986	1
1ex	99.5977	0.048	32.17	2376.9	7.8099	0.9244

Here in Table 3.5 are listed all the main assumptions used in the definition of the HRSG of the bottoming cycle.

Table 3.6 List of assumption for the HRS and steam turbine.

Parameter	*Value*	*Unit*
Condenser Pressure	0.048	[bar]
Max steam temperature	565	[°C]
Organic efficiency steam turbine	98.5	[%]
ΔT_{AP}	25	[°C]
ΔT_{PP}	10	[°C]
ΔT_{SC}	5	[°C]

3.1.7 Flue gas treatment

Natural gas combined cycle usually do not require additional pollutants abatement treatment, such as flue-gas desulfurization (FGD) or SCR, of the flue gas. The FGD in not required most of the time because the sulphur content of natural gas is usually very small if not equal to zero. The SCR section is requested only when very low emissions limits are applied by low for special geographic areas (as urban areas) the use of a premixed burning system usually guarantee an acceptable low level of NO_x emission. Ash capture units such as fabric filters (FF) or electro static precipitator (ESP) are not required as natural gas is ash free.

With this configuration and the assumptions highlighted before, a simulation of the power plant is done to estimate its global performance. This will allow us to compare the results obtained after the application of the CCS system and understand the impact of this one on the power plant performances.
The main results obtained are listed in table 3.7.

Table 3.7 Reference power plant performances.

Parameter	***Value***	***Unit***
$\mathbf{M_{air}}$	621.02	[kg/s]
$\boldsymbol{\eta}_{\mathbf{tot}}$	58.59	[%]
$\mathbf{W_{tot}}$	401.68	[MW]
$\boldsymbol{\eta}_{\mathbf{tg}}$	38.1	[%]
$\mathbf{W_{tg}}$	261.22	[MW]
$\mathbf{W_{tv}}$	140.46	[MW]
$\mathbf{T_{out,GT}}$	615.8	[°C]
$\mathbf{T_{out,HRSG}}$	80	[°C]
Specific emission	352.62	[kgCO2/MWh]

The composition of the flue gas produced by the power plants is of our interest too as it will affect significantly the CCS system performances.
With no recycle of flue gas or CO_2 the composition of the flue gas obtained is shown in table 3.7.

Table 3.8 Chemical composition of the flue gas produced by the reference case power plant.

Chemical species	***Molar fraction [%]***
Ar	0.885
$\mathbf{N_2}$	74.355
$\mathbf{O_2}$	12.323
$\mathbf{CO_2}$	3.994
$\mathbf{H_2O}$	8.442

Table 3.9 Main thermodynamic points of the cycle of figure 3.1

Point	*Description*	*T [°C]*	*P [bar]*	*M [kg/s]*	*Composition [% mol]*							
					Ar	**CO_2**	**H_2O**	**N_2**	**O_2**	**CH_4**	**C_2H_6**	**C_3H_8**
Amb		15	1.01		0.920	0.030	1.034	77.282	20.733	0	0	0
1	T. input	15	1	621.02	0.920	0.030	1.034	77.282	20.733	0	0	0
2	Comb. Inp.	417.6	18.16	501.43	0.920	0.030	1.034	77.282	20.733	0	0	0
3	Turb. Inp.	1448.5	17.61	516.18	0.877	4.895	10.13	73.690	10.412	0	0	0
4	Turb. Out.	615.8	1.04	631.12	0.885	4.023	8.443	74.334	12.262	0	0	0
5	HRSG Out.	81.0	1.01	635.77	0.885	3.994	8.443	74.355	12.323	0	0	0
6	Fuel 1	10	70	14.750	0	0	0	2	0	89.0	7.01	1.10
7	Fuel 2	160	70	14.750	0	0	0	2	0	89.0	7.01	1.10

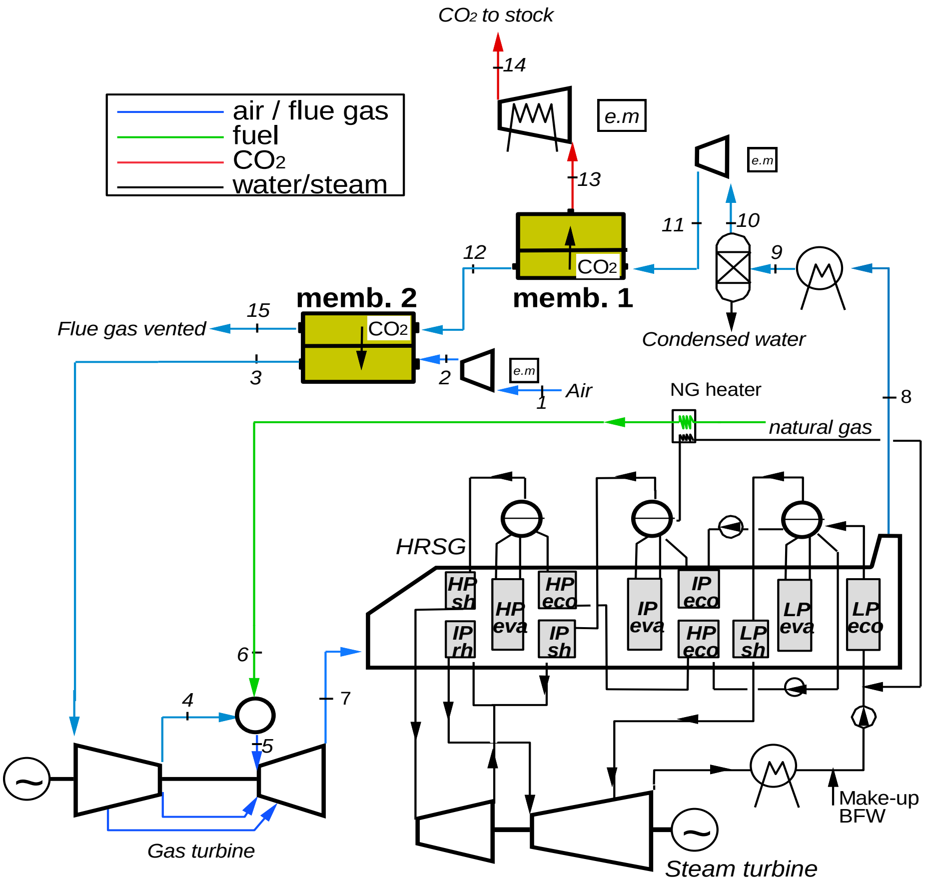
3.2 CO2 capture case with selective recirculation of carbon dioxide.

3.2.1 Plant configuration

The capture system that will be first studied is based on the work of Merkel et al. [39],which managed to achieve a concentration of CO_2 in the flue gas of 23%. In this study the recirculation of CO_2 will be pushed even further in order to significantly increase the carbon dioxide concentration in the flue gas produced by the combustor.

The CO_2 concentration in the flue gas obtained with the simulation of the conventional power plant is extremely low (approximately 4%). This means that applying a simple separation with CO_2 membrane as a post-combustion system would give many problems. The main one is that with a so low concentration of the flue gas it would be extremely difficult to obtain CO_2 with good purity to send to the storage location. But most important is that a high compression of the feed gas of the membrane (the flue gas flow) would be needed to achieve the driving force required for the permeation of CO_2 with a huge energy cost.
That is why we decided to enrich the input flow of the gas turbine recycling CO_2 in order to simplify the separation of carbon dioxide in the capture unit.

The power production section scheme will be substantially unchanged and additional equipment will be added to achieve the CO_2 capture level desired. We will use a post-combustion capture system that uses two different deep eutectic solvents supported membranes (DESSM) to both separate CO_2 to capture and to enrich the input air to the gas turbine with carbon dioxide.



3.4 General equipment scheme of the power plant with selective recirculation of CO2 and CO2 capture.

3.2.2 Gas-turbine

As already said the general scheme of the power section of the plant will not be modified but some of its parameter will significantly change due to the modification of the composition of the gas flowing in the system.

The main differences may be found in the gas turbine equipment. First of all the compression ratio of the Joule cycle that gives the best performances of the overall system may be significantly different from the reference power plant.
The modification of the composition of the stream flowing in the equipment due to the strong CO_2 enrichment can make us expect that the optimum value of the compression value will be higher such as 25-30 instead of 18. Secondly the turbine output temperature (TOT) has to be carefully checked to ensure the integrity of the equipment.

The change of the TOT value can also affect the total energy that can be extracted and converted into electricity from the flue gas by the gas-turbine rather than in the HRSG.

Due to the different characteristics of the flow and the compressor output temperature the amount of gas needed in the cooling system of the turbine may significantly change compared to the reference power plant.

The max TIT that we will assume remains the same of what has been used for the reference case (1360 °C) and will be obtained recycling as much CO_2 as needed in substitution of excess fresh air used in the reference power plant.

3.2.3 Combustor

The combustion process will be significantly different from what happened in the reference power plant. The substantial difference will be in the oxygen present to sustain the combustion process.

In the reference case the amount of fresh air taken from the environment by the turbo-gas compressor was fixed to have enough excess air in the combustor to keep the maximum input temperature in the turbine at a desired value. With this capture system applied we will try to enrich the flue gas with as much CO_2 as possible. The amount of air sucked from the environment will be fixed to just have enough oxygen in the combustor to ensure a complete combustion of the fuel. All the excess air will be replaced by CO_2 recycled from the flue gas.

To ensure enough oxygen for the combustion process we will fix at a desired value the amount of O_2 to be found in the flue gas produced in the combustor. In this way we will decide how much excess fresh air will be used in the power plant.

3.2.4 HRSG and steam cycle

The steam cycle when CO_2 capture is applied is exactly the same. Just very little modification on the assumptions will be done. As the flue gas, once released by the HRSG, will be cooled to a temperature of 35 °C in any case for membrane stability reasons the condition on the minimum output temperature of the HRSG can be released.

In fact it would be better to cool the flue gas as much as possible in the heat recovery steam generator because at least the energy would be recovered in the bottoming cycle. The fraction of heat that will be extracted from the flue gas to bring them to 35 °C after the HRSG will be completely lost. This operation can results also in a smaller, and cheaper, cooling system of the flue gas in the CO_2 capture pre-treatment

The input temperature of the HRSG can be significantly different because of the change in the TOT of the turbine. An increase of this value would modify the total amount of energy that have to be recovered in the bottoming cycle. This would require a bigger boiler and a larger steam turbine meaning a full redesign of the bottoming cycle equipment.

3.2.5 Flue gas cooling

A cooling system has been added to the system to further cool the flue gas released by the HRSG. The final temperature of the gas has been fixed to 35 °C. There are many different reasons why this cooling system has been used.

The first one, and the most important is that most of the membranes available nowadays can have stability problems at high temperature. A high temperature has also proved to negatively affect the selectivity of the whole system. These two reasons are enough already to justify the additional cost for the heat exchangers.

Another reason is that in this way, we can bring the flue gas to the water saturation point that will so condensate in drops. With opportune equipment such as a demister this water can be eliminated from the main stream before entering the real CO_2 capture section.

This will both increase the CO_2 concentration in the flue gas sent to the capture unit and will also reduce the uncertainty given by the unknown impact of water on DESSM. In fact the effect of the presence or not of water vapour has not been deeply studied yet; in this way, reducing the H_2O presence we reduce the possible negative effect on the CCS system.

Reducing the temperature of the flue gas will also reduce the consumption of the venting system needed by the CCS system and of the gas turbine compressor. In fact the CO_2 recycled will be at lower temperature, which means that the input temperature of the gas turbine compressor will decrease allowing a smaller energy consumption in the compression phase of the Joule cycle, increasing the global efficiency of the power plant.

The last good reason to cool the flue gas is that in this way the problem of solvent loss in the supported membrane due to evaporation is minimized.

3.2.6 Membrane separation unit

The membrane that will be used in this study are based on the application of the new deep eutectic solvents (DES) in a supported liquid membrane solution. A complete analyses on DESSM is not still available nowadays, but in table 3.10 are listed the characteristics that the first study made at the TU/e of Eindhoven has recorded.

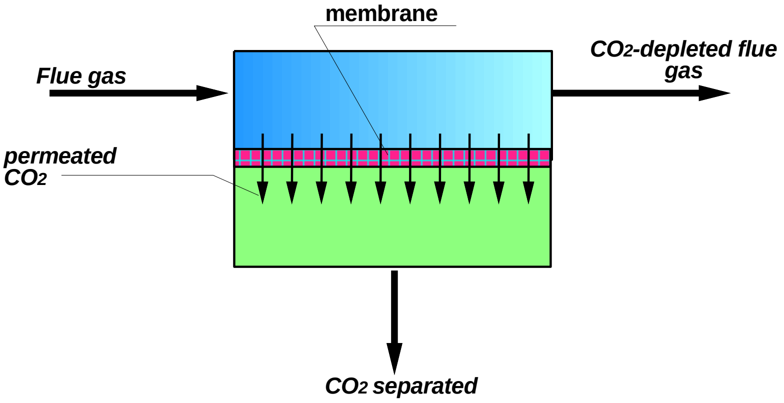
This membrane system for CO_2 capture is formed by using 2 different membranes that do radically different jobs.

Table 3.10 DESSM characteristics

Parameter	***Value***	***Unit***
Permeability	500	[barrer]
CO_2/N_2 Selectivity	60-80	[-]
Membrane thickness	50	[µm]

The direct value on CO_2/O_2 selectivity is still not available but we can expect it to be similar to the CO_2/N_2 selectivity.
The effect of the presence of water in the feed steam is unknown and it can have both a positive or a negative effect on the global performances of this kind of membrane for CCS application.

The first membrane that the flue gas meet once they leave the HRSG has the specific purpose to separate the CO_2 that we want to capture and send to the transport and storage system.
In this study we will consider to use counterflow membranes that give best performances in terms of area of contact needed and purity of the permeate stream.
A vacuum pump will be used to reduce the pressure at the permeate side at approximately 0.2 bar to enhance the driving force of the permeation process obtaining, in this way, a smaller surface and a higher CO_2 purity in the permeate stream.



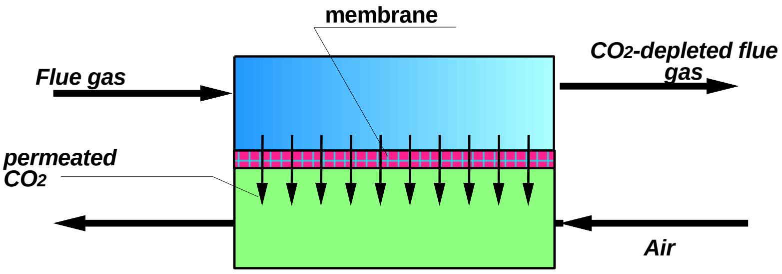
3.5 First membrane functioning

The second membrane will be used to act a selective CO_2 recycle in order to increase the CO_2 concentration in the final flue gas. Different studies [39] conducted on NGCC power plants have already shown that with this particular system it is possible to increase the CO_2 concentration further than using a simple exhaust gas recycle (EGR) thanks to the lower amount of diluent (mainly Nitrogen) recycled.

The idea of this system is to replace the high mass flow of excess air requested by a gas-turbine, which is the reason of the low concentration of CO_2 in the flue gas, with CO_2 recycled in this membrane in order to keep the TIT at a desired value without diluting the CO_2 produced by combustion.

Increasing the CO_2 concentration in the flue gas allow to reduce the size of the first membrane system, but what is more important is that makes possible to obtain a higher CO_2 purity in the captured stream. If CO_2 concentration in the permeate side of the first membrane is high enough (approximately 95%) the use of a purification unit such as a cryogenic system can be avoided reducing the energy cost of carbon capture.

To enhance the driving force of the permeation process of the second membrane will not be used any vacuum pump on the permeate side or compression of the feed gas. Instead the fresh air sucked from the environment will be used as a sweep stream on the permeate side; the extremely low concentration of CO_2 in air (390 ppm) is used to guarantee the driving force of the process.



3.6 Second membrane functioning

3.2.7 Flue gas and air circulation system

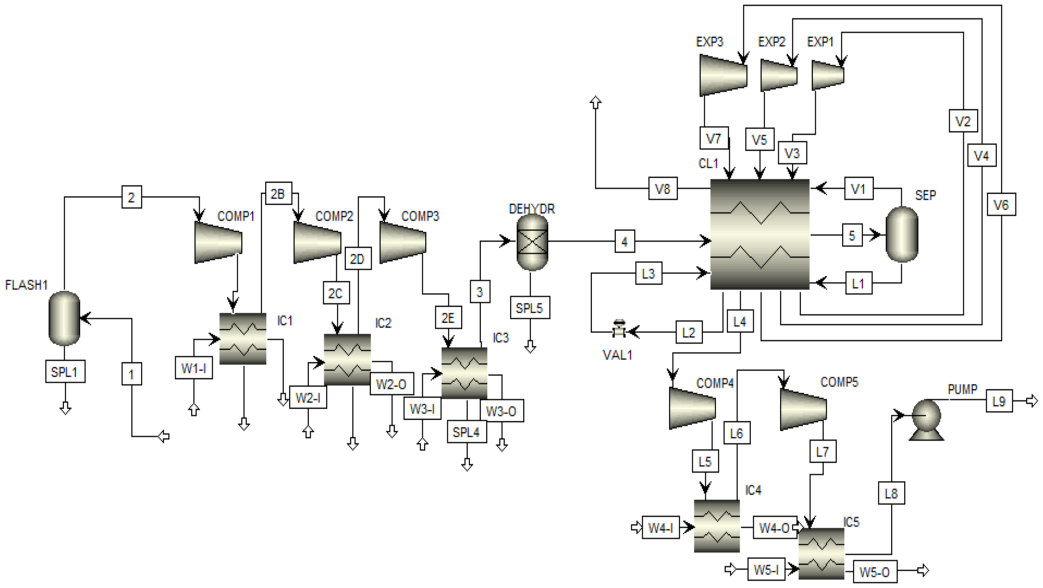
The two membrane systems will cause a pressure drop both in the feed and permeate side; circulation fans will be required to win these pressure losses and will increase the energy penalty of the power plant caused by the application of carbon capture system.

The pressure drop caused at both sides has been assumed to be equal to 3% and two fans at least will be needed in the system. One have been placed just before the first membrane on the flue gas feed side, the second one will be positioned on the air sweep side in of the second membrane in order to fix the input pressure of the gas turbine compressor to 1.01 bar.

3.2.8 CO2 compression and purification system

The CO_2 separated in the first membrane will be compressed till a value of 110 bar in order to be transported in a supercritical state.
The first phase of compression from 0.2 bar to 1 bar will be simulated with a 2 intercooled stages compression; the number of stages have been defined in order to have an output temperature lower than 110 °C.
To better estimated the compression consumption of the CO_2 to the value of 110 bar an ASPEN plus intercooled compression model will be used because the assumptions of ideal gas at high pressure cannot be accepted.

The intercooled compression model will be used only when purification of the carbon dioxide captured is not required. This is the case when infinite selectivity of the membrane is assumed as, in this case, the CO_2 purity would already be 100%. When the selectivity towards all the other gasses that we can find in the flue gas is reduced we can expect a decrease in the purity of CO_2 separated in the first membrane.
When it will happen that the purity of the CO_2 separated is lower than 95% a CO_2 purification and compression unit (CPU) will be used.
A different ASPEN model will be used to evaluate the energy consumption of this equipment and the amount of CO_2 separated by the first membrane that is vented in the purification process in the CPU.
The CPU that will be used is a single flash system that is capable to increase the purity of the CO_2 captured to values higher than 97%.



3.7 Cryogenic CPU used to purify the CO2 captured.

In Figure 3.7 it is shown the ASPEN Plus scheme of the cryogenic system that has been used to evaluate the consumption for the compression of the carbon dioxide to 110 bar.

3.2.9 Flue gas compression system

In the reference CCS solution compression of the flue gas will not be used with the purpose to enhance the driving force of the permeation process, as different studies [40][41]already showed that using a vacuum pump on the permeate side is better cost effective.

The possibility to compress the flue gas to a pressure of 2-10 bar will be taken in consideration to see if it can significantly reduce the surface of the membranes required resulting in a global money saving.
In this case a compressor will be used instead of a simple fan to compress the flue gas coming out of the HRSG, and after the second membrane a gas expander will be positioned to recover part of the energy spent for the compression to reduce the auxiliary consumption and the consequent energy penalty.

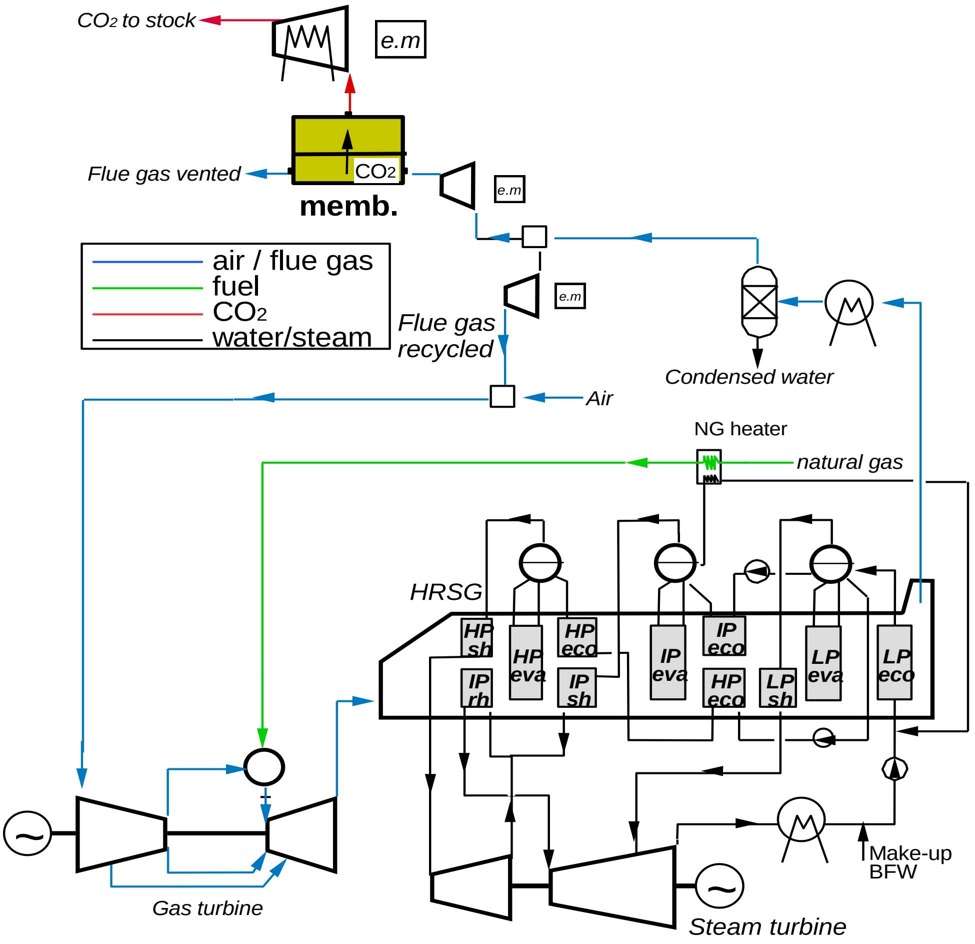
3.3 CO2 capture case with non-selective recirculation of carbon dioxide.

3.3.1 Plant configuration

The second case analyzed uses a simple exhaust gas recycle (EGR) to enhance the CO_2 concentration in the flue gas treated by the capture unit. One single membrane system is theoretically needed, as the recycle is no more selective as in the first capture case considered. The capture system is less sophisticated as the characteristics of the membrane used does not impact on the performances of the power section of the plant.

The non-selective EGR will give a lower enrichment of carbon dioxide concentration in the flue gas as a lot of Nitrogen will be recycled with CO_2. As a result the composition of the flow evolving in the power plant does not change as drastically as with selective recirculation. For this reason we can expect that the operative optimum point (compression value of the joule cycle) will not differ much from the one of the reference power plant. In addition we have to state that with this solution a modification of the structure of the capture unit would not impact in any way on the thermodynamics performances of the power plant, this means that this study is limited to a single case study where the problem will be to optimize the structure of the capture unit rather than understanding deeply the impact of the capture system on the global functioning of the power station.

As shown in fig 3.8 a part of the flue gas released by the HRSG will be simply mixed with the fresh air sucked from the environment and sent to the compressor of the gas turbine.
The remaining share of the flue gas will be sent to the capture unit to be purified.



3.8 General equipment scheme of the power plant with non-selective recirculation of CO_2 and CO_2 capture.

3.3.2 Gas-turbine

Differently from first case the gas turbine compression ratio that gives the best performances will not change. We will assume that the composition change is not strong enough to sensibly modify the power plant performances. For this reason the compression ratio will be fixed at a value of 18 as in the reference power plant.

The TOT of the turbine will not be much different from the reference case and would not give any significant problems to the gas turbine or to the HRSG. The energy converted into electricity in the gas turbine is the same and a redesign of the main equipment will not be needed.

3.3.3 Combustor

The combustor will be set as with the first capture case, the only difference will be that in this case the TIT of the turbine will be fixed by calculating the right amount of flue gas to recycled in the cycle. The amount of excess air will be fixed as in the other case by assuming to have a specific concentration of Oxygen after the combustion process has taken place.

3.3.4 HRSG and steam cycle

As for the gas turbine the steam bottoming cycle will be set as with the selective recirculation of CO_2. the flue gas will be cooled as much as possible in the HRSG in order to recover the energy that would be extracted from the flue gas in the cooler anyway.

