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Topic:

Techno-economic analysis of CO2 capture and its hydrogenation with renewable hydrogen

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Abstract

The escalating impacts of climate change and global warming have intensified the global urgency to reduce greenhouse gas emissions and transition toward low-carbon energy systems. Among the proposed solutions, carbon capture and utilization (CCU) technologies offer promising pathways to mitigate CO_2 emissions, particularly from hard-to-abate industrial sectors. This thesis presents a comprehensive techno-economic analysis of an integrated system combining post-combustion CO_2 capture with renewable hydrogen production and subsequent methanol synthesis. The study focuses on the decarbonization of the pulp and paper industry, selecting a biomass-based cogeneration plant as the case study for CO_2 capture. A detailed Aspen Plus model was developed to simulate the absorption-based CO_2 capture process using monoethanolamine (MEA), and the model was validated against reliable literature data. The captured CO_2 is subsequently hydrogenated using green hydrogen produced via a low-temperature electrolyzer (LTE), with methanol synthesis modeled in a plug flow reactor based on kinetic parameters from literature. A full-process integration was achieved, and the system's technical performance was assessed under different operating scenarios. A techno-economic analysis was then conducted to evaluate capital and operational expenditures, levelized costs, and economic feasibility under various sensitivity parameters. The results show that while the integration of CO_2 capture and utilization for methanol production is technically viable, the system remains economically sensitive to key variables such as electricity price, electrolyser efficiency, and methanol market value. This work contributes to the development of sustainable Power-to-X pathways and offers insights into the challenges and potential of industrial CO_2 valorisation through renewable hydrogen.

Key words:

CO_2 capture, Techno-economic analysis, Post-combustion, MEA absorption, Renewable hydrogen, Low-temperature electrolyzer, Methanol synthesis, Power-to-X

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List of abbreviation

BEC	Bare Erected Cost
CEPCI	Chemical Engineering Plant Cost Index
COM	Cost of methanol
EBIT	Earnings before interest and taxes
EBITDA	Earnings before interest, taxes, depreciation and amortization
EPCC	Engineering, procurement, and construction cost
FCF	Free Cash Flow
HHV	Higher heating value
IRR	Internal rate of return
LCOE	Levelized cost of electricity
LCOM	Levelized cost of methanol
LHV	Lower heating value
MEA	Monoethanolamine
MeOH	Methanol
NPV	Net present value
OPEX	Operating cost
PBP	Payback period
PC	Process Contingencies
PtX	Power-to-X
RES	Renewable Energy Sources
SPECCA	Specific plant energy consumption for CO2 avoided
TIC	Total Invested Cost
TOC	Total Overnight Cost
TPC	Total Plant Cost

Introduction

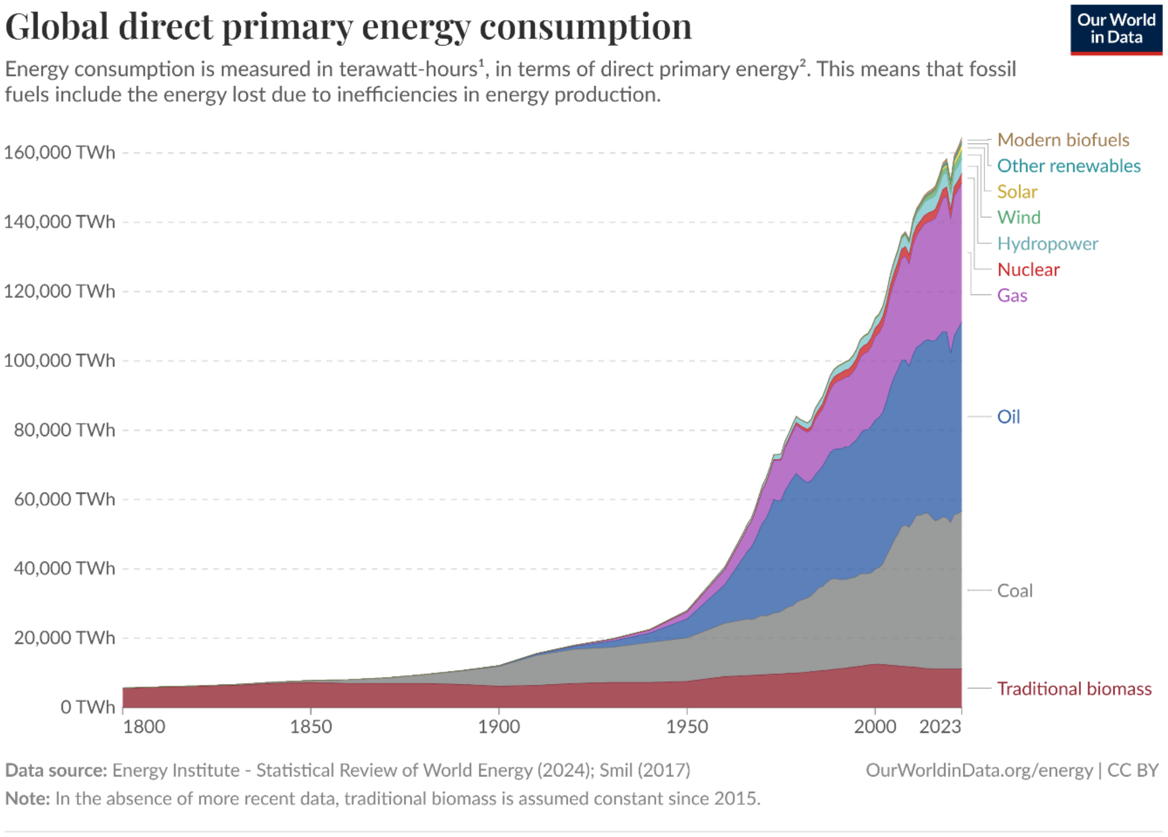
Human life has entered an irreversible stage of complexity due to the advancement of several technologies. Every aspect of our life has been transformed to new levels of modernity which has faced us with different consequences. Comprehending all the consequences is not an easy task, so As long as we continue to innovate and explore new possibilities, we will face quite complex challenges, often with no clear or immediate solutions.

Among the recent challenges we are struggling with, the need for sustainability is one of the vital issues that should be addressed strictly. Technology advancement has both advantages and disadvantages, so as long as there are benefits like economic growth and improved quality of life, there is an increasing pressure on natural systems, particularly through the emission of greenhouse gases. Addressing the environmental impacts of modern industrial activity is no longer a choice but a necessity, one that demands new approaches, new technologies, and new ways of thinking.

To take action, research and development efforts are increasingly focused on exploring effective strategies to mitigate environmental impact, reduce emissions, and promote more sustainable industrial practices. handling these challenges calls for a thoughtful integration of technology, systems thinking, and long-term planning. It is at the intersection of innovation, responsibility, and resilience that meaningful progress can emerge, where scientific inquiry and practical solutions converge to address the complex realities of our time.

Background and Context

In recent years, technological advancements have played a pivotal role in enhancing the quality of human life. From the way we communicate and travel to how we work and consume, innovation has brought about unprecedented levels of comfort and convenience. These developments have redefined our standards of living, integrating digital infrastructure, automation, and smart systems into daily life. While one might assume that such advancements would lead to greater energy efficiency and reduced consumption, the reality has been quite the opposite. The global appetite for energy has continued to grow, driven not only by population growth and urbanization but also by the expanding functionality and accessibility of modern technology.[1] Figure 1 illustrates how the global energy demand has evolved through time and reached to higher levels in recent years.


Global direct primary energy consumption

Energy consumption is measured in terawatt-hours¹, in terms of direct primary energy². This means that fossil fuels include the energy lost due to inefficiencies in energy production.

Data source: Energy Institute - Statistical Review of World Energy (2024); Smil (2017)

OurWorldinData.org/energy | CC BY

Note: In the absence of more recent data, traditional biomass is assumed constant since 2015.

Figure 1. primary energy consumption evolution

As societies become more interconnected and industries more digitized, energy use has expanded across all sectors, including residential, industrial, transportation, and commercial domains. Devices, systems, and services that were once considered luxuries are now seen as essential, and their widespread adoption has significantly increased the baseline demand for energy. According to data from major international energy agencies, this upward trend shows no signs of reversing, with projections indicating a continued rise in global energy demand over the coming decades, particularly in developing economies striving to improve infrastructure and economic stability.

This persistent growth in energy consumption presents a critical challenge: meeting rising demand while ensuring energy accessibility, affordability, and sustainability. Today, global energy needs are met through a diverse mix of energy sources, including fossil fuels (coal, oil, and natural gas), nuclear power, and renewable resources such as hydro, wind, solar, and biomass. Among these, fossil fuels continue to dominate the global energy landscape due to their historical availability, high energy density, and well-established infrastructure. However, the limitations of fossil-based systems, particularly their environmental impact and resource finiteness, have become increasingly apparent. Figure 2 presents the proportion of energy demand met by each source. [2]

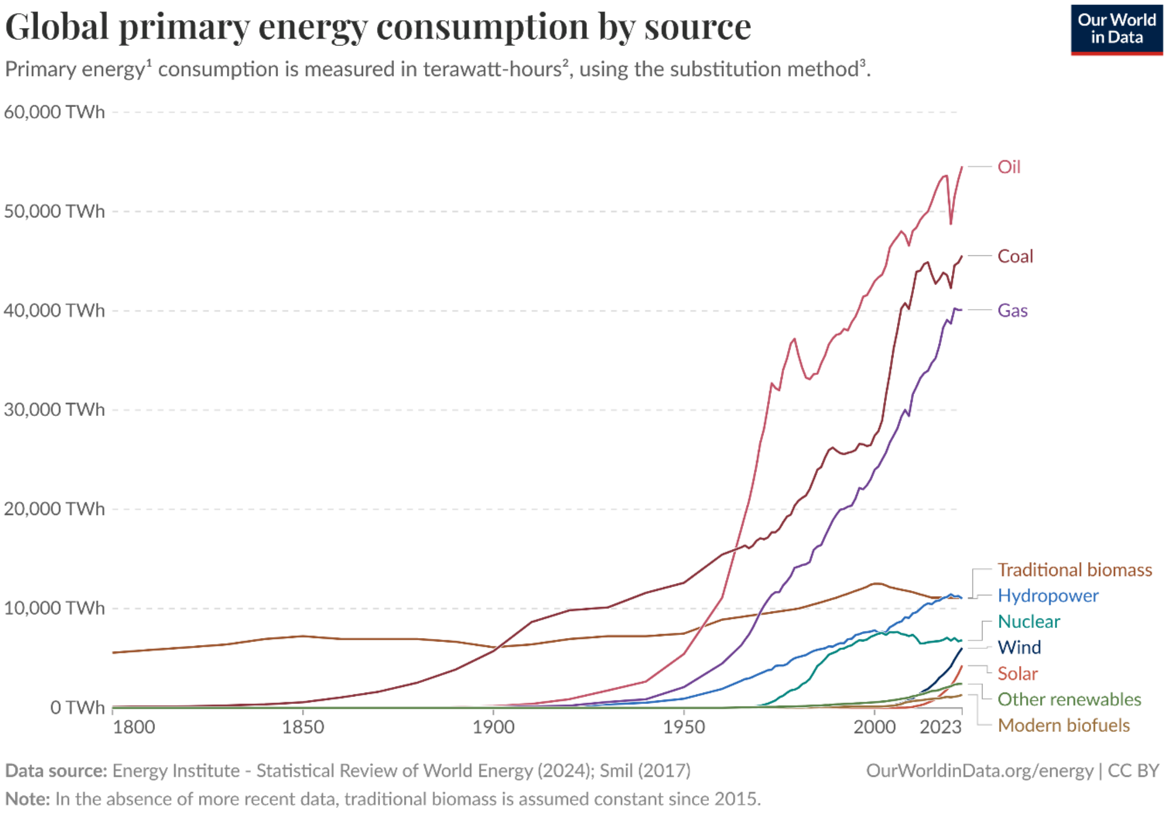


Figure 2. evolution of different energy source utilization

Renewable energy sources have gained significant attention as cleaner and more sustainable alternatives, supported by technological improvements and policy incentives. Yet, challenges such as intermittency, high initial investment costs, and integration into existing energy grids have limited their complete replacement of conventional energy systems. Consequently, despite ongoing efforts to transition toward renewables, a large share of global energy demand is still satisfied through fossil fuel combustion.

This reliance on carbon-intensive energy sources has substantial environmental implications. The combustion of fossil fuels is the primary contributor to anthropogenic greenhouse gas emissions, particularly carbon dioxide (CO_2), which is directly linked to climate change. As energy consumption continues to rise in both developed and developing regions, so too does the urgency to mitigate its environmental impact by accelerating the deployment of cleaner technologies and more sustainable practices.

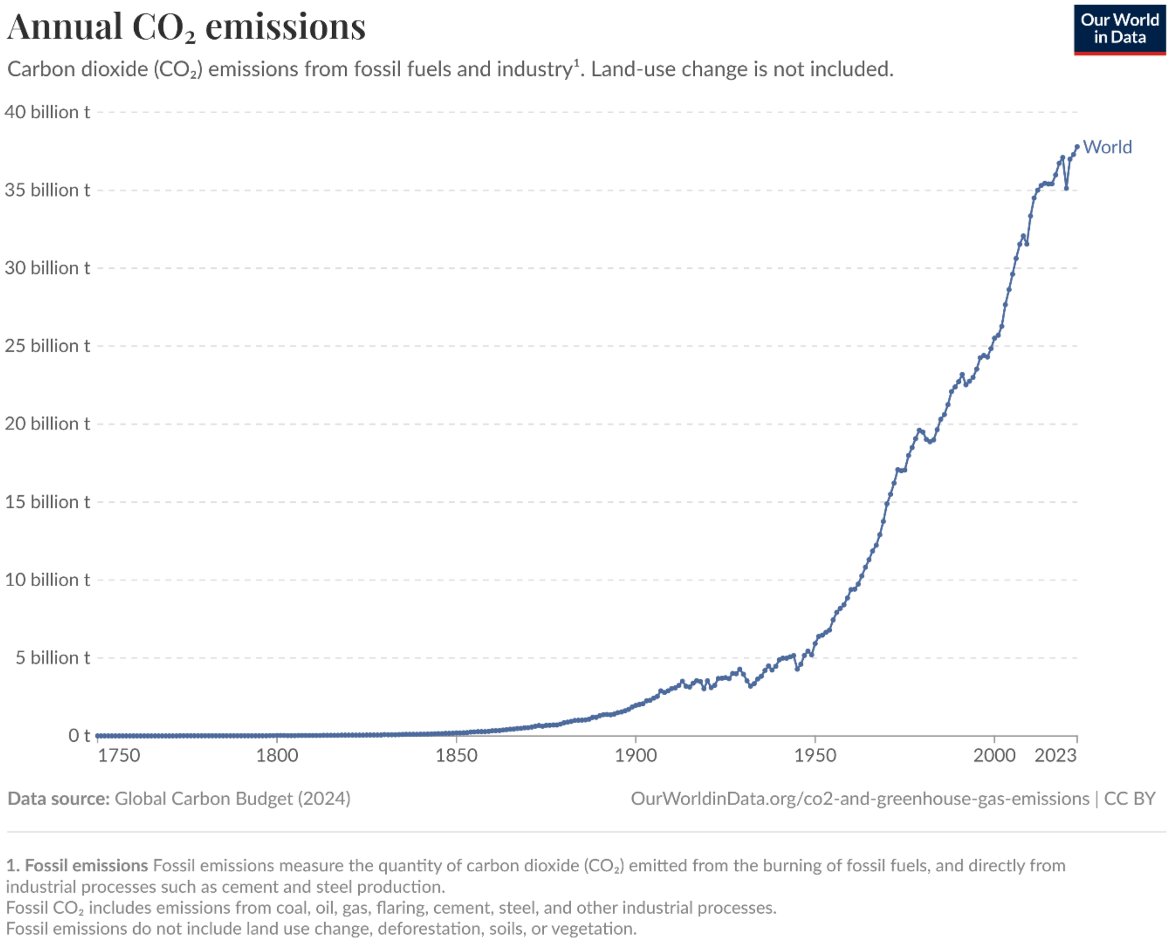


Figure 3. CO2 emissions evolution

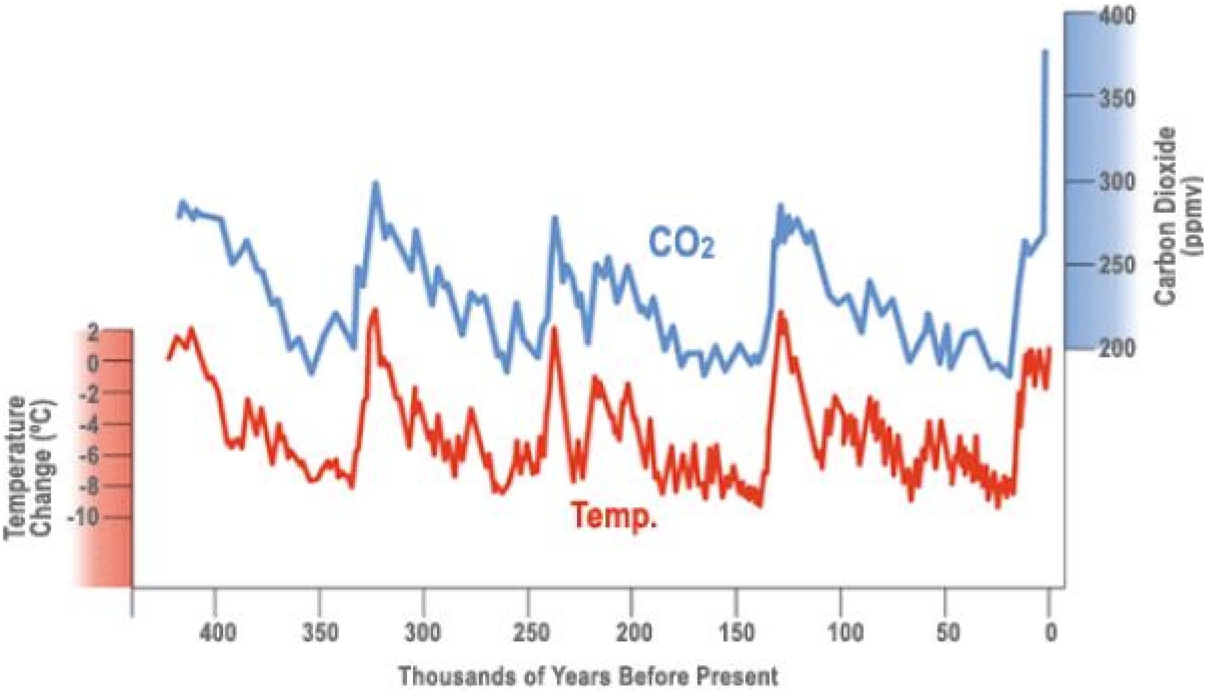


Figure 4. association of CO2 emissions with temperature variations

Carbon dioxide (CO_2) emissions are generally classified into two main categories based on their origin: natural sources and anthropogenic sources. Natural sources are integral components of the Earth's carbon cycle and include processes that have occurred for millions of years. These encompass biological respiration by plants, animals, and microorganisms; volcanic activity that releases CO_2 from the Earth's interior; ocean-atmosphere exchange, where CO_2 is both absorbed and emitted depending on environmental conditions; and the natural decomposition of organic matter or biomass burning during wildfires. Although these natural sources release substantial amounts of CO_2, they are largely balanced by natural carbon sinks such as forests, soils, and oceans, maintaining a relatively stable concentration of atmospheric CO_2 over geological timescales.

In contrast, anthropogenic CO_2 emissions are directly attributable to human activities and are the primary drivers of the recent rise in atmospheric CO_2 concentrations. The most significant contributor is the combustion of fossil fuels—coal, oil, and natural gas—for electricity generation, transportation, industrial processes, and residential heating. In addition, various industrial activities, such as cement production, steel manufacturing, and chemical synthesis, emit CO_2 either through energy use or as part of the chemical reactions involved. Land use changes, particularly deforestation and biomass burning, further contribute to anthropogenic emissions by releasing stored carbon and simultaneously reducing the capacity of natural carbon sinks. Unlike natural emissions, anthropogenic CO_2 emissions are not fully compensated by existing sinks, resulting in a net accumulation of CO_2 in the atmosphere and accelerating the process of global warming and climate change.

Motivation

The continued strong reliance on fossil fuels as the dominant energy source has significantly increased the concentration of greenhouse gases in the atmosphere. Of these gases, carbon dioxide (CO_2) is the primary driver of global warming, accounting for roughly 76% of total greenhouse gas emissions, followed by methane (CH_4) at 16%, nitrous oxide (N_2O) at 6%, and other gases at approximately 2%. [3] This accumulation has become one of the primary drivers of global warming and climate change, leading to severe environmental consequences such as rising temperatures, extreme weather events, and disruptions to ecological and human systems. Despite growing awareness and policy efforts, global CO_2 emissions remain persistently high, driven largely by industrial activities and power generation.

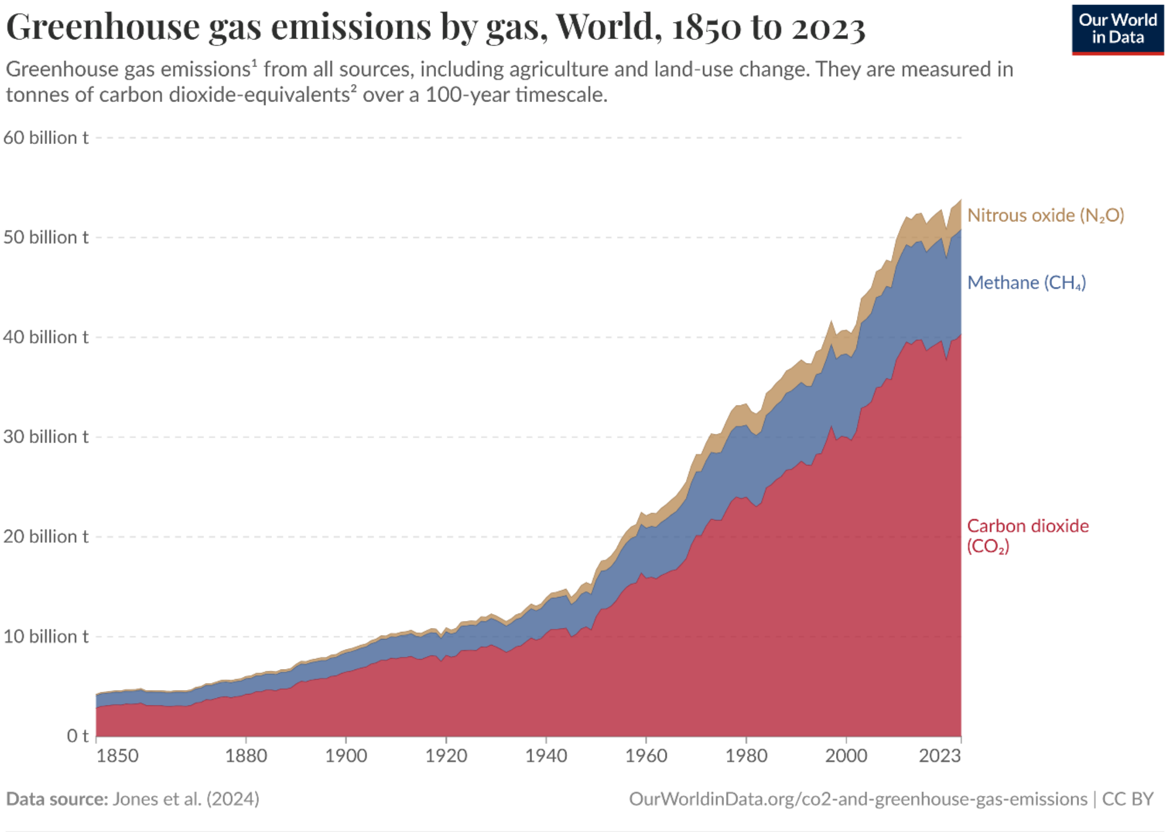
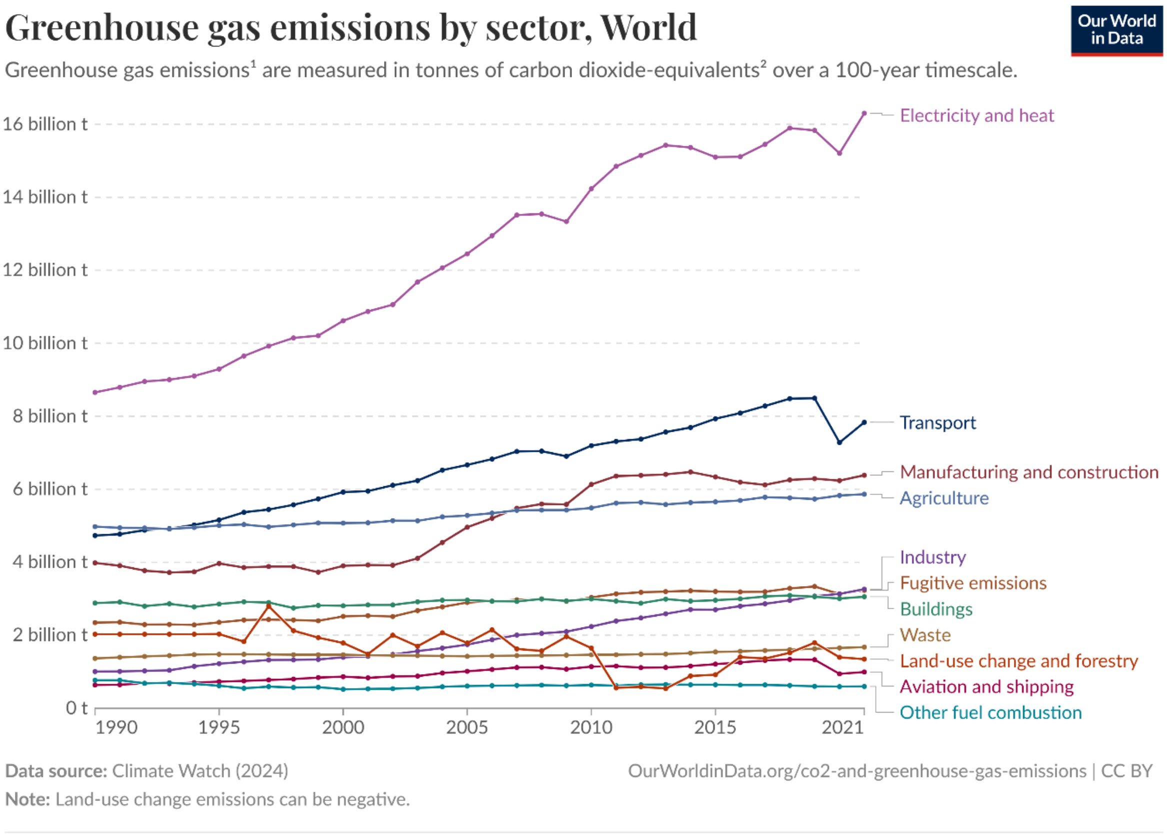


Figure 5. proportion of greenhouse gas emissions by composition

Addressing these challenges requires more than just a transition to renewable energy sources. While renewable technologies are expanding rapidly, they alone cannot ensure deep decarbonization across all sectors, especially those that are energy-intensive and process-dependent, such as the pulp and paper industry. These sectors face unique difficulties in replacing fossil fuels due to the continuous thermal loads and integrated chemical processes involved.


Greenhouse gas emissions by sector, World

Greenhouse gas emissions[1] are measured in tonnes of carbon dioxide-equivalents[2] over a 100-year timescale.

Data source: Climate Watch (2024)

OurWorldinData.org/co2-and-greenhouse-gas-emissions | CC BY

Note: Land-use change emissions can be negative.

Figure 6. greenhouse gas emissions by sector

This reality highlights the need for alternative solutions that can operate alongside renewable energy systems. To mitigate the harmful effects of climate change and reduce emissions, various technologies have been developed in recent decades to capture and recover carbon dioxide (CO_2) in different scenarios. Carbon capture, particularly post-combustion CO_2 capture, emerges as a viable and near-term mitigation strategy that can be retrofitted into existing infrastructure.[4] However, capturing CO_2 is only part of the equation. By introduction of sustainability and circular economy concepts, there is no beneficial point in just capturing the CO2, the important aspect is how to deal with the captured CO2. In this context, carbon utilization has been introduced to convert CO2 to a value-added product to keep the cycle of carbon running. The utilization of captured carbon, particularly through hydrogenation using renewable hydrogen, opens the door to both emission reduction and the creation of value-added products, transforming CO_2 from a waste into a resource.

Despite this potential, the practical implementation of such integrated systems remains uncertain without a clear understanding of their technical and economic feasibility. A comprehensive techno-economic analysis is essential to evaluate these solutions under realistic conditions, identify cost drivers, and assess their scalability and impact. This dual need, for effective emission mitigation and economically viable pathways, forms the core motivation for exploring the integration of carbon capture and utilization in industrial contexts.[5]

Problem Statement

The growing urgency to mitigate climate change, reduce air pollution, and transition away from fossil fuel dependency has intensified the global focus on finding sustainable solutions. Among the most effective responses to these interconnected challenges is decarbonization, which addresses a wide array of environmental, economic, and social issues. Specifically, decarbonization is considered a key solution for:

- Mitigating climate change by reducing greenhouse gas (GHG) emissions
- Lowering the environmental footprint of energy-intensive industries
- Enhancing air quality and reducing public health risks
- Reducing dependence on fossil fuels and increasing energy security
- Meeting national and international climate commitments, such as the Paris Agreement
- Facilitating the transition to a circular and low-carbon economy

In this context, decarbonization refers to the process of systematically reducing carbon dioxide (CO_2) emissions across sectors, primarily through energy transition, process innovation, carbon capture technologies, and the integration of renewable energy sources. It involves a combination of technological, operational, and systemic changes aimed at reducing the carbon intensity of economic activities.

