



National Technical University of Athens

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Diploma Thesis

***Production of Green Hydrogen Through
Methanol: A Technoeconomic Analysis***

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Athens, September 2024

Acknowledgments

This thesis was carried out in Chemical Process Engineering Unit in cooperation with the Thermodynamic and Transport Phenomena Lab in the school of Chemical Engineering, NTUA.

First, I want to express my warm gratitude to Professor Georgios Stefanidis and Professor Epameinondas Voutsas for presenting me the opportunity to work on such an interesting topic as well as their guidance, scientific expertise and availability.

Furthermore, I want to thank PhD Vicky Louli, Laboratory Technical Staff for her day-to-day aid throughout.

With the completion of this thesis, life as a student comes closer to the end. I am very thankful for every moment the last five years and hope for fruitful years to come

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Abstract

Methanol is emerging as a promising green hydrogen carrier due to its favorable chemical properties, ease of storage, and transportability. As a liquid at ambient conditions, methanol offers significant advantages over conventional hydrogen storage methods, such as compressed or liquefied hydrogen.

This thesis explores methanol's role in hydrogen production through reforming processes, where it can be efficiently converted back into hydrogen with low energy demand. In the framework of the thesis, methanol is synthesized from captured CO₂ from the flue gas of a typical cement industry, making it a carbon-neutral option within a circular energy economy. Green hydrogen used for methanol production is generated via water electrolysis in an alkaline electrolyser, which provides a sustainable and carbon-free method essential for transitioning to a clean energy economy. Aspen Plus™ was employed to simulate the whole process: the electrolyser for the H₂ production, the CO₂ capture process and the methanol production process.

The simulation of the electrolyser utilized semi-empirical equations from the original work of Sanchez et al., which describe a 15-kW experimental electrolyser. The stack model was successfully validated, with the results closely matching those from the original paper. An integrated 58.6 MW electrolysis system was subsequently developed, with simulations performed at three different stack pressures (5, 7, and 9 bar) and three inlet temperatures (50°C, 75°C, and 80°C). The feed mixture entering the stack consisted of 65% w/w H₂O and 35% w/w KOH electrolyte. Comparison with a 1.5 MW commercial alkaline electrolyser showed consistent hydrogen production. The optimal operating conditions were identified as 5 bar and 80°C. A techno-economic analysis was conducted, using photovoltaics (PV) as the electrical supply source, resulting in a calculated Levelized Cost of Hydrogen (LCOH) of 6.99 €/kg.

Concerning the carbon dioxide capture process, for a CO₂ flow of 1055.5 ktonnes per year entering the system, it successfully captures 90% of the CO₂ using an aqueous 30% wt. MEA solvent. The process requires 149 MW of heat energy in the stripper column reboiler, for CO₂. A sensitivity analysis indicated an optimal loading of 0.2, which minimizes the reboiler duty while balancing costs such as pump work, heat exchanger surface area, and cooling duty. Increasing the number of stages in both the absorber and stripper columns reduces the reboiler duty and reflux ratio. However, the impact diminishes beyond 10 stages for the stripper column, suggesting that 8 stages are optimal for balancing performance and capital costs, while the absorber column operates with 12 stages. The total equipment cost for the CO₂ capture unit is approximately 45.5 million euros, with the absorber, stripper, scrubber, and heat exchanger contributing the most to the total cost. Utility costs, including cooling water, steam, and electricity, amount to approximately 22 million euros per year. Additionally, the variable operating costs, including MEA makeup, add another 25.6 million euros annually. The levelized cost of the carbon capture process is about 46 €/ton CO₂, which aligns with values found in the literature. However, due to the high annualized revenue from CO₂ capture (73.4 €/ton CO₂ captured), the process is profitable by 27.4 €/ton CO₂.

The methanol production process uses a slightly modified process flow diagram to the one proposed by Kiss et al., replacing the stripper column with a low-pressure separation

vessel. A parametric analysis examines the effects of reactor pressure and temperature on methanol production, focusing on optimizing energy use and production efficiency. Optimal reactor pressure is found to be 50 bar, where energy demand is minimized. The reactor temperature of 250°C is chosen as it provides the best balance for methanol production and carbon dioxide conversion. The economic analysis includes CAPEX of €7.1 million, driven mainly by compression, distillation, and heat exchangers., while the OPEX is €20 million per year, with electricity as the largest contributor. The levelized cost of methanol was calculated to be 533.03 €/tonMEOH.

In conclusion, for methanol production from H₂ produced by electrolysis and CO₂ captured from the flue gas of a typical cement industry, the cost of electrolysis was estimated at 2235.52 €/ton MeOH, the cost of CO₂ capture at -92.66 €/ton MeOH, and the cost of methanol production at 533.03 €/ton MeOH, resulting in a final total cost of 2675.89 €/ton MeOH. Compared to the commercial cost of methanol, which is 535 €/ton MeOH, indicates that there are many steps ahead to achieve a 'greener' world.

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1 Introduction

1.1 Green Hydrogen

The rising global energy demand and the need for sustainable energy solutions have placed hydrogen production at the forefront of renewable energy research. Historically, hydrogen production has heavily relied on fossil fuels, which contribute significantly to greenhouse gas emissions. However, with the global push towards decarbonization and initiatives like the Paris Agreement, there is a shift toward green hydrogen production technologies. Green hydrogen, produced via the electrolysis of water using renewable energy sources such as solar or wind power, offers an environmentally friendly alternative to conventional hydrogen production methods. In this context, the combination of photovoltaic (PV) systems with electrolytic cells represents a promising technology. This system uses solar energy to generate electricity, which is then utilized in water electrolysis to produce hydrogen without any carbon emissions. The shift towards green hydrogen is critical, given that current hydrogen production methods, such as steam methane reforming and coal gasification, contribute to significant CO₂ emissions. For example, brown hydrogen production from coal releases approximately 10-12 tons of CO₂ per ton of hydrogen produced. The alternative, blue hydrogen, involves carbon capture and storage (CCS), which mitigates some emissions but still carries uncertainties regarding long-term CO₂ storage and potential leaks. With renewable-powered green hydrogen, the goal is to achieve a scalable and versatile production process that aligns with global efforts to reduce greenhouse gas emissions. Solar energy offers a vast and untapped resource that can be harnessed for green hydrogen production, contributing to the transition towards a more sustainable and decarbonized energy future. The global demand for energy continues to rise due to population growth, improving living standards, and industrial expansion in developing countries.

As of 2019, the global primary energy supply reached 14,410 MTOE, and projections indicate that energy demand will increase by 50% by 2030. Currently, more than 95% of this energy is generated from fossil fuels, which significantly contribute to greenhouse gas emissions and global warming. This underscores the urgent need for alternative green energy technologies to meet growing energy demands while fostering sustainable development. In response to climate change, international agreements like the Paris Agreement have set targets to limit global temperature increases to below 1.5°C. Many countries are implementing environmentally friendly energy policies aimed at reducing greenhouse gas emissions and achieving decarbonization.

For example, South Korea has introduced a plan to reduce its emissions from 709.1 million tons in 2017 to 536 million tons by 2030. This has prompted research institutions and organizations around the world to develop innovative technologies that can harness renewable energy sources to produce green energy and fuels. Hydrogen is a promising, environmentally friendly renewable energy carrier and the most abundant element in the universe. Despite its abundance, hydrogen does not exist in its pure form on Earth and must be extracted from compounds like water, fossil fuels, and biomass. The challenge lies in efficiently and economically separating hydrogen from these sources. Hydrogen can be produced from various raw materials, both renewable and non-renewable, with annual production totaling around 87 million tons. However, as of 2020, the vast majority of hydrogen (95%) was produced from non-renewable fossil fuels, particularly through

steam reforming of natural gas, which generates 830 million tons of CO₂ annually. Only a small fraction of hydrogen was produced from renewable sources such as water electrolysis. The major hydrogen production methods and their applications are as shown in Table 1.1 [1]

Table 1.1 Hydrogen Production Methods and their applications

Hydrogen Production	Hydrogen Consumption	
Steam Reforming of Natural Gas 49 %	<i>Fuel</i>	<i>Chemical</i>
Partial Oxidation of Hydrocarbons 29 %	Fuel Cells	Petroleum Recovery & Refining 47 %
Coal Gasification 18 %	Engines/Turbines	Methanol Production 4 %
Electrolysis 4 %	Energy Storage	Electronics
		Ammonia Production 45 %
		Metal Processing & Fabrication 2 %
		Food Processing
		Cosmetics

Hydrogen production methods are classified by different color labels based on the technology used, the energy source, and the environmental impact as shown in Table 1.2 [1] [2]

Table 1.2 Hydrogen color shades and their Technology, cost, and CO₂ emissions

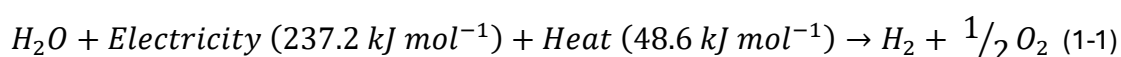
Hydrogen Color	Technology	Source	Products	Cost (\$/kg H ₂)	CO ₂ emissions
Brown Hydrogen	Gasification	Lignite	H ₂ + CO ₂	1.2-2.1	High
Black Hydrogen	Gasification	Black coal (Bituminous)	H ₂ + CO ₂	1.2-2.1	High
Grey Hydrogen	Reforming	Natural Gas	H ₂ + CO ₂ (Released)	1-2.1	Medium
Blue Hydrogen	Reforming & Carbon Capture	Natural Gas	H ₂ + CO ₂ (Captured 85-95 %)	1.5-2.9	Low
Green Hydrogen	Electrolysis	Water	H ₂ + O ₂	4-6	Minimal

Blue hydrogen is generated through the steam reforming of natural gas, where natural gas is broken down into hydrogen (H₂) and carbon dioxide (CO₂). The CO₂ produced in this process is captured at a rate of 85% to 95% and stored underground using carbon capture and storage (CCS) techniques, although some CO₂ cannot be captured. Additionally, the long-term effects of CO₂ storage remain uncertain, and potential leakage poses environmental and climate risks. Gray hydrogen is also produced from non-renewable fossil fuels like natural gas or coal through steam reforming or auto-thermal reforming,

but in this case, the CO₂ generated is not captured and is instead released directly into the atmosphere. Brown hydrogen, the most commonly used type today, is produced from hydrocarbon-rich feedstocks such as brown coal or methane through gasification, releasing 10 to 12 tons of CO₂ for every ton of hydrogen produced. Black hydrogen is also created through coal gasification, where syngas is produced and hydrogen is separated from the other gases, while the remaining gases are emitted into the atmosphere. In contrast, green hydrogen is produced through the electrolysis of water using renewable energy sources like solar or wind power, splitting water into hydrogen (H₂) and oxygen (O₂) without any carbon emissions. As the world moves toward decarbonization, renewable-powered green hydrogen is gaining traction as a viable solution to reduce greenhouse gas emissions and environmental pollution. Consequently, there is growing interest in making green hydrogen production and utilization more scalable and versatile to meet the energy needs of a sustainable future.

1.2 Water Electrolysis

Water electrolysis is a prominent electrochemical technique used for green hydrogen production by splitting water into hydrogen and oxygen with the help of electricity, making it an emission-free technology. The fundamental reaction of water electrolysis is as follows in Eq. (1).



The fundamental reaction of water electrolysis requires a theoretical thermodynamic cell voltage of 1.23 V to achieve this process at room temperature. However, in practice, a cell voltage of 1.48 V is necessary to effectively split the water due to the additional energy needed to overcome the kinetics and the ohmic resistance of the electrolyte and cell components.

Electrolysis is a crucial technology for splitting water into hydrogen and oxygen using renewable energy sources such as solar and wind power. Solar and wind are particularly well-suited for hydrogen production via water electrolysis due to their wide availability and power distribution. Combining renewable energy with water electrolysis offers additional benefits, as excess electrical energy can be stored in the form of hydrogen, helping to balance the gap between energy production and demand. The hydrogen and oxygen produced through this process can be directly utilized in transportation and industrial sectors as primary energy sources. Beyond being a primary energy source, hydrogen also serves as an energy carrier, suitable for use in fuel cell vehicles and various industrial applications. Additionally, hydrogen is a valuable feedstock in chemical and petrochemical industries to produce ammonia and synthetic fuels. Another advantage of using hydrogen as an energy carrier is that hydrogen storage systems generally offer higher efficiency compared to batteries.

Over the past two centuries, water electrolysis has been recognized as a viable technology for green hydrogen production. Despite its potential, only about 4% of global hydrogen production (equating to 65 million tons) is currently derived from water electrolysis, primarily due to economic constraints. A significant portion of this hydrogen is produced as a by-product of the Chlor-alkali industry. The largest electrolysis plant,

with a capacity of 135 MW and capable of producing 30,000 Nm³/h of hydrogen, has been deployed in the fertilizer industry. Since its inception in the 18th century, water electrolysis technologies have evolved across five distinct generations, each marked by specific challenges, technological advancements, and significant contributions to industrial applications. These generations and their developments are illustrated in Figure 1.1 [3]

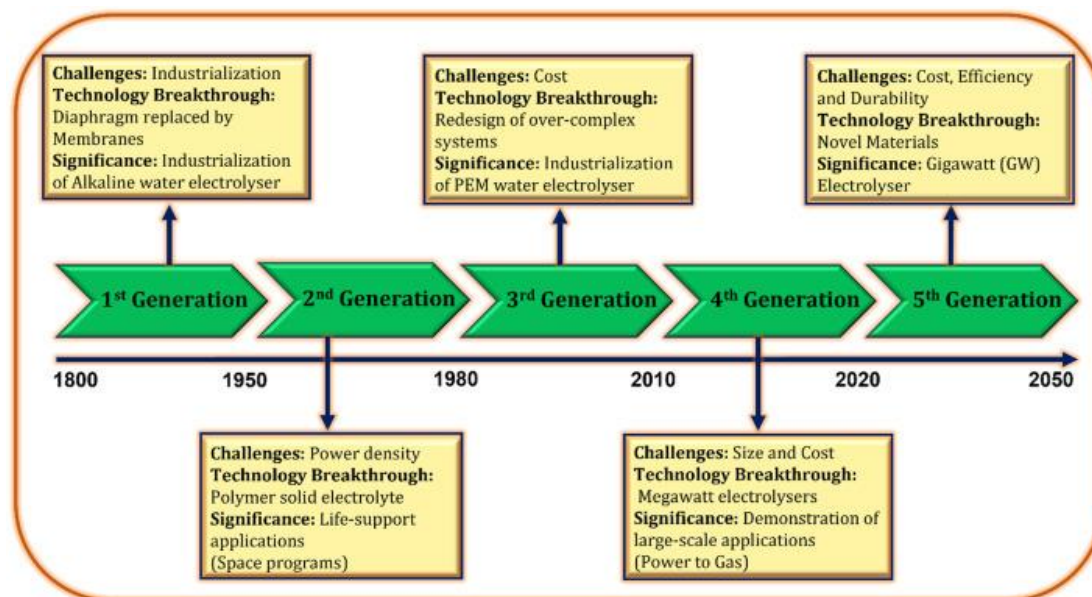


Figure 1.1 Generations of Water Electrolysis Development

Electrolysis technologies play a pivotal role in the sustainable production of hydrogen by splitting water into hydrogen and oxygen using electrical energy. Among the prominent electrolysis methods, alkaline electrolysis (AE), proton exchange membrane (PEM) electrolysis, and solid oxide electrolysis (SOE) are the most widely researched and applied. Alkaline electrolysis, a well-established technology, operates with a liquid electrolyte, typically potassium hydroxide, and offers relatively low-cost hydrogen production. PEM electrolysis, on the other hand, uses a solid polymer electrolyte, enabling higher efficiency, faster start-up times, and better integration with renewable energy sources, although it tends to be more expensive due to the use of noble metal catalysts. Solid oxide electrolysis operates at high temperatures and can utilize both electricity and heat, potentially leading to higher overall efficiency, particularly when integrated with industrial processes. Each of these technologies has its unique advantages and challenges, and ongoing research aims to improve their efficiency, durability, and cost-effectiveness, making them critical components of the future hydrogen economy.

1.3 Alkaline Electrolysis

Alkaline water electrolysis (AWE) is a well-established and mature technology for large-scale hydrogen production, capable of operating in the multi-megawatt range for commercial applications worldwide. The technology was first introduced by Troostwijk and Diemann in 1789, and after further developments, the first large-scale alkaline electrolyser plant began operations in 1939, with a capacity of 10,000 Nm³/h of hydrogen.

By the early 20th century, over 400 industrial alkaline electrolyser units had been successfully installed and were in operation.

AWE operates at relatively low temperatures (30–80°C) and uses a concentrated alkaline solution, typically 5M KOH or NaOH. The system employs nickel-coated stainless-steel electrodes and asbestos or zirconia-based diaphragms as separators. In this process, hydroxyl ions (OH^-) act as the ionic charge carriers, and the electrolyte solution facilitates the electrochemical reactions by permeating through the diaphragm's porous structure.

This technology remains favorable for large-scale applications due to its established design and cost structure. Current investment costs for alkaline water electrolysis range from USD 500 to 1000 per kW [4], with a system lifespan of approximately 90,000 hours. However, this technology faces several challenges. One significant issue is the limited current densities (0.1–0.5 A/cm²) resulting from moderate OH^- mobility and the corrosive nature of KOH electrolytes. The presence of CO_2 in the environment can lead to the formation of potassium carbonate (K_2CO_3), which decreases hydroxyl ion concentration and ionic conductivity. Additionally, K_2CO_3 can clog the pores of the anode gas diffusion layer, reducing ion transfer efficiency and hydrogen production rates. Furthermore, the alkaline electrolysis process typically produces gases with a purity of 99.9%, as the diaphragm does not entirely prevent gas crossover between the cells.

AWE process involves two distinct half-cell reactions: the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. During the alkaline electrolysis process, at the cathode, two moles of the alkaline solution are reduced to produce one mole of hydrogen (H_2) and two moles of hydroxyl ions (OH^-). The generated hydrogen gas is then released from the cathode surface. Meanwhile, the hydroxyl ions migrate through the porous separator and the electric circuit from the cathode to the anode. At the anode, these hydroxyl ions are oxidized to produce one mole of oxygen (O_2) and one mole of water (H_2O), as illustrated in Figure 1.2.

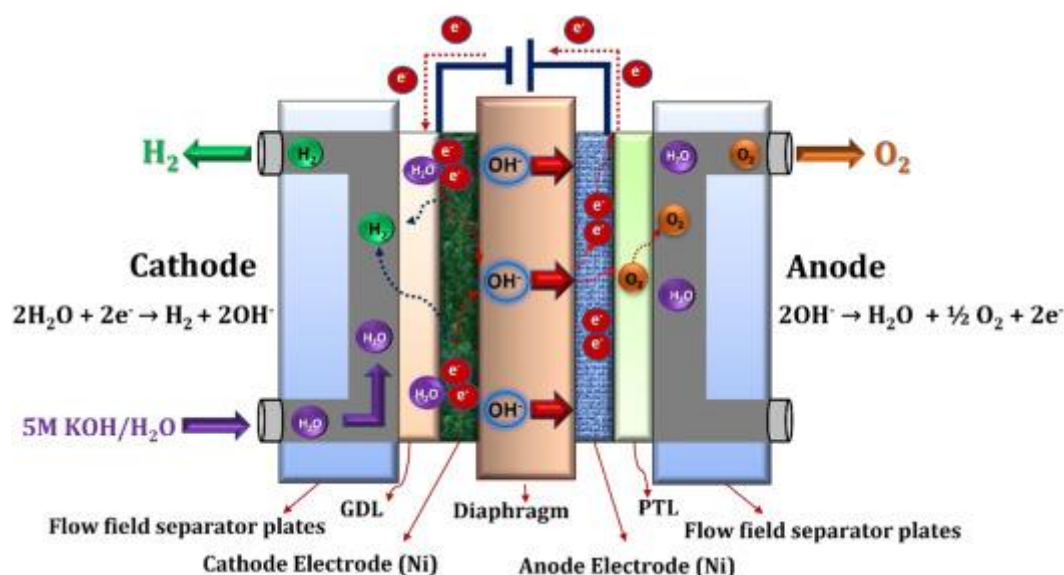


Figure 1.2 Schematic illustration of alkaline water electrolysis working principle

The primary components of an AWE cell include diaphragms or separators, current collectors (gas diffusion layers), separator plates (bipolar plates), and end plates. Typically, asbestos, Zirfon, or nickel-coated perforated stainless-steel materials are used for the diaphragms or separators in alkaline electrolysis. Gas diffusion layers are commonly made from nickel mesh or foam, while the separator plates, also known as bipolar plates, are generally constructed from stainless steel or nickel-coated stainless steel. The end plates are made from stainless steel or similar materials to complete the cell assembly. [5]

1.4 Hydrogen Carriers

Hydrogen carriers for storage and transport are crucial technologies that enable the safe, efficient, and practical handling of hydrogen. Due to hydrogen's low volumetric energy density, storing and transporting it in its gaseous form can be inefficient and costly. Hydrogen carriers offer alternative methods to store hydrogen in a more stable and denser form, which is especially useful for long-distance transport, large-scale energy storage, and industrial use.

Hydrogen can be stored and transported:

- **As compressed hydrogen gas (CH_2):** Hydrogen is compressed at high pressures (usually between 350 and 700 bar) and stored in specialized high-pressure tanks made of strong materials like carbon fiber. CH_2 is widely used and commercially available, suitable for short- to medium-range transport (e.g., vehicles, pipelines). However, high-pressure systems require strong, costly materials for safety. Additionally, compressed hydrogen has lower energy density compared to other carriers and presents potential safety risks due to high pressure.
- **As liquefied hydrogen (LH_2):** Hydrogen is cooled to cryogenic temperatures (-253°C) to convert it into a liquid. LH_2 has a higher energy density compared to compressed hydrogen and is suitable for large-scale storage and long-distance transport. However, liquefaction requires significant energy ($\sim 30\text{--}40\%$ of hydrogen's energy content), and advanced cryogenic tanks are necessary to maintain extremely low temperatures. Boil-off losses can also occur during storage and transport.
- **Ammonia (NH_3):** Hydrogen can be stored in ammonia, which contains 17.6% hydrogen by weight. Ammonia can be decomposed (cracked) into hydrogen and nitrogen at the point of use. NH_3 has high hydrogen content and is liquid under moderate conditions (about -33°C at atmospheric pressure). There is an established infrastructure for ammonia production, transport, and storage. However, ammonia is toxic and corrosive, requiring careful handling and safety measures. Its cracking to release hydrogen is energy-intensive, and the decomposition process can produce nitrogen oxides (NO_x) as pollutants.
- **Liquid Organic Hydrogen Carriers (LOHCs):** LOHCs are organic compounds like methylcyclohexane (MCH), which can chemically absorb hydrogen to form a hydrogenated liquid (e.g., from toluene to MCH). Hydrogen can be released through a catalytic process, and the carrier can be reused. LOHCs remain liquid under ambient conditions, making them easy to handle and transport using existing fuel infrastructure. They are also non-toxic and non-explosive. However, energy is required to release hydrogen from LOHCs, and catalyst degradation can affect efficiency.

- **Methanol:** Methanol is a liquid chemical that contains hydrogen. Through reforming processes, hydrogen can be released from methanol for use in fuel cells or other applications. Since methanol is liquid at ambient temperatures, it makes it easier to store and transport. It can use existing liquid fuel infrastructure and can be produced from renewable sources such as biomass or CO₂. However, hydrogen release requires an energy-intensive reforming process, and CO₂ emissions are produced during reforming unless captured.
- **Metal Hydrides (MHs):** Certain metals (e.g., magnesium) can absorb hydrogen and form solid metal hydrides. Hydrogen can then be released by heating the metal hydride. MHs offer high volumetric hydrogen storage density and are considered a safe, solid-state storage option. However, the materials are heavy, reducing gravimetric energy density, and high temperatures are required for hydrogen release. Additionally, some metal hydrides exhibit slow absorption/desorption kinetics.
- **Adsorbent Materials (e.g., MOFs, Carbon Nanotubes):** Metal-organic frameworks (MOFs) and carbon nanotubes are highly porous materials that can adsorb hydrogen gas at high densities. They offer high surface areas for hydrogen adsorption and have potential for high hydrogen storage capacity. However, this technology is still under development and is not yet commercially viable.

1.5 Methanol

1.5.1 Methanol Synthesis

In the context of utilizing carbon dioxide to produce valuable chemical products, many technologies have been developed to convert CO₂ into various products. One of the promising chemicals that can be produced through the hydrogenation of carbon dioxide, with increasingly growing global demand, is methanol. Methanol is one of the most commercially active chemicals worldwide, with demand estimated to range between 27 and 29 billion cubic meters annually. Methanol is a colorless and highly volatile liquid, with vapors slightly heavier than air, and it is completely miscible with water. Methanol is one of the most valuable chemicals with a wide range of uses and can be produced through the hydrogenation of carbon dioxide, under the concept of "Power-to-Liquid." In the chemical industry, it is used either as a solvent or as a reagent and is found in various everyday products, such as paints, cleaners, synthetic fibers, and fuels. It serves as an energy resource for the shipping, automotive, and electricity sectors. Methanol is also utilized in the production of oxygenates (drop-in-fuels) additives for gasoline, such as MTBE (methyl tert-butyl ether) and TAME (tert-amyl methyl ether), which have replaced toxic tetraethyl lead. Currently, methanol is industrially produced from syngas (synthesis gas) derived from fossil fuels (e.g., coal), natural gas, or through catalytic hydrogenation of atmospheric carbon dioxide over a catalyst. Therefore, in this study, the process of converting carbon dioxide into methanol is examined and simulated. Table ?? presents the physical properties of methanol.

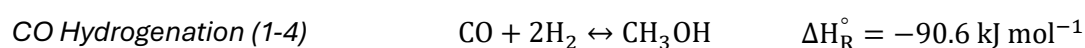
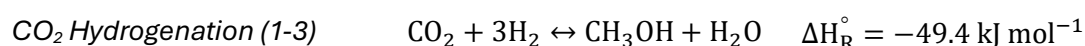
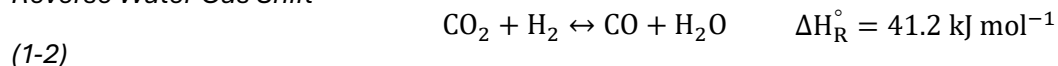
Table 1.3 Physical properties of methanol [6]

<i>Molecular formula</i>	CH₄O / CH₃OH
<i>IUPAC Name</i>	Methanol
<i>Physical state</i>	Liquid
<i>Color</i>	Colorless
<i>Boiling point, 1 atm [°C]</i>	64.7
<i>Density [g/L]</i>	791
<i>Vapor pressure, 20°C [bar]</i>	0.37
<i>Octane rating</i>	110-112
<i>Cetane number</i>	5 (low)
<i>Heating value [kJ/mol]</i>	726.1

1.5.2 Classical Methanol Synthesis Processes

Methanol synthesis on an industrial scale began in 1923 at BASF's facilities in Germany. The process was carried out using a $\text{ZnO/Cr}_2\text{O}_3$ catalyst under very high temperature conditions (350-450°C) and extremely high pressure (250-350 bar). Since the 1960s, when sulfur was removed from syngas, allowing the use of a copper-based catalyst, it has been possible to conduct the process at comparatively lower pressures (50-100 bar) and temperatures between 200-300°C. At lower temperatures, the catalyst remains practically inactive, while at higher temperatures, it deactivates due to limited thermal stability. Catalytic synthesis represents the most developed conversion process for more efficient carbon recovery. Direct hydrogenation of CO_2 results in fewer by-products and lower energy requirements for product purification to meet desired specifications. However, it leads to significantly higher operational costs compared to the conventional methanol production process. The conventional methanol production process is described by the following reaction scheme (Reactions 1-1 to 1-3), which occurs over a Cu/ZnO catalyst.

Reverse Water Gas Shift



The first reaction is referred to as the Reverse Water Gas Shift Reaction (RWGS), a side reaction where carbon monoxide (CO) and water (H_2O) are produced. The reverse of this reaction is known as the Water Gas Shift (WGS) reaction. Both synthesis reactions, from CO_2 and CO (Reactions 1-3 and 1-4), are exothermic and result in a reduction of volume. This leads to the conclusion that methanol synthesis is favored at low temperatures and high pressures. Additionally, it appears that methanol can also be produced via CO hydrogenation, with methanol being the sole product. The presence of CO in the feed has been observed to be beneficial for methanol production. When CO is present, the RWGS reaction (if the CO concentration is higher than its equilibrium concentration) generates more CO_2 , which subsequently leads to increased methanol production.

Moreover, the presence of CO is crucial because it helps "clean" the stream of excess water through the Water Gas Shift (WGS) reaction.

1.5.3 Kinetic Models for Methanol Synthesis

Numerous kinetic models have been proposed in the literature, each assuming different reaction pathways and conditions. **Leonov et al.** [7] were the first to derive a kinetic model for methanol synthesis on a **Cu/ZnO/Al₂O₃** catalyst, without considering the effect of carbon dioxide in the feed. Later, **Villa et al.** and **Klier et al.** proposed models that did not treat carbon dioxide as the primary reactant. [8] [9]

Graaf et al. [10] introduced a kinetic model that accounts for both the hydrogenation of carbon monoxide (CO) and carbon dioxide (CO₂), as well as the Water Gas Shift (WGS) reaction. **McNeil et al.** [11] developed a kinetic model based on mechanistic insights into CO₂ hydrogenation, as reported in the literature, rather than relying on empirical expressions like other models.

The kinetic model of **Froment and Bussche** [12] was derived from a series of experiments, based on a reaction scheme that assumes CO₂ as the main carbon source for methanol synthesis. This model also describes the effects of temperature, pressure, and gas-phase composition.

Kubota et al. [13] considered the hydrogenation of CO₂ as the dominant reaction. **Rovovskii and Lin** [14] proposed a theoretical kinetic model that aligns well with experimental data. **Lim et al.** [15] developed an integrated kinetic model consisting of 48 reaction rates, each based on different reaction stages on a **Cu/ZnO/Al₂O₃/ZrO₂** catalyst.

Table 1.4 summarizes the kinetic models proposed in the literature for methanol synthesis, along with the operating conditions where available.

Table 1.4 Summary of Selected Kinetic Models for Methanol Synthesis via CO₂ Hydrogenation Proposed in the Literature, Along with Their Reported Operating Conditions.