The size of the steam cycle will be approximately the same of the reference cycle as the input temperature of the boiler will be just slightly changed.

3.3.5 Flue gas cooling

The flue gas will be cooled to a temperature of 35 °C for the reasons explained earlier. In Addition to that one we have to say that it is important to remove at least part of the water vapour that can be found in the flue gas in order not to rise too much the H_2O content in the combustor of the gas turbine.

For this reason the cooling system of the flue gas is placed before that the recycled share of the flue gas is separated from the one that will be treated in the capture unit

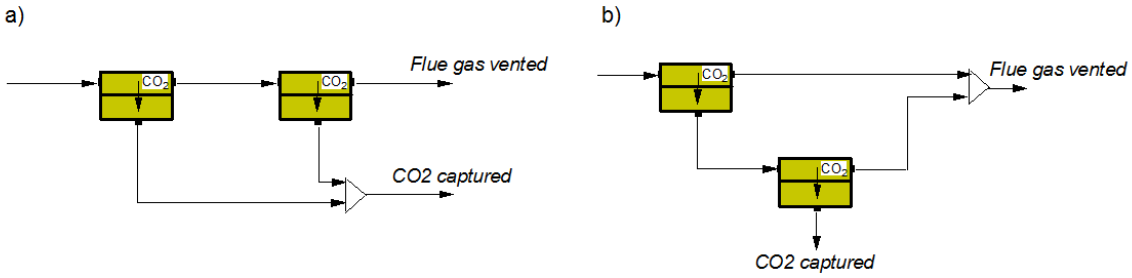
3.3.6 Membrane separation unit

With this solution just one membrane system is used. The recirculation membrane does not exist and the membranes are used just to achieve the separation of CO_2 desired.

As the case that will be analysed is just one, because the technical parameters of the thermodynamic optimum are assumed to be the same of the reference power plant, the input composition to the capture system is a constant in this study.

It has been possible to focus more to understand which disposition of membranes could give the best performances and on its optimization. As the CO_2 concentration in the flue gas obtained with a simple EGR is approximately of 9% on molar base the capture system will be more sophisticated than a single membrane as in the selective recirculation.

More than one membrane will be needed to both achieve the capture ratio desired and a good purity of the separated stream.
Li Zhao et al. [40] already did a study taking in consideration at the same time specific electric consumption and surface membrane studying two main different configuration represented in fig. 3.9.



3.9 The two different capture solution considered.

With the solution A the flue gas pass through two different membrane system in sequence. Membranes can have different selectivity and different pressure can be applied to the permeate side of them. In addition with two compressors; the first placed before the first membrane and the second one between them; two different feed pressure can also be used.
With solution B the two membranes will be placed in a different way. The first membrane will separate all the CO_2 that we desire to capture creating a first enriched stream that will anyway diluted by Nitrogen. The second membrane is fed with the permeate stream of the first membrane, in this way the CO_2 stream produced to be sent to the capture system will be greatly purified as the feed stream of the second membrane has a much higher concentration of CO_2.

The first system revealed to require much smaller membrane surface to achieve the capture ratio required but on the other side showed to not be able to give good purity of the CO_2 captured. A purity of CO_2 higher than 40% has not be reached in any simulation done with the MATLAB model of the membrane.
For this reason we decided to focus our attention on the case B as the low price of the membranes with deep eutectic solvents would reduce the problem of having larger surface for the membranes.

3.3.7 Flue gas and air circulation system

The recirculation system of the flue gas causes a pressure loss that affects both the gas recycled to the turbine input and the gas sent to the capture unit. We can assume that a pressure loss will be found when the fresh air sucked from the environment and the fraction of flue gas recycled are mixed together before the compressor of the gas turbine.

For these two reasons at least 3 fans have to be used to keep the pressure at an acceptable value in every point of the plant. The fan for the fresh air and the one for the recirculation of the flue gas are set in order to keep the input pressure of the compressor of the gas-turbine fixed to 1.01 bar.

The fan on the flue gas that are sent to the capture system is fixed in order to have atmospheric pressure at the chimney.

3.3.8 CO2 compression system

The CO_2 compression system is exactly the same of the selective recirculation case with a final output pressure of 110 bar, suitable for the transportation by pipeline of the captured CO_2.

As the purity of the CO_2 separated will be lower with this scheme because of the lower concentration of CO_2 in the flue gas the consumption for compression cannot be known before the simulation of the capture system has been done and will be calculated independently for each case.

3.3.9 Flue gas compression system

Compression of the flue gas can be used to regulate the feed pressure of both membranes. At the same time we can also fix the permeate pressure of both of them in order to try to optimize the energy consumption for the separation of CO_2 and the surface required by the membranes. In particular the feed pressure of the second membrane can be regulated in function of the purity of the CO_2 that we would want to obtain. Compressing only the permeate stream of the first membrane would results much less energy intense, as the total mass flow that would need to be compressed is much smaller and composed in large quantity by CO_2.

When compression of the feed flows is used (on the first or the second or on both membranes) we have also to consider the possibility to use an expander right after the membrane system to recover as much energy as possible that has been spent in the compression process.

4 THEMODYNAMIC ANALYSIS

In this chapter a description of the simulation programmes, and the methodology used for the calculation of the thermodynamic performances of the different schemes will be first given.
Then a summary of the main thermodynamics results will be given for the two configurations studied explaining the reasons of the behaviours found.

4.1 Methodology for thermodynamic simulations

For the thermodynamic simulation of the power plant and the capture system three different software have been used: GS, Aspen Plus, MATLAB. As different components required different levels of accuracy and different assumptions.

4.1.1 GS

GS (acronym of “Gas-Steam Cycle Simulation Code”) is the main tool that has been used for the thermodynamic simulation and evaluation of the power plant and to obtain the performances of the overall system.
It is a simulation programme developed by the department of Energy of the Politecnico di Milano. This programme is based on a modular structure that allow the simulation of a grate variety of energy system. Every single block is responsible for the calculation of a single component of the global plant. By creating the needed connection between different blocks the plant structure can be completed. The modular structure allow to easily treat even very complex system just by adding the required blocks.
Starting from a “first try solution” the programme calculates the mass and energy balance of every component in sequence modifying the parameters selected to reach a stable convergence of the solution.
After the convergence is obtained the global performance of the power plant are evaluated.

The thermodynamics properties of the mixtures involved in the process are calculated with the hypothesis of ideal mixture without taking in consideration the mixing effects.
This impossibility to treat with real gases forced us to use more sophisticated simulation software like Aspen Plus when the assumption of ideal gas would have been not acceptable.

4.1.2 Aspen Plus

Aspen plus has been used for the simulation of the compression and purification of CO_2. In the GS models we assume to compress the CO_2 captured till a pressure of 1 bar where the assumption of ideal gas is still valid. CO_2 will be compressed then to a value of 110 bar and in this process the assumption of ideal gas cannot been accepted. For this reason Aspen Plus has been used to simulate and have an estimation of the electric consumption of this part of the plant.

For the selective recirculation case a simple intercooled compression unit have been used in most of the cases as the CO_2 captured already has a high purity and further purification would be subordinated to the transport system, that is not take in consideration in this study, rather than the capture unit itself. But in any case when the CO_2 purity obtained was lower than 95% a CPU system has been used.

For the EGR case, as the purity of the CO_2 obtained results to be much lower, a flash cryogenic purification system has been used for most of the cases to achieve a purity of at least 95% of CO_2.

4.1.3 MATLAB

MATLAB has been used for the simulation of the membrane units. The code developed by Marco Maran [42] in his master thesis has already been shortly described in chapter 2. For the selective recirculation case this code has been used to obtain the surface of membrane needed to have a fixed recovery rate of $CO_{2.}$ In the EGR case MATLAB has also been used for the optimization of the whole capture system of the power plant.

4.1.4 Simulation methodology

All these three software have been implemented in an iterative calculation process to obtain as a result the thermodynamic performances of the power plant with capture system and the size of the main equipment needed for a later estimation of the cost of capture.

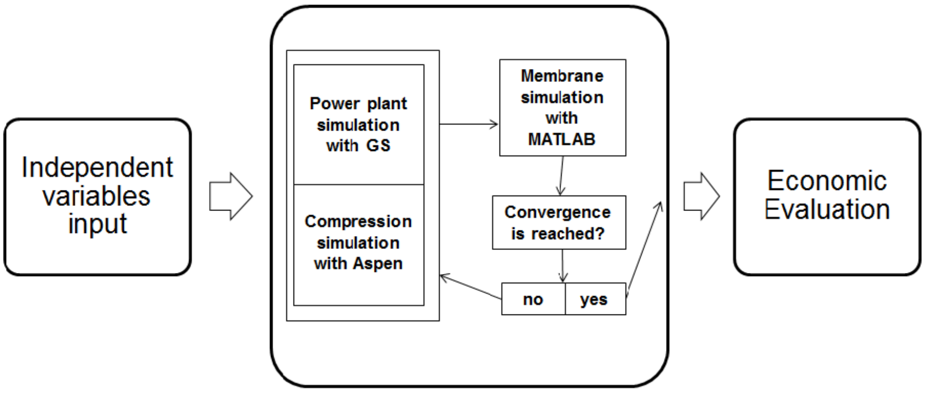
The specific consumptions obtained with the simulation of the compression of the CO_2 using Aspen Plus has been integrated in the GS input file. The composition of the flue gas obtained has been used as input of the capture system simulated with the MATLAB model that calculated the surface required to capture 90% of the entering CO_2 and also the output composition of all the streams involved.

Because with GS the membrane system is just approximately simulated by splitting fixed amount of each chemical compound from the main flow, and because this composition affects the power plant performances (because it changes the composition of the gas flowing in the gas turbine) we have to adjust this value accordingly to what obtained with the MATLAB simulation of the membrane.

Running a new simulation with these new fixed conditions a result closer to the real behaviour of the whole power plant can be obtained. This process has to be repeated until convergence of the composition of the flow permeated in the two membranes is reached.

Now the size of all the main equipment can be calculated by GS and results can be used with the economic models to obtain the total cost of capture.

This calculation process is schematically represented in fig 4.1.



4.1 calculation methodology of the power plant performance and equipment.

It is important to say that this process is required only when the selective recirculation case is considered. This is because the real behaviour of the membranes (that cannot be internally calculated by GS) also affect the part of the power plant that is simulated using GS.

When the EGR case has been studied this iterative process was not required because the performances of the membranes did not affect the power production section of the power plant but only the CO_2 separation unit.

4.2 Reference case power plant performances

4.2.1 Energy balance

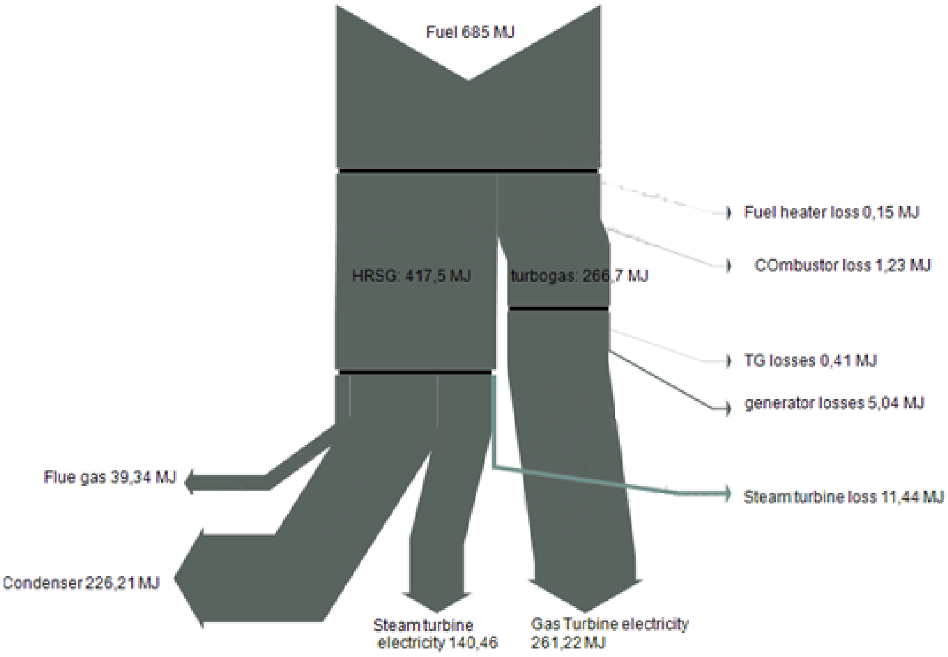
The main performance of the reference power plant have already been showed in chapter 3 and are reported here below in table 4.1

Table 4.1 Reference power plant performances.

Parameter	***Value***	***Unit***
$\mathbf{M_{air}}$	621.02	[kg/s]
$\mathbf{M_{fuel}}$	14.755	[kg/s]
$\boldsymbol{\eta}_{\mathbf{tot}}$	58.59	[%]
$\mathbf{W_{tot}}$	401.68	[MW]
$\boldsymbol{\eta}_{\mathbf{tg}}$	38.1	[%]
$\mathbf{W_{tg}}$	261.22	[MW]
$\mathbf{W_{tv}}$	140.46	[MW]
$\mathbf{T_{out,GT}}$	615.8	[°C]
$\mathbf{T_{out,HRSG}}$	80	[°C]
Specific emission	352.62	[kgCO2/MWh]

A global energy balance can be useful to deeply understand every stage of the process and where energy is lost or converted into electricity.
This energy balance is represented in Fig 4.2 that shows the Sankey diagrams of the reference power plants.

This diagram can be useful to understand how the energy flow would change when capture of carbon dioxide is used.



4.2 Sankey diagram of the reference power plant.

As can be seen the total input power with the natural gas is approximately of 685 MW. Of these just 266 MW are actually used in the gas turbine cycle of which 261 are converted into electricity. The difference is lost in the electricity generator, in the combustor and in other thermal losses in the gas turbine system.

In the flue gas released by the turbine there are still 417 MW that would be lost if the flue gas were sent directly to the chimney. Instead they are sent to a heat recovery steam generator where almost 370 MW are reused in the steam turbine cycle. Just 140 MW are converted into electric power while the remaining are lost mainly in the condenser of the steam cycle as heat at low temperature.

4.3 Selective recirculation of CO2 case performances

4.3.1 Reference case with CO2 selective recirculation

To fully understand the impact of the selective recirculation of CO_2 on the power plant performances different technical parameters have to be investigated. The main parameters that we decided to study are listed here:

- Gas turbine compression ratio.
- O_2 concentration in the flue gas.
- Permeability of gasses other than CO_2.
- Compression of flue gas
- Membrane selectivity

To understand their impact we will vary them one by one and see the impact of these modification of the two parameters that are most important to understand if this capture solution can be considered good or not. The global efficiency of the power plant is the first one and it will be used to evaluate the energy penalty of the capture system as the thermal input (fuel flow) if fixed equal to the reference power plant. The concentration of CO_2 in the flue gas achieved is the other parameter as the size of the membranes and the purity of the CO_2 permeated is strongly influenced by it.

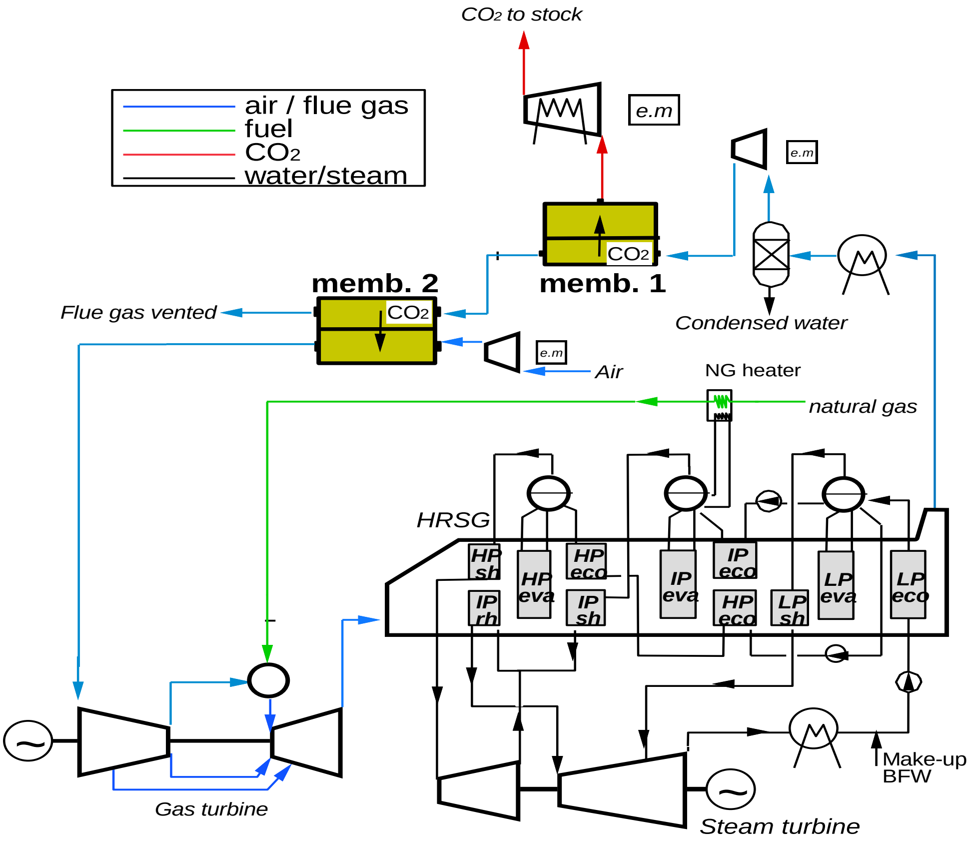
For this reason it is important to clarify the value that the other parameters investigated assumed during the study. A reference power plant with selective recirculation of the CO_2 has, for this reason, been defined and its characteristics are listed in table 4.2

Table 4.2 Base assumptions for CC implementation.

	Value	***Unit***
M_{fuel}	14.755	[kg/s]
$P_{perm,\ first\ membrane}$	0.2	[bar]
O_2 concentration at combustor output	2.5	[%]
$\Delta P_{membranes}$	3	[%]
Temperature of flue gas cooled	35	[°C]
Capture ratio	90	[%]
Membrane selectivity	∞	[-]
Compression ratio	18	[-]
TIT	1360	[°C]

We decided to keep the reference value of the compression ratio equal to the reference power plant one for simplicity. In addition, previous studies shown that for the maximum TIT value assumed (1360°C) the compression ratio that gives the best performances in a combined cycle configuration is approximately 18 [43].

In Fig. 4.3 The scheme of this capture solution is reported.



4.3 General equipment scheme of the power plant with selective recirculation of CO2 and CO2 capture.

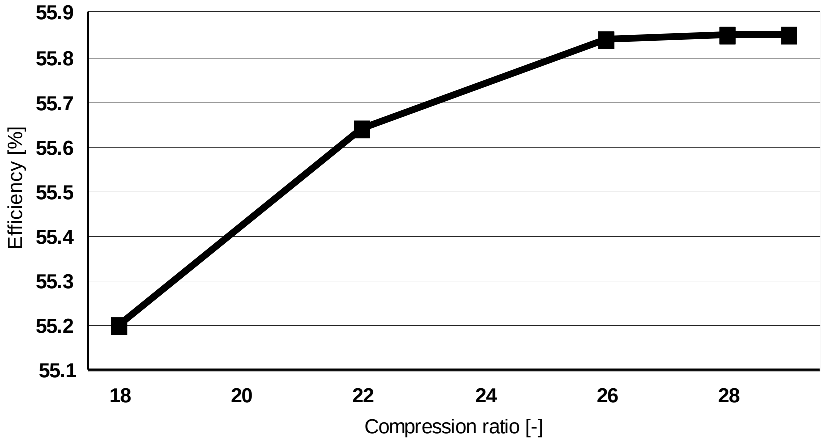
4.3.2 Compression ratio

The compression ratio is the main technical parameter that needs to be defined when a gas turbine is used in a power plants. The system performances, represented by efficiency and net power produced, are both strongly affected by this parameter.

In a conventional combined cycle system the gas turbine operates with a relatively low compression ratio value as results of a tradeoff between the topping (gas turbine) and bottoming cycle (HRSG and steam turbine) once the TIT is assigned.

The increase in CO_2 concentration caused by the recirculation process causes both an increase of the molecular weight and specific heat of the gas treated in the gas turbine. This modifies the turbine performances changing the optimum value of the compression ratio.

Using GS program different simulation have been run with different values of compression ratio and the results obtained were recorded.
The effect on the thermal efficiency of the power plant is shown in the following graph in fig. 4.4. It is important to notice that in fig 4.4 it is included the energy cost for CO_2 compression to 110 bar too.



4.4 Effect the value of compression ratio on the power plant thermal efficiency.

First of all we can notice that with this configuration the efficiency drops to a value of approximately 55.7% from the value of 58.59% obtained by the power plant when carbon capture is not implemented. The global energy penalty caused by the capture system is 5-6%, lower than other capture system analysed in other studies such as MEA absorption which can reach values of 20% for the energy penalty [44].

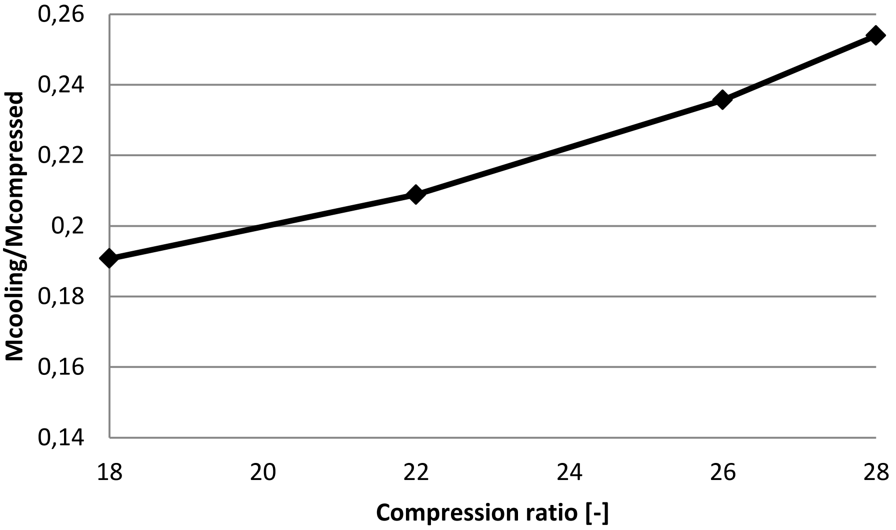
We can also easily notice that the compression ratio value that gives the best performances is approximately 28, a much higher value compared with the reference case without capture that would require a complete redesign of the gas turbine system.
The variation of thermal efficiency is in any cases small as the range of variation is lower than 0.7% and may not justify the complete redesign of the gas turbine.

The decrease of efficiency over a value of 28 of the compression ratio is caused by the increase in the total fraction of fluid compressed in the gas turbine that needs to be used in the cooling system of the turbine blades rather than be heated in the combustor and expanded. This increase is caused by the higher output temperature of the compressor that grows from 376 °C for a compression ratio of 18 to 453 °C when we have a β of 28.

This means that there are smaller ΔT in the cooling system that will require a larger mass flow to cool the blades of the turbine.

As shown in fig. 4.5 the share of gas compressed that is used in the cooling system increases from 19% for a compression ratio of 18 to a value higher than 25% when the compression ratio is 28.

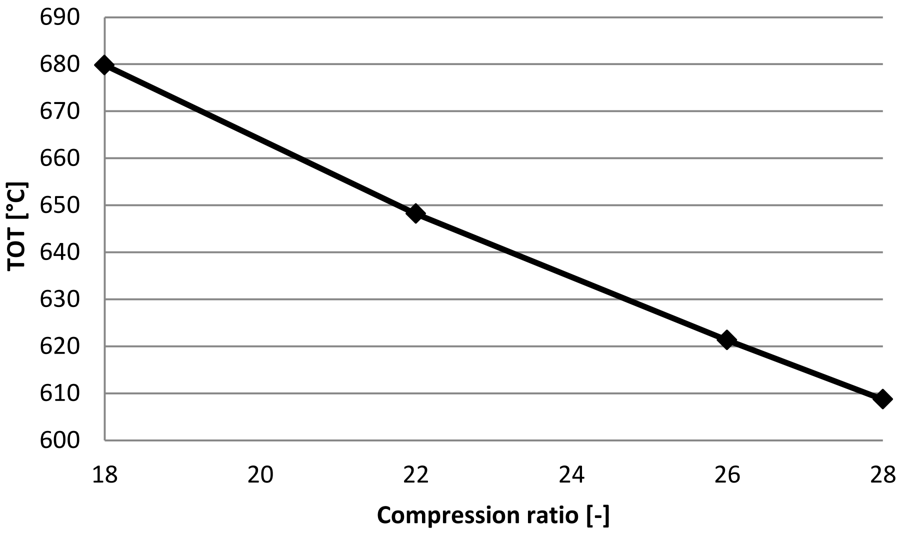
The value of this ratio for the reference power plan was of 18.5% with 115 kg/s used in the cooling system of a total 621 kg/s compressed.



4.5 Effect of the compression ratio on the share of gas used in the cooling system of the turbine on the total flow compressed.

In addition, dealing with an NGCC, we also have to consider the effect of the TOT of the turbine on the bottoming cycle. In a NGCC the TOT of the turbine is usually optimized to have the best integration between gas and steam cycle in order to obtain the best efficiency of the power plant. Changing the TOT, the HRSG and the steam cycle should be modified to fit the new operative condition but this is not our case.

