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Master's degree in
Mechanical Engineering

Master's Thesis

**Simulation of Methanol production plant
through amine-based CO₂ capture system
and CO₂ hydrogenation**



Advisors:

Prof. Massimo SANTARELLI

Ing. Domenico FERRERO

Candidate:

Patrizio BATTAGLIA

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ABSTRACT

Global warming and climate change concerns have powered global efforts to reduce the concentration of carbon dioxide (CO₂) into the atmosphere. Carbon dioxide capture and utilization (CCU) is considered one of the possible strategies applicable in order to reach CO₂ emission reduction targets.

The aim of this work is to assess via techno-economic and environmental metrics the production of methanol (MeOH) using water (H₂O) and flue gas as raw materials.

Through water electrolysis hydrogen (H₂) is obtained, on the other hand CO₂ is captured through CCU process, using absorption with monoethanolamine (MEA).

The attention has been focused on the CCU process. In particular, it has been modelled taking as reference the pilot plant studied by Notz et al. 2011 in the Institute of

Thermodynamics and Thermal Process Engineering of the University of Stuttgart [1].

The model of CCU process has been validated comparing data obtained from literature with the ones acquired from the model simulation. Subsequently, the model has been scaled up in order to meet the mass flow rate requirement for the CO₂ hydrogenation. For this latter part, a model elaborated by Calogero [2] for a thesis project at the Politecnico di Torino has been used with the proper modifications.

After the definition and the simulation of the complete model, a pinch analysis has been done with the purpose to reduce the amount of thermal external sources needed by the plant in order to satisfy the heat and cold requirements, with the final objective to decrease the amount of electricity demanded. Therefore, a Heat Exchanger Network (HEN) has been proposed.

In conclusion, an economic analysis has been carried out in order to evaluate the Total Investment Cost (TIC) of the plant. In this analysis, it has been considered to use only renewable sources in order to cover the demand of electric power.

The analysis has been conducted with the objective to establish a possible methanol price at which it should be sold in order to cover the TIC over the 25-years considered. Then, assuming a possible future methanol price found in literature, the amount of public incentives that should be received, in terms of Euro for tons of CO₂ avoided has been estimated.

1. INTRODUCTION

Our habits, our economy, the devices and services that we use to support our way of life, require ever greater demand of energy. Since the industrial revolution, and especially into the last five decades, the scientific discoveries have allowed the development of even more technological utilities and infrastructure energy demanding with the purpose to satisfy the living standards required by the industrialized societies. The way in which the energy is produced and is managed determines the political power of a country that, consequently, affects the quality of life of the population.

Considering energy sources globally used to support this techno-economic growth, it is possible to notice the high percentage of use of fossil fuels (i.e. coal, crude oil and natural gas) since the industrial revolution [2]. These raw materials are not renewable, limited and, as a result, responsible of an instable global market.

Nevertheless, the most relevant aspect of using of fuel as a energy source is the increase of the emission of carbon dioxide (CO₂), a major anthropogenic greenhouse gas (GHG) [3]. In the following Figure 1, it is showed the increase of the energy demand from 1800, in terms of TeraWatt-hour (TWh), and the subdivision of the energy sources used in the last two centuries.

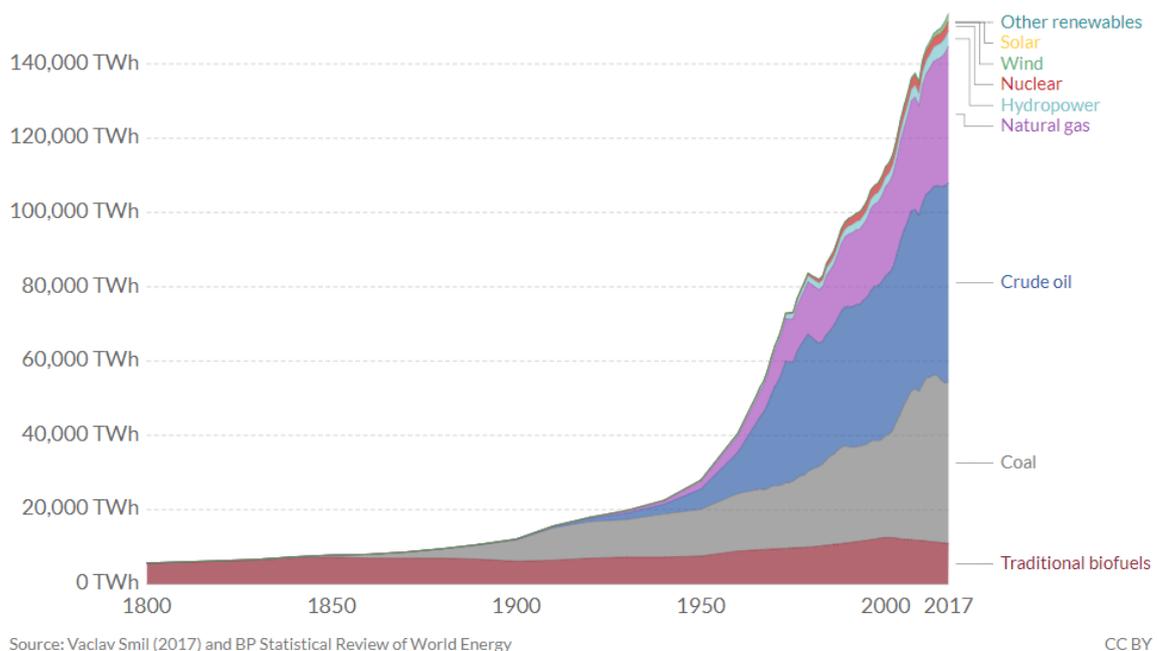


Figure 1. Global energy demand evolution [46]

As it is showed in Figure 1, a rapid increment in global energy demand has been reported especially in the last five decades.

Considering only data of the last two decades, it is possible to appreciate the subdivision of the source of energy and to try to elaborate probable scenarios regarding the energy demand and the energy supplies that can characterize the future of the whole world.

In this work, the data of the International Energy Agency (IEA) have been used as reference, through which it is possible to draw up two scenarios based on the energy policies considered for the future.

In the following Figures 2 and 3, the total primary energy demand of the two considered scenarios is showed, in terms of Million Tonnes of Oil Equivalent (Mtoe), i.e:

- New Policies Scenario (NPS): considers existing energy policies and the assessment of the results that could arise from the implementation of announced policy intentions.
- Sustainable Development Scenario (SDS): it is based on an integrated approach with the purpose to achieve the internationally agreed objectives on climate change, air quality and universal access to modern energy.

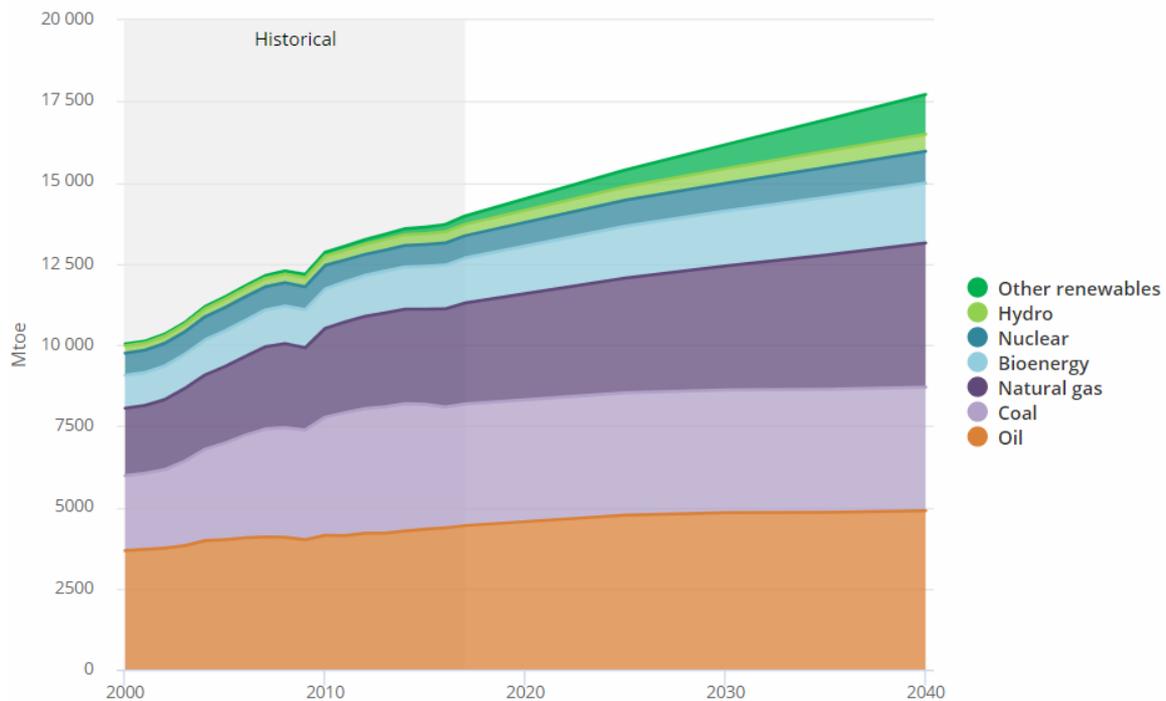


Figure 2. Global Energy Demand Evolution and future perspective based on NPS [5]

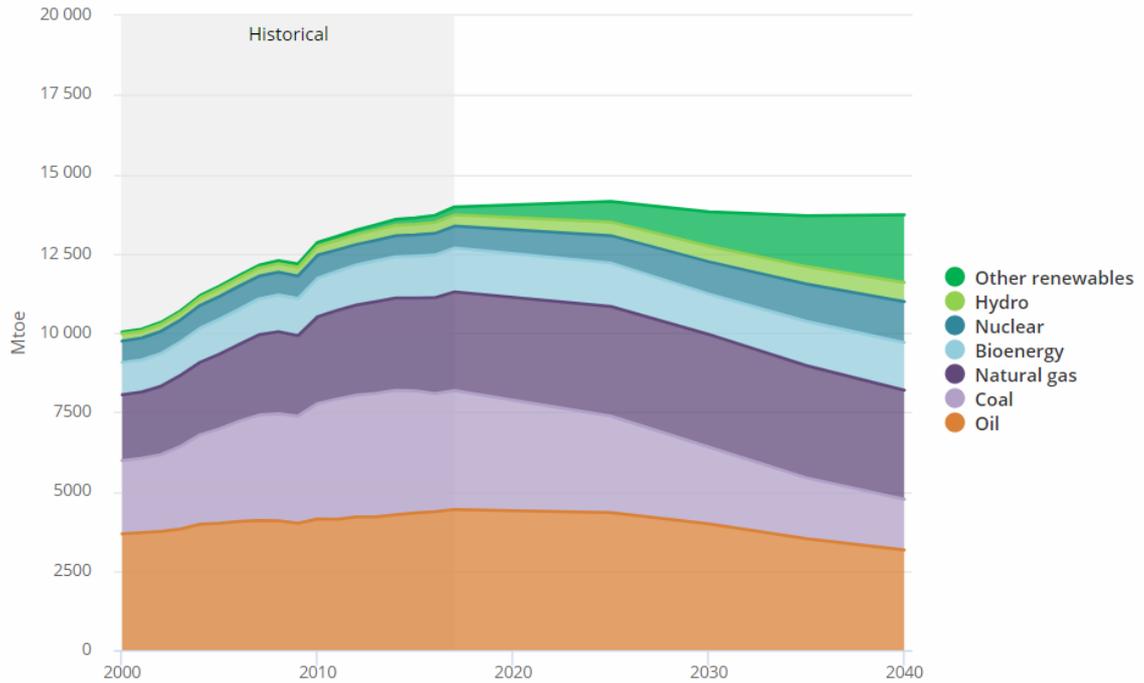


Figure 3. Global Energy Demand Evolution and future perspective based on SDS [5]

Unfortunately, it is worth to underline that, with the actual energy policies, the amount of total energy produced by fossil fuel is expected to increase in the next two decades.

On the other hand, in a sustainable scenario it is desirable that the quantity of total primary energy demand remains constant over the next years, and naturally to have an increase of production of energy from renewable sources.

As obvious consequence of the massive use of fossil fuel as primary source of energy, the amount of CO₂ released into the atmosphere over the years continues to rise, being only the electric power generation based on coal-fired accounted for 30% of global CO₂ emissions [4].

CO₂ is not considered a pollutant but it is one of the most important gases that traps heat in the Earth's atmosphere, called GreenHouse Gas (GHG), and thus contributes to the increase in global temperatures and climate change due to the greenhouse effect.

Regarding the power generation, CO₂ is the principle inevitable product of combustion of fossil fuels, so the ways to reduce its production could be:

- increasing the efficiency of the power production plants;
- switching, partially or totally, to renewable power sources; capturing CO₂ and storing it [3].

The following Figure 4 shows CO₂ and methane emissions recorded in the last decade and the expected ones in the two possible scenarios considered, in terms of Giga-tons carbon dioxide equivalent (Gt CO₂-eq), that is a standard unit for measuring carbon footprints.

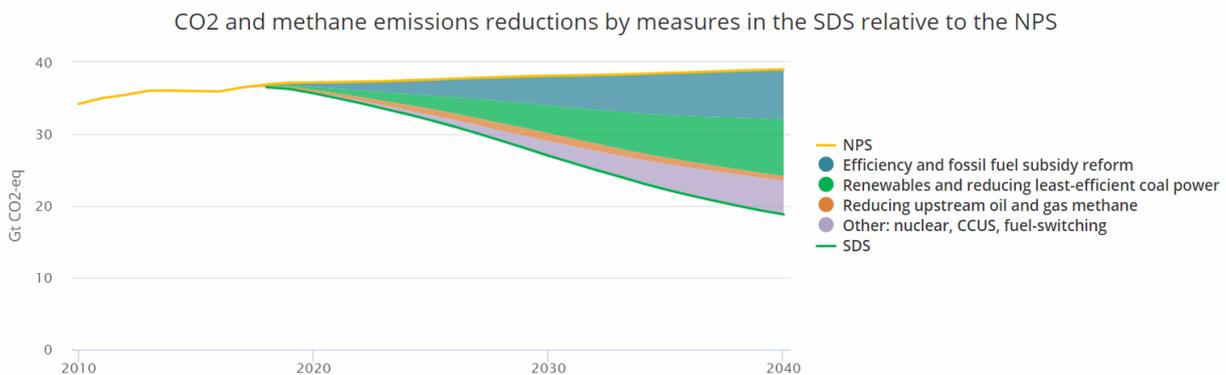


Figure 4. CO₂ and methane emissions reductions by measures in the SDS relative to the NPS. [5]

As anticipated, one of the options in order to reduce CO₂ emissions is represented by the CO₂ capture and storage that is considered one of the most important technologies that can significantly reduce CO₂ emissions from the power generation sector [5].

Of course, there is not a unique solution for the global warming problem, but the approach of the chemical recycling of carbon dioxide to produce carbon neutral renewable fuels and materials can offer a feasible and powerful new alternative and is entering the stage of gradual practical implementation [6].

This type of process is conventionally divided into: Carbon Capture Storage (CCS), which consists into CO₂ capture from flue gas produced by the power production plant, transport to a storage and long-term isolation, for example, in geological formations; Carbon Capture Utilization (CCU), if the CO₂ is involved in other process rather than be stored.

Furthermore, CCU is interesting by policy makers as an alternative to motivate local economies, to manage CO₂ after capture and to decrease CO₂ emissions. Due to these reasons, CCU applications may have different motivating drivers [7].

Another possibility is an integration of CCS and CCU, called as CCUS, which might be able to take advantages of both approaches, as enhancing both environmental and economic incentive [3].

There are three principle way to capture CO₂ into the power production plant: post-combustion capture, pre-combustion capture and oxyfuel process. These processes will be explained more in detail in the next sections.

Among them, post-combustion capture is the most interesting technology because offers the advantage to be easily integrated into the existing plant without radical changes on them.

Post-combustion CO₂ capture typically includes absorption with chemical or physical solvents, membrane mechanical separations, and adsorption using solid sorbents.

Concerning the chemical absorption process, the solvents used are mainly amine solutions, as monoethanolamine (MEA), activated methyl diethanolamine (aMDEA) or hot potassium carbonate solutions. Between them, the MEA is the most mature technology for CO₂ capture in post-combustion processes, even though it requires high regeneration energy [8].

For the reasons explained above, in this work the attention has been focused on the post-Combustion capture process with the use of MEA as solvent (0.3 g/g monoethanolamine in water) [9]. Taking in consideration a pilot plant found in literature, the process will be described in detail. This requires rigorous modelling and simulation of the CO₂ capture process and fundamental understanding of the complex phenomena taking place in the process, therefore it is modelled and simulated in AspenPlusTM and the reached results will be discussed in the Results section of this thesis [2].

With the purpose to limit the amount of CO₂ released into the atmosphere and to utilize the captured CO₂, the latter one will be mixed with H₂, produced by electrolysis, and then the mixture will be hydrogenated in a reactor resulting in the formation of Methanol (CH₃OH), commonly denominated as MeOH.

The first idea of Methanol Economy is presented by Olah in 2009 [6], in which it is assumed to produce methanol by hydrogenation of industrial CO₂. In this context, the necessary energy input is assumed to be provided by renewable energy and not from fossil fuel, resulting in this way in a decrease of CO₂ released.