While significant progress has been made in decarbonizing the power and transport sectors, the industrial sector remains a major source of emissions and presents greater challenges for transformation. Industries such as cement, steel, chemicals, and pulp and paper are classified as hard-to-abate sectors due to their reliance on high-temperature heat, fossil fuel-based feedstocks, and continuous operation processes that are difficult to electrify or modify.

Within this group, the pulp and paper industry is a particularly energy-intensive sector. It consumes substantial amounts of both thermal and electrical energy, and it is responsible for a notable share of global CO_2 emissions. Despite some improvements through energy efficiency and the use of biomass, current mitigation efforts in this sector fall short of the deep emission reductions needed to align with net-zero goals.

To decarbonize such industries, a range of strategies are being explored, including:

- Fuel switching (e.g., from coal to biomass or electricity)
- Process electrification
- Use of renewable hydrogen as a feedstock or energy carrier
- Implementation of carbon capture and storage (CCS) and carbon capture and utilization (CCU)

Among these strategies, Carbon Capture and Utilization (CCU) has emerged as a particularly promising pathway. Instead of treating captured CO_2 as waste, CCU technologies focus on transforming CO_2 into valuable products, with particular emphasis on the production of chemicals and synthetic fuels. This approach aligns with the principles of the circular economy and offers an opportunity to decarbonize industrial processes while creating marketable outputs and playing additional role in decarbonisation of other sectors. [6]

The utilization of CO_2 for chemical synthesis holds significant potential, especially when paired with renewable hydrogen as a reactant. A wide range of chemicals, such as urea, formic acid, methane, and methanol, can be synthesized using captured CO_2, thereby reducing the carbon footprint of both the source process and the downstream chemical products.

Among these, methanol production via CO_2 hydrogenation stands out due to its relatively mature technology and the broad industrial demand for methanol as a platform chemical and alternative fuel. This pathway not only helps mitigate CO_2 emissions from energy-intensive sectors but also reduces dependence on fossil-derived methanol, which is currently the dominant production route.[7]

Despite its potential, however, the integration of CO_2 capture and methanol synthesis into specific industrial sectors, such as the pulp and paper industry, remains underexplored, particularly from a techno-economic perspective. This gap highlights the need to further investigate the integration of CO_2 capture and methanol synthesis in real industrial contexts, not only to assess its environmental benefits but also to determine its economic viability and scalability.

Research Objectives

The overall goal of this research work is to investigate and evaluate the feasibility of decarbonization strategies within energy-intensive industrial sectors, with a particular focus on the pulp and paper industry. The study aims to contribute to the growing body of research on carbon mitigation by focusing on the integration of post-combustion CO_2 capture and CO_2 utilization via hydrogenation for methanol synthesis.

To achieve this, the specific objectives of the thesis are as follows:

- To model and simulate a post-combustion CO_2 capture system using MEA (monoethanolamine) as a benchmark solvent in the context of a representative pulp and paper mill, using Aspen Plus as the primary modeling tool.
- To validate the developed CO_2 capture model against literature data to ensure accuracy, robustness, and applicability to the chosen industrial case.
- To evaluate the techno-economic performance of the CO_2 capture system, including energy requirements, capture efficiency, and cost indicators such as the levelized cost of CO_2 captured.
- To model the hydrogenation of captured CO_2 using renewable hydrogen to synthesize methanol, considering stoichiometric balances, thermodynamics, and reaction conditions based on available process data.
- To assess the integrated CO_2 capture and utilization (CCU) process from both technical and economic perspectives, identifying the main cost drivers and energy penalties, and analysing how different parameters (e.g., electricity price, hydrogen cost, capture rate) affect the overall viability.
- To explore the decarbonization potential of this integrated pathway in the pulp and paper industry by estimating the emission reduction achievable and the conditions under which such a system becomes economically feasible.

This thesis ultimately aims to provide insights into how coupling CO_2 capture with methanol production via renewable hydrogen can serve as a viable decarbonization strategy for hard-to-abate sectors, supporting both climate and industrial sustainability goals.

Scope and Limitations

Scope

This thesis focuses on the techno-economic assessment of integrating post-combustion carbon capture with CO_2 utilization via hydrogenation for methanol synthesis in the context of the pulp and paper industry. The main areas of investigation include:

- Post-combustion CO_2 capture using MEA as the reference solvent technology, modeled using Aspen Plus. The focus is placed on evaluating capture efficiency, energy consumption, and cost implications for an industrial-scale application.
- Hydrogenation of CO_2 to methanol using renewable hydrogen, based on existing reaction pathways and thermodynamic models, with emphasis on process integration and material balance.
- Techno-economic analysis (TEA) of the entire integrated system, including cost estimation (CAPEX/OPEX), energy consumption, and key performance indicators (e.g., levelized cost of methanol, avoided CO_2 cost).
- A case-specific analysis based on a representative pulp and paper facility, used to establish baseline process parameters and emissions profile.

Limitations

Despite its comprehensive focus, the thesis is subject to the following limitations:

- Process simplifications are necessary due to the complexity of real-world industrial operations. Only steady-state simulations are considered, and dynamic behavior is not modeled.
- The hydrogen supply is assumed to come from renewable sources (e.g., water electrolysis powered by renewables), but the electrolysis process itself is not modeled in detail. Instead, standardized values for hydrogen cost and purity are adopted from literature.
- Solvent performance optimization and solvent degradation analysis for MEA are not within the scope of this study. MEA is used as a reference solvent without exploring alternative or advanced capture solvents.

- The methanol synthesis process is simplified based on stoichiometric assumptions and key operating conditions, without detailed reactor design or kinetic modeling.
- Environmental and lifecycle assessments (e.g., full LCA or carbon footprint analysis) are not conducted. The focus is restricted to techno-economic indicators rather than comprehensive sustainability metrics.
- Policy, regulatory, and market factors are acknowledged as important but are not quantitatively assessed in this work. The economic analysis is based on static assumptions rather than dynamic market projections.

Thesis Structure

This thesis is organized into the following chapters:

- Chapter 2 – Literature Review

  Provides a review of the current state of research related to post-combustion CO_2 capture, carbon utilization technologies, and methanol synthesis. Special attention is given to techno-economic assessments of CCU systems and applications within the pulp and paper industry.

- Chapter 3 – Process Description

  Describes the conceptual design of the studied system, including the industrial case considered, the CO_2 capture process, the hydrogenation route, and their integration.

- Chapter 4 – Model Description

  Details the modeling approach, including the simulation setup in Aspen Plus, process assumptions, key input parameters, and validation of the CO_2 capture model.

- Chapter 5 – Techno-Economic Analysis

  Presents the methodology and results of the techno-economic analysis, including cost breakdowns, performance metrics, sensitivity analyses, and a discussion of feasibility.

- Chapter 6 – Conclusions and Future Work

  Summarizes the main findings of the study, reflects on the implications for industrial decarbonization, and suggests directions for future research.

Literature review and background

This chapter provides a comprehensive review of the literature relevant to the topic. It serves two main purposes: first, to establish the necessary technical and theoretical background; and second, to critically assess previous studies in the field in order to identify existing research gaps.

The chapter begins with an overview of CO_2 capture technologies, with particular emphasis on post-combustion carbon capture using chemical absorption with Monoethanolamine (MEA) as a benchmark solvent. Following this, the principles of renewable hydrogen production, especially via low-temperature electrolysis, are presented, including technological developments and economic considerations.

Subsequently, the chapter examines various pathways for CO_2 hydrogenation, highlighting both the chemical fundamentals and techno-economic characteristics of producing value-added chemicals such as methanol. The literature on techno-economic analysis (TEA) is then reviewed in detail, covering methodologies, key performance indicators, and notable case studies relevant to both CO_2 capture and utilization processes.

The chapter concludes by summarizing the key findings from the literature and identifying the gaps that this thesis aims to address. These include limited integration of capture and utilization processes in existing TEA studies, inconsistent economic assumptions, and a lack of focus on specific industrial applications such as the pulp and paper sector.

Introduction

Within the framework of this thesis, because of enormous concern regarding global warming and climate change, the aim is to delve deeper into the context by expanding on applicable solutions regarding the issues our world has faced recently. The main idea is to elaborate on the concept of decarbonisation and explore it in greater detail. Then, bridging it for another important issue of the value-added production chemicals.

Sustainability has attracted considerable attention in different sectors of the economy.

Addressing the urgent challenges posed by climate change, resource depletion, and environmental degradation requires a fundamental transformation of current economic and industrial systems. In this context, sustainability has emerged as a guiding principle for ensuring that development meets present needs without compromising the well-being of future generations. This comprehensive approach is built on three interconnected pillars: protecting the environment, ensuring economic sustainability, and promoting social equity. (Brundtland Commission, 1987; UN, 2015). Achieving sustainability in practice necessitates coordinated efforts across sectors to reduce environmental impact, enhance resource efficiency, and promote long-term societal resilience.

A central strategy for advancing environmental sustainability is decarbonization, which involves reducing or eliminating carbon dioxide (CO_2) emissions from major sources such as power generation, transportation, and industrial processes. Decarbonization is critical for limiting global warming and meeting international climate targets, including those outlined in the Paris Agreement (IPCC, 2021). It is typically pursued through a combination of renewable energy deployment, energy efficiency improvements, electrification, and carbon capture, utilization, and storage (CCUS) technologies (IEA, 2021).

However, decarbonization alone does not guarantee overall sustainability unless it is implemented within a broader systems-based framework. This is where the circular economy comes into play. The circular economy is a regenerative economic model that aims to eliminate waste, extend product life cycles, and maintain the value of materials and resources in the economy for as long as possible (Ellen MacArthur Foundation, 2013). Unlike the traditional linear model based on extraction, production, consumption, and disposal, the circular economy emphasizes reuse, recycling, remanufacturing, and waste valorization as key principles.[8]

The circular economy supports sustainability by enhancing resource efficiency, reducing dependence on virgin raw materials, and minimizing environmental impact (Geissdoerfer et al., 2017). More importantly, it provides systemic pathways to support decarbonization. For example, by integrating CO_2 capture with renewable hydrogen production, industrial CO_2 emissions can be transformed into value-added products such as methanol, synthetic methane, or chemical intermediates (Artz et al., 2018; Hepburn et al., 2019). These Power-to-X (PtX) technologies not only reduce net emissions but also create economic value from waste streams, embodying the essence of both circularity and sustainability.

Furthermore, circular economy principles facilitate the decarbonization of resource-intensive sectors by closing material loops, promoting cleaner production pathways, and enabling sector coupling between energy, chemicals, and transport systems (IRENA, 2021). In doing so, they ensure that carbon neutrality efforts are economically viable and aligned with long-term environmental and societal goals.

In summary, sustainability is the overarching goal in response to pressing global challenges such as climate change and global warming. Decarbonization serves as a critical pathway to achieving environmental sustainability by reducing greenhouse gas emissions, while the circular economy acts as a systemic enabler that makes both sustainability and decarbonization more feasible and effective. These three concepts are not isolated but mutually reinforcing, and their integration is essential to building a low-carbon, resource-efficient, and climate-resilient future.

CO_2 Capture Technologies – decarbonisation

Removal of carbon dioxide as a greenhouse gas from the atmosphere has been considered as a promising solution to climate change. At this stage, different carbon capture technologies have been developed and proposed, but still there are some challenges present in the field. Many approaches for the reduction of carbon dioxide (CO2) emissions into the atmosphere have been developed, with carbon capture and sequestration (CCS) techniques being identified as the promising ones.

Based on the literature, there are three different technologies regarding to carbon capture; post-combustion, pre-combustion, and oxy-fuel combustion. Several methods have been developed for the separation of CO_2 from various gas streams, each with distinct operational principles and suitability depending on the specific carbon capture approach. The most commonly employed techniques include liquid absorption, adsorption, membrane separation, cryogenic distillation, and chemical looping. However, these methods are not universally applicable across for all the three mentioned types of carbon capture due to differences in gas composition, pressure, temperature, and CO_2 concentration inherent to each process.[9]

Liquid absorption, often using solvents such as monoethanolamine (MEA), is the benchmark technology primarily applied in post-combustion capture, where CO_2 is present at relatively low concentrations and atmospheric pressure conditions. Adsorption methods, including pressure or temperature swing adsorption (PSA/TSA), find application in both pre-combustion and post-combustion processes, particularly where higher CO_2 partial pressures enable more efficient capture. Membrane separation technologies are gaining interest for pre-combustion capture due to their ability to selectively separate hydrogen from CO_2-rich gas streams; however, their effectiveness is limited in post-combustion applications because of the dilute CO_2 concentration.[10]

Cryogenic separation is mainly suitable for pre-combustion and oxy-fuel combustion systems where CO_2 is available at higher concentrations and pressures, enabling economical cooling and condensation. Chemical looping, a relatively novel technology, serves as both a combustion method and a CO_2 separation technique, primarily explored as an alternative to oxy-fuel combustion.

post-combustion capture using chemical solvents, particularly monoethanolamine (MEA), remains the most mature and widely implemented, especially for retrofitting existing fossil fuel-based power plants and industrial facilities. Pre-combustion capture is mainly applied in integrated gasification combined cycle (IGCC) systems and hydrogen production plants, while oxy-fuel combustion, although promising, is still in the demonstration phase due to challenges related to air separation and system integration.[11]

Despite technological readiness at pilot and demonstration scales, large-scale deployment of carbon capture and storage (CCS) has been limited by high capital and operational costs, energy penalties, and policy uncertainties. As of 2023, there are over 30 commercial CCS facilities in operation worldwide, with a combined capture capacity of around 45 million tonnes of CO_2 per year. Continued research focuses on improving capture efficiency, reducing costs, and enabling integration with renewable energy and carbon utilization pathways.

although there have been significant advancements in carbon capture technologies, their large-scale implementation remains limited due to a number of persistent challenges. These obstacles span technical, economic, and systemic domains and vary across the main types of capture—post-combustion, pre-combustion, and oxy-fuel combustion. However, several cross-cutting issues are common to all approaches and significantly hinder their widespread adoption.

One of the most critical challenges is the high energy demand associated with CO_2 capture processes. In particular, post-combustion capture using chemical solvents, such as monoethanolamine (MEA), requires significant thermal energy for solvent regeneration, typically in the range of 3.0 to 4.0 GJ per tonne of CO_2. This energy penalty leads to a reduction in overall plant efficiency, often by 7 to 10 percentage points, and results in additional fuel consumption, partially offsetting the environmental benefits of capture.[12]

Closely linked to the energy issue is the challenge of economic viability. CCS systems are capital-intensive, with substantial costs related to the installation of capture units, compressors, pipelines, and storage infrastructure. For many industries and power plants, particularly in the absence of carbon pricing or financial incentives, these costs make CCS economically unattractive. This is especially true for pre-combustion and oxy-fuel systems, which often require complete redesigns of the process layout, further increasing capital expenditure.

Another major concern is the technological maturity and scalability of many capture methods. While post-combustion capture using MEA is relatively well-developed, alternative technologies such as solid adsorption, advanced membranes, cryogenic separation, and chemical looping are still in the early stages of development. Oxy-fuel combustion, for instance, has been demonstrated at pilot scale, but significant challenges remain in improving the efficiency of air separation units and integrating the process within existing facilities. Similarly, direct air capture (DAC), though promising, is currently constrained by high costs and limited deployment.

In solvent-based systems, additional complications arise from solvent degradation and equipment corrosion. Over time, amine-based solvents degrade due to exposure to oxygen, impurities, and high temperatures, forming byproducts that may be toxic or corrosive. This degradation not only affects process performance but also increases operational costs due to solvent makeup and the need for purification systems. Research into more stable, cost-effective, and energy-efficient solvents is ongoing but has yet to yield a definitive solution.[13]

Beyond the capture process itself, the infrastructure required for transporting and storing captured CO_2 presents further challenges. CO_2 must be compressed, transported—often over long distances—and securely stored in geological formations such as depleted oil and gas reservoirs or deep saline aquifers. Developing this infrastructure involves complex regulatory approval, long-term monitoring commitments, and public acceptance, especially concerning the risk of leakage and liability.

Furthermore, integrating carbon capture systems into existing industrial operations can be technically complex. Each industry—whether cement, steel, or pulp and paper—has unique process characteristics that affect how and where capture systems can be installed. Space limitations, variability in flue gas composition, and additional utility demands all complicate implementation. Moreover, CCS increases the plant's electricity and steam requirements, which must be met through low-carbon energy sources to maintain overall emission reductions.

Finally, policy and regulatory uncertainty remains a significant barrier to CCS deployment. In many regions, the absence of strong carbon pricing mechanisms, financial incentives, and long-term regulatory frameworks discourages investment. Additionally, permitting processes for CO_2 storage sites are often unclear, and liability for long-term storage remains unresolved, further slowing progress.[14]

Renewable Hydrogen Production

Hydrogen has emerged as a core contributor in global strategies to decarbonize energy systems and industrial sectors. When produced using renewably derived electricity, hydrogen becomes a clean, versatile energy carrier with the potential to replace fossil fuels in a wide range of applications and for the transition to a low-carbon economy. This form of hydrogen, often referred to as green hydrogen, is considered a key enabler of sector coupling and a vital component of carbon-neutral energy systems, particularly through its role in Power-to-X technologies such as synthetic fuels and CO_2 utilization. In the context of carbon utilization, renewable hydrogen serves as a key reactant for the hydrogenation of CO_2 into valuable products such as methanol, methane, and synthetic fuels.[15]

In recent years, renewable hydrogen has received growing international attention. According to the International Energy Agency (IEA), more than 40 countries have released national hydrogen strategies, and over 1,000 hydrogen projects have been announced globally, many of which involve electrolytic hydrogen production. Renewable hydrogen, commonly referred to as green hydrogen, is primarily produced via water electrolysis powered by electricity from renewable energy sources such as wind, solar, or hydropower.

Among the different electrolysis technologies, alkaline water electrolysis (AWE) and proton exchange membrane (PEM) electrolysis are the most commercially developed and widely studied. AWE is mature and cost-effective, while PEM offers higher efficiency and dynamic operation, making it suitable for integration with intermittent renewable sources. A third option, solid oxide electrolysis cells (SOECs), operates at high temperatures and offers higher theoretical efficiencies, but remains in the demonstration phase.[16]

Despite its technical maturity, green hydrogen production currently accounts for less than 1% of total global hydrogen supply, the vast majority of which is still derived from fossil-based sources such as steam methane reforming. However, global interest is accelerating. According to the reviewed study, global installed electrolyzer capacity reached 510 MW in 2021 and is projected to exceed 60 GW by 2030. China, in particular, is emerging as a leader in green hydrogen deployment, with plans to produce approximately 90% of its hydrogen from water electrolysis by 2060, making up 18% of its primary energy mix. Internationally, over 40 countries have adopted hydrogen strategies aimed at scaling production, reducing costs, and building the necessary infrastructure.[17]

Nonetheless, several barriers hinder the large-scale deployment of renewable hydrogen. Economically, green hydrogen remains expensive, with production costs ranging from 3 to 8 USD/kg—primarily due to the high capital cost of electrolyzers and the need for abundant, low-cost renewable electricity. Technologically, challenges persist in improving electrolyzer efficiency, durability, and cost-effectiveness, especially for newer systems such as PEM and SOEC. Additionally, alternative hydrogen production routes such as solar thermochemical processes, photocatalysis, and biomass-based methods remain at early development stages.[17]

Infrastructure and integration present further challenges. Large-scale storage systems, hydrogen pipelines, and refueling stations are still limited, and comprehensive safety standards and regulations are yet to be fully developed. Furthermore, effective integration with variable renewable energy sources requires robust power electronics, smart control systems, and grid compatibility. From a systems perspective, there is a pressing need for more consistent and regionally adapted techno-economic and life cycle assessments to guide investment and deployment strategies.[16]

CO_2 Hydrogenation Pathways / e-methanol production

Electro-methanol, commonly referred to as **e-methanol**, is methanol produced via the catalytic hydrogenation of carbon dioxide (CO_2) using **green hydrogen** derived from renewable electricity. As a synthetic, carbon-neutral fuel and chemical feedstock, e-methanol plays a pivotal role in Power-to-X pathways and represents a promising strategy for integrating renewable energy with carbon utilization and storage. Unlike fossil-based methanol, which is traditionally produced from natural gas via steam reforming, e-methanol provides a circular and sustainable route by recycling captured CO_2 and utilizing low-carbon energy sources.[15]

The production process involves two main steps: first, water electrolysis is used to generate hydrogen from renewable electricity; second, this hydrogen is reacted with captured CO_2 (typically from flue gas or direct air capture) over a catalyst, usually based on copper and zinc, under high temperature (200–300 °C) and moderate pressure (50–100 bar). The stoichiometric reaction is:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{1}$$

This reaction is exothermic and equilibrium-limited, requiring careful reactor design and thermal integration. The process benefits from mature methanol synthesis technology, originally developed for fossil syngas, but must be adapted for CO_2-rich, H_2-based feedstocks with low CO/CH_4 content. Integrating green hydrogen production with CO_2 capture and methanol synthesis presents both opportunities and technical complexity.[18]

In recent years, e-methanol has received increasing attention as a sustainable alternative to conventional methanol, particularly in the marine fuel sector, chemical industry, and as a platform molecule for further synthetic fuels (e.g., gasoline, DME). Pilot projects and small-scale commercial plants have been launched in countries such as Germany, Iceland, China, and Chile. For example, Carbon Recycling International (CRI) in Iceland and the Haru Oni project in Chile demonstrate the feasibility of large-scale e-methanol production using renewable electricity and captured CO_2. However, global production volumes of e-methanol remain extremely limited, with most methanol (over 98%) still derived from fossil fuels. The levelized cost of e-methanol is currently estimated to range between 800 and 1600 USD/ton, depending on electricity prices, hydrogen cost, CO_2 source, and plant scale—significantly higher than fossil methanol (250–400 USD/ton).[18]

Despite its strong potential, the widespread deployment of e-methanol production faces several technical and systemic challenges that must be addressed to ensure economic and industrial viability. One of the primary barriers is the high production cost, largely driven by the expense of green hydrogen and the capital-intensive nature of electrolyzer systems. In addition, the purity and availability of the CO_2 feedstock significantly affect reactor design, catalyst performance, and overall process efficiency. Optimizing catalysts and reactor configurations for CO_2-rich feedstocks remains a critical research area, particularly in terms of achieving high conversion efficiency, selectivity, and long-term operational stability. [19]

Another key challenge lies in process integration, especially thermal and energy integration across the hydrogen production, CO_2 capture, and methanol synthesis subsystems, which is essential for improving overall system efficiency. Furthermore, comprehensive lifecycle assessments and sustainability frameworks are needed to evaluate the true environmental impact of e-methanol, taking into account the carbon intensity of electricity sources, CO_2 capture pathways, and the eventual use of the product. [20]

A notable limitation in current research is the lack of standardized techno-economic assessment methodologies, which makes it difficult to compare e-methanol systems on a consistent and transparent basis. Beyond these technical issues, the value chain for e-methanol remains underdeveloped, with limited infrastructure for transportation, storage, and end-use applications. Therefore, strong policy support, such as carbon pricing mechanisms, green fuel quotas, and certification standards—will be essential to close the cost gap and accelerate market adoption.[21]

Techno-Economic Assessment (TEA)

An important step toward full-scale industrial application development is to determine the feasibility, guide design decisions, and inform investment and policy-making. TEA serves as a vital tool for evaluating not only the capital and operating costs of emerging technologies but also their potential to compete with conventional fossil-based alternatives. In the context of e-methanol, TEA enables a holistic understanding of the economic implications of coupling water electrolysis, CO_2 capture, and methanol synthesis under realistic process and market conditions.[22]

The importance of TEA in this domain lies in its ability to:

- Quantify cost drivers such as electricity consumption, hydrogen production, CO_2 sourcing, and reactor performance;
- Identify economic trade-offs in system design and integration;
- Compare alternative process configurations, feedstocks, and energy scenarios;
- Provide a consistent framework to evaluate scalability, competitiveness, and environmental co-benefits.

Recent studies have begun to explore the techno-economic potential of e-methanol systems. Most analyses focus on the levelized cost of methanol (LCOM), which currently ranges from approximately 800 to 1600 USD/ton, depending heavily on hydrogen cost, electricity price, CO_2 purity, and plant scale. Some studies integrate process simulations with economic models to assess the impact of operating conditions, while others focus on policy-sensitive parameters such as carbon pricing or green fuel incentives. However, these TEAs often rely on simplified or idealized assumptions, such as steady-state operation, zero CO_2 transport cost, or unrestricted renewable electricity access.[7]

Despite progress, several challenges limit the reliability and comparability of current TEA studies. A major issue is the lack of standardization in methodology, particularly regarding system boundaries, allocation methods, and assumptions about capital cost learning curves. In many cases, TEAs do not fully capture the dynamic interactions between subsystems, such as the variable availability of renewable electricity or the intermittency of CO_2 supply. Moreover, few studies consider the full lifecycle costs or externalities, such as water use, land footprint, or upstream emissions from equipment manufacturing. There is also limited work on industrial integration, especially for sectors like pulp and paper, where CO_2 streams are less concentrated and operational constraints may differ from conventional sources.[23]

Summary and Research Gaps

Overall, based on the comprehensive literature review performed, it is obvious that there are significant research gaps in decarbonisation of pulp and paper industry. the literature lacks reliable studies of decarbonising the pulp and paper mills , There is no serious and practical effort conducting a feasible evaluation of decarbonisation from the pulp and paper industry. Also, methanol synthesis from CO2 captured in pulp and paper industry could be studied to assess its feasibility based on the results of techno-economic analysis. Additional innovative aspects of this integration could also be considered to develop the system for addressing several issues.

Theoretical framework and Process description

In this chapter, a comprehensive description of the key processes involved in the decarbonization pathway analyzed in this thesis, namely carbon capture, hydrogen production, and CO_2 utilization through methanol synthesis is presented. These three elements form an integrated value chain aimed at reducing CO_2 emissions from industrial sectors while enabling the production of low-carbon fuels and chemicals.

The first part of the chapter introduces the concept of Carbon Capture, Utilization, and Storage (CCUS). It provides comprehensive explanation regarding different main technologies of carbon capture and elaborates more by discussing the state-of-the-art of methods. Following this, the chapter discusses hydrogen production via low-temperature water electrolysis, highlighting its compatibility with renewable electricity and its role as a key enabler in Power-to-X systems.

Subsequently, attention is given to the synthesis of methanol from captured CO_2 and green hydrogen. Methanol is a versatile platform chemical and energy carrier, and its production via CO_2 hydrogenation represents a promising route for carbon utilization. The relevant chemical reactions, operating conditions, and process configurations are described, along with considerations for integrating these subsystems into a unified and efficient process.

Together, these sections establish the technological foundation upon which the modeling and techno-economic analysis presented in the following chapters are based.

In order to take action for addressing vital challenges posed by climate change, sustainability has emerged as a core concept for directing all the efforts to develop low-carbon and environmentally friendly systems. As its main goal, sustainability seeks to create a balance among environmental preservation, economic viability, and social well-being, principles that are especially critical in the transformation of energy and industrial sectors. Within this context, the circular economy offers a strategic pathway by prioritizing resource efficiency, waste minimization, and the continuous use of materials through recycling, regeneration, and repurposing. [24]

Unlike the traditional linear model of “take-make-dispose,” circular systems aim to decouple economic growth from environmental degradation by closing material loops and extending product lifecycles. A crucial component of this approach is the valorisation of waste streams, particularly carbon dioxide (CO_2), which is typically treated as an unwanted emission. By capturing CO_2 and converting it into value-added products, such as methanol, synthetic fuels, and chemical feedstocks, not only can emissions be reduced, but new economic opportunities can also be unlocked. This strategy aligns climate mitigation with industrial innovation, offering a synergistic route to achieving both sustainability and circularity objectives.[25]

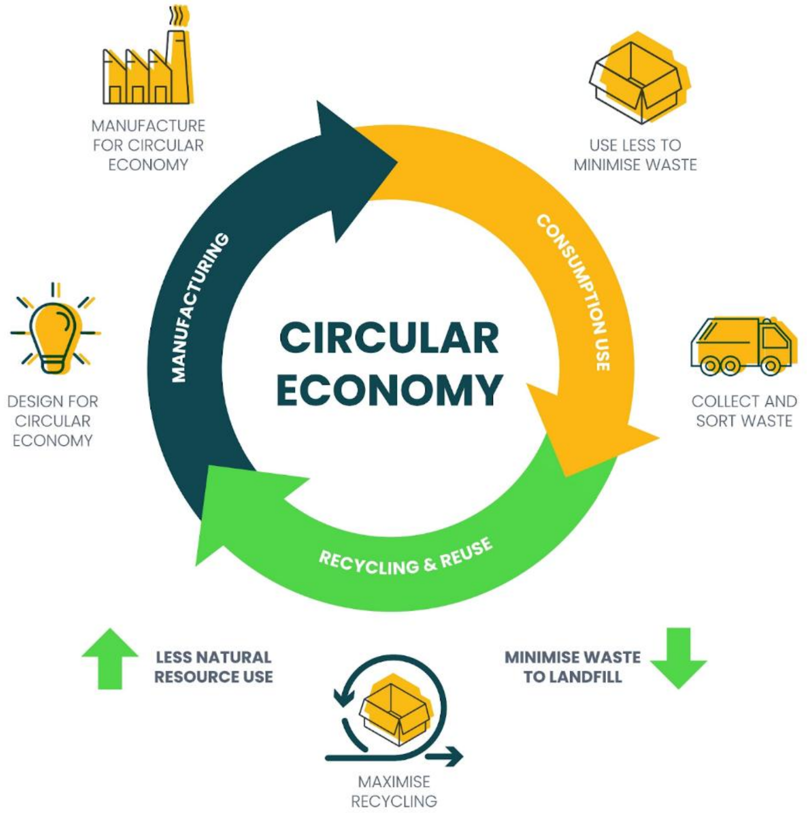


Figure7. schematic of circular economy

carbon capture, utilization, and storage

Carbon Dioxide as a Driver of Climate Change

As previously mentioned, carbon dioxide (CO_2) is one of the most significant anthropogenic greenhouse gases contributing to climate change, primarily emitted through the combustion of fossil fuels such as coal, oil, and natural gas for electricity generation, industrial processes, and transportation. The current trend of rising global temperatures, commonly referred to as global warming, is strongly correlated with increasing atmospheric CO_2 concentrations, which have surpassed 420 ppm in recent years, far above pre-industrial levels (~280 ppm). This accumulation intensifies the greenhouse effect, trapping more heat in the Earth's atmosphere and leading to severe environmental consequences such as melting glaciers, sea-level rise, more frequent extreme weather events, and ecosystem disruptions.[26]

In response to these alarming developments, scientists, engineers, and policy-makers have proposed and are actively pursuing a range of climate change mitigation strategies. These include the decarbonization of the energy sector through the widespread deployment of renewable energy technologies (e.g., solar, wind, hydroelectric), improvement of energy efficiency across all sectors, and the electrification of transport and industry. A particularly important area of focus is the development and deployment of Carbon Capture, Utilization, and Storage (CCUS) technologies, which aim to capture CO_2 emissions from point sources or directly from the atmosphere and either store it in geological formations or convert it into value-added products.