Condition s	Kinetic model	Author, year
220-260 °C 40-45 atm	$r_{CH_3OH} = k \left(\frac{p_{CO}^{0.5} p_{H_2}}{p_{CH_3OH}^{0.66}} - \frac{p_{CH_3OH}^{0.34}}{p_{CO}^{0.5} p_{H_2} K_2^*} \right)$	Leonov et al., 1973 [7]
225-250 °C 75 atm	$r_{CH_3OH} = const \frac{K_{redox}^3 \left(\frac{p_{CO_2}}{p_{CO}} \right)^3 \left(p_{CO} p_{H_2}^2 - \frac{p_{CH_3OH}}{K_2^*} \right)}{\left[1 + K_{redox} \left(\frac{p_{CO_2}}{p_{CO}} \right) \right]^3 (F + K_{CO_2} p_{CO_2})^n + k' \left(p_{CO_2} - (1/K_1^*) (p_{CH_3OH} p_{H_2O} / p_{H_2}^3) \right)}$	Klier et al., 1982 [9]
N/A	$r_{CH_3OH} = \frac{f_{CO} f_{H_2}^2 - f_{CH_3OH} / K_2^*}{(A + B f_{CO} + C f_{H_2} + G f_{CO_2})^3}$ $r_{RWGS} = \frac{f_{CO_2} f_{H_2} - f_{CO} f_{H_2O} K_3^*}{M^2}$	Villa et al. 1985 [8]

210-245 °C 15-50 bar	$r_{CH_3OH} = \frac{k_1 K_{CO} (c_{CO} c_{H_2}^{3/2} - c_{CH_3OH} / c_{H_2}^{1/2} K_1^{eq})}{(1 + K_{CO} c_{CO} + K_{CO_2} c_{CO_2}) (c_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) c_{H_2O})}$ $r_{H_2O} = \frac{k_2 K_{CO_2} (c_{CO_2} c_{H_2} - c_{H_2O} c_{CO} / c_{H_2}^{3/2} K_2^{eq})}{(1 + K_{CO} c_{CO} + K_{CO_2} c_{CO_2}) (c_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) c_{H_2O})}$ $r_{CH_3OH}^* = \frac{k_3 K_{CO_2} (c_{CO_2} c_{H_2}^{3/2} - c_{CH_3OH} c_{H_2O} / c_{H_2}^{3/2} K_3^{eq})}{(1 + K_{CO} c_{CO} + K_{CO_2} c_{CO_2}) (c_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) c_{H_2O})}$	Graaf et al., 1988 [10]
210-240 °C 15-50 bar	$r = \frac{k_f' K_{CH} K_{H_2}^2 K_H^2 K_{CO} (p_{CO} p_{H_2}^2 - p_{CH_3OH} / K_{eq})}{K_{CH} K_{H_2}^{3/2} K_H^{3/2} K_{CO} p_{CO} p_{H_2}^{3/2} + K_{CO_2} p_{CO_2} + K_{H_2}' p_{H_2}} + \frac{k_f'' K_{H_2} K_H K_{H_2} (p_{CO_2} p_{H_2} - p_{CH_3OH} p_{H_2O} / K_{eq}'' p_{H_2}^2)}{K_{H_2}^{1/2} K_H^{1/2} K_{CO_2} K_{CHO_2} p_{CO_2} p_{H_2}^{1/2} + K_{CO_2}'' p_{CO_2}^2 + K_{H_2O} p_{H_2O}^3}$	McNeil et al., 1989 [11]
180-280 °C 15-51 bar	$r_{MeOH} = \frac{k_{5a}' K_2' K_3 K_4 K_{H_2} p_{CO_2} p_{H_2} [1 - (1/K^*) (p_{H_2O} p_{CH_3OH} / p_{H_2}^3 p_{CO_2})]}{(1 + (K_{H_2O} / K_8 K_9 K_{H_2}) (p_{H_2O} / p_{H_2}) + \sqrt{K_{H_2} p_{H_2}} + K_{H_2O} p_{H_2O})^2}$ $r_{RWGS} = \frac{k_1' p_{CO_2} [1 - K_3^* (p_{H_2O} p_{CO} / p_{CO_2} p_{H_2})]}{(1 + (K_{H_2O} / K_8 K_9 K_{H_2}) (p_{H_2O} / p_{H_2}) + \sqrt{K_{H_2} p_{H_2}} + K_{H_2O} p_{H_2O})^2}$	Froment and Bussche, 1996 [12]
200-275 °C 4.9 bar	$R_M = \frac{k_M \{P(CO_2)P(H_2) - P(CH_3OH)P(H_2O) / [K_M P^2(H_2)]\}}{[1 + K_{CO_2} \times P(CO_2) + K_{H_2O} \times P(H_2O)]^2}$ $R_R = \frac{k_R \{P(CO)P(H_2O) / [K_R P(H_2)]\}}{1 + K_{CO_2} \times P(CO_2) + K_{H_2O} \times P(H_2O)}$	Kubota et al., 2001 [13]
240 °C 34-41 bar	$r = \frac{k_3 p_{H_2} \left(1 - \frac{p_m p_{H_2O}}{K_{p_m} p_{H_2}^3 p_{CO_2}}\right)}{1 + K_{-2} p_{H_2O} + K_{-2} p_{H_2O} / (K_1 p_{CO_2})}$	Rozovski i and Lin, 2003 [14]

250-260 °C 5 MPa	$r_A = \frac{k_A K_{CO} K_{H_2}^2 K_{CH_3CO} (P_{CO} P_{H_2}^2 - P_{CH_3OH} / K_{PA})}{(1 + K_{CO} P_{CO}) (1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{H_2O} P_{H_2O})}$ $r_B = \frac{k_B K_{CO_2} K_{H_2}^{0.5} (P_{CO_2} P_{H_2} - P_{CO} P_{H_2O} / K_{PB}) / P_{H_2}^{0.5}}{(1 + K_{CO} P_{CO}) (1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{H_2O} P_{H_2O}) (1 + K_{CO_2} P_{CO_2})}$ $r_C = \frac{k_C K_{CO_2} K_{H_2}^{2.5} K_{CH_3CO_2} (P_{CO_2} P_{H_2}^3 - P_{CH_3OH} P_{H_2O} / K_{PC}) / P_{H_2}^{0.5}}{(1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{H_2O} P_{H_2O}) (1 + K_{CO_2} P_{CO_2})}$	Lim et al., 2009 [15]
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1.5.4 Catalyst

The catalyst primarily chosen for methanol synthesis and used in this study due to its high selectivity and stability, is the Cu/Zn/Al/Zr catalyst. This catalyst is an improved version for the hydrogenation of CO₂ to methanol. In industrial-scale production, methanol is typically synthesized from CO, CO₂, and H₂ using Cu/Zn/Al catalysts, as they have been found effective for methanol synthesis via CO₂ hydrogenation. Al₂O₃ is used to promote the activity and stability of the catalyst, with studies showing that an increase in aluminum content correlates with increased CO₂ conversion. Additionally, the addition of a suitable amount of ZrO₂ significantly enhances the dispersion of copper, leading to improved catalytic activity and selectivity. [16]

In this system, copper serves as the main active component, while ZnO and Al₂O₃ act as supports. The deactivation of the Cu/Zn/Al catalyst is primarily due to copper oxidation and the agglomeration of ZnO species during the hydrogenation of CO₂ to methanol. Some reasons for catalyst deactivation include, poisoning by trace impurities in the feed gas, sintering of copper particles due to high reaction temperatures, and carbon deposition. [17]

According to studies, the main causes of catalyst deactivation are the accumulation of ZnO species and the oxidation of metallic copper. [18]

1.5.5 Methanol Synthesis Process Description

The hydrogenation reactions of carbon monoxide and carbon dioxide to methanol are highly exothermic. As a result, the equilibrium conversion of these reactions is favored at lower temperatures, while the reaction kinetics are more favorable at higher temperatures. Therefore, it is necessary to remove excess heat and recycle the stream containing unreacted components to achieve a reasonable conversion rate. A conventional methanol production unit consists essentially of two sections: the reaction section and the separation section. The feed stream is mixed with the recycle stream, which is heated before entering the reactor. The reactor's output stream is then cooled to allow condensation and the removal of liquid products. However, condensation alone is insufficient to meet the desired product specifications, so further processing is required. A portion of the unreacted gas is purged to prevent the accumulation of inert gases in the recycle stream.

The reactor used in the methanol synthesis process operates isothermally. It functions as both a reactor and a heat exchanger with a shell-and-tube configuration. The reactor shell is typically surrounded by thermal insulation to prevent any heat loss. The tubes within the shell are packed with Cu/ZnO/Al₂O₃ catalyst and are supported by baffle plates, which also enhance heat transfer between the tubes and the shell.

Heating gas flows through the shell, providing an external heat source for the reactions. The reactants flow through the tubes, which contain the catalytic layer where the reactions occur. The reaction heat is removed by circulating cooling water through the shell.

To achieve the desired methanol purity specifications, it is essential to remove unreacted substances and undesirable by-products. The separation section typically includes two pressure vessels—one for high pressure and one for low pressure—to remove dissolved gases from the methanol stream. Additionally, one or more atmospheric distillation columns are used to remove water and obtain the final product.

Instead of using a pressure vessel, a stripping column can be employed to remove dissolved gases, as used by Kiss et al. [19], whose process is also studied in this thesis.

1.5.6 Kinetic Study of Reactions

In this section, we study the chemical reactions occurring during the hydrogenation of carbon dioxide to produce methanol. Initially, we describe the catalyst used for these reactions. Subsequently, we adjust the kinetic constants from Kiss et al. to derive a new kinetic model. This model uses equilibrium constants, calculated via Van't Hoff, to approximate the results from Kiss et al.

1.5.6.1 Kinetic Expressions

Describing the kinetics of the reactions occurring in the process is crucial. The more accurate the kinetic expressions, the more reliable the results from simulations will be. The rate of a catalytic reaction is influenced by the composition, temperature, and the catalyst used. Below is a summary of the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism, which is commonly used in literature for modeling the catalytic reaction of methanol production from carbon dioxide.

1.5.6.2 Langmuir-Hinshelwood-Hougen-Watson (LHHW) Mechanism

The Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model is often used to describe the kinetics of reactions catalyzed by heterogeneous catalysts, where both kinetics and adsorption phenomena are significant. This model is based on describing the stages of internal diffusion of reactants, the surface reaction of intermediates, and the desorption of products, as functions of the surface concentration of active sites occupied by intermediate chemical species. The final form of the rate expression includes only the concentrations of reactants and products in the fluid phase that is in direct contact with the solid catalyst.

According to this kinetic model, the reaction occurs at an active site on the surface of the catalyst. The model assumes that three sequential steps occur on the catalyst surface:

1. **Adsorption:** A molecule absorbs onto the surface and attaches to an active site.
2. **Reaction:** The adsorbed molecule reacts with another molecule adsorbed on a neighboring site (double active site mechanism).
3. **Desorption:** The products are desorbed from the surface, and the active site is freed.

The general form of the kinetic expression for the catalytic reaction is presented in Equation 1-4.

$$\text{Reaction rate} = \frac{(\text{kinetic term})(\text{driving force or distance from equilibrium})}{(\text{resistance term})} \quad 1-5$$

In Equation 3-1, which represents the general form of the rate expression for a catalytic reaction, the kinetic term reflects the dependence of the reaction rate on temperature. The driving force and the resistance term are expressions of the concentrations of the

reacting species and the equilibrium constants of the reactions. For reactions involving polar components, due to deviations from ideal behavior, partial pressures or concentrations are replaced with fugacities or activities of the species, respectively, for gases and liquid mixtures. [20]

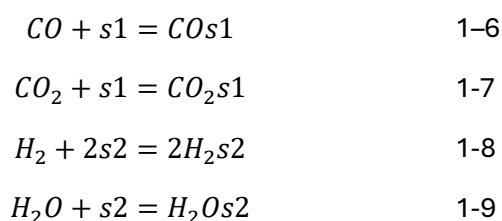
In LHHW mechanism, the overall reaction rate is determined by the rate of the slowest step. This means that the LHHW mechanism does not account for mass transfer and diffusion phenomena through the catalyst, as it assumes these processes are much faster compared to the adsorption, surface reaction, and desorption stages. [21]

1.5.6.3 Kinetics of Kiss et al

In 2015, Kiss et al. published a kinetic model for the methanol production reaction system, which is based on the kinetic model by Lim et al. [15], derived from the experimental data of Graaf et al. [6]. The model considers three reactions, of which two correspond to hydrogenation reactions—one for CO and one for CO₂—and includes the Water Gas Shift reaction. The kinetics are based on the LHHW mechanism, which assumes the presence of two active sites (s1, s2). CO and CO₂ are absorbed onto the s1-sites, while H₂ and H₂O are absorbed onto the s2-sites, respectively. The elementary reactions are described in Table 1.5.

Table 1.5 Elementary reactions for methanol synthesis over a catalyst Cu/Zn/Al/Zr. [15]

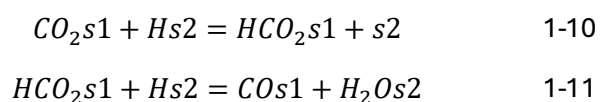
Adsorption reactions



Surface reactions

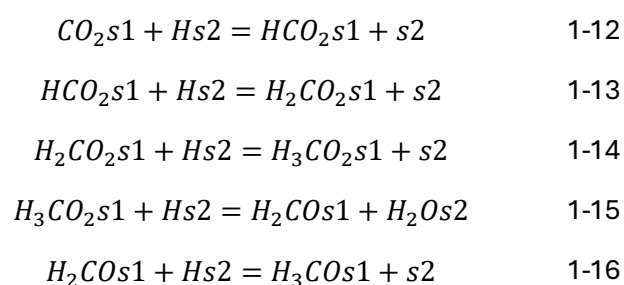
Reaction (1-2)

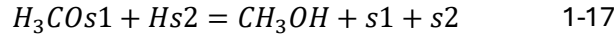
Water-Gas-Shift Reaction



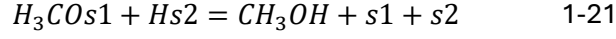
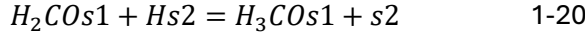
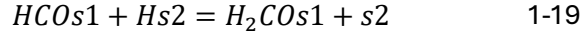
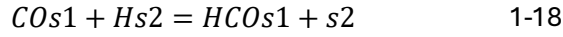
Reaction (1-3)

CO₂ hydrogenation





Reaction (1-4) *CO hydrogenation*



The controlling steps for each reaction from 1-2, 1-3, and 1-4 are 1-11, 1-12, and 1-20, respectively.

The kinetic expressions for the kinetic model (1-7) -(1-14) -(1-20) are functions of temperature and fugacity of the reaction components and are given by equations 1-21 to 1-23.

$$r_{CO,A2} = r_{H_2O,A2} = k_A \frac{K_{CO_2}[f_{CO_2}f_{H_2} - f_{H_2O}f_{CO}/K_A]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})[\sqrt{f_{H_2}} + (K_{H_2O}/\sqrt{K_H})f_{H_2O}]} \quad 1-21$$

$$\begin{aligned} r_{CH_3OH,B3} &= r_{H_2O,B3} \\ &= k_B \frac{K_{CO_2}[f_{CO_2}f_{H_2}^{3/2} - f_{H_2O}f_{CH_3OH}/(f_{H_2}^{3/2}K_B)]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})[\sqrt{f_{H_2}} + (K_{H_2O}/\sqrt{K_H})f_{H_2O}]} \end{aligned} \quad 1-22$$

$$r_{CH_3OH,C3} = k_C \frac{K_{CO}[f_{CO}f_{H_2}^{3/2} - f_{CH_3OH}/(K_C\sqrt{f_{H_2}})]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})[\sqrt{f_{H_2}} + (K_{H_2O}/\sqrt{K_H})f_{H_2O}]} \quad 1-23$$

The temperature dependence of the equilibrium constants for reactions 1-2, 1-3, and 1-4 is expressed through the Van't Hoff equation. Consequently, the expressions for the equilibrium constants used are described by equations 1-23 to 1-25.

$$\ln K_A = 5.031 - \frac{4949}{T} \quad 1-24$$

$$\ln K_B = -21.336 + \frac{5946.3}{T} \quad 1-25$$

$$\ln K_C = -26.367 + \frac{10895}{T} \quad 1-26$$

The thermodynamic model used in this study is the RK-ASPEN, which is essentially an extension of the Redlich-Kwong-Soave equation of state for hydrogen-rich systems.

1.6 Greenhouse gases

In recent years, due to the dimensions that the issue of global warming has taken, due to the enrichment of the atmosphere by gaseous pollutants, the management of air emissions that cause the so-called greenhouse effect, is an issue of particular concern to humanity. Moreover, as tighter and tighter limits are being set on emissions of these gases or fines are being imposed, industry is gradually turning to new technologies for reduced emissions or for their capture.

Since the Industrial Revolution and the discovery of fossil fuels, emissions of man-made greenhouse gases (GHGs) have increased rapidly, with carbon dioxide levels increasing by 68% compared to emission levels prior to industrial development. GHGs include water vapor, carbon dioxide, methane, ozone, nitrogen oxides and chlorofluorocarbons. Carbon dioxide is directly linked to energy production, is emitted into the atmosphere in large quantities, and as a result is a major contributor to GHG emissions. For example, in industrialized countries, carbon dioxide accounts for at least 80% of GHG emissions. Industries such as cement, iron, steel, steel, aluminum, paper and refineries emit quantities of carbon dioxide because of the combustion and transformation of raw materials.

According to research, anthropogenic emissions are estimated to intensify climate change at a rate about 170 times greater than that of natural forcings, such as respiration. To limit global warming and in the broader context of environmental protection, the European Union has committed itself to reducing greenhouse gas emissions to 80-95% below 1990 levels by 2050, according to the Energy Roadmap 2050. However, as the demand for energy is growing, new technologies for CO₂ capture, storage and utilization (CCUS: Carbon Capture Utilization and Storage) are being developed as part of this effort to maintain a competitive and secure energy sector. The EU's objective is to achieve a 40% reduction in CO₂ emissions by 2030 compared to 1990 levels [22]. At the global level, agreements such as the Kyoto Protocol and the Paris Agreement represent a consensus effort to reduce greenhouse gas emissions, emphasizing that reducing emissions of carbon dioxide levels is vital to limiting the greenhouse effect.

1.6.1 Carbon Dioxide

Carbon dioxide (CO₂) is a major greenhouse gas that significantly contributes to global warming and climate change. It is produced primarily through the combustion of fossil fuels such as coal, oil, and natural gas, as well as through deforestation and various industrial processes. Currently, CO₂ is responsible for approximately 76% of global greenhouse gas emissions, making it the most prevalent and impactful greenhouse gas. The concentration of CO₂ in the Earth's atmosphere has risen dramatically since the Industrial Revolution, increasing from about 280 parts per million (ppm) in the pre-industrial era to over 420 ppm today. This surge in CO₂ levels has been linked to rising global temperatures, with current levels contributing to an average increase of approximately 1.1°C (2°F) in global temperatures since the late 19th century. The continued accumulation of CO₂ and other greenhouse gases is a primary driver of the ongoing changes in climate patterns, extreme weather events, and sea level rise,

underscoring the urgent need for effective mitigation strategies to address climate change.

1.6.2 Worldwide Production of CO₂

It is recognized around the world that emissions of carbon dioxide and other greenhouse gases are contributing to global warming, which is one of the major issues of the century and is the result of human activity. Carbon dioxide emissions result from heat and power generation processes, which are mainly based on the combustion of fossil fuels, accounting for 73.2% of global carbon dioxide emissions. In addition to these, major static sources of carbon dioxide emissions include processes such as natural gas sweetening, hydrogen production as a feedstock for ammonia and ethylene oxide production, and installations such as oil refineries, iron, steel, cement and limestone plants.

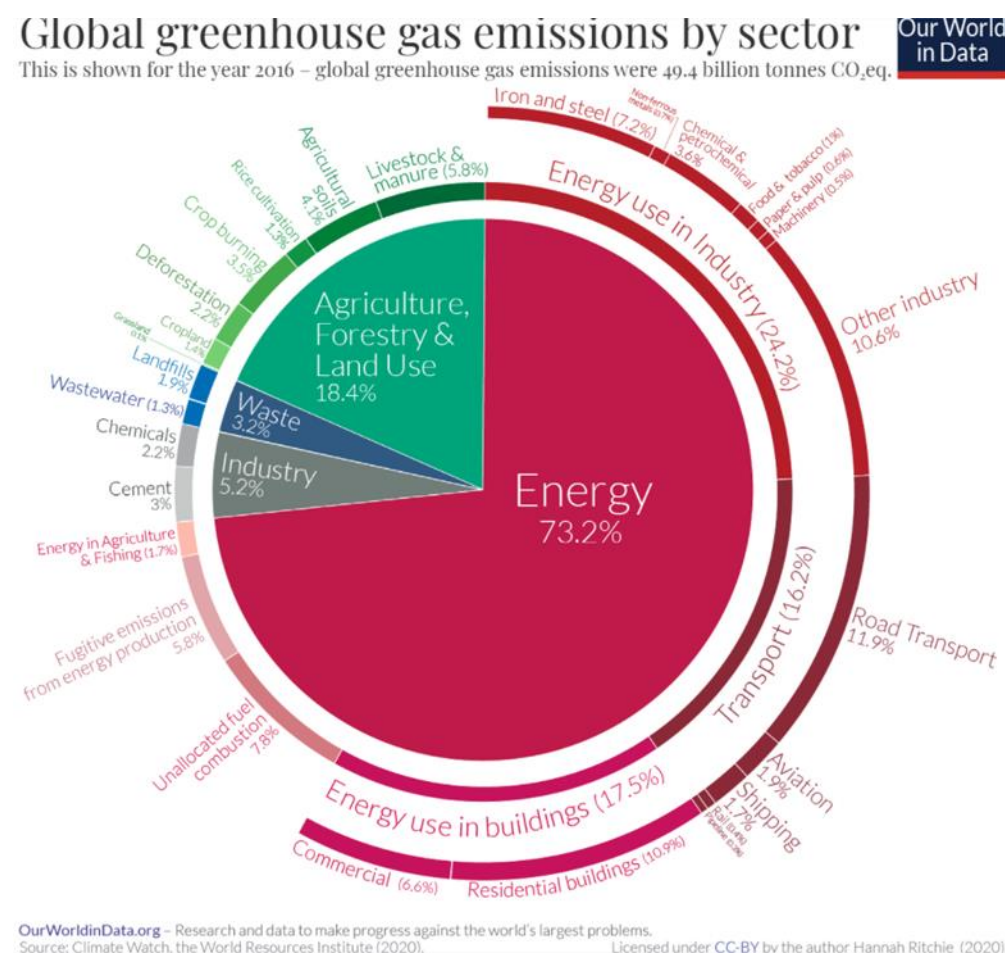


Figure 1.3 GHG Emissions by Sector

As shown in Figure 1.3, of the total GHG emissions in the energy sector, 24.2% is directed to industrial energy use, with the metal industry leading in terms of emissions with 7.2%, followed by the chemicals and petrochemicals industry with 3.6%, and finally the food and paper industry with smaller percentages. In addition to indirect greenhouse gas emissions, which result from energy consumption, there are also direct emissions, with

the cement industry leading the way with 3%, followed by the chemicals industry with 2.2%. The cement industry emits large quantities of carbon dioxide, both because of the clinker production reaction, of which CO₂ is a by-product, and from the combustion of fuels for energy production. Even though efforts are being made to reduce emissions using alternative fuels or biofuels, or through clinker substitution, there is still a growing need for further emission reductions. Especially for this sector, because carbon dioxide must be emitted during the clinker combustion stage, carbon storage and use technologies (CCS, CCU) are becoming increasingly important for reducing and preventing carbon dioxide emissions. Direct carbon dioxide emissions in the chemical industry arise from various chemical production processes, such as ammonia. Carbon dioxide emissions in the chemical industry are becoming increasingly important to reduce and eliminate carbon dioxide emissions.

1.7 Carbon Capture and Storage

Carbon capture and storage (CCS) is a technology designed to mitigate climate change by capturing CO₂ emissions from power plants and industrial processes before they enter the atmosphere. The captured CO₂ is then stored underground with the aim of preventing it from contributing to atmospheric greenhouse gases indefinitely. CCS is viewed as a transitional technology that allows for the continued use of fossil fuels in electricity generation and industry while low-carbon alternatives are developed. It may also be essential for achieving the negative CO₂ emissions needed to meet the 1.5°C and 2°C climate targets.

To make a significant impact, CCS must capture and store substantial amounts of CO₂. The concept of "wedges" developed by Pacala and Socolow in 2004 represents a way to visualize this requirement: each wedge signifies a reduction of 25 gigatons (Gt) of CO₂ over 50 years, and around 10 wedges would be necessary to limit global temperature rise to below 3°C. According to estimates, capturing and storing the CO₂ from 800 large coal-fired power plants would correspond to one wedge, involving the storage of approximately 200 billion cubic meters of CO₂—equivalent to the total global oil and gas production over 50 years. The logistical challenges of injecting such large volumes of CO₂ underground and the additional energy required for CO₂ capture (which can consume up to 30% of a power plant's output) are significant hurdles. Nonetheless, CCS is often included in scenarios aimed at limiting global temperature increases to 1.5°C or 2°C, as it is seen as a crucial element of the energy mix. Studies suggest that achieving these climate targets without CCS would be considerably more costly, if not infeasible. Furthermore, combining biomass energy with CCS (BECCS) could provide a way to achieve negative carbon emissions, as biomass absorbs CO₂ during growth and CCS captures CO₂ during combustion. Additionally, CCS may be the most viable option for reducing emissions from certain industrial processes, such as cement and steel production, where other decarbonization methods are challenging. Consequently, CCS is an important component of a low-carbon energy strategy, particularly for the medium-term future.

CCS operations consist of three major parts: CO₂ capture at a large stationary source (e.g., coal-fired power plant), transport of the captured CO₂ to a storage site, and injection of CO₂ into the subsurface for permanent storage. Capture occurs either through chemical transformation before the fossil fuel is combusted (precombustion) or

through physiochemical processes (e.g., adsorption) from the flue gas (post combustion). The CO₂ is then pressurized to reduce volume and dried to reduce corrosion. Unless the storage site is collocated with the source, CO₂ needs to be transported to the storage site. While trucks or ships may be appropriate for smaller CCS operations, pipeline transport is most appropriate for industrial-scale CCS operations, due to the large volumes of CO₂. At the storage site, CO₂ is injected into the deep subsurface for permanent storage. Storage formations consist of porous rocks, such as sandstone, and are either saline aquifers or depleted/current oil and gas fields. Monitoring in the injection formation and in shallower formations is used to ensure that the injected CO₂ remains in the storage formation, and no significant amount of CO₂ leaks to shallower formations or the atmosphere. Storage in unmineable coal seams and at the bottom of deep oceans has also been considered but has been found to be impractical due to technical issues.

While permanent storage is the ultimate goal of CCS, the captured CO₂ may also be utilized as feedstock for industrial processes [8] and to enhance oil production [9]. In CO₂ enhanced oil recovery (CO₂-EOR), CO₂ is injected into oil fields, and otherwise, immobile oil dissolves into the CO₂ and can thus be produced. Some of the CO₂ remains in the formation during CO₂-EOR, and a large volume of CO₂ is left in the formation at the end of the CO₂-EOR operation, so that CO₂-EOR is considered a form of storage.

At the time of writing of this chapter, the deployment of CCS is lagging far behind compared with what would be required for CCS to have a significant impact on mitigating climate change. Currently, there are only five industrial-scale CCS operations throughout the world, with a combined capture rate of about 6.5 Mt per year (Mt = 10⁹ kg). The projects are the Sleipner and Snøhvit projects (Norway), the Quest CCS Project (Canada), the Illinois Industrial CCS Project (USA), and the Gorgon Project (Australia). It should be noted that none of these projects are related to fossil fuel-fired power plants, but four projects capture CO₂ from natural gas processing and one from ethanol production. However, there are six CO₂ capture operations associated with coal-fired power plants, but CO₂ is being transported to oil fields for CO₂-EOR instead of pure storage. Unfortunately, no new CCS projects are currently under construction, although several projects are in the prefeasibility stage through the US Department of Energy's CarbonSAFE program. Considering that 25 Gt of emissions reduction over 50 years is required for a single stabilization wedge, deployment of CCS needs to be ramped up considerably if it is to have a significant impact on mitigating climate change.

One of the main impediments to the deployment of CCS is a lack of incentives for power plant operators to capture and store CO₂. As long as CO₂ emissions to the atmosphere are free of cost, operators have little reason to spend additional money and energy for CCS. However, operators see CCS as an option when faced with CO₂ emission costs. For instance, the Norwegian oil company Statoil—now Equinor—found it more economical to capture and store CO₂ at two offshore natural gas processing plants rather than pay a CO₂ emission tax. Another taxation example is the 45Q tax credit for CO₂ storage recently implemented in the United States. Monetization of carbon emissions, such as taxation and cap-and-trade systems, needs to increase to make CCS viable. While there are opportunities to improve the energy efficiency and cost of CCS, there do not seem to be any major technological impediments for CCS. Utilization of captured CO₂ for CO₂-EOR is helping the development and operational knowledge of carbon capture, but it should

only be viewed as a steppingstone, as dedicated storage will be necessary for CCS to be effective as a climate mitigation technology.

1.7.1 Carbon Capture with Amines

After over 90 years of development since its introduction in 1930, amine solution scrubbing technology has become a widely used method for acid gas removal, particularly for large-scale purification of industrial gases like biogas, natural gas, coal gas, and flue gases from coal-fired power plants. This advanced wet decarbonization technology is favored for its rapid reaction with CO_2 , high absorption capacity, and ease of regeneration.

The process begins with a series of pre-treatment steps, including drying and desulfurization, before the gas mixture enters the absorption tower. Here, the gas is evenly distributed via a liquid distributor at the top of the tower. Various pretreatment methods are used depending on the gas composition. For instance, gases containing SO_2 can be treated using wet, dry, or semi-dry desulfurization methods. Wet desulfurization employs alkaline solutions, while dry desulfurization includes jet and adsorption methods. Semi-dry desulfurization combines both wet and dry methods using techniques like spray drying and circulating fluidized beds. If NO_x is present, wet and dry stripping processes, such as selective catalytic reduction (SCR), are employed to reduce nitric oxide to nitrogen using reducing agents like ammonia or carbon monoxide.

The gas mixture, now free of moisture and solid particles, is processed in a drying unit and dust catcher. The lean amine solution absorbs CO_2 from the gas, becoming a rich solution. This rich solution is then pressurized and heated in a reboiler and sent to the desorption tower, where it flows from top to bottom. High-temperature water vapor from the reboiler interacts with the rich solution to desorb CO_2 , which is then condensed and separated to minimize absorbent loss. The regenerated lean solution is cooled, pressurized, and returned to the absorption tower for reuse. The water vapor in the desorption tower lowers the partial pressure of CO_2 , aiding the desorption process.

Temperature is a critical variable in the CO_2 capture process. Typically, the absorption temperature is maintained between 25–45 °C, while the regeneration temperature ranges from 90–130 °C. The specific conditions are adjusted based on the gas flow rate, amine flow rate, gas purity, and reactor pressure.

Although decarbonization techniques such as physical solvent absorption, water scrubbing, pressure swing adsorption and ammonia (NH_3)-based technology are also widely used in some specific areas, there are still some shortcomings compared to chemical absorption techniques based on amine decarbonization.

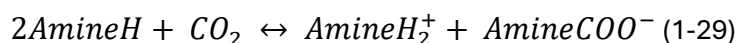
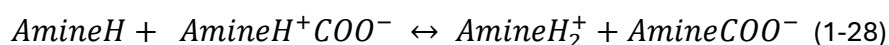
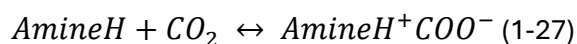
1.7.2 Monoamine solution absorption technique

Amine is the product of the substitution of one or more hydrogen atoms in an ammonia molecule by a hydrocarbon group. Amines are classified according to the number of hydrogen atoms on the nitrogen atom, and are mainly classified as primary amines (with two “active” hydrogen atoms attached to the nitrogen atom), secondary amines (with one “active” hydrogen atom attached to the nitrogen atom), tertiary amines (with no “active” hydrogen atoms attached to the nitrogen atom) and space-site hindered amines (where there is a space-site hindering effect on the nitrogen atom), which can be divided into single-stage and multi-stage amines depending on the number of nitrogen atoms on the amine.) and space-site hindered amines (where there is a space-site hindering effect on the nitrogen atom), which can be divided into single-stage and multi-stage amines depending on the number of nitrogen atoms on the amines. The amino group in the molecular structure of amines provides them with a strong basicity, which allows them to have a fast absorption rate, a high absorption volume and a good selectivity for CO₂.

Primary and secondary amines have good reaction kinetics because they can quickly generate chemically stable carbamates during the reaction with CO₂, and tertiary amines have good absorption kinetics because they generate chemically unstable hydrogen carbamates with water 1 to 1 during the reaction with CO₂, and the specific reaction mechanism will be explained in Section 1.5.3 .Each amine has its own advantages and disadvantages, currently the most widely used is 30 wt% aqueous MEA solution, which has high CO₂ absorption rate, large absorption volume and low cost, but the regeneration energy consumption is too high and difficult to regenerate, so researchers by introducing MDEA and other tertiary amines with low regeneration energy consumption for modification, and get a mixed amine with high absorption capacity, high absorption rate and low regeneration energy consumption at the same time. [23]

1.7.3 Primary and Secondary Amines

The reaction mechanism of amines during the decarbonization process has been thoroughly investigated. For primary and secondary amines, the reaction with CO₂ follows a "zwitterionic" mechanism. This process begins with the formation of a zwitterionic intermediate, which results from the interaction of the amine with CO₂. This intermediate then reacts with additional amine to generate protonated amines and carbamate ions.



where *AmineH*, *AmineCOO* – and *AmineH*₂⁺ + denote free amines, carbamates and protonated amines respectively.

The zwitterionic mechanism indicates that the theoretical CO₂ absorption capacity of primary and secondary amine solutions is approximately 0.5 mol CO₂ per mol of amine. However, due to hydrolysis reactions of some carbamates at higher CO₂ concentrations, as outlined in the equation, free amines and bicarbonates are formed. Consequently, the

actual CO₂ absorption of primary and secondary amines can sometimes exceed the theoretical value of 0.5 mol CO₂ per mol of amine.

1.7.4 Flue gas as an application of amine washing process

Since the onset of the industrial revolution, factors such as increased land use, population growth, and emissions from fossil fuel combustion have intensified the greenhouse effect. Emissions from flue gases, which contribute significantly to global CO₂ emissions, have made CO₂ capture from these gases a critical task. The primary CO₂ capture technologies include pre-combustion capture, post-combustion capture, and oxyfuel combustion, as illustrated in Figure 6. Post-combustion capture focuses on separating and concentrating CO₂ from the flue gases produced by combustion processes using both physical and chemical methods. Typically implemented after desulfurization and denitrification processes, this technology can be adapted to nearly all existing coal-fired power plants with minimal modifications to meet CO₂ removal requirements. In post-combustion capture, CO₂ partial pressures in flue gases are often below 0.15 atm, necessitating the use of chemical absorbers with strong CO₂ binding capabilities. This leads to challenges such as high energy consumption, significant equipment costs, and substantial operational expenses. Among the various methods, amine scrubbing is the most established and widely used technique. Despite its high regeneration energy requirements, amine scrubbing effectively captures CO₂ and provides high separation purity, including the removal of H₂S from flue gases with low CO₂ partial pressures. Additionally, the high initial temperature of the flue gas can be leveraged to aid the amine regeneration process, thereby reducing overall energy consumption.

1.8 Economic Evaluation Methodology

1.8.1 Methodology for Capital Cost Calculation

The calculation of capital costs for chemical process facilities is often based on an estimate of the purchase cost of the main process equipment, while other costs are estimated as factors of the equipment cost. For the precise determination of equipment costs, it is necessary to obtain quotes from a supplier. In this study, a preliminary economic evaluation is carried out, based on cost correlations obtained from the literature in relation to the operating conditions and the scaling of the facility. Although numerous cost estimation methods exist in the literature, this study follows the "Detailed Factorial Method" as described by Towler & Sinnott [24-26].