As it has been anticipated, in order to produce methanol by CO₂ hydrogenation, it is fundamental to have at disposal the necessary H₂ or to include its production in the process. It is worth to underline that regarding its energy property, the use of hydrogen appears very promising. In fact it shows the highest energy content per unit of weight (142 kJ/g) over any other fuel and, furthermore, it is environmentally safe [3]. The limitations that the wide

development of hydrogen as a new energy carrier could meet are related to its purification costs and to the difficulties linked to the infrastructure for its storage and transportation.

On the other hand, methanol is easily stored and transported and can be used as a convenient hydrogen carrier. In the following Table 1 are reported the main methanol's physical properties.

Methanol's physical properties	
Molecular Weight [g/mol]	32,04
Critical Temperature [°C]	239
Critical Pressure [atm]	78,5
Freezing Point (at 1 atm) [°C]	-97,6
Boiling Point (at 1 atm) [°C]	64,6
Latent Heat of Vaporization (at 25 °C) [kJ/mol]	37,43
Vapour Pressure (at 25 °C) [atm]	0,1674
Lower Heating Value (at 25 °C and 1 atm) [kJ/mol]	638,1
Higher Heating Value (at 25°C and 1 atm) [kJ/mol]	726,1
Auto Ignition Temperature [°C]	470

Table 1. Methanol's physical properties

Methanol can be involved in various applications, mainly used as raw material or as energy source. A methanol economy is advisable also considering the increment of methanol demand in the world, as reported in the graph below [3].

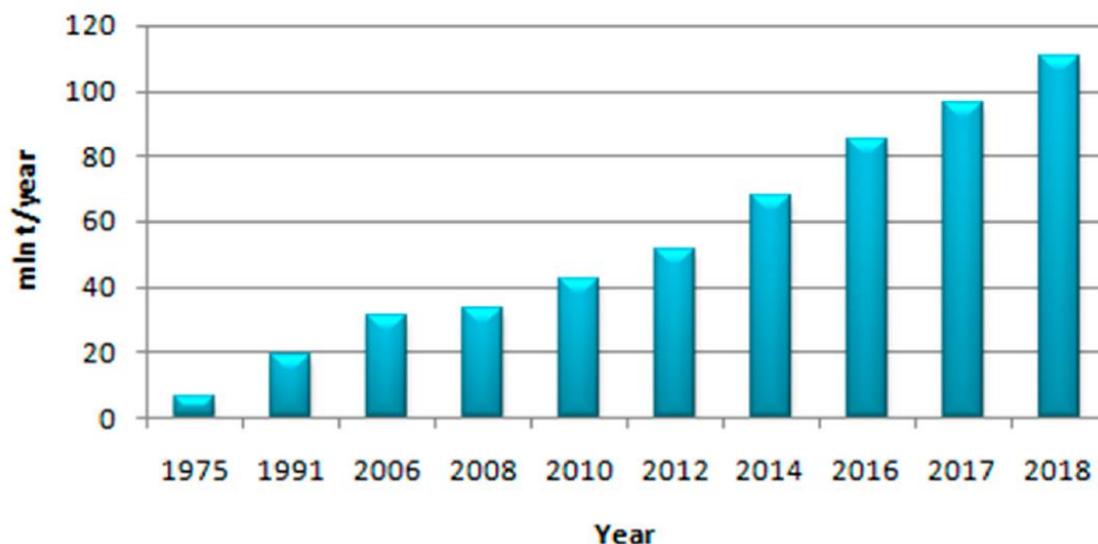


Figure 5. Methanol demand evolution [3]

As raw material, methanol is currently considered one of the most useful chemical products and it is a building block for obtaining more complex chemical compounds. In fact, from MeOH, it is possible to obtain for example: acetic acid, methyl tertiary butyl ether (MTBE), formaldehyde (which uses are various, common applications are into the wood industry as adhesives, disinfectant/biocide and photographic industries), Methanol to Olefins (MTO) and methanol to propylene (MTP).

As energy sources, it can be used both for stationary power generation and mobility. There are essentially two ways of utilization regarding the energetic purpose, the electrochemical conversion, by exploiting the property of the MeOH which oxidation is obtained through electrochemical way, by means of the so-called Direct Methanol Fuel Cell; and the combustion, in the field of power generation or vehicle transportation, using the pure methanol as fuel or using methanol/gasoline mixture.

In fact, in vehicles, the methanol can be mixed with conventional petrol, without requiring any technical modification to the vehicle fleet.

In the following Figure 6, the different methanol utilizations with the correspond percentage in the whole world are showed.

Methanol Applications

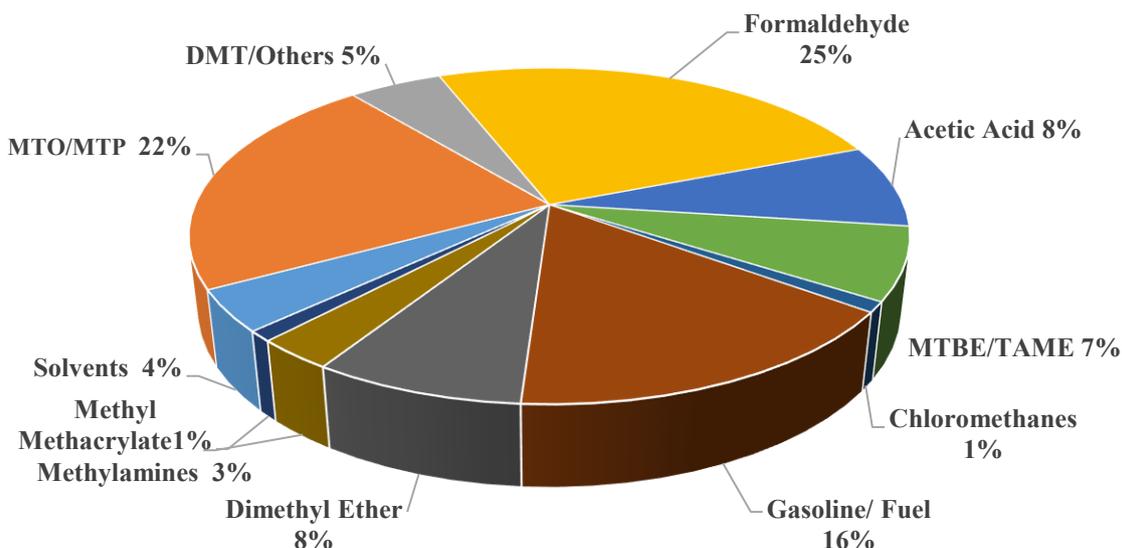


Figure 6. Methanol Application [3]

The aim of this work is to assess via techno-economic and environmental metrics the production of methanol (MeOH) using H₂O and flue gas as raw materials, from which H₂ through electrolysis and CO₂ through CCU process are derived, respectively.

In this study, the attention has been focused especially on the carbon capture and utilisation (CCU) plant that has been modelled and simulated starting only from the data found in literature.

Therefore, the complete process has been elaborated, from the flue-gas rich of CO₂ outgoing by the coal-fired power plant and the H₂ produced through electrolysis of water to the obtained MeOH as final product.

In the last section are presented the consideration on the potential of this type CCU plant focusing on the net reduction of CO₂ emissions and the cost of production of methanol.

2. PROCESS DESCRIPTION

The process that will be simulated in this work is devoted to methanol production through the amine-based capture of CO₂ and the CO₂ hydrogenation.

The process is based on the usage of flue-gas outgoing from a coal-fired power plant production. The CO₂ present in the flue-gas is captured by a chemical absorber system based on the use of a solvent that in this case is monoethanolamine (MEA) which it is considered the most mature technology currently available into the market. After the capture, the carbon dioxide is mixed with hydrogen that it is obtained by electrolysis from water; then the mixture becomes the feed flow rate that is sent into the reactor in which the CO₂ hydrogenation is performed. The process is energy intensive because high quantity of energy is required in order to perform the electrolysis and to permit the amine to release the CO₂ captured from flue gas in the regeneration process [10].

The final products of the process will be oxygen, produced during the electrolysis, and methanol, the goal of the project.

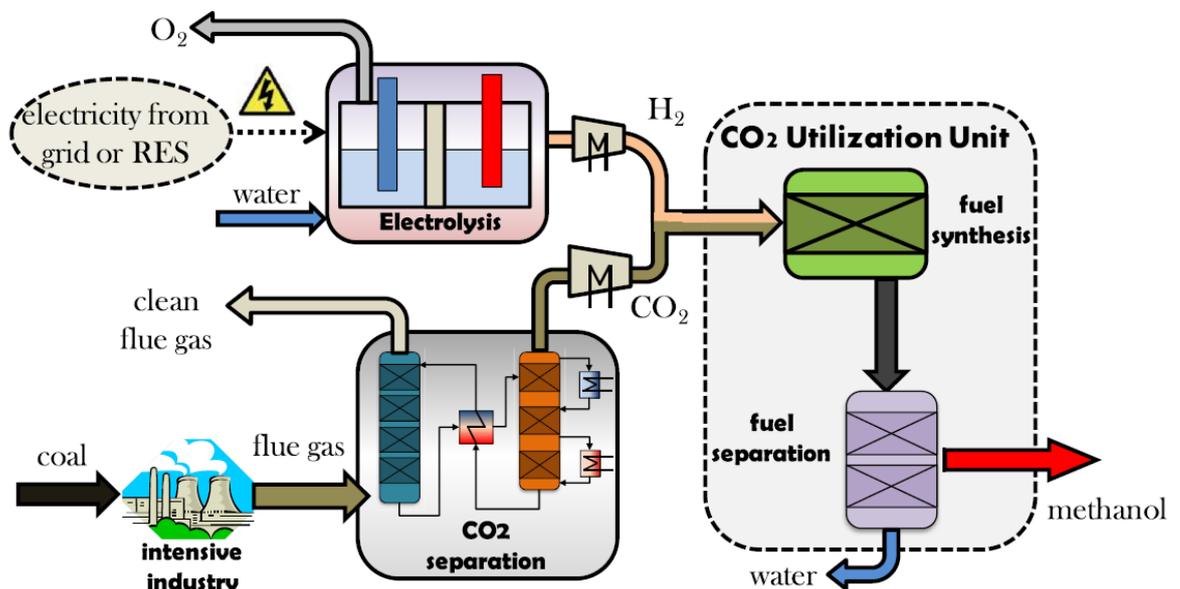


Figure 7. CCU and Methanol Production scheme

As it is possible to see in the Figure 7 above, the process can be divided in three different main sections: CO₂ Capture System, H₂ production, Methanol production.

These three parts will be described in details in the following sections

2.1 CO₂ CAPTURE SYSTEM

Among the options reported on CO₂ capture processes, in this work the attention has been focused on the Post-Combustion Capture (PCC) process with the use of MEA as solvent (0.3 g/g monoethanolamine in water) [9].

Depending on the use of CO₂ captured, CO₂ capture system can be part of Carbon Capture Storage (CCS) or Capture Carbon Utilization (CCU) scheme with the common purpose to prevent to release carbon dioxide into the atmosphere.

In the first case, CCS, the carbon dioxide is transferred to a proper site in which it is stored for long-term, in the second case instead, CCU one, CO₂ is processed and it is utilized for other purposes, and in particular it can be converted in commercial products. In this study, the production of methanol has been considered.

Power plants, oil refineries, biogas sweetening as well as production of ammonia, ethylene oxide, cement and iron and steel are the main industrial sources of CO₂ [11].

Considering that over 40% of the worldwide CO₂ emissions is produced by electricity generation in fossil-fuel power plants, it is easy to understand that the power plants are the main candidates for a potential application of CCS or CCU [12].

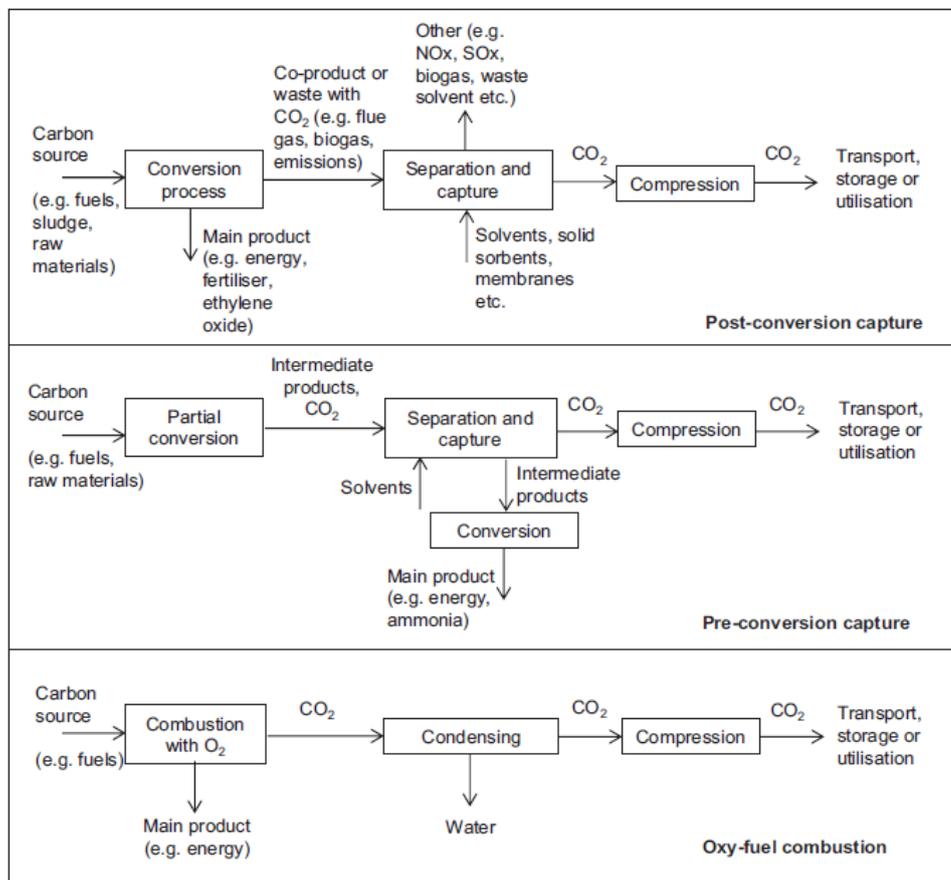


Figure 8. Carbon capture options [10]

On the other side, the high number of application fields involves a high number of possible solutions that could be suitable in each considered case.

As it is possible to note in the Figure 8 above, the first classification that could be done consists in the division into three main approaches to capturing CO₂, namely oxy-fuel combustion, pre-combustion and post-combustion, depending on where the CO₂ is removed.

Oxy-fuel combustion utilizes pure oxygen ($\geq 95\%$ [13]) instead of air to increase the CO₂ concentration in the flue gases and this reduces the amount of N₂ present in the exhaust gas, thus reducing the effects in the subsequent separation processes. The process is technologically feasible but the major disadvantages is the large amount of oxygen consumption which results in high cost that makes it uneconomical, and in high energy consumption, leading to more than 7% energy penalty compared with a plant without carbon capture and storage (CCS) technology [2].

Pre-combustion capture is mainly applied to coal-gasification plant, in this process the fuel is pre-treated before combustion. For coal, the process involves a gasification by means of a gasifier in which at low oxygen level a syngas rich in CO and H₂ is produced, which then undergoes water-shift reaction to produce CO₂. From an economical point of view, this alternative requires a lower capital investment, also because there is the possibility to retrofit to existing plant [2].

Post-conversion capture involves separation of CO₂ from waste gas streams after the conversion of the carbon source to CO₂. It is designed to be placed after traditional cleaning systems. In fact, under this scenario, it is possible to reduce significantly contaminants in the exhaust gas such as SO_x, NO_x, and particulate matters before CO₂ capture process [14]. When it is used in power plants, post-conversion capture is also called Post-Combustion Capture (PCC) [11].

Post-combustion technology is the most attractive among the three technologies and it is currently the most mature process for CO₂ capture [2]. This could be explained considering its high degree of purity for CO₂, captured and the advantage that it could be easily retrofitted to existing power plants and it has been extensively studied with several operational pilot or demonstrational and commercial plants.

The disadvantage of this technique is that the low CO₂ concentration can affect the capture efficiency [2] [13].

Regarding to the post-combustion, there are different methods that could be implemented: absorption, adsorption, micro-algal biofixation, membrane and cryogenic.

Among all these post-combustion technologies mentioned above, chemical absorption is considered so far the most suitable one and most probable to be implemented in the near future, mainly due to its high absorption capacity at low CO₂ partial pressure and relatively high selectivity towards CO₂. Among the different solvents that have been tested in these last years, the monoethanolamine (MEA) one, with the molecular of (C₂H₄OH)NH₂ is the most widespread solvent.

For these reasons, the CO₂ capture system selected in this work is the chemical one based on use of MEA as solvent.

A simple example of conventional flowsheet for amine-based CO₂ capture is proposed below.