Furthermore, sustainable land use practices, such as afforestation and regenerative agriculture, are being promoted to enhance natural carbon sinks. On a systemic level, economic and policy tools like carbon pricing, emission trading systems, and international climate agreements (e.g., the Paris Agreement) are essential to incentivize low-carbon development and ensure collective global action. Together, these measures are vital for limiting global temperature rise to below 1.5–2°C, as outlined by the Intergovernmental Panel on Climate Change (IPCC), and for safeguarding the planet's climate system for future generations.[25]

Among the various mitigation pathways, carbon capture stands out as a critical enabler for achieving deep decarbonization, especially in sectors where emissions are difficult to eliminate entirely, such as heavy industries (e.g., cement, steel, and chemicals) and dispatchable power generation. While transitioning to renewables is essential, it alone may not be sufficient or fast enough to meet near-term climate goals. Carbon Capture, Utilization, and Storage (CCUS) offers a practical and scalable solution to significantly reduce CO_2 emissions from existing infrastructure and to remove CO_2 directly from the atmosphere through Direct Air Capture (DAC). Moreover, when combined with renewable hydrogen, captured CO_2 can be converted into synthetic fuels or chemicals, supporting the development of circular carbon economies. Given the urgent need to bridge the gap between current emissions and climate targets, accelerating the deployment and optimization of carbon capture technologies is not just a technological challenge, but a climate imperative. This underscores the motivation for continued research and innovation in this field, particularly with a focus on improving efficiency, reducing costs, and enabling integration into diverse industrial systems.[27]

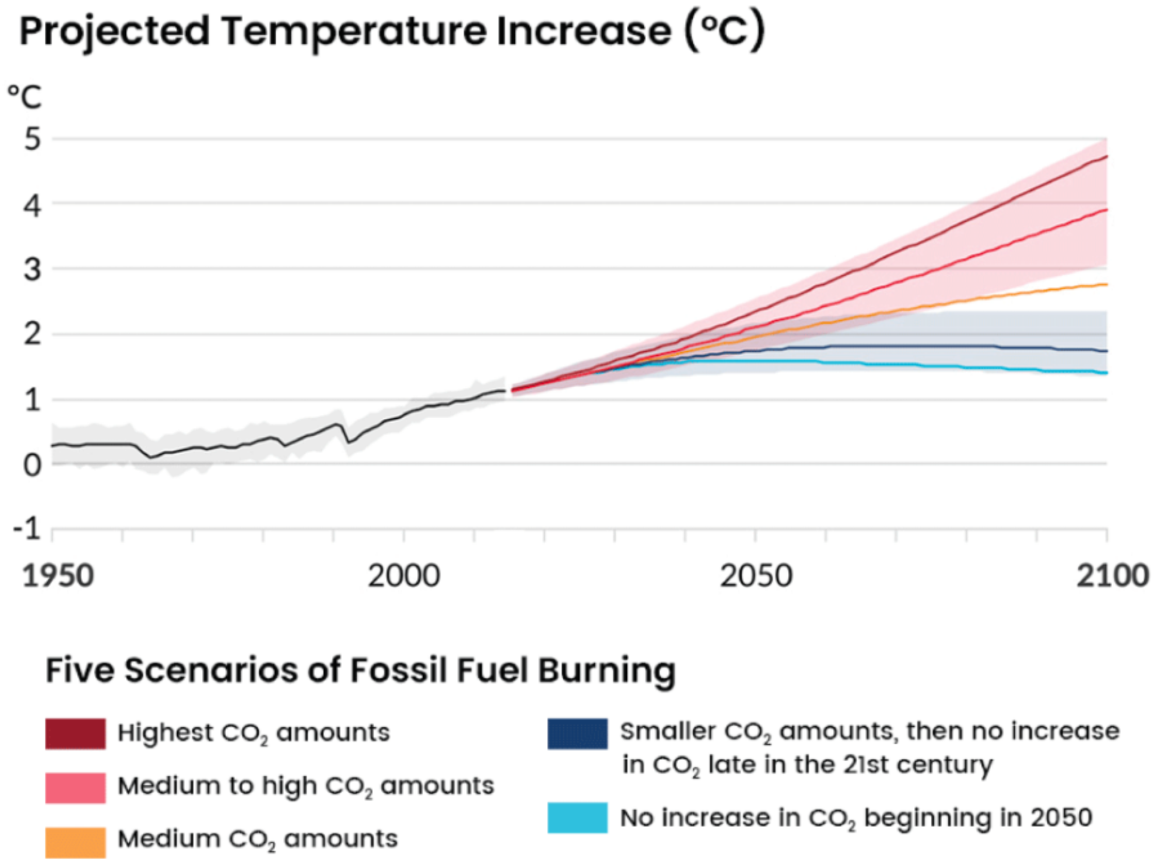


Figure 8. comparison of different temperature levels in different scenarios

Overview of Carbon Removal Pathways

As the global community intensifies its efforts to confront the climate crisis, it has become increasingly clear that reducing greenhouse gas emissions alone will not be enough. To meet the ambitious targets of limiting global warming to below 2°C, and ideally to 1.5°C as outlined in the Paris Agreement, carbon removal has emerged as an essential component of any comprehensive climate strategy. Unlike conventional mitigation approaches that aim to reduce future emissions, carbon removal focuses on actively extracting carbon dioxide from the atmosphere, offering a critical means of addressing legacy emissions and balancing out residual emissions from sectors that are particularly difficult to decarbonize.[28]

Carbon dioxide removal (CDR) plays a uniquely strategic role in climate stabilization. It provides the only viable pathway for achieving net-zero and eventually net-negative emissions, especially as some industrial processes and transport sectors are expected to retain a level of unavoidable emissions for the foreseeable future. Moreover, CDR offers a means to reverse historical emissions, which is vital for restoring atmospheric CO_2 concentrations over the long term. This makes it not just a complementary measure, but a necessary pillar of climate mitigation, particularly in light of delayed global emission reductions and the growing urgency reflected in recent IPCC assessments.[29]

In addition to its environmental importance, carbon removal has broader implications for climate equity and justice. It can help offset emissions from emerging economies that are still in the early stages of industrial development, thereby allowing space for growth while maintaining overall climate goals. Furthermore, carbon removal pathways—if developed responsibly—can offer co-benefits such as improved air quality, ecosystem restoration, and rural employment opportunities.

However, the integration of carbon removal into national and global climate strategies must be approached with caution and credibility. It should not be viewed as a substitute for emission reductions but rather as a complementary solution that fills the gap between what is technically feasible and what is needed to protect the climate. The deployment of CDR must also be guided by sound scientific assessments, robust policy frameworks, and long-term sustainability considerations.

Given its potential to reshape the trajectory of climate action, the exploration and deployment of carbon removal solutions—particularly in synergy with renewable energy and carbon management systems—deserve focused attention. In this context, the role of carbon capture technologies becomes especially relevant, as they form the backbone of many engineered carbon removal pathways and offer a scalable approach to decarbonizing critical industrial sectors.[30]

State-of-the-Art for CO_2 Capture Technologies

Due to the necessity of carbon removal, based on multiple research attempts, different methods have been developed in order to cover wide range of applications and process conditions, and to fit in several contexts. This diversity also stems from the necessity of treating various emission sources and addressing multiple technical, economic, and environmental considerations. All has led to the different choices for carbon capture.

Carbon capture technologies can be broadly classified into three primary categories based on the stage at which CO_2 is separated in the process: post-combustion capture, pre-combustion capture, and oxy-fuel combustion. Each pathway presents distinct technical characteristics, application domains, degrees of technological maturity, and economic implications.[4]

Post-Combustion Capture

Post-combustion capture is the most mature and widely studied approach, particularly suitable for retrofitting existing fossil-fuel-based power plants and industrial facilities. In this method, CO_2 is removed from the flue gas after fuel combustion, typically using chemical solvents such as monoethanolamine (MEA). Its key advantage lies in its applicability to current infrastructure, making it an attractive near-term option. However, the relatively low CO_2 concentration and low pressure of flue gases impose significant energy penalties, especially during solvent regeneration. Consequently, this method often incurs higher operating costs and energy consumption, but remains the most commercially deployed technology to date.[4]

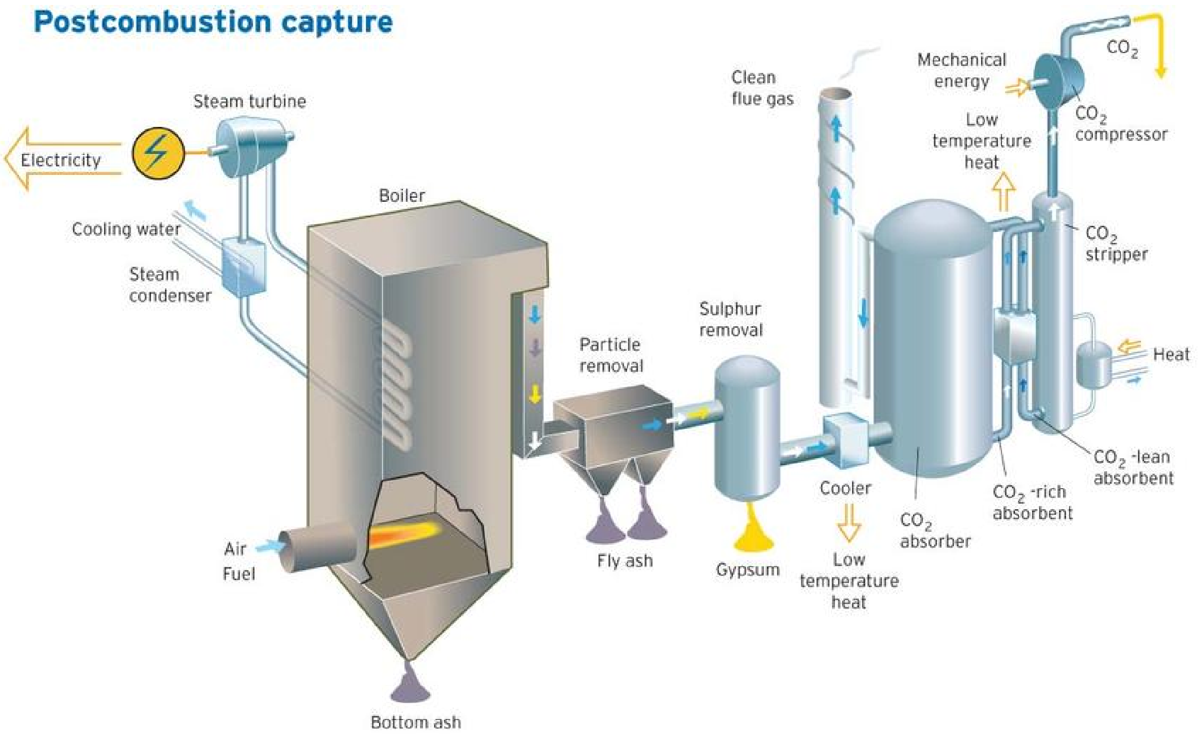


Figure 9. schematic of post-combustion carbon capture

Pre-Combustion Capture

Pre-combustion capture is commonly applied in integrated gasification combined cycle (IGCC) power plants and hydrogen production facilities. It involves converting the fuel into a synthesis gas (syngas), followed by a water-gas shift reaction to increase the CO_2 content, which is then separated—usually with physical solvents or membranes. This method benefits from higher CO_2 partial pressures, which improve separation efficiency and reduce energy costs. However, its application is generally limited to newly designed plants, given the significant changes required in process configuration. While technically promising and more energy-efficient than post-combustion in certain contexts, pre-combustion capture is less mature in large-scale deployment.

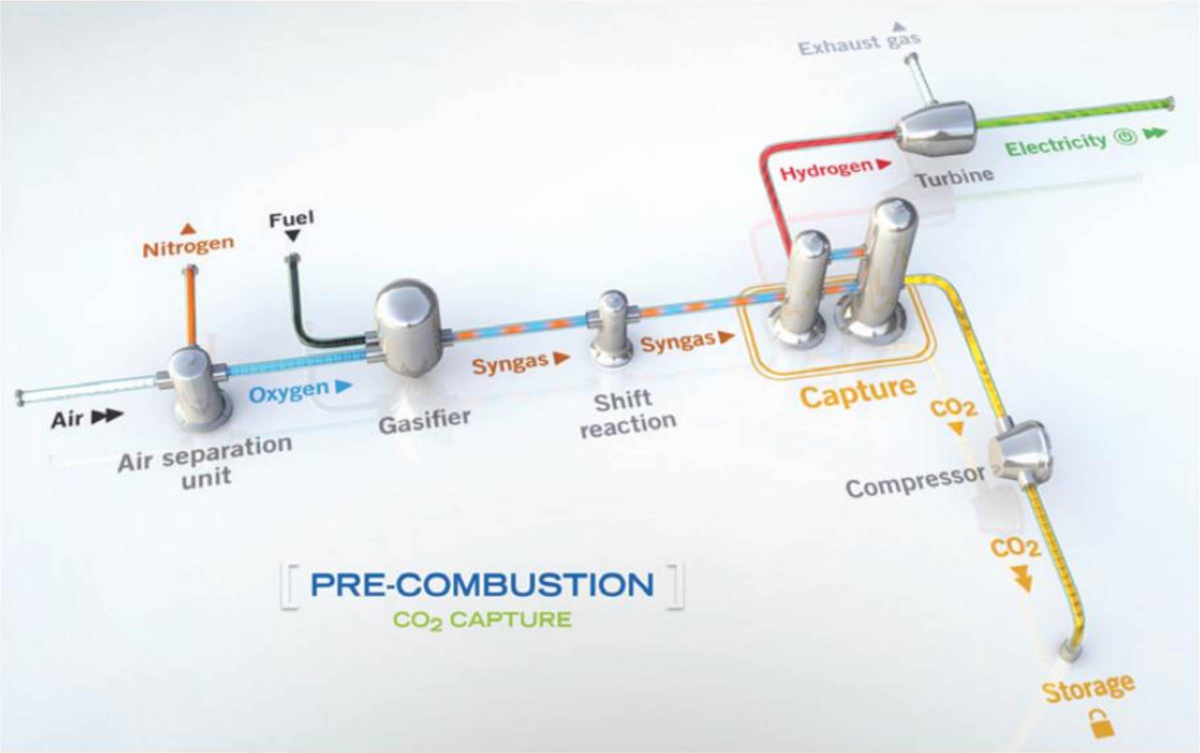


Figure 10. pre-combustion carbon capture

Oxy-Fuel Combustion

In oxy-fuel combustion, the fuel is burned in pure oxygen instead of air, producing a flue gas primarily composed of CO_2 and water vapor. This simplifies the separation process, as water can be condensed, leaving a concentrated CO_2 stream. Although the concept is technologically feasible and offers a relatively pure CO_2 output, the main limitation lies in the high energy cost and complexity associated with oxygen production, typically via air separation units (ASUs). Oxy-fuel systems are still in the pilot or demonstration phase, and are considered promising for new builds rather than retrofits.

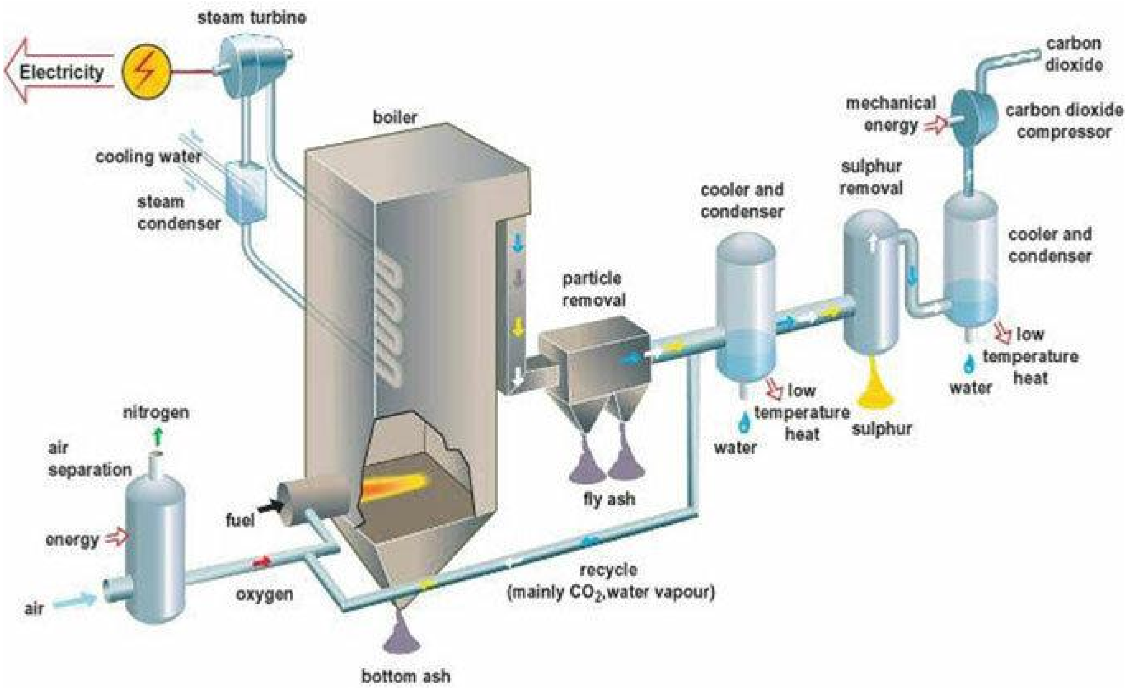


Figure 11. oxy-fuel combustion carbon removal technique

Each of these technologies presents trade-offs between energy efficiency, cost, infrastructure compatibility, and scalability. Therefore, the selection of a suitable capture technology must account for the specific industrial context, emission source characteristics, and long-term deployment objectives.

Classification of CO_2 Capture Methods

The separation of carbon dioxide from gas mixtures is a critical step in carbon capture processes, particularly for applications in power generation and industrial decarbonization. Several techniques have been developed and refined, each based on different physical or chemical mechanisms. The most prominent CO_2 capture methods include absorption, adsorption, membrane separation, cryogenic separation, and chemical looping. These methods differ in their underlying principles, energy requirements, scalability, and readiness for industrial deployment. [31]

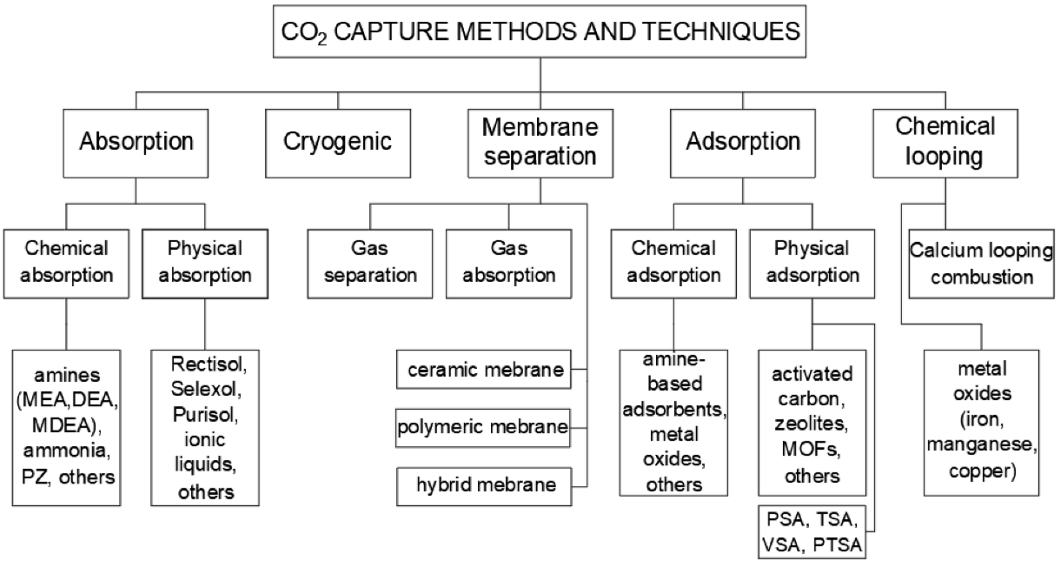


Figure 12. classification of different CO2 capture methods

Absorption-Based CO_2 Capture

Absorption is the most mature and widely deployed CO_2 capture technology, especially in post-combustion systems. It relies on the solubility of CO_2 in a liquid solvent, which selectively captures CO_2 from a gas stream.

Chemical absorption is a widely used method for CO_2 capture, particularly in post-combustion applications. It involves a chemical reaction between carbon dioxide and a reactive solvent, with monoethanolamine (MEA) being the most commonly employed solvent. MEA reacts with CO_2 to form a carbamate compound, enabling efficient separation of CO_2 from flue gases. The process is typically carried out in two primary units: an absorber column, where the flue gas comes into contact with the solvent and CO_2 is captured, and a stripper (or regenerator), where the solvent is heated to release high-purity CO_2 and regenerate the absorbent for reuse. This method offers high capture efficiencies, typically ranging from 90% to 95%, and benefits from extensive commercial deployment and operational experience. However, it also presents several challenges, including high energy requirements for solvent regeneration, solvent degradation over time, corrosion issues, and limited effectiveness at low CO_2 partial pressures.[32]

In contrast, physical absorption relies on the physical solubility of CO_2 in a liquid solvent without forming chemical bonds. Physical solvents such as Selexol and Rectisol are commonly used under conditions of high pressure and low temperature. This method is particularly well-suited for pre-combustion capture, where the gas streams are typically rich in CO_2 and maintained at elevated pressures. While physical absorption requires less energy for regeneration than chemical absorption, it is generally more effective only under specific pressure and temperature conditions.

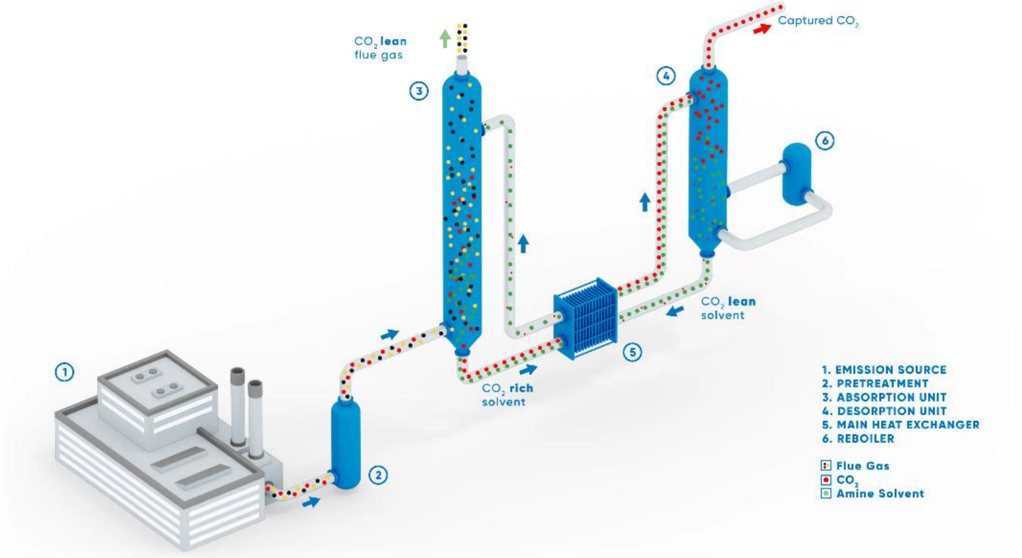


Figure 13. schematic for chemical absorption of CO2

Adsorption-Based CO_2 Capture

Adsorption-based CO_2 capture involves the adhesion of CO_2 molecules onto the surface of a solid material, referred to as an adsorbent. This technique is particularly attractive for separating CO_2 from low-pressure or dilute gas streams, such as flue gas or ambient air. A variety of adsorbents have been explored for this purpose, including activated carbon, zeolites, metal–organic frameworks (MOFs), and amine-functionalized solids. The adsorption process generally operates in a cyclic manner, consisting of two main phases: an adsorption stage, in which CO_2 molecules attach to the adsorbent surface, followed by a desorption or regeneration stage, where the CO_2 is removed and the adsorbent is restored for reuse.

Regeneration is typically achieved using pressure swing adsorption (PSA), temperature swing adsorption (TSA), or vacuum swing adsorption (VSA) techniques. Among its advantages, adsorption offers low thermal energy requirements for regeneration, a modular system configuration, and the potential for high CO_2 selectivity, especially with the development of advanced functional materials. However, the method faces several challenges, including sensitivity to moisture, lower CO_2 loading capacity compared to liquid solvents, and issues related to long-term stability and scale-up for industrial applications.[11]

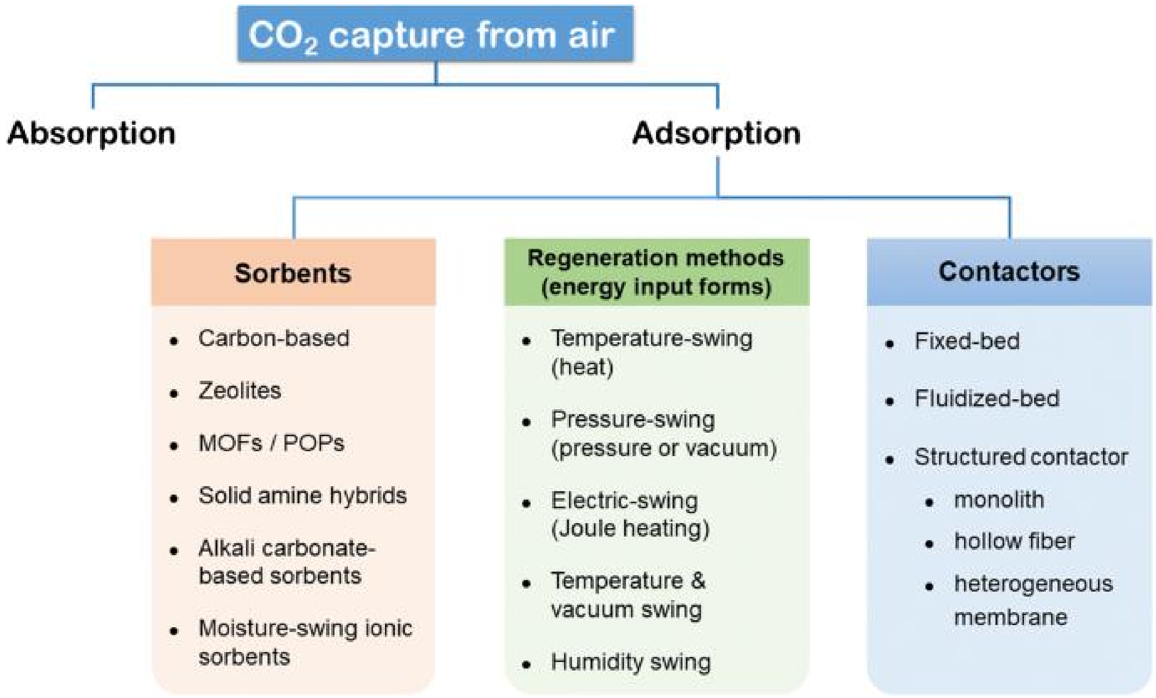


Figure 14. classification of different adsorption-based strategies for carbon capture

Membrane-Based CO_2 Separation

Membrane-based CO_2 separation utilizes selectively permeable materials that enable carbon dioxide to permeate more rapidly than other gas components, such as nitrogen or hydrogen, based on differences in molecular size, diffusivity, or solubility. Membranes used for gas separation are typically classified into three categories: polymeric membranes (e.g., polysulfones and polyimides), which are widely used due to their flexibility and ease of processing; inorganic membranes (e.g., ceramic or zeolite-based), which offer superior thermal and chemical stability; and hybrid membranes, such as polymer–metal organic framework (MOF) composites, which aim to combine the strengths of both types.