The factorial cost estimation method (Detailed Factorial Method) is based on the purchase cost of the necessary equipment, and with the application of appropriate factors, the fixed capital cost required for the project is estimated. The best method for estimating purchased equipment costs relies on actual price data for similar equipment. However, since access to such data is limited, cost correlations are developed to estimate the purchase cost of the equipment, which can be used for the purposes of a preliminary estimation.

To calculate the fixed cost of the equipment, mass and energy balances are first drawn up, i.e., a process flow diagram is created using software to size the equipment of the facility. The equipment sizing for the CO₂ absorption and methanol production is conducted using the Aspen Process Economic Analyzer (APEA) tool within the Aspen Plus V11 software package, and based on these dimensions, the cost is calculated. It should be noted that special attention is required to properly define the equipment in APEA and to correctly choose the category in which the equipment belongs. Subsequently, the appropriate materials for the construction of the equipment are chosen, ensuring they can withstand the process conditions without risk of damage or accidents. Once the equipment has been sized and the construction materials selected, the purchase cost of the equipment is calculated, followed by the installation cost, according to the "Detailed Factorial Method" by Towler & Sinnott.

1.8.1.1 Equipment Purchase Cost

The correlations for calculating the purchase cost of equipment are presented in Table 6-1 for each piece of equipment used in the process. All relationships are of the form:

$$C_e = a + bS^n \quad (1-30)$$

Where:

- C_e : the purchase cost of the equipment as of January 2010, in USD
- a, b : cost constants
- S : equipment size parameter
- n : equipment exponent

For each type of equipment, different constants a , b , and n are defined. Additionally, the size parameter S is specific and different for each piece of equipment. These relationships are only valid within the range of the indicated size parameter S . All prices

are given for equipment made from common steel. For equipment made from other materials, a correction factor, f_m , is required, as described in the next section.

Table 1.6 shows the equation coefficients for the purchase cost for every equipment used in the process.

Table 1.6 Equation coefficients for every equipment used in Carbon Capture Process

Description	S Units	Min S	Max S	Equipment	a	b	n
Vertical Pressure Vessels	kg	160	250000	FLASH	11600	34	0,85
				ABSORBER			
				SCRUBBER			
				STRIPPER			
Horizontal Pressure Vessels	kg	160	50000	RDRUM	10200	31	0,85
U-shell and tube Heat Exchangers	m ²	10	1000	COOLER2	28000	54	1,2
				CROSS-EX			
				COND			
Single-stage centrifuge Pump	L/s	0,2	126	PUMP-1	3300	48	1,2
	kW	1	2500		-1100	2100	0,6
U-tube Kettle Reboiler	m ²	10	500	STRIPPER REBOILER	29000	400	0,9

The pumps in the process are taken as single-stage centrifugal pumps, whose motor is electrically driven (explosion proof motor) to drive the impeller. Therefore, the cost for the in-process pumps is taken as the sum of the cost for the impeller part and the motor part of the pump.

Since three different units have been simulated in this work (Electrolysis, CO₂ absorption, Methanol Production), the correspondence between the equipment and the appropriate cost calculation equation will be presented in detail below for each unit.

1.8.1.2 Equipment Installation Costs

The installation cost of the equipment is calculated according to the "Detailed factorial" methodology as described by Towler & Sinnott. First, the purchase cost of the core process equipment is estimated, and then the total installation cost is calculated.

According to the "Detailed factorial" methodology, the other direct costs, beyond the equipment purchase cost, incurred during the construction of a plant, are as follows:

- Erection of equipment, including foundations and minor structural works
- Piping, insulation, and painting
- Electricity and lighting
- Instruments and automatic control systems
- Auxiliary buildings, offices, laboratories
- Storage spaces for raw materials and final products

- Steam, water, air supplies, fire protection services
- Site preparation

The contribution of each of the above to the total installation cost is calculated by multiplying the equipment purchase cost by an appropriate factor. These factors are derived from historical cost data of similar facilities, and for each part of the process equipment, they are provided in Table 1.7.

Table 1.7 Factors for the calculation of installation costs .

Coefficient	Value
Equipment installation, f_{er}	0.3
Piping, f_p	0.8
Instruments and control, f_i	0.3
Electricity, f_{el}	0.2
Civil engineering work, f_c	0.3
Buildings, f_s	0.2
Insulation and paintin, f_l	0.1

Thus, according to the Detailed Factorial method, the total installation cost of the equipment (C) is given by the equation:

$$C = \sum_{i=1}^{i=M} C_{e,i,CS} [(1 + f_p)f_m + (f_{er} + f_{el} + f_i + f_c + f_s + f_l)] \quad (1-31)$$

Typically, the costs calculated are estimated for equipment made from common steel. For equipment made from different materials, a correction is required using the material factor f_m . Typical values for this factor for common materials are provided in the following Table 1.8.

Table 1.8 Material cost factors, f_m , relative to carbon steel.

Material	f_m
Carbon steel	1.0
Aluminum and bronze	1.07
Cast steel	1.1
304 stainless steel	1.3
316 stainless steel	1.3
321 stainless steel	1.5
Hastelloy C	1.55
Monel	1.65
Nickel and Inconel	1.7

1.8.1.3 Cost Adjustment to Present Value

According to the Detailed Factorial methodology, installation costs are calculated based on the year 2010. Therefore, it is necessary to adjust the calculated amount and convert it to the year under study. This adjustment is made using cost indexes, which change over the years and reflect shifts in economic conditions. The most significant of these indexes are the CEPCI (Chemical Engineering Plant Cost Index) and the MS (Marshall & Swift). The CEPCI index is used in this work, with values for the years 2010-2024 provided in the table below. It is important to note that the Dollar to Euro Exchange Rate is set to 0.94 as of April 2024.

Table 1.9 CEPCI Index Values for the Years 2010 to 2024 [27].

Year	CEPCI
2024	795.1
2023	800.8
2022	816.0
2021	708.8
2020	596.2
2019	607.5
2018	603.1
2017	567.5
2016	541.7
2015	556.8
2014	576.1
2013	567.3
2012	584.6
2011	585.7
2010	532.9

For the year 2024, the CEPCI index is taken as the average value of the index for the months from January to April for which published values are currently available.

To adjust the equipment cost to the present, the following formula is used:

$$\text{Cost at year A} = \text{Cost at year B} \times \frac{\text{Index Value at Year A}}{\text{Index Value at Year B}} \quad (1-32)$$

1.8.1.4 Material Selection for Equipment Construction

When selecting the material for the components of industrial equipment, several factors must be considered. Specifically, for chemical process units, the primary factors examined are resistance to high temperatures and corrosion resistance. The chosen material must meet the process requirements, have mechanical strength, be relatively easy to process, and should not contaminate the product. Additionally, the economic

aspect is crucial, as the material must meet the required specifications at the lowest possible cost, allowing for maintenance and replacement throughout the unit's lifespan.

In summary, some of the most important characteristics to consider when selecting a construction material include:

- Mechanical Properties
 - Tensile strength
 - Fracture toughness
 - Hardness and wear resistance
 - Fatigue resistance
 - Creep resistance
- Temperature Resistance
- Corrosion Resistance
- Ease of Fabrication
- Availability
- Cost

Initially, during material selection, two main parameters are evaluated: the cost and the maximum allowable stress of the material. These data are provided in Table 1.10 for the most common material options.

Table 1.10 Relevant Costs (November 2010) and Maximum Allowable Stress for Common Construction Materials.

Metal	Type	Cost (\$/lb)	Maximum allowable stress (bar)
Carbon steel	A285	0.37	889.4
Austenitic stainless steel	304	1.156	1379.0
	316	1.721	1379.0
Copper	C10400	3.83	461.9
Nickel	99% Ni	9.861	689.5
Incoloy	NO8800	3.733	1379.0
Monel	NO4400	7.76	1289.2
Titanium	R50250	3.35	689.5

From Table 1.10, it is evident that the two cheapest metals are carbon steel and stainless steels 304 and 316. Both carbon steel and stainless steel 304 are widely used in the chemical industry due to their low cost, ease of fabrication, and availability in a wide range of standardized forms and sizes. Thus, the choice between these two types of metals is determined by their resistance to corrosion.

1.8.2 Calculation of Operating Costs

In terms of operating costs, all expenses related to the operation of the unit are considered. For this study, operating costs include auxiliary supplies such as electrical power, cooling water, heating steam, natural gas, the cost of raw materials and consumables, as well as fixed operating costs such as overtime costs, rent and tax costs etc.

1.8.2.1 Varied Operating Costs

The requirements for auxiliary supplies are calculated using the equations using the methodology analyzed below.

The characteristics of the cold and hot utility streams are summarized in the following table.

Table 1.11 Characteristics of the utility streams.

Utility	Input temperature (°C)	Pressure (bar)
Cooling water	20	1
Low-pressure steam	125	2.3

To produce low- and high-pressure steam, natural gas is used as fuel in a steam boiler. Therefore, the cost of steam corresponds to the cost of the fuel used for its production. Table 1.12 summarizes the cost of utilities for calculating the operating cost of the plant.

Table 1.12 Utility costs used in this study. [28] [29]

Utility	Price
Cost of industrial water (EYDAP), Refinery Estimates	0.05 €/ton
Average electricity cost with state subsidy (TEM) from PPC	0.12 €/kWh
Cost of natural gas for industrial use in Greece	0.03485 €/kWh

The cost of natural gas in this study was assessed after a sensitivity analysis, so in this table the base price is shown. The sensitivity analysis is presented in the following chapters.

The calculation of utility costs is performed as follows:

- **For the calculation of electricity cost** required as a utility, the power consumption for the equipment components is obtained from the software and multiplied by the electricity price from Table 6-29.
- **For the calculation of cooling utility costs**, the required cooling water flow rate is calculated using the following equation:

$$Q_{cooler} = \dot{m}C_p\Delta T \quad (1-33)$$

Where:

- Q_{cooler} : the heat load of the heat exchanger in kW, where cooling water is used as a utility
- $\dot{m}$: the mass flow rate of the cooling water in kg/s
- C_p : the specific heat capacity of water, equal to 4.2 kJ/kg/K
- ΔT : the temperature difference between the outlet and inlet water in the heat exchanger

To calculate the cost of heating utilities, the following methodology is used: The energy that the fuel must provide for steam production is calculated using the following equation:

$$Q_{\kappa\alpha\nu\sigma\iota\mu\omicron\nu} = \frac{Q_{heater}}{n_b} \quad (1-34)$$

Where n_b is the boiler efficiency, assumed to be 80%.

The required amount of heating steam is calculated using the following equation:

$$Q_{\kappa\alpha\nu\sigma\iota\mu\omicron\nu} = m_s \Delta H_s \quad (1-35)$$

Where m_s is the mass flow rate of the steam (kg/s) and ΔH_s is the latent heat of condensation of the steam (kJ/kg)

Finally, the cost of steam is derived from the cost of the fuel used for its production:

$$Cost\ of\ fuel = cost\ of\ natural\ gas \times \frac{Q_{heater}}{n_b} \quad (1-36)$$

1.8.2.2 Fixed Operating Costs

The equations used for calculating the fixed operating costs of all processes are summarized in Table 1.13 [26]. In this study, ISBL is assumed to be the whole Capital Cost, while OSBL represents 4 % of OSBL.

Table 1.13 Functions for Fixed Operating Cost Calculation

	Cost Calculation Function
Operation Cost (assumed)	5 M€
Supervision Cost	25 % Cop
Overtime Cost	50 % ($Cop+Cs$)
Maintainance Cost	5 % $ISBL$
Tax and Insurance Cost	2 % $ISBL$
Land Rent Cost	2 % ($ISBL + OSBL$)
General Facility Expenses	65 % ($Cop+Cs+Cot+Cm$)

1.8.3 Calculation of Annual Equivalent Capital Cost

To calculate the annual equivalent capital cost, the Annual Capital Charge Ratio (ACCR) is used. The annual capital charge ratio is defined as the fraction of the capital that must be paid each year to cover the repayment of the capital and all accumulated interest over the life of the investment. The ACCR is calculated using the following formula:

$$Total\ Annualized\ Cost\ (TAC) = OPEX + ACCR \times Total\ Capital\ Cost \quad (1-37)$$

Where:

- i : the interest rate, which is assumed to be 10%
- n : the lifespan of the unit, which is considered to be 25 years

It is noted that the interest rate is related to the proportion of capital taken as a loan, the loan interest rate, the proportion of financing from equity, and the expected return on equity. An interest rate of $i = 0.1$ is considered representative. Thus, the capital charge ratio is calculated as $ACCR = 0.11$.

The annual capital charge ratio can be used to convert the initial capital cost into an annual capital charge. Then, by adding the operating costs, the total annual cost (Total Annualized Cost, TAC) is obtained using the following formula:

$$Total\ Annualized\ Cost\ (TAC) = OPEX + ACCR \times Total\ Capital\ Cost \quad (1-38)$$

2 Electrolyser Process Simulation

In this chapter, green hydrogen production through electrolysis is simulated in Aspen Plus V11, based on a demonstration of KG Engineering Solutions using the equations provided by Sanchez, Tijani et al [30, 31]. Firstly, a model for the stack of an alkaline electrolyser is developed that is later used to simulate in the Aspen Plus an alkaline water electrolysis system of 58.7 MW.

The simulation of the alkaline electrolyser takes place in the Aspen Plus software, although specific components that describe the operation of the stack are not included in the software. Indirect methods could be used to simulate the operation of the stack but important operating variables such as V_{cell} , ηF , HTO (the percentage of hydrogen that immigrates to the anode from the cathode) cannot be calculated dynamically within this software.

The goal is a product of high purity (>99 %), while an effort is made to maintain a high rate of productivity by scaling up the electrolyser stack.

2.1 Process Flow Diagram

In Figure 2.1, the process flow diagram of the electrolyser stack is shown, as extracted from Aspen Plus V11.

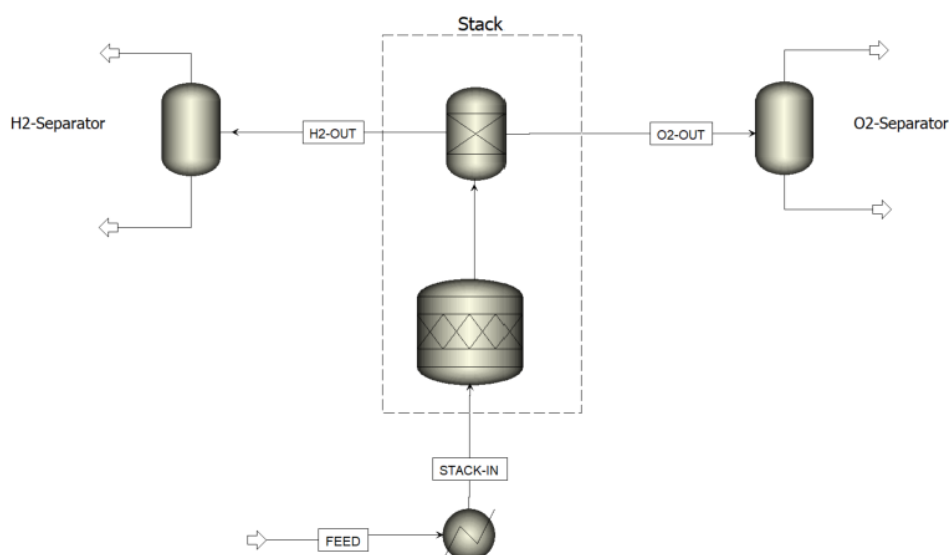


Figure 2.1 Process Flow Diagram of Water Electrolysis

The feedstock enters the stack, passing firstly through a heater operating in 80 °C, where the water splitting reaction occurs. The electrolyser stack is simulated using an RStoic reactor and a vertical separator vessel. After exiting the stack, the two streams of H₂ and O₂ enter a low-pressure flash vessel, operating at 10 °C in order to remove the remaining water. The top product of the H₂ separator is the desired green H₂. In the following tables, the characteristics of every stream as well as the operating conditions are presented.

Table 2.1 Inlet Streams and Characteristics of the Electrolyser**Table 2.2 RStoic-Electrolyser Specs**

Inlet Stack Mass Flow	20000	kg/hr
Inlet Stack Temperature	80	°C
Inlet Stack Pressure	1	bar
Inlet H ₂ O Mass Fraction	65 %	kg/kgtotal
Inlet KOH Mass Fraction	35 %	Kg/kgtotal
Feedstock Temperature	25	°C
Temperature	80	°C
Pressure	5	bar
Nominal Power Input	1.5	MW
Cell surface	0.1	m ²
Number of Cells	12	-
Cell Voltage	1.7902	V
Current Density	2000	A/m ²
Faraday Efficiency	0.902	-
HTO %	1.14 %	-
Stack efficiency	63.2 %	-
Electrical Input	58.7	MW

Table 2.3 Outlet H₂ Stream Specs

Outlet H ₂ Stream Mole Flow	471	kmol/hr
Outlet H ₂ Stream Temperature	10	°C
Outlet H ₂ Stream Pressure	1	bar
Outlet H ₂ Stream Purity	99.9 %	kmol/kmoltot

2.2 Operating Equations

The equations that were used to describe the working conditions of the stack were developed in Sanchez et al. and Tijani et al. [31] [30] work where a 15-kW alkaline water electrolyser was modeled with a semi-empirical mathematical model to predict its electrochemical behavior. When the electrical input, the temperature and the pressure change, operating voltage, Faraday efficiency (n_F [%]), HTO (%), electrical current (I_{cell}) and hydrogen production ($n_{H2,prod}$) vary accordingly. The equations that describe those operating conditions in a semi-empirical way are displayed on the following equations.

$$V_{rev} = \Delta G / zF \quad (2-1)$$

$$V_{cell} = V_{rev} + [(r_1 + d_1) + r_2 * T + d_2 * p] * i_{cell} + s * \log \left[\left(t_1 + \frac{t_2}{T} + \frac{t_3}{T^2} \right) * i_{cell} + 1 \right] \quad (2-2)$$

$$n_F = \left(\frac{i_{cell}^2}{f_{11} + f_{12} * T + i_{cell}^2} \right) * (f_{21} + f_{22} * T) \quad (2-3)$$

$$f_{H2} = n_F \frac{n_c I_{stack}}{zF} \frac{22.41}{1000} \quad (2-4)$$

$$C_E = \frac{\int_0^{\Delta t} i_{stack} V_{stack} dt}{\int_0^{\Delta t} f_{H2}} \quad (2-5)$$

$$HTO = \left[C_1 + C_2 * T + C_3 * T^2 + (C_4 + C_5 * T + C_6 * T^2) * \exp \left(\frac{C_7 + C_8 * T + C_9 * T^2}{i_{cell}} \right) \right] + [E_1 + E_2 * p + E_3 * p^2 + (E_4 + E_5 * p + E_6 * p^2) * \exp \left(\frac{E_7 + E_8 * p + E_9 * p^2}{i_{cell}} \right)] \quad (2-6)$$

$$n_{H2,prod} = \frac{n_F i_{cell} A_{cell} N_{cell}}{zF} \quad (2-7)$$

$$n_{stack} = \frac{n_{H2} LHV_{H2}}{W_{electrical,input}} \quad (2-8)$$

Where i_{cell} [A/cm²] is electrical current density, I_{stack} is the electrical current density of the stack, N_{cell} is the number of the cells, V_{cell} is the voltage of the cell, V_{rev} is the reversible voltage, V_{stack} is the voltage of the stack, A_{cell} [m²] is the area of each cell, LHV is Lower Heating Value, n_F is the Faraday efficiency, $z=2$ is the number of electrons that are transferred per H₂ molecule and $F=96485$ C/mol is the Faraday constant, $W_{electrical,input}$ is the electricity in kWh needed for the stack, $n_{H2,prod}$ are the moles of Hydrogen produced in electrolysis and n_{stack} is the efficiency of the stack.

The coefficients for the calculation of HTO and V_{rev} are shown in Figure

Model	Coefficient	Value	Unit
Polarization curve	r_1	4.45153×10^{-5}	$\Omega \text{ m}^2$
	r_2	6.88874×10^{-9}	$\Omega \text{ m}^2 \text{ }^\circ\text{C}^{-1}$
	d_1	-3.12996×10^{-6}	$\Omega \text{ m}^2$
	d_2	4.47137×10^{-7}	$\Omega \text{ m}^2 \text{ bar}^{-1}$
	s	0.33824	V
	t_1	-0.01539	$\text{m}^2 \text{ A}^{-1}$
	t_2	2.00181	$\text{m}^2 \text{ }^\circ\text{C A}^{-1}$
	t_3	15.24178	$\text{m}^2 \text{ }^\circ\text{C}^2 \text{ A}^{-1}$
Faraday efficiency	f_{11}	478645.74	$\text{A}^2 \text{ m}^{-4}$
	f_{12}	-2953.15	$\text{A}^2 \text{ m}^{-4} \text{ }^\circ\text{C}^{-1}$
	f_{21}	1.03960	—
	f_{22}	-0.00104	$^\circ\text{C}^{-1}$
Gas purity (hydrogen in oxygen)	C_1	0.09901	—
	C_2	-0.00207	$^\circ\text{C}^{-1}$
	C_3	1.31064×10^{-5}	$^\circ\text{C}^{-2}$
	C_4	-0.08483	—
	C_5	0.00179	$^\circ\text{C}^{-1}$
	C_6	-1.13390×10^{-5}	$^\circ\text{C}^{-2}$
	C_7	1481.45	A m^{-2}
	C_8	-23.60345	$\text{A m}^{-2} \text{ }^\circ\text{C}^{-1}$
	C_9	-0.25774	$\text{A m}^{-2} \text{ }^\circ\text{C}^{-2}$
	E_1	3.71417	—
	E_2	-0.93063	bar^{-1}
	E_3	0.05817	bar^{-2}
	E_4	-3.72068	—
	E_5	0.93219	bar^{-1}
	E_6	-0.05826	bar^{-2}
	E_7	-18.38215	A m^{-2}
	E_8	5.87316	$\text{A m}^{-2} \text{ bar}^{-1}$
	E_9	-0.46425	$\text{A m}^{-2} \text{ bar}^{-2}$

Figure 2.2 Coefficient Values for HTO, Vrev and Faraday efficiency calculation

While HTO (Hydrogen to Oxygen Diffusion) is an important variable that should be considered, especially for safety reasons, 2% HTO emergency stop should take place and 1.6% HTO is the alarm value [5], the diffusion of oxygen to hydrogen (OTH) can be considered as negligible quantity around 0.1-0.5% [31]. The mass balance on the anode and cathode side generates the following equations.

$$n_{H_2,cat} = n_{H_2,prod} \quad (2-9)$$

$$n_{H_2,an} = n_{HTO} \quad (2-10)$$

$$n_{O_2,an} = n_{O_2,prod} = 0.5 n_{H_2,prod} \quad (2-11)$$

2.2.1.1 Calculation of Electrical Input

In Table 2.4 [32], the values for the required quantities in order to calculate the electrical input and their respective units of measurement are presented.

Table 2.4 Values and Units for Electrical Input Calculation

Electrolyser Base Energy Requirement (EBER)	39.4	kWh/kg
Electrolysis Efficiency (ne)	63.2 %	-
Electrolyser Energy Requirement (EER)	62.24	kWh/kg
Hydrogen Mass Required	942.17	kg/h

Taken these into consideration, the Electrical Input of the Electrolyser Stack is calculated as follows :

$$EER = \frac{EBER}{ne} \quad (2-12)$$

$$Electrical\ Input = EER * \dot{m}H_2 \quad (2-13)$$

2.3 Validation of Stack model

To validate the stack model that was created a comparison with the original paper figures takes place. Specifically, the diagrams that are compared are the hydrogen flow rate and HTO for different inlet stack temperatures and stack pressures.

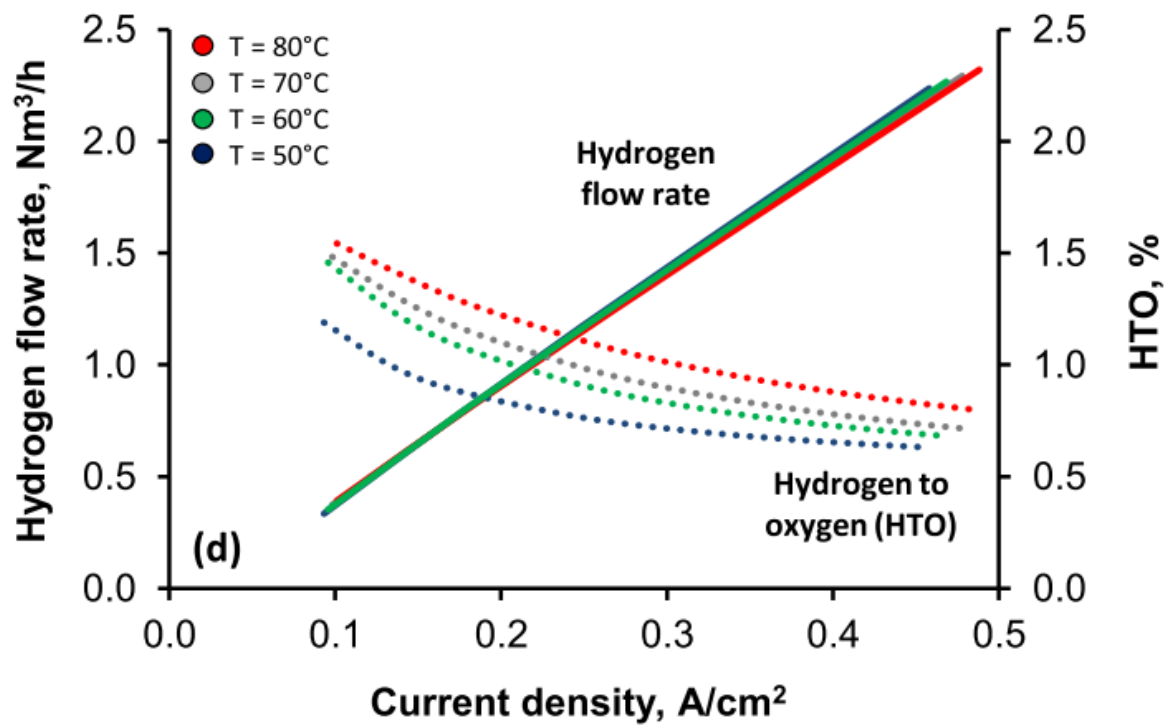


Figure 2.3 Hydrogen flow rate-HTO for different current densities and inlet temperatures for 7 bar stack pressure-Original Paper

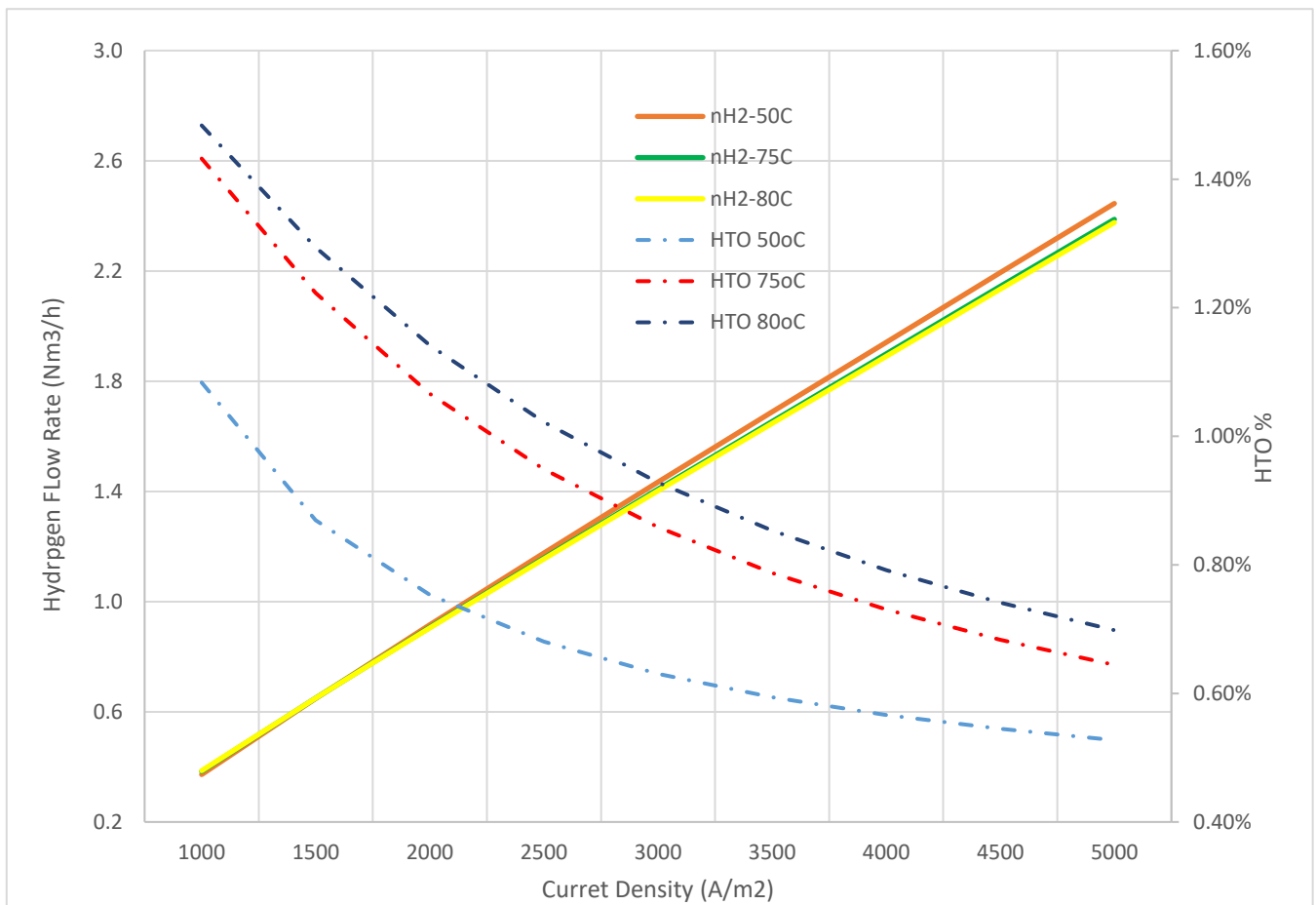


Figure 2.4 Hydrogen flow rate-HTO for different current densities and inlet temperatures for 7 bar stack pressure

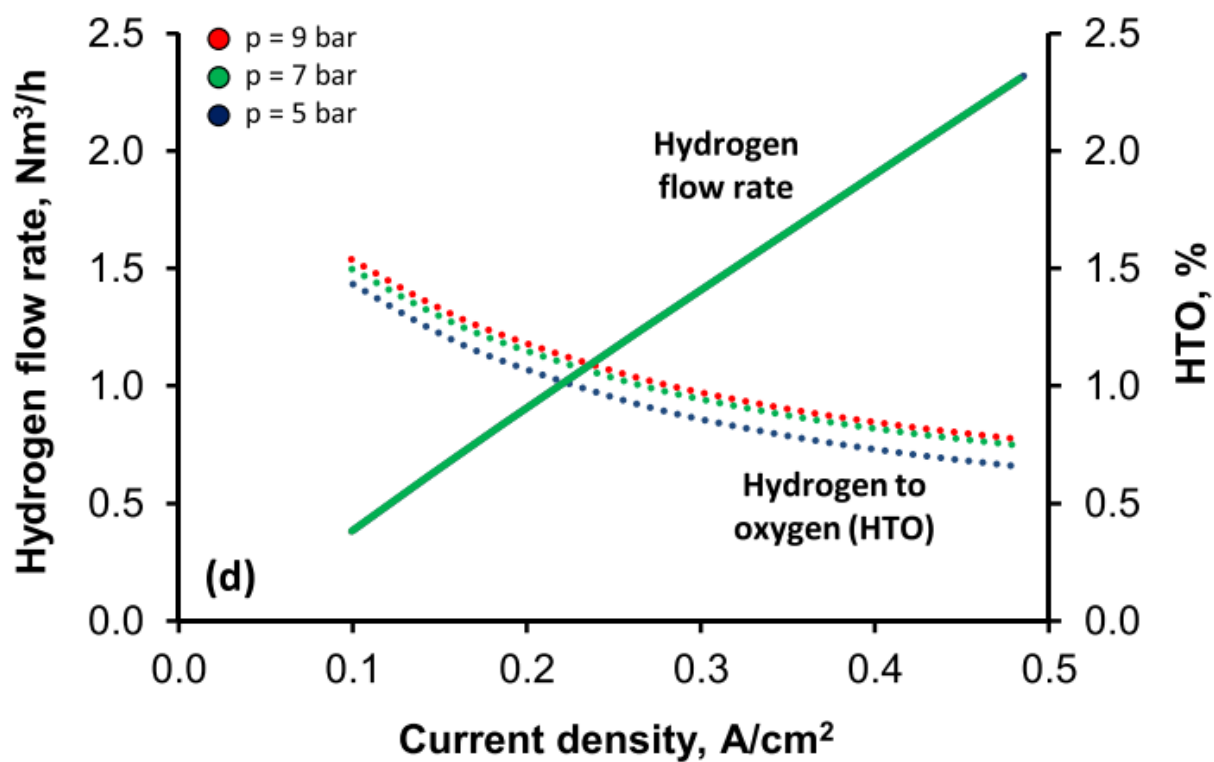


Figure 2.5 Hydrogen flow rate-HTO for different current densities and inlet temperatures for 72°C
Temperature-Original Paper

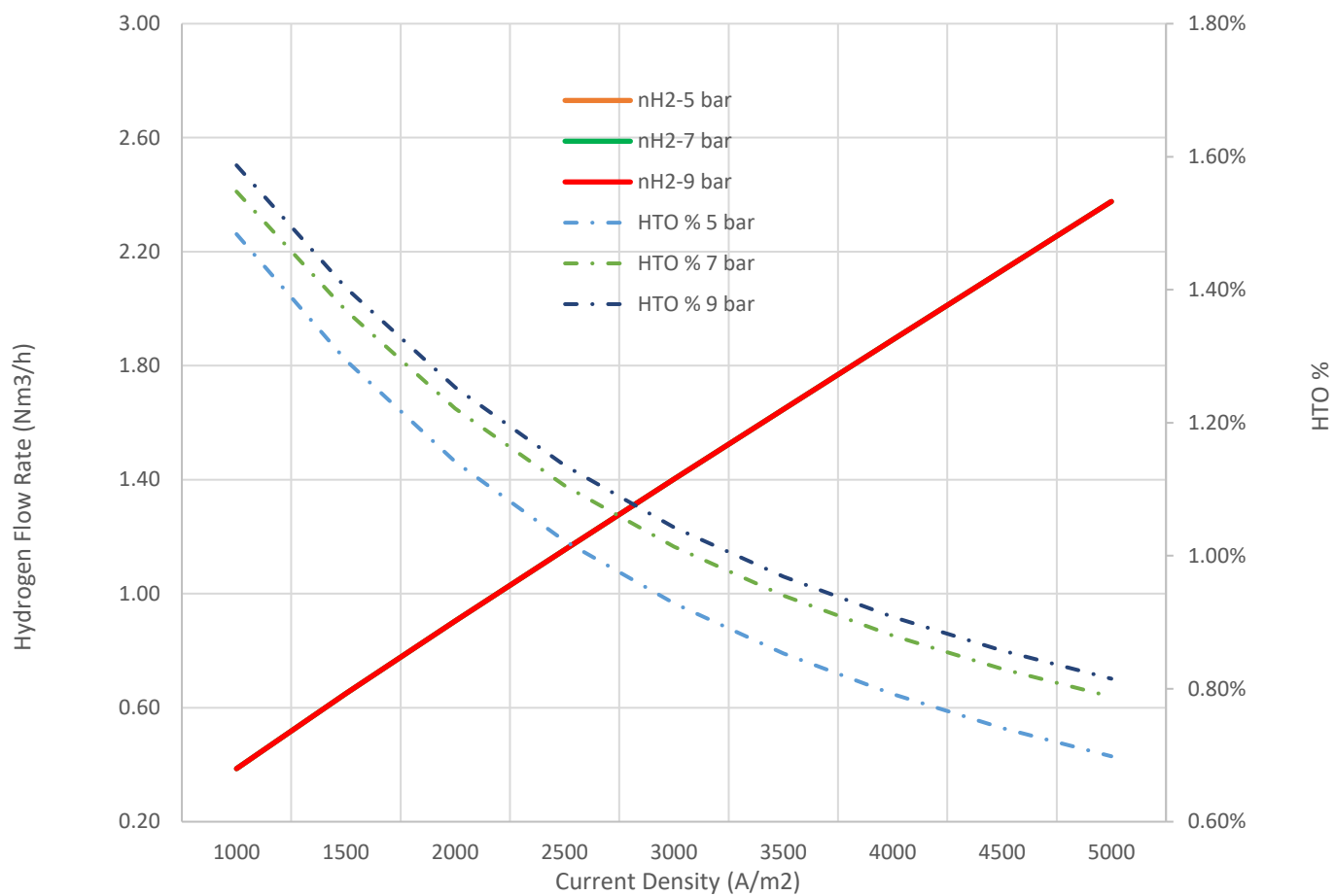


Figure 2.6 Hydrogen flow rate-HTO for different current densities and inlet temperatures for 80°C temperature

As illustrated in Figures 2.2-2.5, the H₂ flow rate, correlated with different pressure and temperatures across the stack, as well as the diffusion of Hydrogen to Oxygen (HTO) shows very similar results with the work of Sanchez and al. Thus, it is assumed that the stack developed in this thesis is validated.