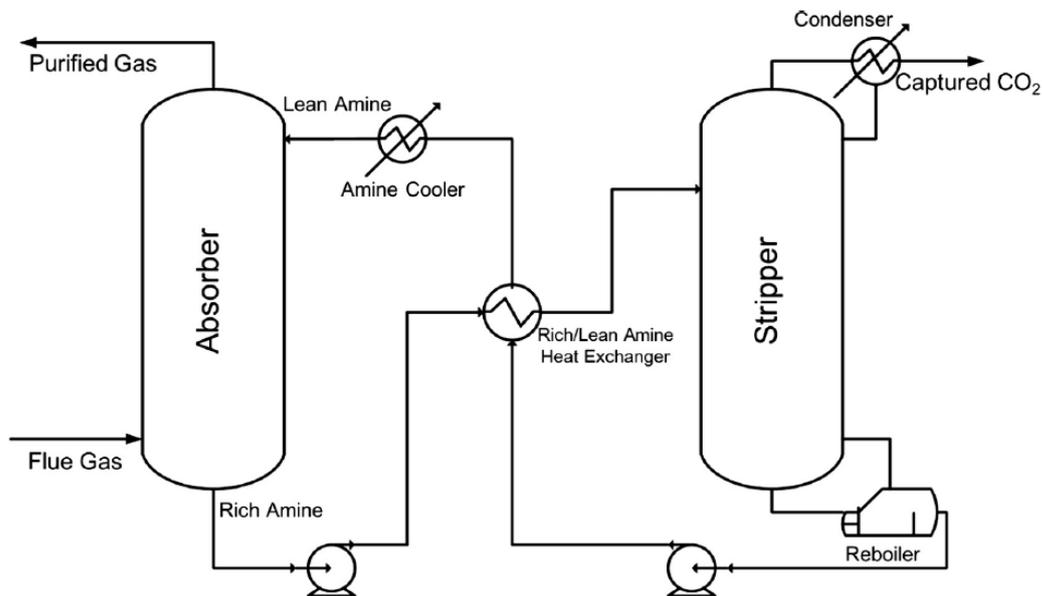


Figure 9. Example of conventional flowsheet for amine-based CO₂ capture [16]

The conventional equipment configuration for a CO₂ absorption process using amine solvents are an absorber, heat exchangers and pumps in order to guarantee the right

thermodynamic conditions of the fluid in the process, a stripper with a condenser and a reboiler. The process can be divided into two parts: the first one consists in the absorption of CO₂ in the absorber; the second one regards the desorption of CO₂ in the stripper in which the amine solvent is regenerated using the heat supplied to the reboiler.

The capture process is energy intensive and the reduction of heat energy required for solvent regeneration [16].

In fact, as part of CCS capture system, the chemical absorption has been studied in the last years in pilot plant and also in demonstration power plant, as for example in the first and largest commercial-CCS project in Boundary Dam [14], in order to improve the knowledge about the process. From all these studies appears that the major drawback of this technology is the elevated energy required for the regeneration of the solvents.

2.2 H₂ PRODUCTION

In the last years, with the growing of renewable energy, the role of the hydrogen has become even more important and it could be a green way to store the excess energy generated because, considering for example a wind plant, during windy periods, the electricity grid cannot absorb all the energy generated by wind turbines [15].

Hydrogen can be burnt with the production of only water as waste product and this makes it an environmental friendly energy storage medium. In alternative H₂ can be used to produce methanol, in case of this work, that it could be used as fuel and could be a type of storage of the hydrogen.

There are several technologies available for hydrogen production, including reforming, decomposition, hydrolysis of fossil fuels, and electrolysis which is the one chosen in this work. One of the advantages of hydrogen as an energy carrier are not only its high energy density, but also that hydrogen and electricity can be interconverted through water electrolysis.

Nowadays, approximately 95% of hydrogen production derived from fossil fuel, which also produces CO₂ so it cannot be considered as renewable source of hydrogen.

On the contrary, if hydrogen is produced through the water electrolysis powered by renewable energy source zero CO₂ emissions are produced and a product with high purity (99.9%) can be reached. Wind energy is the most promising way to produce hydrogen with a relative low cost and with a production of zero CO₂ emissions, which can produce cheap hydrogen [15] [16].

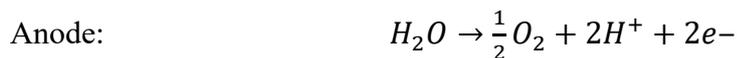
However, the coupling of the electrolyzers with renewable energy it is not an easy task to manage, and there are different aspects that can be improved in order to make it easier, as the control system in order to permits it to operate under variable energy supply, the reduction of cost of manufacturing, installation and distribution.

2.2.1 ELECTROLYSIS OF WATER

In the electrolysis, the water is the reactant and it is dissociated in hydrogen and oxygen under the passage of the direct current. The current flows between two electrodes which are separated and immersed in an electrolyte in order to raise the ionic conductivity.

As it is possible to see through the reactions reported below, Oxygen (O₂) and Hydrogen (H₂) are produced at the anode and cathode respectively.

The electrolysis reactions taking place are:



The elements that configure an electrolytic cell are the electrodes, the electrolyte and also the diaphragm in the case of alkaline electrolyzers.

Concerning the stability of the cell, it is important that the electrodes, which usually are made of different types of steel, are able to resist to corrosion, to guarantee a good electric conductivity and catalytic properties and also to guarantee a structural stability [17].

The electrolyte works not only as vector for transporting ionic charges to promote the decomposition of water into hydrogen and oxygen but also it has to prevent to prevent any interaction between the electrodes without react with them, preventing the effects on cell's integrity that this interaction would produce.

Depending on the materials of the elements used in the electrolytic cell, more than one technology have been studied and developed in the years. Their main characteristics are reported in Figure 10.

	Alkaline	PEM	Solid Oxide
Electrolyte	Liquid alkaline KOH	Solid acid polymer	Ceramic metal compound
Electrodes	Ni/Fe electrodes (Raney)	Noble metals (Pt, Ir)	Ni doped ceramic
Temperature	40-90°C	20-100°C	700-1000°C
Pressure	<30 bar	<200 bar	Atm.
Module size (commercial)	Max. 760 Nm ³ H ₂ /h, ~3,2 MW _{el}	Max. 30 Nm ³ H ₂ /h, ~170 kW _{el}	~1 Nm ³ H ₂ /h, kW range
Charge carrier	OH ⁻	H ⁺	O ²⁻
Anodic reaction	2OH ⁻ → 1/2O ₂ +H ₂ O+2e ⁻	H ₂ O → 1/2O ₂ +2H ⁺ +2e ⁻	O ²⁻ → 1/2O ₂ +2e ⁻
Cathodic reaction	2H ₂ O+2e ⁻ → H ₂ +2OH ⁻	2H ⁺ +2e ⁻ → H ₂	H ₂ O+2e ⁻ → H ₂ +O ²⁻

Figure 10. Main electrolyzers' characteristics [20].

The main difference between the electrolytic cells relates on their working conditions. Especially, their working temperature range permits to classify them in low-temperature electrolyzers, that can be used in fuelling stations, and high-temperature ones, characterized by an high electrical efficiency and more suitable for use at solar thermal facilities.

At present, from a technological point of view, the advanced alkaline electrolyzers, that are low-temperature electrolyzers, are sufficiently developed as to begin the production of renewable hydrogen at significant rates. However, it is generally agreed that in case of explosion of hydrogen economy, there will be a massive hydrogen production required, and in order to support the economy, there is the necessity to develop electrolysis units with production capacities much higher than the ones existing now. [19]

Another low-temperature electrolyzer is the Polymer electrolyte membrane (PEM) one, it is commercially available but its high cost is a limiting parameter. This technology seems more suitable for low-scale applications.

On the other hand, as high-temperature electrolyzer, the solid oxide electrolyzers (SOEs) for hydrogen production from steam are in a research and development stage. They seem to have great potential because the use of high-temperature heat reduces their electricity usage.

Among the different types of electrolytic cell, the alkaline one is chosen, because it represents a very mature technology that is current standard for large-scale electrolysis as reported in numerous works available in literature [17] [18] [15] [19].

2.2.2 ALKALINE CELL

As described before, Alkaline water electrolysis operates at low temperature (60–80 °C), with KOH and/or NaOH aqueous solution as the electrolyte.

The cell consists of two electrodes separated by a gas-tight diaphragm. In the cathode, there is the formation of hydrogen, while hydroxide anions go through the diaphragm and recombine at the anode producing water, oxygen, and releasing electrons that go to the electric circuit, as it is possible to see in Figure 11.

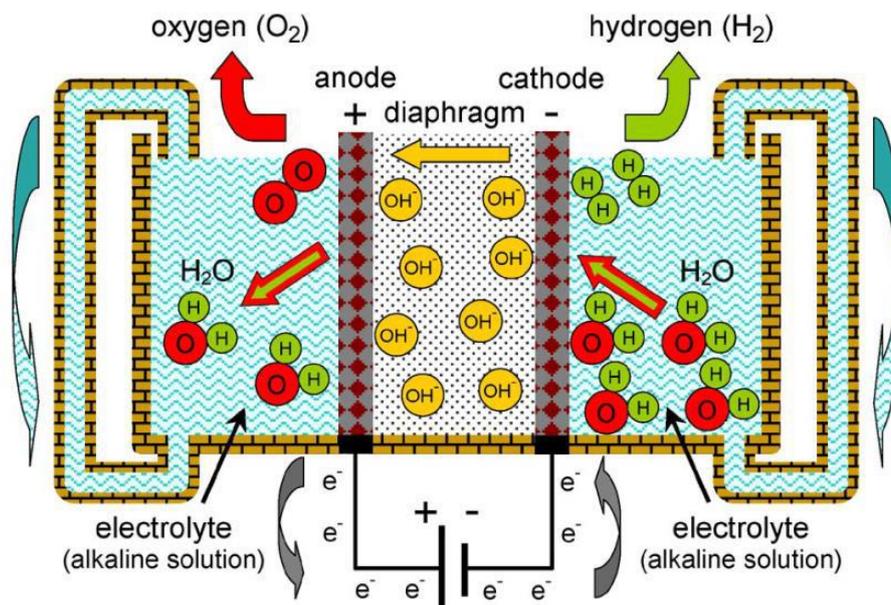


Figure 11. Scheme of an alkaline electrolyser [19]

Regarding the maximum operating current density, for an alkaline electrolyzer is less than $400 \frac{mA}{cm^2}$, and the power consumption is approximately $4.5-5.5 \frac{kWh}{Nm^3}$ with an efficiency of roughly 60% [19].

If the operating current density reach too high values, the cell could work in operating condition that could damage the structure itself. On the contrary, if it is too low, there could be the formation of a flammable mixture.

So, in order to prevent these types of damage, the production range usually in restricted to 25-100% of the nominal range [17].

Furthermore, the pressure between the anode and cathode sides must be balanced in order to avoid hydrogen/oxygen penetration through porous asbestos diaphragm resulting in an explosion risk.

In this type of cell, the electrolysis cells are connected in series, and hydrogen is produced on one side of the cell, oxygen on the other. An high level of purity can be reached in this type of cell, 99,9% vol. for hydrogen and 99,7 vol. without auxiliary purification equipment [15] [20].

2.3 METHANOL PRODUCTION

Methanol is currently considered one of the most useful chemical products in the world, and, as it has been discussed in the introduction of the thesis, it represents a valid alternative to the fossil fuel in order to reduce the Greenhouse Gas Emissions.

Methanol (CH_3OH is an alcohol (organic compound) with a boiling temperature of 64.6 °C, soluble in water, and with a melting temperature of -98 °C.

The most important properties that has to be kept in mind during its synthesis are the flammability limits in air ($6.7 - 36.5$ % v/v) and its toxicity

Methanol is producible from a number of technologies that have been developed over the years, including several feedstocks, such as natural gas, coal, biomass and CO_2 . The latter could be directly recoverable from the atmosphere [3].

In this work, as mentioned before, will be analysed the case in which the CO₂ is captured through a CCU system and the hydrogen is produced through the electrolysis of water with the further benefit of significantly reducing CO₂ emissions into the atmosphere.

The process flow diagram of a typical methanol synthesis unit from CO₂ is shown in Figure 12. The unit consists of the methanol synthesis, gas separation and product purification.

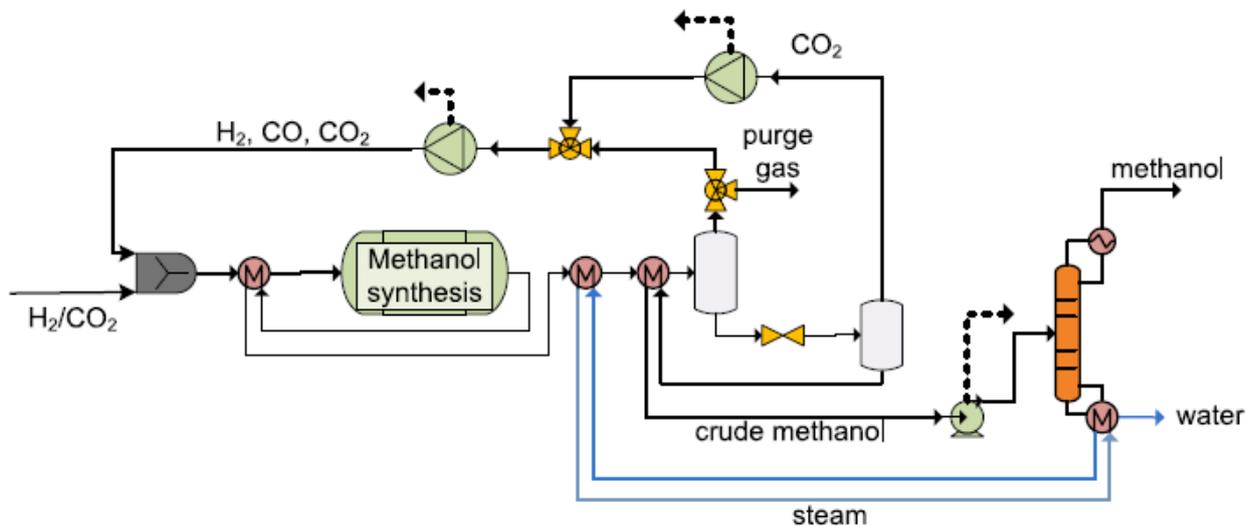
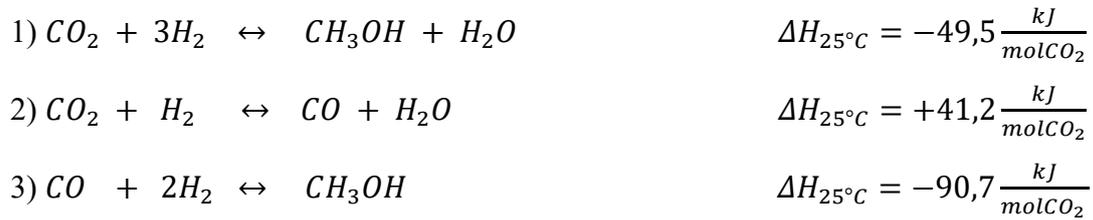


Figure 12. Example of model of Methanol production [21]

The MeOH synthesis process can be divided into three different stages. In the first process stage, the feed gases are compressed up to the reactor feed pressure, with the use of several compression stages with intercooling. In the second one, the pressurised feed is heated up and fed to the reactor. In the third one, MeOH is separated from water in a distillation column.

As regard the second stage of the process, it is the main part of the methanol production. The feed gas enter in the reactor at the pressure and temperature predefined that will be discussed later.

In the reactor, the methanol is formed through CO₂ hydrogenation under the following three-phase reactions:



The reaction 1) represents the direct CO₂ hydrogenation: considering a feeding mole flow rate composing by 3 moles of hydrogen per each mole of carbon dioxide, there will be the formation of 1 mole of methanol and 1 mole of water. This reaction is exothermic with a decrease in the number of moles from the reactants to the products; therefore, from the definition of Gibbs free energy and the Le Chatelier – Braun Law, it can be deduced that methanol production is favoured at low temperature and high pressure.

However, a part of the carbon dioxide and of the hydrogen not takes part at the first reaction and undergoes reaction 2), called RWGS, which converts one mole of H₂ and one mole of CO₂ in one mole of H₂O and one of CO and it is endothermic.

At this point, the generated carbon monoxide undergoes a hydrogenation (reaction 3), which leads to the formation of methanol. This reaction is exothermic with a reduction in moles from the reactants to the products; therefore, also this reaction is favoured at low temperature and high pressure.

In conclusion, the CO₂ hydrogenation (both the direct one and the indirect one) is globally an exothermic phenomenon.

Before entering the distillation column, which is operated at ambient pressure, the process stream that comes from the reaction section is depressurised.

In order to promote the reaction, in the reactor there is the needed of a catalyst. In fact, the carbon dioxide molecule is very stable and its reactivity, and consequently its conversion, could be enhanced acting on the thermodynamic conditions, but as reported before, the process is globally exothermic and not tolerate high temperature. Therefore, the use of catalyst is crucial in order to guarantee the development of the reactions.

The principal methods of optimization of the considered process are:

- the regulation of the thermodynamic (temperature and pressure)
- the regulation of the kinetic (space velocity) conditions,
- the use of a catalyst
- the separation of reactants and products.

The state of art consists of a process carried out at a temperature of 250 - 300 °C and a pressure of 5 – 10 MPa with the aid of a Cu-based catalyst [21] [22] [23].

3. MODEL DESCRIPTION

The main purpose of the model is to simulate the operational condition of a methanol plant production, composed by the CO₂ amine-based capture system, the electrolysis section and the CO₂ hydrogenation section in order to describe the plant through the energy consumption for kg/h of CO₂ captured, the methanol production (kg/h), and efficiency (%).

Regarding the CO₂ capture system, a pilot plant model has been chosen and has been taken as reference in order to build a model that respects the experimental values obtained in the experiments made by the reference work found in literature. Then, it has been modified and scaled-up in order to reach the value of CO₂ captured required into the other parts of the plant.

Concerning the second and third section of the plant, a reference model built and studied by Calogero [21] has been used and adapted with the objects to simulate the overall process and to continue the investigation on methanol production with the use of CCS system.

Each section has been simulated by using the software Aspen Plus™.