Membrane technologies offer several advantages, including the elimination of chemical solvents, a compact and modular design, and continuous operation with few moving parts, making them attractive for scalable deployment. Nevertheless, significant challenges remain, particularly the inherent trade-off between permeability and selectivity, which limits overall performance. Additionally, polymeric membranes are prone to plasticization and aging, which can degrade performance over time. In some applications, high-pressure operation is required to achieve adequate separation efficiency, which can increase energy consumption and infrastructure costs. Membranes are particularly suitable for pre-combustion capture or natural gas sweetening, and are under development for post-combustion applications.[11]

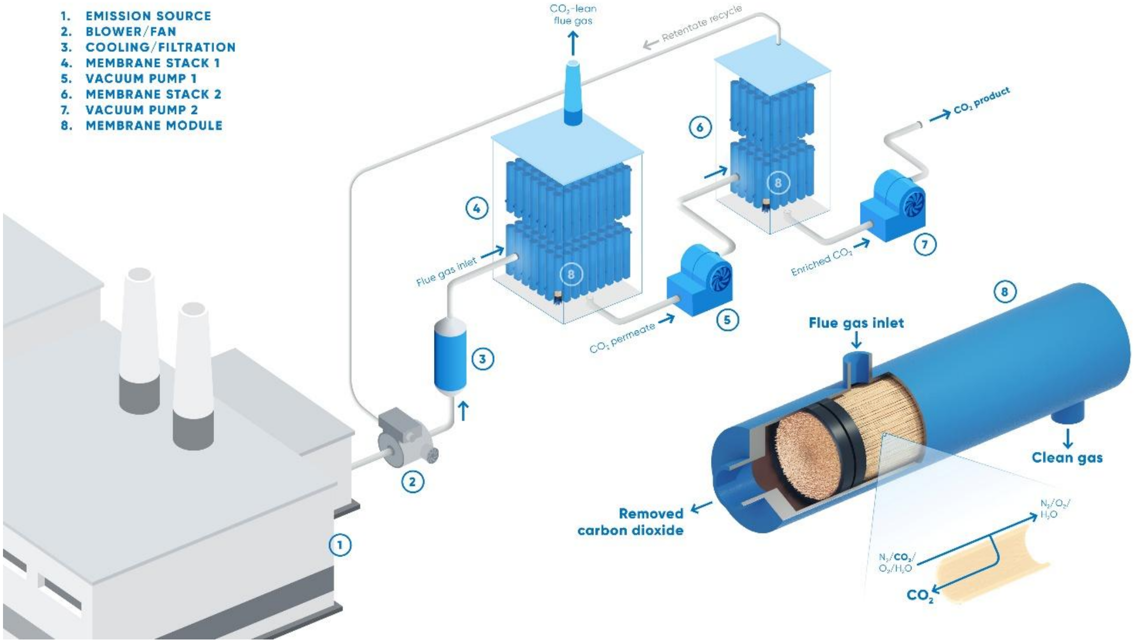


Figure 15. membrane based configuration for carbon capture

Cryogenic Separation

Cryogenic CO_2 capture leverages the differences in boiling and sublimation points between carbon dioxide and other gases to achieve separation. By cooling the gas stream to extremely low temperatures, CO_2 can be selectively condensed or solidified, while other gases such as nitrogen or hydrogen remain in the gaseous phase and are separated accordingly. This process involves cooling the gas stream below the condensation or sublimation temperature of CO_2, enabling its recovery in either liquid or solid form.

One of the main advantages of cryogenic separation is that it can produce high-purity CO_2 without the use of chemical solvents or the need for regeneration processes. Additionally, it is particularly well-suited for high-pressure, CO_2-rich gas streams, such as those found in liquefied natural gas (LNG) processing or syngas purification. However, the method faces notable limitations, including a high energy demand for refrigeration, as well as operational complexity and increased costs. There are also practical issues such as frosting and clogging of equipment, which can hinder reliability and long-term operation. Although cryogenic CO_2 capture is not yet widely adopted for large-scale post-combustion applications, it is increasingly being considered for niche scenarios and hybrid systems, where its unique advantages can be leveraged efficiently.[11]

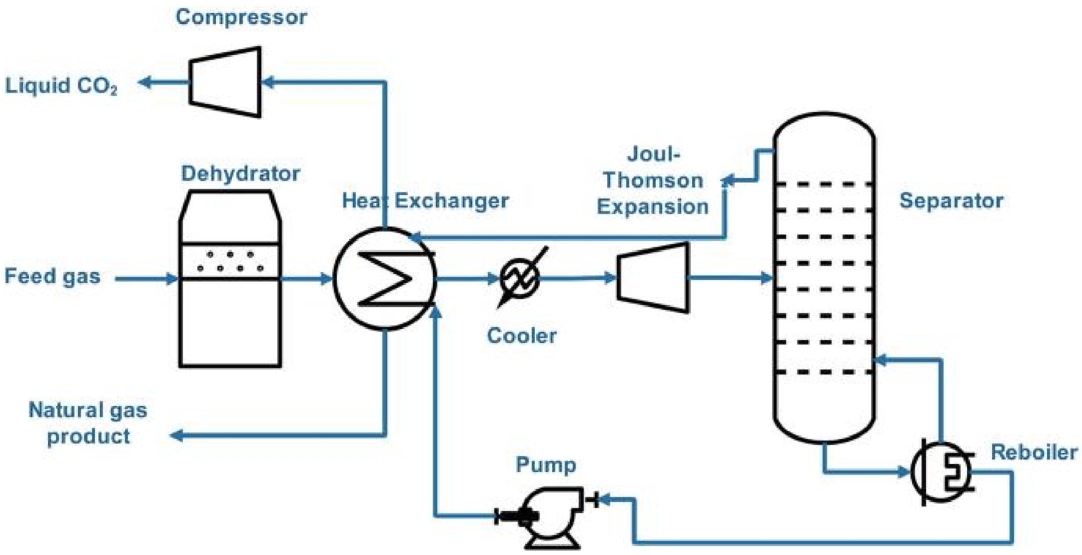


Figure 16. cryogenic separation of CO2

Chemical Looping Combustion (CLC)

Chemical looping is a novel indirect combustion process where a solid oxygen carrier (typically metal oxides like Fe_2O_3, CuO) transfers oxygen to the fuel. It inherently separates CO_2 from other gases without the need for external separation.

Chemical looping combustion (CLC) is an innovative CO_2 capture technology that indirectly oxidizes fuel using a solid oxygen carrier, typically a metal oxide, instead of direct contact with air. The process is carried out in two separate reactors. In the fuel reactor, the metal oxide reacts with the fuel (e.g., natural gas, syngas), producing CO_2 and H_2O. After water is condensed, a nearly pure CO_2 stream remains, free from nitrogen dilution due to the absence of air in the combustion zone.

In the air reactor, the reduced metal is reoxidized with air, regenerating the oxygen carrier for reuse. This cyclical operation allows for inherent CO_2 separation without additional capture steps. The key advantages of chemical looping include the production of a CO_2-rich stream that simplifies separation, high thermal efficiency, and the avoidance of direct mixing between fuel and air, which reduces NO_x formation. However, several challenges limit its widespread adoption. These include the development and long-term stability of oxygen carrier materials, the complexity of solid circulation and reactor design, and the lack of large-scale demonstration beyond pilot projects. Despite these challenges, chemical looping remains a promising candidate for future power plants and hydrogen production systems, particularly in applications aiming for integrated CO_2 capture and energy generation.[11]

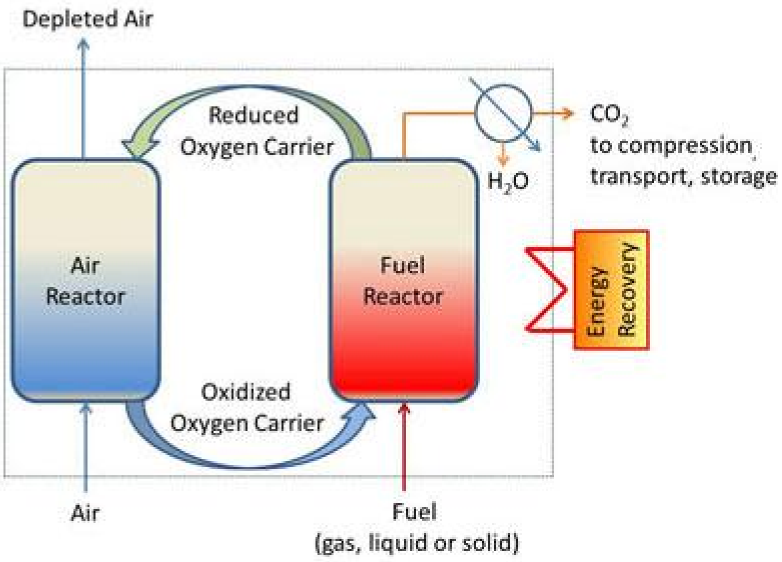


Figure 17. chemical looping as a CO2 capture method

Carbon Dioxide Storage and Utilization Pathways

After that the CO2 content present in the stream has been captured, its long-term management becomes a critical aspect of any carbon mitigation strategy. Two main pathways could exist for handling captured CO_2: geological storage and utilization in value-added processes. These pathways play distinct yet complementary roles in reducing net greenhouse gas emissions and contributing to a more sustainable, circular carbon economy.[2]

1. CO_2 Storage (Carbon Sequestration)

Geological storage, or carbon sequestration, involves the injection of compressed CO_2 into deep underground rock formations, where it is expected to remain securely trapped for centuries or longer. The most common storage sites include saline aquifers, depleted oil and gas reservoirs, and unmineable coal seams. Among these, saline formations are considered the most abundant and globally distributed. The storage process typically involves three trapping mechanisms: structural trapping (where CO_2 is held beneath impermeable rock layers), residual trapping (where CO_2 is immobilized in pore spaces), and mineral trapping (where CO_2 reacts with the host rock to form stable carbonates over time). While technically feasible and well-understood through decades of experience in enhanced oil recovery (EOR), large-scale storage deployment still requires robust regulatory frameworks, monitoring systems, and public acceptance.

2. CO_2 Utilization (Carbon Recycling)

Instead of storing CO_2, various utilization pathways seek to convert it into useful products, thereby turning a waste stream into a resource. These pathways can be broadly categorized into chemical, biological, and mineralization-based approaches. Chemical utilization includes processes like the hydrogenation of CO_2 to produce methanol or synthetic fuels, the synthesis of urea and salicylic acid, and polymer production. These applications often require a source of renewable hydrogen and significant energy input, limiting their feasibility to regions with abundant low-carbon energy. Biological utilization, such as algae cultivation using CO_2, provides a means to produce biofuels, feed, and bioplastics. Mineralization involves the reaction of CO_2 with calcium- or magnesium-rich materials to form stable carbonates, which can be used in building materials like concrete.

Although the market for CO_2-derived products is still emerging and relatively small compared to global CO_2 emissions, CO_2 utilization offers an opportunity to create economic incentives for carbon capture, particularly when integrated into Power-to-X or industrial symbiosis strategies. Importantly, these utilization routes can only contribute to climate mitigation if the CO_2 is permanently removed or if it displaces more carbon-intensive products.

In summary, both storage and utilization are essential components of the carbon management chain. While geological storage offers the most direct path to permanent carbon removal, utilization pathways provide value-added incentives and potential integration with clean energy and circular economy strategies. The appropriate choice between storage and utilization depends on factors such as site availability, economic viability, energy supply, and overall carbon balance.[2]

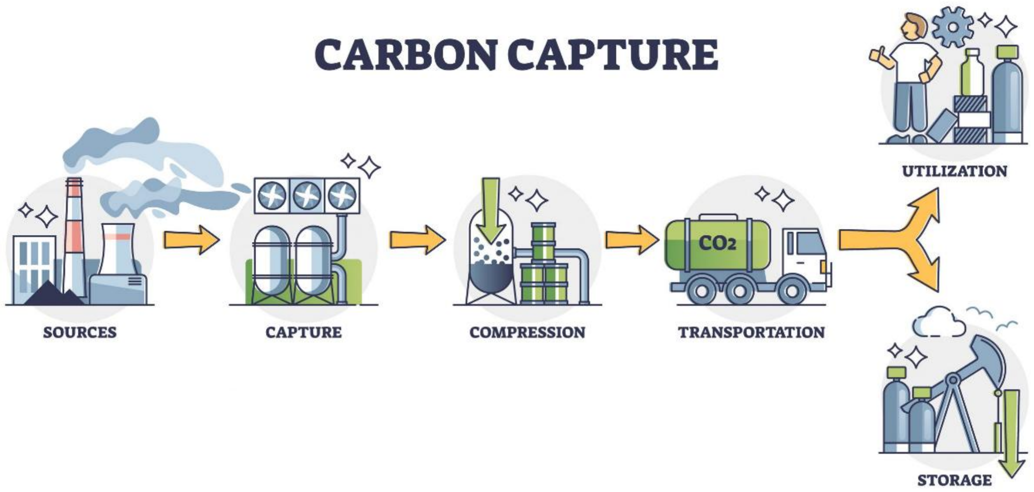


Figure 18. carbon capture – storage and utilization overview

Hydrogen production

Hydrogen, the lightest element in the periodic table, is a fundamental component of matter and the most abundant element in the universe. On Earth, it is not found freely in nature due to its high reactivity and instead exists in compound forms such as water, hydrocarbons, and biomass. Despite this, hydrogen is gaining renewed global attention as a strategic enabler of the energy transition, thanks to its versatility, clean usage profile, and potential role in deep decarbonization.

The growing interest in hydrogen is due to a mix of technological, environmental, and political reasons. One of the main drivers is the need to reach climate goals by the middle of this century, as set by international agreements like the Paris Agreement and national plans such as the EU Hydrogen Strategy and the IEA Net Zero Roadmap. These goals have shown that hydrogen can play an important role in cutting emissions from sectors where using electricity directly is difficult or expensive. These sectors, often called "hard-to-abate," include heavy industries like steel, cement, and chemicals, as well as high-temperature heating, long-distance transport, shipping, and aviation.[33]

Furthermore, the accelerated deployment of renewable energy sources—notably solar and wind—has introduced significant variability into power systems. Hydrogen offers a unique solution for large-scale and long-duration energy storage, enabling the temporal and spatial balancing of renewable electricity. Through Power-to-Hydrogen and Power-to-X (PtX) pathways, surplus renewable electricity can be converted into hydrogen and further processed into synthetic fuels, thus enhancing system flexibility and sector coupling.

At the industrial level, hydrogen is already widely used, especially in petroleum refining, ammonia production, methanol synthesis, and food processing. However, the vast majority of this hydrogen is currently produced from fossil fuels via carbon-intensive processes such as steam methane reforming (SMR) and coal gasification, collectively referred to as grey hydrogen. These methods account for approximately 830 million tonnes of CO_2 emissions annually, undermining the sustainability of current hydrogen use.

The urgency of addressing these emissions has spurred global efforts to transition toward low-carbon hydrogen production methods. As a result, hydrogen is now categorized into color codes—grey (fossil-based), blue (fossil-based with carbon capture and storage), green (renewables-based), and others—to denote the carbon intensity of its production. Among these, green hydrogen, generated via water electrolysis powered by renewable electricity, is considered the most promising pathway for aligning hydrogen production with net-zero goals.[34]

The growing momentum behind hydrogen is further supported by:

- Falling costs of renewable electricity, especially from solar PV and wind;
- Technological advancements in electrolyzers and hydrogen storage;

- Government incentives, funding programs, and national hydrogen strategies;
- International collaborations aiming to establish cross-border hydrogen value chains.

In summary, hydrogen is increasingly recognized not only as a clean energy carrier but also as a strategic vector for decarbonization, energy system integration, and the production of sustainable fuels and chemicals. Its ability to enable circular economy approaches, particularly when combined with captured CO_2, places it at the heart of emerging low-carbon industrial ecosystems.

The following sections explore the various hydrogen production routes, with a particular focus on electrolysis technologies, which are key to unlocking the potential of green hydrogen in sustainable energy systems.

hydrogen production

Hydrogen can be produced through a wide range of processes that differ in terms of feedstock, energy source, technological maturity, and environmental impact. The choice of production method significantly affects the overall sustainability, cost, and carbon footprint of hydrogen. Today, the vast majority of hydrogen is generated from fossil fuels through mature, large-scale industrial processes. However, as the demand for low-carbon and renewable hydrogen increases, alternative production methods based on clean energy sources are gaining attention.

In this section, hydrogen production pathways are broadly classified into two main categories: common (conventional) methods, which are currently dominant in the global hydrogen market, and innovative (emerging) methods, which aim to reduce environmental impact and support the transition to a sustainable hydrogen economy. In the following, hydrogen production methods will be presented and explained.

Common Hydrogen Production Methods

Today, the majority of hydrogen is produced through well-established fossil-based thermochemical processes, which account for more than 95% of global production. These methods are technically mature and widely used in industry, especially for hydrogen used in refineries, ammonia, and methanol production. However, they are associated with significant CO_2 emissions and are not sustainable in the long term without carbon capture integration.[35]

Innovative Hydrogen Production Methods

Hydrogen production from low-carbon and renewable sources is essential for decarbonizing the energy system. Green hydrogen is primarily produced via water electrolysis powered by renewable electricity. Among the main technologies, Alkaline Electrolyzers (AEL) are mature and cost-effective but have slower response times. Proton Exchange Membrane (PEM) electrolyzers offer fast dynamics and compact design, though they rely on expensive materials. Solid Oxide Electrolysis Cells (SOEC) operate at high temperatures, enabling high efficiency when coupled with industrial heat sources, but face material durability challenges.

Biomass-based hydrogen production offers another sustainable route. Gasification thermochemically converts biomass into hydrogen-rich syngas, while dark fermentation uses anaerobic bacteria to produce hydrogen from organic waste, albeit with lower yields.

Emerging methods include photofermentation and algal hydrogen production, which use light and biological systems to generate hydrogen, though they remain at the research stage. Methane pyrolysis, or turquoise hydrogen, thermally splits methane into hydrogen and solid carbon without CO_2 emissions, assuming renewable energy input.

Finally, solar-driven water splitting can be achieved via photoelectrochemical (PEC) systems or solar thermochemical cycles, both of which aim to directly convert solar energy into hydrogen. These approaches are still under development but hold long-term potential for clean hydrogen production.[36]

water electrolysis

Water electrolysis is a well-established electrochemical process utilized to split water (H_2O) into hydrogen (H_2) and oxygen (O_2) using electrical energy. Its basis is on the principle of applying a direct current across two electrodes immersed in water, where the anode facilitates the oxygen evolution reaction (OER), and the cathode facilitates the hydrogen evolution reaction (HER). The result is the generation of pure hydrogen at the cathode and oxygen at the anode.

The significance of water electrolysis lies in its ability to produce high-purity hydrogen without emitting carbon dioxide, provided that the electrical input is derived from renewable energy sources such as wind, solar, or hydroelectric power. In this context, the process enables the production of green hydrogen, which is increasingly seen as a critical pillar of future sustainable energy systems.

Historically, water electrolysis was used for small-scale hydrogen production, especially in remote areas or in applications requiring very pure hydrogen (e.g., electronics, pharmaceuticals, and aerospace). However, with the global shift towards decarbonization and the increasing penetration of variable renewable energy sources, electrolysis is being reconsidered and developed at industrial scale. It offers a flexible and modular solution for both centralized and decentralized hydrogen production and can be strategically deployed to absorb surplus renewable electricity, thereby playing a role in sector coupling and energy storage.[16]

Moreover, water electrolysis presents a technically viable pathway for decarbonizing so-called "hard-to-abate" sectors such as steelmaking, chemical production, long-distance transport, and aviation, which cannot be easily electrified. It also aligns with broader climate goals and hydrogen strategies set by governments and international agencies (e.g., EU Green Deal, Hydrogen Roadmap Europe, IEA Net Zero Roadmap), which emphasize the role of clean hydrogen in achieving carbon neutrality by mid-century.

While the basic principles of electrolysis are well understood, ongoing research and industrial efforts aim to improve the process efficiency, reduce system costs, and scale up production capacity. This is done through the development of more advanced electrolyzer technologies (e.g., PEM and SOEC), optimization of materials, and integration into renewable energy systems and hybrid plants. Figure represents a general schematic of water electrolysis. [37]

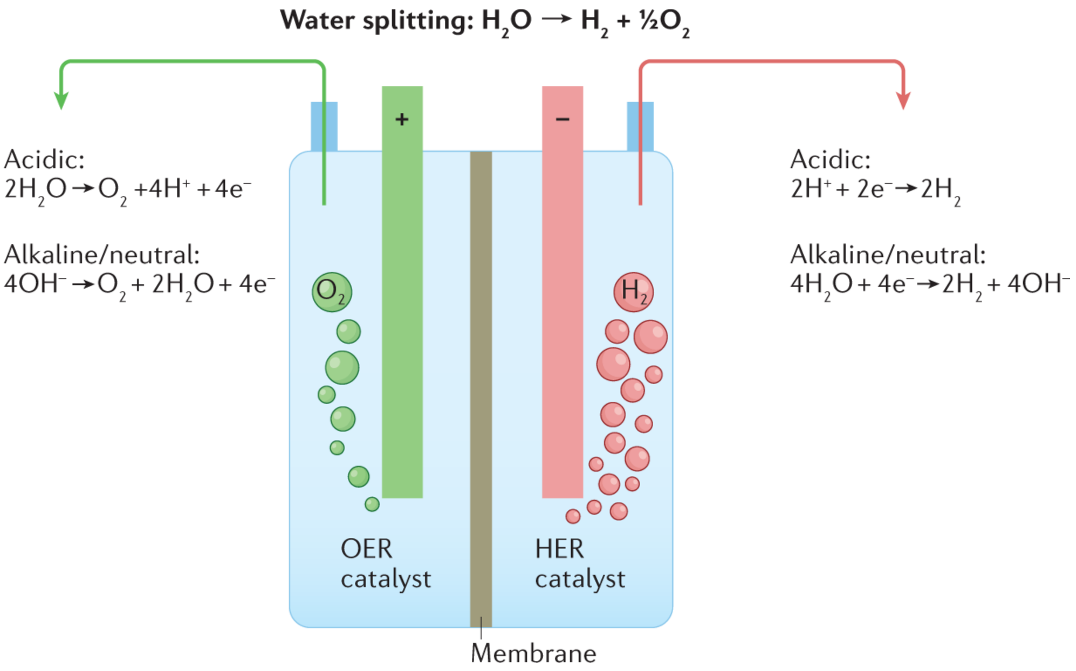


Figure 19. schematic of operation of water splitting

Advantages of Water Electrolysis

- Zero Carbon Emissions: When powered by renewable electricity, electrolysis produces hydrogen without any direct CO_2 emissions.
- Flexible Integration: Electrolyzers can be operated dynamically and are compatible with intermittent renewable energy sources.
- High Purity Hydrogen: Electrolysis delivers high-purity hydrogen, which is particularly important for fuel cell applications.
- Energy Storage Potential: It enables conversion of surplus renewable electricity into hydrogen, which can be stored and later used for power, heat, or transport.
- Scalability and Modularity: Electrolysis systems can be scaled and installed in distributed or centralized configurations based on demand.

Technical Aspects of Water Electrolysis

Water electrolysis involves several components and parameters:

- **Electrodes:** Typically made of metals or metal oxides; they serve as sites for redox reactions.
- **Electrolyte:** Can be a liquid or solid medium that allows ion transfer between the electrodes.
- **Cell Voltage:** Usually ranges between 1.6 and 2.0 V depending on current density and cell type.
- **Operating Conditions:** Includes temperature (from ambient up to 850°C), pressure, current density, and electrolyte concentration.
- **Faradaic Efficiency:** Measures how efficiently electrical current is converted into chemical energy (usually close to 100%).

Types of Electrolyzers

Different electrolyzer technologies exist, each with its own characteristics, advantages, and maturity level. The most common types are:

- **Alkaline Electrolyzers (AEL):**
    - Electrolyte: Liquid potassium hydroxide (KOH)
    - Operating Temp: 60–90°C
    - Pros: Technically mature, low cost

  - Cons: Less suitable for dynamic operation and low current densities
- **Proton Exchange Membrane Electrolyzers (PEM):**
  - Electrolyte: Solid polymer membrane (e.g., Nafion)
  - Operating Temp: 50–80°C
  - Pros: High current density, compact design, good load-following capability
  - Cons: Expensive due to precious metal catalysts (e.g., platinum, iridium)
- **Solid Oxide Electrolyzers (SOEC):**
  - Electrolyte: Solid ceramic (typically YSZ – yttria-stabilized zirconia)
  - Operating Temp: 700–850°C
  - Pros: High efficiency, potential integration with industrial heat
  - Cons: High temperature leads to material durability challenges; still under development

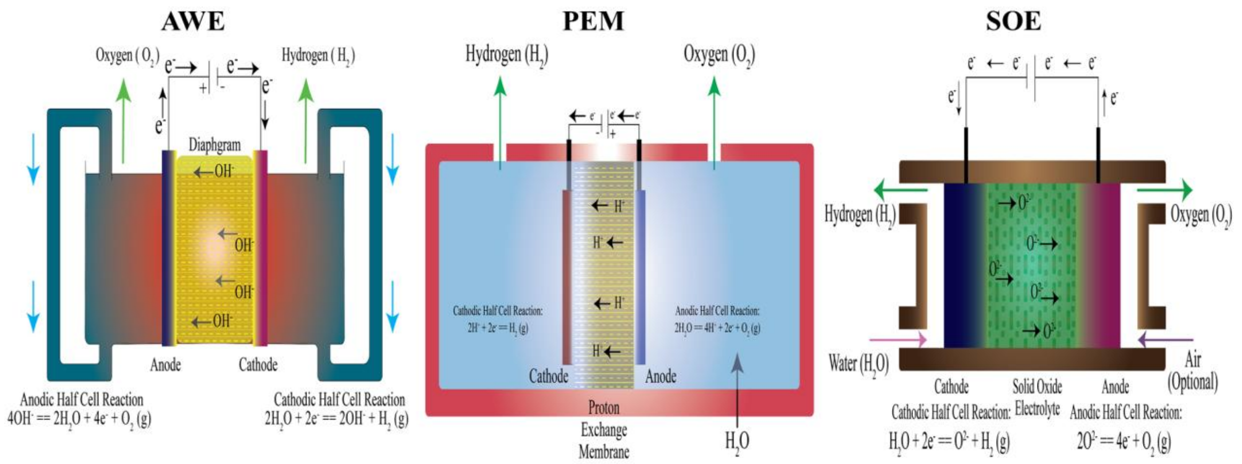


Figure 20. different types of electrolyser

Methanol production

In the context of a low-carbon and circular economy, the conversion of captured carbon dioxide (CO_2) into value-added products has emerged as a strategic approach to mitigate greenhouse gas emissions while generating useful commodities. Among the various carbon-derived chemicals, methanol stands out as a versatile and high-demand product with significant potential for decarbonization across multiple sectors.[38]

Methanol is not only a fundamental building block in the chemical industry, used in the production of formaldehyde, acetic acid, and various polymers, but also it plays an increasingly important role in the energy sector. As an energy carrier and alternative fuel, methanol can be used directly in internal combustion engines, blended with gasoline, or reformed to produce hydrogen for fuel cells. Its liquid form at ambient conditions and high energy density make it especially attractive for applications such as maritime transport, stationary power generation, and seasonal energy storage.

From a sustainability perspective, methanol synthesis from CO_2 and renewable hydrogen presents a compelling route for carbon utilization. This pathway not only helps reduce dependence on fossil-derived methanol but also contributes to the reduction of atmospheric CO_2 when coupled with green hydrogen produced via water electrolysis powered by renewable electricity. As such, methanol embodies the core principles of the circular economy: valorizing waste (in this case, CO_2) into a reusable and marketable product.[39]

Given its wide-ranging applications, compatibility with existing infrastructure, and potential for carbon neutrality, methanol is increasingly recognized as a key enabler of sustainable industrial transformation. This section explores methanol's properties, its various production routes, classification based on carbon intensity, and a specific focus on green methanol produced from captured CO_2 and renewable hydrogen which is the main goal of this thesis.

Methanol characteristics

Methanol (also called methyl alcohol) is an organic chemical compound and the simplest aliphatic alcohol, with the chemical formula CH_3OH (a methyl group linked to a hydroxyl group, often abbreviated as MeOH). It is a light, volatile, colorless and flammable liquid with a distinctive alcoholic odor similar to that of ethanol (potable alcohol), but is more acutely toxic than the latter. Methanol acquired the name wood alcohol because it was once produced through destructive[7] distillation of wood.

Methanol is a colorless, volatile, and polar liquid with excellent solvent properties and diverse chemical reactivity. It participates in key reactions such as combustion, steam reforming, and dehydration to dimethyl ether (DME), making it valuable in energy and chemical sectors. Physically, it has a low boiling point (64.7 °C), is fully miscible with water, and possesses favorable thermal properties such as a heat of vaporization of 35.2 kJ/mol and a specific heat capacity of 2.51 J/g·K.

Thermodynamically, methanol has a standard enthalpy of formation of −238.7 kJ/mol and a lower heating value of ~19.9 MJ/kg, indicating strong potential as an energy carrier. Its synthesis from CO_2 and H_2 is exothermic, requiring careful temperature control to optimize yields and catalyst stability.

Despite its utility, methanol is toxic and must be handled with care to avoid health hazards. From an environmental and operational perspective, methanol offers several advantages, including easy storage, low emissions, high hydrogen content, and infrastructure compatibility, which collectively position it as a promising fuel and chemical intermediate in sustainable energy systems.

Methanol Production Methods

Methanol can be produced through several technological pathways, each characterized by different feedstocks, reaction mechanisms, and sustainability implications. The selection of a production method is closely tied to resource availability, energy sources, environmental regulations, and economic feasibility. Broadly, methanol production methods can be classified into fossil-based and renewable-based routes.