2.4 Results and Discussion

In this chapter, data from the simulation are used in order to study the alkaline system behavior. Additionally, a simple techno-economic analysis is performed using the exported data, in order to calculate the LCOH for a PV electrical source, is done.

2.4.1 Influence of temperature in stack system

To understand the influence of temperature in the electrolysis stack system, three different temperature values of 50°C, 75°C and 80°C were selected. Afterwards, combining equations (5)-(11), the values of stack efficiency for these temperature values were calculated and plotted as a function of current density. The results are shown in Figure 2.6

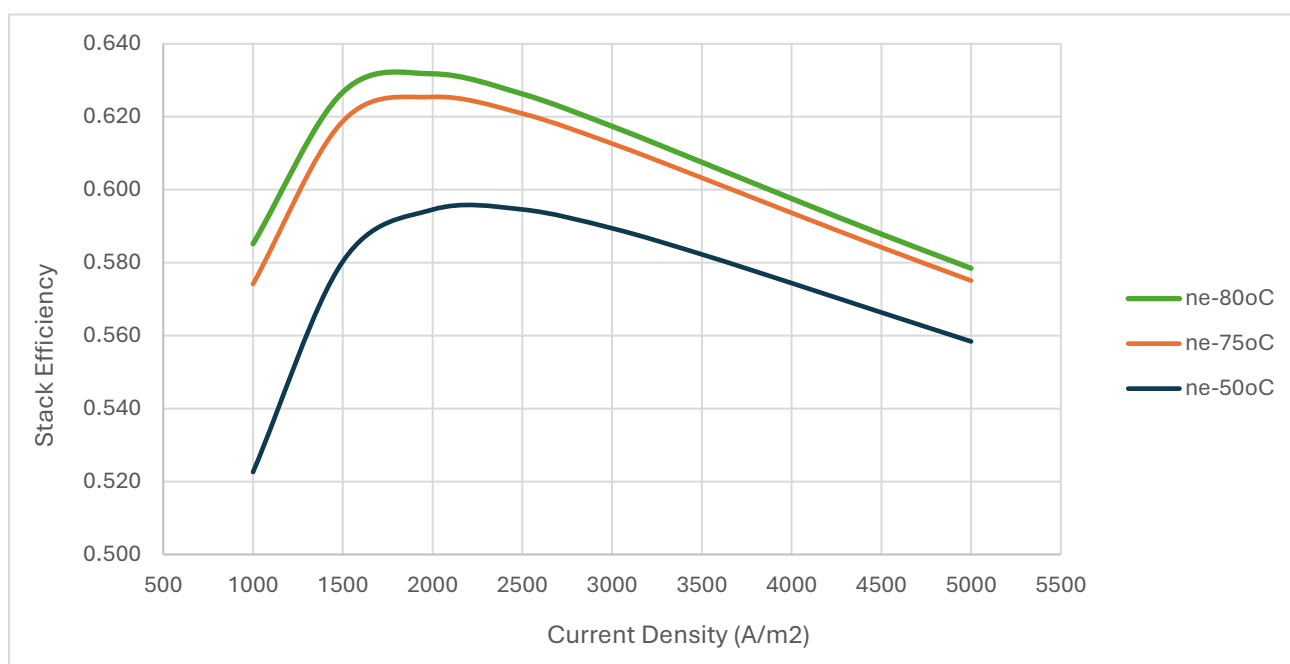


Figure 2.7 Stack Efficiency vs Current Density for different temperature values

As illustrated in Fig.2.6, stack efficiency is highly dependent on temperature, with a clear increase as temperature increases. Furthermore, it is evident that high values of current density don't facilitate the electrolysis process, with the peak value being 2000 A/m². Additionally, examining Fig.2.3 presented in the previous chapter, temperature has a relatively minor effect on the hydrogen flow rate of in the stack, yet at 80°C the rate is indeed higher. Therefore, from a temperature standpoint, the optimal scenario involves the stack system temperature set at 80°C.

2.4.2 Influence of pressure in stack system

Same as in chapter 2.6, Figure 2.7 is made, presenting the results for stack efficiency in different pressures when changing the current density.

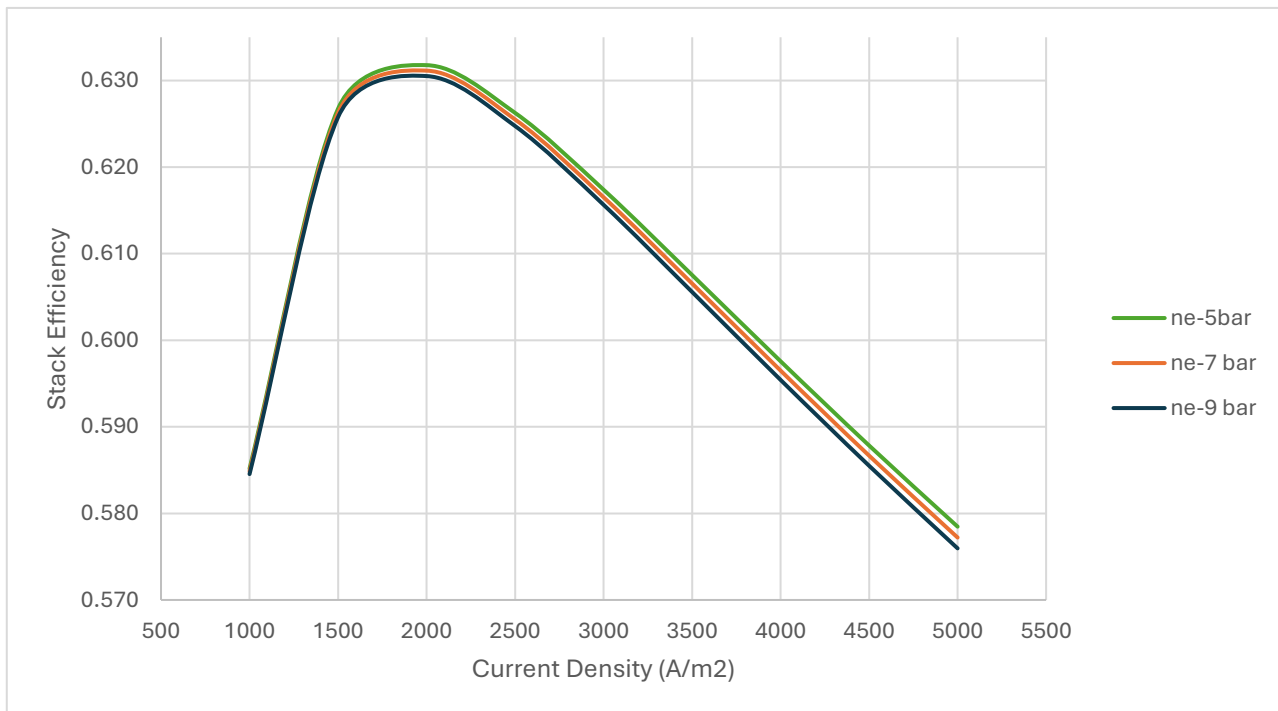


Figure 2.8 Stack Efficiency vs Current Density for different pressure values

As illustrated in Fig.2.7, stack efficiency is not highly dependent on pressure changes, despite the slight decrease as pressure increases. Furthermore, as previously mentioned, it is evident that high values of current density don't facilitate the electrolysis process, with the peak value being also 2000 A/m². Examining Fig.2.5 presented in the previous chapter, pressure does not significantly impact the hydrogen flow rate, as there's a clear overlap between the lines. However, given the slight increase in stack efficiency and the existing tendency to operate at lower pressures when it is feasible, the optimal scenario involves the stack system pressure set at 5 bar.

The chosen operating conditions ultimately lead to a stack efficiency of **63.2 %**.

2.5 Economic Analysis and LCOH evaluation

This chapter presents a simple techno-economic analysis takes, in order to calculate the Levelized Cost of Hydrogen (LCOH) of the simulated electrolyser system. The LCOH is calculated for the optimal scenario of 80°C and 5 bar, operational parameters in present time (2024) and solar photovoltaic electricity source (PV). Intermittency issues regarding PV panels are not taken into consideration, so the electricity feed is considered constant. It is assumed that the electrolyser works 8000 hours (CF=91,32 %) yearly. The lifetime of the system is assumed to be 25 years.

2.5.1 Economic Analysis

For the calculation of the LCOH the following formula was used:

$$LCOH = \frac{CAPEX [\text{€}] * ACCR + OPEX \left[\frac{\text{€}}{\text{year}} \right] + SolutionCost \left[\frac{\text{€}}{\text{year}} \right] + LCOE \left[\frac{\text{€}}{\text{year}} \right]}{H_{2,prod} \left[\frac{\text{kg}}{\text{year}} \right]} \quad (2-14)$$

$$ACCR = \frac{(1+i)^n * i}{(1+i)^n - 1} \quad (2-15)$$

where, i is the discount ratio assumed to be 10 %, while n is the lifespan of the system assumed to be 25 years.

- **CAPEX Costs**

For the CAPEX of present time scenario, the following equations were used. [33]

$$CAPEX_{stack, 2024} = 600[\text{€kW}] * 58643.76[\text{kW}] = 35,186,254.03 \text{ €} \quad (2-16)$$

- **OPEX Costs**

The OPEX was calculated as 4% of the CAPEX [33]. The stack needs replacement every 80000 working hours due to degradation and it adds an 30% of the CAPEX cost [34]. In our case system-for a plant life of 25 years- the stack will be replaced 2 times; hence this adds 60% of the CAPEX cost.

- **Feed water solution Cost**

The feed water solution cost, as it is not pre-made, is evaluated using the following formula:

Table 2.5 Values of Quantities for Solution Cost Calculation

Deionised Water Mean Cost (€/m ³) [34]	2
KOH 99% cost (€/ton) [35]	756.7
% Water Composition	65
% KOH Composition	35

$$Solution\ Cost = \left(\frac{\%WaterComp * WaterCost}{1000} + \frac{\%KOHComp * KOHCost}{1000} \right) * 1000 \quad (2-17)$$

- **LCOE Cost**

The LCOE for a primary PV electricity source is $0.045 \frac{\text{€}}{\text{kWh}}$ [36]

2.5.2 LCOH Results and Discussion

The results of the techno-economic analysis are shown in Table 2.6.

Table 2.6 Results of Electrolyser Techno-economic analysis

BOP Scenario	PV Connection	
Hydrogen Production	kg/year	8,264,736
CF	%	91.32
CAPEX,stack	€	35,241,928.48
OPEX, stack	€/year	1,409,677.14
Stack Replacement	€	21,145,157.09
Solution Cost	€/m ³	266.15
Solution Need	m ³ /year	114,434
Solution Cost	€/year	30,456,252.56
LCOE	€/year	21,145,157.09
MEOHproduction	kg/year	25,828,151.5
LCOH	€/kg	6.99

Examining Table 2.6, several conclusions can be reached:

- The price of green H₂ is on average 2-3 times higher than the price of grey H₂ in Europe in 2024. [37]
- While market prices may vary, the LCOH produced by this study's electrolyser is within the lower bound of the market prices for 2024. [2]
- Although the electrical input, capital costs, and operational costs are relatively high, the overall cost is balanced by the high capacity of the system.
- Although, a 58.6 MW electrolyser is not currently available in the market, the desired electrical input is reached by connecting several 1.5 MW electrolyzers currently abundant in the market [38]

3 Carbon Capture Process with MEA

In this chapter, the simulation of carbon capture process with MEA is presented using Aspen Plus V11. The optimization of the process, the sensitivity analysis as well as a thorough techno-economic analysis are also included in this chapter.

3.1 System Components

Table 3.1 lists the components entered in the Aspen Plus computational environment to carry out the simulation of the CO₂ capture process.

Table 3.1 Chemical Components for the Carbon Capture Process as listed in Aspen Plus software

Component ID	Type	Component Name	Alias
CH4	Conventional	METHANE	CH4
C2H6	Conventional	ETHANE	C2H6
C3H8	Conventional	PROPANE	C3H8
I-C4	Conventional	ISOBUTANE	C4H10-2
N-C4	Conventional	N-BUTANE	C4H10-1
I-C5	Conventional	2-METHYL-BUTANE	C5H12-2
N-C5	Conventional	N-PENTANE	C5H12-1
HEXANE	Conventional	N-HEXANE	C6H14-1
N2	Conventional	NITROGEN	N2
CO2	Conventional	CARBON-DIOXIDE	CO2
H2	Conventional	HYDROGEN	H2
CO	Conventional	CARBON-MONOXIDE	CO
H2O	Conventional	WATER	H2O
O2	Conventional	OXYGEN	O2
NEO-C5	Conventional	2,2-DIMETHYL-PROPANE	C5H12-3
ARGON	Conventional	ARGON	AR
SULFU-01	Conventional	SULFUR	S
CARBO-01	Conventional	CARBON-GRAPHITE	C
CO3--	Conventional	CO3--	CO3-2
MEA	Conventional	MONOETHANOLAMINE	C2H7NO
MEA+	Conventional	MEA+	C2H8NO+
MEACOO-	Conventional	MEACOO-	C3H6NO3-

3.2 Selection of Thermodynamic Package

The ELECNRTL model of Aspen was considered the most suitable to describe the chemical CO₂ uptake process. Accordingly, the electrolyte-NRTL model is used for the liquid phase, while the Redlich-Kwong equation of state is used for the gas phase. Henry's law is used to describe the phase equilibrium of non-condensable components (CO₂, N₂, O₂, CO, H₂, CH₄, C₂H₆). The definition of these Henry components is done in the Components|HenryComps tab. The reference state for calculating the activity factor for Henry components and ions is defined in the Setup|Calculation Options|Reactions and Chemistry|Specifications forms, respectively. In this work, the Henry components are defined as Mixed-Solvent and the ions as Unsymmetric.

3.3 Chemical and Phase Equilibria

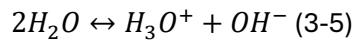
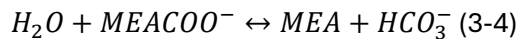
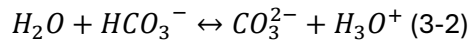
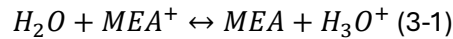
For the correct description of the carbon capture process, it is necessary to determine the exact composition of the two phases in contact at equilibrium. In this section, the equilibrium reactions governing the system are analyzed and the interaction parameters used in the software are presented.

3.3.1 Reactions and equilibrium constants

During the process of carbon capture in an aqueous amine solution, electrolytic reactions occur in the liquid phase. In Aspen, when determining the electrolytes, it is necessary to define the reactions governing this system. Because these reactions are rapid, they are assumed to reach chemical equilibrium. The calculation of the solution composition is done by introducing the appropriate equilibrium constants.

To define the set of reactions, a new Chemistry ID is created in Properties|Chemistry. At this point, all reactions that affect the system are defined, as well as the corresponding thermodynamic equilibrium constants. In this task, the thermodynamic constants are calculated based on the mole fractions (Mole-Frac) of the chemical species.

During the CO₂ absorption process in an aqueous MEA solution, the reactions that take place are as follows:



Each equilibrium reaction is accompanied by its corresponding equilibrium constant, which relates the concentrations and activity coefficients of reactants and products:

$$K_j^{eq} = \frac{\prod_{i=1}^{prod} (\gamma_i x_i)^{v_i}}{\prod_{i=1}^{react} (\gamma_i x_i)^{v_i}} \quad (3-6)$$

where: γ_i is the activity coefficient, x_i the molar fraction and ν_i the stoichiometric coefficient of component i in j reaction.

In Aspen Plus, the thermodynamic equilibrium constants are approximated in the form of polynomial equations. The correlation used is the following:

$$\ln(K_{eq}) = A + \frac{B}{T} + C * \ln(T) + D * T \quad (3-7)$$

where K_{eq} in units of molar fraction and T in K .

The values of the coefficients of the equilibrium constants, for each reaction, are shown in Table 3.2 below:

Table 3.2 Thermodynamic Coefficients parameters in CO₂ capture reactions

Reaction	A	B	C	D
19	-3.038325	-7008.3569	0.0	-0.003135
20	216.050446	-12431.7	-35.481899	0.0
21	231.465439	-12092.10	-36.781601	0.0
22	-0.52135	-2545.53	0.0	0.0
23	132.89888	-13445.9	-22.477301	0.0

Then, the Chemistry ID that has been created is selected in the Methods|Global|Electrolyte calculation options field and thus constitutes the general model based on which electrolyte calculations are performed. Note that the input of the reactions above is particularly important because they affect the phase equilibrium, physical properties and other characteristics of the system.

3.3.2 Interaction parameters of the Electrolyte-NRTL model

To describe the phase equilibrium with the $\gamma - \phi$ approach, it is necessary to calculate the activity coefficient for each component, and therefore, to use the appropriate interaction parameters. In this study, the default molecule-molecule interaction parameters from the Electrolyte-NRTL model were used. These parameters are for the H₂O-CO₂ and H₂O-MEA molecule interaction and are presented in Table 3.3

Table 3.3 Molecule to molecule interaction parameters of NRTL model

Component i	Component j	AIJ	AJI	BIJ	BJI	CIJ
H2O	CO2	10.064	10.064	-3268.135	-3268.135	0.2
H2O	MEA	1.438498	-1.046602	99.02104	-337.5456	0.2

For the molecule-ion pair and ion-molecule pair interactions, the parameters obtained from Freguia's regression procedure [39] were used. These parameters are of high accuracy, as they give very good results for higher loadings and for this reason they were used in this work. These parameters were entered in the respective tabs in Methods|Parameters|Electrolyte Pair and are summarized in Table 3.4.

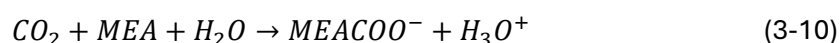
Table 3.4 Interaction Parameters for the molecule-ion pair introduced in Aspen Plus

	GMELCC-1	GMELCD-1
H ₂ O - (MEA ⁺ MEACOO ⁻)	10.4	-119.92
(MEA ⁺ MEACOO ⁻) - H ₂ O	-5.963	336.45
H ₂ O - (MEA ⁺ HCO ₃ ⁻)	6.88	969.63
(MEA ⁺ HCO ₃ ⁻) - H ₂ O	-3.89	-91.35

3.4 Reaction Kinetics

Some reactions in the absorption tower do not occur fast enough, so the use of finite rate models is required. To address this issue, an additional set of reactions valid only in the absorption column (Absorber) is incorporated. More specifically, to introduce finite rate reactions, such as those identified by the RadFrac model, a new Reaction ID is defined in the Blocks|ABSORBER|Specifications|Reactions form. This makes it possible to identify reactions at equilibrium and reactions with finite rates.

It is important to model the kinetics of the reactions in the system with rate expressions that depend on temperature and concentrations. Thus, the reactions characterized by finite rates replace two of the ways in which CO₂ can react directly in the mixture:



Of the above reactions, only the reaction of CO₂ with MEA contributes significantly to the absorption of dioxide, because the concentration of hydroxides is low. However, the reaction with the hydroxides is not negligible at high carbonation rates when the reaction of CO₂ with the MEA is slow and thus both are considered.

Aspen calculates reaction rates with Power Law-type kinetic expressions, i.e. of the form $r = k \cdot C$, where k is calculated from the Arrhenius equation. The full form of the rate is:

$$r = k \left(\frac{T}{T_o} \right)^n \exp \left[\left(-\frac{E}{R} \right) \left(\frac{1}{T} - \frac{1}{T_o} \right) \right] \prod_{i=1}^{reac.} C_i^{v_i} \quad (3-12)$$

In the case where T_o is not defined and $n = 0$, the rate equation takes the form:

$$r = k \cdot \exp \left(-\frac{E}{RT} \right) \prod_{i=1}^{reac.} C_i^{v_i} \quad (3-13)$$

The above rate expression is also used in this work. Molarity is defined as the basis for calculations. Note that in reaction (26), where water is the reactant, it is not considered in the rate expression, i.e. $v_{H_2O} = 0$.

The kinetic parameters of reactions are taken from the works of Pinsent et al. [40] and Hikita et al. [41] Table 3.5 summarizes the pre-exponential factor and activation energy of each reaction.

Table 3.5 Kinetics of reactions taking place in absorber tower using MEA solution

Reaction	k	E (cal/mol)
(3-8)	4.23E+13	13249
(3-9)	2.38E+17	29451
(3-10)	9.77E+10	9855.8
(3-11)	3.23E+19	15655

Overall, the reactions included in the absorption column are the equilibrium reactions (19), (20), (23) and the finite rate reactions (26), (27), (28), (29). The values of the reaction parameters are taken from Tables 3.2 and 3.5 and introduced into the respective Equilibrium and Kinetic forms in Aspen Plus.

In addition, the loading, α , is defined as a design parameter for the simulation, which is the ratio of the molar fractions of all CO₂-bearing species to all MEA-bearing species.

$$\alpha = \frac{x_{CO_2_{tot}}}{x_{MEA_{tot}}} = \frac{x_{CO_2_{dis}} + x_{HCO_3} + x_{CO_3^{-2}} + x_{MEACOO^{-}}}{x_{MEA} + x_{MEA^{+}} + x_{MEACOO^{-}}} \quad (3-14)$$

3.5 Simulation of Carbon Capture Process

Fig.3.1 presents the Process Flow Diagram of the process, as simulated in Aspen Plus V11 environment.

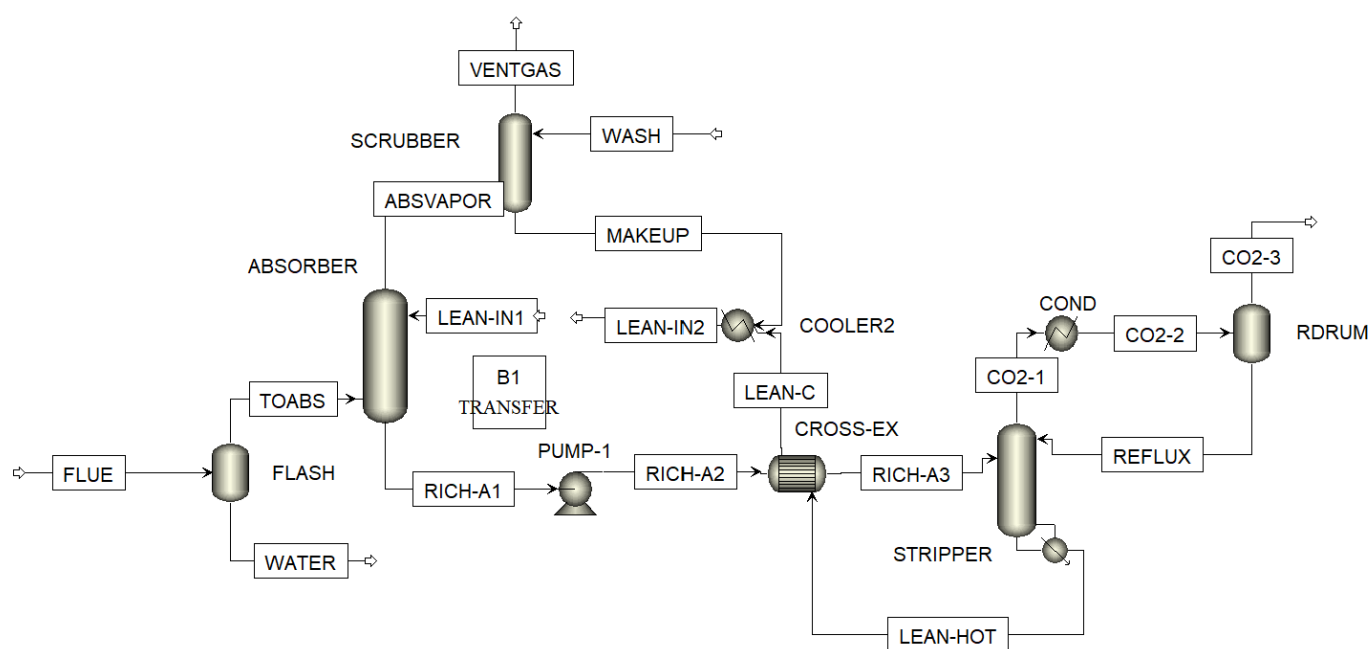


Figure 3.1 Process Flow Diagram of Carbon Capture Process in Aspen Plus

The inlet stream from the cement plant blast furnace enters the FLASH to remove a significant amount of water. The top product of the distillation column is then directed to the absorption column (ABSORBER), with the stream remaining in the gas phase at 50°C. In this way the amount of solvent required and the load of the absorber on the STRIPPER is reduced. According to the literature [19], the exhaust gas stream is introduced at the bottom of the absorption column at a temperature in the range of 40-50°C. In the present work the upper limit of 50°C was chosen.

Next, the resulting stream is led to the absorption column (ABSORBER), where CO₂ is captured by amine. The process takes place usually in a packed column, where the gas mixture containing CO₂ enters from the bottom and exits from the top of the column, while the amine stream flows in the opposite direction. The packing increases the contact surface between the two fluids, improving the transport phenomena. The outgoing gas contains traces of CO₂ since the main amount of CO₂ has been absorbed by the amine. The top product from the absorption column is then fed to the SCRUBBER, which removes any amine that may have passed into the process stream during absorption. This results in the VENTGAS stream, which is free of CO₂ and any amount of amine.

The rich stream resulting from the absorption column after being compressed and heated is led to the stripper to separate the amine and CO₂. The resulting stream is directed to a separation column to separate the CO₂ from the water contained in the stream. The CO₂ is recovered for other industrial processes (including sales). The main solvent used for CO₂ capture is the aqueous amine solution, monoethanolamine (MEA). The amine used is recovered and reused in the absorption unit.

In this simulation, some basic assumptions have been made. These are:

- Stream FLUE comes from the blast furnace of a cement industry without containing any sulfur oxides which poison the amine
- The goal of the process is a 90 % capture of CO₂
- In this simulation, dehydration and compression of CO₂ are not included.

Table 3.6 summarizes the blocks used in Aspen Plus and their respective function.

Table 3.6 Aspen Plus Models and their function

Όνομα	Aspen Plus Model	Function
FLASH	Flash2	Flash Vessel
ABSORBER	Radfrac	Absorption
PUMP-1	Pump	Pump
CROSS-EX	HeatX	Heat Exchanger
STRIPPER	RadFrac	Stripper Column
COND	Heater	Condenser
RDRUM	Flash2	Reflux Drum
COOLER2	Heater	Cooler
SCRUBBER	Radfrac	Scrubber Tower

Moreover, the conditions of the feed streams of the process are shown in the following tables (Table 3.7, Table 3.8, Table 3.9, Table 3.10)

Table 3.7 Feed Stream characteristics in Carbon Capture Unit

Temperature (°C)	50
Pressure (atm)	1.01
Molar Fraction (Vapor)	1
Molar Flow Rate (kmol/hr)	12000

Table 3.8 Composition of Feed Stream in Carbon Capture Unit

Component	(mol-%)
N2	62.4
CO2	22.8
H2O	7.3
O2	7.5

Table 3.9 MEA Solvent stream Characteristics in Carbon Capture Unit

MEA Solvent 30% wt.	
Temperature (°C)	50
Pressure (atm)	1

Table 3.10 MEA Solvent Composition in Carbon Capture Unit

Component	(mol-%)
H ₂ O	88.78
MEA	11.22

For the carbon dioxide absorption process, a standard aqueous solution containing 30% w/w of amine is used. In addition, the loading has been set at the top of the column equal to 0.2. This choice has been made based on thorough studies showing that it provides optimum performance at low operating costs. The effect of loading in the process will be analyzed in the next chapters.

The amount of carbon dioxide is calculated by mixing the amine fraction with the carbonation ratio and normalizing the molar fraction values. Thus, the solvent stream finally fed to the absorption column has the following characteristics and composition.

Table 3.11 Composition of solvent stream fed in CO₂ absorption unit (LEAN-IN1)

MEA 30% wt. – $\alpha = 0.2$	
Temperature (°C)	50
Pressure (atm)	1
Composition (mol%)	
H ₂ O	86.83
MEA	10.98
CO ₂	2.20

The solvent flow rate depends on the CO₂ capture rate, the geometric characteristics of the absorption column and the loading of the solvent at the top of the column. In the simulation, 90% carbon dioxide removal is selected in the simulation and the solvent flow rate is adjusted in this way.

Table 3.12 details the simulation characteristics of all individual processes.

Table 3.12 Characteristics of all equipment used in CO₂ absorption with MEA

FLASH	Temperature	50 °C
	Pressure	1.13 atm
ABSORBER	Number Of Theoretical Stages	8
	Pressure	1 atm
	Packing	IMTP NORTON 25 mm
	HETP	1.88 m
	Flooding fraction approach	0.7
PUMP-1	Efficiency	0.75
	Discharge Pressure	3.7 atm (equal to the saturation pressure of the solution at the inlet temperature of the stripping column)
CROSS-EX	$\Delta T_{\min}$ (Hot in – Cold out)	10 °C
	Operation	Counter-current
STRIPPER	Number Of Theoretical Stages	8
	Pressure	1.7 atm
	Packing	IMTP NORTON 25 mm
	HETP	1.5 m
	Flooding fraction approach	0.7
	Reboiler Type	Kettle
COND	Temperature Out	40 °C
	Pressure	1.7 atm
RDRUM	Temperature	40 °C
	Pressure	1.7 atm
COOLER2	Temperature Out	40 °C
	Pressure	1 atm
SCRUBBER	Pressure	1 atm
	Number Of Stages	2
	Water Temperature	20 °C

The flash vessel (FLASH) is added to remove most of the water from the inlet stream to the Absorber. In this way, the temperature of the TOABS stream can be reduced to 40°C, with the stream remaining entirely in the gas phase. This reduces the amount of solvent required and the load of the absorber on the STRIPPER.