In the simulation of a real process as the one investigated in this work, there are a considerable number of different sections and subsections, both real and fictitious. These sections are connected by material, thermal and energy flows that enhance the number of variables of the system, making the results impossible to find in a single solution.

In these cases, it is necessary to use an iterative procedure in order to determine the operation of the whole plant, with the progressive adjustment of the variables that characterize the system.

For this purpose, it has been used the process simulator Aspen Plus™, that use a modular approach for definition and calculation of processes.

The simulation programme predicts the behaviour of chemical reactions and steps using standard engineering relationships, such as mass and energy balances, rate correlations, or also phase and chemical equilibrium data [24].

3.1 MODEL OF CO₂ CAPTURE SYSTEM

As already stated in the previous paragraphs, for what concern the CO₂ capture system, a reactive absorption process based on the use of amine as solvent has been chosen because it is the most promising one for Post Combustion Carbon Capture (PCC) from power plant flue gases.

The design, optimization and scale-up of PCC plants has been based on modelling and simulation. The model has been developed basing the construction on information on the physico-chemical properties of the chosen reactive systems and has been validated using pilot plant data. For this simulation, a rate-based process model such as RateSep has been chosen which represents a second generation rate-based process dynamic modelling software for multistage separation operations. This dynamic model needs a large amount of input for describing fluid dynamics and physico-chemical properties. It requires based-models for various transport properties that are fundamental for correlations of mass transfer, heat transfer, liquid holdup, interfacial area, pressure drop, etc. The input data affects directly the simulation results that can be extrapolated from the model.

In order to elaborate a reliable model, a real pilot plant has been taken as reference with the purpose to compare the results obtained through the model simulation with the ones available from the experiments conducted on the real model.

For the comparison, the standard parameters that characterize this type of plant has been chosen for the description of the process [1], i.e.:

Description	Definition	Unit
CO ₂ removal rate	$\psi = \frac{\dot{m}_{CO_2}^{abs}}{\dot{m}_{CO_2}^{FG,in}}$	[%]
Specific energy requirement of the evaporator	$q^{evap} = \frac{\dot{Q}^{evap}}{\dot{m}_{CO_2}^{abs}}$	[GJ/tCO ₂]
Ratio between solvent mass flow rate and gas mass flow rate in the absorber (L/G ratio)	$\frac{L}{G} = \frac{\dot{m}^{Sol}}{\dot{m}^{FG}}$	[kg/kg]

Table 2. Parameters for process characterisation independent of the scale [1]

3.1.1 REFERENCE PILOT PLANT

The pilot plant taken as reference in this part of the work is described in the studies conducted by Notz et al. 2011 in the Institute of Thermodynamics and Thermal Process Engineering of the University of Stuttgart.

The basic scheme of the absorption/desorption process for CO₂ capture from flue gases and a picture of the pilot plant are shown in Figure 13, in which it is possible to see the high number of sensors that has been installed in order to control the thermodynamic condition of the fluid.

The flue gas is produced by a gas burner with the scope of simulate the flue gas that exits from a natural-gas power plant or a coal fired power plant, they differ mainly for the partial pressure of the CO₂. The experiments presented in this paper has been considered without adding NO_x and SO₂.

A blower feeds the flue gas into the pre-washer column and then it goes directly at the bottom of the absorber inlet with a temperature of approximately 40-50 °C. The maximum gas flow rate through the absorber is limited to approximately 100 kg/h due to fluid dynamic restrictions.

The lean solvent that comes from the desorber enters on the top of the absorber. The latter one has five sections equipped with the structured packing BX 500 (Sulzer Chemtec) each of which contains a liquid redistributor at the top and a collector at the bottom. The total packing height is 4,25 m; the diameter is 0,125 m. To reduce solvent loss by flue gas, there is a washing section at the absorber top above the solvent inlet.

A pump that guarantees that the circulation of the rich solvent into the desorber controls also the liquid level in the absorber bottom. Before entering into the desorber, or stripper, the rich-solvent is heated until a temperature of approximately 110°C. The desorber is equipped with three sections of BX 500 similar to the absorber. The total packing height in the desorber is 2,55 m and the diameter is 0,125 m as the absorber, and at the bottom an electrical reboiler is present in order to permit the partial evaporation of the solvent that releases a vapour at the top of the desorber. This vapour consists of water, CO₂ and some traces of amine. To retain the amine, also at the desorber top a washing section is installed, which is similar to that of the absorber. Then, there is a condenser on the top of the desorber that guarantees to remove the water present in the vapor so that almost pure

O₂ is obtained. A part of the condensate is used in the washing section of the desorber and another part if necessary is withdrawn to fulfil the water balance of the process. More details over the description of the pilot plant is given in reference [1].

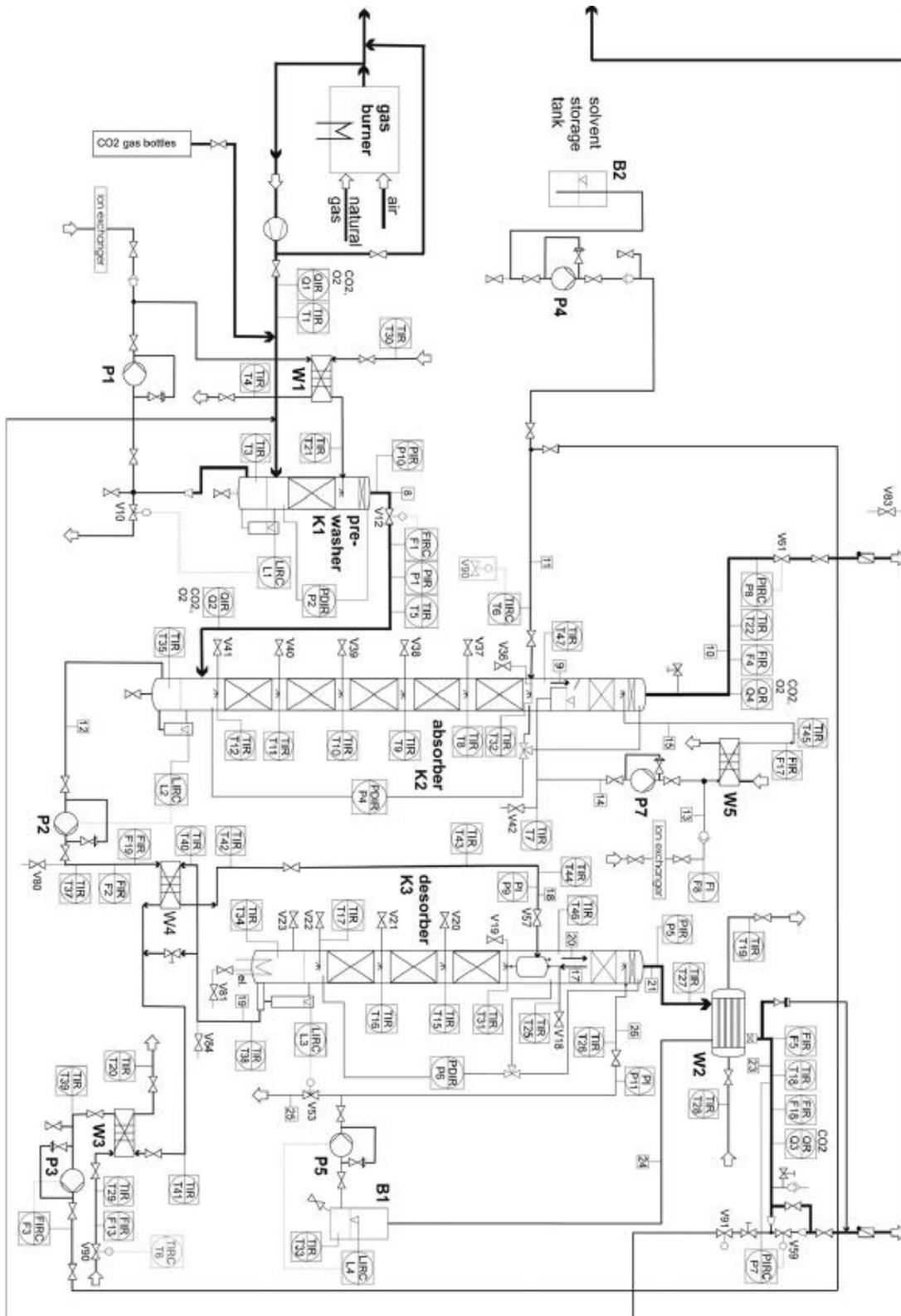


Figure 13. Process flow diagram of the absorption-desorption process of the pilot plant [1].

3.1.2 MODEL DESCRIPTION

At this point, the model of the pilot plant described above has been built. The modelling has been based on the input conditions of the pilot plant, i.e., the temperature, pressure, flow rate, and composition of the lean solvent and the flue gas to the absorber, and also the temperature and pressure at the inlet of the stripper, which are equal to the one presented in the pilot plant. Instead, the temperature, flow rate and composition of the lean solvent, the gas out of the desorber have been calculated as results of the simulation. In the present model, the washing section has not been taken into account in the simulation.

In order to model the pilot plant and to simulate the non-idealities in the liquid phase the Electrolyte-NRTL activity coefficient model has been chosen [25].

A crucial aspect of the configuration of the model to set the chemical reactions that take place in the absorber and into the desorber. Chemical reactions are divided in equilibrium-controlled reactions and kinetic-controlled reactions. The kinetic reactions have been considered mainly into the absorber, because due to the high temperature it has been sufficient to model the desorber considering that the chemical equilibrium is reached [26].

The reboiler at the desorber bottom has been considered as an equilibrium stage.

To describe the kinetic reactions, concentration based kinetics for the forward and backward reaction have been used [13].

Starting from the absorber, the equilibrium-controlled reaction equations used in this study are reported below.

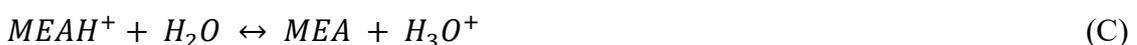
Dissociation of water:



Dissociation of bicarbonate:



Dissociation of protonated alkanolamines:

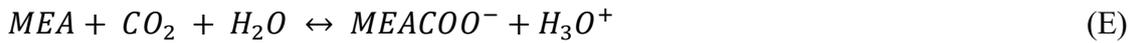


Kinetic-controlled reaction equations used in this study are as follows.

Bicarbonate formation reaction:



Carbamate formation reaction:



Regarding the stripper, as reported in the reference of the chemical reactions used [13], the follow equilibrium reaction has been added:

Dissociation of hydrogen sulphide:



Dissociation of bisulphide:



After the definition of the chemical species and reactions that are involved in the process, the next step of the elaboration of the model consists in the definition of the block used in the simulation.

Concerning the simulation of the absorber and the stripper, it has been chosen to use the RadFrac column, and for both, respecting the dimensions of the considered plant, the Flexipac Type is used. Furthermore, for the desorber, a condenser and a reboiler have been considered.

RadFrac allows the user to discretize the liquid and gas films and incorporates kinetic of reactions involved and provides four different flow models which determine the bulk properties required to evaluate the mass and energy fluxes and reaction rates.

The Film discretization facilitates an accurate modelling of the chemical reactions taking place in the liquid film. In particular, without film discretization, the liquid film reaction rates are evaluated based on an average liquid phase composition, instead with film discretization, the liquid film reaction rates are evaluated by multiple sets of liquid phase compositions, where each set expresses the average liquid phase composition for the particular film segment [27].

In this study, the “Vplug” flow model has been considered, in which the outlet conditions are used for the liquid and average conditions are used for the vapor; the liquid phase is set to “Discrxn”, in which the film is discretized and the diffusion resistance in the film is considered. Furthermore, the non-ideality correction has been set. Regarding the correlations used in this two blocks, as reported in [28], the 1985 correlations of Bravo et al. has been used to calculate the mass transfer coefficients and the interfacial area, the Chilton and Colburn correlation has been employed to calculate the heat transfer coefficients [28], the Stichlmair et al. (1989) correlation has been used to calculate the holdup [27].

As regards the Rate-Based modelling, RateSep calculates film thickness as the ratio of the average mass transfer coefficient and average diffusivity. It allows several options for modelling film resistance. The “reaction condition” factor, has been set to 0.9. The condition used is the “factor \times bulk condition + (1 - factor) \times interface”, where a factor of 0 represents the interface, and a factor of 1 indicates the edge of the film next to the bulk. The “film discretization” option has been chosen and set the number of discretization points for the liquid film to 5, which gives six film segments. The film discretization ratio, that is the ratio of the thickness of the adjacent discretization regions, has been set to 5 [27].

For both the components, the Wallis pressure drop calculation method has been used. The others components used in this part of the process are the counter-flow heat exchangers, a simple mixer and a pump with an efficiency of 0.75 has been considered. Finally, a mechanical separator with an efficiency of 0,83 has been considered in order to summarize in this value the approximation made into the model and to fit the model. This value, obviously, has not been modify in the different simulations made.

The model is showed in the Figure 14 below, in which it is also possible to see the thermodynamic properties of the fluid in the various step of the process for one of the two cases considered in this study. In particular is showed the experiment 2 in which a CO₂ partial pressure of 109.4 mbar is considered (see validation section), thus to represent the conditions of the flue gas outgoing from a coal fired power plant.

It is worth to underline that, due to Aspen PlusTM convergence limit, the plant has been modelled as an open system and, moreover, in the following analysis it has been taken in consideration the regeneration of the solvent. These have been take into account with the described coefficient inserted into the mechanical separator.

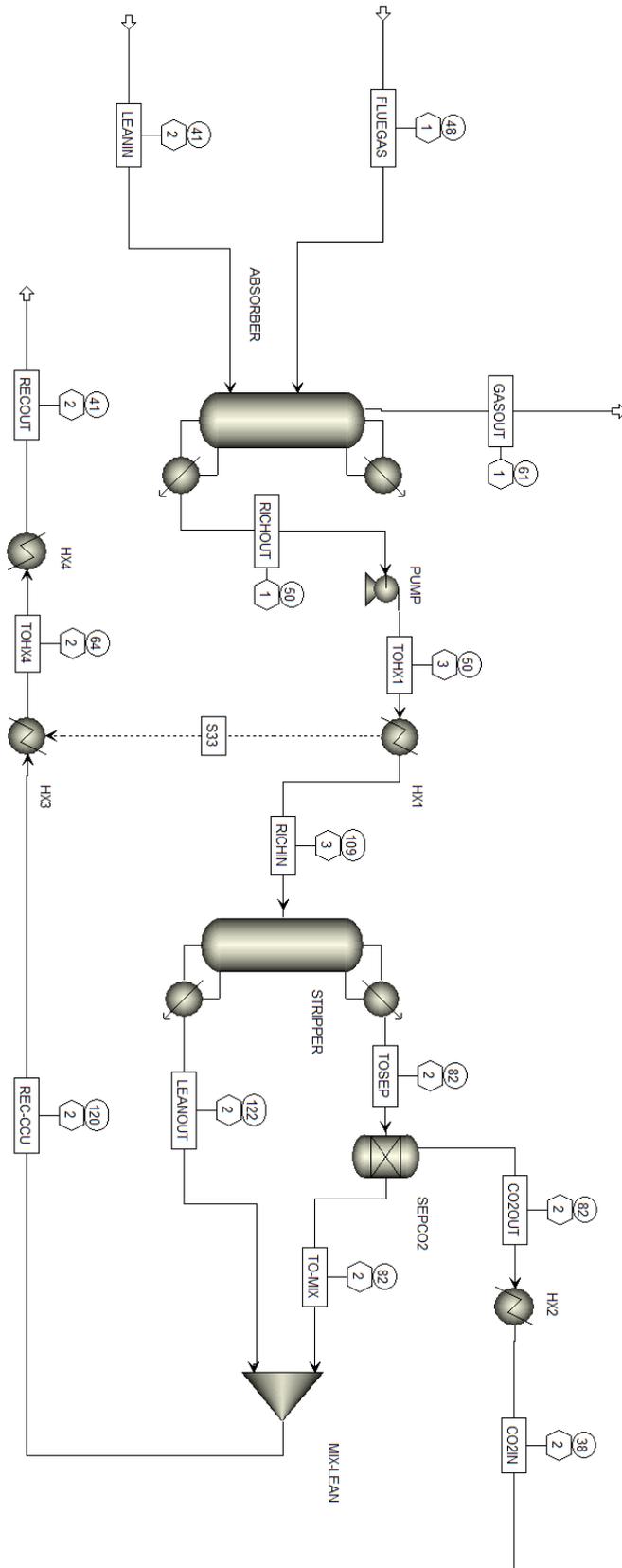


Figure 14. CO₂ capture pilot plant model

3.1.3 VALIDATION AND RESULTS

In this section are presented the results obtained from the real experiments made with the use of the pilot plant and the results extrapolated from the elaboration of the model. Then, a comparison between them will be done in order to verify the reliability of the model, based on the qualitative value of the plant described in the section 3.2.

In order to do this, two reference experiments will be reported, one at low CO₂ partial pressure in the flue gas, experiment 1, and one at high CO₂ partial pressure, experiment 2. The first one, with a CO₂ partial pressure of 54.6 mbar in the flue gas, corresponds to conditions in gas turbine power plants, whereas the second one with a CO₂ partial pressure of 109.4 mbar closer to the conditions of a coal fired power plant [1].

In Table 3 below the main process conditions of the two reference experiments are given.