Conventional (Fossil-Based) Methanol Production

The most established route for industrial methanol production is via steam reforming of natural gas, followed by syngas (CO + H_2) conversion over a heterogeneous catalyst.

a) Steam Methane Reforming (SMR) + Methanol Synthesis

- **Step 1: Reforming**

$$\mathrm{CH_4 + H_2O \rightarrow CO + 3H_2} \quad \Delta H = +206\,\mathrm{kJ/mol}$$

- **Step 2: Water-Gas Shift (WGS)**

$$\mathrm{CO + H_2O \rightarrow CO_2 + H_2} \quad \Delta H = -41\,\mathrm{kJ/mol}$$

- **Step 3: Methanol Synthesis**

$$\mathrm{CO + 2H_2 \rightarrow CH_3OH} \quad \Delta H = -91\,\mathrm{kJ/mol}$$

$$\mathrm{CO_2 + 3H_2 \rightarrow CH_3OH + H_2O} \quad \Delta H = -49.5\,\mathrm{kJ/mol}$$

This process is thermodynamically favorable at high pressure (50–100 bar) and moderate temperature (200–300 °C), typically over a $Cu/ZnO/Al_2O_3$ catalyst.

b) Coal Gasification Route

Used predominantly in coal-rich countries like China. Coal is gasified to produce syngas, which is then processed similarly to the SMR route. It has a significantly higher carbon footprint.

Renewable and Alternative Methanol Production

In response to climate and energy concerns, several alternative methods are being developed or deployed at pilot/commercial scale to produce low-carbon or carbon-neutral methanol:

a) CO_2 Hydrogenation (Power-to-Methanol)

- Reacting captured CO_2 with green H_2 from water electrolysis.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{2}$$

- Operates under similar conditions to fossil-based synthesis, but feedstock is sustainable.
- Integration with renewable electricity enables carbon-neutral or even carbon-negative methanol production.

b) Biomass Gasification (Biomethanol)

- Biomass is thermochemically converted to syngas, followed by methanol synthesis.
- Feedstocks: forestry residues, agricultural waste, energy crops.
- Offers CO_2 neutrality depending on lifecycle emissions.

c) Municipal Solid Waste (MSW) Conversion

- Waste-to-methanol via gasification of MSW and conversion of the syngas.
- Addresses waste management and clean fuel production simultaneously.

d) Electrochemical and Photocatalytic CO_2 Conversion (Emerging)

- Direct conversion of CO_2 and water into methanol using electrocatalysts or photocatalysts.
- Still under development with low efficiency and selectivity, but promising for long-term innovation.

Key Process Considerations

Several critical factors influence the efficiency and performance of methanol synthesis from CO and CO_2. Firstly, the reaction thermodynamics play a central role, as the process is exothermic and limited by chemical equilibrium, requiring careful temperature management to favor methanol formation. Secondly, catalyst performance is vital; copper-based catalysts are commonly employed due to their high activity, but challenges such as catalyst deactivation and limited selectivity persist, particularly under long-term operation. Additionally, heat integration is essential to enhance overall energy efficiency, as the exothermic reactions generate significant thermal energy that can be recovered or reused within the process. Finally, the purity of CO_2 and the hydrogen-to-CO_2 ratio, ideally close to 3:1, are critical parameters. These directly affect the conversion rate and overall yield, making precise control of feed composition a key operational requirement. [40]

Green Methanol Production

The synthesis of methanol through CO_2 hydrogenation represents one of the most promising pathways for producing green methanol, a renewable, low-carbon alternative to conventional methanol derived from fossil fuels. This approach fits into the broader framework of Power-to-X (PtX) technologies, which seek to convert renewable electricity into chemical energy carriers. Green methanol production effectively combines CO_2 utilization, green hydrogen, and renewable power, contributing to climate change mitigation, energy system flexibility, and sustainable fuel production.

Green methanol is defined not only by its chemical identity (CH_3OH) but by the sustainability of its feedstocks and energy inputs. To qualify as “green,” methanol must be produced from:

- Renewable hydrogen: Typically from electrolysis using renewable electricity (solar, wind, hydro).
- Captured CO_2: From biogenic sources, direct air capture (DAC), or post-combustion capture from industrial processes.
- Sustainable energy inputs: Ensuring the process energy (compression, separation, etc.) is supplied by low-carbon or renewable sources.

The carbon balance of green methanol can be nearly neutral or even negative, depending on the origin of the CO_2 and the energy mix used.[41]

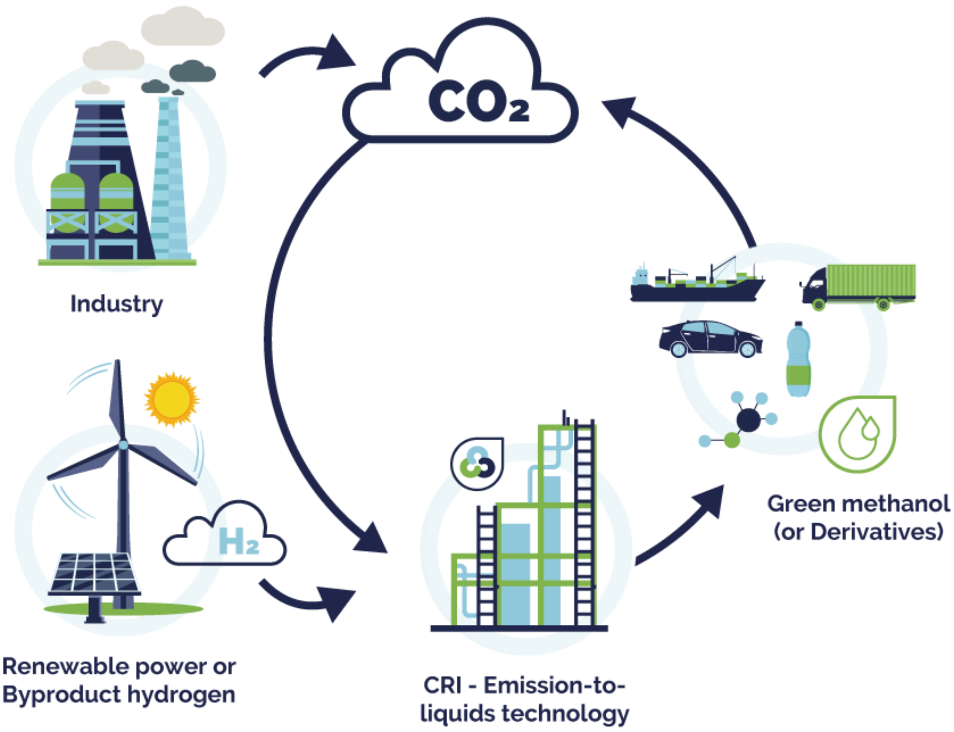


Figure 21. green methanol production pathway

Chemical Reactions and Process Thermodynamics

The primary reaction is the catalytic hydrogenation of carbon dioxide:

$$\mathrm{CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O} \quad \Delta H = -49.5\,\mathrm{kJ/mol} \tag{3}$$

It is mildly exothermic and equilibrium-limited, which necessitates:

- **Moderate temperatures** (200–280 °C): Lower temperatures improve equilibrium yield but reduce reaction rate.
- **High pressures** (50–100 bar): To shift equilibrium towards methanol formation.

Side reactions (especially the reverse water-gas shift) may compete with methanol formation, producing CO and water, thus reducing selectivity. Catalyst development and reactor design are therefore critical in optimizing yield and efficiency.

Process Configuration and Components

A typical green methanol production plant integrates several interconnected units designed to convert renewable inputs, primarily CO_2 and water, into methanol using clean energy. The process begins with a CO_2 capture unit, which sources CO_2 from flue gases originating from biomass combustion, cement plants, or directly from the atmosphere via direct air capture (DAC). Common capture technologies include chemical absorption (e.g., MEA), membrane separation, and adsorption, all aiming to deliver CO_2 at purities exceeding 99%, necessary to prevent catalyst degradation in downstream processes.[42]

The captured CO_2 is then fed into a hydrogen production unit, where hydrogen is generated via electrolysis. The main technologies used are Proton Exchange Membrane (PEM), Alkaline Electrolyzers (AEL), or Solid Oxide Electrolyzers (SOE), each requiring demineralized water and powered by renewable electricity such as wind, solar, or hydropower. The typical energy consumption for electrolysis is approximately 50–55 kWh per kilogram of H_2, making energy sourcing a critical factor for plant efficiency and sustainability.[43]

Hydrogen and CO_2 are subsequently reacted in the methanol synthesis reactor, typically employing a $Cu/ZnO/Al_2O_3$ catalyst within fixed-bed reactors, which may be operated under isothermal or adiabatic conditions. Recent advancements also explore membrane-assisted and modular microreactors. Due to the exothermic nature of the CO_2 hydrogenation reaction, efficient heat removal is essential to maintain catalyst activity and ensure stable reactor operation.

Following synthesis, the process enters the gas recycle and separation section, where unreacted gases are recovered and fed back into the reactor. The methanol–water mixture is condensed, separated, and subsequently purified via distillation to achieve high-purity methanol, typically above 99.85%, suitable for fuel or chemical applications.

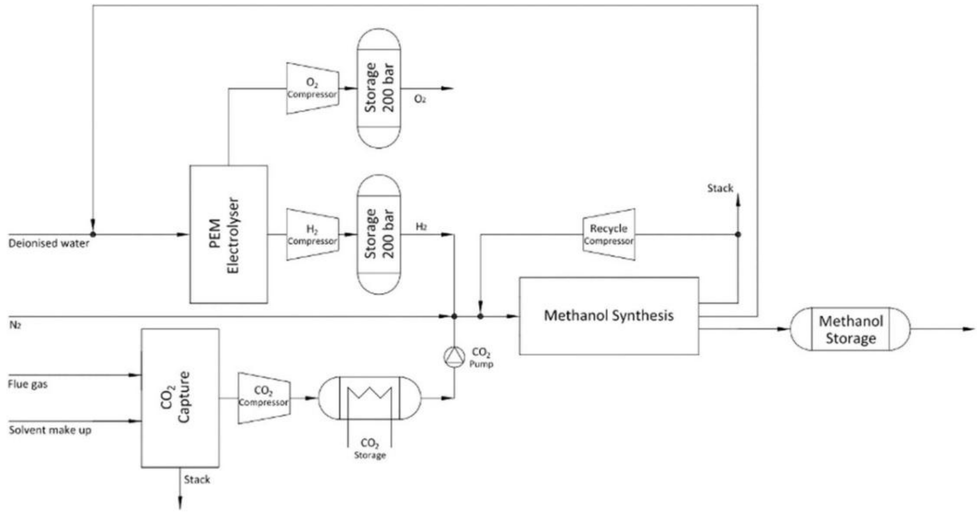


Figure 22. schematic of methanol synthesis through CO2 hydrogenation[23]

From a techno-economic and environmental perspective, the efficiency of green methanol production largely depends on the electrolyzer efficiency and reactor conversion rates, with current overall conversion efficiencies ranging between 40–60% on a lower heating value (LHV) basis. If powered entirely by renewable electricity, the process offers significantly reduced life-cycle greenhouse gas (GHG) emissions compared to fossil-based methanol routes.

However, the economic viability remains challenged by the high operational costs, particularly the cost of electricity, which can account for approximately 70% of total OPEX. Additionally, the plant is capital-intensive due to the need for CO_2 capture infrastructure, electrolyzers, and high-pressure synthesis systems. Nonetheless, policy incentives such as carbon pricing, green fuel mandates, and the classification of green methanol under Renewable Fuels of Non-Biological Origin (RFNBO) in the European Union can significantly enhance its market competitiveness and deployment potential.[44]

Process Modeling and Simulation Framework

This chapter provides a comprehensive detailed description of the model developed in Aspen plus® software for simulating the desired process. As discussed in previous chapters, there are three main sections for the modelling and each section will be accompanied by its theoretical framework. The main goal of this work is to construct a reliable and flexible modeling framework capable of analyzing the performance and interactions of the subsystems involved in Carbon Capture and Utilization (CCU).

Aspen Plus® is selected as the simulation platform due to its robustness, industry-wide acceptance, and suitability for steady-state process modeling and performance evaluation. The overall modeling strategy is chosen in order to reflect the real-world process configuration proposed in this thesis, which targets the decarbonization of industrial flue gas emissions through methanol synthesis—a value-added chemical and a promising energy carrier.

The chapter is organised into the following sections: CO_2 capture using MEA, hydrogen production via low-temperature electrolysis, and methanol synthesis through CO_2 hydrogenation. Each section details the modeling approach, operating conditions, and necessary assumptions, with validation where applicable to ensure reliability. The integration of the modules is also addressed, focusing on material and energy flows to support a consistent techno-economic analysis. Overall, the chapter establishes a modular and transparent simulation framework that forms the technical basis.

Process modelling of CO2 hydrogenation serves as the core aspect of this research work. The main goal is to simulate and provide a proper model in Aspen plus® software in order to gain a deep understanding of the process. This model will present the operational conditions of CO2 hydrogenation leading to methanol production. CO2 capture, hydrogen production, and CO2 hydrogenation are the three main sections of the global plant. Based on this integration, there are several parameters involved for proper operation of the overall process and these parameters will be discussed.

Regarding the CO2 capture system, a basic model is developed based on the conventional capture systems to simulate the process of carbon capture and familiarize reader with the operational conditions, and it has been validated considering a case study. This case study has become a reference to ensure the reliability, validity and flexibility of the model developed to proceed further with the main job of this research work. The validation procedure takes place by a strict comparison of the simulated results with the experimental ones to assure the reliability of the model by taking into account the high alignment with experimental results as a sign to satisfy the physical nature of the phenomena.

The basic model, then, is adjusted to comply with our need to model the carbon capture for the principle case study we desire to focus in this research. It goes under a scale-up and sizing step to design the components in order to respect our desired goal, to comply with the overall flow process of the plant.

The second section which is the modelling of hydrogen production through electrolysis is conducted in different set-up and a combination of CO2 stream with produced H2 occurs at the same environment leading to a stream with a composition of H2/CO2, ready for the main reaction. The modelling of H2 production is based on a simple electrolysis reference which will be explained further.

The last and the important part of the overall process is the CO2 hydrogenation. The provided stream of CO2/H2 will go through some adjustments to better prepare for the reaction in the methanol synthesis reactor. It is worth noting that the basic process of methanol synthesis might be different in some aspects due to the difference of the source and reactions utilized to perform this task.

The combination of different sections of the overall process requires proper adjustments for the continuous operation of the procedure. There are multiple technical aspects involved which should be addressed carefully leading to the satisfaction of desired goal.

Finally, as mentioned earlier, Aspen plus® software is employed as the process simulator, which utilizes a modular approach for defining and calculating chemical processes. The software predicts the behavior of reactions and process units based on standard engineering principles, including mass and energy balances, reaction kinetics, and phase or chemical equilibrium data.

carbon capture modelling

This section will provide a fully-detailed understanding of the carbon capture process simulation and modelling in Aspen plus® software. We will start with a detailed description of the carbon capture method utilized for the goal of this research work, and will continue by providing important fundamental information regarding the modelling procedure. A basic model will be developed in order to have an in-depth visual of the process and finally, the main model required to satisfy our goal will be constructed.

Post-combustion carbon capture

In chapter 3, an overview of post-combustion carbon capture was presented, but at this point, a detailed explanation will be provided. post-combustion carbon capture is based on removing the CO2 after that combustion reaction takes place. This is a general rule, and to be specific, any stream that contains CO2 and it is a product of the combustion of a fuel, could be considered for the carbon capture process. After burning carbonaceous materials, CO2 is captured from the flue gas. This method makes it particularly attractive for retrofitting existing infrastructure without major modifications to the combustion system as there is no need to perform adjustments to the whole system.

In a typical fossil fuel combustion, the resulting flue gas contains a relatively low concentration of CO_2 (usually between 3% and 15% by volume, depending on the fuel), mixed with nitrogen, water vapor, oxygen, and trace pollutants. The dilute nature of CO_2 and the presence of impurities pose technical challenges, particularly in terms of separation efficiency and energy requirements.

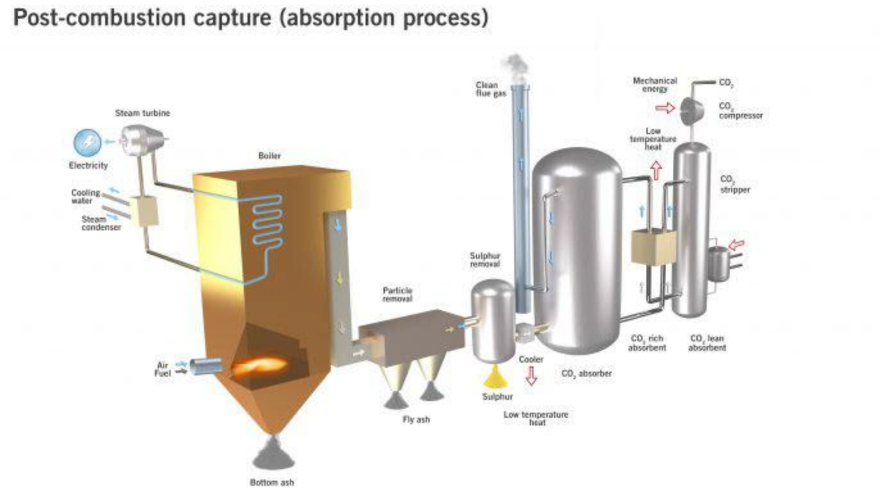


Figure 23. a schematic of Post-combustion carbon capture

Post-combustion carbon capture (PCC) is applicable across a wide range of industrial and power generation sectors that rely on the combustion of fossil fuels or biomass. One of the most vital applications is in fossil-fuelled power plants. In particular, coal-fired power plants are among the largest stationary sources of CO_2 emissions, with flue gas streams containing relatively high CO_2 concentrations (typically 12–15%). Natural gas-fired power plants, while emitting less CO_2 overall, also represent a significant application area for PCC, despite the more dilute nature of their flue gas (around 3–5% CO_2).

Beyond the power sector, PCC can be effectively implemented in various energy-intensive industries. Cement production is a major contributor to global CO_2 emissions, not only due to fuel combustion but also due to process emissions from the calcination of limestone. In such cases, PCC can be applied to the kiln exhaust streams. Similarly, the steel and iron industry, particularly in integrated steel mills using blast furnaces, produces CO_2-rich off-gases that can be treated using PCC. Relevant sources include reheating furnaces, coke ovens, and sinter plant flue gases.

Refineries and petrochemical plants are also key candidates for PCC, with emissions originating from both combustion processes (e.g., heaters and boilers) and process units such as catalytic reformers. In the pulp and paper industry—especially in kraft mills—PCC can be applied to flue gases from recovery boilers and lime kilns, supporting the decarbonization of biomass-based operations.

Waste-to-energy (WtE) facilities, which incinerate municipal solid waste, generate significant CO_2 emissions and represent another suitable application for PCC. Furthermore, chemical and fertilizer plants, particularly those producing ammonia or hydrogen via steam methane reforming (SMR), can benefit from PCC when pre-combustion capture is not feasible, by capturing CO_2 from combustion off-gases.

Other high-temperature industries, such as glass and ceramics manufacturing, also emit CO_2-rich flue gases that can be treated using PCC. Finally, when applied to biomass combustion systems in combined heat and power (CHP) plants or dedicated biomass power plants, PCC enables Bioenergy with Carbon Capture and Storage (BECCS), a negative-emission strategy that is gaining increasing attention in climate mitigation pathways.

PCC's wide applicability stems from the fact that it treats flue gas after combustion, making it a flexible and retrofittable solution without requiring major modifications to existing process configurations. One of the key advantages of post-combustion carbon capture (PCC) over pre-combustion and oxy-fuel methods is its ability to be retrofitted to existing power plants and industrial facilities without requiring major modifications to the core combustion system. This makes PCC particularly attractive for the decarbonization of current infrastructure, providing a flexible and immediately deployable solution.

Moreover, PCC is compatible with a wide range of fuels—including coal, natural gas, and biomass—and is well-suited for flue gas streams at atmospheric pressure, which are common in many industrial applications. Importantly, PCC—especially when based on amine solvent systems such as monoethanolamine (MEA)—has reached a high level of technological maturity, with several pilot and full-scale commercial demonstrations worldwide, reinforcing its position as the most developed CO_2 capture option available today.

The necessity of coverage of different sectors has led to the development of several methods to use as a carbon capture technique. Absorption, adsorption, cryogenic methods, chemical looping, and membrane separation are the main technologies implemented to perform separation of CO2 from the flue gases. Among these, chemical absorption with amine-based solvents, especially monoethanolamine (MEA), is the most mature and commercially deployed solution. The process involves the chemical binding of CO_2 in a liquid solvent within an absorber, followed by its thermal release in a stripper or regenerator for CO_2 recovery and solvent reuse.

Despite its proven effectiveness, PCC systems often impose a significant energy penalty on power plants or industrial operations due to the heat required for solvent regeneration. As a result, current research and engineering efforts are focused on improving capture efficiency, reducing energy consumption, enhancing solvent stability, and integrating capture units into broader decarbonization systems.

PCC plays a vital role in Carbon Capture, Utilization, and Storage (CCUS) strategies and is considered essential for achieving near-term emissions reduction targets, especially in hard-to-abate sectors such as cement, steel, and pulp and paper industries.

chemical absorption

In the context of post-combustion carbon capture, as mentioned earlier, absorption plays a vital role in CO2 separation. Two different kinds of absorption exist which based on a combination of process conditions, gas composition, and performance requirements the choice might vary. The chemical absorption of CO2 is a commercially viable technology due to its many advantages, including technical efficiency, handling capacity, and sophistication. The working principle is simple. CO2 is separated from flue gas by absorption using a liquid sorbent and It is possible to regenerate the sorbent via a regenerative process or stripping by depressurizing and/or heating. This is the latest and most advanced method for separating CO2.

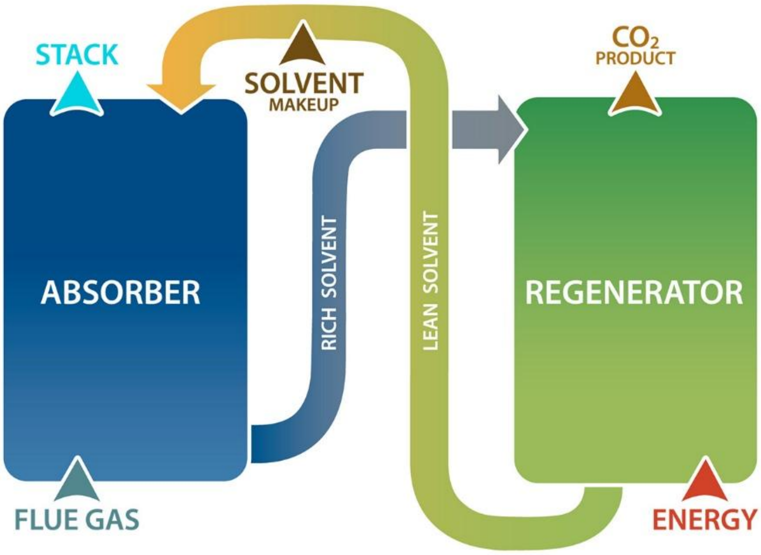


Figure 24. process flow of chemical absorption of CO2

Chemical absorption is a gas separation technique in a gas–liquid separation process that originates from fundamental principles of mass transfer and chemical reaction engineering. It involves the transfer of gaseous component, carbon dioxide, into a liquid solvent where it reacts chemically to form stable compounds. CO2 is selectively removed from a gas mixture through irreversible or reversible chemical reactions with a liquid solvent. This process is governed by thermodynamics, mass transfer theory, reaction kinetics, and chemical equilibrium. At the interface between gas and liquid phases, CO_2 first dissolves into the solvent and then reacts with reactive species, such as amine groups, to form compounds like carbamates or bicarbonates. These reactions are typically reversible and exothermic, allowing the absorbed CO_2 to be released later during the regeneration step.

The theoretical basis of chemical absorption is often described using film theory, which accounts for the resistance to mass transfer across a thin liquid film, and rate-based models that consider the kinetics of the gas–liquid reaction. The concept has been applied industrially for decades, particularly in the natural gas processing industry, where amine-based systems have been widely used to remove CO_2 and H_2S. Its extension to post-combustion carbon capture emerged as a promising strategy for decarbonizing fossil fuel-based power generation and industrial emissions. Due to its high selectivity, scalability, and maturity, especially with solvents like monoethanolamine (MEA), chemical absorption has become the benchmark method for post-combustion CO_2 capture systems.

In CO_2 capture, the most widely used solvents are aqueous amines, which chemically react with CO_2 to form carbamates or bicarbonates, depending on the amine type and system pH. The overall absorption process involves the following fundamental steps:

1. **Gas-phase diffusion** of CO_2 to the gas–liquid interface.
2. **Physical dissolution** of CO_2 into the solvent film at the interface.

3. **Chemical reaction** of CO_2 with the active component of the solvent (e.g., MEA).
4. **Liquid-phase diffusion** of the reaction products into the bulk of the solvent.

For **primary amines** such as monoethanolamine (MEA), the main reaction is:

$$\mathrm{CO2+2RNH2 \rightleftharpoons RNH3++RNHCOO-} \tag{4}$$

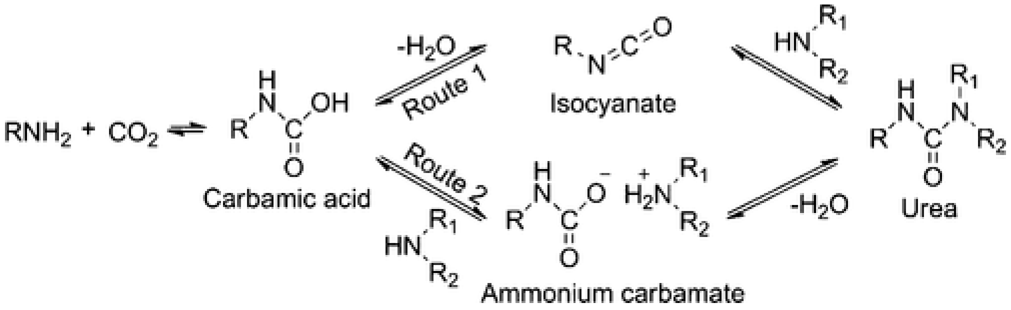


Figure 25. reaction schematic of carbon capture through amine

This reaction is **exothermic** and reversible. The equilibrium favors absorption at lower temperatures and desorption at higher temperatures, an essential feature for regeneration in the stripper.

The absorption rate is influenced by:

- The CO_2 partial pressure in the flue gas.
- The amine concentration and type.
- Temperature and pressure of the system.
- Mass transfer coefficients and interfacial area (linked to column design and packing).

In the regeneration step, the rich solvent is heated to break the chemical bonds and release CO_2, shifting the equilibrium back toward the original amine. The thermodynamic behavior of the system is typically described using activity-based models (e.g., **NRTL**, **ELECNRTL**, or **Kent–Eisenberg**) that account for electrolyte interactions and non-ideal solution behavior.

Overall, chemical absorption combines mass transfer, thermodynamics, and chemical kinetics in a tightly coupled manner, making **rigorous modeling essential** for performance prediction and process optimization. In this work, the Aspen Plus® simulation employs rate-based or equilibrium-stage modeling depending on the data availability and accuracy needed, as explained in the following sections.

Absorption method

The post-combustion CO2 capture using amine aqueous solutions consists in a reactive absorption-solvent regeneration process. Two main sections can be identified in the plant: the absorption, where carbon dioxide is transferred from the vapor/gas phase to the liquid one, and the stripping, where the solvent is regenerated. In particular, the absorption process is enhanced by the reaction between the CO2 transferred in the liquid phase and the solvent. On the other hand, the reverse reaction happens in the stripper to detach the amine from the CO2, which is then transferred back to the gaseous phase. The two sections are interconnected by a cross heat-exchanger. A simplified flowsheet of the system is presented in Fig. 26. It highlights the main equipment, flow directions of the flue gas, rich and lean solvent loops, and the CO_2 product stream.

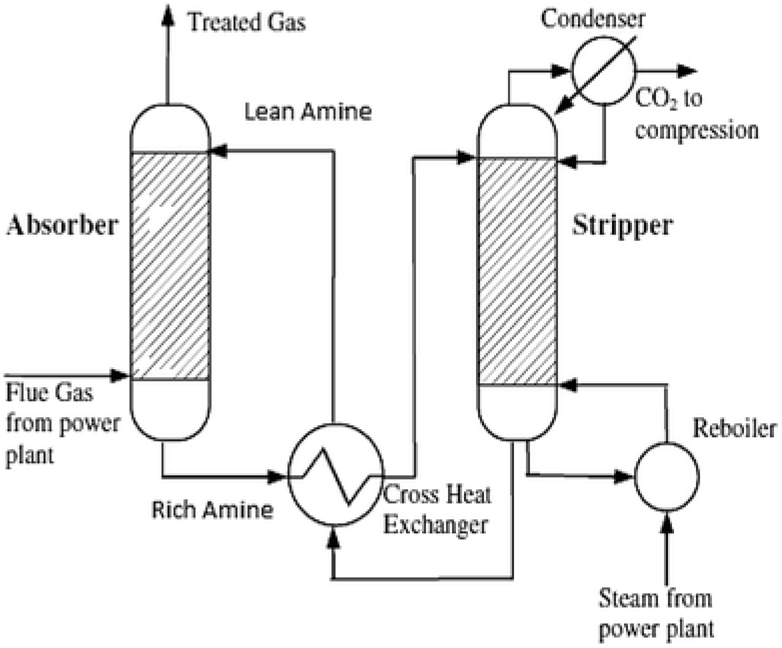


Figure 26. equipment setup for chemical absorption of CO2 capture

The flue gas rich in CO2 enters the absorber from the bottom and flows countercurrent with respect to the liquid solvent. Following the absorption process, the exhaust gas exits the top of the column and after solvent recovery is sent to the stack. The rich solvent is pumped from the bottom of the absorber to the cross heat-exchanger where it is heated and then sent to the top of the stripper. In this second section, the liquid flows countercurrent with the vapor flow generated by the reboiler.