The absorption and stripping columns are simulated according to the equilibrium stage model. In this model, the column is divided into several theoretical stages, and it is assumed that the vapor and liquid phases leaving each stage are in thermodynamic equilibrium with each other. Thus, in the absorption column, in the Blocks|ABSORBER|Specifications|Setup field and in the corresponding STRIPPER field, "Equilibrium" is selected as the "Calculation Type". Furthermore, for the convergence of both columns the option "Strongly non-ideal liquid" is set, which is provided by Aspen.

In the absorption column, the solvent stream (LEAN-IN1) is introduced at the first stage of the column, while the CO₂-rich stream (TOABS) is introduced at the last stage of the column (on-stage). Similarly, in the stripping column the reflux stream (REFLUX) is introduced above the first column stage (Above-Stage) and the CO₂-rich amine stream (RICH-A3) in the second column stage (On-stage). Note that in STRIPPER, 8 theoretical stages are defined in the "Configuration" of the column, however the last one corresponds to the column reflux stream.

The assumption of the equilibrium tier model is quite simplistic and coefficients such as HETP and tray efficiency estimation methods are used to correct for model inaccuracy. In this work, for packed columns (ABSORBER, STRIPPER), the HETP (Height Equivalent to Theoretical Plate) factor is used to convert the theoretical grades to packing height. The values for the HETP factor were taken from the literature [42] and are entered in the Column Internals|Sections|Geometry field for the absorption and stripping columns.

In packed columns, for a given liquid flow, the gas velocity at the loading point (usually corresponding to 70% of the flooding velocity) is very often used to calculate the internal column diameter [42]. Thus, in absorption and stripping columns the % Approach to maximum capacity ($\frac{L}{V}$) is defined in the Column Internals|Sections|Design Parameters field equal to 70%. Thus, Aspen calculates the minimum diameter to meet the flooding criterion.

In the Absorber some rate-controlled reactions take place. Thus, it is necessary to set the liquid holdup at each stage (liquid holdup) in the Blocks|ABSORBER|Specifications|Reactions|Holdups form. To assign a value to the holdup, the Column Internals option of the Radfrac model was used. It is particularly important that the holdup units are set correctly, as these also determine the units of the predictor of the reactions. In this work the holdup is calculated in m³.

In the stripping column, due to the high temperatures involved, it is assumed that all reactions are very fast and reach equilibrium. Thus, there is no need to set the holdup to perform the calculations. Furthermore, in STRIPPER there is no need to redefine reactions as was done in Absorber, as the Chemistry ID is already defined in the Methods tab.

3.6 Simulation details

Initially, the simulation was solved in an open loop to achieve easier convergence and shorter computational time. Then, after the simulation had converged and all design specifications had been met, the simulation was solved using a Transfer Block in a closed loop.

More specifically, three design specifications are used in the simulation to obtain the desired results. The Design Specs used in the simulation are:

1. **CAPTURE:** The CO₂ capture rate is adjusted by defining the ratio of the CO₂ supply in the gaseous stream leaving the Absorber to the CO₂ at the inlet of the column. In particular, it is set that $\frac{CO_2 \text{ mole flow}|_{ABSVAPOR}}{CO_2 \text{ mole flow}|_{TOABS}} = 0.1$, or the percentage of CO₂ capture to be 90 %. This is achieved by varying the solvent flow at the top of the column (LEAN-IN1).
2. **LOADING:** The amount of heat in the STRIPPER reboiler is varied so that the loading of the LEAN-IN2 stream is identical to that in the LEAN-IN1 stream, i.e. in our case equal to 0.2.
3. **BALANCE:** The flow of the WASH stream is adjusted to the SCRUBBER to maintain the mass balance for the water throughout the process and ensure convergence. Specifically, the amount of water in the WASH stream plus that in the process input stream (FLUE stream) is set equal to the sum of the amount of water in the VENTGAS, CO2-3 and WATER streams.

However, the use of design specifications combined with the existence of recycling loops make the overall convergence of the simulation challenging. It requires the use of several solvers by the program, through which a large iterative loop, including several nested loops, must be solved. Thus, the following steps are followed to converge the simulation:

Initially, the simulation was solved without the Design specs in operation, with the REFLUX stream not connected to the Stripper. A different reflux stream was assigned to the Stripper, to which an initial recommendation and supply was given. In addition, the LEAN-HOT stream was defined as a tear stream, for which Aspen makes an initial recommendation estimate. It should be noted that this stream must also be given initial conditions, otherwise, due to its selection as a tear stream, Aspen assumes zero flow and errors result.

Thus, results were obtained for the REFLUX and LEAN-HOT streams, which were set as inputs for the subsequent simulations, i.e. a reconcile of these two was performed. Then, the reflux current was connected to the Stripper and defined as the cutoff current. This resulted in the order of resolution of each block and thus the entire simulation. Finally, all Design specs were enabled to obtain the desired results. Note that after performing the above steps, the LEAN-IN1 and LEAN-IN2 streams, which are essentially the same stream, are almost identical in all their properties. At this point the simulation can practically be solved in a closed loop using a Transfer block. Thus, through this block the LEAN-IN1 stream is copied to the LEAN-IN2 stream at each iteration. Note that this can only be achieved if the above path has been followed to satisfy the mass balances.

3.7 Results

Upon solving the simulation, it is found that for capturing 90% of the carbon dioxide from the feed stream to the absorption column (TOABS stream), i.e. for the capture of **116,523** kg/hr of CO₂, the following are required:

- **81,179** kmol/hr of 30% wt. MEA solvent with an input carbonation ratio equal to 0.2 in the absorption column
- **149** MW in the STRIPPER column reboiler
- **4259** kmol/hr of pure water in the SCRUBBER column

Table 3.13 summarizes the properties and composition of the main streams in the simulation of the CO₂ absorption process with MEA.

Table 3.13 Table of streams for the CO₂ capture process

Stream	TOABS	ABSVAPOR	VENTGAS	RICH-A1	RICH-A3	LEAN-HOT	LEAN-C	CO2-3
Temperature (°C)	50.0	78.1	73.6	55.8	109.1	119.1	66.5	50.0
Pressure (bar)	1.01	1.01	1.01	1.01	3.75	1.72	1.72	1.72
Molar Vapor Fraction	1	1	1	0	2.59E-05	0	0	1
Molar Flow (kmol/hr)	12000	13956	13586	76764	76852	76554	76552	2855
Mass Flow (ton/hr)	374.75	346.21	339.36	1972.65	1972.65	1852.38	1852.38	120.74
Molar Fraction								
CH4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C2H6	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C3H8	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
I-C4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N-C4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
I-C5	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N-C5	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
HEXANE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N2	0.624	0.537	0.551	0.0000	0.0000	0.0000	0.000	0.0000
CO2	0.228	0.020	0.020	0.0000	0.0012	0.0000	0.0000	0.927
H2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H2O	0.073	0.379	0.363	0.876	0.869	0.879	0.880	0.073
O2	0.075	0.064	0.066	0.0000	0.0000	0.0000	0.000	0.0000
NEO-C5	0.000	0.000	0.000	0.000	0.000	0.0000	0.000	0.0000
H3O+	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.000
OH-	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.000
HCO3-	0.000	0.000	0.000	0.005	0.011	0.0013	0.0005	0.000
CO3--	0.000	0.000	0.000	0.0002	0.0001	0.0000	0.0002	0.000
MEA	0.000	0.0003	0.0000	0.007	0.016	0.073	0.072	0.0000
MEA+	0.000	0.000	0.000	0.058	0.057	0.024	0.024	0.000

MEACOO-	0.000	0.000	0.000	0.053	0.045	0.022	0.023	0.000
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3.8 Sensitivity Analysis

Table 3.14 shows the results of the sensitivity analysis on the ABSORBER column, which was performed by setting the carbonation ratio a as the independent variable.

Table 3.14 Results when changing the carbonation ratio on the entrance of the ABSORBER

Carbonation Ratio	Reboiler Duty (MW)	Reflux Ratio (L/G)	LEAN-IN1 (kmol/hr)	Wpump (kW)	Aexchanger (m ²)	Cooling Duty (MW)
0.05	723.14	3.39	49937.41	125.42	8117.15	-14.89
0.10	334.36	3.89	56231.37	142.97	8582.83	-18.39
0.12	264.56	4.14	59281.89	151.48	8744.23	-20.31
0.14	215.47	4.42	62723.27	161.14	8923.36	-22.58
0.16	180.44	4.76	66646.96	172.13	9241.85	-25.11
0.18	155.96	5.15	71184.94	184.88	9694.91	-28.04
0.20	139.98	5.63	76477.76	199.76	10213.03	-31.61
0.22	130.99	6.22	82758.06	217.52	10790.40	-36.11
0.24	127.55	6.96	90343.27	238.91	11414.57	-41.80
0.26	127.25	7.93	99675.12	265.38	12199.62	-49.11
0.28	129.37	9.21	111284.99	298.13	13109.56	-58.19
0.30	132.07	10.87	125548.82	338.47	14235.63	-68.76
0.35	139.90	16.56	174715.50	475.42	18688.38	-94.19

Examining Table 3.14, the following conclusions are drawn:

- With the increase of the inlet loading in the absorption column, there is a decrease in the reboiler duty of the stripping column until minimum for loading 0.26, as well as an increase in the L/G suction ratio in the absorption column
- With the increase of the loading, there is a particular increasing trend in the solvent flow rate (LEAN-IN1), as well as in other selected parameters, such as pump work, surface area of the exchanger and cooling work in the COOLER.

It is therefore clear that the choice of the optimal loading is a complex process, which will be largely determined by the subsequent economic analysis of the plant.

A composite graph (Figure 3.2) was constructed which relates the loading in the absorption column to the work of the boiler - a key economic parameter - and the reflux ratio.

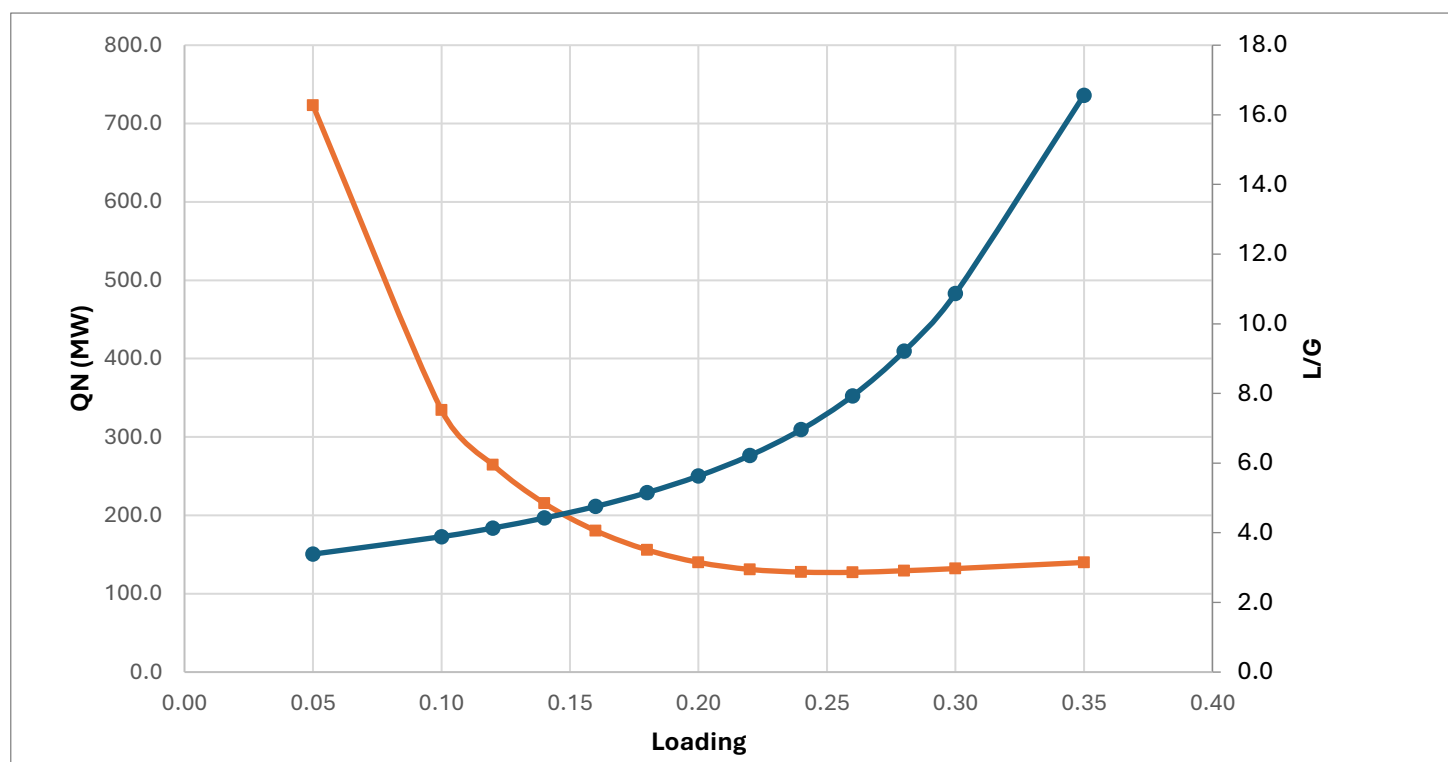


Figure 3.2 Reboiler Duty and Reflux Ratio vs Loading

Studying the composite graph, a minimum for the reboiler duty for a loading of 0.24 is obtained. However, considering the costs that will result from the subsequent economic analysis, especially for the heat exchanger, the optimum loading was chosen to be 0.22.

In Table 3.15, the composition of the amine stream at the inlet of the absorption column was also calculated for an optimum loading equal to 0.22.

Table 3.15 Molar Composition of LEAN-IN1 for optimal loading $a=0.22$

LEAN-IN1 Composition	
xCO ₂	0.02415
xMEA	0.10976
xH ₂ O	0.86610
a	0.22

Subsequently, the number of stages in both the absorption and stripping column was set as an independent variable in the analysis, since it was considered as a key design parameter for capital expenditure. The results of the sensitivity analysis are shown in Tables 3.16 and 3.17.

Table 3.16 Results of variation of the number of stages in Absorber column

<i>a=0,22</i>	<i>Stripper Stages : 8</i>	
Absorber Number of Stages	Reflux Ratio (L/G)	Reboiler Duty (MW)
2	8.08	147.68
3	7.33	140.95
4	6.92	136.90
5	6.65	134.55
6	6.46	133.16
7	6.32	131.93
8	6.22	131.20
9	6.14	130.26
10	6.08	129.86
12	5.98	128.68
14	5.92	127.77
16	5.87	127.77
18	5.84	127.42

Table 3.17 Results of variation of the number of stages in Stripper column

<i>a=0,22</i>	<i>Absorber Stages : 8</i>	
Stripper Number of Stages	Reflux Ratio (L/G)	Reboiler Duty (MW)
2	1.051	672.074
3	0.929	263.805
4	0.822	188.534
5	0.738	158.551
6	0.678	144.298
7	0.635	136.515
8	0.602	131.089
9	0.578	127.640
10	0.561	125.388
12	0.541	122.584
14	0.534	121.974
16	0.531	121.758
18	0.530	121.691

Commenting on the results in Table 3.16, the following conclusions can be drawn:

- An increase of the number of stages in the absorption column leads to a decrease of both the reflux of the column and the reboiler duty of the stripper in the stripping column.
- However, the reboiler duty shows less sensitivity to this reduction than the reflux ratio, as especially after the 10th stage, the reduction of the work in the riser is very small.

Looking in Table 3.17, the conclusions for the stripping column show similarities, with the sole additional difference being that apart from the very low values of the number of stages, the reflux ratio shows a higher resistance to variation.

To visualize these conclusions, 4 graphs were also constructed, which correlate the number of stages with the suction ratio and the work in the riser respectively.

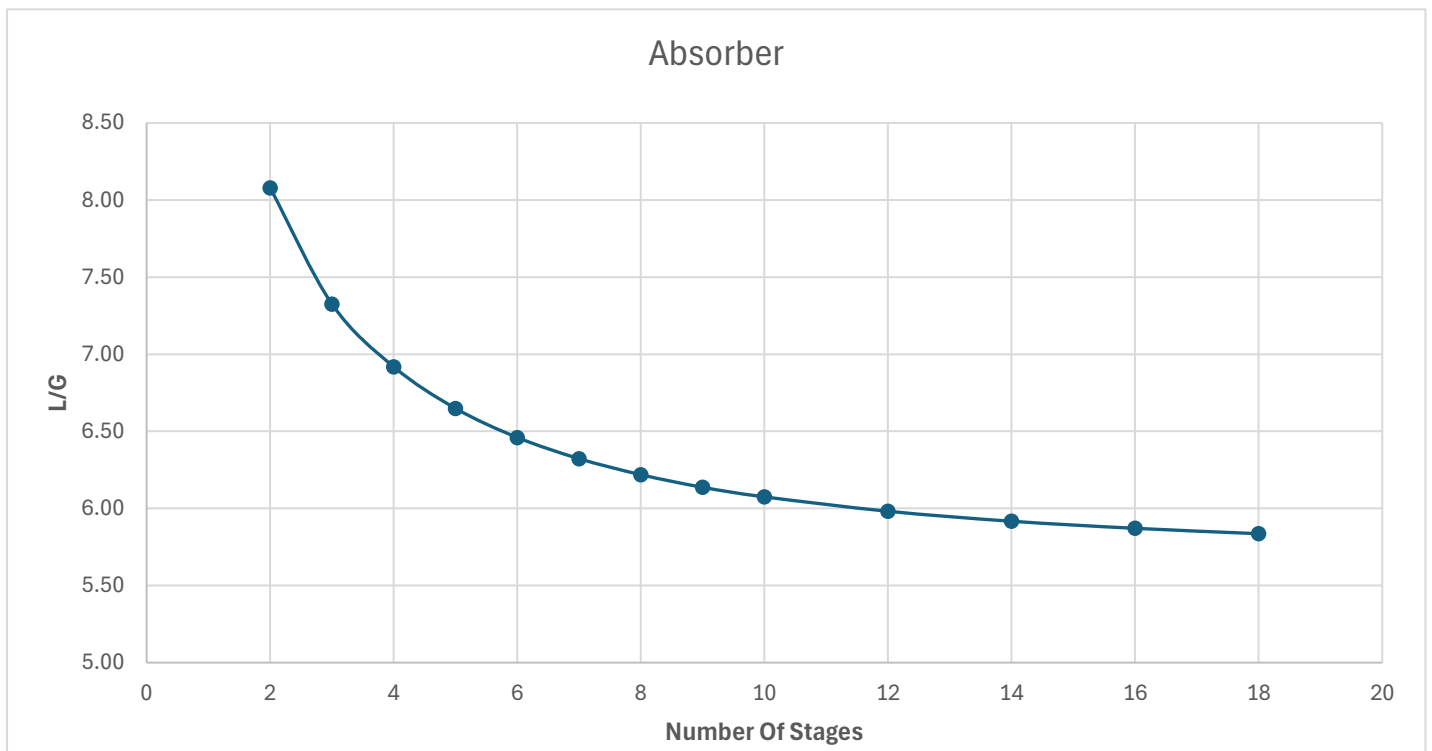


Figure 3.3 Reflux Ratio vs Number of Stages on ABSORBER column

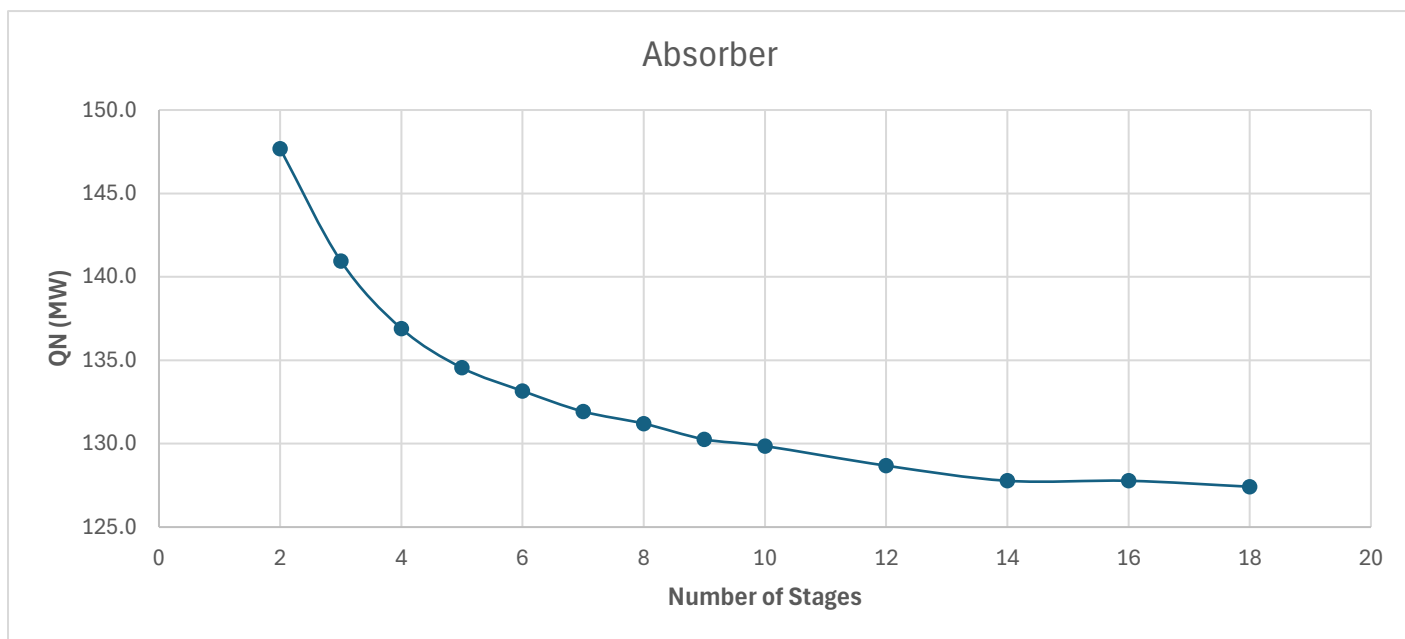


Figure 3.4 Reboiler Duty vs Number of Stages on ABSORBER column

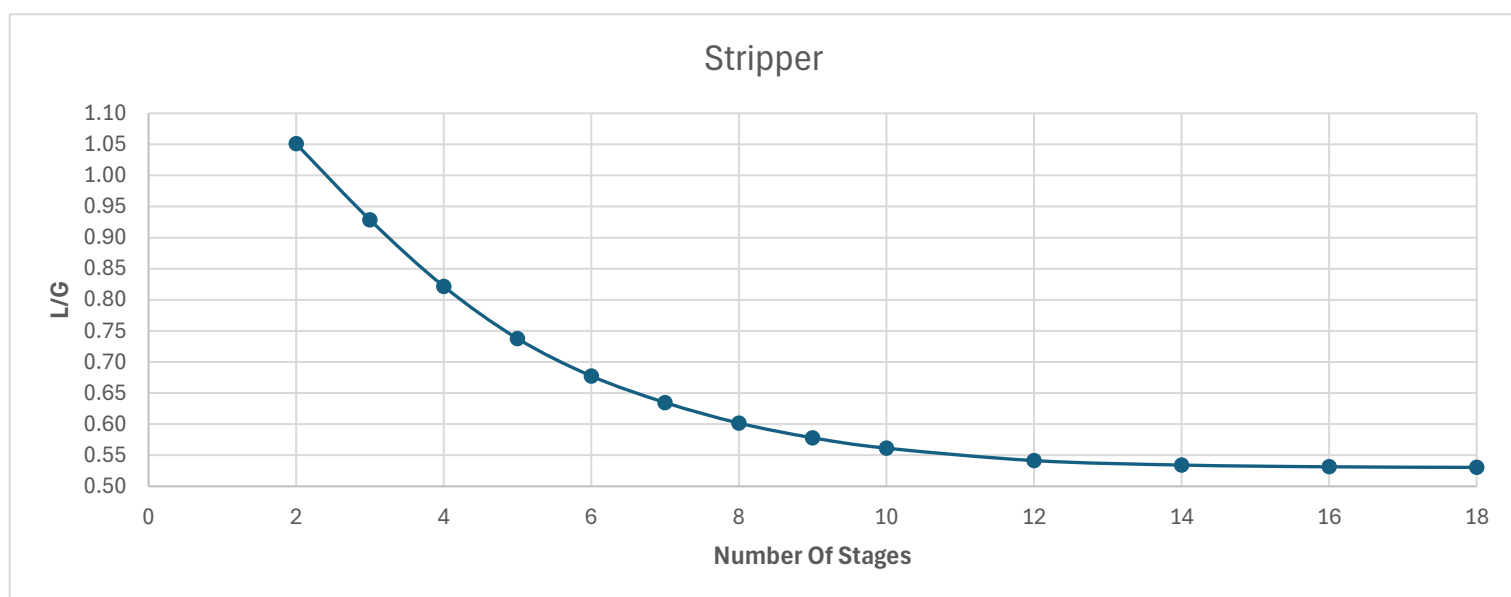


Figure 3.5 Reflux Ratio vs Number of Stages on STRIPPER column

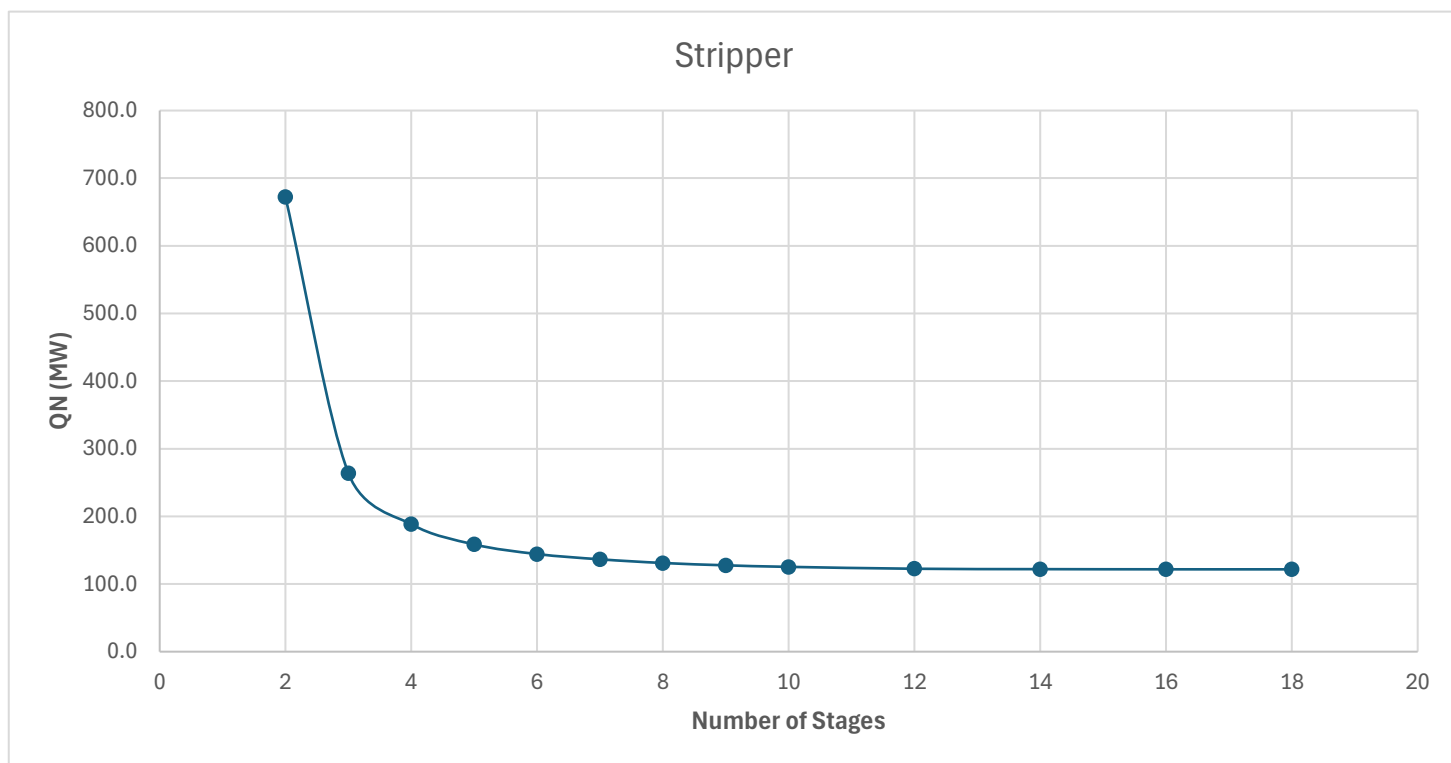


Figure 3.6 Reboiler Duty vs Number of Stages on STRIPPER column

From the previous figures, it can be understood that the initial choice of the number of 8 stages in the simulation is reasonable, since on the one hand it maintains both the reboiler duty and the reflux ratio at modest levels, while on the other hand the capital cost is not inflated.

Admittedly so, the choice of the number of stages will be clarified in the subsequent economic analysis.

3.9 Economic Analysis

In this chapter, the economic analysis of the CO₂ absorption unit with MEA is carried out. First, the fixed costs of the process are calculated, including the cost of installing the equipment as well as the cost of purchasing the solvent for the CO₂ absorption process. The calculation of the plant operating costs is then carried out, which includes the cost of utilities and the operating costs for the feed streams.

3.9.1 Capital Cost Evaluation

To carry out the capital cost evaluation, all equations presented in subchapter 1.8 were used.

Table (Table 3.18) shows the dimensions of the equipment as derived from the Aspen Plus APEA calculation tool.

Table 3.18 Dimensions of the equipment as derived from Aspen Plus APEA calculation tool

<i>Equipment</i>	<i>S</i>	<i>N</i>	<i>Sfinal</i>
FLASH	34,790.54	-	34,790.54
ABSORBER	180,302.97	-	180,303
SCRUBBER	59,692.76	-	59,692.76
STRIPPER	89,539.13	-	89,539.13
RDRUM	3674.10	-	3674,098
COOLER2	1,079.11	2	539.557
CROSS-EX	11,082.28	11	980.9
COND	1,090.70	-	1090.704
PUMP-1	582.94	1	582.9
	212.64	-	212.6
STRIPPER REBOILER	2,964.80	6	494.1

For equipment outside the boundaries of the cost equation, it is assumed that the *S* calculated is divided by the appropriate number to produce an *Sfinal*. Thus, i.e. for COOLER2, it is assumed that there are 2 coolers in the unit which combined represent COOLER2. For the block CROSS-EX, due to the high inlet flows, surface area tends to be quite extensive leading to vast equipment costs, completely inadequate to the actual ones. This situation is also due to the type of heat exchanger. Towler and Sinott equations are not compatible for plate heat exchangers which are the main heat exchangers used in carbon capture processes. Therefore, a different route was followed.

Table 3.19 [43] shows a correlation between the surface area of a heat exchanger and its cost in million €.

Table 3.19 Values of surface area for a plate HEX and their respective cost

Area (m ²)	Cost M€
40	19
50	21
60	23
70	25
80	27
100	31
120	36
140	39
160	42
200	49
220	54
240	57
260	61
280	65
300	71

These values, then, were plotted (Fig. 3.7), the linear equation linking them was extracted, so the cost for a 11082.28 m² plate heat exchanger was calculated in **2,145,993.89 €** (2010).