Process Variables	Process Specification	Experiment 1	Experiment 2
Flue gas at absorber inlet	Mass flow rate [kg/h]	72	72,4
	Temperature [°C]	48	48,2
	Pressure [mbar]	1004,5	1009,7
	p [mbar]	54,6	109,4
Solvent at absorber inlet	Mass flow rate [kg/h]	200,1	200
	Temperature [°C]	40	40,2
MEA mass fraction in the CO ₂ free solvent	$x_{MEA}^{m,S}$ [g/g]	0,288	0,303
Desorber	Pressure [mbar]	1999,1	1999,5
Evaporator	\dot{Q}_{evap} [kW]	7,95	7,94

Table 3. Process conditions for the reference experiments 1 and 2 [1].

In the model of the process, it is important to focus the attention on the evaporator that has a significant rule. In fact, in this type of plant the CO₂ removal rate cannot be adjusted directly, thus the thermal power that is available in the evaporator determines the level of CO₂ that is possible to capture. So, in order to verify the reliability of the model is

essential to set the same values of thermal power that have been used in the two experiments.

Finally, in the Table 4 below, are reported the results of the two experiments conducted on the pilot plant, those ones obtained from the model and the differences that there is between the two results.

Experiment	Parameter	Pilot Plant	Model	Deviation
1	CO ₂ removal rate [%]	75,91	75,92	~ 0 %
	Specific energy requirement [GJ/t _{CO2}]	6,16	6,17	~ 0 %
	L/G ratio [-]	2,78	2,78	--
2	CO ₂ removal rate [%]	51,3	51,7	~ 1 %
	Specific energy requirement [GJ/t _{CO2}]	4,68	4,64	~ 1 %
	L/G ratio [-]	2,76	2,76	--

Table 4. Results of the experiments

As it is possible to see in the Table 4 above, the elaborated model in Aspen PlusTM reflects perfectly the results obtained in the experiments conducted in the pilot plant. Even though in the present model has not been considered the water washing section, these results has been reached with the help of a coefficient added into the flash separator located at the exit of the stripper that permits to takes into account the approximations that have been made and to fit the model. This value has been maintained constant for the two experiments and also for the following analysis conducted in this work.

With these results, it is possible to confirm the reliability of the model. This is the starting point for the realistic simulation of a methanol plant production that is the goal of this work and that will be reported in the next sections.

3.2 MODEL OF CO₂ HYDROGENATION

This part of the thesis is devoted to the description of the model used for the simulation of the CO₂ hydrogenation process, in which the captured carbon dioxide is converted into methanol through hydrogen obtained by water electrolysis. In order to reach this goal, the model elaborated by Calogero [21] has been used as reference, and in which it is possible to find more details of the plant and of the model.

In the study of Calogero, the model has been defined inspiring to Atsonios model [29] that consists in a methanol production plant, starting from carbon dioxide and hydrogen obtained as previously specified, with a purity of the 99.9%. Furthermore, in his study, an accurate design of the reactor has been made, defining a reliable kinetic scheme on which the reactor has been modelled.

Then, the model has been modified in order to adapt it to the CO₂ capture model with the purpose of the construction of a unique model that simulates the overall process from the capture of CO₂ to the production of the methanol as final product.

This has been done maintaining constant the variable that characterize the model of CO₂ hydrogenation, i.e.:

$$CO_2 \text{ conversion} = \frac{\text{reacted moles of } CO_2}{\text{fed moles of } CO_2} \quad (1)$$

$$MeOH \text{ selectivity} = \frac{\text{produced moles of } MeOH}{\text{reacted moles of } CO_2} \quad (2)$$

$$MeOH \text{ yield} = \frac{\text{produced moles of } MeOH}{\text{fed moles of } CO_2} = CO_2 \text{ conversion} * MeOH \text{ selectivity} \quad (3)$$

In the following tables are summarized the operational conditions that has been chosen into the model. For simplicity reasons these operating parameters are constant regardless of the plant size.

Basic operating conditions	
H ₂ /CO ₂ ratio	3
Inlet gas preheating temperature	150,7 °C
MeOH reactor temperature/pressure	250°C/ 65 bar
Flash separator 1 temperature/pressure	30°C/ 64,4 bar
Flash separator 2 temperature/pressure	24,5°C/ 0,2 bar
Crude methanol preheating	85°C
Distillation column, number of stages	60
Distillation column, inlet pressure	1,3 bar
Compressors isentropic efficiency	75%
Pump efficiency	70%

Table 5. CO₂ hydrogenation basic operating conditions [21]

Properties of catalyst	
Pellet diameter [m]	0.0048
Pellet porosity [-]	0.3
Pellet tortuosity [-]	2.5
Void fraction [-]	0.39
Bulk density [kg/m ³]	952

Table 6. Properties of catalyst [22]

Properties of reactor	
Tube's length [m]	4.3
Tube's diameter [m]	0.11103
Number of tubes	3000
T [°C]	250
P [bar]	65

Table 7. Properties of reactor [22]

Properties of fluid	
Mass flow rate [kg/s]	0,01742
Feeding H ₂ /CO ₂ (or H ₂ /CO)	Stoichiometric
WHSV [h ⁻¹]	2

Table 8. Properties of fluid [22]

	Inlet H ₂ O	Inlet CO ₂
Mass flow rate [kg/h]	1525,83	1243,265
Temperature [°C]	15	25
Pressure [bar]	1,01325	1,01325

Table 9. Thermodynamic properties of fluid [22]

3.2.1 MODEL DESCRIPTION

The model has been divided into two main parts:

- The gas conditioning section, in which the reactants are led to the process conditions.
- The processing section, in which the reactions take place and the unused reactants are separated from the products, the first one are recirculated, from the second one instead, the methanol is extrapolated.

The two sections will be explained separately in the following paragraphs.

3.2.1.1 GAS CONDITIONING SECTION

The analysis is based on the basic aspects that affect the techno-economic evaluation, for this reason the water electrolysis process has not been modelled in detail in this study.

At the inlet, it has been assumed to use water taken from the network. The water supply has to be pumped and heated in order to reach the operating conditions required in the electrolysis block.

It has been considered to use an alkaline electrolyzers that, from the studies found in literature, seems to be the most promising solution for large scale production.

The thermodynamic condition chosen are: $T=80\text{ }^{\circ}\text{C}$ and $p=10\text{ bar}$. It is assumed to produce H_2 at high purity ($>99,9\%$) and O_2 that, as it will be possible to see in the section of economic analysis, can be sold in order to increase the revenues of the plant. Concerning the electrolyzers, it is worth to underline that it works much above the thermoneutral point, thus the process is globally exothermic and it is necessary to remove the part of the electrical power supplied that is converted in heat with the purpose of maintain the operative conditions (T and p).

Then, the H_2 produced is cooled and compressed in order to permit the mixing with the CO_2 captured.

Regarding the CO_2 , it is progressively brought to the reaction pressure with the use of a series of compressors with intercooling, composed by four compressors with an efficiency of 0,75 and three heat exchangers as it is possibile to see in the figure 15 below. Finally, the two flows are mixed.

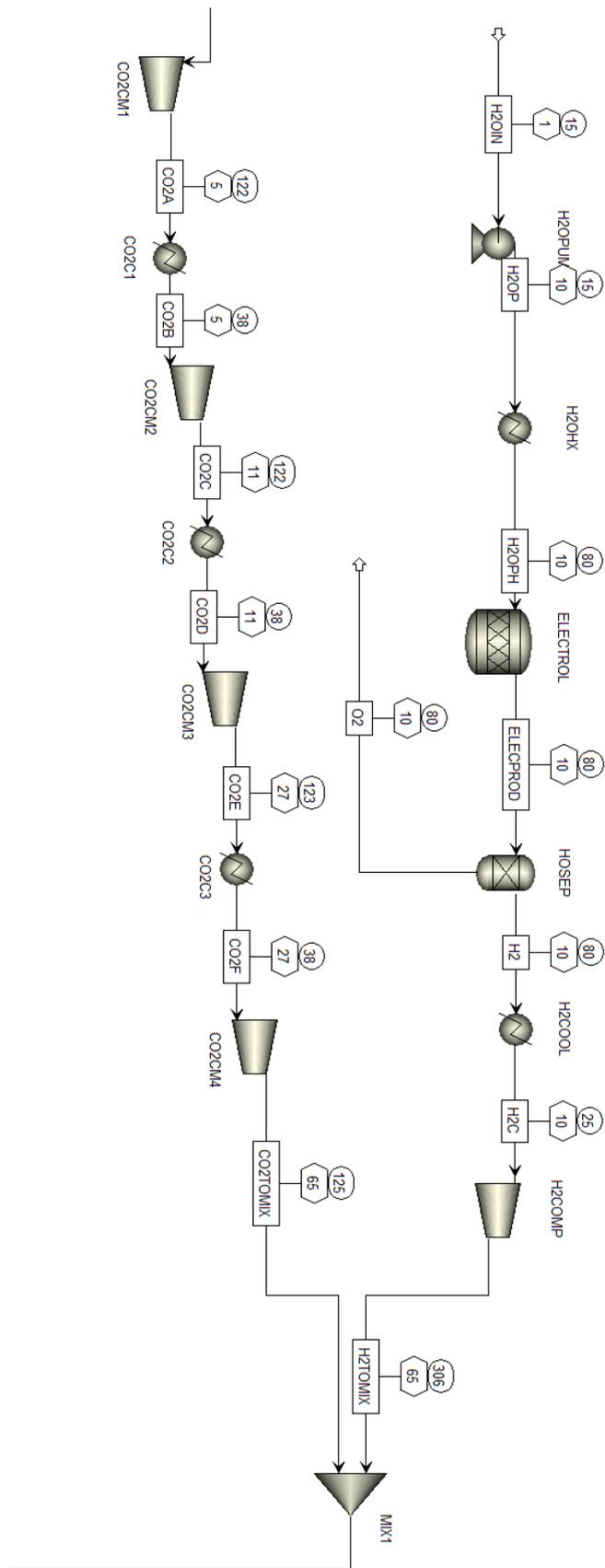


Figure 15. Model of preparation line

3.2.1.2 PROCESSING SECTION

The processing section is the part of the plant in which the transformation of H_2 and CO_2 in methanol is performed. As showed in the Figure 16 below, the feeding flow, that is characterized by composition H_2/CO_2 equal to 3, is mixed with the recirculated reactants. The temperature of obtained fluid is lower than the temperature of the reaction ($150^\circ C$), thus, before entering the reactor, the resulting flow has to be preheated. Using the out-going flow from the reactor, through an heat exchanger, the feeding flow is preheated until the temperature of $150,7^\circ C$ [29]. After that, a second heater brings the temperature to the process one.

After the reaction, in order to reach the operating conditions of the first flash separator, ($T=30^\circ C$, $p=65$ bar) the fluid undergoes other two cooling in addition to the one described before, which one of that is used to preheat the fluid that goes to the distillation column.

In the flash separator, the separation of methanol and water from a considerable part of the reactants occurs. However, this is not sufficient to “purify” the fluid that has to fed the distillation column. So, another flash separator is needed. Before entering into the second flash separator, the fluid crosses two rolling valves that reduce its pressure up to 18,8 and the temperature up to $24.5^\circ C$. Subsequently, the separator causes a flash separation, bringing the pressure to 2.2 bar; in this way, most of the reactants previously mixed with the products pass into the gaseous state and are recirculated. However, the problem of traces in each flow leaving the separator is not solved.

The gaseous flows that goes out from the separators are mixed, in a condition in which their operating condition are the same, so the one that leaving the component at lower pressure is previously compressed. Afterwards, a small fraction ($<1\%$) of the flow is removed (to avoid the accumulation of the products in the reactor, which would damage the position of the equilibrium of the reaction). Then, the fluids are mixed.

On the other hand, the liquid fluid that goes out from the second flash separator is bring to the operational temperature of the distillation column ($T=85^\circ C$), as mentioned before, with the help of the second heat exchanger at the exit of the reactor, in which the MeOH is separated from the rest. The distillation column has been modelled considering 60 number of stages with pressure equal to the atmospheric one at the condenser and to 1.1 bar at the reboiler. Then, in order to produce methanol with a degree of purity of 99.9%, a mechanical separator has been added in the plant.

3.3 COMPLETE MODEL

The complete model permits to simulate the whole process, from the capture of CO₂ to the methanol production. In the elaboration, given the appreciable differences in the dimensions of the two parts of the plant considered, it has been decided to maintain constant the operating conditions of the section in which the methanol production is described, and to modify the model of the CO₂ capture section.

Concerning the section of the methanol production, the design of the plant has been based on the assumption that in the electrolysis block the installed power is equal to 10 MW. This assumption fixes the water input and the CO₂ flow rate required in order to form a fluid with a composition H₂/CO₂ equal to 3 [21].

At this point, considering that an Alkaline Hydrogen Generator has been chosen, and that at nominal load, it produces 100 Nm³/h of hydrogen at a pressure of about 10 bar with a conversion efficiency of 5.4 kWh/ Nm³_{H₂} [30]; an electrolysis train made of 19 components has an installed power equal to 10.26 MW. Consequently, a CO₂ flow rate equal to 1243,265 kg/h is needed.

As it is possible to see from the tables in the previous section, there is a notable difference between the required inlet mass flow rate of CO₂ and the captured one of the pilot plant taken as reference. In fact, the mass flow rate captured in the second experiment, the one that assumes to simulate the flue gas exit from a coal-fired power plant, is equal to 6.17 kg/h.

Therefore, in order to connect the two models, it has been necessary a scaling up of the CO₂ capture plant model.

With this purpose, the following assumptions has been made:

- The thermodynamic conditions of the pilot plant have not been modified;
- The L/G ratio is maintained equal to 2,8;
- The chemical reactions has not been modified;
- The number of stages in the columns has been maintained constant.
- The blocks used for the simulation of the absorber and the stripper have been changed, the more efficient IMTP ones are chosen.

Thus, in order to reach the goal, apart from the mass flow rate of the flue-gas and of the amine solvent, only the size of the absorber and of the stripper has been increased.

Over the test done using the possible dimensions found in literature, for example the ones proposed in the papers [31] [27] [32] [33] the dimensions that has been chosen in this work, due the better results obtained, are the ones proposed in the work of Thomas Marx-Schubach and Gerhard Schmitz [34]. Considering also the limitations into the diameter of the columns imposed from [35] (12,2 m), the final size of the columns are:

	Absorber	Stripper
Diameter [m]	12,2	8,51
Height [m]	15	10

Table 10. Dimensions of absorber and desorber

Furthermore, as it has been described in the section 3.1.3, the removal rates reached in the experiments are 75,92% and 51,3%, but it is common in this type of plant, in order to compare them, to reach a removal rate of 90%. Thus, acting on the evaporated power of the reboiler, in this studied case, this goal has been reached.

Another modification that has been done in the proposed model, in the part of methanol production, precisely in the preparation section, is the pressure ratio used in each compressor. In fact, in the connection of the models, the CO₂ captured is available at a pressure of 1,9995 bar, that is higher than 1,01325 bar supposed into the model taken as reference.

So, the total pressure ratio is:

$$\beta_T = \frac{65}{1,9995} = 32,5 \quad (4)$$

Then, the new pressure ratio at each stage will be:

$$\sqrt[4]{\beta_T} = 2,387 \quad (5)$$

The results obtained from the simulation will be presented in the section 5, simulation and results.

4. PINCH ANALYSIS

In many industrial processes, in order to guarantee the right operational condition it is important to satisfy the heat and cold requirement. For this purpose, the simplest solution could be the use of external sources, as steam produced by a boiler or refrigerated water produced by a refrigeration unit.

Nevertheless, this solution requires the use of components that need high quantity of energy and are characterized by a high cost, thinking about the fuel, or the electricity as in this studied case, necessary for the boiler and the electricity needed by the refrigeration system.

In many of these industrial processes, it is possible to couple fluids that are involved in a temperature change in order to use the hot fluid to increase the temperature of the cold fluid that need to be heated and vice versa. In this way, it is possible to take advantages from internal sources and to reduce the number of external sources necessary.

In order to reach this type of result, it is necessary to consider a high number of heat exchangers, this is called Heat Exchanger Network (HEN). This network could be quite complicate because in the coupling of the fluid it is important to respect some restrictions and constraints, the procedure will be described in the follow paragraphs.

The pinch analysis, introduced by Linnhoff and Vredeveld in 1982, is a useful technique that permits to synthesize the heat exchanger network in order to reach a prefixed objective, that generally is to satisfy, through the use of external sources, the minimum energy requirement of the system.

The pinch analysis could be used also to identify energy cost and heat exchanger network capital cost targets for a process and recognizing the pinch point. The pinch point is the crucial point in the process in which falls the minimum difference between hot and cold fluids.

4.1 PROCEDURE DESCRIPTION

The procedure after the characterization of the process and the identification of the fluids involved, predicts the minimum requirements of external energy in terms of heating and cooling needs. After this, the coupling of the fluids permits to design a heat exchangers network and to determine the type and the number of components required [36].

1) Fluids identification and characterization

The first step of the analysis consists into the identification and characterization of the components and of fluids involved in the process. It is important to describe the fluids through their chemical composition, mass flow rate, temperature at which they are available and the temperature that they have to reach.

In the following Figures 17 and 18, it is possible to see the components and the fluids that are considered in this work, in which it is possible to distinguish between the hot fluids that have to be cooled, in orange, and the cold ones that have to be heated, in blue.