As the gas rises, CO_2 diffuses into the liquid phase and reacts with the amine to form carbamate and bicarbonate species. The cleaned or "sweet" flue gas exits the top of the absorber, typically vented to the atmosphere after water wash stages to minimize solvent losses. From the top of the stripper, a gaseous mixture of carbon dioxide and water is sent to a partial condenser where the CO2 is concentrated in the gas phase and then sent to compression, while the water is recovered in the liquid phase.

Exiting from the bottom of the stripper, the regenerated solvent is sent to the heat-exchanger where it supplies its sensible heat to the rich solvent and recycled back to the top of the absorber. Typically, the two columns are packed columns, chosen over the plate ones because the packing is able to provide a higher contact area between the gaseous and the liquid phase and ensures less pressure drop.

The released CO_2 exits the top of the stripper, where it passes through a **condenser** to remove any entrained water vapor. The resulting gas stream is highly concentrated CO_2, which can be compressed for transport or storage. The regenerated lean solvent, after passing through the lean/rich heat exchanger, is cooled further in a **solvent cooler** and pumped back to the top of the absorber to continue the cycle.

Overall, the post-combustion CO_2 capture system comprises several key equipment components that enable efficient separation and regeneration of the solvent. The absorber column, typically a packed tower, provides a large surface area to facilitate gas–liquid contact, operating near atmospheric pressure and at moderate temperatures ranging from 40 to 60°C. The stripper column, which can also be either packed or tray-based, is used to regenerate the solvent by heating the CO_2-rich stream to approximately 100–120°C, often using steam as the heat source. To enhance energy efficiency, a lean/rich heat exchanger is implemented to preheat the rich solvent before it enters the stripper, thereby reducing the thermal load on the system. A reboiler is connected to the bottom of the stripper to supply the necessary heat for CO_2 desorption. At the top of the stripper, a condenser is used to remove water vapor from the product CO_2 stream, ensuring its purity. Finally, a solvent cooler and pump are included to cool the regenerated lean solvent and circulate it back into the absorber, completing the solvent loop.

The presence of the chemical reactions adds complexity to the process, where different phenomena are involved, as following:

- non-ideal thermodynamics
- chemical equilibrium and kinetic reactions
- simultaneous material and energy transfer
- vapor-liquid and gas-liquid equilibria
- distribution of the components between the liquid and the gaseous phase

One of the challenges in chemical absorption is the significant energy required for solvent regeneration. Integration of a **lean/rich heat exchanger** is therefore essential to recover sensible and latent heat from the hot lean solvent exiting the stripper. Moreover, using **low-**

pressure steam from an existing power plant for the reboiler minimizes external energy demand.

Due to the complex nature of the process, a model that is able to take contemporarily into account all of these phenomena is needed in order to obtain a correct mathematical description of the system. In this work, the process was modeled using Aspen Plus® v14.0 and a step-by-step procedure is presented in the following sections.

basic model development and validation

modeling tool

As mentioned previously, taking into account the complexity of the absorption process, a highly reliable and comprehensive model is required to study correctly the MEA-CO2-H2O system physics and also cover all the details associated with the phenomena involved in the physical process, leading to obtain a correct mathematical description.

The modelling software considered to simulate the process is Aspen Plus® v14.0. this software is one of the most utilized applications that is capable of simulating both steady-state and dynamic processes in chemical, process and energy engineering disciplines. It offers the possibility to model a broad spectrum of processes, from the classic distillation columns to different kinds of reactors, and includes also all the auxiliary equipment typical of a chemical plant, such as valves, pumps, compressors, mixers, and pipelines.

The suite offers the possibility to link the modeling part with Aspen Properties®, that gives the possibility to access an extremely large database of physical properties. Aspen Plus operates using a modular and block-based approach, where each unit operation (e.g., reactor, heat exchanger, column) is represented by a model block connected via process streams. Users define the chemical components, property methods, operating conditions, and equipment configurations, and the simulator performs mass and energy balances, phase equilibrium calculations, and reaction modeling.

First, the simulation must be fully specified with no missing variables or parameters. This is determined through a degrees-of-freedom analysis, where the number of equations must match the number of unknowns for each unit. In addition, the selection of an appropriate thermodynamic property method is critical. For chemical absorption processes involving aqueous amine solvents and electrolytic systems, property methods such as Electrolyte NRTL, Kent–Eisenberg, or RKSMHV2 are commonly used to account for non-ideal solution behavior, phase equilibrium, and heat of absorption.

All chemical components involved in the process, including CO_2, H_2O, and MEA, must be defined, and relevant chemical reactions must be incorporated when a rate-based or equilibrium-based model is used. For example, the absorption of CO_2 by MEA involves the formation of carbamate and protonated amine species, which are modeled through appropriate reaction sets. Each unit block, such as RadFrac for columns or Heater for thermal conditioning, must be configured with specified operating conditions, such as pressure, temperature, and stage numbers.

Aspen Plus uses a combination of sequential modular and equation-oriented solution strategies. In systems with recycle streams, tear streams are introduced to break recycles and allow iterative solution of the flow network. The software uses convergence algorithms such as Broyden’s method, Wegstein acceleration, or Newton-Raphson techniques to solve non-linear systems and update flow conditions until convergence criteria are met.

Convergence is facilitated by supplying reasonable initial guesses for key process variables (e.g., temperature, flow rate, composition), defining tolerances for mass and energy balances, and using design specifications judiciously. For particularly complex or sensitive models, such as those involving electrolyte chemistry or tightly coupled energy loops, tighter convergence tolerances and systematic debugging may be required.

Aspen Plus also supports detailed rate-based modeling, especially in RadFrac columns, which allows for the simulation of mass transfer across film layers and within reaction zones. This is especially useful for simulating gas–liquid absorption processes such as CO_2 capture with MEA. The software enables the inclusion of electrolyte chemistry, which is necessary to accurately model ionic species, acid-base equilibria, and CO_2 solubility in aqueous media.

Other important modeling features include heat integration using heat exchanger blocks or energy streams, and built-in sensitivity and optimization tools for analyzing the effect of process variables on key performance indicators such as reboiler duty, CO_2 capture efficiency, and solvent circulation rates.

modelling procedure – theoretical framework

the post-combustion CO2 capture by means of amine aqueous solutions consists in a reactive absorption-stripping process. In Aspen Plus® this kind of processes are typically modeled using the so called RadFrac™ model, which allows to model absorbers and strippers with chemical reactions. The modelling procedure covers a wide range of involved phenomena regarding the physics and complicated nature of the system desired to study.

From a mathematical point of view, in Aspen Plus®, it is not necessary to write the model equations. In fact, each block contains the material and energy balances used to describe each unit operation. Though this gives the possibility to save time in writing the equations, it rises the necessity to set the model parameters in an appropriate way to ensure the correct process description. In general, an Aspen Plus® model is built in two distinct environments:

Properties and Simulation. In the first environment, the components are defined and the methods for the computation of the thermodynamic properties are chosen. In the second environment, the streams and the equipment are represented in a flowsheet and the main parameters of the model are set.

To start describing the basic model developed for the post-combustion carbon capture in Aspen plus, some theoretical background is needed to be explained first, and then the main procedure of the simulation will be presented.

The CO2-MEA-H2O system is an electrolyte system characterized by a nonideal behavior due to the presence of ions. For this reason, the thermodynamic model for the liquid phase must be able to describe the interactions between electrolytes. In particular, the correct evaluation of the components activity coefficients is crucial, since these parameters are involved in the calculation of the vapor-liquid and gas-liquid equilibria, the equilibrium and kinetic reactions and the calculation of the driving force for the interphase material transfer.

The definition of the reaction scheme is essential for the correct description of the CO2-MEA-H2O system, where the chemical reactions are limited to the liquid phase only. A significant number of reactions sets have been proposed in the literature. Some authors have proposed a purely equilibrium reactions set while others have considered only one kinetic reaction between CO2 and MEA or two kinetic reactions involving CO2 and MEA and OH^- ions. With regards to the reaction between CO2 and MEA, different forms have been proposed in the literature, depending on which equilibrium reactions are considered for their derivation. The desired reactions are presented as below:

$$2\mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{OH^-} \tag{5}$$

$$\mathrm{MEA^+} + \mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{MEA} \tag{6}$$

$$\mathrm{HCO_3^-} + \mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{CO_3^{2-}} \tag{7}$$

$$\mathrm{CO_2} + \mathrm{MEA} + \mathrm{H_2O} \rightleftarrows \mathrm{MEACOO^-} + \mathrm{H_3O^+} \tag{8}$$

$$\mathrm{CO_2} + \mathrm{OH^-} \rightleftarrows \mathrm{HCO_3^-} \tag{10}$$

The basic aspect of this phenomena is the reaction of CO2-H2O-MEA system. We have to thoroughly understand what is the underlying physics of this phenomenon in order to obtain the ability to model this system correctly.

Modelling – practical framework

Based on the overall path of post-combustion carbon capture by reactive absorption-stripping process, the selection of the equipment is necessary to follow the logical route. It was previously stated that the main equipment involved in the process are absorber and regenerator (stripper), and there are other equipment utilized for the process flow of the procedure. As a start to model the post-combustion carbon capture process, a simple model has been considered to develop in order to obtain a basic understanding of physical nature of the process. Then, this model is validated considering a reference case to assure the reliability of the model developed based on experimental data.

The starting point for modelling the post-combustion carbon capture is to define the involved components in the reactions present in our processes. The overall procedure is consisted by two steps: definition of the properties environment and moving to the simulation phase. Definition of the components has a great importance since it defines the basic chemistry of the reactions and the following processes. At this point, after the specification of components, Aspen plus will recognise all the technical aspects associated with each component of the reactions. Since this composition, CO2-MEA-H2O, has a complex nature, there will be some ions present in our system which the subsequent considerations will be explained.

Based on the system that we are dealing with, two phases are involved in the process: the gaseous and the liquid one. In the first phase, nitrogen, oxygen and water vapor are present together with the CO2. Depending on the specific case, other components such as H2S can be present as impurities in the flue gas. As the source for CO2 cover a wide range of industries, a variety of components could be available in the fluegas.

In the liquid phase, the system CO2-H2O-MEA is characterized by the presence of ions due to ionic dissociation. In this work, monoethanolamine (MEA) was chosen as target solvent, since it is by far the most studied and proven to be the most mature one for chemical absorption of post-combustion carbon capture.

Once the main components are specified in the Components—Specifications panel, Aspen Properties® recognizes the possible presence of ions and asks if the user wants the program to work with one of the following approaches:

- Apparent components: In this case the components in the liquid phase are considered undissociated;
- True components: In this case for the liquid phase the dissociation of the components in free and dissociated forms is taken into account.

The true components approach is used for the model development to give a more realistic description of the system. Once the option is activated, the software generates all the components involved, including the ions. For the CO2-MEA-H2O system, 11 components are generated. Moreover, the software proposes a set of ionic equilibrium reactions and salts dissociation reactions that are used to determine the compositions of all the streams involved in the process. The user has the possibility to choose which reactions are to be used.

The salts dissociation reactions are assumed negligible and, subsequently, a set of five chemical equilibrium reactions is considered.

After the introduction of species, it is possible to specify the model to be used for the evaluation of the thermodynamic properties. In particular, this model must be able to take into consideration the strong non-ideality of the liquid phase due to the presence of ions. Based on the literature, the Electrolyte Non-Random Two Liquid is the most suitable model for the description of the electrolytic interactions present in the CO2-MEA-H2O system. Then, the Elec-NRTL model was used for the evaluation of the thermodynamic properties in the liquid phase. It must be highlighted that this method is also the one suggested automatically by Aspen Properties®. Furthermore, the Elec-NRTL model was coupled with the ESPSAFT Equation of State for the computation of the non-idealities of the vapor/gas phase. Once the thermodynamic model is specified, Aspen Properties® automatically retrieves all the parameters from the database. There is also the possibility to change the value of the parameters, which might be necessary in specific cases.

The henry components are defined, chemistry of the problem is set, and UNIFAC groups are specified. After the components and the system thermodynamics are set-up, it is possible to move from the Properties to the Simulation environment which is a place that the equipment set-up and stream network is defined. the simulation environment should be defined properly in order to have a proper alignment between theory and practice.

The Simulation environment is the part of the software where the equipment and the streams involved in the process are specified. Furthermore, all the parameters necessary for the development of the model are defined in this section. Streams and equipment in Aspen Plus® are reported in the Main Flowsheet panel by a specific symbolic notation, giving a clear representation of the process.

In the simulation environment, the choice of the blocks are important. Since two vital equipment involved in this process are the absorber and stripper, the type of these two components is important. Based on the literature, a RADFRAC column is selected as the type of these two blocks. For other blocks in the flowsheet, there is no specific considerations and the typical layout is fine to proceed with.

Once the streams characterization and the reactions are defined, the next step is to describe what happens inside the columns. The first decision to be taken regards the degree of approximation of the model. It was highlighted in the previous sections the complex nature of the process that involves several different phenomena. Then, in order to obtain a correct mathematical description of the system, a model that is able to describe contemporarily the non-ideal thermodynamics, the chemical reactions, the interphase transfer, the component transport in the two phases and the fluid dynamics is needed. This section deals with the modeling of the interphase transfer and the components transport in the two phases in the presence of chemical reactions. In the RadFrac™ model, two different approaches are present: the equilibrium stages mode and the rate-based mode. In both cases, the column height is discretized into a certain number of parts, which are referred to as stages in Aspen Plus®, though in the case of the rate-based mode they should be referred to as segments.

This process is far from the phase equilibrium condition. For this reason, the most used approach in the case of the reactive absorption-stripping of CO2 with MEA is the so-called rate-based one. With this approach it is possible to take into account the limitations to mass transfer due to the presence of the chemical reactions. The rate-based mode was chosen for the description of both the absorber and the stripper.

For modelling the absorber and stripper blocks, we need to take the following:

First, the configuration of the block should be specified which contains the type of the column, number of stages, and stream location specification. Also, the reference operating pressure should be determined for the columns. The reactions involved in the column, the configuration of the column, and the rate-based set-up modelling of the column should be determined.

RadFrac column allows the user to discretize the liquid and gas films and incorporates kinetic of reactions involved and provides four different flow models which determine the bulk properties required to evaluate the mass and energy fluxes and reaction rates. The Film discretization facilitates an accurate modelling of the chemical reactions taking place in the liquid film. In particular, without film discretization, the liquid film reaction rates are evaluated based on an average liquid phase composition, instead with film discretization, the liquid film reaction rates are evaluated by multiple sets of liquid phase compositions, where each set expresses the average liquid phase composition for the particular film segment.

For the rest of the components, the characterisation phenomena follows a simple data input, and there is no specific consideration. Thermodynamic specifications should be determined and the component will be connected to other ones through the streams.

Once the set-up of the model is complete, the simulation will be performed based on the input data of the reference case-study. In this work, two reference case studies were considered in order to validate the reliability of the model developed in Aspen plus. One case study is a laboratory-scale plant and the other one is a large-scale plant. The type of the columns are also different in these two case studies in order to study the difference between them.

After that we have validated the correct process simulation of the model, the main job starts from this point. Since we desire to propose a carbon capture section for a specific case study, there is no available experimental data to validate the proposed model, so it should be validated before. At this point, it is determined that the developed model is reliable and we will proceed with the specified settings to design the model for new case study.

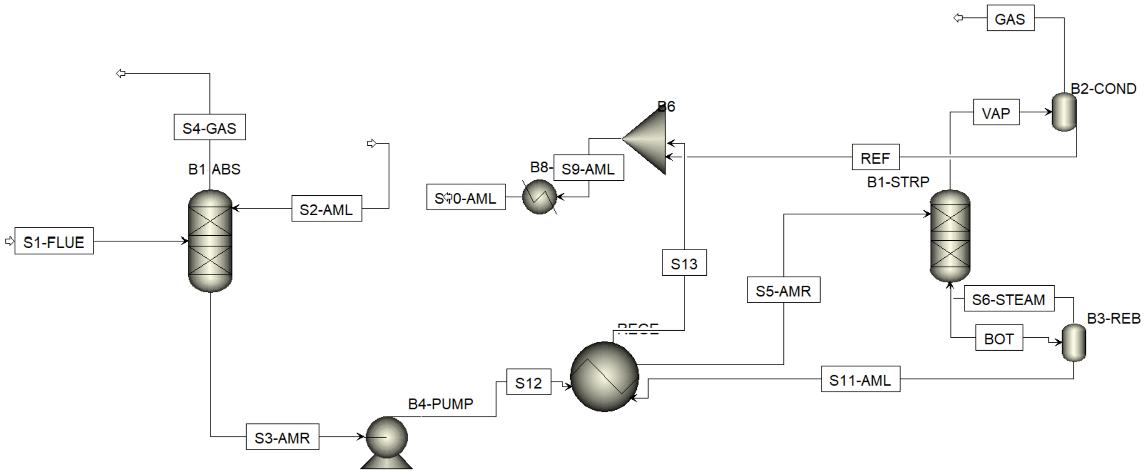


Figure 27. basic model development for carbon capture

Model up-scaling

The base model developed for post-combustion carbon capture was based on a simple case study. As this research work aimed at carbon capture from a different plant and CO2 source, it was essential to size and up-scale the model to fit for the new layout that this thesis is considering.

The carbon capture section of the plant should be designed and sized in order to adapt for the new input variables of the plant. Since we consider carbon capture of a pulp and paper plant, the input streams from the pulp and paper plant contain different composition and should be treated in another way.

The global set-up of the simulation environment for carbon capture is the same, but there are some modifications like additional components in the flowsheet. Since based on the configuration of pulp and paper plant, there are three exit streams containing the CO2, a combination of these streams takes place first. Then, due to the impact of the temperature on the deterioration of MEA, a cooler is added to reduce the temperature of the mixed stream before entering to the absorber.

Basically, the scenario for sizing and design of the absorber and stripper is the same and consists of two stages. The procedure starts with an assumed number of stages for both absorber and the stripper, since in the modelling section we have come up with specific value for stage number, and the configuration of the absorber and regenerator is similar to the previous model.

Generally, the only variable parameters for the absorber and the stripper are the height, diameter, and the base stage considered for the equipment. So, by performing a trial-and-error procedure, the geometrical specifications of the both absorber and stripper for new configuration of carbon capture plant could be determined. The design and sizing procedure is as follows:

First, for the initial design scenario, a specific value for height of the column is set. At this case, the value is 100. Then, an initial value for the diameter of the absorber and an amount for base stage is considered. After that the convergence reaches, the outlet stream for gas outlet is analyzed to determine the CO2 removal rate. Since our desire is to design a 90% carbon removal rate, our convergence criteria is to reach 90% removal rate. At this point, based on the CO2 composition of the outlet gas stream and the inlet fluegas, the carbon removal rate could be calculated.

This procedure, modification of the diameter and base stage, continues until the desired carbon removal rate is reached. Another important variable which is highly important for the absorber is solvent flow rate. This parameter is also monitored during the sizing procedure in order to satisfy the overall convergence criteria. The design specification for solvent flow rate could be backed up by the theory which the L/G ratio should be less than about 4 for structured packing equipment. Based on this fact, it is possible to adjust the value of solvent flow rate.

The first scenario is called infinite packing height. But, the second scenario which could be considered more realistic and practical for design considerations, is called effective packing height. This sizing approach is based on the fact that the minimum solvent flow rate is fixed in previous step, and then the packing height is modified step by step to satisfy the desired objectives. At this point, based on the plant configuration layout, the height is set to 50, 40, 30, 20, and based on these values the diameter of the column is sized for satisfying the desired carbon removal rate.

The same procedure is applied to the stripper, and after performing the trial-and-error procedure, the sizing of the stripper for our case study is done. At this point, the convergence is checked based on the CO2 loading in the solvent flow.

hydrogen production

hydrogen production through water electrolysis

Hydrogen plays an important role for our main goal of fuel synthesis. As for the methanol production, hydrogen is a component which the captured CO2 enters a reaction with in order to produce methanol. So, it is required to provide the sufficient amount of hydrogen at least as the stoichiometry of the reaction for proceeding to methanol synthesis. As stated earlier, there are some production methods for hydrogen, but for our case, to move along with sustainability framework, it is our desire to use renewable hydrogen production method.

Renewable hydrogen production occurs through water electrolysis, and a brief overview of this method is explained in chapter 3. Based on the explanation about different types of water electrolysis cells, it is important to choose a cell for satisfying our goal, so the selection criteria should consider different aspects of integration and production of methanol.

At this point, to take into account the synthesis of methanol and also the simplicity of the procedure, we have decided to utilize and model alkaline water electrolyser. This choice is also backed up by the fact that this type of electrolyser is less expensive than the other types of electrolyser, so the capital expenditure would be low.

The water is used as the input to the cell for splitting, and the required power for the hydrogen production is satisfied through renewable energy. Alkaline electrolyser is a promising choice based on the literature for our purpose to work in a large-scale production plant. Alkaline water electrolysis is one of the most mature and commercially available technologies. Its operation is based on an electrochemical reaction in an aqueous alkaline solution, typically potassium hydroxide (KOH) or sodium hydroxide (NaOH), with water as the reactant. The reaction is endothermic, meaning it requires an external energy source in the form of electricity.

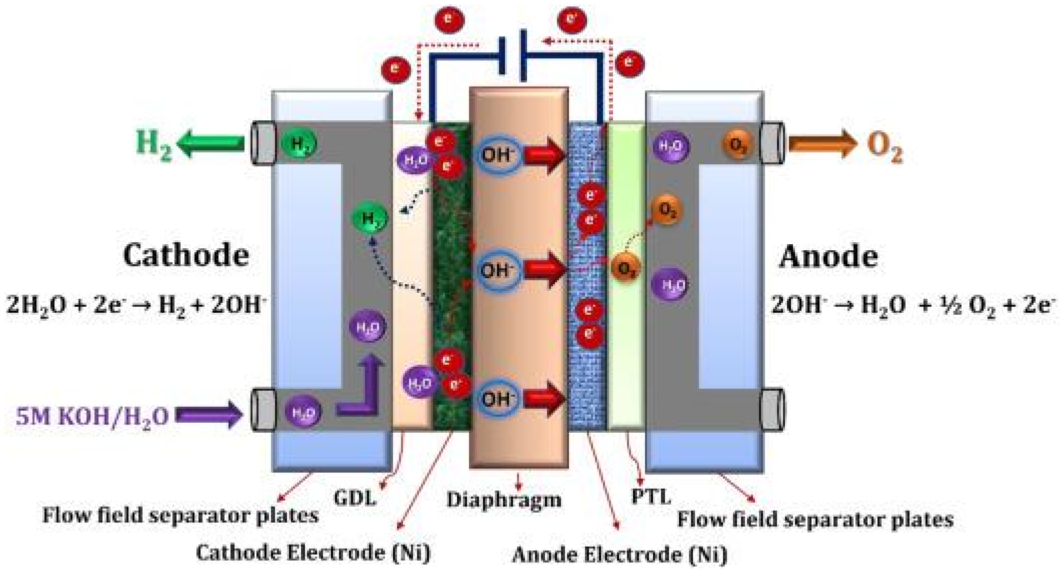


Figure 28. water electrolysis operation schematic

The cell operates based on the principle of applying a direct current across two electrodes submerged in an aqueous alkaline solution, typically potassium hydroxide (KOH) or sodium hydroxide (NaOH). In this setup, water molecules are decomposed into hydrogen gas at the cathode and oxygen gas at the anode. The overall chemical reaction is the decomposition of water into hydrogen and oxygen: H_2O (l) → H_2 (g) + ½ O_2 (g).

Thermodynamically, this is an endothermic reaction that requires a minimum electrical input equivalent to the Gibbs free energy change of the reaction, which is approximately 237.2 kJ/mol at 25°C. However, the total energy demand, including the thermal contribution represented by the enthalpy change ($\Delta H \approx 285.8$ kJ/mol), must be considered for a complete energy balance. The minimum theoretical cell voltage, known as the reversible voltage, is about 1.23 V under standard conditions. In practice, due to kinetic and resistive losses, including activation overpotentials, ohmic resistance in the electrolyte and membrane, and concentration polarization, the actual operating cell voltage typically ranges between 1.8 and 2.2 V.

The alkaline electrolyser operates at relatively low temperatures, generally between 60 and 90°C, which helps enhance reaction kinetics and improve the ionic conductivity of the electrolyte. Pressure can vary from atmospheric conditions up to 30 bar, depending on the system configuration and whether pressurized hydrogen is desired for downstream use. The electrolyte is maintained in a highly basic state, with pH values above 13, to facilitate the transport of hydroxide ions (OH^-) from the cathode to the anode through a porous diaphragm or separator.

At the cathode, water molecules accept electrons from the external power source, producing hydrogen gas and hydroxide ions. These hydroxide ions migrate through the electrolyte to the anode, where they release electrons and form oxygen gas and water.

The electrodes are typically made of nickel or other corrosion-resistant materials suitable for the harsh alkaline environment. Overall, the process is characterized by high durability, relatively low capital cost, and moderate energy efficiency, making alkaline electrolysis a reliable choice for large-scale hydrogen production when powered by renewable electricity.

modelling of alkaline cell in Aspen plus

To model the water electrolysis in Aspen plus, a simple process flow has been considered. Since we have assumed an inlet stream of water in standard conditions, water should undergo a pretreatment stage before entering to the stack of electrolyser. Its pressure and temperature are modified by using a pump and a heater, and then it is ready to enter the stack.

Water electrolysis is performed through a Rstoic reactor and a separator which both of them are considered as a stack. The thermodynamic conditions will be explained further. The process flow diagram is presented in figure 29.

After the exit from the stack, considering the thermodynamic requirements, produced H2 goes through a cooler to reduce its temperature, and then it enters a compressor to bring its pressure close the desired pressure for methanol synthesis as it will undergo a mixing stage with captured CO2. A flowsheet of the proposed model is presented in fig.

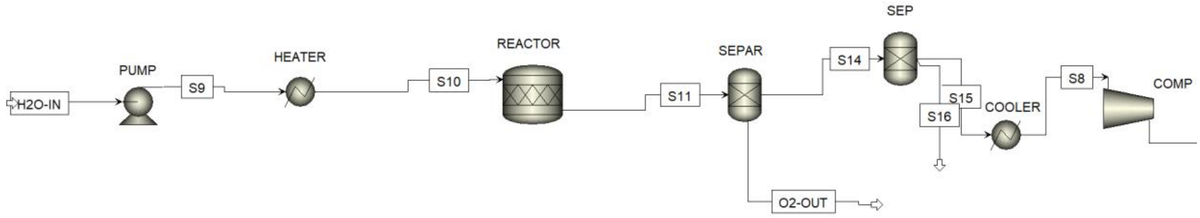


Figure 29. proposed model in Aspen plus for water electrolysis

For the electrolysis itself, a simple procedure is considered for the modelling. Based on the modelling criteria, a reference paper is considered to utilize the values for the alkaline cell electrolysis. At this step, also some assumptions have been made to be consistent with the physical nature of the process and the reactions. There are also some calculations required to perform in order to specify some input data for the reactor and the reaction itself which all are based on the reference paper considered.

One parameter that plays an important role in water electrolysis is the power input to the stack. This value is adjusted based on the produced H2, since there are some mathematical equations governing the relation between the power and the molar flow rate of the produced hydrogen.

Up to now, the overall procedure is explained. For the thermodynamic aspects of the problem, the pressure of electrolysis is fixed on 7 bar to be consistent with the reference we have considered for the simulation.

The main component involved in this procedure is the reactor which the reaction takes place in. all the settings required to set-up for the reaction are utilized from the reference paper. At this point, the specifications required for setting up the reactor is its operating pressure and the reactions performed inside. Also, the conversion rate of the reactants is determined. For the last section, it is required to decrease the outlet stream which is the produced H2 and increase its pressure for the mixing action.

Methanol Synthesis via CO_2 Hydrogenation

theoretical framework

The core part of this research work, after preparing all the pre-requisites, is the green methanol synthesis. Two pathways of methanol production from H2 and CO2 do exist: direct methanol synthesis and indirect one. The direct methanol synthesis consists of one reactor in which CO2 hydrogenation takes place.

Methanol synthesis reaction in direct form is an exothermic reaction. Meaning that the temperature conditions should be kept low with high pressures. the model developed for this purpose mainly consists of a reactor which methanol production occurs inside and a series of additional components to adjust the process flow for desired conditions. A flowsheet of the process is presented in figure 31.