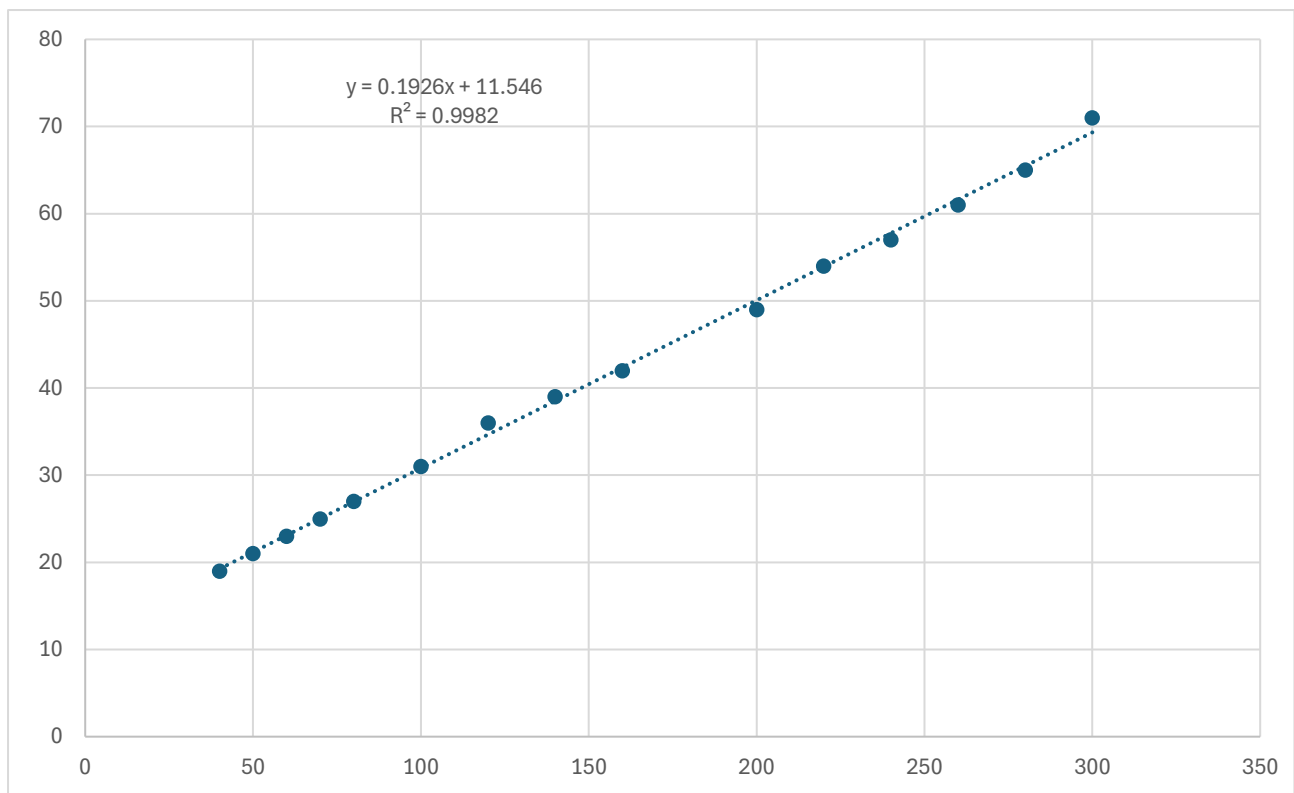


Figure 3.7 Correlation between cost and surface area for a plate HEX.

Table 3.20 shows the purchase and installation costs of all the equipment for the CO₂ capture process with MEA according to the Detailed Factorial methodology of Towler and Sinnott.

Table 3.20 Purchase and Installation costs of equipment in CO₂ capture process

Equipment	C_{ei} (\$ 2010)	fm	C (\$ 2010)	C (\$ 2024)	C (€ 2024)
FLASH	\$258,045	1	\$825,745	\$1,232,032	1,158,110 €
ABSORBER	\$1,009,487	1.3	\$3,775,481	\$5,633,111	5,295,124 €
SCRUBBER	\$401,553	1.3	\$1,501,808	\$2,240,735	2,106,291 €
STRIPPER	\$562,014	1.3	\$2,101,934	\$3,136,137	2,947,969 €
RDRUM	\$43,446	1.3	\$162,488	\$242,436	227,890 €
COOLER2	\$499,091	1.3	\$1,866,600	\$2,785,013	2,617,912 €
CROSS-EX	\$2,282,972	1.3	\$8,538,316	\$12,739,379	11,975,016 €
COND	\$266,584	1.3	\$997,025	\$1,487,586	1,398,331 €
PUMP-1	\$103,297	1.3	\$386,333	\$576,418	541,833 €
	\$51,236	13	\$191,624	\$285,908	268,754 €
STRIPPER REBOILER	\$3,227,947	1.3	\$12,072,522	\$18,012,502	16,931,752 €

In total, the equipment capital cost of the unit is about **45.47 M€**

As expected, and confirmed by Table 3.20, most of the cost comes from the three columns (ABSORBER, STRIPPER, SCRUBBER) and then the plate HEX. Especially, the

reboiler presents an enormous cost mainly due to the high duty needed to be maintained throughout the process.

3.9.1.1 Fixed solvent purchase cost

For the carbon dioxide absorption process, a fixed cost is considered for the purchase of a quantity of solvent for the initial operation of the plant and then an operating cost for the replacement of a certain quantity of amine that has been destroyed. The following table summarizes the costs of the solvent used in the process [44]:

Table 3.21 Solvent Cost for Carbon Capture with MEA

Vabsorber (m ³)	1172.6
LEAN-IN1 (m ³ /hr)	2013.7
Absorber 70% (m ³)	820.81
Time to 70 % flood (hr)	0.41
MEA in LEAN-IN1 (ton/hr)	314.55
Required MEA (ton)	128.2
MEA Cost (\$/ton)	1470
MEA Cost (€/ton)	1381.8
MEA 30 % w/t Cost (€/ton)	414.54
MEA Cost	53,149.86 €

The solvent flow in the LEAN-IN1 stream in Table 3.21 refers only to the flow of the amine solution and not to the total LEAN-IN1 stream, as this stream also contains CO₂ based on the loading selected.

As can be seen from the above results, the fixed cost for the purchase of the solvent is negligible compared to the fixed cost of installing the plant equipment.

In total, the fixed cost of the CO₂ capture process with MEA, including the equipment installation cost and the solvent purchase cost equals **45,522,137.58 €**

3.9.2 Operating Cost

3.9.2.1 Varied Operating Cost

Table 3.22 summarizes the cost of utilities in CO₂ capture unit.

Table 3.22 Cost of utilities in CO₂ capture unit

Equipment	Utility	Units	Utilities Demand	Calculated Cost (€/hr)	Calculated Cost (€/yr)
COOLER	Cooling Water	ton/hr	5494.60	274.73 €	2,197,839€
STRIPPER REBOILER	Low-Pressure Steam	kg/hr	52,000.87	1812.23 €	14,497,842 €
COND	Cooling Water	ton/hr	5494.60	274.73 €	2,197,839€
PUMP-1	Electricity	kW	212.64	25.52 €	204,133 €

Finally, the utility cost adds up to **21,962,303.92 €**

The cost of the raw materials for the absorption process includes the cost of replenishing the amine solution.

In the process, a quantity of solvent is replenished, as after a certain time of use the amine solution builds up in the amine solution and needs to be replaced. In addition, a small amount of amine is lost in the outgoing vapors from the absorption column. Typically, in amine scrubbing processes, this cost adds up to 15 % of the fixed operating cost according to TCM DA [45]. Thus, plus the MEA makeup the varied operating cost adds up to **25,622,125.11 €**

3.9.2.2 Fixed Operating Cost

The methodology of calculating the fixed capital cost is presented thoroughly in subchapter 1.8.

In Table 3.23, the calculations for the fixed operational cost are presented.

Table 3.23 Fixed Operational Cost for Carbon Capture Process

ISBL	45,522,137.58 €
OSBL	18,208,855.03 €
Cop	5,000,000 €
Cs	1,250,000 €
Cot	3.125.000,00 €
Cm	2,276,106,88 €
Cti	910,442.75 €
Cr	1,274,619.85 €
Cg	7,573,219.47 €

Total	21,409,388.95 €
--------------	------------------------

In total, all operating cost for the CO₂ capture with MEA unit is **47,031,514.07 €**

3.9.3 Results Analysis

In this section, the results for the fixed installation costs (CAPEX) and operating costs (OPEX) of the CO₂ capture process are analyzed and compared with available results from the literature.

The total fixed costs (CAPEX) for the case of MEA are about 45.5 MEUR. The following graph shows the percentage of the fixed installation costs of each piece of equipment. The solvent cost is negligible and not shown in the graph.

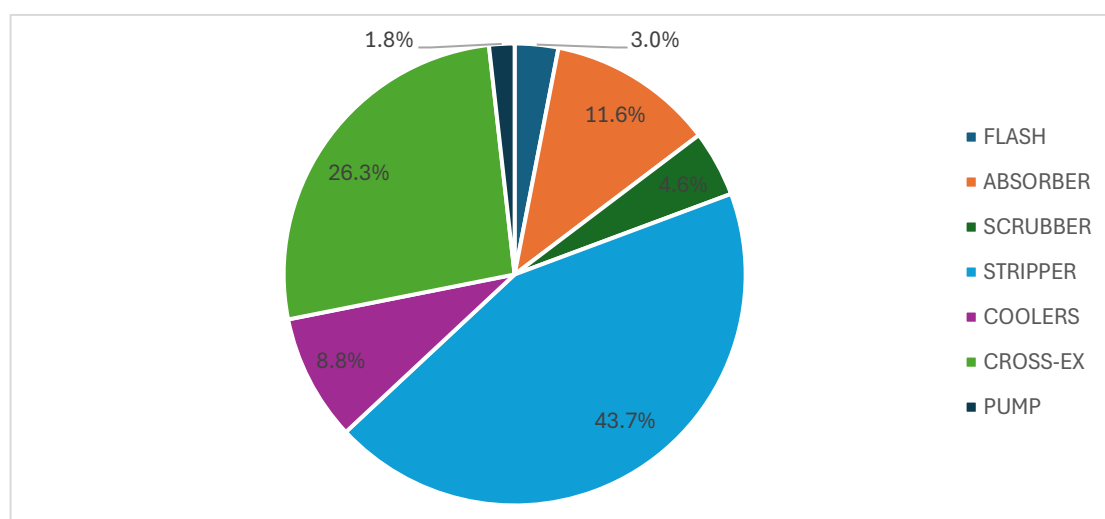


Figure 3.8 Equipment installation costs compared to total installed equipment cost

It appears that the cost of the stripper column is near half of the total cost due to the high cost of the reboiler that has been already discussed in previous subchapters. The Cross Exchanger also is of high value, even with the plate type used, due to the extensive surface area needed for the heat transfer of tens of thousands of kilomoles every hour and the large temperature range it operates.

As far as the operational cost is concerned, the sum adds up to 47 MEUR using MEA. IN Figure 3.9, the percentage of the utilities used in the unit compared to the total varied operating cost is shown.

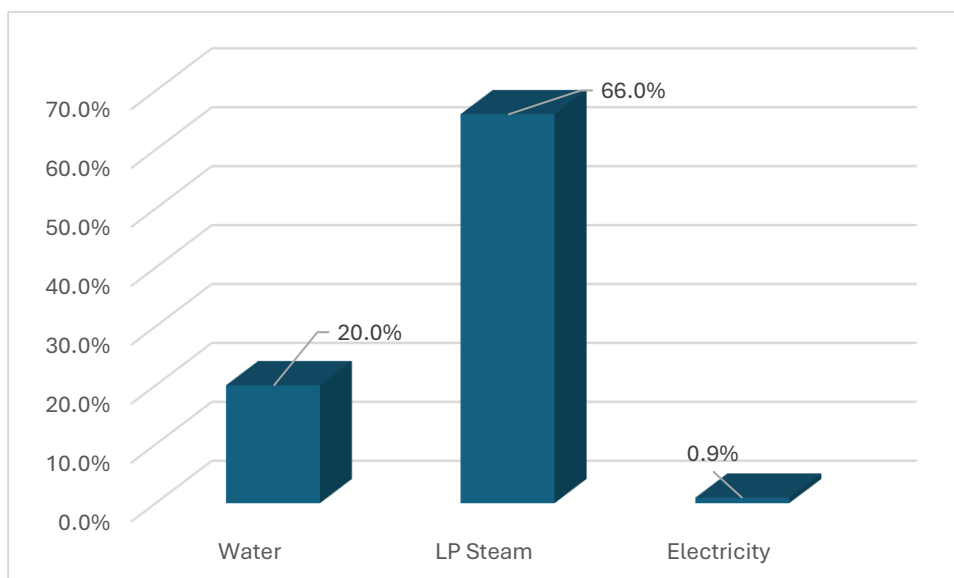


Figure 3.9 Percentage of Utilities to total operating cost in Carbon Capture Process

Most of the cost comes from the LP Steam usage in the unit and consequently from the price of the natural gas, while cooling water comes in a distant second. However, despite the respectable percentage the cost of cooling water is rather low, so it doesn't have a serious effect in the end result. The electricity usage on the other hand is negligible, thus the adjusted price presented previously is taken as the mean average of the industrial prices in Greece in 2024.

NG price plays an important role in determining the varied operating cost. For this reason, as mentioned before, a mini sensitivity analysis was carried out, presenting a plethora of scenarios for best to worst concerning the price of natural gas and its effect on the levelized cost of CO₂. The results are shown in Table 3.24.

Table 3.24 Variations on NG Price and their effect on CO₂ levelized cost.

		Adjustmen t	NG Price (€/kWh)	Total Cost (€/tonCO ₂)
NG Price (€/kWh)	0,03485	-30%	0,0244	41,14
		-20%	0,0279	42,73
		-10%	0,0314	44,32
		0%	0,0349	45,88
		10%	0,0383	47,45
		20%	0,0418	49,04
		30%	0,0453	50,62

The price selected is 0.03425 €/kWh due to an accordance with the actual prices.

3.10 Levelized Cost of CO₂

The levelized cost of carbon dioxide capture is the most important factor when assessing the success of a plant. In this subchapter, the levelized cost of carbon dioxide is calculated with the operational parameters extracted from the previous analysis. Then, an analysis is carried out in which already stressed parameters such as the number of stages in the absorber and stripper column as well as the carbonation ratio are varied. The optimal scenario is determined by the levelized cost of CO₂.

The methodology for the calculation of the ACCR is also extensively explained in subchapter 1.8.

In Table 3.25, the characteristics of the investment are presented in order to assess the levelized cost of CO₂.

Table 3.25 Characteristics of the investment in Carbon Capture Unit

ACCR	0.110
i	0.1
n	25

Thus, the levelized cost of carbon dioxide in this study's plant is shown in Table 3.26

Table 3.26 Levelized cost of CO₂ in Carbon Capture process

Annualized CAPEX	4.76	€/tonCO ₂
OPEX	41.13	
Total	45.88	

The scenarios are presented graphically in the following figures.

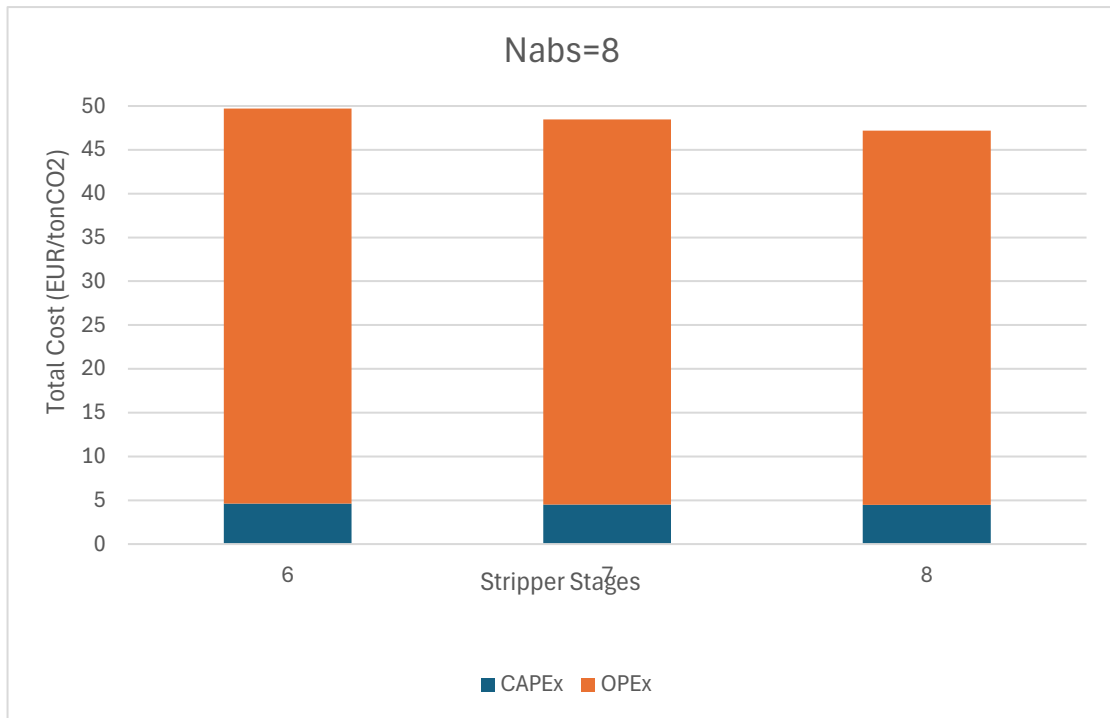


Figure 3.10 Total Levelized Cost correlated with the number of Stripper Stages for 8 Absorber Stages

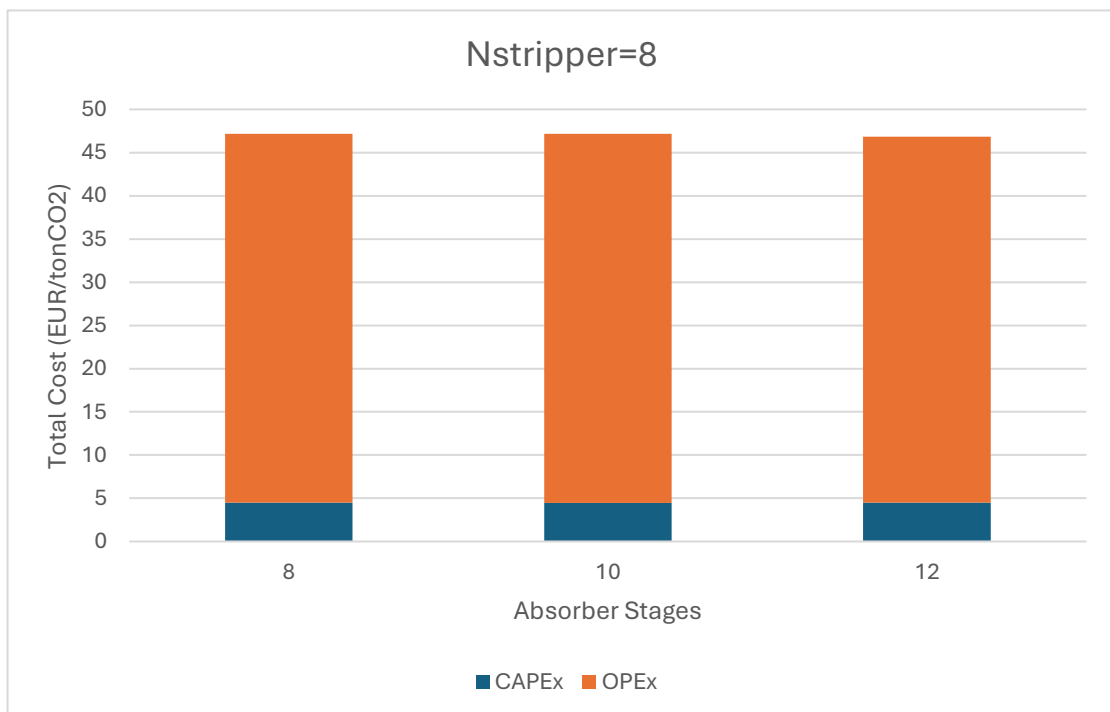


Figure 3.11 Total Levelized Cost correlated with the number of Absorber Stages for 8 Stripper Stages

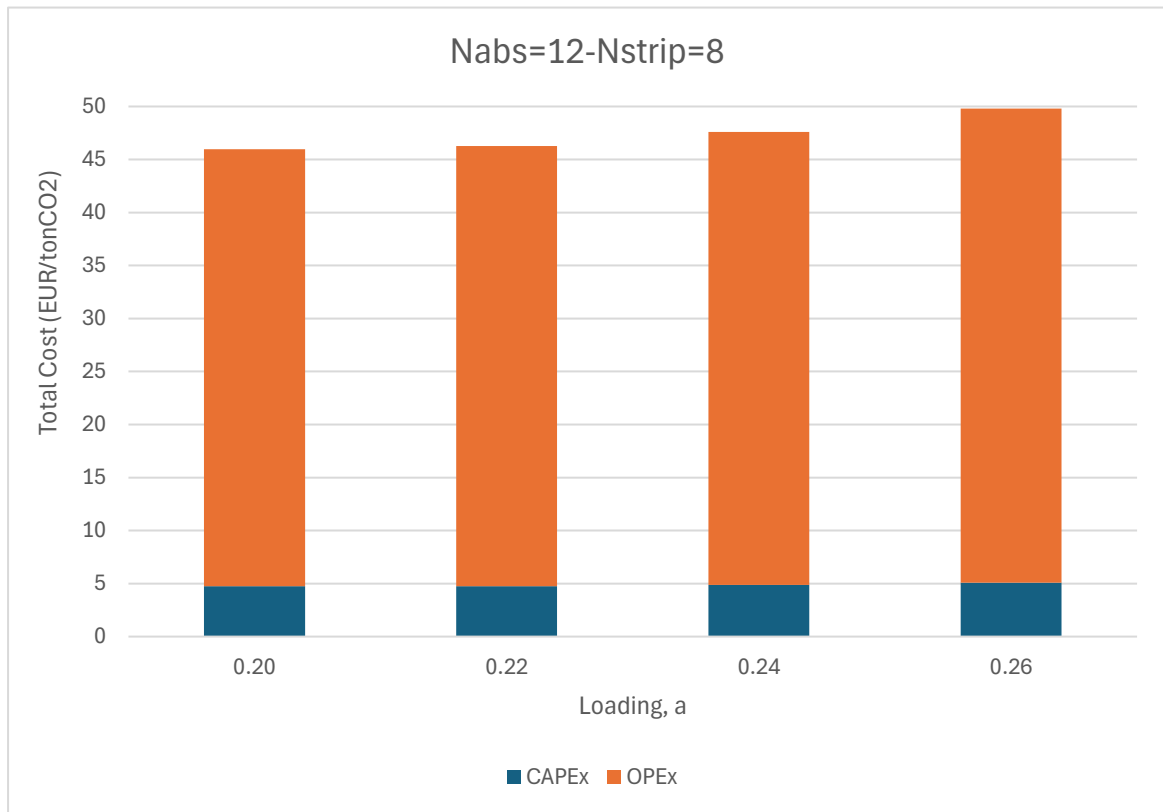


Figure 3.12 Loading vs Levelized Cost for Nabs=12 and Nstrip=8

Examining Fig.3.10-3.12, the final conclusions can be drawn:

- The optimal number for stripper stages is 8
- The optimal number for absorber stages is 12
- The optimal loading as already discussed is 0.2

4 Methanol Production Process

4.1 Process Flow Diagram with Low-Pressure Flash Vessel

The process flow diagram used in this work, as developed in the Aspen Plus computing environment, is shown in Figure 4.1. Essentially the process is identical to the one proposed by Kiss et al. [19], except that the STRIPPER stripping column is replaced by a low-pressure LP-SEP separation vessel. This replacement is carried out as it is considered necessary to introduce a cleaner hydrogen stream, with a smaller amount of water. With STRIPPER the hydrogen stream is contaminated with carbon oxides, methanol and water, resulting in hydrogen of a final purity of 73,5 %. The low-pressure vessel is placed in place of the former STRIPPER, immediately after the high-pressure vessel, in order to remove the carbon dioxide from the methanol-water stream. The pure hydrogen is fed directly into the process together with the carbon dioxide, after being compressed to the appropriate pressure.

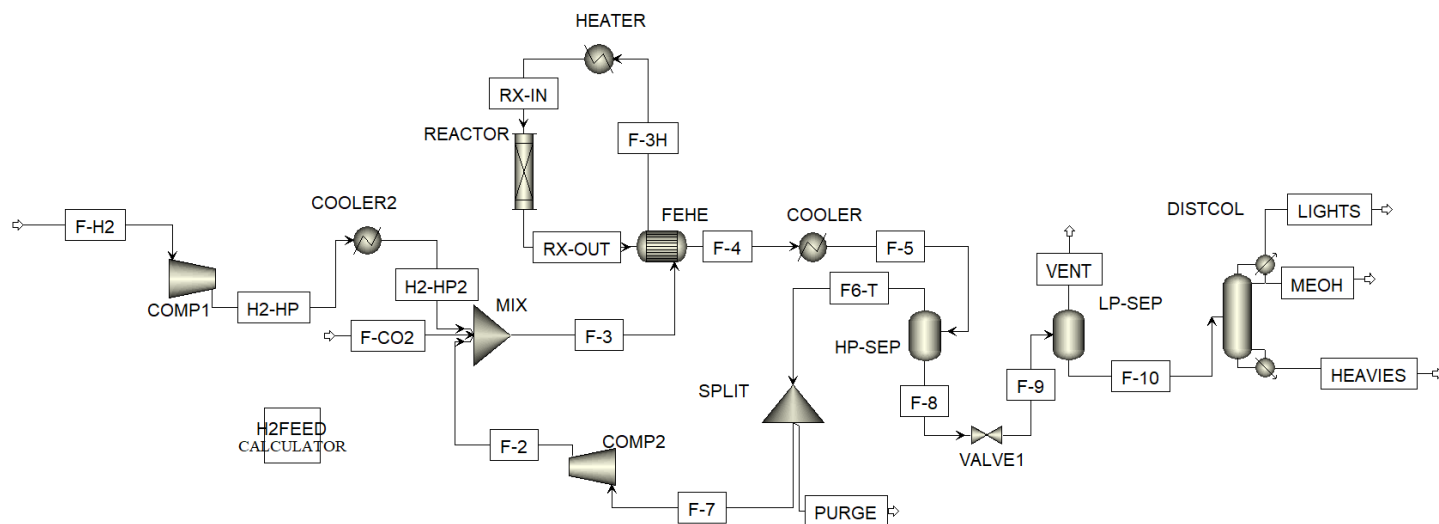


Figure 4.1 Methanol Production Process as developed in Aspen Plus

The fresh hydrogen feed, produced by alkaline salt electrolysis, is compressed to 50 bar in a single-stage compressor (COMP1). The fresh carbon dioxide feed stream is mixed with the recycle stream and compressed hydrogen, and the resulting gas mixture is heated in the FEHE heat exchanger by the RX-OUT reactor outlet stream. This stream is then heated in a second heat exchanger and fed into a plug-flow type reactor with shells and tubes, which operates isothermally at a temperature of 250 °C and a pressure of 50 bar. The reactor outlet stream is cooled in the FEHE exchanger and then in a second cooler before entering the HP-SEP high pressure separation vessel, which is designed to separate the methanol-water mixture from the residual gases (CO_x, H₂). The residual gases separated by the high-pressure separation vessel are then compressed in a single-stage compressor (COMP2) at 50 bar and returned to the reactor feed. The liquid stream from the separation vessel is vented to a relief valve at a pressure of 5 bar, and then fed to the second separation vessel, which operates at a low pressure of 1,5 bar. The top stream

of the separator vessel is discharged, while the bottom stream, which is rich in methanol and water, is passed to a distillation column (DISTCOL), of the same operating pressure, in which water is separated as the bottom product and methanol as the high-purity top product.

4.2 Process Description

4.2.1 Definition of Stoichiometric Number

The conversion of carbon dioxide and carbon monoxide to methanol requires hydrogen in different mole ratios, so a standard of the stoichiometry of the line mole fractions of hydrogen, monoxide and carbon dioxide, the Stoichiometric Number (SN), is defined. The stoichiometric number is defined by equation 4-1.

$$SN = \frac{[H_2] - [CO_2]}{[CO_2] + [CO]} \quad 4-1$$

For a stoichiometric ratio of reactants, the stoichiometric number is equal to SN=2. Feed gas to the reactor with SN<2 means an excess of carbon oxides relative to H₂, resulting in increased by-product formation. In contrast, feed gas to the reactor with SN>2, means excess H₂ and carbon deficit, which results in increased product recycling, and hence lower reaction efficiency and more expensive installation. [46]

4.2.2 Reactants Feed

The process feed consists of three streams, a carbon dioxide stream (F-CO₂), a hydrogen stream (F-H₂) and a stream consisting of all process components (F-2), as shown in Figure 4-2. The F-CO₂ and F-H₂ streams contain pure carbon dioxide and hydrogen of 99% wt. purity, respectively, while the F-2 stream, the recycling stream of the process, is rich in monoxide, dioxide and hydrogen. All three streams are mixed in a mixer (MIX). The hydrogen stream H₂-HP is cooled down in COOLER2 due to high temperature increase achieved during compression. Kiss et al. resolved this issue by utilizing a multi-stage compressor with embedded cooling mechanism. However, in this work, a multi-stage compressor was difficult to model as the intermediate temperatures and pressures are almost impossible to forecast, except experimentally.

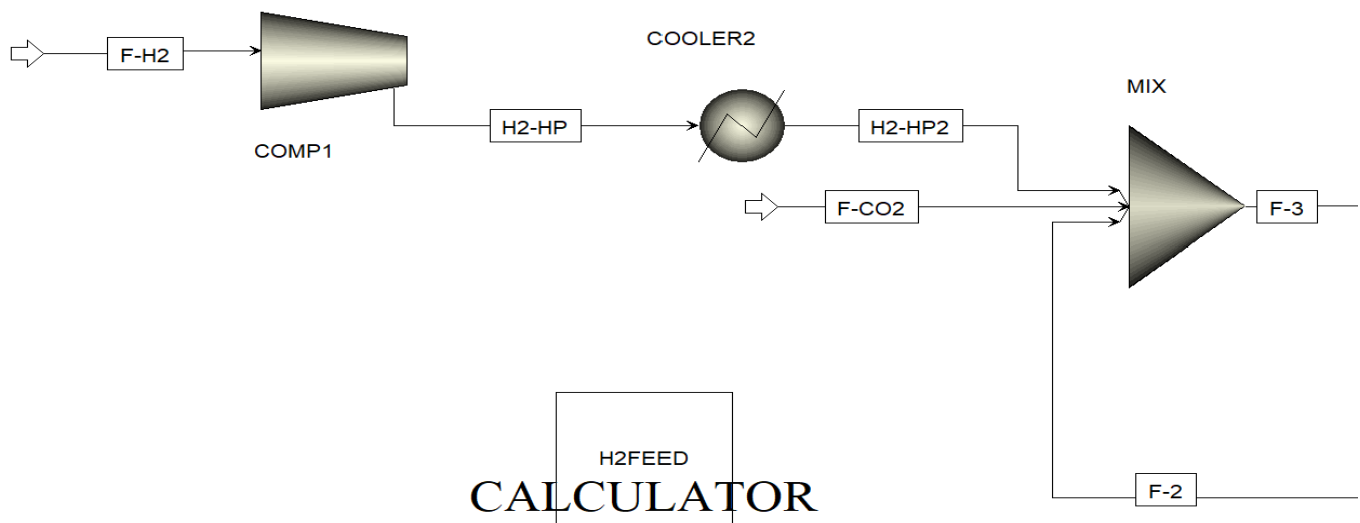


Figure 4.2 Reactants feed process flow diagram as developed in Aspen Plus

The operational parameters in COMP-1 are shown in Table 4.1.

Table 4.1 Operational parameters of COMP-1 in Methanol production process

Compressor COMP1	
Compressor Type	Isentropic
Discharge Pressure (bar)	50
Utility	Electricity

It should be noted here that the calculation of the required amount of hydrogen is carried out using a Calculator Block, which depending on the final amount of the recycling stream calculates the amount of hydrogen, so that the reacting components in the reactor inlet stream are in a stoichiometric ratio (SN=2).

4.2.2.1 Results of reactants feed section

Table 4.2 Results of reactants feed part

	H2-HP	H2-HP2	F-CO2	F-H2	F-2	F-3
Temperature [°C]	744	170	50	15	42.1	64
Pressure [bar]	50	50	1.72	1	50	50
Vapor frac	1	1	0.53	1	1	0.95
Mole flow [kmol/h]	472.9	472.9	323.9	472.9	2204.6	3001.5
Mass flow [kg/h]	1036.5	1036.5	9973.1	1036.5	27374.3	38383.9
Volume flow [m³/h]	808.2	356.5	2659	11336.3	1169.2	1619.1
Mol Fractions						
CO	0	0	0	0	0.020	0.015
CO ₂	0	0	0.491	0	0.233	0.225
H ₂	0	0.989	0.509	0.989	0.743	0.702
H ₂ O	0.011	0.011	0	0.011	0.000	0.057

CH ₃ OH	0.989	0	0	0	0.002	0.002
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4.3 Reaction Section

4.3.1 Reaction Section Description

The process reactor is the same as in the previous simulation in the literature. Again, i.e., a plug-flow catalytic bed, shell and tube reactor loaded with Cu/ZnO/Al₂O₃ catalyst is used. The reactor operates at a temperature of 250°C and a pressure of 50 bar. Due to chemical equilibrium constraints, the reactor outlet stream will consist of the unreacted reactants (CO_x and H₂), in addition to the products, which are methanol and water.

4.3.1.1 Catalyst Mass Calculation

As already mentioned, a Cu/ZnO/Al₂O₃ catalyst is used. The data for the Cu/ZnO/Al₂O₃ catalyst used in the process for the conversion of carbon dioxide are shown in Table 4.3.

Table 4.3 Data for Cu/ZnO/Al₂O₃ catalyst

Density [kg/m ³]	1775
Particle Diameter [m]	0.006
Catalyst Bed Porosity	0.4

A typical porosity for the bed is assumed to be equal to $\varepsilon_{bed} = 0.4$, so the density of the catalytic bed is calculated as follows:

$$\rho_{catalyst} = \frac{\rho_{bed}}{(1 - \varepsilon_{bed})} \rightarrow \rho_{bed} = 1065 \text{ kg/m}^3$$

The total amount of catalyst in the isothermal catalytic bed reactor:

$$m_{catalyst} = \rho_{bed} V_{bed} \rightarrow m_{catalyst} = 29269 \text{ kg} = 29.3 \text{ ton}$$

For the simulation, it is chosen to place the amount of catalyst calculated, for a typical catalyst bed porosity, as a number that represents the industry.