The maximum temperature of the steam generated in the HRSG and the pressure levels are fixed affecting, or the recovery efficiency of the boiler or the efficiency of the steam cycle.



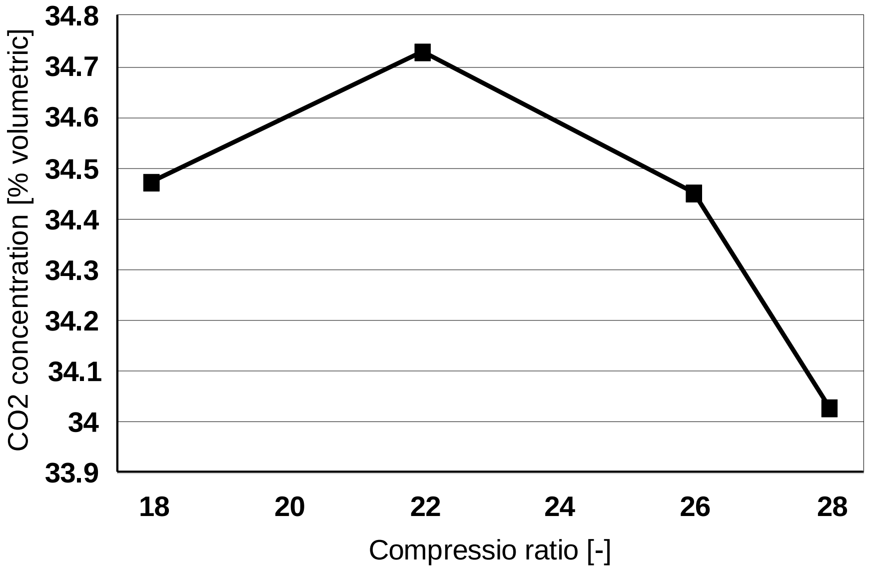
4.6 Effect of the compression ratio on the TOT of the turbine.

As can be easily seen in Fig. 4.6 the TOT of the turbine is significantly higher than the reference power plant where its value is of 613.9 °C.
We can see that the best efficiency of the NGCC with capture is reached when the TOT is closer to the value of the reference power plant without capture for which the HRSG had been optimized. This occurs for a compression ratio value of 28 where the TOT is equal to 609 °C, which is the closest results to the reference power plant we obtained.

Looking at fig 4.6 we can also notice that the variation of TOT with the compression ratio is wide and that for high compression ratio lower temperature can be easily achieved.
The higher value of TOT when the compression ratio is the same of the reference power plant (18) is caused by the different nature of the gas expanding in the turbine. In fact CO_2 has a different specific heat from air and for the same expansion rate (from 18 to 1.04 bar) the resultant reduction of temperature is smaller. Being the starting value of the temperature (TIT is fixed) the same, it results in a higher TOT. When the compression ratio increases the expansion ratio in the turbine increases too causing a gradual reduction of TOT with the value of compression ratio, as the gas will be cooled more by the grater expansion that it undergoes.

This means that in any case a redesign of the gas turbine is required. If the compression ratio is not changed the last stages of the turbine have to be redesigned to ensure the material resistance to higher temperature. If the compression ratio is increased a redesign of the compressor and the turbine is required as the pressure difference to achieve are drastically different.

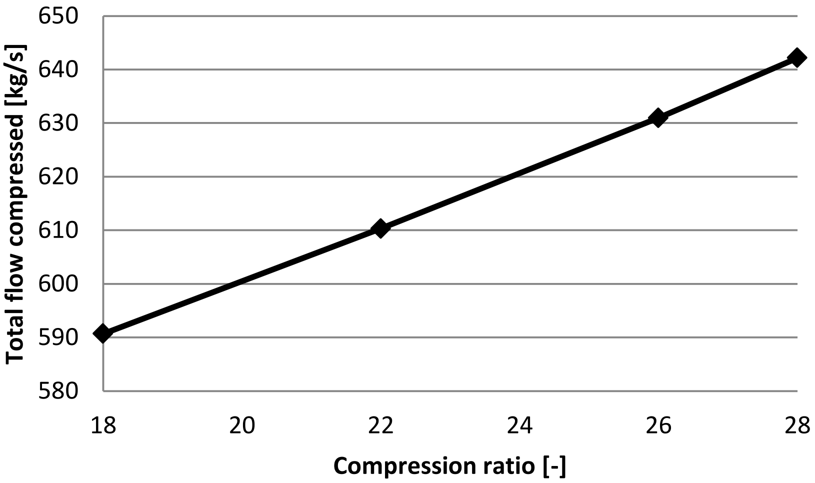
Looking at the effect of the recirculation system on the CO_2 concentration in the flue gas we found interesting results.
First of all as can be seen from the following graph of Fig. 4.7 we can say that the effect is significant. The concentration of CO_2 reaches levels below 30%, more than 10 times higher than the reference case without selective recirculation.



4.7 Effect of the value of compression ratio on the CO2 concentration in the flue gas produced.

It can be immediately noticed that there is a maximum in the CO_2 concentration in the flue gas for a compression ratio of 22. This particular trend is caused by the change in the amount of gas compressed in the gas turbine which is used in the cooling system rather than be sent to the combustor to be heated.
To provide the gas required by the cooling system of the turbine keeping the O_2 concentration fixed, a larger amount of air has to be taken from the environment. In fact, increasing the compression ratio, the ratio between fresh air sucked from the environment and CO_2 recycled, increases as It will be explained better soon.

Increasing the compression value the total mass flux flowing in the gas turbine (sum of the fresh air taken from the environment and the CO_2 recycled) increases as shown in fig. 4.8.



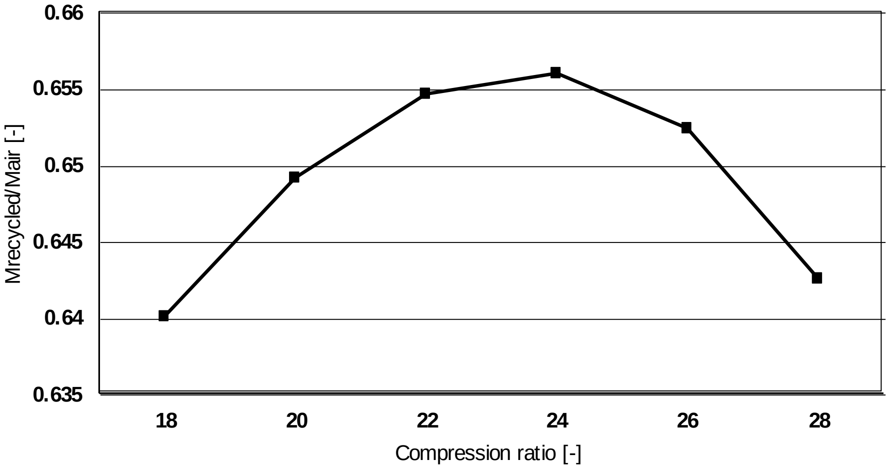
4.8 Effect of the compression ratio on the total input flow of the gas-turbine

The ratio between CO_2 recycled and fresh air changes because for lower value of compression ratio a larger share of the total flux is sent to the combustor where oxygen in consumed generating CO_2 and is than mixed with a lower amount of gas rich of O_2 used in the cooling system of the turbine blades. This results in an increase of CO_2 presence in the flue gas till a value of 22 of the compression ratio.

For higher value of compression ratio the share of gasses compressed in the gas turbine used in the cooling system of the turbine increase due to the higher compressor output temperature. This flux, which is not burned in the combustor and is for this reason richer in O_2, significantly dilute the flue gas produced in the combustion process reducing the CO_2 concentration released by the gas turbine.

This behaviour of the cooling system of the turbine also explains the variation of the ratio between the fresh air taken from the environment and the CO_2 recycled by the membranes shown in fig 4.9. As the share of compressed gas used in the cooling system increases, the amount of fresh air has to grow to keep the amount of oxygen in the combustor at the fixed value.

This also affect the amount of CO_2 that we can find in the flue gas as with less carbon dioxide recycled this parameter has to decrease and it will cause the particular trend of the CO_2 concentration in the flue gas shown in fig 4.7



4.9 Effect of compression ratio variation on the recycled flue gas on fresh air ratio.

Anyway even in this case we can notice that the effect of the compression ratio on the CO_2 concentration is really small as the range of variation is smaller than 0.8%. this means that with this configuration we could chose the value of compression ratio that gives the best thermodynamic performances without worrying about effecting the carbon capture system performances too much.

Anyway, as the benefit achieved in terms of thermal efficiency increasing the compression ratio to higher value is really small, this option needs to be carefully evaluated from an economic point of view. The increase in the power section (as the cost of a gas turbine increases with its compression ratio) and of the capture plant cost (as the total mass flux to be treated is increased) may exceed the additional revenue obtained due to a slightly higher efficiency of the global power plant.

4.3.3 Oxygen concentration in the combustor

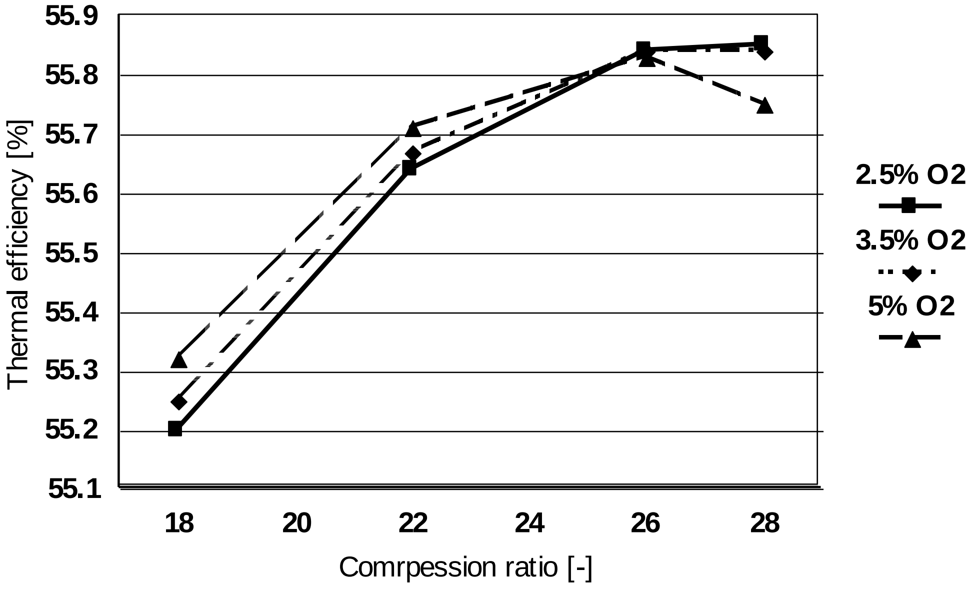
In the previous analysis the concentration of O_2 in the flue gas produced by the combustor was fixed to 2.5% in order to ensure a complete combustion of the natural gas and, at the same time, to do not take too much fresh air from the environment. The excess air needed as diluent to keep the TIT below the

maximum value acceptable, required without recirculation, is replaced by CO_2 recycled in the second membrane.
The variation of this parameter can significantly affect the concentration of carbon dioxide in the flue gas, changing the operative conditions of the capture system.

Increasing the O_2 concentration allowed in the combustor product will reduce the amount of CO_2 that needs to be recycled in the second membrane but will, on the other hand, reduce the CO_2 concentration in the flue gas sent to the capture system. This could result in a decrease in the size of the second membrane but at the same time in an increase of the size of the first one and a lower CO_2 purity. This parameter then needs to be carefully optimized to find a trade-off between the cost of the two membranes.

Increasing the O_2 concentration in the flue gas will also affect the thermal efficiency of the power plant as will modify the composition of the gas flowing in the gas turbine.
The O_2 concentration has been varied starting from the 2.5%, minimum required to ensure a complete combustion of the fuel, to the value of 3.5% and 5% respectively.

The results obtained are shown in Fig 4.10.



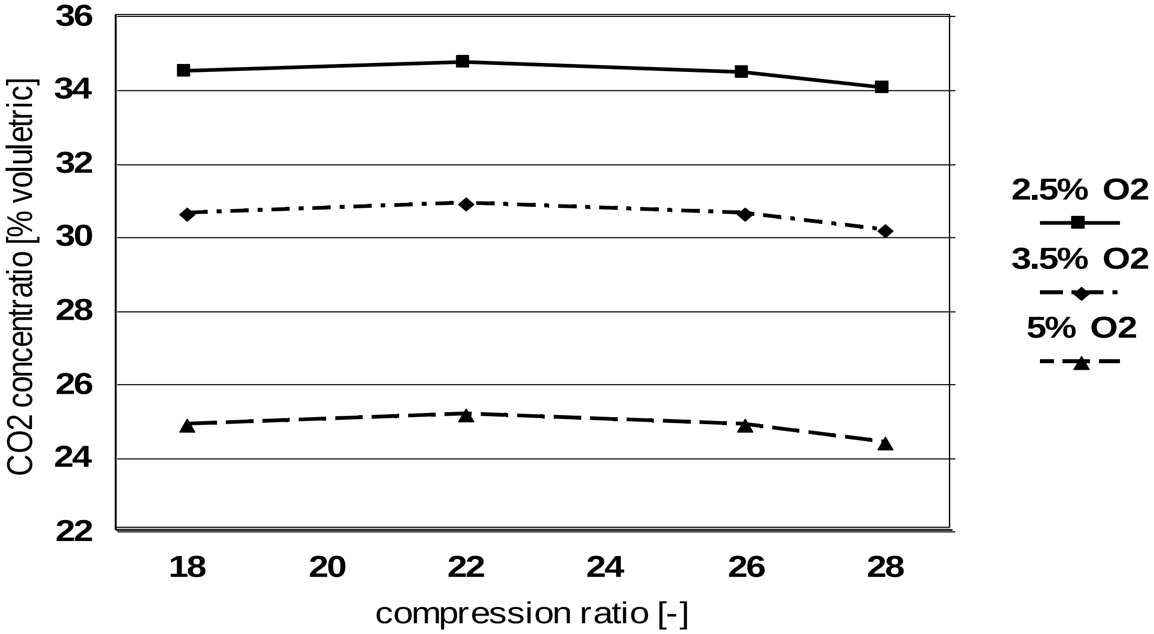
4.10 Effect of O2 concentration in the flue gas on the thermal efficiency of the power plant.

As can be seen for higher value of O_2 in the flue gas, which means a smaller recycle, the optimum compression ratio moves to slightly lower value. These results are consistent with the fact that the optimum compression ratio for the reference case (without any recycle of CO_2) is obtained for a compression ratio of 18. If we would further decrease the amount of CO_2 recycled we would gradually move toward the reference power plant.

The variation of the value of thermal efficiency is, in any case, very small as can be easily seen from Fig. 4.10. The variation in fact is in the order of 0.1% approximately.

The maximum value of the thermal efficiency achieved is almost constant as the consumption for the venting for the capture system is not significantly altered by the variation of composition of the flue gas.

More important is to understand the effect of a higher O_2 concentration at the combustor output on the composition of the flue gas released by the gas turbine.



4.11 Effect of the concentration of oxygen in the combustor on the CO2 concentration in the flue gas

As can be seen in fig. 4.11 an increase in the O_2 concentration allowed in the combustor output has a strong effect on the global CO_2 concentration in the flue gas produced by the power plant.

The effect is very strong as both the gas produced by the combustor and the flux used in the cooling system of the turbine will be richer of oxygen, decreasing sensibly the concentration of carbon dioxide.

Doubling the value of O_2 fraction to 5% cause a drop of approximately 10% in the CO_2 concentration (equal to a relative decrease of 30%).
The operative conditions of the capture system results strongly changed resulting in a strong reduction of purity of the CO_2 separated.

4.3.4 Flue gas compression

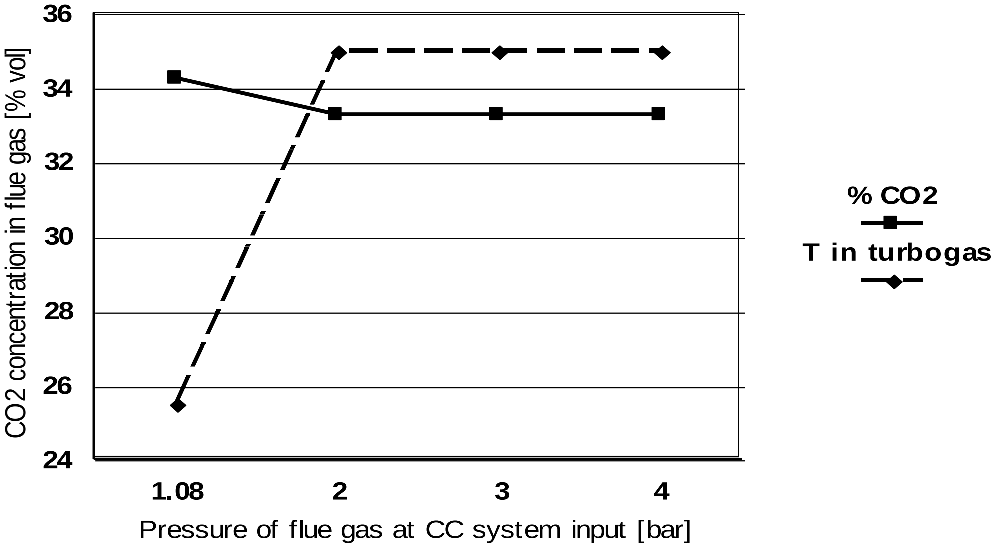
In all the previous simulation compression of the flue gas is not taken in consideration. A fan is used just to cover the pressure losses caused by the two membrane systems allowing the flue gas to correctly flow.
The difference in partial pressure of the CO_2 needed to ensure the driving force for the permeation process in the membranes are given respectively using a vacuum pump in the first one, and using fresh air as sweep stream in the second one.
This solution allow to minimize the energy penalty caused by the capture system [40], but will require a larger membrane area for the separation of the desired amount of CO_2 as the resulting driving forces of the permeation process are very small.

Further decrease of the vacuum on the permeate side of the first membrane is not applicable to significantly increase the driving force as we already assume to use a value close to the minimum achievable with currently available industrial equipment. Furthermore this option would increase the driving force of the first membrane system only without affecting the second one.

Compression of the flue gas can be an interesting solution as can be used to greatly reduce the membranes surfaces needed and increase the purity of CO_2 separated. In addition compressors are well known equipment and largely used in the range of pressure of our interest if compared with vacuum pumps.

Compressing the flue gas would rise the gas turbine compressor input temperature as the CO_2 recycled in the second membrane would be at higher temperature due to the compression process in the capture system. An additional cooler requires to be used to cool the gasses before the gas turbine in order to limit the input temperature to a reasonable value. We have assumed a maximum input temperature for the gas turbine compressor of 35°C.

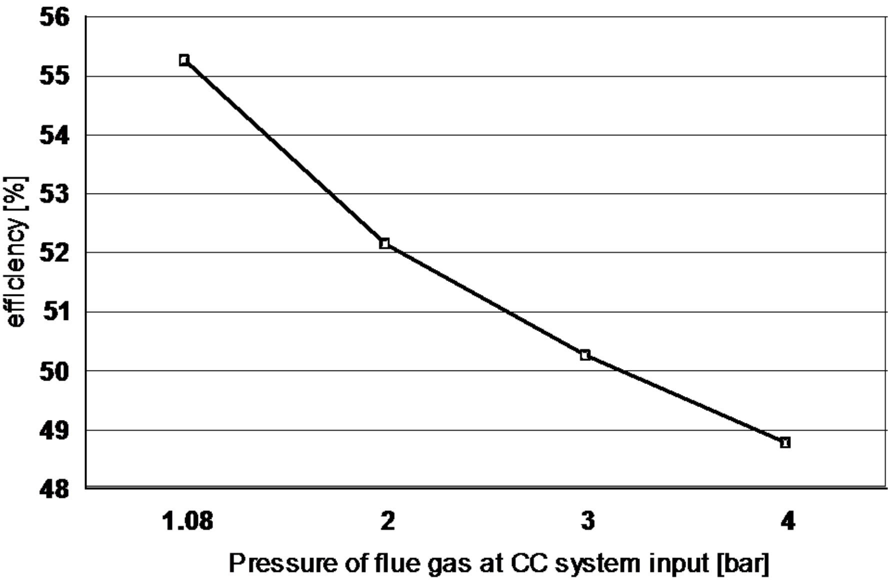
Once the maximum input temperature assumed is reached the effect of compressing the flue gas on the CO_2 concentration is null as the cooling flow required by the turbine will not change as can be seen in fig 4.12.
before the maximum input temperature for the gas-turbine compressor is reached the concentration of CO_2 in the flue gas slightly reduce because with an increase of the temperature of the flow, a larger share of compressed gas is used in the cooling system of the turbine diluting the combustion process.



4.12 Input temperature at the gas turbine compressor and CO2 concentration in the flue gas on final pressure of flue gas after compression.

The results, are shown in function of the final pressure of the flue gas before being sent to the capture system. The compression ratio of the power plant has been fixed for a value of 18 that best approximates the condition of best performances.

As the volumetric flux of flue gas produced by the power plant is large, the energy cost for this compression is significant and increases with the ratio of compression that we want to obtain. The reduction in membranes surfaces obtained could, however, overcome the grater energy penalty making this option economically competitive.



4.13 Effect of the flue gas compression on the thermal efficiency of the power plant.

From the results obtained (shown in fig 4.13) we can say that even for low compression ratio the efficiency loss is considerable reaching an absolute loss of more than 6% (more than 10% of relative loss) to compress the flue gas to 4 bar.

4.3.5 Membrane selectivity

Till this point the questions about the effect of membrane selectivity have been avoided assuming an infinite selectivity towards CO_2. This assumption could be an oversimplification of the real problem and for this reason the effect of permeability of other chemical species on the plant performances have been investigated.

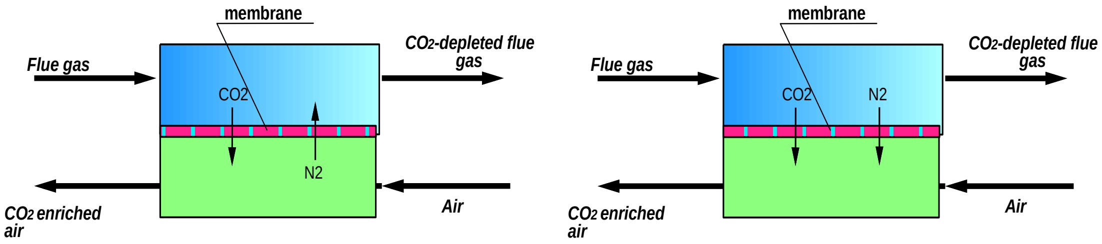
To simplify the problem in this analysis we will, however, consider exclusively the selectivity of N_2 on CO_2. The concentration of the other chemical species involved in the process (Oxygen and Argon) are much lower and will be neglected here. For what concerns water we have already assumed to cool the flue gas released by the HRSG to a temperature of 35°C and to remove all the condensed liquid produced in the process. We have also to consider that an eventual permeation of water, especially in the second membrane, could be considered a benefit as it would reduce the partial pressure of CO_2 at the permeate side increasing the driving force of the process.

Rather than imposing a specific CO_2/N_2 selectivity we have considered different cases changing the ratio between the molar flux of CO_2 and N_2 permeated. We simulated three cases where relatively in the permeated streams there will be 2.5%, 5% and 10% of Nitrogen and the results have been compared with the infinite selectivity simulation.

Considering the behaviour of the first membrane (the one in charge of the CO_2 separation) we can immediately say that the application of a flue gas compression system would not change anything. In fact, being the permeate pressure always lower of the feed side one Nitrogen would always permeate together with carbon Dioxide.
The effect of the permeation of Nitrogen will then only to reduce the purity of the CO_2 separated and sent to the compression unit to be then stored.

If we take into consideration the second membrane instead it can seems at first glance that the behaviour may be more complex. When a flue gas compression system is used there would not be any unexpected behaviour as the partial pressure of carbon dioxide and Nitrogen in the feed side (the flue gas input side) would always be higher then what we find in the fresh air side. Nitrogen would for this reason always flow in the same direction of CO_2.

When compression of the flue gas is not used, instead, we noticed that the input partial pressure of N_2 on the feed side (N_2 concentration is approximately 60%) would be smaller of what we have in the sweep air side. For this reason we can expect that, while carbon dioxide permeates from the flue gas to the sweep side, Nitrogen should permeate in the opposite direction.



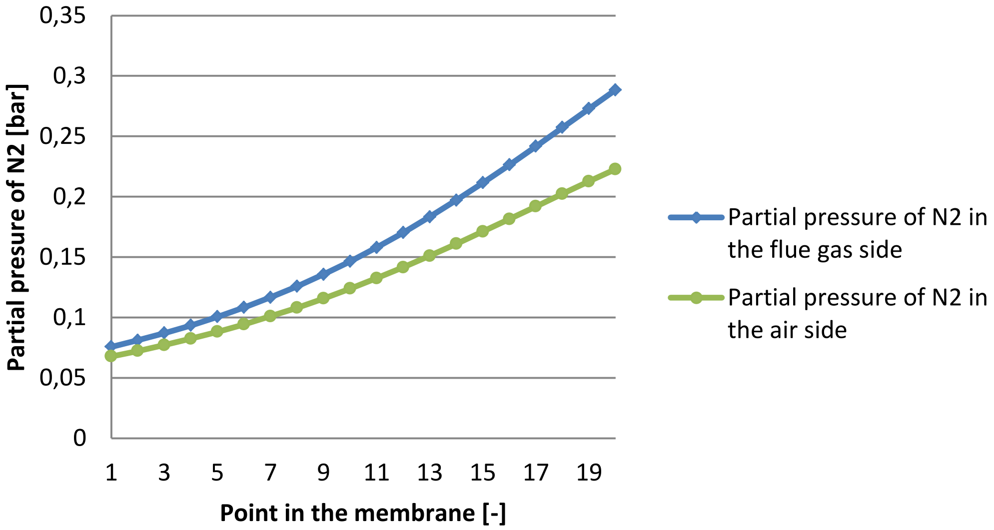
4.14 difference that could be found in the permeation process in the second membrane without and with flue gas compression.