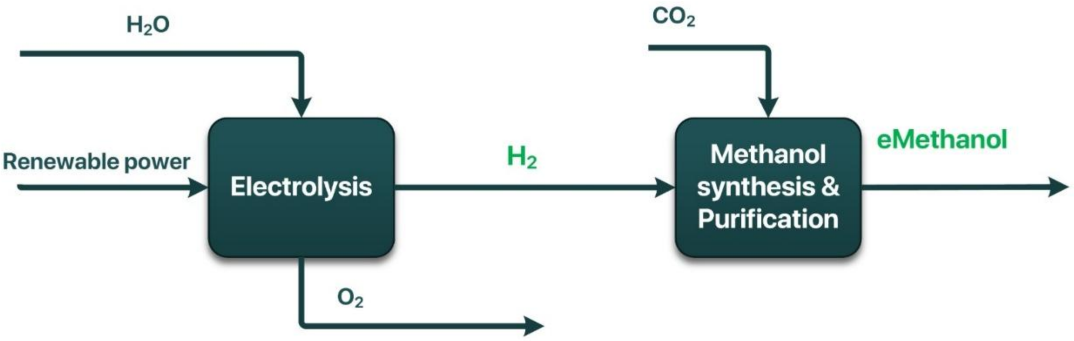


Figure 30. overall process of green methanol production

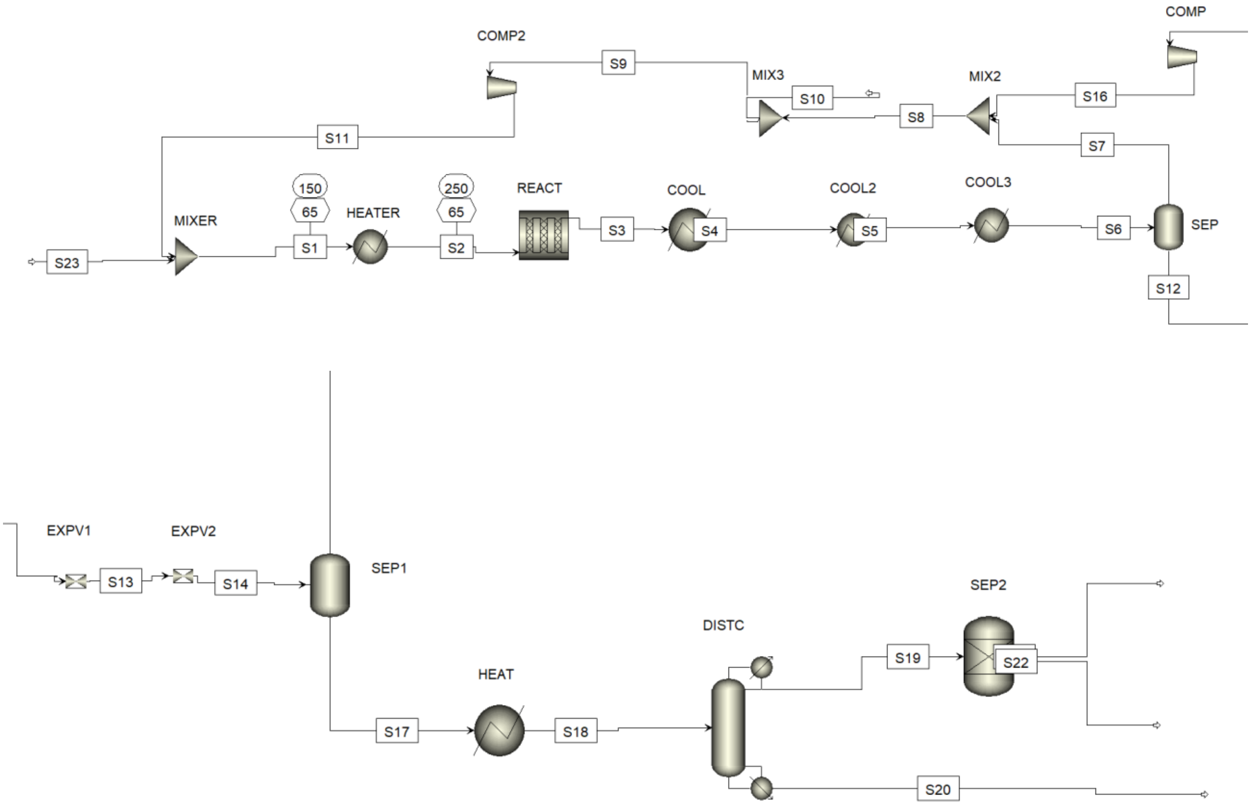


Figure 31. Aspen model for methanol synthesis

process description

the process is simple; the feeding stream containing the stoichiometric composition of CO2 and H2 with is about to enter the reactor. It undergoes two stages of heating to reach the temperature of the mixture to be suitable for the methanol synthesis reaction. Meanwhile, the pressure of the stream is controlled at the desired amount. The stream is fed to the reactor and the outlet stream is passing through three stages of cooling to reduce the temperature of the mixture.

Following the cooling section, the mixture enters a flash type separator in order to separate the inert gases from the liquid phase. The trace amount of gases in a recycle stream mixes with the inlet stream which helps to convert more percentage of the CO2/H2 mixture into methanol. The outlet liquid phase stream should be expanded to reduce the pressure, and again enters the second flash separator.

By splitting the residual amount of gas from the liquid mixture, the resulting liquid stream is sent to a distillation column to separate the water present in the mixture and methanol. By passing through a separator, the final result of methanol produced is available.

The major aspect of methanol synthesis is the choice of reactor model in Aspen plus. As there are some considerations regarding the methanol production based on the objective of the problem, it is necessary to satisfy the boundaries of the desired problem. Since the objective of this research is to model industrial-scale production of methanol, it is highly required to develop a proper model to approach the desired goal.

The selection of an appropriate reactor model is a fundamental step in process simulation, particularly for methanol synthesis from CO_2 and renewable hydrogen. Aspen Plus provides several reactor models, each based on different assumptions and levels of detail. The choice of reactor model directly influences the accuracy of the predicted performance, heat duty, conversion, and ultimately the techno-economic feasibility of the process. This section outlines the key reactor types available in Aspen Plus and discusses their relevance and suitability for simulating green methanol synthesis.

Given the objective of the current work, the RPlug reactor is the most appropriate choice. It provides a realistic representation of the industrial fixed-bed reactor used for methanol synthesis, enabling the integration of detailed kinetic models, thermal effects, and catalyst properties. It also supports the implementation of heat exchange and recycle loops, which are critical for achieving high conversion and process efficiency.

To represent the actual chemistry involved in methanol synthesis, the following three reactions should be included in the reactor model, even if the feed contains only CO_2 and H_2:

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \text{ (main synthesis reaction)}$$

$$CO + 2H_2 \rightleftharpoons CH_3OH \text{ (secondary synthesis pathway from in-situ CO)}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \text{ (reverse water-gas shift reaction, RWGS)}$$

The RWGS reaction produces CO as an intermediate, which can subsequently react with hydrogen to form additional methanol. Omitting the second reaction would lead to an underestimation of methanol yield and incorrect modeling of carbon flow within the system.

By incorporating these reactions using a kinetic model such as the Vanden Bussche & Froment (1996) LHHW formulation, the RPlug reactor can simulate the system with a high degree of accuracy. This approach will also allow for realistic estimation of reactor size, conversion efficiency, heat duty, and ultimately, production cost, essential elements for a reliable techno-economic analysis.

reactor design

For the specific purpose of methanol production from the CO2 contained streams of pulp and paper plant , it is required to size a reactor based on the specifications desired for the methanol synthesis.

There are two stages of specification set-up for reactor modelling. The first stage is to determine the thermodynamic conditions related to the reaction and the reactor, while the second stage is to specifically focus on the reaction kinetics and reaction determination. For the second stage, also, a catalyst is considered.

After component set-up in the property environment and method specification, the geometrical characteristics of the reactor should be determined. This is based on the fact that a specific value is desired for CO2 conversion and methanol yield, so the required dimensional characteristics like length, number and diameter of the tubes of the reactor should be set based on the mentioned parameters since these variables have a great impact on the performance of the reactor. These parameters influence both residence time and heat and mass transfer rates, which in turn determine the extent of reaction within the catalytic bed.

The total reactor volume, defined as the sum of the internal volumes of all catalytic tubes, determines the residence time of the reacting gas mixture inside the reactor. A longer residence time generally allows the reactions to proceed closer to equilibrium, thereby increasing both the CO_2 conversion and methanol yield per pass. In an RPlug reactor model, the volume is a critical parameter because the axial profiles of temperature, concentration, and reaction rate are computed along the reactor length.

However, due to the exothermic nature of methanol synthesis reactions, increasing the volume without adequate heat removal can lead to hot spots, which may reduce catalyst activity, favor reverse reactions (especially RWGS), and ultimately decrease selectivity. Thus, optimizing volume must be done in conjunction with heat management strategies.

The diameter and length of each reactor tube affect the axial dispersion and pressure drop within the reactor. Smaller diameters generally improve heat transfer but may result in higher pressure drops. Longer tubes increase residence time, allowing more complete conversion, but again raise the risk of non-uniform temperature profiles and catalyst deactivation if not properly cooled.

In industrial practice, tube diameters typically range from 1 to 2 inches (25 to 50 mm), while lengths vary between 5 and 10 meters. These dimensions strike a balance between achieving sufficient conversion and maintaining manageable pressure drops and heat transfer conditions.

The number of tubes in a multi-tubular reactor determines how the total catalyst volume is distributed across the system. For a fixed total reactor volume, increasing the number of tubes reduces the flow rate per tube, increasing residence time and enhancing conversion, but it also increases the heat transfer area and associated cost.

In Aspen Plus, the number of tubes can either be specified directly or computed automatically based on the total reactor volume and the geometry of individual tubes. The catalyst loading is typically expressed in terms of either total catalyst mass or catalyst volume per tube, and the choice directly affects the reaction rate through the kinetic expression.

Overall, based on the specific considerations related to our case study, the reactor design has been performed and the specific characteristics will be provided.

Results, analysis and discussion

In this chapter, the main results obtained from the simulations and modelling are presented. Techno-economic analysis also are discussed with a complete technical explanation. The focus is on evaluating the performance and feasibility of the integrated system for CO_2 capture using MEA, hydrogen production via electrolysis, and methanol synthesis through CO_2 hydrogenation.

The chapter begins with the validation of the base model for post-combustion carbon capture using monoethanolamine (MEA), comparing the simulation results with reference data from literature to ensure the reliability of the model. Following the validation, the model is scaled up to represent a larger industrial-scale case study, and the results of this up-scaling are analyzed in terms of process performance and energy requirements.

Subsequently, the hydrogen production process is introduced, with attention given to the electrolyzer performance and operating assumptions. The next section covers the methanol synthesis reactor, analyzing CO_2 conversion, methanol yield, and the influence of key operating parameters.

Finally, the techno-economic analysis (TEA) of the integrated system is presented, including capital and operational cost estimations, economic performance indicators, and sensitivity analyses. The discussion throughout the chapter aims to provide a critical interpretation of the results, identifying key trade-offs and highlighting the technical and economic implications of the proposed process configuration.

validation of the base model for carbon capture

In chapter 4, we provided a fully-detailed theoretical explanation framework about the basic model developed in Aspen plus for post-combustion carbon capture. The proposed model was based on the elementary aspects of post-combustion carbon capture modelling in Aspen plus as we desired first to obtain the primary understanding regarding the carbon capture process. At this point, the validation results of the model are presented. There have been previous works which utilized different experimental setups for validation of the model, and in this work, we also take advantage of one of the existing plants for validating our results.

In the literature, two case studies have been validated by the experimental results of the existing carbon capture plants. One is a laboratory-scale setup and the other one is called large-scale plant. It is worth mentioning that the procedure of the validation of the results is divided to verify the two vital components of the process, absorber and the stripper, separately. Therefore, the absorber of both laboratory-scale and large-scale plants are validated first and then the same procedure is applied to the stripper.

Validation of the absorber for both cases, the laboratory-scale and the large-scale, takes place by simulation of the basic model of the equipment in Aspen plus and then comparing the performance results with the considered case study. The differences among the models of laboratory-scale and the large-scale plants only exist in some geometrical specifications and the basic modelling criteria is fixed.

After following the model setup criteria, for validation of the developed model, the initial values for verification of the model are utilised from the laboratory-scale plant designed in the work of Tontiwachwuthikul et al. the main features related to the plant are reported in table 1.

In the reference experimental study of the post-combustion carbon capture plant, several measurements have been performed to record data of the operation of the plant. In this regard, for validation of our case, a specific experiment has been chosen to verify the results of the proposed model. The main data used for the validation of the model and process flow are interphase temperature profile between the liquid and gas phase confronting in the absorber and the CO2 vapor composition for the gas phase. In the experimental setup, each section is equipped with sensors for the measurement of the liquid temperature and the CO2 vapor composition in the gaseous phase.

Tables 1 and 2 are presenting the specifications for the experimental setup which also have been used to simulate the model developed in Aspen plus.

Table 1. column and packing features for the case study

Source	Tontiwachwuthikul et al.[45]
Packing height (m)	6.55
Column diameter (m)	0.1
Packing type	12.7 mm Berl Saddles
Void fraction ($\frac{m^3}{m^3}$)	0.62
Dry specific area ($\frac{m^2}{m^3}$)	465

Table 2. Feed characterization for the selected experiment

source		
Stream	Fluegas	Lean amine
Temperature (k)	288.15	292.15
Molar flow (mol/s)	0.14	1.04
CO2 (mol frac)	0.191	0
MEA (mol frac)	0	0.055
H2O (mol frac)	0.1	0.945
N2 (mol frac)	0.709	0
Pressure (kpa)	103.15	103.15

Based on the entry data of experimental setup, the process flow is simulated and the results are available. Since liquid temperature profile of the interface and CO2 vapor composition exist, the validation procedure will take place by the comparison of these two profiles. At this point, the validation for absorber of the laboratory-scale will be presented, and the rest of this section will elaborate on verification of the absorber for large-scale and stripper consequently.

Regarding the simulation criteria in Aspen plus, there are some parameters which contribute to the better understanding of the physics of the problem. Temperature bulge which is referred to a pronounced bulge in the temperature profile could be considered a symbol of validation for the absorber. Based on different configurations and simulations done on the absorber, this bulge occurs in different places in different absorber layouts.

Another vital parameter affecting the operation of the columns is the number of segments requested to be specified while determining the characteristics of the absorber and stripper. By setting up the basic details of the model, the main validation burden is on this parameter. As the rest of the settings are the same for all the configurations, the only variable which is responsible for following the experimental trend is this number of segments. To validate the model, we start with 20 segments and increase this value up to 90 segments to see which configuration is valid. The results are shown below.

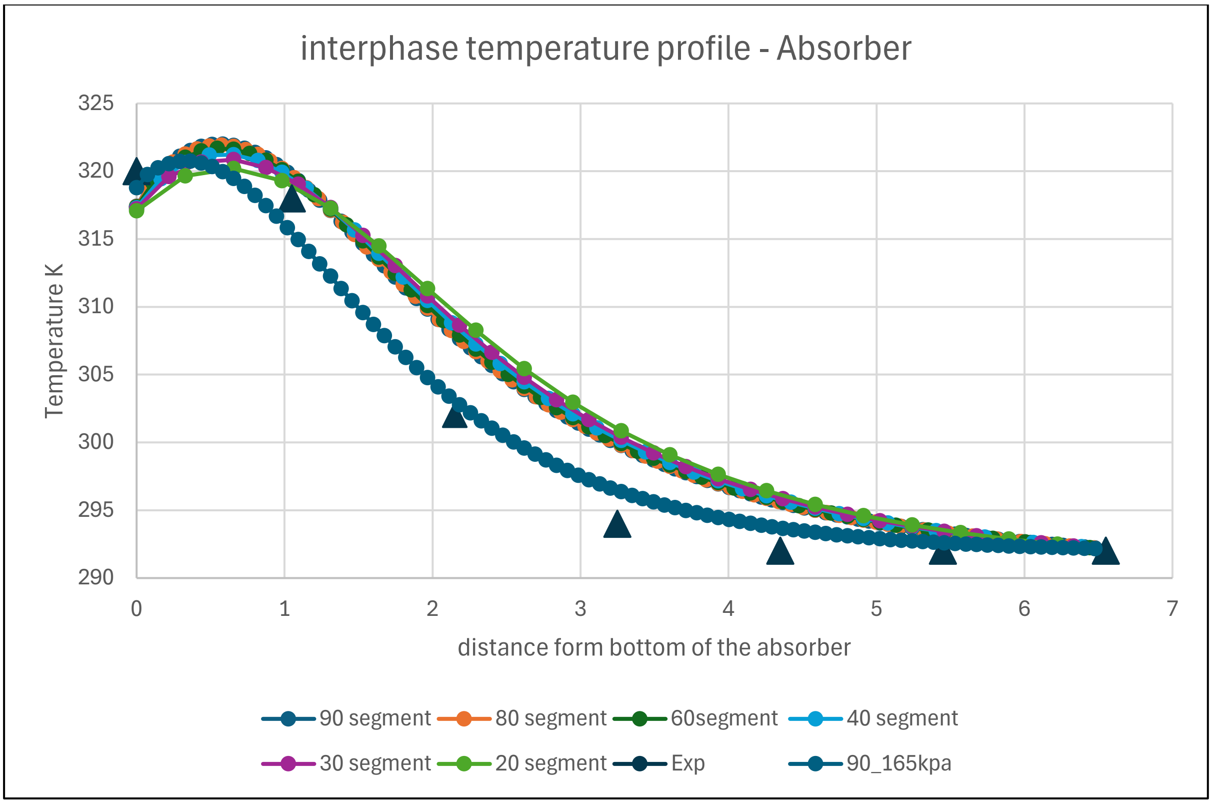


Figure 32. validation of Absorber results for laboratory-scale configuration

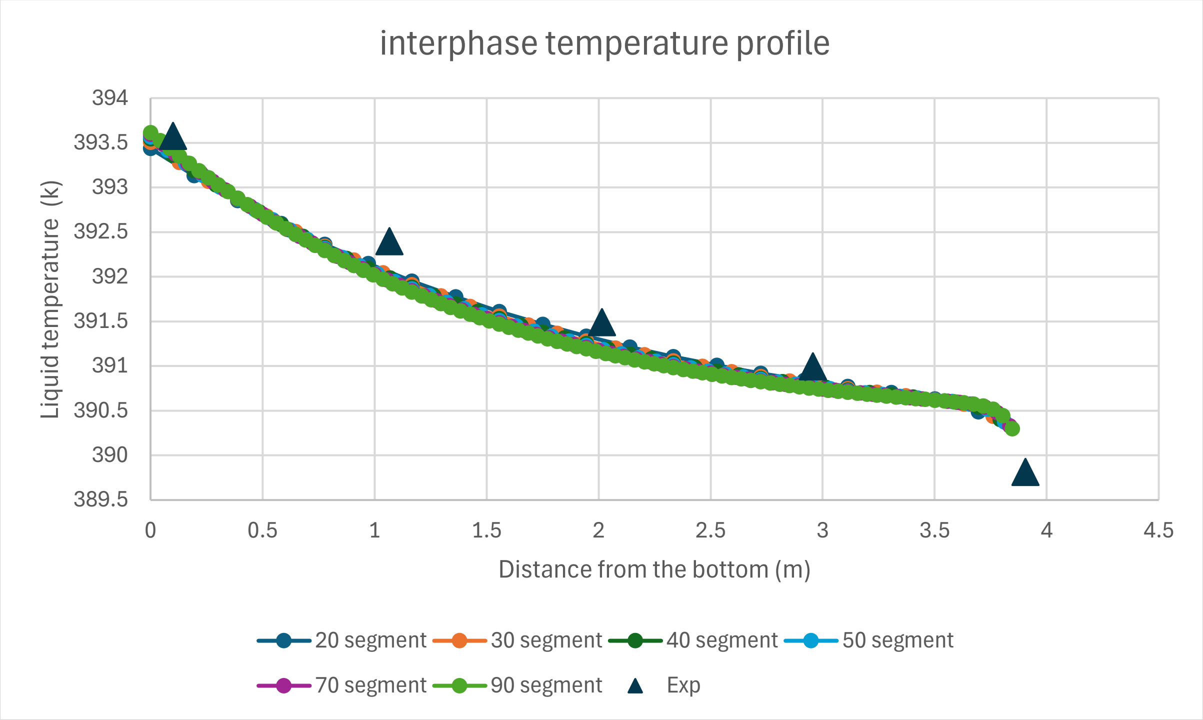


Figure 33. validation of stripper results for laboratory-scale configuration

Through a deep analysis, it can be understood that the temperature profile approaches the experimental data in higher number of segments. This observation is also valid for the previous validation tasks performed. Figure 32 is presenting the interphase temperature profile for the large-scale plant and in this case also, it can be seen that the higher number of segments is the most accurate approach for absorber segment. After determining the proper number of segments for the absorber, the same procedure is applied to the stripper which figure 33 shows this validation.

Both cases, laboratory-scale and large-scale, are considered for the validation. Step-by-step by increasing the number of segments, the validity of the results are checked. In this case also, by increasing the number of segments, interphase temperature profile shows a proper validity in high number of segments.

For the large-scale plant, the validation procedure is as the previous one. A case study has been considered and the model is developed based on the data provided by the experiments on that plant.

Table 3. column and packing features for the case study

Source	Razi et al[46]
Packing height (m)	17
Column diameter (m)	1.1
Packing type	Sulzer Mellapak 2X
Void fraction ($\frac{m^3}{m^3}$)	0.99
Dry specific area ($\frac{m^2}{m^3}$)	205

Table 4. Feed characterization for the selected experiment

source		
Stream	Fluegas	Lean amine
Temperature (k)	326.92	332.57
Molar flow (mol/s)	52.33	214.55
CO2 (mol frac)	0.12	0.0263
MEA (mol frac)	0	0.102
H2O (mol frac)	0.12	0.8717
N2 (mol frac)	0.76	0
Pressure (kpa)	106.391	101.325

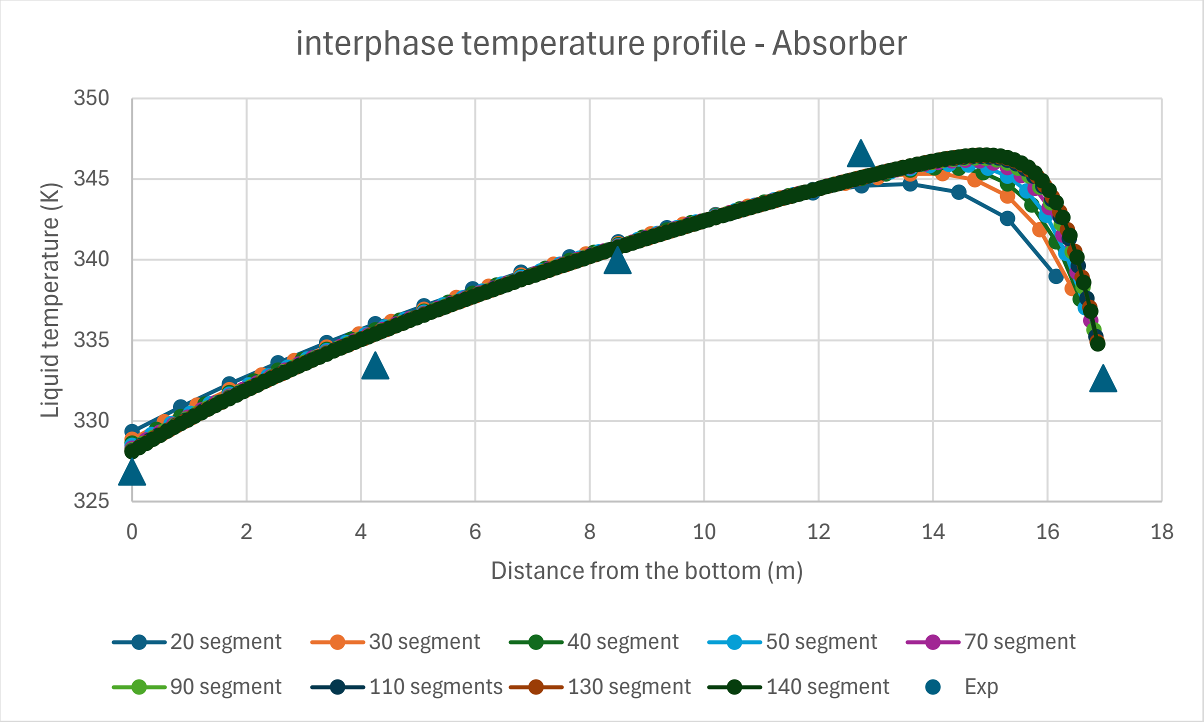


Figure 34. validation of Absorber results for large-scale configuration

There is a notable difference between the results of the laboratory-scale and the large-scale plants. Temperature bulge is near the bottom of the column in the laboratory-scale but it happens in the upper side of the large-scale column. This phenomena is backed up with the fact that laboratory-scale layout is a packed column with random packing structure but the large-scale one is shaped with structured packing. There is a specific theory behind this phenomena but we will not explain it in detail.

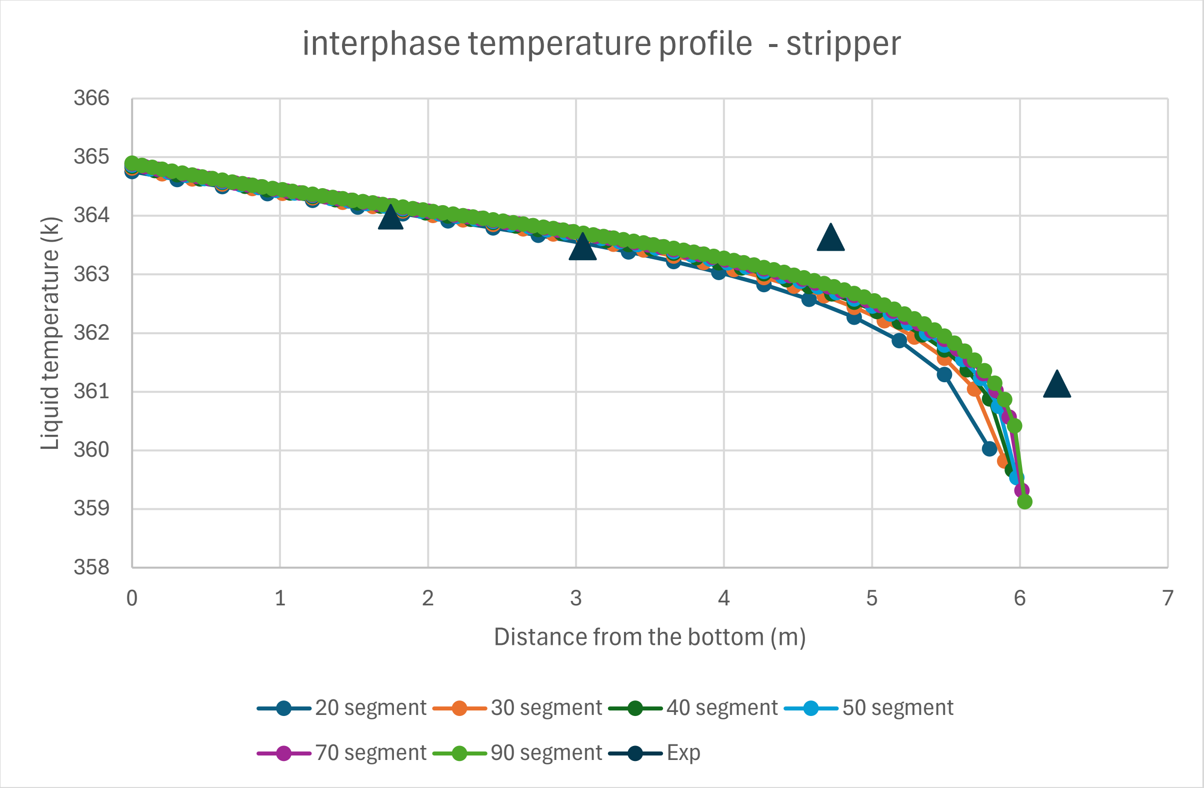


Figure 35. validation of stripper results for large-scale configuration

Built on the simulation work done on both models, it has been concluded that the developed model is valid to proceed with to utilize as our main model.

model up-scaling and performance evaluation

While the developed model in Aspen follows the basic aspects of post-combustion carbon capture procedure, to comply with the desired objective of our work, it is necessary to adjust the model in accordance with the case study considered. To do so, an overall understanding of the pulp and paper plant structure should be performed. Based on the process flow and streams involved in this plant, there are three exiting streams consisting of CO2 species. It is possible to conduct carbon capture on each stream but in that case, including equipment for capturing CO2, would be extremely costly.

The exiting streams containing CO2 from pulp and paper plant are mixed before entering the carbon capture section of the plant which is shown in figure . The characteristics of each stream are provided in the following table, and it should be noted that based on the thermodynamic conditions of the inlet stream, considering the degradation issue for solvent, a pre-cooling stage is provided to decrease the temperature of the inlet stream to the absorber.

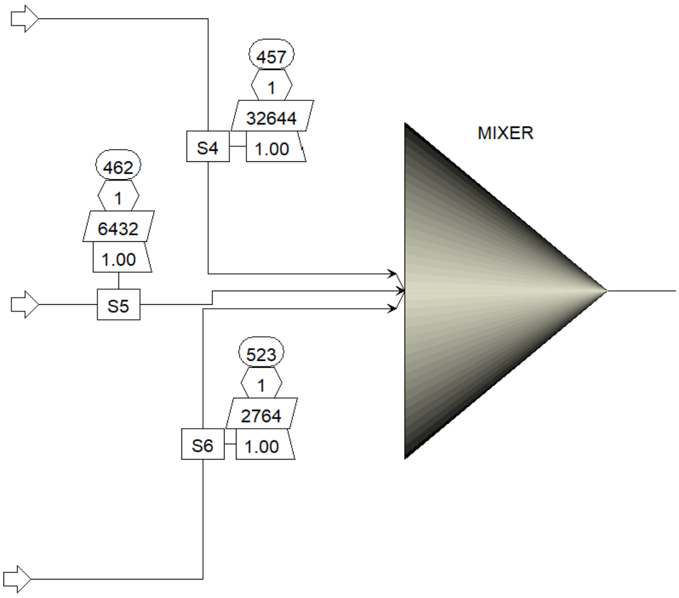


Figure 36. mixing of pulp and paper streams

for up-scaling the carbon capture plant, it is needed to redesign the equipment and size them based on the new characteristics we are dealing with. As it has been mentioned previously, there are two design strategies for sizing the absorber and the stripper, and based on this strategies, we size our equipment to operate properly in accordance to the desired plant.