4.3.1.2 Operational Parameters for Reaction Section

Table 4.4 Reactor Operational Parameters

REACTOR	
Tube Length (m)	12
Internal Tube Diameter (m)	0.06
Number of Tubes	810
Catalyst	Cu/ZnO/Al ₂ O ₃
Catalyst mass (kg)	29269
Catalyst Bed Porosity	0.4
Bed Density (kg/m ³)	1065

Utility
Cooling Water at 20°C

Table 4.5 Exchangers Operational Parameters

Exchanger FEHE	
Cols Stream Outlet Temp [°C]	225
Exchange Surface Area [m ²]	785
Exchanger HEATER	
Outlet Temp [°C]	250
Pressure [bar]	50
Heating Utility	HP-STEAM

The process flow diagram of the reaction part is presented in Figure 4.3.

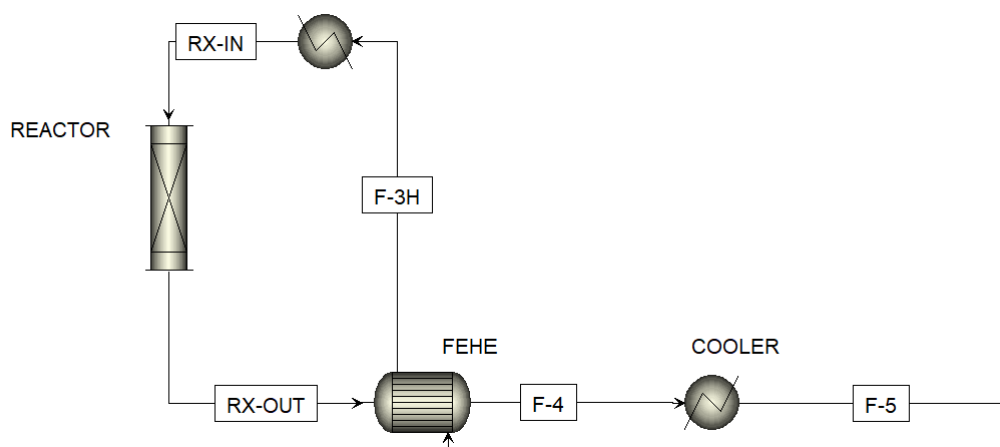


Figure 4.3 Reaction Part of Methanol Production Process as developed in Aspen Plus

4.3.2 Stream Results in Reaction Section

Table 4.6 Streams Results in Reaction Section

	F-3H	RX-IN	RX-OUT	F-4	F-5
Temperature [°C]	225	250	250	109.1	31
Pressure [bar]	50	50	50	50	50
Vapor frac	1	1	1	0.92	0.92
Mole flow [kmol/h]	3001.5	3001.5	2814.4	2814.4	2814.4
Mass flow [kg/h]	38383.9	38383.9	38383.9	38383.9	38383.9
Volume flow [m³/h]	2525.0	2652.6	2476.0	1666.7	1666.7
Mole Frac					
CO	0.015	0.015	0.017	0.017	0.017
CO ₂	0.224	0.224	0.204	0.204	0.204
H ₂	0.702	0.702	0.647	0.647	0.647
H ₂ O	0.057	0.057	0.096	0.096	0.096

CH ₃ OH	0.002	0.002	0.035	0.035	0.035
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4.4 Recycle Section

4.4.1 Recycle Section Description

The top stream of the high-pressure vessel, which is rich in hydrogen, monoxide and carbon dioxide, returns to the feed, after being compressed from the operating pressure of the high-pressure vessel (45 bar) to the operating pressure of the reactor (50 bar).

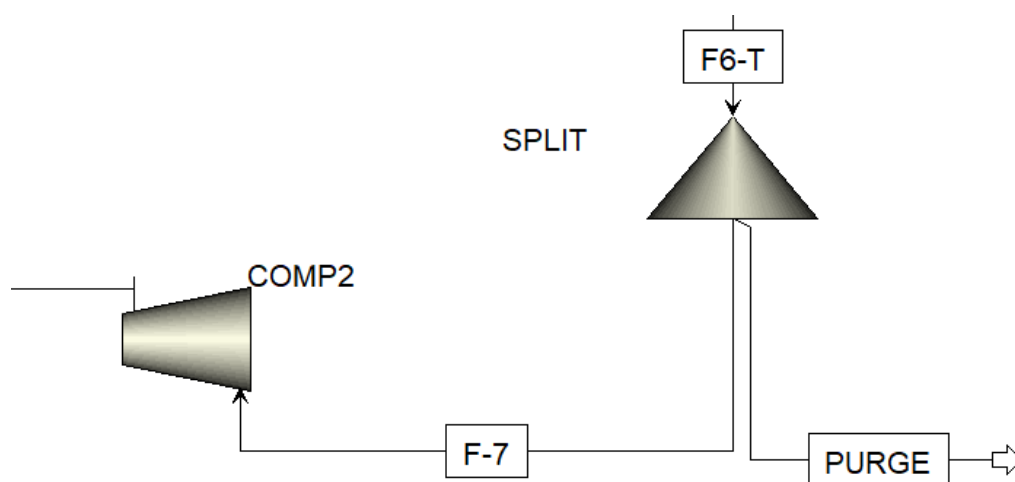


Figure 4.4 Process Flow Diagram of Recycle in Methanol Production Process

The operational parameters of COMP2 in the Recycle Section are presented in Table 4.7.

Table 4.7 Operational parameters of COMP2 as developed in Aspen Plus

Compressor COMP2	
Compressor Type	Isentropic
Discharge Pressure (bar)	50
Utility	Electricity

4.4.2 Results of Recycle Section

Table 4.8 Stream Results of Recycle Section in Methanol Production Process

	F6-T	F-7	PURGE
Temperature [°C]	30	30	30
Pressure [bar]	45	45	45
Vapor frac	1	1	1
Mole flow [kmol/h]	2449.5	2204.6	245.0

Mass flow [kg/h]	30415.9	27374.3	3041.6
Volume flow [m³/h]	1383.6	1245.2	138.4
Mole Frac			
CO	0.020	0.020	0.020
CO₂	0.233	0.233	0.233
H₂	0.743	0.743	0.743
H₂O	0.000	0.000	0.000
CH₃OH	0.002	0.002	0.002

4.5 Separation Section

4.5.1 Separation Section Description

The methanol produced in the reactor must then be separated from the remaining reactants, as well as from the excess reactants and any by-products of the reaction (CO_x and H₂). This part of the unit is designated as the separation section, followed by the reaction section.

The reactor outlet is cooled by a pressure drop equal to 5 bar, i.e. to a pressure of 45 bar, and fed into the first high-pressure separation vessel HP-SEP. The bottom stream of the high-pressure separation vessel is then discharged into the VALVE1 valve at a pressure equal to the operating pressure (1,5 bar) of the second low-pressure separation vessel LP-SEP, while the top stream of HP-SEP, after being compressed, is returned to the feed as a recycle stream. The bottom stream of the LP-SEP low pressure separation vessel, which consists mainly of methanol and water, is fed to a distillation column, of the same operating pressure, for the final separation of methanol from water. The LP-SEP peak stream, which consists mainly of gases, is discarded because its quantity is negligible in relation to the total quantity introduced into the separation vessel. It is also worth noting that the compression of this stream, from an initial pressure of 1.5 bar to a final pressure of 50 bar, is highly energy-intensive, and therefore costly, so since its quantity is negligible in relation to the quantity of feed, it is decided to discard it.

Figure 4.5 shows the flow diagram of the methanol separation section.

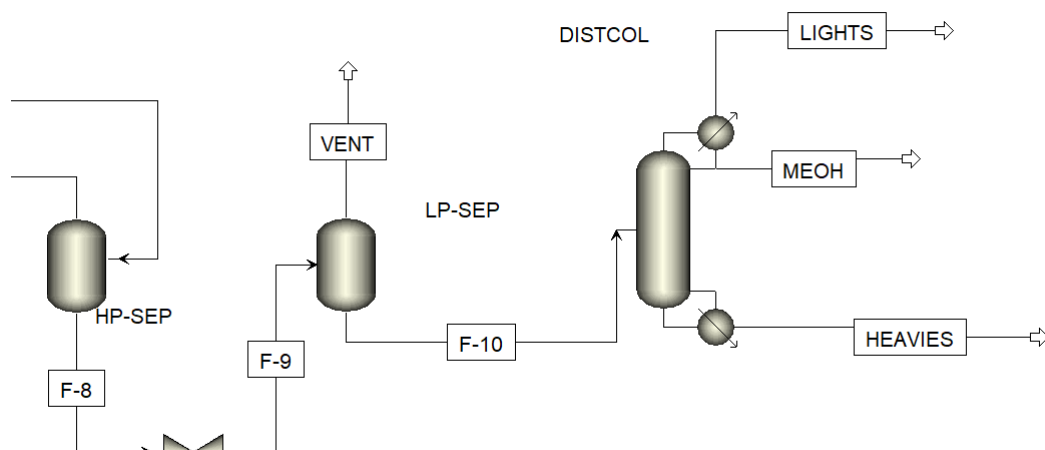


Figure 4.5 Process Flow Diagram of Separation Section as developed in Aspen Plus

4.5.2 Operational Parameters in Separation Section

Table 4.9 Operational Parameters for separation vessels HP-SEP, LP-SEP as well as VALVE1 and PUMP

HP-SEP	Temperature [°C]	30
	Pressure [bar]	45
LP-SEP	Temperature [°C]	30
	Pressure [bar]	1.5
VALVE1	Outlet Pressure [bar]	5
PUMP	Discharge Pressure [bar]	1.5
	Utility	Electricity

Table 4.10 Operational Parameters for Distillation column (DISTCOL)

DISTCOL	
Number of Theoretical Stages	30
Feed Stage	15
Condenser	Partial
Condenser Temperature [°C]	64
Condenser Pressure [bar]	1.5
Convergence Method	Standard
Specifications	
Top Methanol Purity [% w/w]	99
Bottom Water Purity [% w/w]	99
Utilities	
Reboiler	LP Steam
Condenser	Cooling Air

4.5.3 Results for Separation Section

Table 4.11 Streams Results in Separation Vessels HP-SEP and LP-SEP

	F-8	F-9	F-10	VENT
Temperature [°C]	30	30.6	30	30
Pressure [bar]	45	5	1.5	1.5
Vapor frac	0	0.005	0	1
Mole flow [kmol/h]	364.8	364.8	361.5	3.38
Mass flow [kg/h]	7968.1	7968.1	7827.8	140.3
Volume flow [m ³ /h]	11.0	20.7	10.8	56.4
Mole Frac				
CO	0.000	0.000	0.000	0.000
CO ₂	0.010	0.010	0.001	0.898
H ₂	0.000	0.000	0.000	0.033
H ₂ O	0.735	0.735	0.742	0.021
CH ₃ OH	0.255	0.255	0.257	0.047

Table 4.12 Streams Results in Distillation Column (DISTCOL)

	LIGHTS	MEOH	HEAVIES
Temperature [°C]	64	64	111.3
Pressure [bar]	1.5	1.5	1.5
Vapor frac	1	0	0
Mole flow [kmol/h]	0.92	92.3	268.2
Mass flow [kg/h]	33.2	2958.2	4836.4
Volume flow [m ³ /h]	17.0	5.2	6.9
Mole Frac			
CO	0.000	0.000	0.000
CO ₂	0.333	0.002	0.000
H ₂	0.000	0.000	0.000
H ₂ O	0.000	0.000	0.998
CH ₃ OH	0.666	0.996	0.001

4.6 Parametric Analysis

In this subchapter, a parametric analysis is carried out on several operating variables in the reaction section to draw conclusions on their effect on the reaction conversion, methanol production efficiency and energy loads consumed in the process. This analysis is intended to determine the optimal operating conditions in terms of methanol production and operating costs.

The parameters studied are the following:

- Reactor operating pressure
- Reactor operating temperature

In each case, the change in only one independent variable is considered, leaving all other parameters at their values in the basic simulation

4.6.1 Definition of evaluation parameters

The definitions of the parameters that will be used for the evaluation are described in equations 4-1 and 4-2.

$$\%CO_2 \text{ Conversion} = \frac{(CO_2)_{in} - (CO_2)_{out}}{(CO_2)_{in}} \quad \mathbf{4-2}$$

$$\% \text{ Methanol Production Efficiency} = \frac{(CH_3OH)_{out} - (CH_3OH)_{in}}{(H_2)_{in} - (H_2)_{out}} \quad \mathbf{4-3}$$

Equation 4-1 describes carbon dioxide conversion. The second parameter used is the methanol production efficiency, which is based on the key limiting reactant consumed, in this case hydrogen, and is defined according to Equation 4-2.

4.6.2 Equilibrium Calculations

During parametric analysis, the comparison of the situation in equilibrium state versus the reaction state is mandatory for the validation of the process. Thus, calculations needed to be carried out to assess the conversion of carbon dioxide and the production of methanol in equilibrium state. These calculations were executed as follows:

Firstly, the three reaction (Eq.1-2 to 1-4) tables were constructed assuming that all reactions occur simultaneously in gas phase.

Table 4.13 Mole Balance for Reaction 1-2 (A)

(kmol)	CO ₂	H ₂	CO	H ₂ O
Initially	711.8	2238.4	51.4	172.1
Reacted/Produced	-e1	-e1	+e1	+e1
Equilibrium	711.8-e1	2238.4-e1	51.4+e1	172.1+e1

Table 4.14 Mole Balance for Reaction 1-3 (B)

(kmol)	CO ₂	3 H ₂	CH ₃ OH	H ₂ O
Initially	711.8-e1	2238.4-e1	4.8	172.1+e1
Reacted/Produced	-e2	-3e2	+e2	+e2
Equilibrium	711.8-e1-e2	2238.4-e1-3e2	4.8+e2	172.1+e1+e2

Table 4.15 Mole Balance for Reaction 1-4 (C)

(kmol)	CO	2H ₂	CH ₃ OH
Initially	51.4+e1	2238.4-e1-3e2	4.8+e2
Reacted/Produced	-e3	-2e3	+e3
Equilibrium	51.4+e1-e3	2238.4-e1-3e2-2e3	4.8+e2+e3

To calculate the equilibrium conversion for CO₂ and the equilibrium production for MEOH, variables e1, e2 and e3 need to be found.

The total moles for every substance taking part in the reactions are:

$$N_{CO_2} = 711.8 - e1 - e2$$

$$N_{CO} = 51.4 + e1 - e3$$

$$N_{H_2} = 2238.4 - e1 - 3e2 - 2e3$$

$$N_{H_2O} = 172.1 + e1 + e2$$

$$N_{CH_3OH} = 4.8 + e2 + e3$$

$$N_{total} = 3178.5 - 2e2 - 2e3$$

The values for the equilibrium constants K_A , K_B , K_C are calculated by Van't Hoff equation, are shown in Table 4.16.

Table 4.16 Equilibrium constants calculated by Van't Hoff equation

KA	0,011926
KB	4,67984E-05
KC	0,0039217

Moreover, equilibrium constants can also be expressed with the following relations:

$$K_A = K_{yA} K_{fA} P^{vA} \quad (4-4)$$

$$K_B = K_{yB} K_{fB} P^{vB} \quad (4-5)$$

$$K_C = K_{yC} K_{fC} P^{vC} \quad (4-6)$$

While $vA = 0$, $vB = -2$, $vC = -2$

Pressure's effect on K_y and K_f is negligible except in high pressures surpassing 100 bar. This system operates in 40 bar, so it is assumed that $K_f = 1$. With this assumption, equations (4-4) -(4-6) are simplified into:

$$K_A = K_{yA} P^{vA} \leftrightarrow K_{yA} = \frac{K_A}{P^{vA}} \quad (4-7)$$

$$K_B = K_{yB} P^{vB} \leftrightarrow K_{yB} = \frac{K_B}{P^{vB}} \quad (4-8)$$

$$K_C = K_{yC} P^{vC} \leftrightarrow K_{yC} = \frac{K_C}{P^{vC}} \quad (4-9)$$

Constants K_{yA} , K_{yB} and K_{yC} can also be expressed as follows:

$$K_{yA} = \frac{N_{CO} N_{H2O}}{N_{CO2} N_{H2}} \quad (4-10)$$

$$K_{yB} = \frac{N_{CH3OH} N_{H2O}}{N_{CO2} N_{H2}^3} N_{total}^2 \quad (4-11)$$

$$K_{yC} = \frac{N_{CH3OH}}{N_{CO} N_{H2}^2} N_{total}^2 \quad (4-12)$$

For the system's solution, the following mathematical equalities are intended:

$$\begin{aligned} \frac{K_A}{P^{vA}} &= \frac{N_{CO} N_{H2O}}{N_{CO2} N_{H2}} \\ \frac{K_B}{P^{vB}} &= \frac{N_{CH3OH} N_{H2O}}{N_{CO2} N_{H2}^3} N_{total}^2 \\ \frac{K_C}{P^{vC}} &= \frac{N_{CH3OH}}{N_{CO} N_{H2}^2} N_{total}^2 \end{aligned}$$

Then, variables F_1 , F_2 and F_3 were assumed. Their mathematical expressions are shown below:

$$F_1 = \left| \frac{K_A}{P^{vA}} - \frac{N_{CO} N_{H2O}}{N_{CO2} N_{H2}} \right| \quad (4-13)$$

$$F_2 = \left| \frac{K_B}{P^{vB}} - \frac{N_{CH_3OH} N_{H_2O}}{N_{CO_2} N_{H_2}^3} N_{total}^2 \right| \quad (4-14)$$

$$F_3 = \left| \frac{K_C}{P^{vC}} - \frac{N_{CH_3OH}}{N_{CO_2} N_{H_2}^2} N_{total}^2 \right| \quad (4-15)$$

It is now understood that the system is solved when:

$$F_1 + F_2 + F_3 = 0$$

Using the Solver Excel Add-in, the values of conversion e1, e2 and e3 as well as the composition in equilibrium are presented in Tables 4.17 and 4.18 respectively.

Table 4.17 Values for reactions conversions

e1	e2	e3
22.806	89.359	27.354

Table 4.18 Equilibrium Composition

N _{CO2}	N _{CO}	N _{H2}	N _{H2O}	N _{CH3OH}
599.7	46.9	1892.8	284.2	121.5

Finally, for operational parameters of 40 bar and 250°C in equilibrium the CO₂ conversion is **15.8 %** while Methanol production is **33.8 %**

4.6.3 Reactor Operating Pressure

According to Graaf et al [10], the conversion reaction of carbon dioxide to methanol takes place in the pressure range 15 - 50 bar. However, to study the effect of pressure, the variation of the reactor operating pressure in the range of 30 - 70 bar is considered to observe the behavior of the system at higher pressure.

The composition of the reactor inlet stream is characterized by the stoichiometric number (SN) (Equation 4-1). When $SN=2$ the reactants are in stoichiometric ratio, whereas when $SN<2$ and $SN>2$, there is a hydrogen deficit and excess respectively, as has been mentioned in subsection 4.2.

The sensitivity analysis is performed by adjusting the hydrogen supply so that the reactants are in a stoichiometric ratio of $SN=2$ and by keeping the reactor operating temperature constant and equal to 250°C .

Lastly, the cooling duty, heating duty, electricity and total energy in kWh per every kg of methanol produced were extracted from Aspen Plus software and placed into the comparative graphs. The goal is to determine the optimal pressure value by obtaining the total energy minimum.

Figures 4.6 through 4.10 show the influence of pressure in the evaluation parameters.

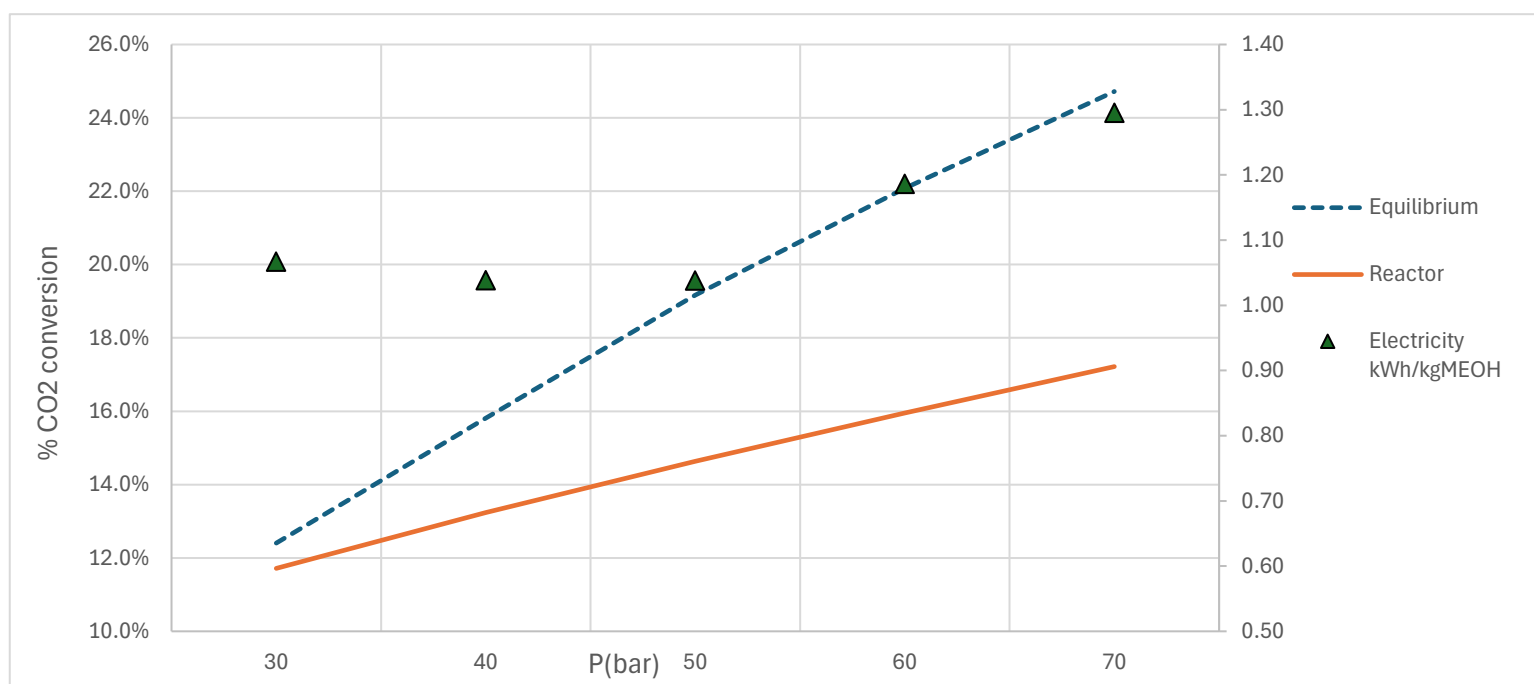


Figure 4.6 CO₂ Conversion for different pressures correlated with electricity per methanol produced

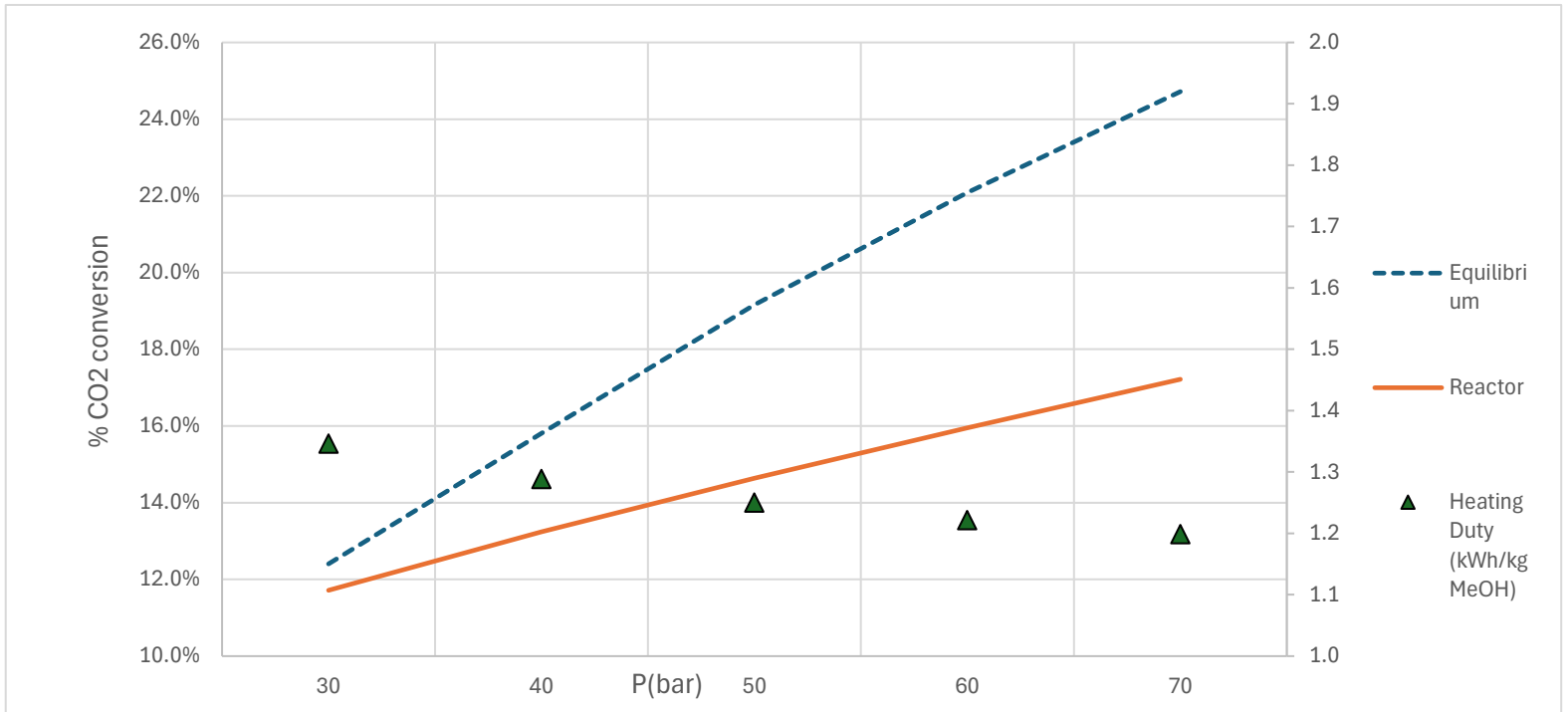


Figure 4.7 CO₂ Conversion for different pressures correlated with heating duty per methanol produced

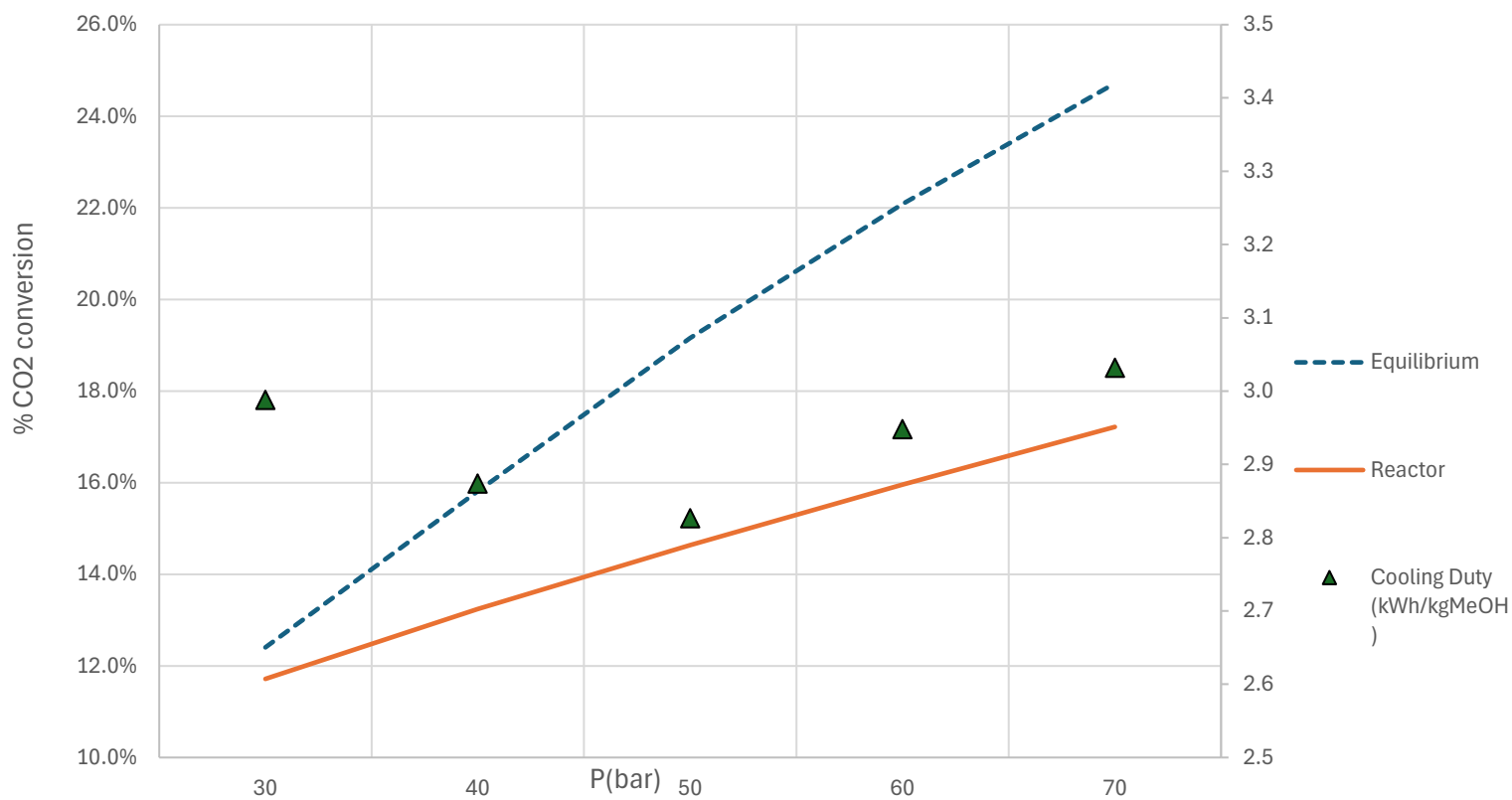


Figure 4.8 CO₂ Conversion for different pressures correlated with cooling duty per methanol produced

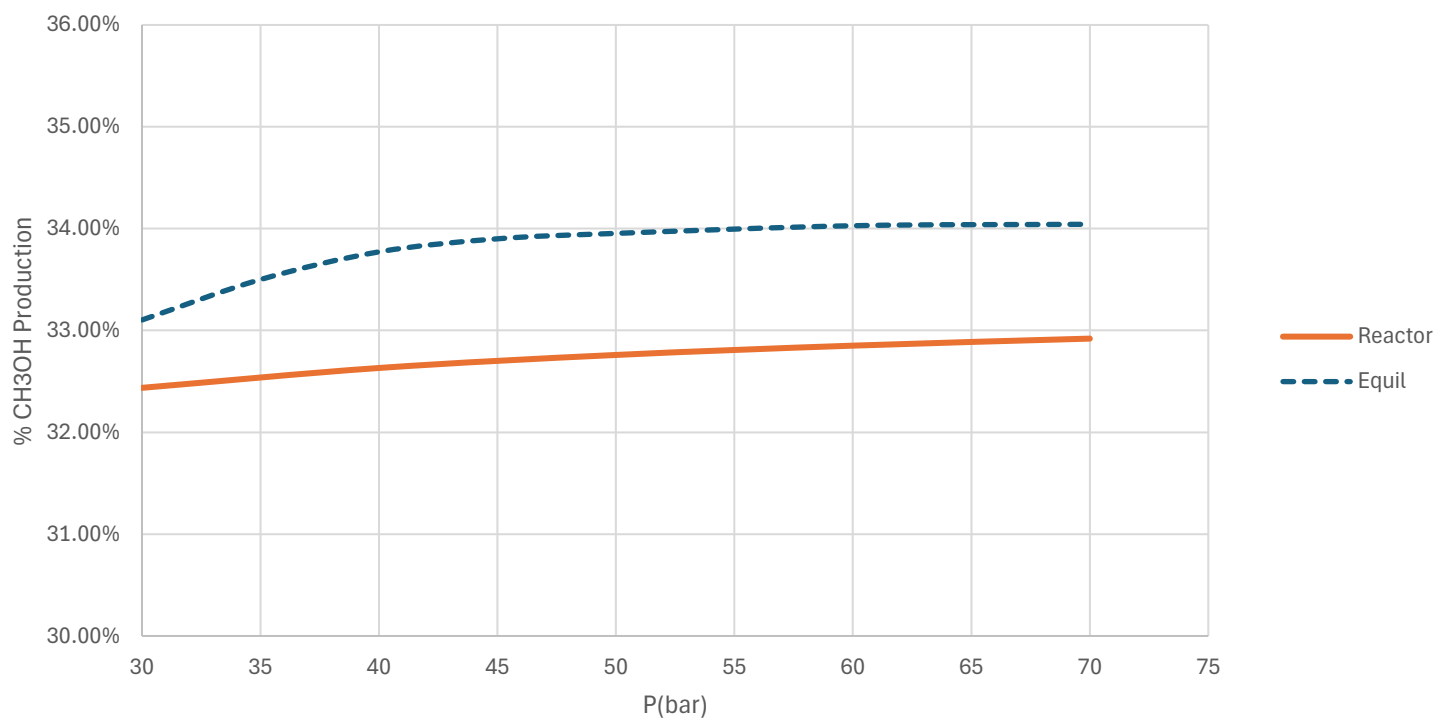


Figure 4.9 Methanol production for different pressures

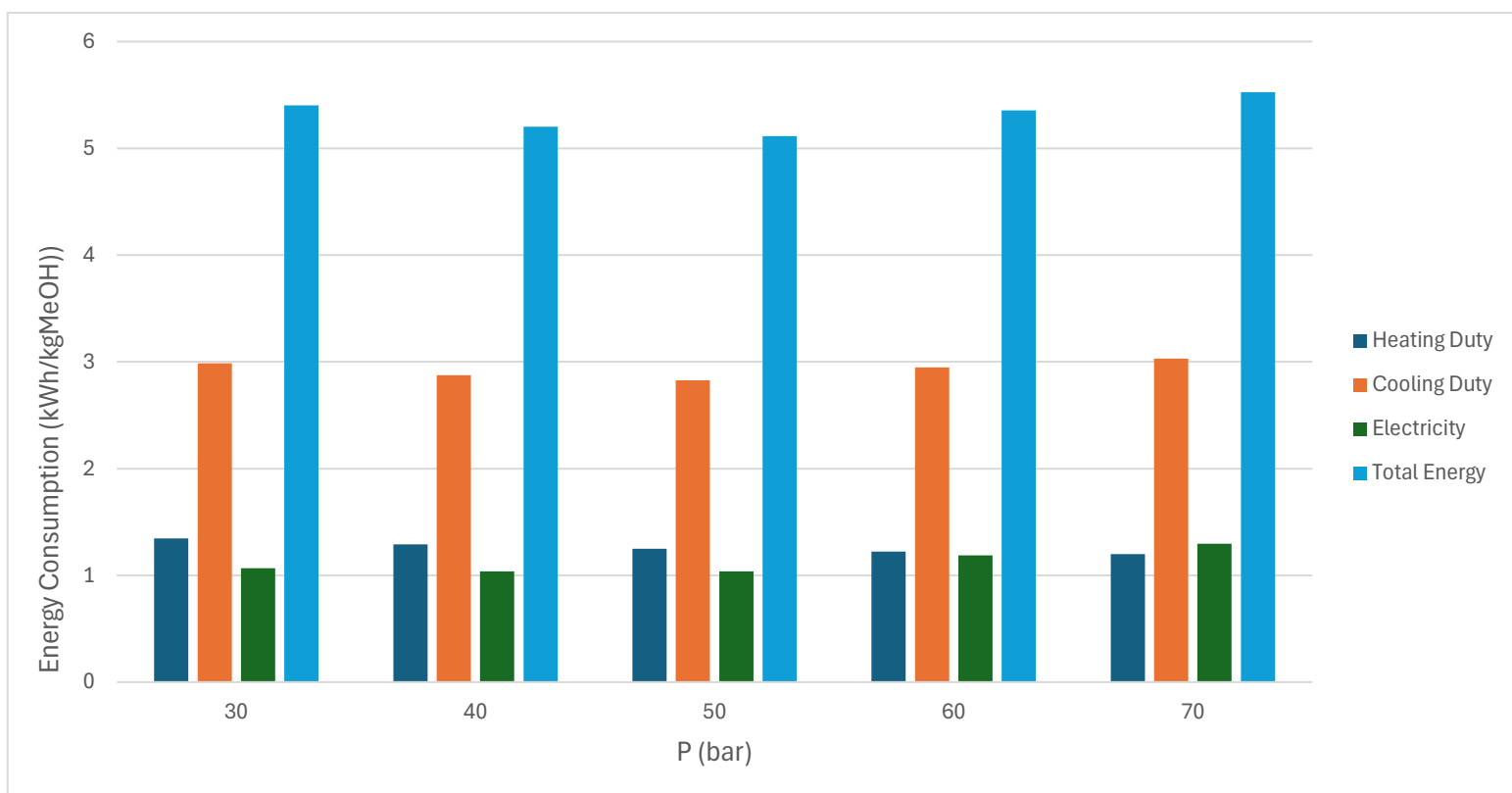


Figure 4.10 Comparative Graph for Total Levelized Energy Consumption for Different Pressures

Examining Figures 4.6 to 4.10, it is evident that reactor pressure is crucial for the process in terms of carbon dioxide conversion. The higher the pressure the more carbon dioxide reacts both in equilibrium and in reactor conditions. However, process optimization is based on reducing the required energy demands. As seen in Figure 4.6 to 4.8, levelized energy demands for the process explode beyond 60 bar except for heating duty, the values of which though are not exceptionally high.