Anyway after the simulation of the membrane have been done using the MATLAB model described in chapter 2 we found out that this distinction is not valid.

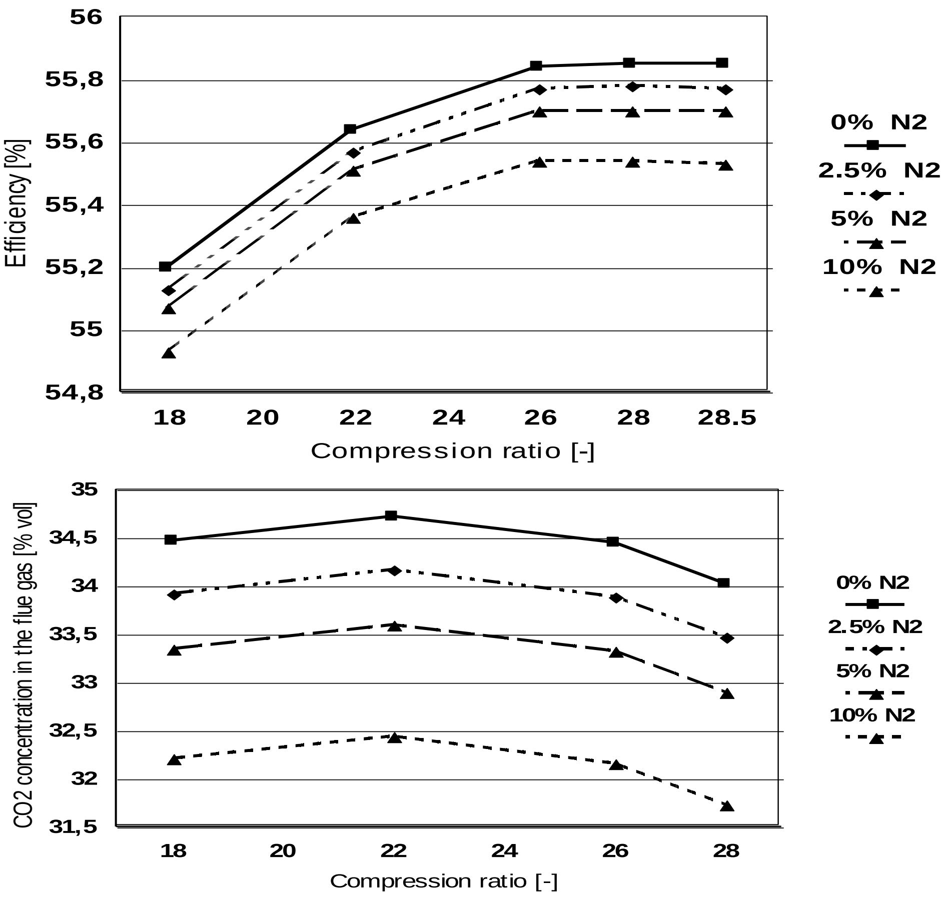
In fact even when the flue gas compression is not used Nitrogen will permeate from the flue gas to the air side anyway. This is because of the counter flow disposition of the membrane and the large amount of CO_2 permeating from the flue gas to the air side. In fact, as CO_2 permeates from the feed to the permeate side, increase the concentration and so the partial pressure of Nitrogen in the feed side continues to increase despite also part of it permeates. This allow to have a constant positive pressure difference of Nitrogen from the flue gas to the fresh air side of the membrane as can be seen in fig. 4.15

Then there is no difference in the behaviour of the membrane if flue gas compression is used or not and the effect of membrane selectivity is exactly the same.

(it is important to notice that the input of the two flows are at opposite sides of the membrane: flue gas entrance is at point 1, fresh air entrance is at point 20)



4.15. Nitrogen partial pressure trend on the flue gas and air side of the second membrane.



4.16 Effect of membrane selectivity.

In figure 4.16 are summarized the results obtained changing the amount of N_2 permeated together with the carbon dioxide.

Considering the effect on the power plant efficiency we can notice that the trend with the variation of the compression ratio is almost the same of what we obtained with the infinite selectivity case. The absolute value of the efficiency is anyway reduced with the increase of the flow of permeated Nitrogen. Looking more into detail of the consumptions of the different equipment we found out that the decrease of efficiency is caused almost exclusively by the increase of consumption of the intercooled compression on the permeate stream of the first membrane and the increase of energy required to compress captured CO_2 to 110 bar.

This increase of consumption is both caused by the larger flow that have to be compressed (the amount of CO_2 is exactly the same and there is just more Nitrogen that increases the total mass flow) and the increase specific energy required by the CO_2 compression system due to the presence of impurities.

The effect on the power section of the whole plant is very modest as the change of composition of the gas flowing into the gas turbine is very small. This is why the optimum is still found out for a value of 28 of the compression ratio. The global decrease of efficiency is in the order of 0.3% that is not that significant.

The effect on CO_2 concentration instead is particularly strong as can be seen in Fig 4.16. When Nitrogen flows in the same direction of CO_2 the results is a lower concentration of carbon dioxide in the flue gas. This happens because in the second membrane we do not have a recycle of pure CO_2 as the Nitrogen permeating will dilute the gas. Anyway the decrease of concentration is not drastic; in fact even when 10% of the recycled stream is nitrogen the CO_2 concentration in the flue gas drops of only 2%.

4.3.6 Water behaviour

Analysing the selectivity of the membrane we did not take in consideration the water permeation in the membranes. Permeation of water in the first membrane would be beneficial for the purity of the CO_2 separated as it would increase the driving force of CO_2 permeation reducing its partial pressure at the permeate side and could be easily removed by condensation. In the second membrane the problem would not exist either because in the input air sucked from the environment humidity is already present.

The problem related to water is the possibility of its condensation of the feed side of the membrane that could affect the membrane performances covering its surface and preventing gas permeation.

The gas entering the capture system is, in fact, saturated with water vapour due to the flue gas cooling system. The permeation of carbon dioxide and Nitrogen would cause the partial pressure of water vapour to rise over the saturation pressure causing condensation of water.

As the content of water is relatively much lower than the Nitrogen one, we could not apply the same system used to simulate the permeation of Nitrogen as it would give problems to the simulation programme.

We simulated different cases applying a selectivity of water on carbon dioxide of 10-50-100 and for a value of the compression ratio of 18 and 28 to see if condensation of water could be found in any point of the capture system.

For all these cases we found out that condensation of water is not reached in any point of the capture system as the permeation of water in the two membranes is large enough to reduce the partial pressure of water below the saturation point.

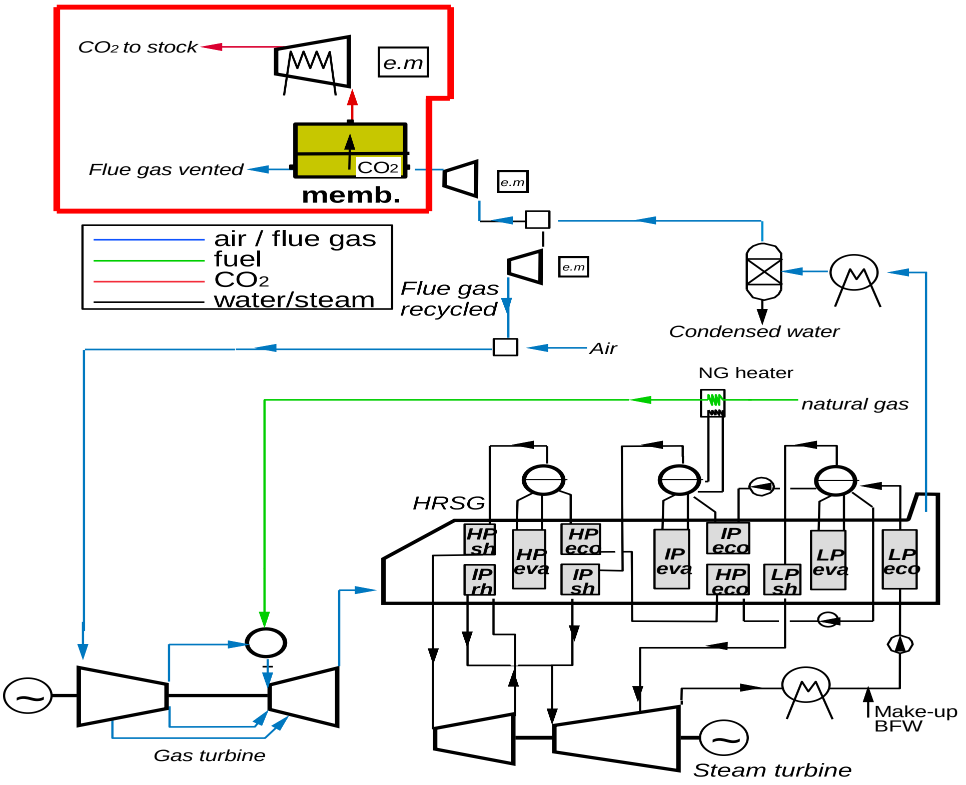
We can then say that condensation of water should not be a problem for this plant configuration

4.4 Non-selective recirculation of CO_2 case performances

As already said in chapter 3 a single case will be considered when the EGR system will be analysed. The technical parameters that have been assumed and the reasons to do so are described in chapter 3 too. Here we will describe the main output performances obtained with the simulation of the power plant.

It is important to notice that in this case we did not simulate the CO_2 capture unit. In fact, as the study is limited to just one case, we decided to operate in a different way compared to the selective recirculation case.
A MATLAB code has been created to optimize the capture unit configuration. This code will be better described in chapter 6.

The part that has not been simulated with GS is the one that is encircled in the red line in Fig. 4.17



4.17 EGR scheme with indication of which part has been simulated using GS.

We can then say that the GS simulation is limited to the power section of the whole plant and to the smaller auxiliary equipment needed for the recirculation of the exhaust gasses and the pre-treatment for the capture unite.

The consumptions of the whole capture system is not taken in consideration by these firsts data that will be used as input for the MATLAB optimization of the membrane system.
The most important data that we obtain with the GS simulation of this part of the power plant is the composition and the amount of the flue gas that will be treated by the capture unit.
In fact we can calculate it independently from the capture system itself as the recycle of the flue gas is before the separation unit of CO_2 and it is not affected by its configuration.

The main results that are obtained with the GS simulation are listed in table 4.3.

Table 4.3 EGR power plant performances.

Parameter	***Value***	***Unit***
η_{tot}	58.41	[%]
W_{tot}	400.43	[MW]
W_{tg}	238.43	[MW]
W_{tv}	144.43	[MW]
M_{air}	304.57	[kg/s]
M_{EGR}	322.91	[kg/s]
$M_{to\ capture}$	297.52	[kg/s]

These data will be used as a starting point for the calculation of the optimum configuration of the membrane capture system. The second most important information we get from the GS simulation of this part of the power plant is the composition of the flue gas that will be treated by the capture unit, where the most important thing is the concentration of CO_2 because it is the parameter that will affect most the membranes performances.

The composition of the flue gas produced using the exhaust gas recirculation is shown in table 4.4.

Table 4.4 molar composition obtained in the combined cycled using simper exhaust gas recycle.

Chemical species	***Molar concentration in percentage***
CO_2	8.729
N_2	80.026
O_2	4.745
H_2O	5.548
Ar	0.952

As can be immediately seen the CO_2 concentration in the flue gas is extremely different from what obtained with the selective recirculation system.

The CO_2 percentage drops from a value higher than 30% to less than 9%. This is caused by the huge amount of Nitrogen that is recycled together with the carbon dioxide to keep the TIT at the desired value, while with the selective recirculation system all the recycled flux required was CO_2 only.

The concentration of carbon dioxide in the flue gas is, anyway, almost double of the value that is obtained with the reference power plant without any recirculation of flue gas.

Another important difference from the selective recirculation case that needs to be noticed is the amount of flue gas effectively treated by the membrane system. When selective recirculation is used all the flue gas produced in the gas turbine flow through the membrane system both for the capture and the recirculation of carbon dioxide. This means that a flow of approximately 630 kg/s needs to be treated that will results in larger membrane surface. When non selective recirculation is used only the fraction that is not recycled is sent to the membrane system. In the capture unit only 297 kg/s flow and are purified. If the concentration of carbon dioxide had been the same, a much smaller area of the membrane would have been needed. As the concentration of CO_2 is much smaller as it was said before, we cannot say in advance if the membrane in this case will be smaller or bigger.

5 TECHNO-ECONOMIC ANALYSIS

Selective Recirculation Plant

In this chapter the methodology used by the CO2CRC research group will be used to estimate the cost of CO_2 avoided for the selective recirculation capture system. An integration between GS and MATLAB software will be used in order to calculate a configuration closer to the real one and calculate the size of the main equipment needed.
Using this data as an input the impact of different technical parameter of the power plant will be studied from an economic point of view, looking at how they impact on the cost of the CO_2 avoided.

5.1 Economic evaluation methodology

5.1.1 Assumptions for the cost of capture.

For the calculation of the cost of CO_2 avoided more assumptions have to be made. In fact the assumptions taken in chapter 4 on the technical parameters of the power plant are not enough to estimate the economic result of the selective recirculation capture system. Assumptions about the load factor, expected life of the power plants have to be made.

In this work CO2CRC guidelines [45] have been used to set these assumptions and the methodology for the economic calculation of the avoidance cost of CO_2

The assumptions are both economic (discount rate, equations for the cost estimation of every single components etc.) and technical for the power plant (expected life, construction period, load factor etc.).

The main assumptions used are listed in table 5.1.

Table 5.1 assumption for the evaluation of the avoidance cost.

	Value	***Unit***
Cost year	2012	[-]
Discount rate	7	[%]
Project life	25	[years]
Construction period	2	[years]
Plant load factor	90	[%]
Currency	US$	[-]
Cost of electricity	43	[$/MWh]
Capture ratio	90	[%]

Construction period and project life are essential for the calculation of the present value of the equipment, the operative costs, and the CO_2 avoided. While the load factor and the cost of electricity will be used to evaluate the effect of the energy penalty on the cost of capturing CO_2.

We also have to notice that in chapter 4 the membrane was assumed with infinite selectivity or permeable just to CO_2 and Nitrogen when the effect of the membrane selectivity was studied. Here a real membrane has been used for the membrane areas required estimation, giving the possibility to water vapor, Oxygen and Argon too to flow through the membrane.

5.1.2 Capital costs definition

The costs estimates are mainly divided into two category: capital and operative costs; where capital costs take account of the costs for acquiring the equipment needed in the system and the physical construction of the capture unit.

The methodology used for the estimation of the capital cost of the CCS project is, as it has already been said, the CO2CRC research group one and is briefly described in the following tables

In table 5.2 is shown the methodology for the capital expenditure (Capex) of the capture system.

Table 5.2 Capex calculation methodology.

	Parameter	*Value*
A	**Process equipment costs (PEC)**	Sum of all equipment cost
B	**General cost**	30% PEC
C	**Total equipment costs (TEC)**	A + B
D	**Instrumentation**	15% TEC
E	**Electrical**	7% TEC
F	**Piping**	20% TEC
G	**Total installed cost (TIC)**	TEC+D+E+F
H	**Set-up cost**	8% TIC
I	**Engineering**	5% TIC
L	**Owners costs**	7% (G+H+I)
M	**Engineering, procurement, construction and owner's costs (EPCO)**	G+H+I+L
N	**Contingency**	10% EPCO
O	**Total capital cost (CAPEX)**	M+N

Each voice listed in table 5.2 will now be explained here:

PEC: It is nothing more than the sum of all main equipment purchasing at their nominal cost and represents the amount of money paid to the equipment sellers.

General cost: It represents the additional expenditure that have to be done for the freight of the purchased equipment to the site where the CCS plant is being built. It include both international and local transportation.

TEC: The total equipment cost represents the amount of money to be spent to have all the required equipment at the building site ready to be installed. It simply the sum of the Process Equipment Cost and the General Cost.

Instrumentation/Electrical/Piping: These three costs give an approximated evaluation of the costs of all auxiliary equipment required to operate the power plant and they are, for this reason, calculated as a percentage of the total equipment cost.

Total Installed costs: TIC is the final cost of all the main and auxiliary equipment that will be installed at the project site.

Set-up costs: These costs take into account the amount of money that have to spent fort the installation of all the equipment in order to have the whole capture unite ready to operate.

Engineering: It is an estimation of the cost for the engineering design of the capture system.

Owners costs: These are the costs for obtaining approval, including environmental ones, land purchase, negotiation and legal process.

EPCO: It is simply the sum of all the previous costs explained.

Contingency: This covers the cost of miscellaneous equipment not included above and it takes account of the uncertainties on the costs estimation. (more a technology is known lower this value is)

Total Capital Cost: It is the total amount of money to be spent for the whole realization of the process.

For the Process equipment costs estimation different equations given by the CO2CRC have been used. The equipment used in the membrane our CCS system are: compressors, fans, vacuum pumps, heat exchangers, expanders, membranes and a dryer unit.

The equation used are listed below; the results obtained are all in the same unit which is [$].

-Gas blower:

$$Cost_{gas\ blower} = 555650 * \frac{Total\ flow\ rate}{160} \qquad (5.1)$$

Where Total flow rate is [m^3/s]

-Gas compressor and expander:

$$Cost_{comp/exp} = 45.37776 * \ {W_{el}}^{0.7934} \qquad (5.2)$$

Where W_{el} is [MW_{el}]

-Heat exchangers:

$$Cost_{heat\ exchangers} = 62000 * \ W_{th} \tag{5.3}$$

Where W_{th} is [MW_{th}]

-Demister:

$$Cost_{demister} = 2144 * N_{water} \tag{5.4}$$

Where N_{water} is [$kmol_{H2O,liquid}$ / h]

-Membrane:

$$Cost_{memb} = S * \ C_{spec\ membrane} \tag{5.5}$$

Where S is [m^2]

$C_{spec\ membrane}$ = [$/$m^2$]

-Membrane housing:

$$Cost_{housing} = 250000 * \left(\frac{S}{2000}\right)^{0.7} \tag{5.6}$$

Where S is [m^2]

-Vacuum pump:

$$Cost_{vacuum\ pump} = 1.1e06 * \frac{Total\ flow\ rate}{70} \tag{5.7}$$

Where Total flow rate is [m^3/s]

-Intercooled compressor:

$$Cost_{intercooled\ compressor} = \ Cost_{compressor} + \ Cost_{heat\ exchangers} \tag{5.8}$$

-Cryogenic

$$Cost_{crio} = 102.33e06 * \left(\frac{W_{crio}}{62.2}\right)^{0.67} \tag{5.9}$$

Where W_{crio} is [MW_{el}]

5.1.3 Operative costs definition

Operative costs are the expression of the maintenance, replacement and operation of the equipment over time and represents the costs that each year have to be sustained to keep the capture unit working.

The assumptions for the operative expenditure (Opex) estimation, as for the Capex, the CO2CRC methodology has been used and it is shown in table 5.3.

Table 5.3 Assumptions of the operative costs evaluation.

	Value	*Unit*
Fixed operational and maintenance (FOM) cost		
General and maintenance cost	6	[%Capex/year]
Variable operational and maintenance (VOM) cost		
Cooling water	0.025	[$/m^3]
Membrane replacement price	50 $/m^2	[$/m^2]
Expected membrane life	3 years	[years]

In addition we have to include to the operative costs the cost due to the energy penalty caused by the capture system. In fact part of the electricity that the combined cycle produce will be consumed to operate the equipment of the capture unit. This will results in a loss of money because less electricity could be sold to the market for the assumed price.

5.1.4 CO_2 avoided cost calculation

The evaluation of the economic performance of the capture system will be done by the final calculation of the avoidance cost of CO_2 expressed as cost per ton avoided [$\$/t_{CO2,avoided}$].

The present value of the project is the additional cost of a plant with CCS compared with an equivalent non-CCS power plant with the same production rate.

Once the operative and capital costs have been evaluated they will be actualized for the calculation of their present value and the same will be done with the amount of CO_2 avoided.

In this way we will be able to compare these two parameters and calculate the cost for each tonne of carbon dioxide avoided with the equation (5.11).

$$Cost\ of\ CO_2\ avoided = \frac{Present\ value\ of\ project}{Present\ value\ of\ CO_2\ avoided} \qquad (5.10)$$

$$Cost\ of\ CO_2\ avoided = \frac{\sum_{i=1}^{n} \frac{C_i + O_i}{(1+d)^i}}{\sum_{i=1}^{n} \frac{(CO_2\ avoided)_i}{(1+d)^i}} \qquad (5.11)$$

Where: -C_i is the capital cost paid in year *i*
-O_i is the operative cost paid in year *i*
-d is the discount rate

Calculated in this way the cost of CO_2 avoided represents the amount of money that the electricity generator should receive for each ton of CO_2 he avoids building the capture system, to recover the whole money spent (both for capital and operative investment) during the operative life of the capture plant.(The cost of CO_2 avoided is the breakeven price that would be needed to match the present value of the capture project)

5.2 Economic results

5.2.1 Cases studied

For this study the reference power plant with selective recirculation of carbon dioxide is completely identical to the one described in Chapter 4. The only difference is that permeability of Nitrogen, Oxygen, Argon and water vapour is added to the membrane. The reference selectivity value that has been chosen is 50 for every gas. This is the lowest value of the range of selectivity expected for DESSM and it has been chosen because it is the case where selectivity of other gasses will give grater effects on the power plant performances.

Table 5.4 Base assumptions for CC implementation.

	Value	*Unit*
$P_{perm, first\ membrane}$	0.2	[bar]
O_2 concentration at combustor output	2.5	[%]
$\Delta P_{membranes}$	3	[%]
Temperature of flue gas cooled	35	[°C]
Capture ratio	90	[%]
Membrane selectivity	50	[-]
Compression ratio	18	[-]
TIT	1360	[°C]

The effect of the variation of the parameters already shown in chapter 4 will be here repeated with the addition of the membrane area, and the cost of avoidance evaluation.
In chapter 4 the analysis was purely theoretical to understand the impact we could expect applying this capture system to the power plant.

The parameter that have been analysed are the compression ratio, the O_2 concentration in the combustor, the membrane selectivity and the membrane specific price.

5.2.2 Capture reference case results

With the methodology described we calculated the value of the cost of avoidance of the capture system. The amount of CO_2 separated in the first membrane is set to be equal to the 90% of the CO_2 outgoing from the power plant boundaries. When infinite selectivity of the membrane was supposed all these CO_2 was captured. The amount of CO_2 avoided anyway results lower than 90% due to the energy penalty.
When real selectivity is used we have to additionally subtract from the CO_2 avoided the amount of CO_2 captured in the first membrane that is vented by the cryogenic system in the purification process.

The thermodynamic results of the reference capture plant are listed in the following table.

Table 5.5 Thermodynamic results of the reference power plant with selective recirculation of CO2.

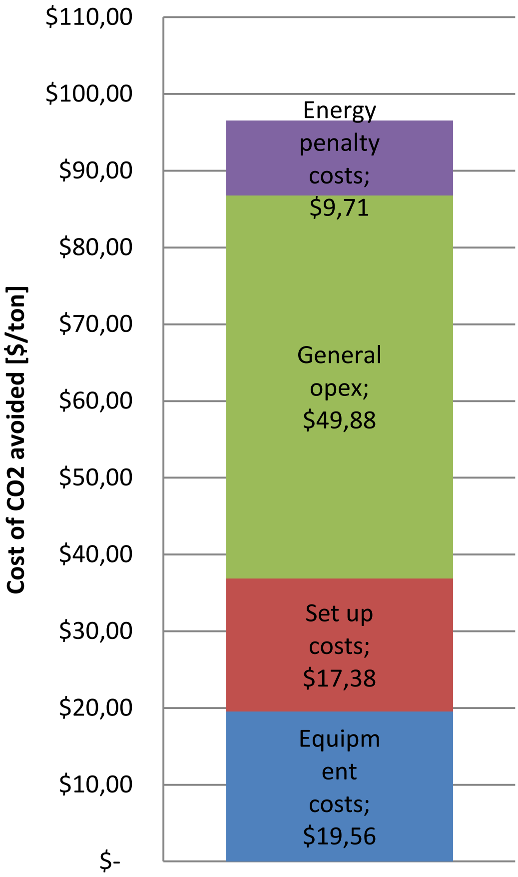
	Value	***Unit***
η_{tot}	54.79	[%]
W_{tot}	375.67	[MW]
M_{air}	360.27	[kg/s]
M_{ric}	231.47	[kg/s]
CO_2 concentration in flue gas	32.23	[% mol]
CO_2 avoided	81.35	[%]
S memb.1	14693	[m^2]
S memb.2	1257600	[m^2]

The energy penalty of the capture system is equal to 26 MW, and the biggest contribute to the energy loss is the consumption of the cryogenic purification system that needs a power of 15.77 MW.