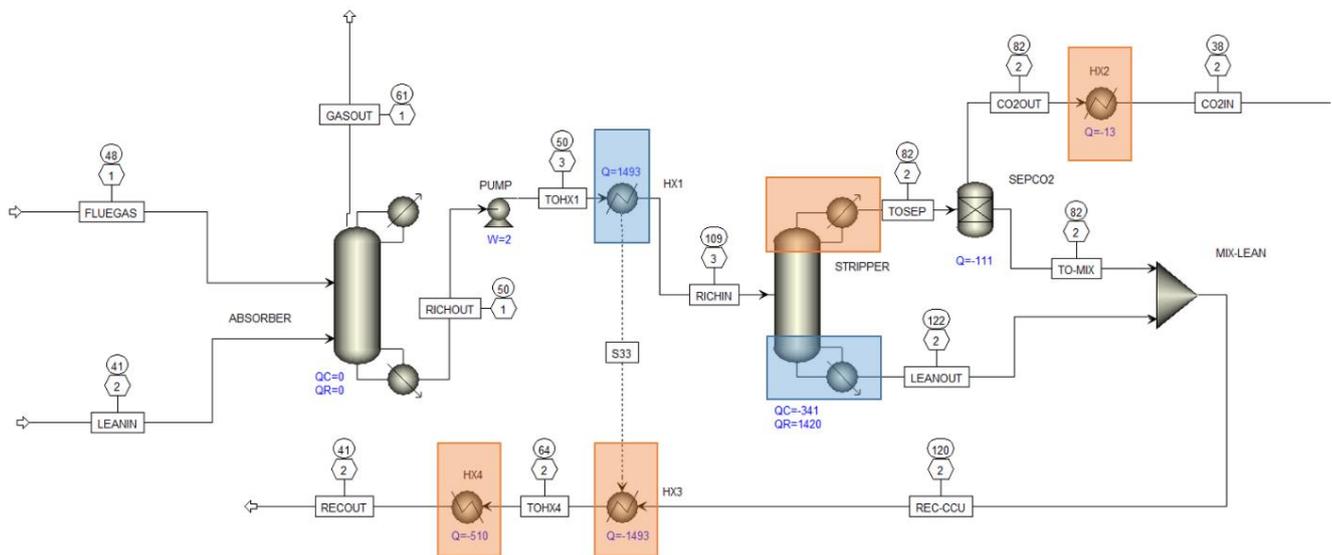


Figure 17. Scheme 1 of the considered

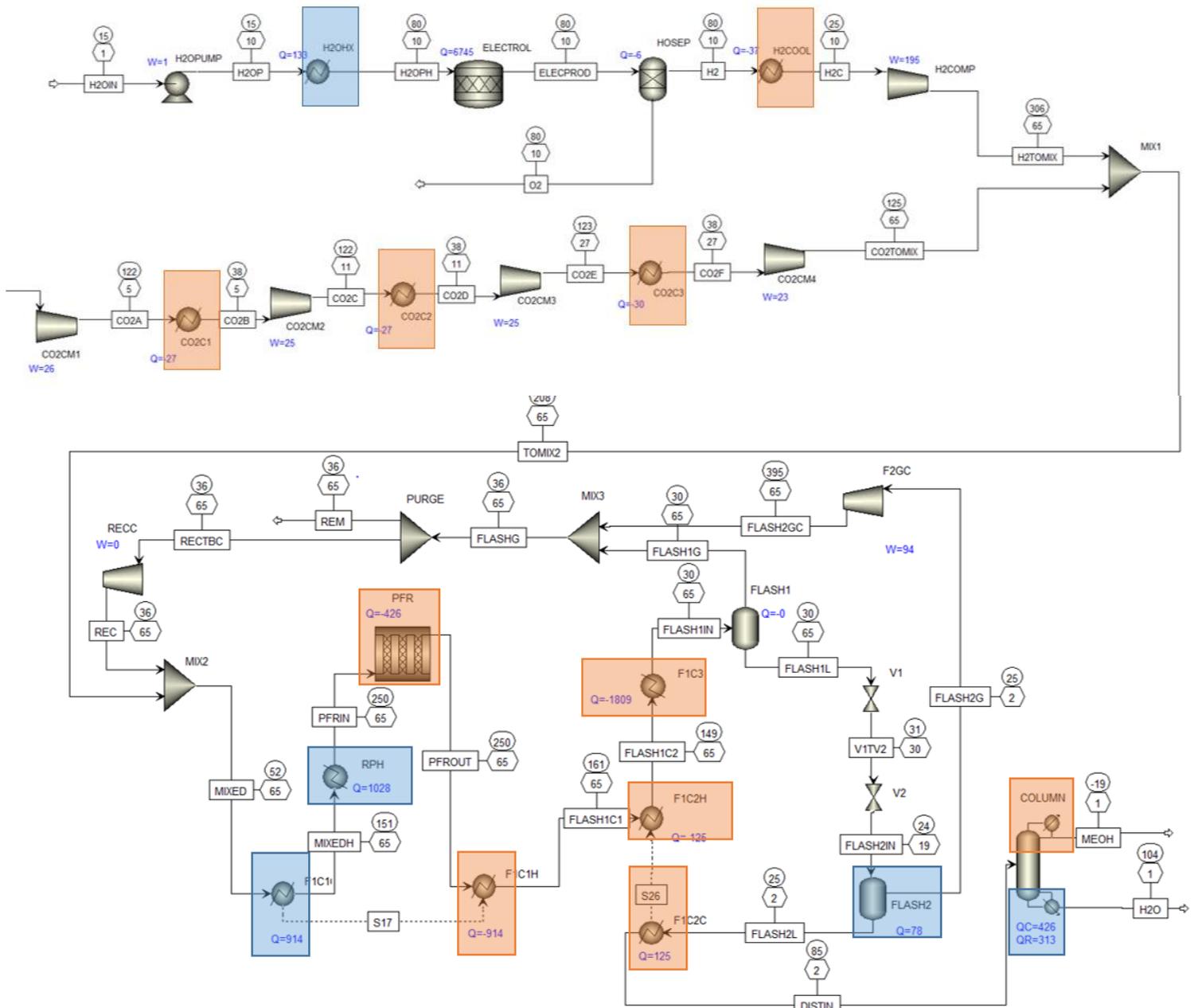


Figure 18. Scheme 2 of the considered

In the Table 11 below, the fluids and their characteristics to be combined in order to minimize the external heat requirement are reported.

Fluid name	Type	T _{in} [°C]	T _{out} [°C]	h _{in} [kJ/kg]	h _{out} [kJ/kg]	c [kJ/(kgK)]	G [kg/h]	Gc [kW/K]	Q̇ [kW]
H2OHX	cold	15,1	80,0	-16081,20	-15768,21	4,82	1525,83	2,043	-132,66
H2COOL	hot	80,0	25,0	794,64	4,30	14,37	170,74	0,682	37,48
CO2C1	hot	122,1	38,0	-8857,56	-8934,43	0,91	1243,21	0,316	26,55
CO2C2	hot	122,4	38,0	-8860,95	-8940,33	0,94	1243,21	0,325	27,41
CO2C3	hot	123,3	38,0	-8869,00	-8955,78	1,02	1243,21	0,351	29,97
F1C1C	cold	51,7	150,7	-6466,05	-6176,93	2,92	11379,78	9,228	-913,92
RPH	cold	150,7	250,0	-6176,93	-5851,78	3,27	11379,78	10,351	-1027,81
PFR	hot	251,0	250,0	-5851,78	-5986,63	134,84	11379,78	426,252	426,25
F1C1H	hot	250,0	161,3	-5986,63	-6275,75	3,26	11379,78	10,299	913,93
F1C2H	hot	161,3	148,6	-6275,75	-6315,28	3,11	11379,78	9,847	124,96
F1C3	hot	148,6	30,0	-6315,28	-6887,29	4,82	11379,78	15,250	1808,16
FLASH2	cold	23,5	24,5	-	-	125,17	2231,71	77,592	-77,59
F1C2C	cold	24,5	85,0	-10575,46	-10232,82	5,66	1312,93	2,065	-124,96
COND	hot	-17,8	-18,8	-	-	1774,27	863,95	425,802	425,80
REB	cold	103,5	104,5	-	-	2507,25	449,01	312,715	-312,72
HX1	cold	49,7	108,6	-12134,86	-11911,08	3,797	24023,49	25,341	-1493,33
CONDCO2	hot	82,6	81,6	-	-	718,507	1710,172	341,325	341,33
REBCO2	cold	120,8	121,8	-	-	229,149	22313,32	1420,300	-1420,30
HX2	hot	81,6	38,0	-8893,37	-8931,96	0,886	1243,213	0,306	13,33
HX3	hot	120,3	63,5	-11922,87	-12158,86	4,159	22780,28	26,316	1493,33
HX4	hot	63,5	40,5	-12158,86	-12239,52	3,503	22780,28	22,166	510,40

Table 11. Fluid definition

For each fluid, it is necessary to determine the thermal flux that it is required or available for other fluids.

The thermal flux exchanged by each fluid can be calculate as [36]:

$$\dot{Q} = G \cdot c \cdot (T_{in} - T_{out}) \quad (6)$$

Where:

- G : the mass flow rate in [kg/h];
- c : the specific heat capacity [kJ/(kgK)];
- T_{in} the temperature at which the fluid is available;
- T_{out} the temperature that the fluid has to be reach;

Collecting the data of the variation of temperature and enthalpy available from the simulation programme used, Aspen PlusTM, and considering the simplified following correlation between these two variables, it was possible to evaluate an average specific heat capacity of the considered fluid.

$$c = \frac{\Delta h}{\Delta T} \quad (7)$$

As it is possible to see in the Table 6541, there are components in which the temperature evolution of the fluid was not obtainable but the exchanged thermal power and the mass flow rate are known. In those cases, it has been considered a fictitious variation of temperature of 1°C, considering a $\Delta T = 1^\circ\text{C}$ if a hot fluid needs to be cooled down, and a $\Delta T = -1^\circ\text{C}$ if a cold fluid needs to be heated.

Once supposed the variation of temperature, knowing the exchanged thermal power and the mass flow rate, it has been possible to determine the specific heat capacity from the formula 1. This is a conservative way to deal with this type of evolution

2) Restrictions and constrains

Before to start the elaboration of the heat exchanger network of the process it is necessary to define the constrains and the boundary condition that have to be respected.

In order to make possible the exchange of the heat, it is essential to have a difference in temperature between the hot and the cold fluid involved in the exchange.

For this process, a $\Delta T_{MIN} = 10^{\circ}C$ has been chosen.

Table 12 reports the fluids, subdivided in hot ones and cold ones, with the respective fictitious temperatures.

Fluid's name	Type	Fluid's n°	T _{in} [°C]	T _{out} [°C]	T _{in} *[°C]	T _{out} *[°C]	G _c [kW/K]	Q̇ [kW]
H2COOL	hot	1	80,0	25,0	75,0	20,0	0,68	37,48
CO2C1	hot	2	122,1	38,0	117,1	33,0	0,32	26,55
CO2C2	hot	3	122,4	38,0	117,4	33,0	0,32	27,41
CO2C3	hot	4	123,3	38,0	118,3	33,0	0,35	29,97
PFR	hot	5	251,0	250,0	246,0	245,0	426,25	426,25
F1C1H	hot	6	250,0	161,3	245,0	156,3	10,30	913,93
F1C2H	hot	7	161,3	148,6	156,3	143,6	9,85	124,96
F1C3	hot	8	148,6	30,0	143,6	25,0	15,25	1808,16
COND	hot	9	-17,8	-18,8	-22,8	-23,8	425,80	425,80
COND_CO2	hot	10	82,6	81,6	77,6	76,6	341,33	341,33
HX2	hot	11	81,6	38,0	76,6	33,0	0,31	13,33
HX3	hot	12	120,3	63,5	115,3	58,5	26,32	1493,33
HX4	hot	13	63,5	40,5	58,5	35,5	22,17	510,40
H2OHX	cold	14	15,1	80,0	20,1	85,0	2,04	-132,66
F1C1C	cold	15	51,7	150,7	56,7	155,7	9,23	-913,92
RPH	cold	16	150,7	250,0	155,7	255,0	10,36	-1027,81
FLASH2	cold	17	23,5	24,5	28,5	29,5	77,59	-77,59
F1C2C	cold	18	24,5	85,0	29,5	90,0	2,07	-124,96
REB	cold	19	103,5	104,5	108,5	109,5	312,72	-312,72
HX1	cold	20	49,7	108,6	54,7	113,6	25,34	-1493,33
REB_CO2	cold	21	120,8	121,8	125,8	126,8	1420,30	-1420,30

Table 12. Reordered fluid with fictions temperature

Summing up the heat requirements of cold fluids and the heat releases of the hot ones, the maximum heating and cooling needs were obtained.

The obtained values are high in comparison to the dimension of the plant, with the help of the pinch analysis and the coupling of the fluid will be possible to reduce them significantly.

$\dot{Q}_{\max, \text{heating}}$ [kW]	$\dot{Q}_{\max, \text{cooling}}$ [kW]
5503,29	6178,89

Table 13. Maximum heating and cooling requirements

3) Pinch point and Minimum energy requirement calculation

The determination of the pinch point and the minimum energy requirement it is important in order to determine if an implementation of the heat exchanger network can bring to a significant reduction of the thermal energy requirement compared to the maximum one, covering the investment of the network itself.

In order to do this, in this work it has been applied an algebraic procedure with the help of the programme excel.

The first step is the attribution of fictitious temperature at each fluids, as it is showed in Table 14. This guarantees that in all the process the minimum difference of temperature is respected.

Then, all temperatures are ordered in a decreasing way, so the formation of range of temperature between the T^*_i and T^*_{i+1} takes place.

For each range, the net thermal flux that it is available is calculated.

All fluids present in the considered range undergo the same variation of temperature, so the net thermal flux has been obtained summing the product between the heat specific capacity (c) and the mass flow rate (G) of the hot fluid of the considered range and subtracting the product of G and c of the cold ones.

Then this value has been multiply for the difference in temperature of the interval as expressed in the following formula:

$$\dot{Q}_{h,j} = (\Sigma Gc_{hots} - \Sigma Gc_{colds})_j \cdot (T_i^* - T_{i+1}^*) \quad (8)$$

If the value of the \dot{Q}_h is positive it means that in the considered temperature interval there is a surplus of thermal power that could be used in the following interval. Instead, in case of negative value of \dot{Q}_h this means a deficit in thermal power in this interval that has to be compensate by the previous interval or by an external source. [36]

At this point, it is possible to calculate the cumulative value of all intervals, starting from the one with the higher temperatures. In this way, if the cumulative value is negative, it is possible to affirm that in that case there is the need of an external source. At the end of the calculation, the minimum value, i.e the maximum negative value, will be the minimum value of heat that an external source has to provide to the plant.

As it is possible to see in the Table 14 below, in this studied case, the maximum negative value is present in the interval 14, between 109°C and 108°C.

At this point, as the procedure requires, it is possible to consider to provide the maximum heating required by the plant at the maximum temperature, in order to bring to zero the cumulate in this point.

The point in which the cumulative value is zero represents the Pinch Point of the plant.

The described calculations and the results in terms of temperature of pinch point, minimum of heating and cooling requirements are showed in the following tables, in which are reported also the involved fluids and the equivalent Gc product of each interval

Range n°	T_i^* [°C]	T_{i+1}^* [°C]	Involved Fluids	$\Sigma Gc_{hots} - \Sigma Gc_{colds}$	\dot{Q}_h [kW]	\dot{Q}_{cum} [kW]	\dot{Q}_{cum2} [kW]
		255,0					(+1138,47)
1	255,0	246,0	16	-10,35	-93,15	-93,15	1045,31
2	246,0	245,0	5;16	415,90	415,90	322,75	1461,21
3	245,0	156,3	6;16	-0,05	-4,61	318,13	1456,60
4	156,3	155,7	7;16	-0,50	-0,28	317,85	1456,32
5	155,7	143,6	7;15	0,62	7,51	325,36	1463,83
6	143,6	126,8	8;15	6,02	101,15	426,51	1564,97
7	126,8	125,8	8;15;21	-1414,28	-1414,28	-987,77	150,70
8	125,8	118,3	8;15	6,02	45,13	-942,64	195,82
9	118,3	117,4	4;8;15	6,37	5,75	-936,89	201,57
10	117,4	117,1	3,4;8;15	6,70	2,03	-934,86	203,60
11	117,1	115,3	2;3;4;8;15	7,01	12,63	-922,23	216,24
12	115,3	113,6	2;3;4;8;12;15	33,33	55,73	-866,50	271,97
13	113,6	109,5	2;3;4;8;12;15;20	7,99	32,76	-833,74	304,73
14	109,5	108,5	2;3;4;8;12;15;19; 20	-304,73	-304,73	-1138,47	0,00
15	108,5	90,0	2;3;4;8;12;15;20	7,99	147,82	-990,65	147,82
16	90,0	85,0	2;3;4;8;12;15;18; 20	5,92	29,62	-961,02	177,44
17	85,0	77,6	2;3;4;8;15;14;15;1 8;20	3,88	28,87	-932,16	206,31
18	77,6	76,6	2;3;4;8;10;12;14;1 5;18;20	345,21	345,21	-586,95	551,51
19	76,6	75,0	2;3;4;8;11;12;14;1 5;18;20	4,19	6,55	-580,40	558,06
20	75,0	58,5	1;2;3;4;8;11;12;1; 15;18;20	4,87	80,21	-500,20	638,27
21	58,5	56,7	1;2;3;4;8;11;13;1; 15;18;20	0,72	1,34	-498,86	639,61
22	56,7	54,7	1;2;3;4;8;11;13;1; 18;20	9,95	19,78	-479,08	659,38
23	54,7	35,5	1;2;3;4;8;11;13;1; 18	35,29	676,45	197,37	1335,83

24	35,5	33,0	1;2;3;4;8;11;14;18	13,12	32,80	230,17	1368,63
25	33,0	29,5	1;8;14;18	11,82	41,38	271,55	1410,01
26	29,5	28,5	1;8;14;17	-63,70	-63,70	207,84	1346,31
27	28,5	25,0	1;8;14	13,89	48,61	256,45	1394,92
28	25,0	20,1	1;14	-1,36	-6,70	249,75	1388,21
29	20,1	20,0	1	0,68	0,05	249,80	1388,27
30	20,0	-22,8	-	-	0,00	249,80	1388,27
31	-22,8	-23,8	9	425,80	425,80	675,60	1814,07

Table 14. Procedure of determination of the minimum heating and cooling requirements and of the pinch point

$\dot{Q}_{\min, \text{heating}}$ [kW]	$\dot{Q}_{\min, \text{cooling}}$ [kW]
1138,47	1814,07

Table 15. Minimum heating and cooling requirements

T^*_{pp} [°C]	$T_{pp, \text{hots}}$ [°C]	$T_{pp, \text{colds}}$ [°C]
108.5	113.5	103.5

Table 16. Pinch point

As it is notable from the Table 15, the calculated values are significantly lower than the ones, showed in the Table 13, obtained considering only the external sources as solutions in order to satisfy the cooling and heating requirements.