Ultimately, in Figure 4.10 a minimum is observed for 50 bar which is the optimal value for the reactor pressure.

Hydrogenation reactions of dioxide and monoxide reduce the total number of moles in the direction of the reaction, i.e. they produce fewer moles of gas. According to thermodynamics, and the "Le Chatelier Principle", due to the reduction of molecules in the direction of hydrogenation, the equilibrium is shifted in that direction when the pressure is increased to bring the system to chemical equilibrium. Therefore, the formation of methanol is favored at high pressures, since it is in the direction of the reaction where the line molecules are decreasing.

In this work, methanol production isn't greatly affected by pressure variations as seen in Fig.4.9, with methanol production being in every case studied between 32 % - 33 % and close to equilibrium. This is reasonable due to relatively low methanol quantities present in the reactor. Thus, the system moves closer to equilibrium state, while simultaneously being not very dependent on external environment variations.

4.6.4 Reactor Operating Temperature

The mechanism proposed by Graaf et al [10] assumes that both the CO₂ hydrogenation reaction and the CO hydrogenation reaction are involved in methanol production, along with WGS. The methanol formation reactions are exothermic, with a decrease in the total number of line molecules, while RWGS is endothermic with no change in the total number of line molecules, so high pressure is required to achieve high conversions. The CO₂ hydrogenation reaction takes place in the range of 483 to 543 K [47]. According to Graaf et al. [10], the conversion reaction of carbon dioxide to methanol takes place in the temperature range of 210 - 250°C and pressures of 15 - 50 bar. It is also noted that in the range 473 - 553 K the Cu/ZnO/Al₂O₃ catalyst ensures satisfactory reaction rates . [48]

Therefore, according to Graaf et al. [10], the conversion reaction of carbon dioxide to methanol takes place in the temperature range 210 – 250°C. Thus, as part of the analysis, a sensitivity analysis will be carried out at a slightly lower temperature than 210°C and a slightly higher temperature than 250°C to study the behavior of the system. In particular, the analysis is carried out in the temperature range 200 - 270°C, at a pressure of 50 bar and for a stoichiometric ratio of the reactants.

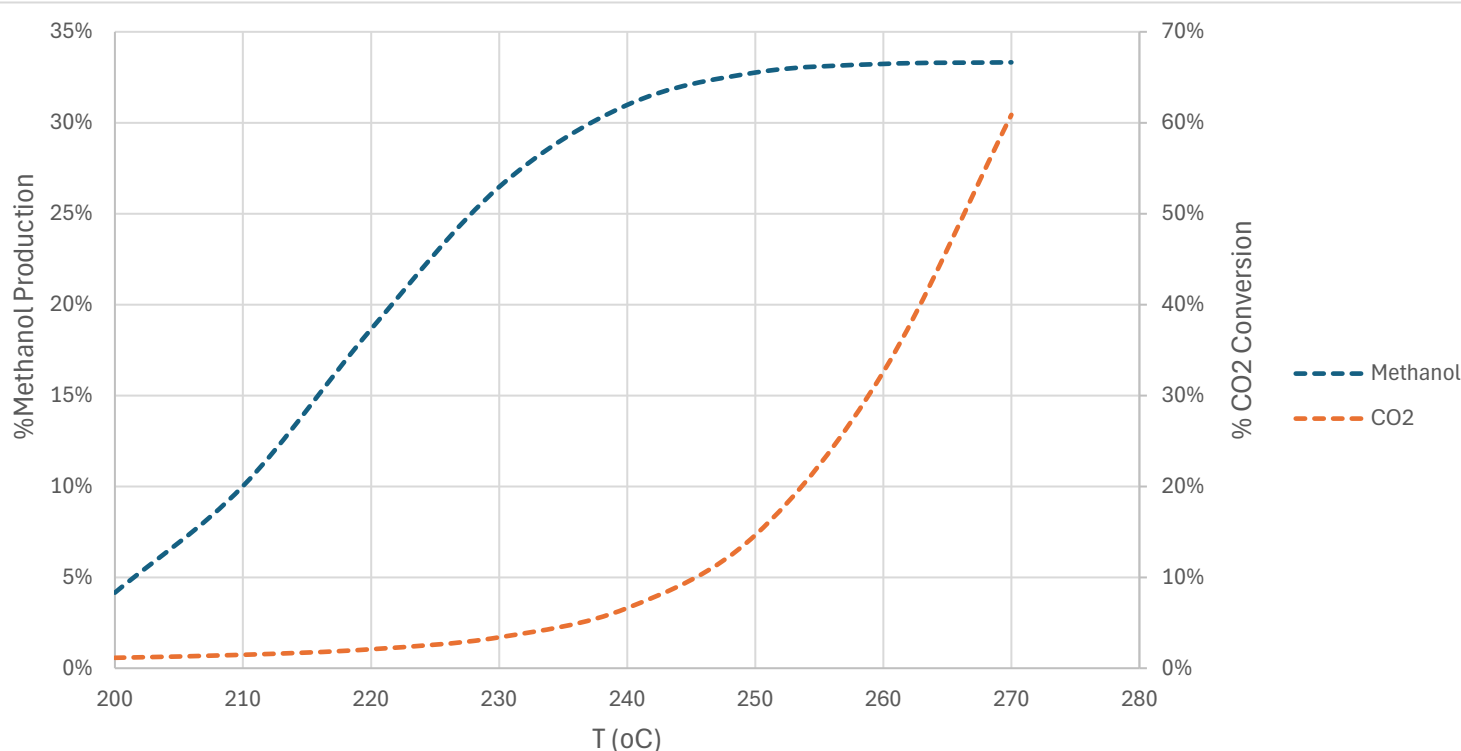


Figure 4.11 Influence of Reactor Temperature in CO₂ conversion and Methanol Production

According to the Le Chatelier Principle, high pressures (due to the reduction of moles) and low temperatures are required because methanol synthesis reactions are exothermic. However, because the third reaction is endothermic (Reaction 1-2 - RWGS), according to the kinetics of the reactions, as shown in Figure 4.11, an increase in temperature is required to increase conversion and methanol production efficiency. However, after 250°C methanol production presents a plateau, as temperature increase does not highly affect it. So, the value of 250°C is chosen where methanol production and carbon dioxide conversion are at 32.7 % and 14.6 % respectively.

4.7 Economic Analysis

In this subchapter, the economic evaluation of the process of methanol production is carried out. The methodology is the same as in CO₂ absorption's case, while all the equations, the utilities cost and factors needed are extensively analyzed in subchapter 1.8.

4.7.1 Manufacturing Materials Choice

Our process involves five substances, carbon monoxide and carbon dioxide, hydrogen, water and methanol. Carbon monoxide and carbon dioxide are not corrosive to metals and metal alloys. Thus, the effect of methanol and hydrogen on corrosion is studied, as the concentration of water in the process is very low. Due to the presence of hydrogen, two phenomena are the ones that may cause equipment failure. The first is High Temperature Hydrogen Attack, or methane reaction, while the second is Hydrogen Embrittlement, or crack initiation, and both occur at temperatures higher than 500°C. These phenomena are described in detail in section 1.10.5, and based on these it is decided whether ultimately mild steel can be used or whether the use of another alloy is required. In addition to hydrogen, the resistance of mild steel to methanol is also considered. It is known that methanol is corrosive to certain metals, such as aluminum, zinc and manganese, with which it reacts and releases hydrogen. However, there are about a dozen classes of alloys that are suitable for handling methanol, and they are suitable for lining pumps and valves, and as casings for containing pressurized liquids. [46]

The process reactor is operated at a pressure of 50 bar (725.2 psia) and a temperature of 250°C (481.73 °F). If it is assumed that the partial pressure of hydrogen can reach up to 725.2 psia at a temperature of 250°C, there is no risk of a "High Temperature Hydrogen Attack" occurring. Similarly, because the operating temperature of the reactor is lower than 500°C, there is no risk of cracking (Hydrogen Embrittlement phenomenon), using common carbon steel. Also, common steel is suitable for methanol handling, as long as the corrosion rate is in the range of safe use. Therefore, mild steel can be safely used for process equipment. In other cases where mild steel would not be suitable, stainless steel (304 stainless steel) would be selected, but the cost of the plant in this case would be several times higher.

4.7.2 Capital Cost Estimation

Table 4.19 presents the dimensions of every equipment as extracted from APEA calculation tool in Aspen Plus.

Table 4.19 Dimensions of equipment as extracted from APEA calculation tool in Aspen Plus.

Equipment	a	b	n	S	N	Sfinal
HP-SEP	11600	34	0.85	5,352.39	1	5352.39
LP-SEP				1,542.21	1	1542.21
REACTOR				5,352.39	1	5352.39
DIST RDRUM	10200	31	0.85	816.47	1	816.47
DIST COLUMN				18,189.05	1	18189.05
COOLER	28000	54	1.2	99.99	1	99.99

COOLER2				94.71	1	94.71
FEHE				785.00	1	785.00
HEATER				37.39	1	37.39
DIST COND				1,288.37	1	1288.37
DIST COL REBOILER	29000	400	0.9	202.83	1	202.83
DIST COL TRAYS	100	120	1.2	0.61	1	0.61
COMP1	-8400	3100	0.6	2,839.65	1	2839.65
COMP2				231.39	1	231.39

In Table 4.20, the equipment and installation costs are shown using the ‘Detailed Factorial’ by Towler and Sinott.

Table 4.20 Installation and Equipment Costs for Methanol Production Process

<i>Equipment</i>	<i>Cei (\$ 2010)</i>	<i>fm</i>	<i>C (\$ 2010)</i>	<i>C (\$ 2024)</i>	<i>C (€ 2024)</i>
HP-SEP	\$61,804.7	1. 3	\$231,149.63	\$344,880.98	324,188.12 €
LP-SEP	\$29,034.2	1. 3	\$108,587.88	\$162,015.81	152,294.86 €
REACTOR	\$61,804.7	1. 3	\$231,149.63	\$344,880.98	324,188.12 €
DIST RDRUM	\$19,457.8	1. 3	\$72,772.27	\$108,578.04	102,063.35 €
DIST COLUMN	\$139,679.3	1. 3	\$522,400.52	\$779,434.52	732,668.45 €
COOLER	\$41,561.9	1. 3	\$155,441.42	\$231,922.45	218,007.11 €
COOLER2	\$40,707.8	1. 3	\$152,247.04	\$227,156.36	213,526.98 €
FEHE	\$188,782.0	1. 3	\$706,044.57	\$1,053,435.9 9	990,229.83 €
HEATER	\$32,165.8	1. 3	\$120,300.27	\$179,490.99	168,721.53 €
DIST COND	\$610,734.7	1. 3	\$263,132.36	\$392,600.00	369,044.00 €
DIST COL REBOILER	\$76,695.9	1. 3	\$286,842.60	\$427,976.26	402,297.69 €
DIST COL TRAYS	\$166.3	1. 3	\$621.80	\$927.75	872.08 €
COMP1	\$357,464.8	1. 3	\$1,336,918.2 1	\$1,994,715.0 8	1,875,032.18 €
COMP2	\$72,877.1	1. 3	\$272,560.53	\$406,667.06	382,267.03 €

Furthermore, the cost of catalyst Cu/ZnO/Al₂O₃ is determined as fixed capital cost. Thus Table 4.21 shows the results for catalyst cost.

Table 4.21 Catalyst Cost for Methanol Production Process [49]

Catalyst Cost	
Catalyst Cost (\$/kg)	30
Catalyst Cost (€/kg)	28.2
Catalyst Mass (kg)	29629
Catalyst Cost	835,537.80 €

Adding up, the total capital cost sums up to **7,090,939.12 €**

4.7.3 Operating Cost Estimation

4.7.3.1 Varied Operating Cost

Table 4.22 summarizes the utilities cost for the process exactly as presented in subchapter 1.8

Table 4.22 Varied Operating Cost for Methanol Production Process

Equipm ent	Utility	Uni ts	Utility Demands	Calculated Cost (€/hr)	Calculated Cost (€/yr)
HEATER	Νερό Θέρμανσης	ton/ hr	120.77	6.04 €	48,306.55 €
COOLE R2	Νερό Ψύξης	ton/ hr	383.65	19.18 €	153,458.48 €
COOLE R	Νερό Ψύξης	ton/ hr	653.90	32.70 €	261,560.66 €
DIST REBOIL ER	Ατμός Χαμηλής Πίεσης	kg/h r	1043.96	36.38 €	291,055.66 €
COND	Νερό Ψύξης	ton/ hr	401.69	20.08 €	160,676.16 €
COMP1	Ηλεκτρική Ενέργεια	kW h	2839.66	340.76 €	2,726,073.60 €
COMP2	Ηλεκτρική Ενέργεια	kW h	231.394	27.77 €	222,138.24 €

The total varied operating cost adds up to **3,641,131.11 €**

4.7.3.2 Fixed Operating Cost

Table 4.23 summarizes the fixed operating cost calculated for Methanol Production Process

Table 4.23 Fixed operating cost for Methanol Production Process

ISBL	7,090,939.12 €
OSBL	2,836,375.65 €
Cop	5,000,000.00 €
Cs	1,250,000.00 €

Cot	3,125,000.00 €
Cm	354,546.96 €
Cti	141,818.78 €
Cr	198,546.30 €
Cg	6,324,205.52 €
Total	16,394,117.56 €

The whole operating cost for the process adds up to **20,035,248.67 €**

4.7.4 Results Analysis

In this section, the results for the fixed installation costs (CAPEX) and operating costs (OPEX) of the Methanol Production process are analyzed and compared with available results from the literature.

The total fixed costs (CAPEX) are about 7.1 MEUR. The following graph shows the percentage of the fixed installation costs of each piece of equipment.

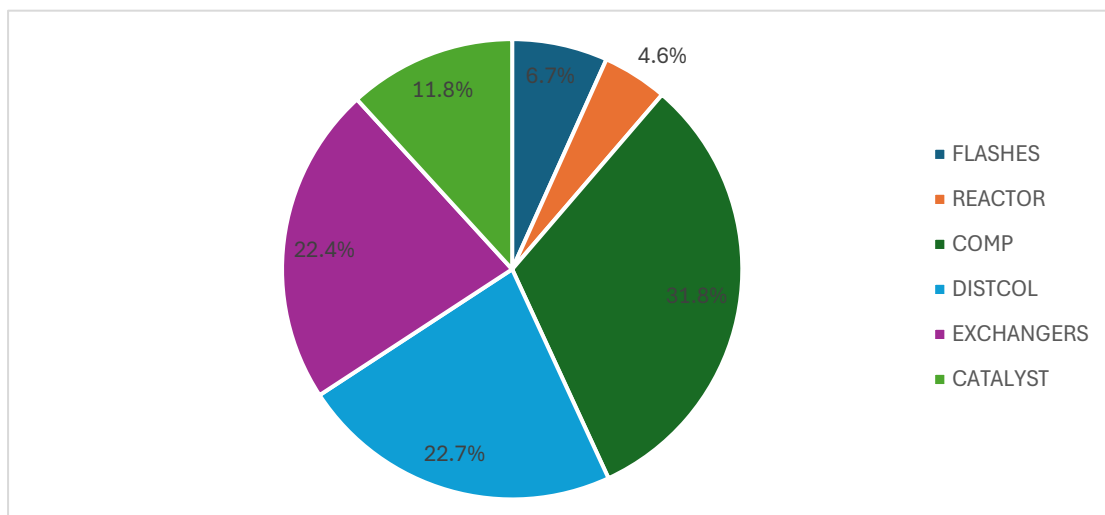


Figure 4.12 Equipment installation costs compared to total installed equipment cost

It appears that the cost of compressing is the highest among all equipment installed as there's a need for compression of large-capacity streams to a great pressure range. The Distillation column, with high reboiling duties, and the heat exchangers, due to the extensive surface area needed for the heat transfer of tens of thousands of kilomoles also account for more than half of equipment cost. Ultimately, a notable fact is the cost of the catalyst, accounting for more than 11 % of total costs.

As far as the operational cost is concerned, the sum adds up to 20 MEUR using MEA. In Figure 4.13, the percentage of the utilities used in the unit compared to the total varied operating cost is shown.

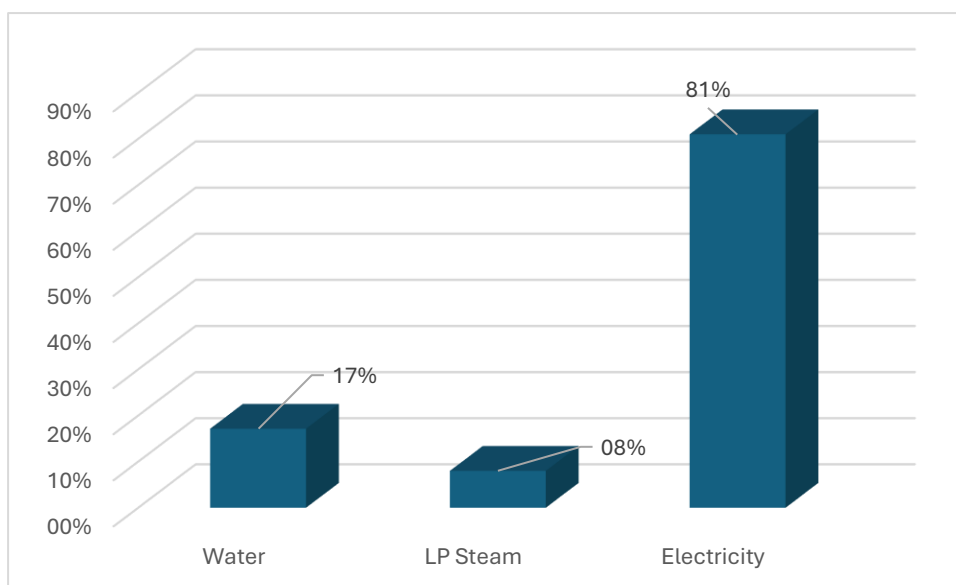


Figure 4.13 Percentage of Utilities to total operating cost in Carbon Capture Process

Most of the cost comes from the electricity usage in the unit, while cooling water comes in a distant second. However, despite the respectable percentage the cost of cooling water is rather low, so it doesn't have a serious effect in the result. The LP steam usage on the other hand is negligible, thus the adjusted price considered is the same as the Carbon Capture Unit presented in Chapter 3.

Electricity price plays an important role in determining the varied operating cost. For this reason, as mentioned before, a mini sensitivity analysis was carried out, presenting a plethora of scenarios for best to worst concerning the price of electricity and its effect on the levelized cost of Methanol. The results are shown in Table 4.24.

Table 4.24 Variations on Electricity Price and their effect on MEOH levelized cost.

Electricity Price (€/kWh)	Adjustment	Electricity Price (€/kWh)	Total Cost (€/tonMEOH)
0.12	-30%	0.084	501.49
	-20%	0.096	512.01
	-10%	0.108	522.52
	0%	0.12	533.03
	10%	0.132	543.54
	20%	0.144	554.06
	30%	0.156	564.57

The price selected is 0.12 €/kWh due to an accordance with the existing literature.

4.7.5 Levelized Cost of Methanol

The levelized cost of methanol is the most important factor when assessing the success of a plant. In this subchapter, the levelized cost of methanol is calculated using the parameters extracted from the parametric analysis.

The methodology for the calculation of the ACCR is also extensively explained in subchapter 1.8.

In Table 4.25, the characteristics of the investment are presented in order to assess the levelized cost of CO₂.

Table 4.25 Characteristics of the investment in Methanol Production Unit

ACCR	0.110
i	0.1
n	25

Thus, the levelized cost of methanol in this study's plant is shown in Table 4.26. The levelized cost of methanol is calculated minus the revenue generated from CO₂ sales, which will be explained thoroughly in Chapter 5.

Table 4.26 Levelized cost of CH₃OH in Methanol Production Process

Annualized CAPEx	30.12	€/tonMEOH
OPEx	772.61	
Revenue from CO ₂	269.7	
Total	533.03	

The total levelized cost of 533.03 €/tonMEOH responds in an accurate way in 2024 prices in Europe. [50]

5 Levelized Cost of the Overall Process

In this study, an effort was made to assess the total cost for methanol production using green Hydrogen and CO₂ captured with MEA. In this context, it is mandatory to transform the levelized cost for each process into levelized cost of methanol (€/tonMEOH). This transformation was made for both hydrogen and carbon dioxide using the following formula:

$$LCOM_{H_2} = LCOH \left[\frac{\text{€}}{\text{tonH}_2} \right] * \frac{H2_{prod}}{MEOH_{prod}} \left[\frac{\text{tonH}_2}{\text{tonMEOH}} \right] \quad (5-1)$$

$$LCOM_{CO_2} = LCOCD \left[\frac{\text{€}}{\text{tonCO}_2} \right] * \frac{CO2_{fed}}{MEOH_{prod}} \left[\frac{\text{tonCO}_2}{\text{tonMEOH}} \right] \quad (5-2)$$

Due to high productivity in CO₂ capture unit and lower demand for the methanol production process, a large percentage of the carbon dioxide produced needs to be sold to the listed price (Table 5.1).

Equation (5-2) uses the amount of CO₂ fed in Methanol production process instead of CO₂ produced. This is since only a certain amount of CO₂ produced participates in methanol synthesis to maintain stoichiometric balance.

Table 5.1 summarizes the streams produced and revenues from CO₂ processes.

Table 5.1 Carbon Capture Unit Revenue Results

CO2out (tonne/year)	1,054,578
CO2feed(tonne/year)	87,424.32
CO2sold (tonne/year)	967,153.73
CO2cost(EUR/ton Jan'24) [51]	80
CO2 revenue(EUR/year)	77,372,298.14 €
Annualized CO2 revenue (EUR/tonCO2prod)	73.37 €

Table 4.25 includes the revenue generated from Carbon Dioxide sales. The calculations for CO₂ cost saved are shown in Table 5.2

Table 5.2 CO2 cost saved per ton of Methanol produced

MEOH prod (tonne/year)	25931.88
CO2feed(tonne/year)	87424.32
CO2cost(EUR/ton Jan'24) [51]	80
CO2costsaved(EUR/year)	6,993,945.77
CO2costsaved(EUR/tonMEOH)	269.70

Ultimately, the levelized cost of Methanol in CO₂ capture and Electrolysis processes are presented in Tables 5.3 and 5.4

Table 5.3 Levelized Cost of Methanol from CO₂ capture process

45.88	EUR/tonCO₂
73.37	Annualized CO₂ revenue (EUR/tonCO₂prod)
-27.49	EUR/tonCO₂
3.37	tonCO₂/tonMEOH
-92.66	EUR/tonMEOH

Table 5.4 Levelized Cost of Methanol in Electrolysis

0.32	tonH₂/tonMEOH
2,235.52	Cost of H₂/ ton MEOH (€/tonMEOH)

Examining Tables 5.2 to 5.4, it is evident that Carbon Capture is the only profitable process in the whole methanol production chain due to the income generated from CO₂ sales. On the contrary, electrolysis appears as a costly process to produce high purity methanol in large capacities

The total levelized cost of methanol in the whole production chain is shown in Table 5.5

Table 5.5 Total levelized cost of methanol produced by Green H₂ and Carbon Capture

H ₂ production process	2235.52	€/tonMEOH
CO ₂ capture process	-92.66	€/tonMEOH
Methanol production process	533.03	€/tonMEOH
TOTAL COST	2675.89	€/tonMEOH

6 Conclusions

Energy carriers play a vital role in modern energy systems by enabling the storage, transport, and conversion of energy into usable forms. They bridge the gap between energy production and consumption, allowing energy generated from various sources—such as solar, wind, or fossil fuels—to be efficiently delivered to end users. Energy carriers, such as electricity, hydrogen, and biofuels, are essential for integrating renewable energy into the grid and ensuring a stable energy supply. Their ability to store and transport energy over long distances helps mitigate the intermittency of renewable sources and ensures energy availability when and where it is needed. As the world transitions toward cleaner energy, the development of efficient and sustainable energy carriers will be key to reducing carbon emissions and meeting global energy demands.

Methanol is gaining attention as a potential green hydrogen carrier because of its beneficial chemical characteristics, as well as its easy of storage and transport. Being a liquid under normal conditions, methanol presents considerable benefits compared to traditional hydrogen storage options like compressed or liquefied hydrogen.

This thesis investigates the role of methanol in hydrogen production through reforming processes, where it can be efficiently reconverted into hydrogen with minimal energy input. Within the scope of the study, methanol is synthesized using CO₂ captured from the flue gas of a typical cement plant, positioning it as a carbon-neutral solution within a circular energy economy. The green hydrogen used in methanol production is generated via water electrolysis using an alkaline electrolyser, offering a sustainable and carbon-free approach, which is vital for the transition to a clean energy future. The entire process—encompassing hydrogen production in the electrolyser, CO₂ capture, and methanol synthesis—was simulated using Aspen Plus™.

The results from the simulation of the electrolyser and the LCOH of 6.99 €/kg of H₂ produced are considered well-adapted to reality in 2024. The integrated 58.6 MW electrolysis system developed seems quite energy-costly and out of reach at first glance. Nevertheless, given the fact that an electrolysis system can encompass several 1.5 MW commercial electrolysers and Greece's heavy solar PV capacity, an integrated system of 58.6 could be feasible. The best operating conditions of the system at 5 bar and 80°C present no technical obstacle and allow for further optimization, both in materials (such as membranes) and in processes. However, the competitiveness of alkaline electrolysis is still in question, because despite the rapid progress and extensive research, it remains still at least 3 times more costly than every other hydrogen colors.

Concerning the carbon dioxide capture process, for a CO₂ flow of 1055.5 ktonnes per year entering the system, it successfully captures 90% of the CO₂ using an aqueous 30% wt. MEA solvent. Over the years, carbon capture technology has evolved, becoming more efficient and cost-effective, and it is now considered a well-established technology. The total equipment cost for the CO₂ capture unit is approximately 45.5 million euros, with the absorber, stripper, scrubber, and heat exchanger contributing the most to the total cost. Utility costs, including cooling water, steam, and electricity, amount to approximately 22 million euros per year. Additionally, the variable operating costs, including MEA makeup, add another 25.6 million euros annually. The levelized cost of the carbon capture process is about 46 €/ton CO₂ captured, which aligns with values found

in the literature. These numbers describe carbon capture process as a safe investment, with a high return, given the purchase price for a ton of CO₂ is around 80 €. Lastly, carbon capture is the only process in the whole production chain which produces profitable levelized cost in methanol production. Due to high capacity, most of the CO₂ is assumed to be sold at the listed price of 80 €/ton, producing revenue of 73.4 €/ton of CO₂ captured and the process is profitable by 27.4 €/ton CO₂ or 92.7 €/ton MEOH.

The methanol production process proposed by Kiss et al., is considered a novel approach. In this thesis, the use of green hydrogen enhanced the novelty of this approach focused on sustainability and the results are considered promising. Analyzing the key factors affecting the process, Kiss et al. work is validated. Optimal reactor pressure is found to be 50 bar, where energy demand is minimized. The reactor temperature of 250°C is chosen as it provides the best balance for methanol production and carbon dioxide conversion.

The economic analysis includes CAPEX of €7.1 million, driven mainly by compression, distillation, and heat exchangers., while the OPEX is €20 million per year, with electricity as the largest contributor. Given the plant's high capacity of 26 ktonnes/year, the investment's cost is considered viable. The levelized cost of methanol was calculated to be 533.03 €/tonMEOH, a value directly proportional to current methanol prices.

In conclusion, for methanol production from H₂ produced by electrolysis and CO₂ captured from the flue gas of a typical cement industry, the cost of electrolysis was estimated at 2235.52 €/ton MeOH, the cost of CO₂ capture at -92.66 €/ton MeOH, and the cost of methanol production at 533.03 €/ton MeOH, resulting in a final total cost of 2675.89 €/ton MeOH.

The price of methanol produced in this work is 4 times higher on average than the price of methanol produced by fossils in Europe in 2024 [50], with hydrogen production contributing to the base cost of the overall production process. Even though each one of the three separate steps of production is deemed viable, the general picture looks yet bleak. Although there is political will for the energy transition, with tax incentives being implemented to replace carbon-emitting plants. Being financially not competitive, the current process indicates that clear steps must be taken for the optimization and replacement the existing production methods.

7 Future Work

Future work in methanol production from green hydrogen could likely focus on optimizing the efficiency and scalability of the process to meet growing energy demands. This could involve advancements in electrolyser technology to reduce costs and energy consumption in hydrogen production, making it more economically viable. A special focus could be given to membrane materials or to new emerging technologies to replace alkaline electrolysis.

Additionally, improvements in CO₂ capture techniques and integration with industrial processes could enhance the carbon-neutrality of methanol synthesis. Optimization of the carbon capture process might focus on determining the most compatible heat-exchanger so as to reduce the surface area consequently the equipment cost. This will transform the industry and the carbon stock even more than today.

Efforts may also be directed towards development decentralized methanol production systems to localize energy storage and reduce transportation costs. Process-wise, the optimization focus should be on improving compression, to minimize energy requirements.

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