The purity of CO_2 in the permeate stream of the first membrane is already particularly high (92.22 %) which results in a very small amount of CO_2 lost in the vent stream but in a larger specific consumption of the CPU.

Using the methodology explained earlier we obtained a cost of avoidance of CO2 equal to 96.53 $/t.

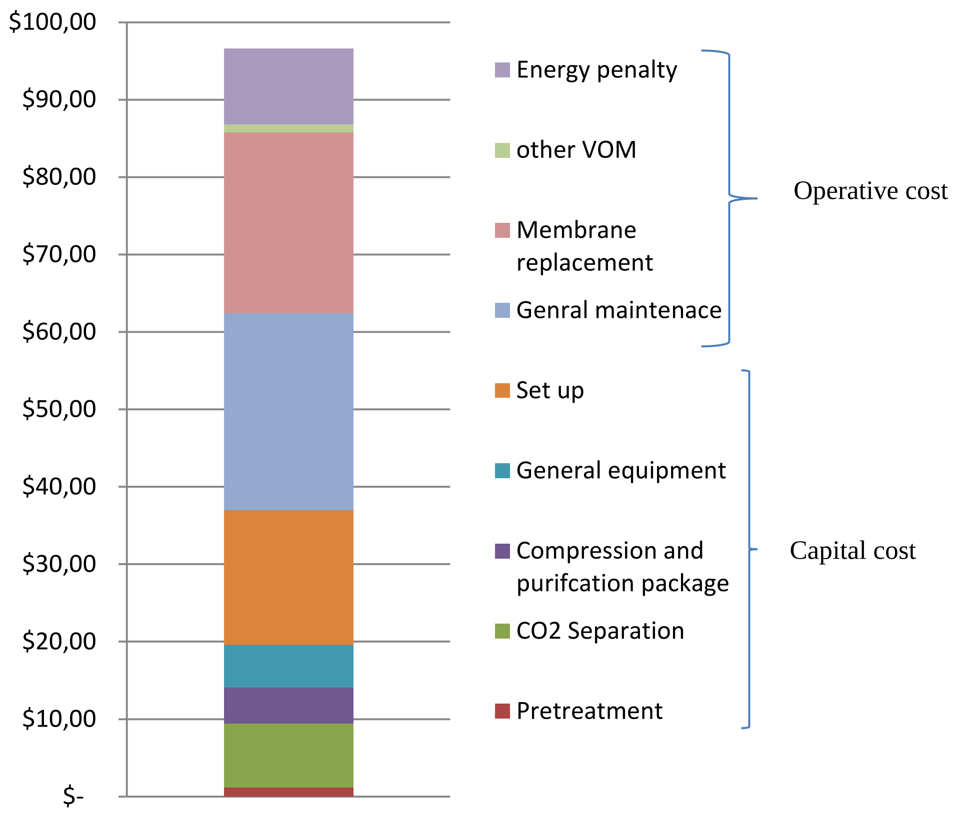
In fig. 5.1 it is shown a general cost breakdown of this solution to show how the different cost entries contribute to the final result.



5.1 Cost breakdown of the reference capture plant.

As can be immediately seen the greatest part of the cost of capture is caused by the operative costs of the CCS unit. While the Capex cause only the 36% of the total cost. The energy penalty cost results to be relatively small due to the low loss of energy caused by the capture system as no compression of the flue gas is used in this case.

It can be interesting now to see a more detailed cost breakdown in order to understand the impact of every component of the power plant to the cost of capture.



5.2 Detailed cost breakdown of the reference capture case

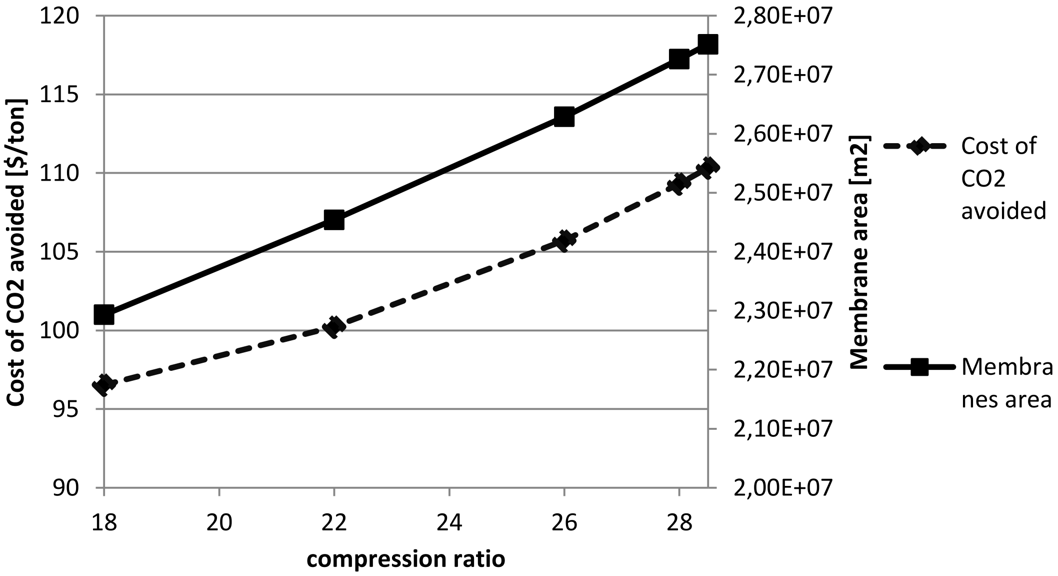
We can see that the main equipment required for the CO_2 separation unit account for less than 10 $/ton, especially the cost of the pre-treatment is extremely low. This is because in this case we only used fans to guarantee the circulation of the gas streams in the membranes.

What really needs to be discussed is the impact of the membranes replacement during the operative life of the capture system. We can see that, despite the first purchase of the membrane is relatively cheap (CO_2 separation part in fig 5.2), its periodical replacement drastically rise the cost of CO_2 avoided causing more than 23.5 $/ton over a total of 96.53 $/ton. This means that in future development of the membranes it could be more important to focus on a longer membrane life than on it technical performances like sensibility and permeability. In addition we could consider to use a membrane, whose specific price is higher, that presents a longer operative life.

The general maintenance cost is also very significant and it is due to its methodology of calculation. Being set as 6% of the total Capex every year, it results to be equal to approximately 65% of the Total Capex when actualized over the 25 year of operation of the capture system.

5.2.3 Effect of compression ratio

We already saw in chapter 4 that an increase of compression ratio to a value of 28 would allow to operate with a higher global thermal efficiency of the power plant without affecting the CO_2 concentration in the flue gas significantly. This would results in smaller energy penalty that would allow to save money over the 25 year of life of the power plant.



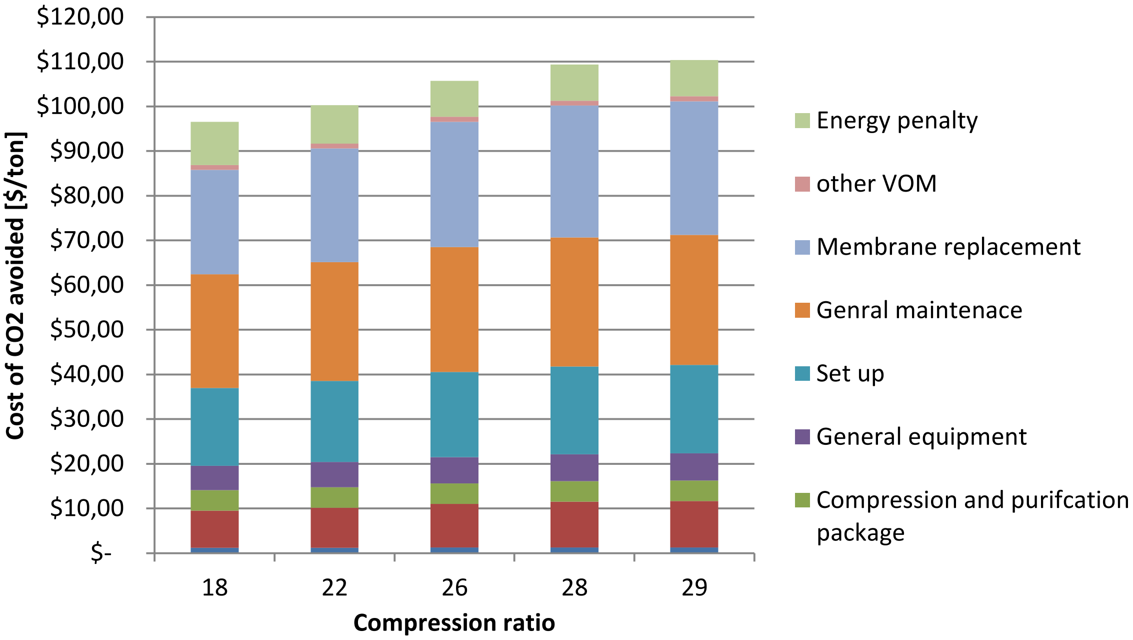
5.3 Effect of compression ratio on membrane area and CO2 avoided cost.

In fig. 5.3 is represented the total membranes area (sum of the first and the second one) because it is the real parameter of our interest and the cost of CO_2 avoidance.
fig 5.3 tells us that the economic evaluation would make us opt for a configuration which is completely different to what the technical analysis suggested us. In fact the cost of CO_2 avoided increases with the compression ratio instead to decrease for the thermal efficiency benefit.

Moving from a value of 18 to a value of 28 of the compression ratio we see that the cost of CO_2 avoided grows of approximately of 14.2% (from 96.53 to 110.3 $/t). This increment of the cost is caused by the large increase of the membrane area that overcomes the benefit of having a better thermal efficiency.

The membrane area increases mainly because, increasing the compression ratio of the gas turbine, the combustor output temperature increases and for this reason a larger amount of coolant is required in the turbine to keep the desired value of TIT. The recycled flow in the second membrane then increases causing a larger membrane to be needed.

Another particular, that we have not taken in consideration, but that needs attention is that different compression ratio means different cost and complexity of the gas turbine. For this analysis we have considered that the cost of the power section of the power plant remains constant even when the compression ratio value change, in order to simplify the study. This assumption is very strong as in real fact, when the composition of the gasses is given, a higher compression ratio would mean a higher cost of the turbine as the compressor would be much more complex and expensive.
However if this fact would be taken in consideration the final conclusion of this results would not change. The solution with high compression ratio would result to be even more expensive than what we have calculated, due to a more expensive gas turbine.



5.4 Cost breakdown with the variation of compression ratio.

As we can see in fig. 5.4 the cost due to the energy penalty decreases increasing the compression ratio.
But we have to consider that increasing the membrane area does not only increase the Capex of capture. The cost of membrane replacement, in fact,

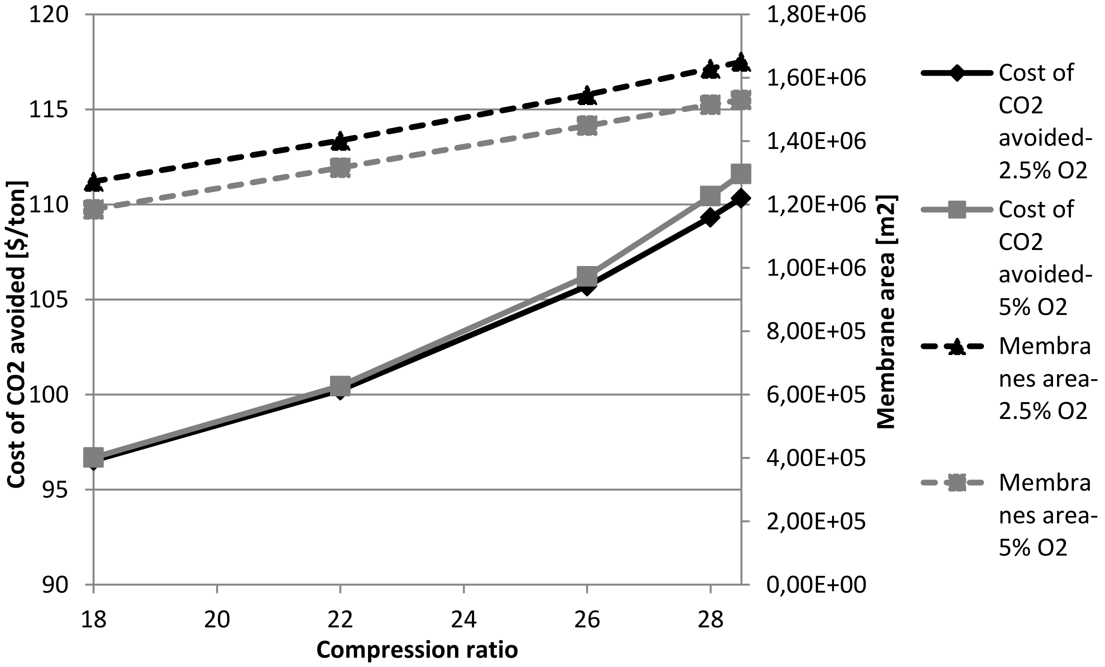
changes in function of the membrane area, resulting in a higher Opex too that overcomes the lower energy penalty cost.

5.2.4 Effect of O2 concentration

Increasing the concentration of O_2 fixed at combustor output we have already seen that drastically change the flue gas composition and we can expect then that will affect significantly the capture system.

The membrane simulations show that for this kind of capture system the second membrane area constitutes usually more than 90% of the total. Conceptually we could think to reduce the amount of CO_2 recycled in order to see if a trade-off between the first and the second membrane is achievable. Reducing the amount of CO_2 recycled in fact would decrease the CO_2 concentration of the flue gas increasing the area required in the first membrane system to separate the amount of CO_2 desired but would decrease at the same time the area of the recirculation membrane.

In fig. 5.5 are summarized the results obtained with a concentration of Oxygen at the combustor output of 5%, and they are compared with the reference capture case results already discussed.



5.5 Effect of O2 concentration on membrane area and cost of avoided CO2.

As it was expected, we can see that the total amount of membrane area required for the process decreases. Anyway we notice that the reduction is very modest, especially if compared with the reduction of the total mass flux recycled in the second membrane. The second membrane reduces its area of only 8.21% even if the total mass flux recycled decreases of 26.89%. The membrane reduction is much smaller because even if less CO_2 have to be recycled, its concentration at the membrane input is much smaller than the reference capture case, and for this reason more membranes is required to separate 1 kg/s of CO_2.

In addition we found out that the stream separated by the first membrane (the one that is sent to the CPU) has a lower concentration of CO_2 resulting in a larger amount of CO_2 lost in the purification process that reduce the total CO_2 avoided from 88% to 83%.

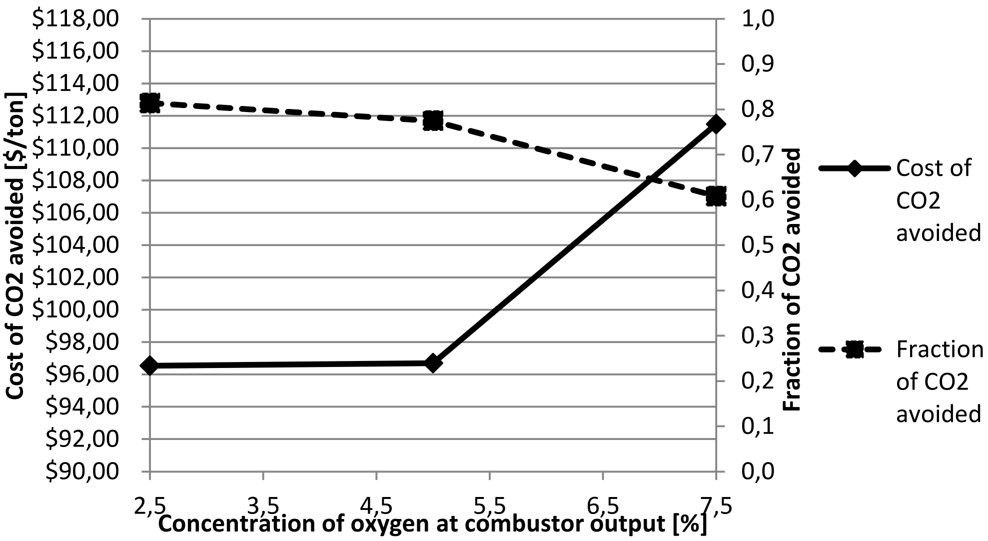
Table 5.6 Results with compression ratio equal to 18 and O2 concentration at combustor output to 5%

	Value	***Unit***
η_{tot}	54.94	[%]
W_{tot}	376.67	[MW]
M_{air}	434.47	[kg/s]
M_{ric}	169.22	[kg/s]
CO_2 concentration in flue gas	24.22	[% mol]
CO_2 avoided	77.44	[%]
S memb.1	30460	[m^2]
S memb.2	1154300	[m^2]

The thermal efficiency of the power plant results to be slightly higher due to the purification system. In fact being the stream separated by the first membrane more impure the specific work required for the purification is smaller at the expenditure of a larger fraction of CO_2 lost.

Due to the two different solution gave very similar results we introduced a third case in the analysis to better understand the effect of the concentration of Oxygen fixed at the combustor. In the third case considered we fixed a value of O_2 concentration equal to 7.5%.

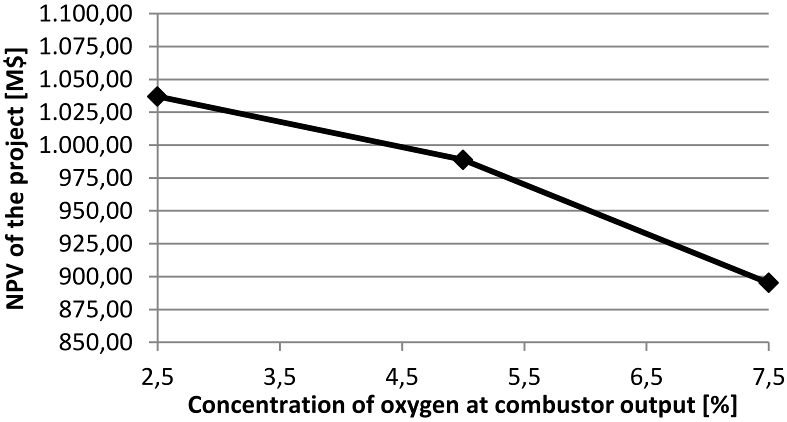
In fig. 5.6 are shown the results obtained.



5.6 Effect of O2 concentration at the combustor on the cost of CO2 avoided.

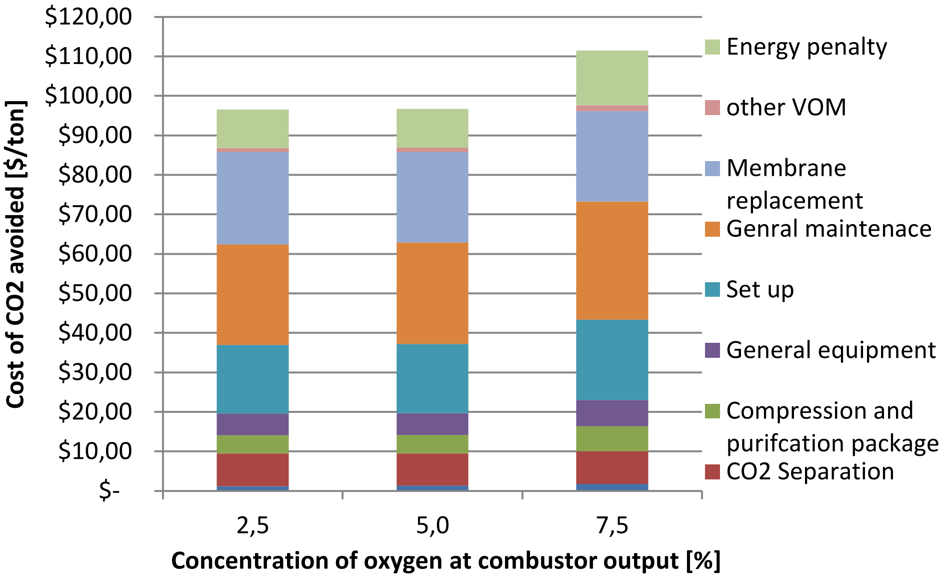
Increasing the Concentration of Oxygen in the flue gas causes a strong reduction of the fraction of CO_2 avoided that drops from a value close to 80% to a level of 60%. The increase of the cost of CO_2 avoided in then caused not for an increase of the costs of the capture project but because the amount of CO_2 avoided drastically drops.

It is the denominator of eq. (5.2) that decreases and not the nominator to increase. In fact if we look at the trend of the NPV of the whole project we can see in fig. 5.7 that it significantly decrease due to the smaller membranes when we increase the concentration of Oxygen in the flue gas.



5.7 NPV of the project with the variation of O2 concentration at the combustor.

The global cost of CO_2, taking into account every factor, results to be higher than a solution with less Oxygen at the combustor output. In fig. 5.8 is shown the comparison between the cost breakdown with different concentration of O_2 to understand what causes this difference.



5.8 comparison of the cost breakdown with different concentration of O2. (compression ratio equal to 18).

Comparing the first two solutions (2,5% and 5%) we can see that the total avoided cost change of less than 1 $/ton. We can also notice that there is not any significant distribution change of the costs.

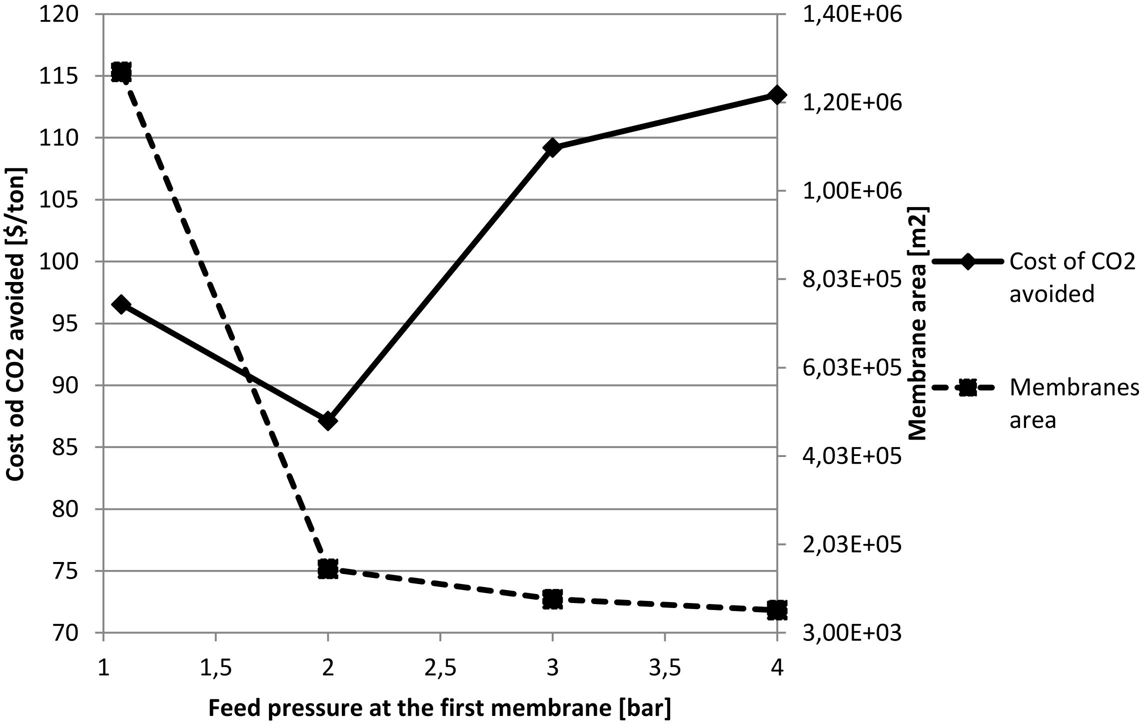
A significant difference instead is found when the 7.5% concentration case is considered. This increase is, as it has already been said, caused by the strong decrease in the amount of CO_2 avoided rather than in an increase of cost of the plant and, in fact, we can see that all the different cost items increase. Even the pre-treatment part of the cost increases its weight even if the capital expenditure for this equipment is almost constant with the other two cases.

Knowing this behaviour of the capture plant we could think to not send directly the stream vented by the CPU to the chimney. In fact it is here that most of the additional CO_2 vented is lost. Recycling it into the capture unit, for examples at the first membrane input point, we could recover most of it, reducing significantly the cost of capture. This solution has not been considered in this study and could be an interesting development of this research.

5.2.5 Effect of flue gas compression

We already saw that using a flue gas compression system to enhance the driving force in the membrane system, instead of simple fans, drastically increase the energy penalty of the capture system.
It is now time to see if this additional loss can be overtaken by the benefit of having smaller membranes for the separation process.

We have to notice that the vacuum pump on the permeate side of the first membrane will be used in combination of the compression of the flue gas and the permeate pressure of the first membrane will remain equal to 0.2 bar.