In this condition, it is possible to state that the pinch analysis can provide appreciable advantages in terms of energy savings, and that it could be convenient to continue the analysis with the fluid coupling.

4.2 FLUID COUPLING

As already stated, the coupling of the fluid is finalized to the realization of a Heat Exchanged Network that permits to satisfy the heating and cooling requirements of the plant. In order to reach the prefixed goal of the analysis the first step to do is to divide the overall process into two parts, i.e. above and below the pinch point temperature. This is made because the two parts are energetic independent, without any thermal exchange between them. Above the pinch point the goal is to cool down the hot fluids until the hot temperature of pinch point or until the prefixed final temperature that the fluid has to reach, instead below the pinch point the goal is to heat the cold fluids until the cold pinch point temperature or, as before, until the prefixed final temperature. It is important to start the calculation from the pinch point because this is the point that have the more stringent constrains in terms of minimum temperature difference.

Furthermore, there are two important rules that have to be observed in order to respect the thermodynamic constrains of the plant. Respecting these rules, it is sure that the minimum difference temperature is satisfied [36]:

Above the pinch point:

- $(Gc)_{cold\ fluid} > (Gc)_{hot\ fluid}$
- $Number_{hot\ fluid} < Number_{cold\ fluid}$

Below the pinch point:

- $(Gc)_{cold\ fluid} < (Gc)_{hot\ fluid}$
- $Number_{hot\ fluid} > Number_{cold\ fluid}$

If the property of the fluids of the plant and their subdivision do not permit to observe these rules, it is possible to divide the fluids, cold or hot based on needs, in order to find a feasible solution. This is of course a fictitious division.

In the following figure, the solution proposed for this plant is showed. The fluids are represented by lines that go from the left to right in case of hot fluid, and from right to left in case of cold fluid. Each heat exchanger is represented with a circle with a progressive letter to identify them. The coolers and heaters are represented with the letters C and H respectively.

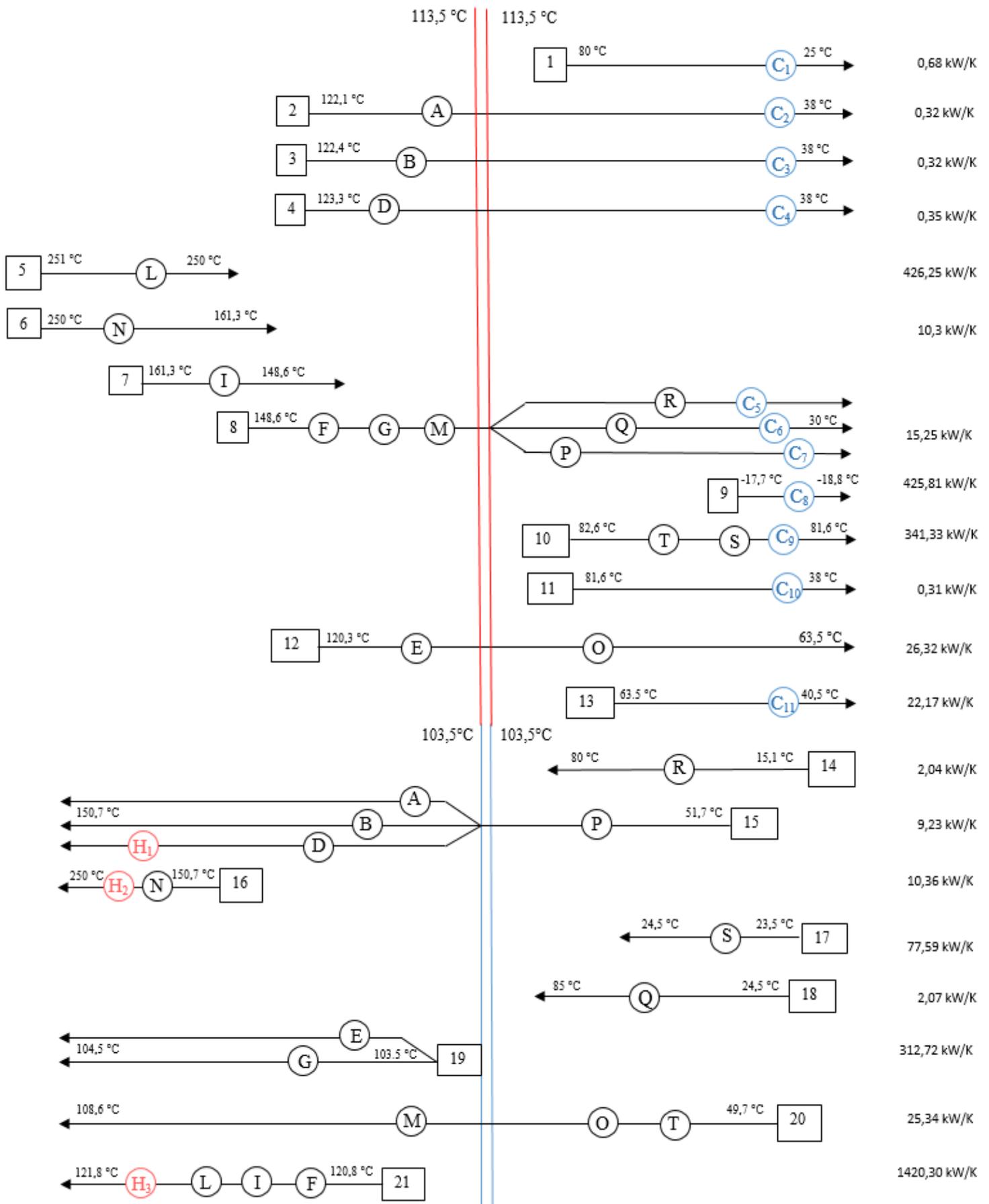


Figure 19. Scheme of fluid coupling

After that all possible connection has been evaluated for each fluid in order to find the best configuration of the heat exchanger network, the solution in the figure above it is chosen.

As it is possible to see in the figure 354, above the pinch point, the number of hot fluids is lower than the one of the cold ones, thus it has been necessary to divide the cold fluids 15 and 19 to satisfy one of the two fundamental rules of the analysis.

Below the pinch point, the hot fluid 8 has been divided into three fluids with the purpose to satisfy the constrain linked to the product between the mass flow rate G and the specific heat capacity c , in order to bring to the pinch point temperature the cold fluid 15, and to the required temperature the fluid 14 and 18.

The thermal flux exchanged for each heat exchanger it has been evaluated through the following formula:

$$\dot{Q}_{HE} = G \cdot c \cdot (T_{in} - T_{out}) \quad (9)$$

Then, each temperature has been controlled in order to verify if the minimum difference of temperature is respected.

When all possible connection has been evaluated, the remain fluids that are not even at the desired point, an external source is added, i.e. heater or cooler.

In the following Table 17, the thermal flux exchanged in each heat exchanger, the duty of the coolers and heaters, and also the intermediate temperature of the fluids involved are reported

Heat Exchanger	Fluids involved	\dot{Q} [kW]	T _{OUT, hot side} [°C]	T _{OUT, cold side} [°C]
A	2 - 15	2,71	113,5	150,7
B	3 - 15	2,88	113,5	150,7
D	4 - 15	3,44	113,5	103,87
E	12 - 19	178,21	113,5	104,5
F	8 - 21	271,38	130,87	120,87
G	8 - 19	134,50	121,95	104,5
I	7 - 21	124,96	148,6	121,05
L	5 - 21	426,25	250	121,37

M	8 – 20	129,24	113,5	108,6
N	6 – 16	913,93	161,3	239
O	12 – 20	1315,11	63,5	103,5
P	8 – 15	478,38	79,97	103,5
Q	8 – 18	124,96	53	85
R	8 – 14	132,66	61,66	80
S	10 – 17	77,59	82,42	24,5
T	10 - 20	48,97	82,19	51,6
TOT		4365,17		

Table 17. Heat Exchanger characterization

Coolers	Fluid involved	\dot{Q} [kW]	$T_{\text{hot side}}$ [°C]
C1	1	37,48	25
C2	2	23,84	38
C3	3	24,53	38
C4	4	26,53	38
C5	8	197,75	30
C6	8	47,51	30
C7	8	292,13	30
C8	9	425,80	-18,8
C9	10	214,76	81,6
C10	11	13,33	38
C11	13	510,40	40,5
TOT		1814,07	

Table 18. Coolers characterization

Heaters	Fluid involved	\dot{Q} [kW]	$T_{\text{cold side}}$ [°C]
H1	15	426,52	150,7
H2	16	113,70	250
H3	21	597,71	121,6
TOT		1137,93	

Table 19. Heaters characterizations

At the end of the calculation, it can be affirmed that it is possible to design a Heat Exchanged Network that respect the thermodynamic constrains imposed.

The total number of heat exchangers is 16 with a total thermal power exchanged of 4365,17 kW.

Furthermore, in order to satisfy the heating and cooling requirement of the plant, there is the need of 11 coolers and 3 heaters that, after the analytic calculation, provide the same quantity of thermal power calculated in the previous section during the pinch point analysis. This is an indicator that verify the fluid coupling.

5. SIMULATION RESULTS

As described in the previous part of the thesis, the simulated plant can be divided into two parts: one regarding the CO₂ amine-based capture system and one regarding the methanol production.

In this section, the results obtained are presented. Firstly, the ones derived from the simulations of the two parts of the plant separately and then the ones of the overall plant. Before the calculation of the efficiency that characterizes the plant, it is useful to evaluate the electrical power that is used by the components into the plant.

Furthermore, in the previous section, the minimum heating requirement is calculated, and it is worth to underline that it is assumed to be satisfied by the use of an electric heater.

The electric power required by each component is shown in the Table 20 below.

Component	Power [kW]
PUMP	2,165
H2OPUMP	0,561
ELECTROLYSIS	6745,343
H2COMP	194,919
CO2CM1	25,693
CO2CM2	25,381
CO2CM3	24,637
CO2CM4	22,801
RECC	0,00055758
F2GC	94,11
Q _{min, heating}	1137,93
W_{el, global}	11788,197

Table 20. Electric power requirement

5.1 CO₂ CAPTURE SYSTEM

Concerning the CO₂ capture system part, in the Table 21 below are reported the variables that characterize the system that has been modified in order to guarantee the quantity required of CO₂ captured.

Process Variables	Process Specification	Result
Flue gas at absorber inlet	Mass flow rate [kg/h]	8372,39
	Temperature [°C]	48,2
	Pressure [mbar]	1009,7
	p [mbar]	109,4
Solvent at absorber inlet	Mass flow rate [kg/h]	23442,690
	Temperature [°C]	40,2
MEA mass fraction in the CO ₂ free solvent	$x_{MEA}^{m,S}$ [g/g]	0,303
Desorber	Pressure [mbar]	1999,5
Evaporator	\dot{Q}_{evap} [kW]	7,94

Table 21. Process conditions for the scaled model

In the follow Table 22 are presented the results obtained from the simulation of this part of the plant.

Variable	Model
CO ₂ removal rate [%]	90
Specific energy requirement [GJ/tCO ₂]	4,113
L/G ratio [-]	2,8

Table 22. Results of the scaled model for CO₂ capture system

As it is possible to see in the Table 23, the CO₂ removal rate has been increased until the value of 90% and this has been done rising the evaporated power required in the stripper. Despite this, the specific energy requirement decreases in comparison with the values obtained in the experiments 1 and 2, available in Table 4.

In particular, a value of specific energy requirement 4,113 GJ/t_{CO₂}, that is a consistent with the other data found in literature concerning this type of process [37] [38] [8].

This can be explained because the increment of the size of the stripper and especially of the absorber, would decrease the required driving force for the mass transfer of CO₂ [1].

5.2 METHANOL PRODUCTION

Once the part of the process that regards the methanol production has been simulated, the efficiency of the conversion process has been evaluated.

This efficiency is obtained with a plant MeOH yield with respect to inlet CO₂

$$Y = \frac{\text{Produced kmol of MeOH [kmol/hr]}}{\text{Captured kmol of CO}_2 \text{ [kmol/hr]}} * 100 = \frac{24,5963}{28,2485} * 100 = 87.07\% \quad (10)$$

5.3 COMPLETE MODEL

At this point, in order to describe the entire process, it is useful to introduce the following efficiency definition, in which the chemical power stored in the methanol is compared with the global electrical power required by the plant.

$$\varepsilon = \frac{\text{Chemical power of produced MeOH}}{\text{Electrical power used for the production}} * 100 = \frac{\dot{m}_{\text{MeOH}} LHV_{\text{MeOH}}}{W_{el,global}} * 100 \quad (11)$$

The numerator that represents the mass flow rate of produced methanol has been obtained from Aspen PlusTM, while the lower heating value was taken from literature with the data showed in the Table 23 below.

MeOHout [kg/s]	MeOHout [kmol/s]	LHV _{MeOH} [kJ/kg]	MeOH chemical power [kW]
0,2189218	0,0068	19920	4361,331

Table 23. Complete model obtained results

Finally, the global efficiency of the plant can be evaluated:

$$\varepsilon = \frac{\dot{m}_{MeOH} LHV_{MeOH}}{W_{el,global}} * 100 = \frac{4361,331}{11788,197} = 37,01\% \quad (12)$$

6. ECONOMIC ANALYSIS

In this section, a preliminary economic analysis is carried out in order to evaluate the economic feasibility of the plant presented in the previous section.

The aim of this part of the thesis is to estimate, through a methodology explained in the following sections, the total cost of the methanol production plant, and in particular its Cost of Product, (COP), that represents the methanol price which allows the economic feasibility of the initial capital, the operating and maintenance investment for the 25 years considered. Regarding the determination of the electricity cost needed by the plant, various renewable energy sources have been considered in different scenarios.

Due to low amount of examples of large-scale constructed plant present into the world, and consequently due to even less information over this type of plant reported, the analysis performed is characterized by a quite elevated uncertainty.

Furthermore, the public incentives for tons of CO₂ avoided that the government should provide in order to cover part of the initial capital cost have been calculated.

In the next sections, the procedure followed, the costs estimated and the results obtained, will be described.

6.1 USED PROCEDURE

Before the description of the methodology followed in this study, it is useful to report the assumptions on which the calculation have been based, as the considered Project Life, the Operating Hours per year, the Basis Year and the expected Land.

Parameter	Assumption	Reference
Project Life [year]	25	[39]
Operating hours per year [h]	8000	[39]
Basis Year	2018	-
Land [m^2]	500.000	[40]

Table 24. Basic assumptions of economic analysis

The procedure followed into the determination of the Total Investment Cost (TIC) of the overall plant is mainly based into the evaluation of the cost element, called Bare Erected Cost (BEC). The BEC includes the cost of all the process equipment considered in the project.

After the definition of all costs of the considered components, the calculation continues with the definition of the main components of analysis, the capital expenditures (CAPEX) and operating expenses (OPEX) for the project. The elements of CAPEX and the OPEX have been evaluated mainly considering a percentage of the BEC or through considerations found in literature. The elements and the procedure for the cost determination will be explained in detail in the next section [39].

6.1.1 COST ESTIMATION

Regarding the cost of each component, the calculation has been based on purchasing costs of similar equipment found in literature. It is often the case that a price is known for a different size than what needed. In order to scale each equipment price according to its size, the following equation has been used [1] [41] [40] [42]:

$$C_{i_{ry}} = C_0 \cdot \left(\frac{S_i}{S_0}\right)^f \quad (13)$$

Where:

- C_0 : is the cost of a similar equipment found in literature;
- $C_{i_{ry}}$: is the cost of the selected element in the year considered into the reference;
- S_0 : is the Reference Size of the based equipment;
- S_i : is the Size of the considered element;
- f : is the Scale Factor;

Starting from the reference erected costs C_0 found in the various reference papers used for the calculation, $C_{i_{ry}}$ are evaluated comparing the selected element with the reference element found in literature through a Scaling Factor that characterize the component. This relation is done through a Scale Factor (f) that depend on the considered component.

The Scale Factor has been chosen considering the value found in the reference paper, but in case of absence of this information the “Six-Tenths-Rule” has been used, in which a value equal to $f = 0,6$ is considered [42].