5.9 Effect of flue gas compression on capture cost and membranes area.

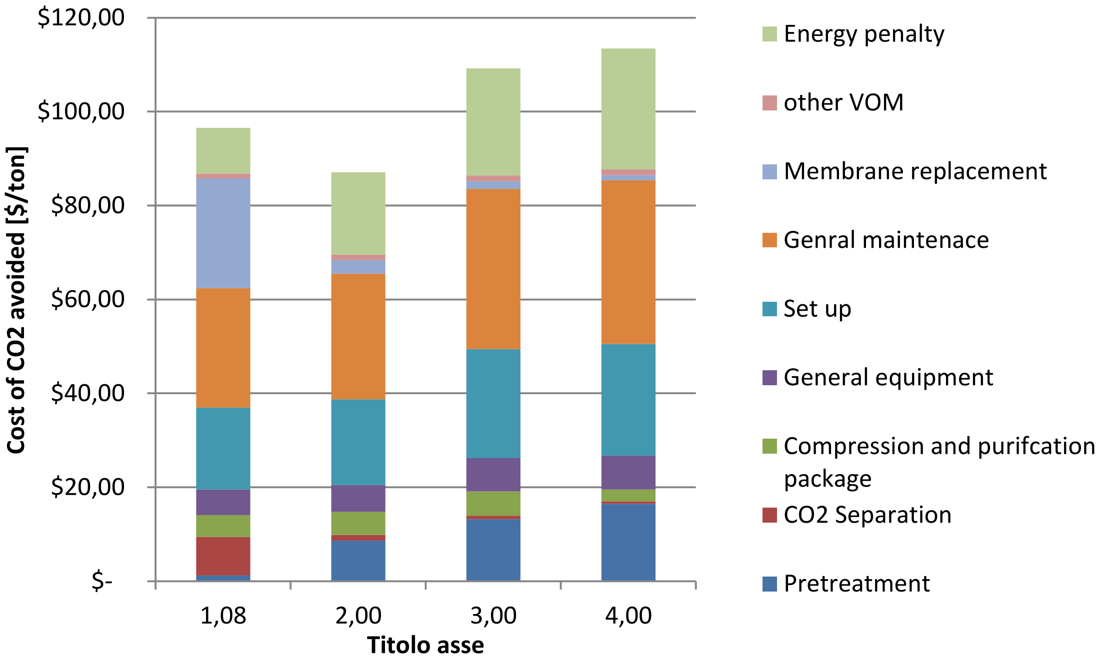
As can be seen in fig. 5.9 the reduction of total membrane area achievable compressing the flue gas in highly significant. Just compressing the flue gas to a final pessure of 2 bar (instead of 1.08 bar requested due to pressure losses) we obtained a reduction of membrane area of more than one order of magnitude.

This figure also shows us that a further increase in the flue gas compression could achieve smaller area surface but that the relative saving gests smaller and smaller as we increase the final pressure.

Looking at the final cost of CO_2 avoided we can see that a minimum can be obtained for low level of compression as a trade-off between the cost of the membrane (function of the total surface) and the energy spent to increase the flue gas pressure.
Compressing the flue gas to a pressure of 2 bar we achieved a saving in the avoidance cost of approximately 10 $/ton getting to the value of 87.12 $/ton .

In this analysis we have also considered the additional cost caused by the need to cool the gas before the turbine compressor for the reasons described earlier in chapter 4.

Looking at the cost breakdown of the different cases considered we can have a better explanation of the trade-off between membrane area and energy penalty.



5.10 Cost breakdown of the avoidance cost with different compression of the flue gas.

As can be immediately seen from fig. 5.10 the contributes of each cost drastically change when compression of the flue gas is used.

First of all the costs due to the membrane area (CO2 separation and membrane replacement) are drastically reduced by the increase of compression of the flue gas being almost negligible for the 4 bar case while when no compression of the flue gas is used they account together for almost 30 $/ton.

At the same time we can see that the cost for the pre-treatment and the energy penalty increase when a stronger compression is used. This is caused by the fact that larger compressors are more expensive to purchase and consume more electric power. The increase of the capital cost also affect the general maintenance cost causing it to increase.

Going from the case without flue gas compression and a compression of 2 bar the best case is obtained. In fact the increase of capital cost for the compressors is almost perfectly balanced by the reduction of capital cost of the membrane systems which is reduced to approximately 11% of the case without compression. The increase of energy penalty is largely overtaken by the reduction of the membrane replacement cost.

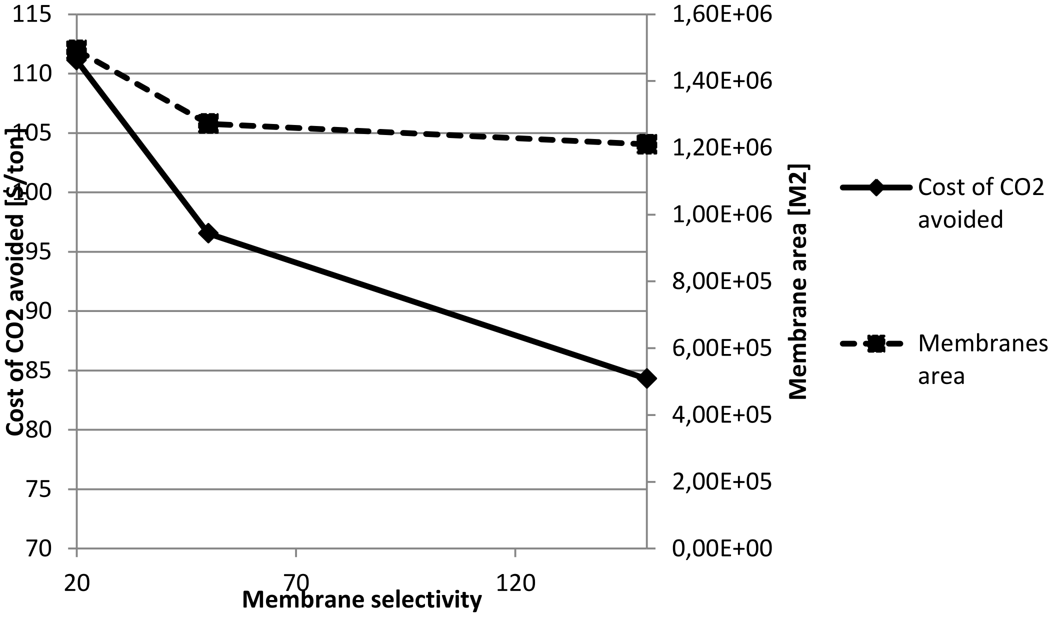
We also have to notice that for the last case considered, when we compress the flue gas to 4 bar the cost of the purification unit is almost halved as its consumption. This is caused by the fact that the stream permeated in the first membrane is already pure enough (the purity of CO_2 is higher than 95%) that the CPU is not required. Instead we could simply use and intercooled compression of the CO_2 which results less expensive and a less energy intense process.

5.2.6 Effect of membrane selectivity

In the previous cases we assumed to use a fixed membrane selectivity of 50. This is the lower value of the expected range for DESM and it has been used as a conservative hypothesis. In fact we can expect to obtain a captured stream in the first membrane with more impurities which would results in higher cost for CO_2 purification.

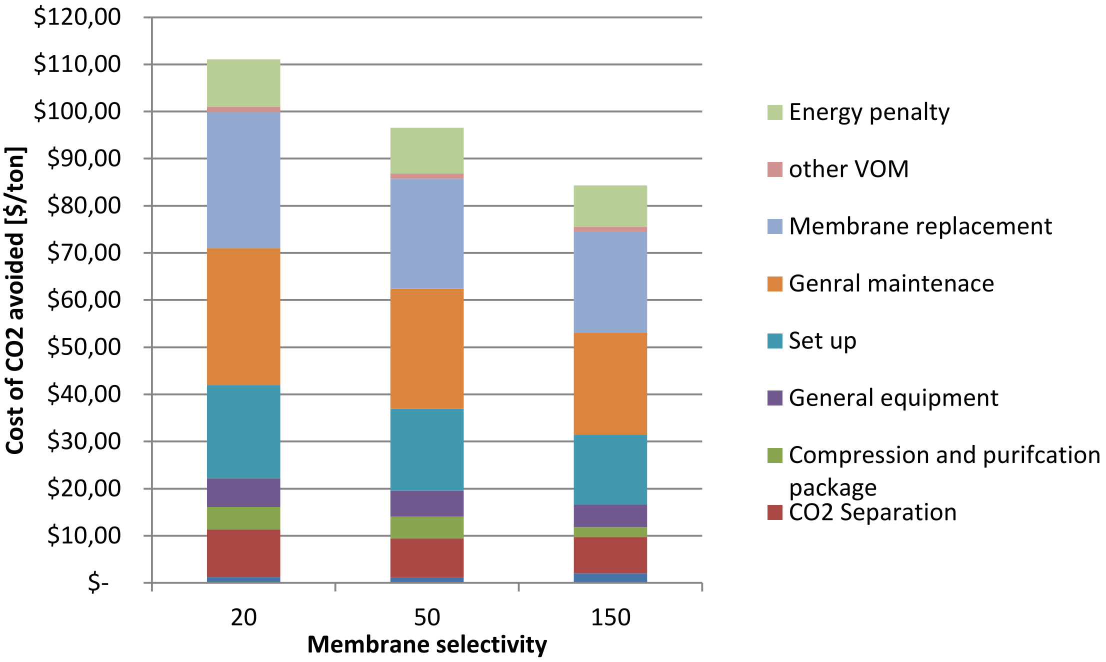
Three values have been assumed: 20-50-150 for the membrane selectivity. A selectivity higher than 150 has not been considered as at a first analysis we found out that the further improvement of this value would not give any significant difference in the results.

In fig. 5.11 are shown the results that we found out. What we can see is that the effect is different from what expected; in fact, usually, an increase of selectivity causes an increase of the total membrane area for the lower driving forces of the process resulting.



5.11. Effect of membrane selectivity on cost of CO2 avoided.

The system obtain a substantial cost benefit when selectivity of the membrane increases. This is caused by the reduction of the total surface of the two membranes required in the process. With a lower selectivity value the first membrane would be smaller but the first one would be much bigger. In fact more Oxygen would move in the opposite direction and more Nitrogen in the same direction of CO_2. This would result at the same time in a lower CO_2 concentration in the flue gas and a smaller pressure difference of CO_2 partial pressure at the two sides of the second membrane. This results in larger membrane required in the second membrane causing the cost of capture to rise. In addition the input flow of the CPU will be more impure and will result in larger fraction of CO_2 separated vented to the atmosphere. The opposite happens when the selectivity of the membrane increases.



5.12 Cost breakdown of the avoidance cost with different membrane selectivity.

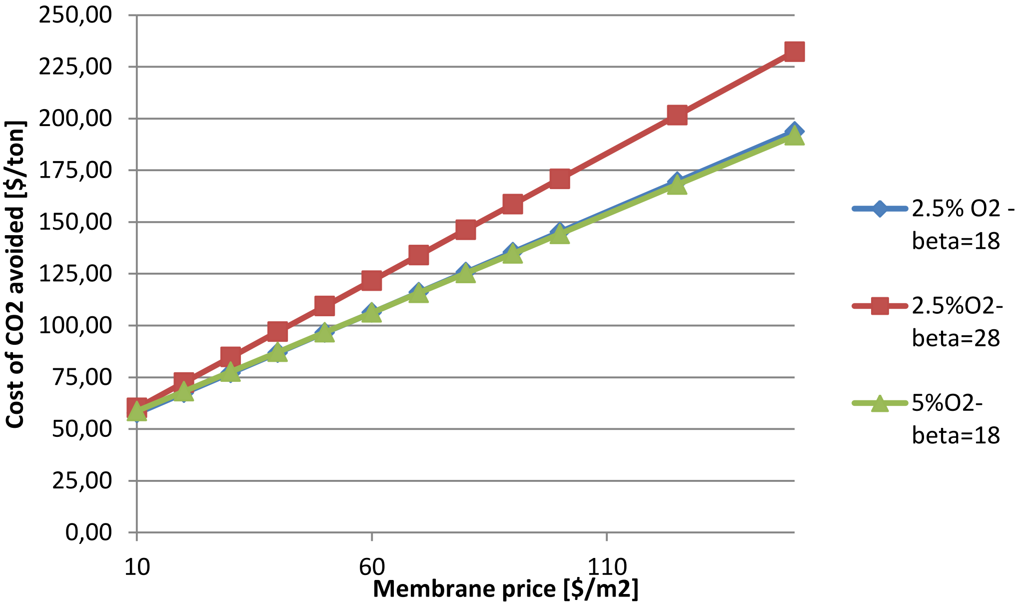
As can be seen in fig. 5.12 the membrane replacement, and membrane share of the total costs decreases with the increase of selectivity. The cost of the purification and compression of carbon dioxide decreases too, and for a selectivity value of 150 it is more than halved as the purity of CO_2 separated in the first membrane is already higher than 95% and a simple intercooled compression is used instead of a CPU.

In addition this causes less CO_2 to be lost in the purification process; in fact the CO_2 avoided changes from 77.1% when selectivity is 20 to 83.4% when it is 150 and this contributes to the reduction of cost of avoidance too.

5.2.7 Effect of membrane specific cost

In all previously analysis we have assumed a cost of 50 $\$/m^2$ to estimate the final cost of the membranes. All the equipment used in this capture system is well known technology, whose cost can be foreseen quite accurately, but the membrane itself.

Being the deep eutectic solvents supported membranes (DESSM) a new technology we do not have accurate estimation on the their cost. For this reason we conducted a sensitivity analysis to see how the cost of capture change for different value of cost of the membrane.



5.13 Effect on avoidance cost of membrane specific price.

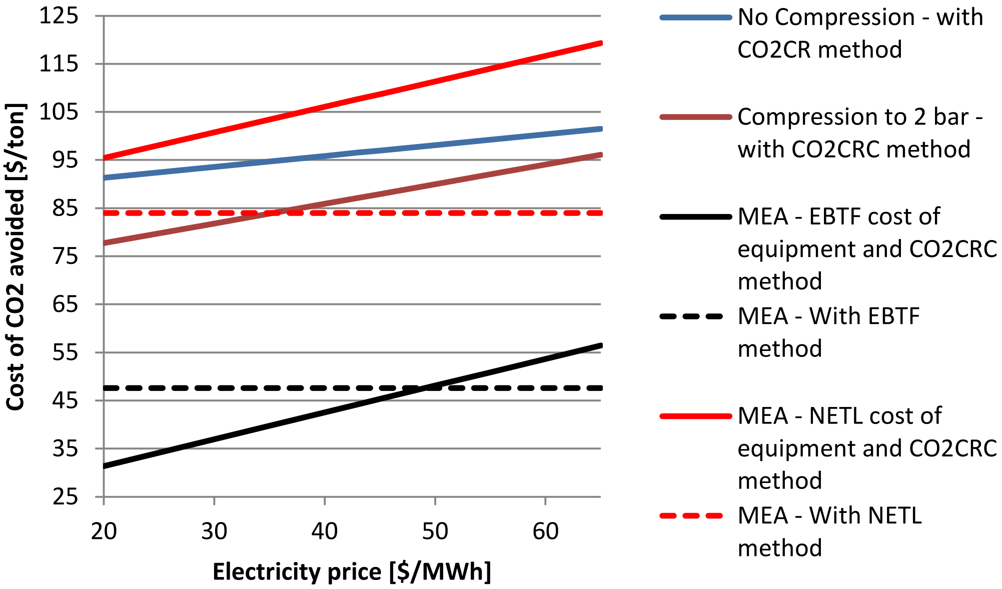
As expected we can see that with an increase of the specific price of the membranes the cost of CO_2 avoided continue to rise. It is interesting to see that reducing the cost of the membrane to a value of 30 $\$/m^2$, that with the progress of technology of DESSM can be achieved, the cost of avoidance is reduced to approximately 75 $/ton which is a decrease of almost 20% of the total cost.

We notice that the lines that represents cases with different Oxygen concentration are almost overlapped. In particular we see that they cross for a value of 70 $\$/m^2$ of the specific price of the membrane. This is due to the fact that the solutions with more oxygen have smaller membranes. When the impact of this component is not important (when the membrane is cheap) the negative effect on the avoidance ratio for the case with 5% of oxygen is relatively heavier and it cost more than the case with less oxygen. When the membrane saving becomes more relevant (when the membrane is expensive) a solution with more Oxygen in the flue gas can be more competitive.

5.3 Comparison with MEA solution.

It can be now interesting to compare the solution obtained with our methodology with a reference MEA absorption solution, as it is now considered the current benchmark of CO_2 capture technologies.

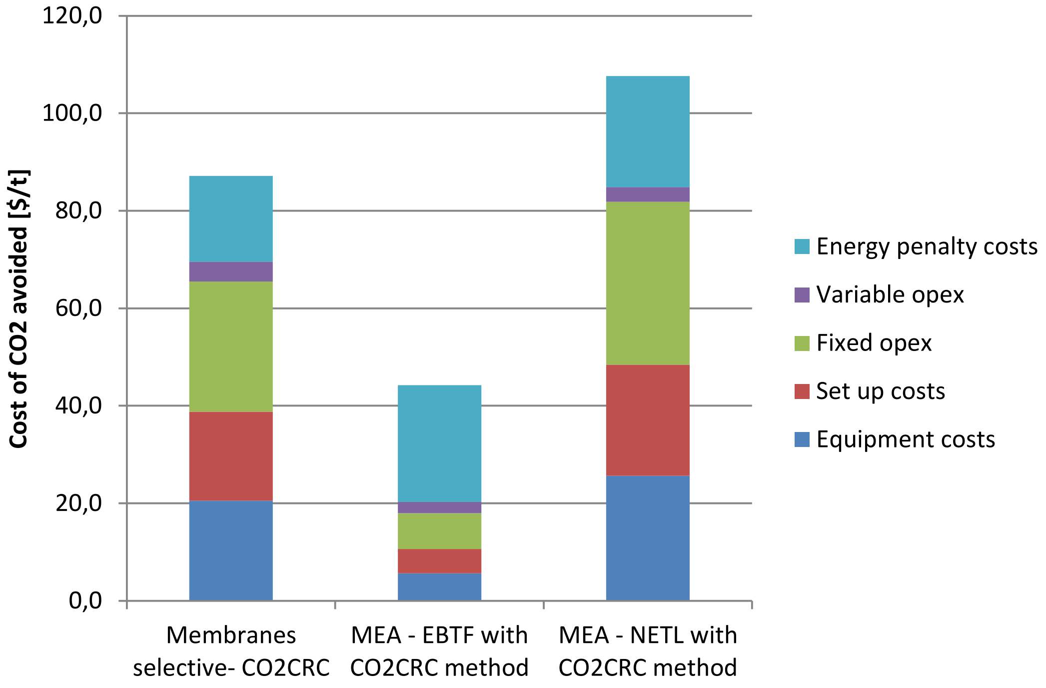
We will compare our solution to the EBTF [46] report one and the NETL too [47]. In our solution, the assumption of a price of electricity is required to evaluate the contribute of the energy penalty on the cost of CO_2 avoided, for this reason we compared the results obtained changing this value.



5.14 Comparison of CO2CRC results with EBTF ones

In figure 5.14 we compared the result obtained. The dashed horizontal lines are the values of cost of CO_2 avoided reported in the EBTF and NETL report using their assumptions ant methodology.
The red and black lines instead are the results we obtained using the CO2CRC methodology starting from the value of total equipment cost and variable costs estimated in the other two reports instead of using our estimation of the equipment cost, and varying the electricity price.
We compared these values with two selective recirculation cases; the first one is the reference one, and the second one is with a compression of the flue gas to 2 bar. We can see that the solutions analysed in this thesis have a smaller energy penalty (their steepness is lower) than the MEA absorption solution. In addition we obtained better results if compared with the NETL-MEA case, which means that this configuration can be competitive to the already available technology. The results of the EBTF case anyway tell us that a lot of uncertainties still exist on the estimation of costs of the required equipment for carbon capture.

If we look at fig. 5.15 we can see in fact that the substantial difference between the results of EBTF and NETL method is the first estimation of the capital cost that is less than 25% of the NETL (and approximately our) estimation.



5.15 Cost breakdown of different methodology results.

6 THECNO-ECONOMIC ANALYSIS

Non-selective recirculation plant

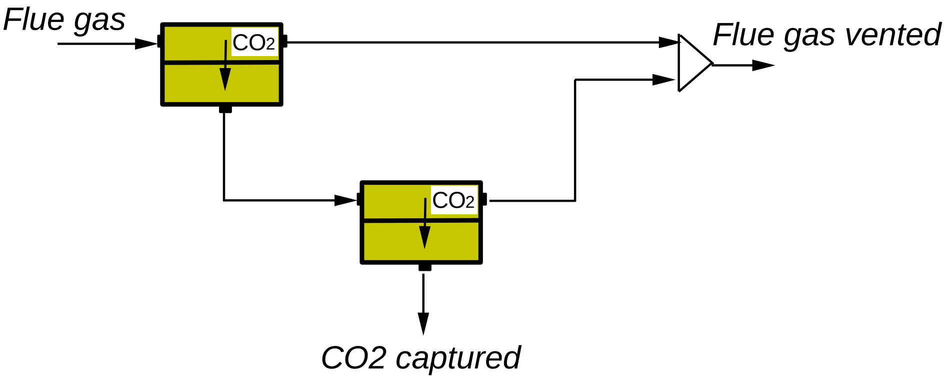
In this chapter the methodology used for the simulation and the optimization of the capture system for the EGR case will be presented. First the technical parameters and structure of the membrane system will be explained and in a second moment the methodology for its calculation will be highlighted.

For the economic evaluation of this solution the same assumptions and methodology explained in chapter 5 will be used in order to obtain consistent results with the selective recirculation case.

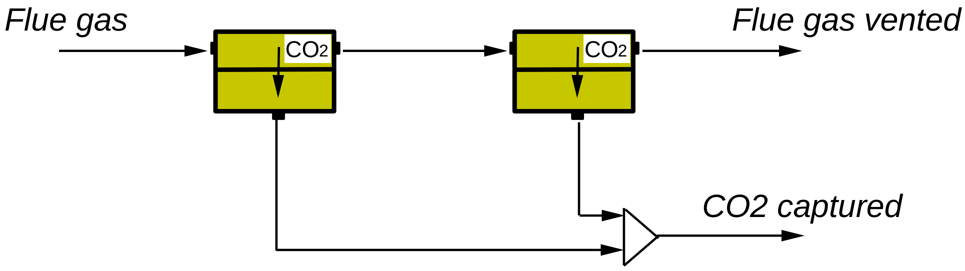
6.1 Membranes system description

6.1.1 Membranes disposition

As it has already been said in chapter 3.3.6 the membrane system that have been considered are two that are shown in figure 6.1 and 6.2.



6.1 Disposition of the membranes in the EGR capture system.



6.2 Different possible disposition of the membranes for the EGR capture system.

The solution shown in Fig 6.2, has been immediately discarded as the preliminary simulation done using the MATLAB model of the membranes showed that a purity of CO_2 captured higher than 40% was never reached. An additional membrane system would be then required anyway to increase the purify the permeate stream of both membranes in order to reach a minimum CO_2 purity level that can be accepted by the CPU.

Using and additional membrane to purify the permeate of the two membrane of the case we would obtain a situation absolutely identical to the case shown in figure 6.1 and this is why we decided to focus exclusively on this solution.

Table 6.1 Composition of the flue gas treated by the capture system.

Chemical species	***Molar concentration in percentage***
CO_2	8.729
N_2	80.026
O_2	4.745
H_2O	5.548
Ar	0.952

In the solution considered the flue gas produced by the combined cycled, whose composition is shown in table 6.1, enter the first membrane system that has the objective to recover as much CO_2 as possible from the flue gas. The gas that does not permeate here are immediately sent to the chimney and all the CO_2 contained would be vented to the atmosphere.
For this reason it is important that this first membrane operates with the right condition to separate as much CO_2 as possible from the flue gas and that is why the surface used will be relatively large.

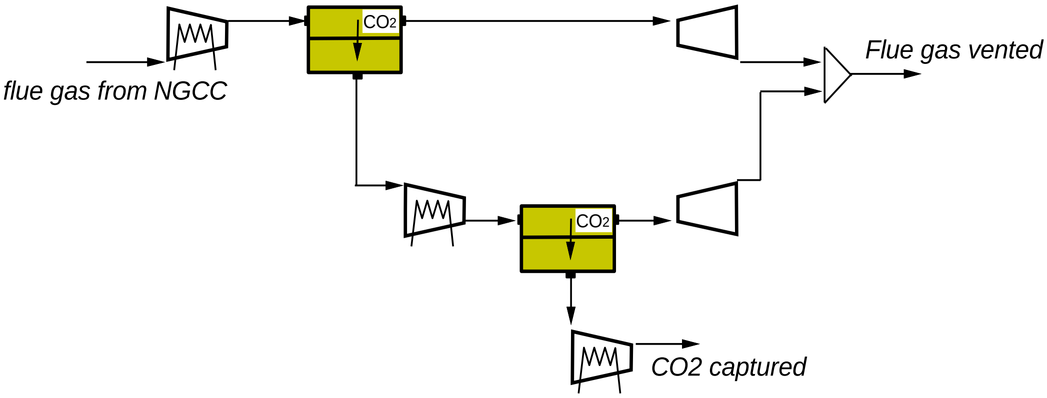
The CO_2 enriched flow produced on the permeate side of the membrane can be now sent to the second membrane unit. Due to the higher

concentration of carbon dioxide of the flow treated the permeate of this second membrane will have a much higher purity of CO_2. The stream produced in this way can have purity relatively high (around 80%) that could be now accepted by the capture and purification unit that will further purify the CO_2 to values beyond 97%.
Even in this case what remains in the feed side of the membrane is sent to the chimney and vented to the atmosphere.