After that, it is worth to consider that the obtained costs $C_{i,ry}$ of each component are referred to the year in which the considered year is based. In order to adapt them to the reference year of this work (2018) the chemical engineering plant cost index (CEPCI) has been used through the following formula:

$$\frac{C_i}{C_{i,ry}} = \frac{I_i}{I_{i,ry}} \quad (14)$$

Where

- C_i : Element Cost in the Basis Year of the analysis;
- $I_{i,ry}$: CEPCI of the reference year;
- I_i : CEPCI of the Basis Year;

The cost obtained are reported in the Table 27 and 28 in the section Results 6.2.

6.1.2 CAPEX COST

It is possible to evaluate the CAPEX as a percentage of the BEC as anticipated before, following the methodology used in the reference paper [40].

It includes the engineering services costs, project contingency costs, process contingency costs and the costs related of the instrumentation & control.

The engineering services cost, which includes for example the process design and the project management, has been considered as 8,4% of BEC.

With the Process contingency has been taken into account the uncertainty in cost estimates associated with processes that do not have sufficient commercialisation history, and it has been considered as 20% of BEC, due to the low amount of informations found in literature.

The same considerations could be done for the project contingency that has been taken into account as 15% of the sum of BEC, engineering services cost and process contingency.

The Instrumentation & control cost takes into account the necessary advice related to the control of the system has been evaluated as 5% of the Bare Erected Cost.

The sum of the BEC and of the engineering services costs, project contingency costs, process contingency costs and the costs related of the instrumentation & control forms the Total Purchasing Cost, (TPC).

Furthermore, into the calculation of the CAPEX, other variables have been considered in order to take in account Owner's costs. These parameters are evaluated as percentage of the above calculated TPC. Where, in particular [42]:

- Pre-production cost includes waste disposal cost for one month and an additional term;
- Inventory capital takes into account the replacement parts;
- Financing cost covers the cost of securing financing (excluding interest during construction);
- Other's owner cost including initial feasibility studies, local economic improvement, construction of infrastructures, legal fees, permitting costs and owner's engineering;

Then, also the cost of the Land has been considered and has been estimated as 0,6607 €/m². The assumptions for the calculation of the other elements of the CAPEX are reported in the Table 25 below.

Parameter	Assumption [% of TPC]	Reference
Pre-Production	2	[40] – [34]
Inventory Capital	0,5	[40] – [42]
Financing Cost	2,7	[40] – [42]
Other's Owner Cost	15	[40] – [39]

Table 25. Assumptions CAPEX

The sum of these elements listened in the table above and of the TPC calculated before, represents the Total Overnight Cost, (TOC)

The total results of the elements of the CAPEX will be reported in the section Results 6.2.

6.1.3 OPEX COST

The other main cost that has been taken into account into the methodology used for the economic analysis represents the operating and maintenance cost, considered in this work as OPEX.

This category has been divided into two components:

- Fixed OPEX cost, which is independent of power generation;
- Variable OPEX cost, which is proportional to power generation.

In particular, into the fixed cost have been considered: operating labour cost, maintenance labour cost, administrative & support labour cost and the insurance. The operating labour cost has been fixed as 75.000€/year, instead, for the other elements of the fixed OPEX, a percentage relative to the TOC calculated before has been considered as reported in the Table 26 below.

Parameter	Assumption [% of TOC]	Reference
Maintenance	2	[42]
Administrative and support labour	30	[42]
Insurance	1	[42]

Table 26. Assumptions fixed OPEX

Regarding the variable part of the OPEX, it includes the raw material and its replacement and the electricity needed by the plant.

In this specific case, the following elements have been taken in consideration: the water, the electricity used by the electric components, the cold and hot utility expressed in MW necessary to guarantee the right conditions into the plant and the cost for the compensation of the loss of MEA that is expected during the project life. [42]

Concerning the electricity necessary into the plant, it has been considered to use only electricity derived from renewable sources in order to follow the idea of the plant, the reduction of the CO₂ produced.

In order to examine all possible solutions available at the moment as renewable sources, the follow options have been considered

- Hydro
- Solar photovoltaics
- Concentrating solar power
- Offshore wind
- Onshore wind

For each of these options, the total cost over the project life has been calculated, and, as it will be reported in the next section, different considerations on the required methanol price or public incentives have been investigated.

As stated for the other categories, the results will be showed in the section 6.2.

6.1.4 REVENUES

In order to cover the investment required for the construction and the maintenance of the plant, it has been considered to sell the methanol, obviously being the objective of the plant, and also the oxygen, that is a product of the electrolysis.

The prices of the oxygen has been found in literature and has been considered constant in the 25-years considered as project life. The considered price of the oxygen is 150€/ton which represents a typical market value [43].

As it has been anticipated in the description of the analysis, the goal of the study is to obtain a selling price of the methanol that guarantees to balance the Total Investment Cost. The calculated value will be reported in the next section.

Furthermore, in this analysis it has been assumed to receive public incentives that are evaluated through the amount of tons of CO₂ not released into the atmosphere.

The results of the analysis are reported in the following section.

6.2 RESULTS

In this section are reported the results obtained from the calculation described in the previous section.

As anticipated, the first step of the calculation is the determination of the costs of each component. Based on the obtained cost, the Bare Erected Cost will be showed.

In the following Table 27 are reported the costs of the component in the Reference Year.

Components CCU	Scaling Parameter	C_0 [k€]	S_0	S_1	f	$C_{i,ry}$ [k€]	Ref.
Absorber	Volume [m ³]	3184	1131,0	1753,5	0,60	4142,3	[39]
Stripper	Volume [m ³]	482	69,1	568,8	0,60	1707,2	[39]
Pump	Power [kW]	155	227,0	2,0	0,60	9,1	[39]
Reboiler	Power [kW]	328	117100, 0	1420,3	0,60	23,2	[39]
Condenser	Power [kW]	71	29275,0	341,0	0,60	4,9	[39]
Components Meth							
Pump_H ₂ O	Power [kW]	155	227,0	1,0	0,60	6,0	[39]
Comp_H ₂	Power [kW]	12080	10000,0	194,9	0,67 ^a	863,5	[29]
Comp_CO ₂	Power [kW]	12080	10000,0	98,51	0,67 ^a	546,6	[29]
Column	MeOH. flow rate [kg/h]	1658	6,8	0,7881	0,70 ^a	368,7	[29]
Comp_F2GC	Power [kW]	12080	10000,0	94,1	0,67 ^a	530,2	[29]
Comp_Recc	Power [kW]	-	-	-	-	29,8	[44]
Heat Exchanger	Power [MW]	39260	355	4,365	1,00 ^a	482,7	[29]
PFR	Gas production [t/d]	12000	300,0	17,3	0,60	2164,2	[45]

^a Scale factor f from reference [27]

Table 27. Cost determination in the references' year

As it is possible to see in the table above, the cost of the Comp_Recc has not been evaluated following the same procedure used for the other components. Due to its small size, it has been supposed a based cost for this type of element found in the reference paper [44]. Regarding the electrolyzer, in order to evaluate the cost of the component the data elaborated by Gamba [18] have been used. So, it has been considered a specific cost for kW equal to 601€/kW that will be reported later. The results obtained in the Basis Years (C_i) taken in consideration in this work are showed in the table below, in which also the Bare Erected Cost is reported.

Components CCU	Reference Year	$I_{i,ry}[-]$	$I_i[-]$	C_i [k€]
Absorber	2016	541,7	603,1	4611,8
Stripper	2016	541,7	603,1	1900,7
Pump	2016	541,7	603,1	10,1
Reboiler	2016	541,7	603,1	25,9
Condenser	2016	541,7	603,1	5,5
Electrolyzer	-	-	-	6166,3
Components MeOH				
Pump_H ₂ O	2016	541,7	603,1	6,7
Comp_H ₂	2006	525,0	603,1	992,0
Comp_CO ₂	2006	500,0	603,1	659,3
Column	2006	500,0	603,1	444,7
Comp_F2GC	2006	500,0	603,1	639,5
Comp_Recc	2007	525,0	603,1	34,3
Heat Exchanger	2006	500,0	603,1	582,3
PFR	2016	541,7	603,1	2409,5
TOT (BEC) [k€]				21480,2

Table 28. Costs determination in the basis year

Regarding the CAPEX of the studied plant, the following results have been obtained. Where the value of the TPC represents the sum of the BEC and the elements of the Capital Cost.

Furthermore, the TOC is the sum of the TPC and the elements of the Owner's cost.

From this point, the results will be presented in Millions of Euro (M€) in order to make the calculation easily to understand.

Capital Cost	Cost [M€]
Engineering services cost	1,80
Process Contingencies	4,30
Project Contingencies	4,53
Instrumentation & control	1,07
TOT (TPC) [M€]	33,2
Owner's Cost	
Pre-Production	0,66
Land	0,33
Inventory Capital	0,17
Financing Cost	0,90
Other's Cost	4,98
TOT (TOC) [M€]	40,22

Table 29. Results CAPEX

Concerning the OPEX components, the fixed and variable cost of the considered elements are reported in the table below.

Fixed OPEX	Annual Cost [M€]	25-years Cost [M€]
Operating labour	0,75	18,75
Maintenance	0,80	20,11
Administrative and support labour	0,47	11,66
Insurance	0,40	10,06
TOT (FO) [M€]		60,57

Table 30. Results fixed OPEX

Variable OPEX	Quantity	Unitary Cost	Annual Cost [M€]	25-years Cost [M€]
Water [m^3]	1,57	6 [74]	0,07554	1,89
Cold Utility [MW]	1,81	6,88 [105]	0,35919	8,98
Hot Utility [MW]	1,14	6,07 [105]	0,19898	4,97
MEA make-up [kg]	1,86	1,042 [74]	0,01555	0,39
TOT (VO) [M€]				16,23

Table 31. Results variable OPEX

Regarding the electricity cost, element of the variable OPEX, as anticipated in the previous section of the thesis, various alternatives have been considered, all derived from renewable sources. After the calculation of the electricity required by the electric components of the plant, as reported in the Table 31, (10650,10 kW not considering the thermal power required), the annual quantity necessary in kWh has been evaluated, equal to 85200779,9 kWh. Basing the calculation on average data found in literature from the IRENA agency [44] and considering the electricity needed by the plant, the obtained costs of the various options are reported in the table below.

Sources	Cost [€/kWh]	Annual Cost [M€]	25-years Cost [M€]
Hydro	0,042	3,6	89,4
Solar photovoltaics	0,076	6,5	161,7
Concentrating solar power	0,165	14,1	351,8
Offshore wind	0,113	9,7	241,5
Onshore wind	0,050	4,3	106,5

Table 32. Cost of Electric energy sources considered

Finally, considering the sum of the components described into the methodology, TOC, FO, VO, equal to 117,03 M€, the Total Investment Cost (TIC) for all the possible sources of electricity have been obtained and are reported in the table below.

Sources	TIC [M€]
Hydro	206,41
Solar photovoltaics	278,88
Concentrating solar power	468,86
Offshore wind	358,56
Onshore wind	223,53

Table 33. Total Investment Cost of the various options considered

As it is notable from the Table 33 above, the most convenient option, from an economical point of view, is the use the electricity derived from a hydropower plant.

At this point, it is possible to evaluate the revenues of the plant. Through this analysis it has been determined the selling price at which the methanol should be sold in order to cover the TIC just calculated.

The calculation has been carried out considering a fixed selling price of the oxygen equal to 150€/ton. This assumption allows to evaluate the total revenues that the oxygen sold in 25–years can provide, i.e. 40,65 M€.

Taking into account to cover the residual part of the TIC with the selling of the methanol without any public incentives, the following Cost of Products (COP) have been obtained. It is worth to underline that they have been considered constant over the 25-years of the plant for all the options considered.

Sources	COP [€/ton]
Hydro	1051,6
Solar photovoltaics	1510,1
Concentrating solar power	2716,6
Offshore wind	2016,8
Onshore wind	1160,2

Table 34. Cost of Product (COP) for the various scenarios

Nowadays, the average price of the methanol available into the market is equal to 400€/ton [43] As it is reported in the table above, the obtained price of the methanol are much higher than the actual selling price. However, the price of the methanol is expected to raise in the next years considering an increase of the methanol demand. As reported in the study conducted by D.Bellotti et al. [43], in the future the methanol price could probably increases from 400€/ton to 800€/ton. For this reason, in this analysis it has been investigate the cases in which the selling price of the methanol is maintained constant at the values equal to 400, 600, 800€/ton. In these considered cases, the remaining part of the TIC has been considered to be covered by the public incentives calculated as a price for tons of CO₂ not released into the atmosphere.

Among the renewable sources considered, only the most convenient option, the hydropower one, has been considered.

Sources	MeOH Price [€/ton]	CO ₂ Incentives [€/ton]	Total CO ₂ Incentives [M€]
Hydro	400	549,54	102,71
	600	380,87	71,19
	800	212,20	39,66

Table 35. Hypothetical necessary public incentives

From the calculation made, as it was to be expected, from an economical point of view, the considered plant is not the most attractive option for the production of methanol.

Although has been followed a simplified procedure, it is possible to note the high cost of some components, like the electrolyser and the absorber, that very affect the final value of the Bare Erected Cost, and consequentially the other terms that are based on the BEC.

Furthermore, the elevated required energy for the electrolysis and for the regeneration of the solvent into the CCU process has a big impact on the Total Investment Cost of the plant. These are the main reasons that limit the development of this type of plant.

In fact, as it is possible to see from the latest tables that report the results of the economic analysis, the most attractive option is based on the assumption that the price of the methanol should double in the next years and that the total public incentives received should be approximately equal to 40 M€. In addition, it is worth to underline that, in this simplified methodology, the considered prices or costs are maintained constant over the 25-years assumed as Project Life and that, with the calculation made, the goal of the analysis is to balance the investment, without any economic gain.

However, hoping in a reduction of the required energy and its relative cost, and trusting on the public incentives that could help the construction of these type of plants, a methanol economy could represents a possible scenario of the future.

7. CONCLUSIONS AND FUTURE WORKS

The aim of this thesis is to model and to simulate a Carbon Capture Utilization (CCU) process, based on post combustion carbon dioxide (CO₂) capture from a combined heat and power plant by the use of chemical absorption. The captured CO₂ has been used, as required in CCU system, in order to produce methanol (CH₃OH) by the hydrogenation of the CO₂, using hydrogen (H₂) obtained through water electrolysis.

Regarding the CO₂ capture system, it has been chosen to use the chemical absorption technology based on the utilization of monoethylamine (MEA) that represent the most mature option available at the moment. The model has been based on a real pilot plant.

The model of CCU part has been successfully validated comparing the data found in literature for the considered plant with the ones obtained from the model, in terms of specific energy requirement, CO₂ removal rate and L/G ratio.

After this, using the CO₂ hydrogenation model previously elaborated by Calogero [21], it has been possible to connect the models in order to simulate the whole process, from the CO₂ capture to methanol production. Therefore, the CCU model has been scaled up with the purpose to meet the mass flow rate of CO₂ required by the hydrogenation part.

The complete model has been described through the specific energy requirement, the CO₂ removal rate and the energy efficiency of the plant. In particular, considering to reach a removal rate equal to 90%, a value of specific energy requirement 4,113 GJ/tCO₂, that is a consistent with the other data found in literature concerning this type of process [37] [38] [8].

In addition, a pinch-point analysis has been performed in order to reduce the amount of heating and cooling requirement of the whole plant, being this aspect one of the most important disadvantage of this type of plant. Therefore, a Heat Exchanger Network (HEN) has been proposed.

Finally, an economic analysis based on simplified considerations has been done with the aim of evaluating the economic feasibility of the plant and to underline the critical issues of the process.

After the abovementioned analysis, it is possible to state that this type of plant represents one of the possible options in order to reach a net reduction of CO₂ emissions in Europe, thus contributing to climate change mitigation.

As notable by the results obtained, there is a need for research and development focused on CCU options in order to reduce the energy consumption required for the regeneration of the solvent, which is one of the most relevant cost of the plant that limits the development of this technology. It is worth to underline that it has been considered to use only renewable sources in order to satisfy the electric power requirement of the plant, according to the final goal of the reduction of CO₂ released into the atmosphere. Among various options considered, the hydro-power electric generation has been identified as the most convenient one.

Regarding the results obtained from the economic analysis, considering the high capital cost of the plant (columns, pumps, heat exchangers and initial solvent, reactor, electrolyser) and the high operating cost (mainly reboiler duty and electrolyser but also electrical power for machinery and solvent makeup), it appears that the theoretical methanol price which it should be chosen in order to cover the total investment of the plant is approximately 2,5 times higher than the actual one.

Considering an increase of methanol price from 400€/t_{CO2} to 800€/t_{CO2}, as reported in many reference papers that take into account a development of methanol economy, public incentives are necessary in order to permit the economic feasibility of the plant. These incentives have been estimated in terms of euro for tons of CO₂ not released into atmosphere [€/t_{CO2}].

In conclusion, it is possible to state that while this capture technology is being considered for largescale application on existing power plants, it is necessary to further optimize the individual process units and improve the overall process economics.

7.2 FUTURE WORKS

In order to improve the CCU technology and consequently the methanol production plant, with the purpose to overcome the limits that have been found through the simulation of the complete model and especially through the economic analysis, further developments of this topic could take into account:

- To use different solvent;
- To test different sizes of the absorber;
- To evaluate possible increment in the O₂ price;
- To include in the model water recirculation and washing sections;
- To evaluate the storage conditions of methanol;
- To scale up overall plant in order to analyse the proportion between the increment into the Total Investment Cost and the increase of revenues;
- To perform an economic analysis based on future scenario considerations, regarding the component and electricity price.

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