6.1.2 Compression of the flue gas

To enhance the driving force of the permeation process of both membranes a compression system can be used. Both the compression of the feed stream and a depression on the permeate side of the membrane will be used in order to reduce the surface required for the separation of CO_2 and increase the purity of both permeate streams.
When compression of the flue gas is used we also have to consider the utilization of gas expanders at the output on the feed side of the membrane. In fact here we could have a pressurized gas that can be used to recover at least part of the energy spent for the previous compression reducing the energy penalty due to the capture system.

The disposition of compressors and expanders is shown in fig. 6.3, and as we can see using three compressors and two expanders we can independently choose the input and permeate pressure of both membranes.



6.3 Compressors and expanders disposition in the membrane capture system

Intercooled compressors have been used instead of simple compressors to keep the temperature of the gas flowing in the membrane system to a

reasonable value that would not give problems to the chemical and mechanical stability of the membranes.
This will reduce for sure the maximum amount of energy that can be recovered by the two expanders and will increase the operative costs due to the cooling process in the compressors.

It is important to notice that according to the different value of the pressure that will be used one or more of the equipment considered may not be needed.

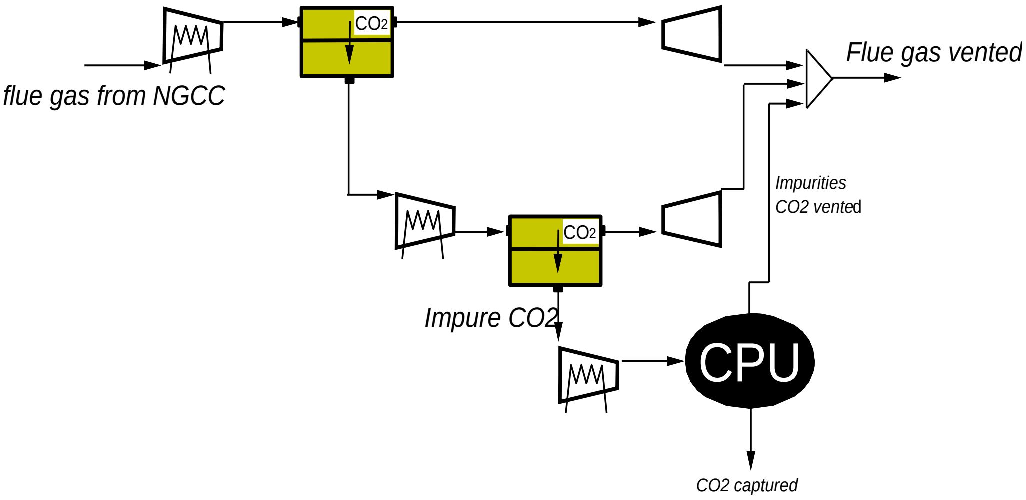
6.1.3 Purification system (CPU)

The permeate flow of the second membrane is highly enriched in CO_2 but is still not pure enough to be directly compressed to high pressure and sent to the storage location by the different transport technologies available nowadays. As the presence of impurities dramatically increases the cost of transport a purity of even 90% of the CO_2 cannot be accepted in any case.

The impurities that we can find in the stream are mainly Nitrogen and Oxygen. Water can be found in the form of water vapour and can be easily removed just by cooling the flue gas to low temperature and condensing it.
To remove the other impurities a much more complex system have to be used.

The system we used is exactly the same cryogenic CPU described in chapter 3 that has been used for the selective recirculation case. The intercooled compression has never been used within the EGR case analysis as the low purity of the captured stream always require a cryogenic purification.

With the addition of the purification system the scheme of the separation unit used becomes as shown in fig 6.4



6.4 CO2 capture system with purification unit

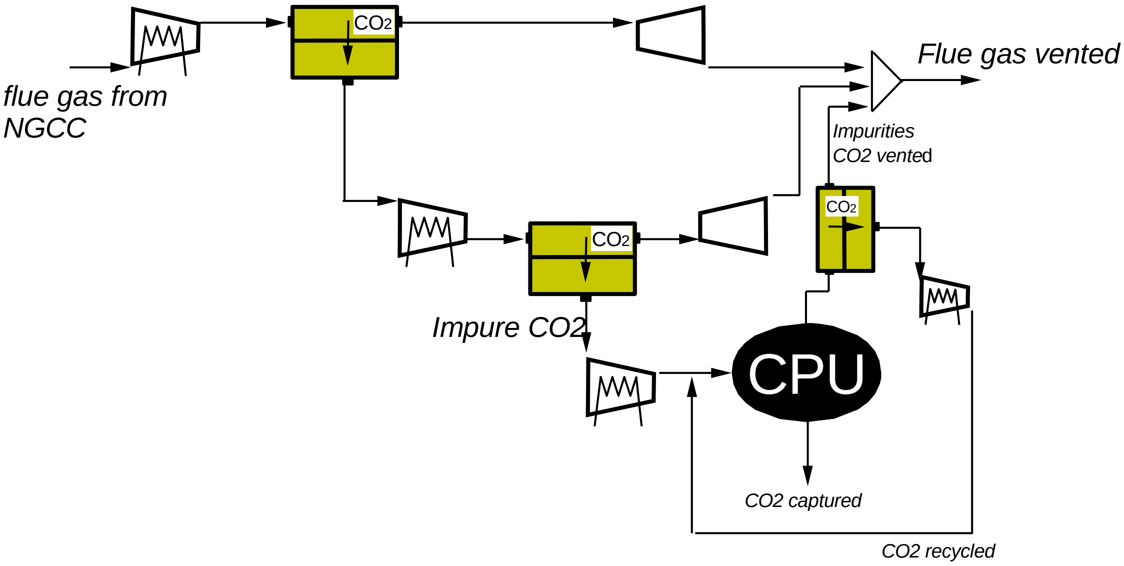
An important thing to notice is that with this configuration part of the CO_2 that we can find in the permeate stream of the second membrane will be lost in the purification process. In fact together with the impurities a small part of the CO_2 entering the CPU will be vented. The fraction of CO_2 lost is proportional with the CO_2 initial impurity.

6.1.4 Vented CO2 recovering process

As it has already been said in paragraph 6.1.3 some CO_2 will be lost in the purification process when a cryogenic system is used.
The fraction of CO_2 lost on the total amount that is treated by the CPU is inversely proportional to the starting purity of the stream treated in the CPU. For very low CO_2 concentration the amount of CO_2 lost can be relevant and cannot for this reason been neglected in the calculation of the total CO_2 avoided.
When the concentration of CO_2 in the stream entering the CPU is 70% approximately 17% of the total CO_2 treated is lost with the impurities.
The large amount of carbon dioxide lost can make economically competitive to recover at least part of it in order to reduce the loss.

For this reason a third membrane has been used to capture part of the CO_2 vented by the compression and purification system. The CO_2 recovered in this way is then recycled at the CPU input in order to be retreated and captured.

The final configuration of the scheme that we obtained adding this component is represented in fig 6.5.



6.5 Final scheme of the capture unit considered.

As can be noticed the additional membrane will require to add one more intercooled compressor to the system to create a driving force big enough for the permeation of carbon dioxide. As the impurities flow vented by the CPU is at atmospheric pressure a low pressure needs to be kept at the permeate side of the third membrane. To simplify the recirculation system of CO_2 in the purification process we assumed to keep a constant pressure at the permeate side of the third membrane.

It is important to say that the application of the CO_2 recovery from the gasses vented by the CPU can be not competitive in every circumstance. When the purity of CO_2 reached at the permeate side of the second membrane is particularly high, the fraction of CO_2 vented in the purification system can be so small that the cost of the recovery system can overcome the benefit of a smaller CO_2 final emission.

6.2 Simulation methodology

6.2.1 Independent variables of the system

For the whole simulation of the system many different independent variables have to be defined. Each membrane system requires 4 input for the simulation with the MATLAB model of the membrane. These variables are the pressure at the feed and permeate side of the membrane, the composition and the total flow of the feed stream and the membrane surface. Given these inputs the MATLAB code calculates the composition of the two output streams.
In this way the independent variables of this system would be 12.
The size and the consumption of the compressors and the expanders is a function of the ΔP on the membranes and they are then function of the same variables that impacts on the membranes.

The initial composition of the flue gas flows into the first membrane is fixed. The composition of all the other flows is a dependent variable of the other operative conditions (feed and permeate pressure and membrane surface) of the two membranes. The input composition of the other two membranes is a direct consequence of the permeation in the first one that is calculated starting from the flue gas composition that is fixed. For this reason also these two variables are dependant and the total amount of independent variables of the system decrease to 9.

The feed pressure of the third membrane is fixed as the flow vented by the CPU is at atmospheric pressure. In this way the number of independent variables is 8.

To further simplify the optimization of the whole system we have decided to fix the permeate pressure of the three membranes. This decision has been taken because in any case, the variation on the permeate pressure admissible is relatively small due to the low concentration of carbon dioxide in the flue gas. The plausible range of variation of the permeate pressure is from 0.15 bar (lower value is not easily reachable with current industrial equipment) and 0.3 bar as a higher value would seriously affect the purity of CO_2 separated.
The value of the permeate pressure has then been fixed to the value of 0.2 bar for all three membranes. In this way the total amount of independent variables that we have to study for the optimization is reduced to 5. The 5 remaining variables are the feed pressure of the first two and the surface of the all three membranes.

6.2.2 Calculation of gas properties

For the calculation of the energy spent for the compression of the gasses in the capture system it is important to define a methodology for the gas mixture properties calculation. All the gas streams are assumed to be formed be composed of 5 chemical species that are carbon dioxide (CO_2), Nitrogen (N_2), Oxygen (O_2), water vapour (H_2O) and Argon (Ar).

To evaluate the specific heat of a mixture, that is needed for the calculation of the compression work of the different compressors, we used the NASA polynomials. The range of temperatures interested in this system is relatively small; a temperature higher than 100 °C is never reached to ensure the mechanical stability of the membranes. For this reason the specific heat of the gasses has been evaluated at a fixed temperature of 35 °C and it has been considered constant with the variation of temperature of the gasses. The error committed by this assumption is negligible for the final calculation of the cost of capture.

6.2.3 Simulation of the compression equipment

The evaluation of the compression duty of the 4 compressors and the energy recovered with the 2 expanders is one of the most important part of the simulation. The variation of these values strongly influence which parameters allow the capture unit to separate CO_2 at the minimum cost per ton.

To calculate the compression duty we decided to use an intercooled compression process for mainly two reasons. First of all the total duty for compression is, in this way, lower, which allows a great energy saving over the operative life of the capture system. Secondly, and probably more important, we cannot accept an indefinite increase of the compressed gas temperature. This is because the membrane can have both mechanical and chemical stability problems at high temperature. Another reason is that a strong increase in the temperature of the gas treated could strongly affect the membranes performances. An increase of temperature, in fact, usually increase the permeability of every chemical species strongly decreasing the membrane selectivity towards carbon dioxide, This would result in a much lower purity of the CO_2 separated.

For these reasons we decided to fix the maximum temperature admissible at the compressor output at a value of 100 °C.

The input temperature is accepted without any problem as long as it is lower than the maximum value admissible that we assumed equal to 35 °C. when the flow to be compressed is at a higher temperature it is first cooled to this value and then the compression can start.
To simplify the simulation we calculated the compression duty assuming an isentropic compression. The energy consumed is then reported to a real value using an isentropic efficiency that have been assumed equal to 0.8 for the compressors.

First of all the maximum isentropic output temperature is calculated according to equation 6.1

$$T_{max,is} = T_{min} + \eta_{is} * (T_{max} - T_{min}) \qquad (6.1)$$

Where: -T_{min} = 35 [°C]
-T_{max} = 100 [°C]

This value is used to calculate the maximum compression ratio achievable without overcoming this output temperature, and the relative specific work of compression according to equation 6.2.

$$\beta_i = \left(\frac{T_{max,is}}{Tmin}\right)^{\left(\frac{K}{K-1}\right)} \qquad (6.2)$$

Where - K = Cp/Cv

The number of compression stages required to obtain the total compression ratio needed is then calculated. With this methodology the number of stages calculated is a real number and not an integer. This choice has been done to give a better stability to the calculation.

Equation 6.3 shows how the number of stages required is calculated.

$$\beta_{TOT} = \log\left(\frac{\beta_{TOT}}{\beta_i}\right) \qquad (6.3)$$

The total energy required for the compression is then calculated simply as the product of the number of stages and the energy needed for every single stage of compression.
Once it is known the number of stages we can also calculate the thermal power that needs to be extracted from the gasses as the product of the number of stages and the heat released to cool the gas from the max temperature to the minimum one.

The energy recovered in the expanders is calculated in the same way as an isentropic expansion then corrected using an isentropic efficiency of 0.85. The calculation of the expanders is much easier as there is just a single expansion without any particular technical problem.

6.2.4 Membranes calculation

In the selective recirculation case the membrane calculation was carried out by fixing the amount of carbon dioxide that had to permeate from the feed to the permeate side of the membrane. The surface was unknown and iteratively calculated, in order to make permeate the desired amount of carbon dioxide. With the EGR case a different approach will be used. The capture ratio of the CCS unit will not be fixed to a desired value as done before, as, from the economic point of view, a solution that captures a smaller amount of CO_2 could be more interesting. For this reason the calculation of the membranes will be done by fixing the value of the surface and the composition of the permeated stream is calculated.

The reference characteristics of the membrane system that we used in the simulations are the same used in the selective recirculation system. The lack of need to integrate the two different software (MATLAB and GS) allows us to directly calculate the system using real membranes without infinite selectivity.

The characteristics of the reference membrane are shown in table 6.2.

Table 6.2 characteristics of the membranes used

	Value	***Unit***
CO_2 permeability	500	[barrer]
Membrane thickness	50	[µm]
CO_2/N_2 selectivity	50	[-]
CO_2/O_2 selectivity	50	[-]
CO_2/H_2O selectivity	50	[-]
CO_2/Ar selectivity	50	[-]

As already said in paragraph 6.2.1 the permeate pressure of each of the three membranes will be fixed to a value of 0.2 bar in order to reduce the number of independent variables required to fully define the system.

6.2.5 CPU calculation

The purification system has to be calculated together with the third membranes used to recover part of the CO_2 vented by the cryogenic system. this necessity comes from the fact that this recovered CO_2 (that comes with some impurities) are remixed with the flow that is going to be treated by the purification equipment. We do not know at first both the mass flow and the composition of the recycled stream and for this reason in the first calculation it is set to zero.

After the first iteration we know a first estimation of the composition of the recycled flow that will change the input flow of the CPU. This modification does not only affect the size (and so the consumption) of the purification system, but also the purity of the gas treated modifying the fraction of CO_2 lost in the vented stream that will then change the composition of the flow recycled in the membrane.

This is why an iterative calculation is required to have an accurate simulation of this part of the capture plant. The convergence condition that needs to be met is that the composition between two subsequent iteration has to be constant.

When convergence is reached we can then calculate the real size and consumption (and then the cost) of the CPU unit.

6.2.6 System optimization

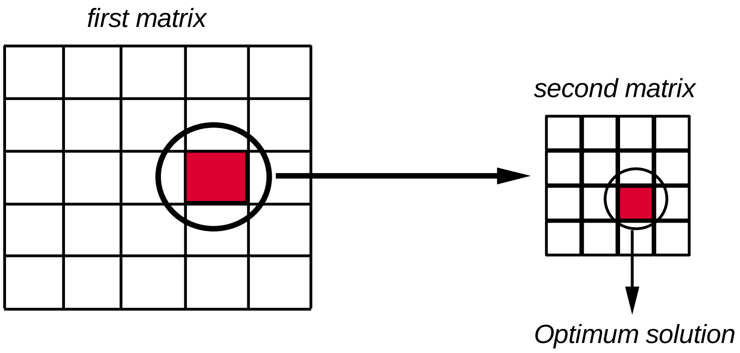
The number of independent variables of the system that have to be optimized are 5 and are the three membrane surface and the feed pressure of the first and second membrane.

The optimization of the system will be done just by calculating the cost of capture that are obtained with different combinations of values of the 5 independent variables. The one that gives the best performance (the minimum price) will be the best solution.
The values that will be used for the calculation of the cost of capture have been chosen in a plausible range to reduce the number of case to calculate.
The range of the feed pressure considered have been chosen taking as example what we obtained with the selective recirculation case and is goes from atmospheric pressure to a maximum of 5 bar.
The range of variation of the membrane surfaces considered has been evaluated in order to have the permeation of a good fraction of the CO_2

flowing into the capture system but not big wnough force the permeation of all the CO_2 that would strongly affect the purity of the carbon dioxide captured.

With an iterative calculation all the possible combinations of the 5 parameters are done, a 5 dimension matrix with the results of all the cases considered is created. Finding the minimum value of the matrix and its position inside the matrix we can then find out which combination of parameters gives the best performances.
To have a better estimation of the optimum point, after this 5 dimension matrix has been calculated and the minimum point found, a second matrix is calculated fixing a more dense range of cases around the optimum solution found in the first matrix. In this way a better accuracy of the solution could be found.

This process is schematically represented in Fig (6.6).



6.6 schematic representation of the optimization process.

6.3 Economic evaluation methodology

6.3.1 Economic methodology

The methodology that has been used for the calculation of the cost of capture is almost identical to the one used with the selective recirculation system that has already been shown in chapter 5. All the assumptions made for the cost estimation remain the same but one is added.
As the capture ratio is not fixed in this simulations we will find the capture unit configuration that operates in the most cost effective way. The amount of CO_2 avoided then could be very different from case to case and no additional penalties have been applied to those configuration that capture a low fraction of the CO_2 initially emitted.

Differently from the selective recirculation capture system we will also take into consideration the possibility to apply a carbon tax on the CO_2 emitted by the power plant.

The reference capture plant that we will consider is characterized by a specific membrane cost of 50 $\$/m^2$ and of selectivity of the membrane equal to 50. The carbon tax in the reference case has been assumed equal to 0 $/ton; this choice has been done in order to be able to compare most of the results we obtained for the EGR capture case with the previous analysis of the selective recirculation one. In fact in that study no carbon tax has been used and, if we would do so in every case considered for the EGR solution, the results could not be compared.

We have to explain why we decided to optimize the capture unit searching for the minimum cost of CO_2 avoided instead of the minimum LCOE. First of all we would be able to calculate only the differential LCOE of the capture system (the increase or reduction of the price of electricity compared with the reference power plant without capture) as we do not exactly know the LCOE of the reference power plant and we do not know its costs. Secondly, as in the reference EGR system analysis no carbon tax is applied, we would not be able to take account in any way in the LCOE of the amount of CO_2 avoided as it is a ratio only between financial quantities. If no monetary value is assigned to the CO_2 avoided or emitted this parameter would be completely ignored. If the capture ratio of the power plant was assigned in the capture unit calculation, it could have been done, because the optimization would have been carried out just among the configuration that avoided the amount of CO_2 chosen; but this is not our case.

Last but not least the analysis of the other configuration considered have been done calculating the cost of avoidance of CO_2, and this allow us to keep the coherence of the results obtained in the two different analysis carried out in this thesis.

When no carbon tax is applied we used the same equation for the cost of CO_2 avoided:

$$Cost\ of\ CO_2\ avoided = \frac{Present\ value\ of\ project\ costs}{Present\ value\ of\ CO_2\ avoided} \quad (6.1)$$

When a carbon tax is applied to the emissions of the power plant with and without capture this eq. (6.1) is changed to the one shown here below:

$$CCA = \frac{PV_{CCS\,project} + \left(PV_{cost\,of\,emission\,CCS} - PV_{cost\,of\,emission\,no\,CCS}\right)}{PV_{CO_2\,avoided}}$$

(6.2)

Being the PV of the emission the product between the ton of CO_2 emitted every year and the carbon tax of the all 25 years of operation, actualized at year 0. The $PV_{cost\,of\,emission\,no\,CCS}$ will always be higher than the CCS case one and, for this reason, the cost of CO_2 avoided will be lower than in the other case. In some cases a negative CCA could be obtained. This happens when the carbon tax is so high that is more economically competitive to invest in a capture system rather than to emit all the CO_2 produced by the power plant.

6.3.2 Cases studied

Now that all the methodology for the simulation of the capture system and its economic evaluation is set we have decided to analyse the impact of different parameters on the optimization of the capture system.

Different characteristics of the membranes and the whole power plant itself can deeply affect the optimum point due to a variation of the different costs.

We decided to limit the analysis to three different parameters that will be:

-Price of the carbon tax.
-Membrane selectivity.
-Specific cost of the membrane.

6.4 Results discussion

6.4.1 Reference case results

For the calculation of the reference case we will make some assumptions of the properties and the cost of the membranes and the value of the carbon tax.

The assumptions that we well use are listed here:

-Membrane selectivity: 50.
-Membrane cost: 50 \$/m^2.
-Carbon tax: 0 S/ton.

As there are no problems of integration between different simulation programmes we did not limit the permeability to Nitrogen and carbon dioxide only but we will extend it to Oxygen, water and Argon too.

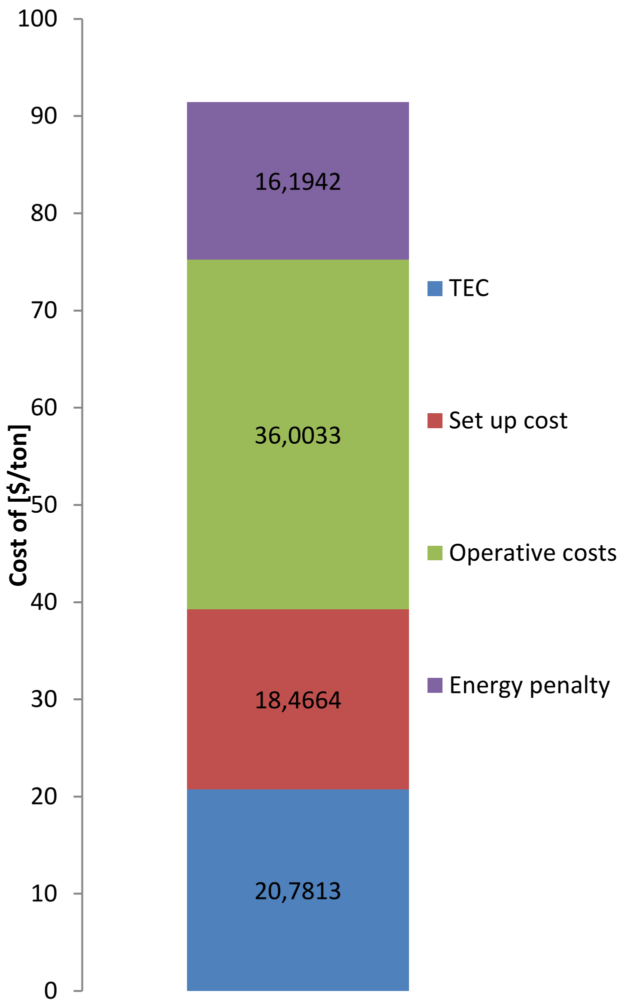
The result obtained with the optimization described earlier and the values of the independent variables that give the best performances are shown in table 6.3.

Table 6.3 Reference EGR capture unit optimization results

	Value	***Unit***
Minimum cost	91.44	[\$/ton]
Capture ratio	64.79	[%]
CO_2 avoided	57.29	[%]
Energy penalty	7.6	[%]
Feed pressure memb.1	104000	[Pa]
Feed pressure memb.2	175000	[Pa]
Memb.1 surface	225000	[m^2]
Memb.2 surface	15000	[m^2]
Memb.3 surface	3000	[m^2]

The minimum cost of capture obtained is of 91.44 $/ton, the global capture ratio of 64.79 % and a purity of the captured CO_2 of 97.26 % is reached.

Feed pressure of the first membrane is atmospheric, while in the second one a slight compression of the feed stream is used. In this system a large first membrane is used to recover CO_2 avoiding to compress all the input mass flux in order to save energy and reduce the total consumption of the capture unit. In this way the second membrane is used to further purify a stream that has already been enriched in CO_2 using a small membrane area.



6.7 Breakdown cost of the reference EGR capture system.

Looking at the breakdown cost of the reference case we can immediately see that how the biggest part of the cost of the capture system is due to the operative costs and not the capital of the equipment. In particular we can see that cost for the equipment (TEC) is just a small share of the total being less than the 23% of the total price of capture.

It could be interesting to additionally split the different components of the cost in order to better understand what is it to drive up the cost of capture.

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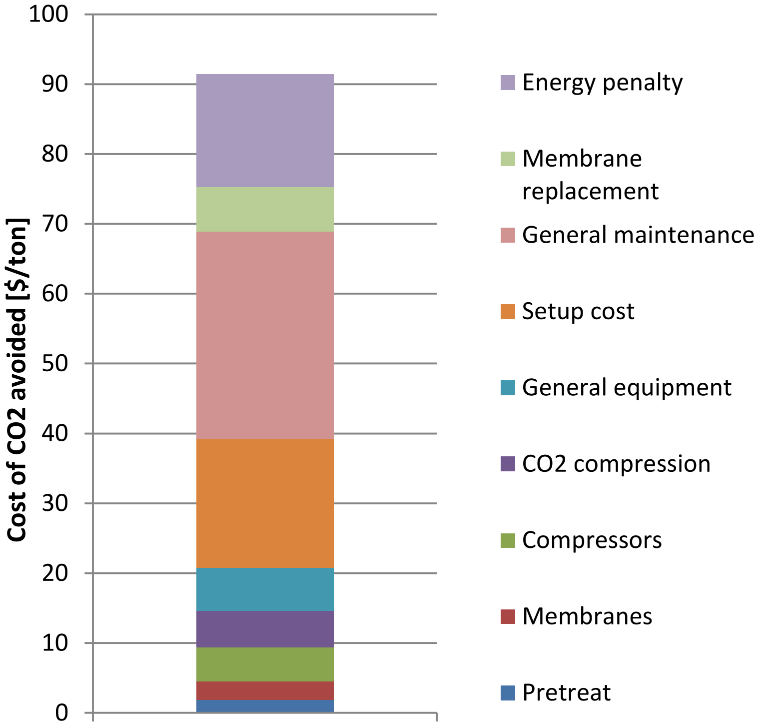


6.8 detailed cost breakdown of the reference EGR capture system.

As can be seen from the graph in fig. 6.8 the three most important parts of the total costs are the setup cost, the general maintenance and the energy penalty cost. General maintenance is set as a fixed percentage per year of the total capex and this is the reason why it is so big being in any case the capex cost equal to almost 40 $/ton.

Particular attention can be given to the fact that the capex cost for the membranes is extreamely low, and it period sobstitution as a consequence. Especially if compared with the selective recirculation case the costs of membrane replacemente are much smaller. This is caused because in thies case we only have membranes for the separation and capture of CO_2, the membrane for the selective recirculation of carbon dioxide does not exists here resulting in a great saving of costs on membranes.

6.4.2 Carbon tax

To evaluate the effect of the carbon tax on the final cost of capture we just repeated the same simulation keeping selectivity and membrane cost equal to the EGR capture reference case and changing the value of the carbon tax.

Three cases have been analysed with a carbon tax of 0, 50 and 100 $/ton of CO_2 emitted to the atmosphere.

The results obtained changing the value of the carbon tax are listed in table 6.4

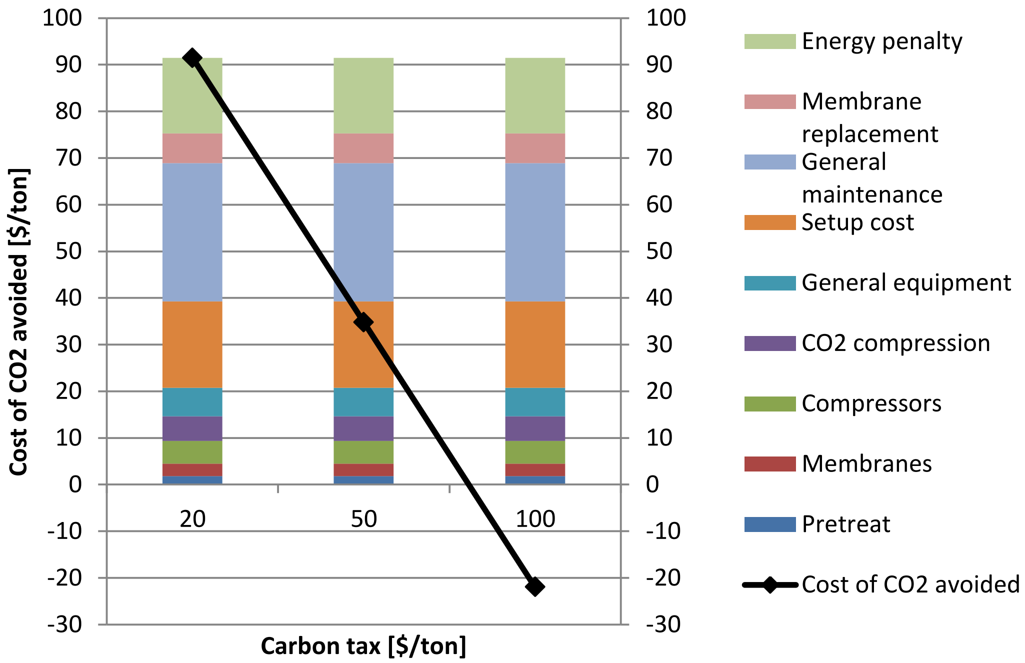
Table 6.4 Carbon tax effect on the cost of capture

Value of the carbon tax	***0***	***50***	***100***	***[$/ton]***
Minimum cost	91.44	34.80	-21,98	[$/ton]
Capture ratio	64.79	64.79	98.31	[%]
CO_2 avoided	57.29	57.29	60.32	[%]
Energy penalty	7.60	7.60	8.09	[%]
Feed pressure memb.1	104000	104000	104000	[Pa]
Feed pressure memb.2	175000	175000	104000	[Pa]
Memb.1 surface	225000	225000	250000	[m^2]
Memb.2 surface	15000	15000	15000	[m^2]
Memb.3 surface	3000	4000	4000	[m^2]

It can be seen that an increase of the carbon tax in general causes a drastic decrease of the cost of the avoidance that goes from 91.44 $/ton to a negative value of -22.56 $/ton

This happen because a carbon tax has the same effect of a discount on the total costs of the capture unit equal to the amount of carbon dioxide avoided multiplied for the value of the carbon tax itself. When the value obtained is a negative one, it means that the electricity generator could actively save money by investing in a capture system rather than emitting all the CO_2 he produces.

The optimum solution obtained are exactly the same. This is obtained because we decided to minimize the CCA instead of the LCOE; so if the technical characteristics of membranes are the same, the configuration of that gives the best performances when carbon tax is not used will also be the one that does it when carbon tax is used.



6.9 Detailed Cost breakdown for the study of the effect of the carbon tax on the total capture cost.

In fig 6.9 it is shown the cost breakdown of the three different cases considered. As the solution found is exactly the same the cost part (the bars) are identical. It is also shown the total CO_2 avoided cost and as and it decrease with the increase of the carbon tax. That results is obtained subtracting from the total costs the amount of money recovered due to the different emission with and without carbon capture thanks to the carbon tax (that is not shown in fig 6.9). Everything that is over the point that shows the CO_2 avoided cost and the top of the costs columns represents that contribute.

6.4.3 Membrane selectivity

To evaluate the effect of the membrane selectivity on the cost of capture we repeated the simulation by changing the properties of the membrane keeping the value of the carbon tax and of the membrane costs constant to the EGR reference case.

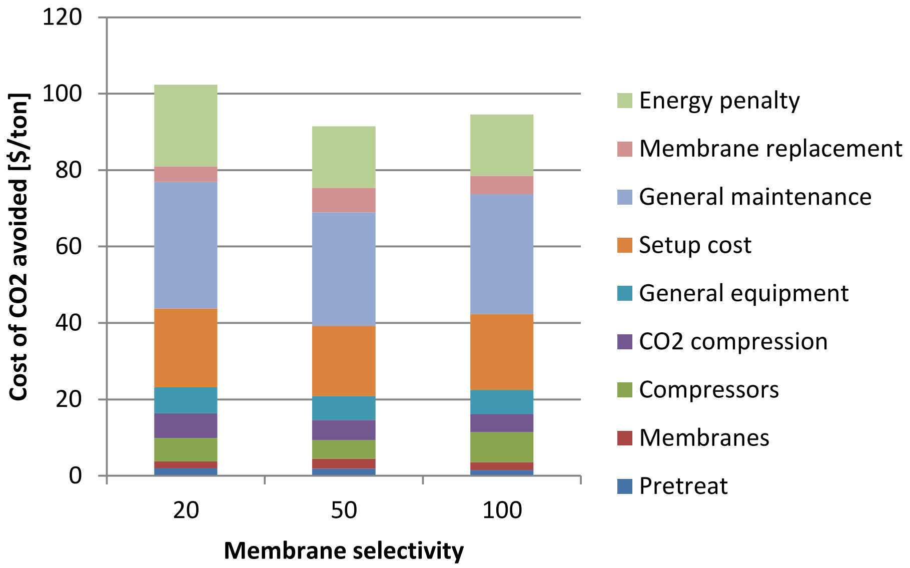
Three value have been evaluated and are respectively: 20, 50, 100.
We decided to modify the selectivity of every chemical species that we have in the gasses treated and to keep the same value for all of them.

The results obtained are listed in table 6.4.

Table 6.4 Selectivity effect on the cost of capture

Value of selectivity	***20***	***50***	***100***	***[-]***
Minimum cost	102.32	91.44	94.33	[$/ton]
Capture ratio	63.34	64.79	79.40	[%]
CO_2 avoided	54.00	57.29	70.17	[%]
Energy penalty	9.45	7.60	9.29	[%]
Feed pressure memb.1	104000	104000	175000	[Pa]
Feed pressure memb.2	150000	175000	104000	[Pa]
Memb.1 surface	125000	225000	175000	[m^2]
Memb.2 surface	15000	15000	45000	[m^2]
Memb.3 surface	10000	3000	2000	[m^2]

From table 6.4 we can see that the effect of membrane selectivity on the optimum solution is quite complex. Both for very low and very high selectivity value the cost of CO_2 avoided increases for different reasons.



6.10 Detailed Cost breakdown for the study of the effect of the membrane selectivity on the total capture cost.

When selectivity is low, smaller compression is required to create an adequate driving force for the process of permeation and the membrane surfaces obtained are smaller. On the other hand the permeated stream in the second membrane will have much more impurities that at the same time increases the size of the CPU needed and the fraction of CO_2 lost in the purification system. This cause a decrease of the total CO_2 avoided to a value of 54 % rather than 57.29 % obtained with a selectivity of 50. This affects the costs causing it to rise.

When selectivity of the membrane is high (100) the cost of capture rises to 94.33 $/ton. This happens because bigger compressors are required for the permeation process (a compressor on the feed side of the first membrane has to treat much more gas than on placed on the feed side of the second one) that causes a much larger money expenditure. In addition the total membrane required in the process is approximately the same even if compression of the flue gas is used. The capture purity of CO_2 treated by the CPU is higher and this is why a smaller third membrane is required, because there is less CO_2 vented by the cryogenic system.

Anyway we can see from table 6.4 that the avoidance rate of the system strongly increases to a value of 70 but this increase (and the consequent redistribution of costs on more ton of CO_2 captured) is not enough to compensate the increase of equipment cost. As can be seen in fig 6.10

6.4.4 Specific cost of the membrane

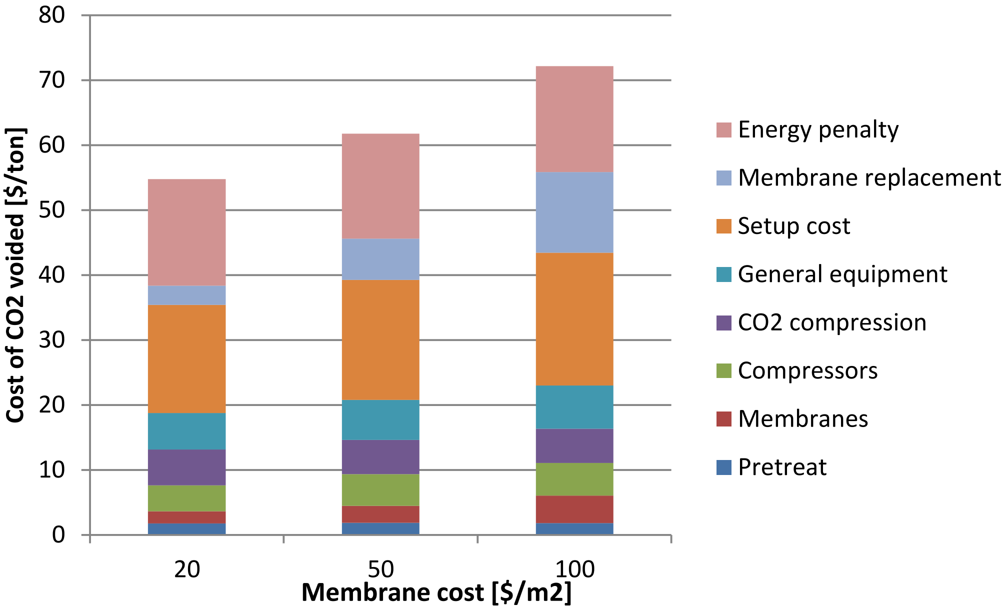
To evaluate the effect of the membrane cost on the final cost of captured we repeated the simulation changing the specific price of the membrane ($/m^2)

The selectivity of the membrane will be kept constant to 50 and the carbon tax to the reference value of 0 $/ton. Three cases have been evaluated; we considered a price of the membrane equal to: 20, 50, 100 $/m^2.

Table 6.5 Membrane cost effect on the cost of capture

Value of selectivity	***20***	***50***	***100***	***[$/m^2]***
Minimum cost	81.58	91.44	104.69	[$/ton]
Capture ratio	68.31	64.79	65.47	[%]
CO_2 avoided	60.32	57.29	57.84	[%]
Energy penalty	8.09	7.60	7.74	[%]
Feed pressure memb.1	104000	104000	104000	[Pa]
Feed pressure memb.2	104000	175000	200000	[Pa]
Memb.1 surface	225000	225000	225000	[m^2]
Memb.2 surface	40000	15000	12500	[m^2]
Memb.3 surface	10000	3000	3000	[m^2]

As we expected the increase of the membrane price results in bigger cost of capture. The optimum point changes in order to try to reduce the surfaces of the membranes of the system. As can be seen from table 6.5 the value of the feed pressure of the second membrane increases and the membranes surface decreases.

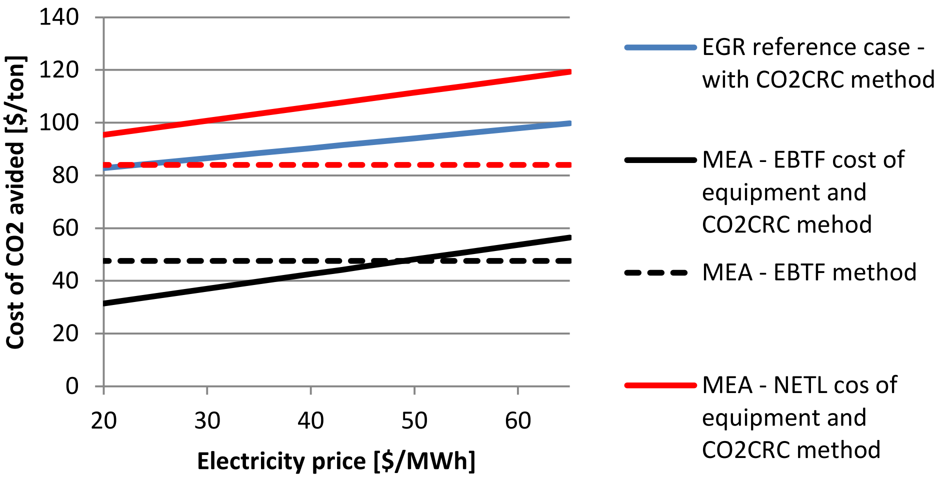


6.11 Detailed Cost breakdown for the study of the effect of the membrane price on the total capture cost.

We can see from fig. 6.11 that the increase of the capture cost is caused mainly by the higher membrane cost that increases both the capital cost (and them the general maintenance) end the cost of replacement of the membrane.

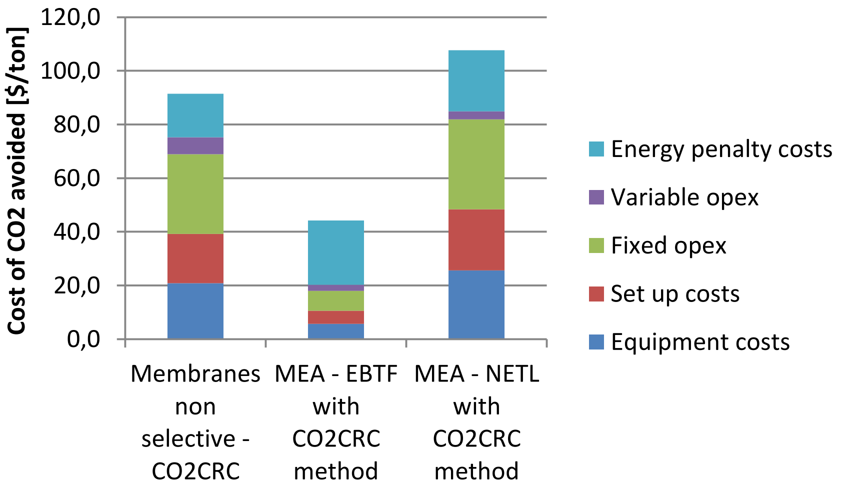
6.3 Comparison with MEA solution.

As it has already been done in paragraph 5.3 we will compare these results obtained for the non-selective recirculation system with the MEA solution studied in the EBT report of 2008 and the NETL report.
We compared the non-selective recirculation solution with the MEA one obtained with the CO2CRC methodology starting from the equipment estimation of the EBTF and NETL report.
The value of cost of CO_2 avoided are represented in figure 6.12 are exactly the same of what found in chapter 5.3 but the EGR case that has been calculated starting from the optimum solution of the reference condition of the EGR case.



6.12 Comparison of CO2CRC results with EBTF and NETL ones for non-selective recirculation solution

As for the selective recirculation case we can see that our solution looks competitive if compared with the NETL MEA case, while it seems to be much more expensive if compared with the EBTF report. This tells us that our configuration could be competitive in the field of CO_2 capture technologies but that still great uncertainties exists on the cost estimation of these systems.
The large difference of cost obtained with the EBTF MEA case is due to smaller cost of the equipment estimation that impacts on the operative cost too reducing drastically the total cost of capture as can be seen in the cost breakdown comparison in fig.6.1



6.13 Cost breakdown of different methodology results.

7 CONCLUSIONS AND FUTURE DEVELOPMENTS

For the selective recirculation system the first objective has been reached using mainly the GS simulation programme. The capture system simulation showed a modest energy penalty when compression of the flue gas is not used of approximately 6% of the net electricity produced by the combined cycle. We found out that a strong enrichment of the CO_2 concentration is possible; a value of approximately 33% molar can be reached reducing the amount of excess air and recycling CO_2 instead. This value have been obtained when the Oxygen concentration in the flue gas produced by the combustor was set to 2,5%, doubling this value the concentration of CO_2 in the flue gas dramatically drops to 23% strongly affecting the purity of the CO_2 captured.

The great change in the composition of the gas flowing in the gas turbine changes the optimum value of the compression ratio that has been found to be 28; a value much higher than the common one used in NGCC.

The effect of the variation of the compression ratio didn’t show to significantly affect the CO_2 concentration reached in the flue gas that stays almost unchanged.

The second objective for the selective recirculation case has been obtained integrating the GS simulation model with a MATLAB code that allowed to simulate the membrane behaviour calculating the membrane area required for the capture process. This data, together to the GS one, has been used following the CO2CRC methodology to estimate the cost of each ton of CO_2 avoided. First of all we calculated the fraction of CO_2 avoided by the capture system that revealed to be 80% of the CO_2 emitted by the reference power plant without CCS applied. The cost of CO_2 avoided was estimated to be equal to 96.53 $/ton. Then the effect of the same technical parameters has been analysed from an economic point of view. First of all we found out that the capture process results to be an operative intense operation, where the costs for the regular membrane substitution account for a large share of the final cost.

We discovered that an increase of value of the compression ratio of the power plant, even if it gives better efficiencies, results in a marked increase of the cost of the CO_2 avoided by the system due to the increase of the mass flow of the gas that has to be treated by the membranes. This means that the starting value of compression ratio of 18 should be kept, implying less modification to the combined cycle. The effect of the Oxygen concentration in the combustor showed to affect mainly the amount of CO_2 avoided by the capture system. In fact with a concentration of 5% of O2 in the combustion products the share of CO_2 avoided drops from 80% to approximately 70%, this results, even if the cost of the CCS unit decreases, in a stable or higher cost of CO_2 avoided.

We also found out evidence that compression of the flue gas should be used as an increase of the pressure of the flue gas just to 2 bar results in a decrease of the total membrane required by the process of 90%, which result in a money saving that far exceed the cost for the larger energy penalty, that reaches the 11% of the electricity produced by the NGCC.

The first and the second objective have been achieved at the same time when the non-selective recirculation system has been studied. After a first analysis of the possible configuration of this capture system we found out that the one that gave the best performances in terms of purity of the CO_2 separated was to connect two separate membrane system in series in order that the second one could purify the permeate stream of the first one, which was in charge to recover all the CO_2 desired by the flue gas.

The GS simulation of this power plant showed that much lower level of CO_2 concentration can be reached with this system. In fact recycling more than half of the flue gas in the turbine we reached a concentration of CO_2 of 8.73% molar.

The two objectives have been reached by the implementation of the CO2CRC methodology in a MATLAB code that, automatically varying the independent variables of the system, (the operative condition of the membranes) estimated the size and consumption of all the main equipment and calculated the resulting cost of CO_2 avoided. A cost of CO_2 avoided similar to what obtained with the selective recirculation has been found. The reference EGR capture system showed a cost of CO_2 avoided equal to 91.44 $/ton but a lower fraction of CO_2 avoided of 57.29 %.

In general we can say that compared with the selective recirculation system lower rates of avoidance are reached and that the process seems to be more energy intense as compression of the flue gas is largely used at least on the feed stream of the second membrane to enhance the driving force of the process to both reduce the membrane area and increase the purity of CO_2 captured. This is caused by the fact that the concentration of CO_2 in the flue gas treated is much smaller than the selective recirculation case.

Both solution (selective and non-selective) achieve a much higher cost of CO_2 avoided than the MEA absorption system studied in EBTF CO_2

capture technology report. The value for the MEA solution obtained is of approximately 48 $/ton, it results a cheaper even if a more energy intense process. Instead if we compare out results with what is obtained starting from the NETL report we see that our two solutions could be both competitive with a MEA capture system. These two opposite conclusions tells us that the technology studied in this work could be competitive to already existing ones but that still great uncertainties exist for the cost estimation of the equipment used in CO_2 capture system.

The integration of a recovery system of the CO_2 vented by the CPU in the selective recirculation capture case is a possible future development of this thesis. In this work, in fact, we assumed to lose all the CO_2 vented in the purification system when one is needed. This CO_2 could be partially recovered with a selective process (like using a third membrane as it has been done in the EGR capture case) or a non-selective recirculation of the CPU vented stream at the input point of the CPU itself, or at the entrance of the whole capture system.

Another upgrade of the current work would to consider not only the cost of the capture system, but also the increase (o decrease) of cost of the power section of the whole plant. The great changing of the composition of the stream flowing in the gas turbine would require a different design of the turbine itself in order to adapt it to the new operative conditions. This would most probably require a money expenditure that has not been considered in this thesis.

A MATLAB modelling of the selective recirculation system, like it has been done for the EGR case, would in addition make possible to analyse the combined effect of the variation of the different technical parameters. In this study their effect has been considered but just one at a time.

For the EGR optimization a possible development could be a better estimation of the energy required for compressions that here has been calculated just correcting, with an assumed value of isentropic efficiency, the result obtained with an isentropic compression.

In addition a more dense matrix of cases could be calculated to obtain a better approximation of the optimum case. Especially for the membrane surfaces as their effect on the permeate purity is very important.

Acronyms

CCS Carbon Capture and Storage
TPES Total Primary Energy Supply
EP Energy Penalty
SE Specific Emission
SPECCA Specific Primary Energy Consumption for Carbon Avoided
HR Heat Rate
CCA Cost per CO_2 Avoided
LCOE Levelized Cost of Electricity
DES Deep Eutectic Solvents
NGCC Natural Gas Combined Cycle
SLM Supported Liquid Membrane
NG Natural Gas
EOR Enhanced Oil Recovery
ASU Ait Separation Unit
USC Ultra Super Critic
IGCC Integrated Gasification Combined Cycle
MEA Monoethanolamine
MCFC Molten Carbon Fuel Cell
IL Ionic Liquids
NDES Natural Deep Eutectic Solvents
HRSG Heat Recovery Steam Generator
LHV Lower Heating Value
SCR Selective Catalytic Reduction
TIT Turbine Inlet Temperature
TBC Thermal barrier coating
CPU Compression and Purification Unit
FGD Flue Gas Desulfurization
FF Fabric Filters
ESP Electrostatic Precipitator
DESSM Deep Eutectic Solvent Supported Membrane
TOT Turbine output temperature
EGR Exhaust gas recycle
CAPEX Capital Expenditure
OPEX Operative Expenditure

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RINGRAZIALMENTI

I più sentiti ringraziamenti alla mia famiglia. A Mamma e Papà per essermi sempre stati di sostegno nei momenti di difficoltà e di sprone nei momenti di scoraggiamento. A Chiara e Matteo, per essere oltre che fratelli, amici impareggiabili.

Un ringraziamento ai mie nonni Felice, Anna, Angela e Mario per avermi mostrato che con l’impegno e il duro lavoro si può arrivare ovunque si voglia.

Grazie a Gloria e Giovanni, la vostra carica ed energia infinita mi contagiano, ogni volta che passo del tempo con voi, un po’ di più.

Un ringraziamento speciale al Professor Romano per l’enorme disponibilità che ha dimostrato nel guidarmi nella stesura di questa tesi e a Davide Turi senza il quale, probabilmente, non avrei mai domato GS.

Thanks to Minh and Prof Dianne Wiley and all the CO2CRC staff for welcoming me with no hesitation, allowing me to spend 5 splendid months in the wonderful Sydney!

Grazie ai miei amici storici per tutti i bei momenti passati insieme e ai miei amici “ingegneri” che hanno alleggerito le lunghe ore di lezione e studio passate al Politecnico.

Un enorme grazie a Vinka per essermi sempre stata vicina anche se lontana e per l’enorme pazienza con cui ha affrontato questi ultimi anni.