Referring to the up-scaling, there had been some assumptions related to the thermodynamics and operating conditions of the plant in order to strictly follow the physical nature of the carbon capture. Thermodynamic conditions were kept constant. Chemical reactions are the same as before. The only differences are the size of the components and the modification related to the solvent mass flow rate to satisfy the carbon removal rate of 90%.

The results of the up-scaling of the carbon capture section is as follows:

Table 5. up-scaling characteristics of the plant

	absorber	stripper
diameter	11.27 m	10.99 m
height	20 m	10 m
Solvent flow rate	7.2 e6	----
Number of stages	100	100
Energy requirement for the reboiler	-----	355 MW

To ensure that the up-scaled model is valid, there is another way to check. It is possible to draw the interphase temperature trend and compare it with the basic trend applicable for large-scale plant.

Methanol Synthesis via CO_2 Hydrogenation

Following the preparation of captured CO2 for mixing with produced H2 through water electrolysis, the methanol synthesis section produces MeoH. The efficiency of conversion process is evaluated based on the captured CO2 and the methanol yield. Also, a specific ratio is defined representing the chemical power stored in the methanol based on the global electrical power. This ratio could be considered as a global efficiency for the methanol synthesis plant.

$$\gamma = \frac{produced\ kmol\ of\ methanol\ [\frac{kmol}{hr}]}{captured\ kmol\ of\ CO2\ [\frac{kmol}{hr}]} * 100$$

$$\varepsilon = \frac{chemical\ power\ of\ produced\ MeoH}{electrical\ power\ used\ in\ the\ process} * 100$$

Techno-Economic Analysis of the Integrated Process

As the final part of the research work done, in this section, the results of the techno-economic analysis for the methanol production are provided. As already stated, this evaluation is performed to determine the feasibility of the methanol production through the captured CO2 from pulp and paper industry. We aim at specifying the total cost of methanol production plant and the determination of levelized cost of methanol to figure out the economic feasibility of the initial capital, the operating and maintenance investment for the 20 years considered.

Techno-economic evaluation (TEE), also known as techno-economic analysis (TEA), is a systematic approach that integrates both technical and economic perspectives to assess the viability of a process, technology, or system. It serves as a critical tool in determining whether a given project is not only technically feasible but also economically sustainable and competitive in the market.

The core purpose of techno-economic evaluation is to provide a comprehensive understanding of the performance and cost-effectiveness of a technology. It helps identify key cost drivers, technical bottlenecks, and economic trade-offs, supporting informed decision-making for technology developers, investors, policymakers, and researchers. Additionally, TEE enables comparison among alternative technological pathways and plays a vital role in guiding research and development priorities.

A typical techno-economic evaluation consists of two main components: technical assessment and economic assessment.

The **technical assessment** focuses on evaluating the functionality and performance of the system or process. It involves designing and simulating the process using engineering tools (e.g., Aspen Plus), conducting mass and energy balances, analyzing equipment sizing and operating conditions, and estimating yields and efficiencies. The maturity level of the technology, often expressed in terms of Technology Readiness Level (TRL), is also considered.

The **economic assessment** involves estimating both capital and operating costs. Capital expenditure (CAPEX) includes costs associated with equipment, construction, and commissioning, while operating expenditure (OPEX) accounts for raw materials, energy, maintenance, labor, and utilities. In addition to cost estimation, the economic analysis calculates financial indicators such as Net Present Value (NPV), Internal Rate of Return (IRR), Payback Period, and Levelized Cost of Product (e.g., €/kg of methanol). These indicators help evaluate the profitability and financial attractiveness of the project.

Regarding the determination of the electricity cost needed by the plant, various renewable energy sources have been considered in different scenarios. Due to low amount of examples of large-scale constructed plant present into the world, and consequently due to even less information over this type of plant reported, the analysis performed is characterized by a quite elevated uncertainty. Furthermore, the public incentives for tons of CO2 avoided that the government should provide in order to cover part of the initial capital cost have been calculated.

For conducting the TEA, there is a need to specify some basic assumptions in order to proceed with the calculations. These input data are important as they are building the foundation of the techno-economic calculations. considered Project Life, the Operating Hours per year, the Basis Year and the expected Land are the parameters which should be considered first.

The main job of the procedure starts by determination of the Total Investment Cost (TIC) of the overall plant which is based on the evaluation of the cost element, called Bare Erected Cost (BEC). The BEC includes the cost of all the process equipment considered in the project.

After the definition of all costs of the considered components, the calculation continues with the definition of the main components of analysis, the capital expenditures (CAPEX) and operating expenses (OPEX) for the project. The elements of CAPEX and the OPEX have been evaluated mainly considering a percentage of the BEC or through considerations found in literature.

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

$$C_{i,year} = C_0 * (\frac{S_i}{S_0})^f \tag{11}$$

Where:

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

Starting from the reference erected costs $C0$ found in the various reference papers used for the calculation, $Ci\ ry$ are evaluated comparing the selected element with the reference element found in literature through a Scaling Factor that characterize the component. This relation is done through a Scale Factor (f) that depend on the considered component.

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

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

$$\frac{C_i}{C_{i_{ry}}} = \frac{I_i}{I_{i_{ry}}} \tag{12}$$

Where

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

CAPEX :

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

It includes the engineering services costs, project contingency costs, process contingency costs and the costs related of the instrumentation & control. The engineering services cost, which includes for example the process design and the project management, has been considered as 8,4% of BEC.

With the Process contingency has been taken into account the uncertainty in cost estimates associated with processes that do not have sufficient commercialisation history, and it has been considered as 20% of BEC, due to the low amount of information found in literature. The same considerations could be done for the project contingency that has been taken into account as 15% of the sum of BEC, engineering services cost and process contingency. The Instrumentation & control cost takes into account the necessary advice related to the control of the system has been evaluated as 5% of the Bare Erected Cost.

The sum of the BEC and of the engineering services costs, project contingency costs, process contingency costs and the costs related of the instrumentation & control forms the Total Purchasing Cost, (TPC). Furthermore, into the calculation of the CAPEX, other variables have been considered in order to take in account Owner's costs. These parameters are evaluated as percentage of the above calculated TPC. Where, in particular:

- Pre-production cost includes waste disposal cost for one month and an additional

term;

- Inventory capital takes into account the replacement parts;

- Financing cost covers the cost of securing financing (excluding interest during

construction);

- Other's owner cost including initial feasibility studies, local economic

improvement, construction of infrastructures, legal fees, permitting costs and

owner's engineering;

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

Table 6. basic assumptions for economic analysis

parameter	Value [% of TPC]
Pre-production	2
Inventory capital	0.5
Financing cost	2.7
Other owner's cost	15

The sum of these elements listed in the table above and of the TPC calculated before, represents the Total Overnight Cost, (TOC). The total results of the elements of the CAPEX will be reported.

OPEX:

The other component of the considered costs that should be taken into account in the methodology used for the economic analysis represents the operating and maintenance cost, considered in this work as OPEX.

This cost has been divided into two components:

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

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

Table 7. assumptions for OPEX

parameter	Value
Maintenance	2
Administrative and support labor	30
Insurance	1

Regarding the variable part of the OPEX, it includes the raw material and its replacement and the electricity needed by the plant. In this specific case, the following elements have been taken in consideration: the water, the electricity used by the electric components, the cold and hot utility expressed in MW necessary to guarantee the right conditions into the plant and the cost for the compensation of the loss of MEA that is expected during the project life.

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

Revenues:

In order to cover the investment required for the construction and the maintenance of the plant, it has been considered to sell the methanol, obviously being the objective of the plant, and also the oxygen, that is a product of the electrolysis. The prices of the oxygen has been found in literature and has been considered constant in the 25-years considered as project life. The considered price of the oxygen is 150€/ton which represents a typical market value.

As it has been anticipated in the description of the analysis, the goal of the study is to obtain a selling price of the methanol that guarantees to balance the Total Investment Cost. The calculated value will be reported in the next section. Furthermore, in this analysis it has been assumed to receive public incentives that are evaluated through the amount of tons of CO2 not released into the atmosphere. It is worth mentioning that due to the requirement of huge investments, as the size of the plant is large, incentives are an inevitable part of the process. The results of the analysis are reported in the following section.

Results

At this point, after performing the calculations regarding the techno-economic analysis, the results are presented. It is worth noting that at this stage only the levelized cost of methanol is calculated. The first stage of the calculations is to determine the costs of each component. Based on the obtained cost, Bare Erected Cost will be presented. The costs of each component is resented in the table below.

Table 8. equipment cost calculation

Component	Assumed Scaling Basis	Estimated Cost (k€)
Absorber	3534 m^3 (20 m height, 15 m Ø)	6307.8
Stripper	785 m^3 (10 m height, 10 m Ø)	2072.1
Reboiler	360 MW	643.5
Pump (CCU)	1 MW	377.3
Condenser	300 kW	4.5
Pump_H_2O	1 MW	377.3
Compressor H_2	200 kW	878.5
Compressor CO_2	100 kW	552.2
Methanol Column	1000 kg/h methanol	433.3
Comp. F2GC	100 kW	552.2
Comp. Recc	50 kW	347.0
Heat Exchanger	4 MW	442.4
PFR Reactor	30 t/day methanol	3014.3

Regarding the electrolyzer, in order to evaluate the cost of the component the data elaborated by Gamba have been used. So, it has been considered a specific cost for kW equal to 601€/kW that will be reported later. The results obtained in the Basis Years (Ci) taken in consideration in this work are showed in the table below, in which also the Bare Erected Cost is reported.

Table 9. BEC calculation

Category	Parameter	Value
Capital Costs	Updated Bare Equipment Cost (BEC)	€19.20 million
	Total Plant Cost (TPC)	€38.41 million
	Indirect Costs (13% of TPC)	€4.99 million
	Contingency (10% of TPC)	€3.84 million
	Total Capital Investment (TCI)	€47.24 million
Operating Costs	Annual OPEX (5% of TCI)	€2.36 million/year
Production	Annual Methanol Output	9,900 tonnes/year
Financial Parameters	Project Lifetime	20 years
	Discount Rate	8%
	Capital Recovery Factor (CRF)	0.1019
	Annualized CAPEX	€4.81 million/year
Final Result	Total Annual Cost (CAPEX + OPEX)	€7.17 million/year
	LCOM (€/ton methanol)	€725/ton

Regarding the CAPEX of the studied plant, the following results have been obtained. Where the value of the TPC represents the sum of the BEC and the elements of the Capital Cost. Furthermore, the TOC is the sum of the TPC and the elements of the Owner's cost. From this point, the results will be presented in Millions of Euro (M€) in order to make the calculation easily to understand.

Table 10. CAPEX calculation

CAPEX calculation		
BEC		45
Engineering services cost		4.05
process contingences		9
project contingences		6.75
instrumentation & control		2.25
total (TPC)		67.05

Table 11. owner’s costs

owner's cost		
pre-production		2.682
land		0.5
inventory capital		0.33525
financing cost		3.3525
other costs		10.0575
TOC		83.97725

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

Table 12. fixed OPEX calculations

fixed OPEX		annual cost (M€)	20 year cost
operating labour		1	20
maintanance		1	20
administrative		0.8	16
insurance		0.7	14
TOT			70

At this point, it is required to perform calculations based on the electricity price. The cost of electricity, as an element of variable OPEX, could be derived from different renewable sources, and this difference impacts the results significantly. For this case, as there was no such a limit for the source, electricity from solar photovoltaic systems could be considered. But, in general, we just considered a price that electricity from grid could be bought.

Table 13. variable OPEX

variable OPEX	quantity	unitary cost	annual	20 year cost
water	1.57	6	0.07554	1.5108
cold utility	1.81	7	0.35919	7.1838
Hot utility	1.14	6	0.19898	3.9796
MEA make-up	1.86	1.042	0.01555	0.311
TOT				12.9852

After the calculations regarding the amount of electricity required by the electric components of the plant, the annual quantity necessary in kWh has been evaluated. Basing the calculation on average data found in literature, the obtained cost is available. As the final calculation, it is possible to determine the Total Investment Cost (TIC).

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

The calculation has been carried out considering a fixed selling price of the oxygen equal to 250€/ton. This assumption allows to evaluate the total revenues that the oxygen sold in 20–years can provide, i.e. 40,65 M€.

Taking into account to cover the residual part of the TIC with the selling of the methanol without any public incentives, the following Cost of Products (COP) have been obtained. It is worth to underline that they have been considered constant over the 20-years of the operation time of plant.

Based on the developed techno-economic model, a reference value for the cost of methanol production has been obtained under current assumptions regarding process performance, equipment costs, and energy prices. This value serves as a representative baseline, providing insight into the economic feasibility of the integrated CO_2-to-methanol pathway. While the present analysis focuses on a single set of input parameters, further exploration through sensitivity analysis, such as evaluating alternative cost scenarios or policy conditions, can offer a deeper understanding of the system's robustness and potential for improvement.

Capital costs were initially estimated at the equipment level using scaling laws, adjusting reference costs obtained from literature according to equipment size and capacity. The Bare Equipment Cost (BEC) was estimated at approximately €16.0 million based on historical data from 2016. To reflect 2024 cost levels, the Chemical Engineering Plant Cost Index (CEPCI) was used to update costs, with CEPCI rising from 541.7 (2016) to 650.2 (2024). This adjustment resulted in an updated BEC of approximately €19.2 million.

The Total Plant Cost (TPC) was calculated by applying an installation factor of 2.0, accounting for equipment erection, piping, instrumentation, and other direct construction costs. Indirect costs—including engineering, legal, and construction management—were estimated at 13% of the TPC. A contingency factor of 10% was then applied to cover uncertainties and potential cost overruns. Collectively, these factors yielded a Total Capital Investment (TCI) of approximately €47.2 million.

Operating and Production Assumptions

Operating expenses (OPEX) were estimated at 5% of the TCI, corresponding to an annual OPEX of approximately €2.36 million. The plant operation was assumed to be 330 days per year, producing 30 tonnes of methanol per day, which corresponds to an annual methanol output of 9,900 tonnes.

Financial Parameters and Levelized Cost Calculation

The Capital Recovery Factor (CRF) was calculated using a discount rate of 8% and a plant lifetime of 20 years, resulting in a CRF value of 0.1019. This was used to annualize the capital costs, yielding an annualized CAPEX of approximately €4.81 million per year. The total annual cost—sum of annualized CAPEX and OPEX—was thus approximately €7.17 million.

The Levelized Cost of Methanol (LCOM) was then calculated by dividing the total annual cost by the annual methanol production, resulting in: LCOM≈725€/tonne

Discussion and Perspective

The estimated LCOM of €725 per tonne aligns with the upper range of reported costs for green methanol production, which typically exceeds that of conventional fossil-based methanol, usually ranging between €200 and €400 per tonne depending on market conditions. This cost premium is primarily attributable to the high capital intensity of renewable hydrogen production via electrolyzers, the energy demands of CO_2 capture, and the relative immaturity of the integrated technology.

It should be noted that this analysis assumes constant prices and operational parameters throughout the plant's lifetime and does not consider revenues from byproducts such as oxygen or possible financial incentives for carbon mitigation. Incorporation of such factors could significantly improve economic viability. Furthermore, future work should include sensitivity analyses to investigate the impacts of key parameters—such as electricity cost, plant capacity factor, and methanol market prices—on overall project feasibility.

Nowadays, the average price of the methanol available in the market is equal to 283€/ton, the obtained price of the methanol are much higher than the actual selling price. However, the price of the methanol is expected to raise in the next years considering an increase of the methanol demand.

The market price of methanol varies depending on its production route, geographic region, and market conditions. As of recent data (2024–2025), the price of conventional methanol—primarily produced from natural gas or coal—ranges between €300 and €450 per tonne in Europe and globally, with regional fluctuations due to feedstock costs, demand, and logistics.

In contrast, green methanol, which is synthesized using captured CO_2 and renewable hydrogen, carries a significantly higher production cost and market price due to the current capital intensity and energy requirements of electrolysis and carbon capture. According to several techno-economic studies and market reports, the price of green methanol typically falls in the range of €800 to €1,500 per tonne, depending on assumptions about electricity price, electrolyzer efficiency, CO_2 capture cost, and scale.

This elevated price reflects both the premium associated with low-carbon fuels and the immaturity of large-scale production infrastructure. However, increasing policy support, carbon pricing mechanisms, and demand from shipping and chemical sectors are gradually improving the market outlook for green methanol. For this reason, in this analysis it has been assumed a quite fixed selling price of the methanol.

For calculation of LCOM, it is required to determine NPV.

$$NPC = CAPEX_0 + \sum_{J=1}^{n} [\frac{OPEX_j}{(1+d)^j} + \frac{RC_j}{(1+d)^j}]$$

Where:

- *n=20* is the analysis period, in years;
- d is the corrected discount rate (considering an expected inflation rate);
- $CAPEX_0$ represents the capital expenditures due to the investments done at the beginning of the analysis period;
- $OPEX_j$ represents the cost of the operational phase in the j-th year. It accounts for the maintenance of the plant as well as all the expenditures necessary during the year;
- RC_j accounts for the replacement cost as periodically it is necessary a periodic substitution of components to maintain reliable the operation of the system.

The discount rate variable, d, extends the economic analysis to the entire life of the plant and it can be calculated through an economic formulation used in reference. In this way it is possible to determine any future cost at the present value.

$$d = \frac{d' - ir}{1 + ir}$$

Where:

- d'is the nominal discount rate, assumed equal to 7%;

- ir corresponds to inflation rate, equal to 2%

Such that the real discount rate is 5%.

Another hypothesis that has to be fixed is the capacity factor of the plant, defined as the ratio between the operating hours of the system and the total yearly hours:

$$CF = \frac{working\ hours}{8760}$$

For the analysis, a CF equal to 90% is fixed, so the total working hours of the plant are 7884. This ratio is important for assessing the total production of SNG as well as the consumption of fuels and the frequency of substitutions.

In the Operating Expenditure are included all the cost for activities that occur once the system starts to operate. In particular, the following expenditures are considered:

- Electrolyzer Operation and maintenance costs: the general maintenance cost is fixed from 4- 5% of the total CAPEX per year, reaching a value of 53625€ ;

- Replacement stack cost: the stack replacement is fixed to the 30% of the total investment cost and the substitution is performed every 6 years with a cost of 321750€;

- Methanation Operation and maintenance costs: maintenance cost is fixed at 10% of the total CAPEX per year, reaching a value of 100915,2€. This value includes also include costs

for catalyst replacement;

- Labour cost: 120.000 € per year obtained for 4 workers.

- The expenditure relating to electricity depend on plant utilization. Electricity is used to run both AWE and methanation sections, and its cost is fixed to 50 €/MWh. For the electrolyzer and the methanation, the electricity cost is 281853€ and 179361€ respectively.

at the values equal to 400, 600, 800€/ton. In these considered cases, the remaining part of the TIC has been considered to be covered by the public incentives calculated as a price for tons of CO2 not released into the atmosphere.

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

$$LCOM = \frac{NPC}{\sum_{J=1}^{n} \frac{SNG\ produced_J}{(1+d)^j}}$$

From the techno-economic evaluation carried out, it becomes evident that, under current market and technological conditions, the integrated system for methanol synthesis from captured CO_2 and renewable hydrogen presents limited economic attractiveness. While the analysis follows a simplified yet consistent methodology, key cost drivers such as the electrolyzer and the CO_2 capture unit—particularly the absorber and stripper columns, significantly increase the Bare Erected Cost (BEC), which subsequently elevates the Total Capital Investment.

Moreover, the high energy demand associated with water electrolysis and solvent regeneration further burdens the operating expenditure, highlighting the substantial impact of energy consumption on the overall feasibility of the process. These factors combined restrict the competitiveness of such configurations, especially when compared to conventional methanol production routes.

As reflected in the economic indicators, favorable outcomes largely depend on optimistic scenarios, such as a substantial rise in methanol market prices or the availability of considerable public incentives. In the most promising case examined, economic viability could only be achieved if methanol prices doubled over the project lifetime and public subsidies reached levels around 40 million euros. It's important to note that all economic assumptions—such as feedstock cost, electricity price, and product value—were considered constant over a 25-year project horizon, with the primary objective being investment recovery rather than profit generation.

Nonetheless, in view of potential advancements in electrolyzer efficiency, declining costs of renewable electricity, and stronger policy support for CO_2 utilization technologies, the deployment of methanol synthesis systems based on carbon capture and green hydrogen could become a viable pathway within a future decarbonized economy.

Conclusion and future works

At the final point, This chapter concludes the work carried out in this thesis, which focused on the techno-economic analysis of CO_2 capture from industrial sources and its subsequent hydrogenation with renewable hydrogen for the production of methanol. The study involved the development and validation of process models in Aspen Plus for CO_2 capture using MEA, hydrogen production through electrolysis, and methanol synthesis, followed by a comprehensive techno-economic evaluation of the integrated system. In this final chapter, the main findings are summarized, key conclusions are drawn, the contributions and limitations of the study are discussed, and recommendations for future research are proposed to support further advancement in sustainable fuel production and industrial decarbonization.

research highlights

Overall, this thesis aimed at moving toward zero-emissions and addressing critical issues we are dealing with these days. Specifically, the aim of this research was to evaluate the feasibility of methanol production from pulp and paper industry through methanol synthesis through CO2 captured and renewable hydrogen production. biogenic CO_2 emissions are considered part of the natural carbon cycle, since the carbon was recently absorbed from the atmosphere by plants during photosynthesis.

Despite this difference, biogenic CO_2 emissions can be substantial—particularly in sectors like waste-to-energy, biomass combustion, pulp and paper production, and bioethanol manufacturing. Therefore, as decarbonization efforts intensify across all sectors, it is increasingly important to address biogenic CO_2 alongside fossil-derived emissions.

Capturing CO_2 from biogenic sources is not only technically feasible but also strategically significant. When coupled with permanent storage or utilization pathways, such as geological sequestration or conversion into fuels and chemicals, carbon dioxide removal (CDR) can be achieved. In this way, biogenic CO_2 capture transforms into a negative emissions strategy, actively reducing atmospheric CO_2 concentrations. This makes it a vital component in climate mitigation pathways, especially in scenarios aiming to limit global warming to 1.5°C or 2°C.

Carbon capture strategy utilized in this work was based on post-combustion carbon capture through liquid absorption with MEA, as it has been proved to be the state-of-the-art technology for this procedure. The model of CCU part has been successfully validated comparing the data found in literature for the considered plant with the ones obtained from the model, in terms of specific energy requirement, CO2 removal rate and L/G ratio.

The complete model has been described through the specific energy requirement, the CO2 removal rate and the energy efficiency of the plant. In particular, considering to reach a removal rate equal to 90%, a value of specific energy requirement 4,15 GJ/tCO2, that is a consistent with the other data found in literature concerning this type of process.

Finally, an economic analysis based on simplified considerations has been done with the aim of evaluating the economic feasibility of the plant and to underline the critical issues of the process. It is obvious that this concept, CCU, represents one of the possible options in order to reach a net reduction of CO2 emissions, thus contributing to climate change mitigation.

As this work followed the concept of CCU, the other objective was to produce methanol

Key Conclusions

As evidenced by the results obtained, there is a clear need for further research and optimization of integrated CO_2 capture and utilization (CCU) systems, particularly in sectors such as the pulp and paper industry, which emit significant amounts of biogenic CO_2. While biogenic emissions are often considered carbon-neutral, capturing and converting this CO_2 into value-added products such as methanol offers the potential for carbon-negative pathways, making these systems especially attractive in the context of climate change mitigation.

One of the major limitations identified is the high energy requirement for solvent regeneration in the post-combustion capture process using monoethanolamine (MEA). The thermal duty of the reboiler constitutes a significant portion of the operating costs and directly impacts the overall process efficiency. Further improvements in solvent formulation, heat integration, and column design are crucial to reducing this energy penalty.

The system was evaluated assuming full reliance on renewable electricity, primarily sourced from solar or wind power, to ensure a net-zero operational footprint. This renewable energy is primarily consumed in the hydrogen production unit via water electrolysis, which is both capital- and energy-intensive. Although electrolyzer costs are expected to decline due to technological advancement and scale-up, they currently represent a major share of the total investment cost.

From a techno-economic standpoint, the integration of CO_2 capture, hydrogen production, and methanol synthesis results in high capital expenditures (CAPEX)—driven by the electrolyzer, capture columns, heat exchangers, and reactor units—as well as high operating expenditures (OPEX), largely associated with electricity consumption and solvent make-up. The levelized cost of methanol produced through this route was found to be substantially higher than the prevailing market price, reinforcing similar findings in recent literature.

However, policy mechanisms such as carbon pricing, subsidies, or incentives for avoided emissions (€/tCO_2) can significantly improve the project's financial viability. Moreover, the increasing demand for low-carbon fuels and chemicals, combined with anticipated future methanol price increases driven by a shift toward e-methanol in shipping and chemical sectors, could further support economic justification.

In conclusion, while the integration of post-combustion CO_2 capture from biogenic sources with renewable hydrogen-based methanol synthesis represents a technically feasible and environmentally compelling route, the current economic landscape necessitates further process optimization and external support mechanisms.

Advancements in capture efficiency, electrolyzer performance, and renewable energy integration, alongside supportive policy frameworks, are essential to enabling large-scale deployment and contributing meaningfully to industrial decarbonization and circular carbon economy objectives.

Contribution to the Field

This thesis contributes to the ongoing research and development efforts in the field of industrial decarbonization by focusing on the integration of post-combustion CO_2 capture with renewable hydrogen-based methanol synthesis, specifically applied to the pulp and paper industry. The key contributions are as follows:

- It addresses the underexplored potential of biogenic CO_2 capture in the pulp and paper sector, highlighting its role in enabling carbon-negative pathways through utilization and permanent removal.
- A comprehensive Aspen Plus® process model was developed for the post-combustion CO_2 capture system using MEA, validated against literature data, and adapted to suit the specific characteristics of biogenic flue gas.
- The thesis presents a detailed techno-economic analysis (TEA) of the full value chain—from CO_2 capture to renewable hydrogen production and methanol synthesis—offering insights into cost structures, key economic drivers, and integration challenges.
- Renewable electricity assumptions were integrated throughout the system to align with net-zero emissions targets, providing a realistic framework for assessing future energy scenarios.
- The work supports decision-making for future investments and research by quantifying the levelized cost of methanol, identifying required policy support (€/tCO_2 avoided), and proposing optimization strategies.

This study therefore provides both methodological and strategic value to the research community and industry stakeholders working on Power-to-X, CCU, and the decarbonization of biomass-based industrial sectors.

Limitations of the Study

While this study provides valuable insights into the integration of post-combustion CO_2 capture and renewable hydrogen-based methanol synthesis in the pulp and paper industry, certain limitations must be acknowledged:

- Limited Availability of Industrial Data: One of the key challenges encountered in this work was the limited number of pulp and paper plants with publicly available or detailed operational data. This constrained the ability to generalize the results or calibrate the model based on multiple case studies. The simulation and techno-economic analysis were therefore based on a single representative plant configuration, which may not fully capture the diversity of real-world installations.
- Assumptions in Process Modeling: The Aspen Plus® models rely on a number of simplifications, such as idealized absorber/stripper performance, fixed stage numbers, and default thermodynamic property methods. While efforts were made to validate the model with literature data, uncertainties remain due to assumptions on heat integration, pressure drops, and solvent degradation, which are difficult to capture precisely without plant-scale measurements.
- Fixed Operating Conditions: The study focuses on steady-state operation and does not account for dynamic or off-design conditions, which are critical in industrial settings, especially when dealing with intermittent renewable energy sources or load variability in the plant.
- Hydrogen Supply Assumptions: The analysis assumes continuous and reliable access to renewable hydrogen at specific purity and pressure levels. In practice, variability in renewable electricity supply and electrolyzer operation can impact hydrogen availability, system flexibility, and storage requirements, which were not explicitly modeled.
- Economic Input Uncertainty: The techno-economic analysis depends on cost assumptions that are time- and location-sensitive (e.g., electrolyzer CAPEX, electricity price, methanol selling price). While sensitivity analyses were performed, fluctuations in market conditions or technology maturity could significantly affect the results.
- Exclusion of Lifecycle and Environmental Impacts: Although the study discusses CO_2 avoidance and the use of renewable electricity, a full life cycle assessment (LCA) was not conducted. Potential environmental trade-offs, such as upstream

emissions from material inputs or end-of-life impacts, were therefore not addressed.

These limitations suggest that while the conclusions are indicative and meaningful, they should be interpreted within the context of the defined system boundaries and assumptions. Future studies involving more diverse case studies, detailed process dynamics, and real-time data from pilot or commercial facilities would help to strengthen the findings and enhance their applicability.

Recommendations for Future Work

While this work attempts a techno-economic evaluation of integrating post-combustion CO_2 capture with renewable hydrogen-based methanol synthesis in the pulp and paper industry, several areas remain open for further investigation. Future work can build upon the current findings to enhance process performance, economic feasibility, and environmental sustainability. The following suggestions are proposed:

- Evaluate alternative solvents (e.g., blended amines or phase-change solvents) to reduce regeneration energy and improve long-term solvent stability over MEA.
- Investigate advanced heat integration strategies to recover and reuse waste heat within the system, particularly from the pulp and paper process, to lower the reboiler duty.
- Extend the process model to dynamic and off-design operation, accounting for load variations and transient behavior in real industrial settings.
- Analyze the use of next-generation electrolyzers, such as solid oxide or high-efficiency PEM systems, to reduce energy demand and investment costs.
- Study the integration of variable renewable energy sources, such as solar or wind, and assess their impact on electrolyzer sizing, hydrogen storage, and system reliability.
- Explore alternative CO_2 utilization pathways, such as the production of dimethyl ether or synthetic fuels, based on regional market needs and infrastructure readiness.
- Assess the influence of catalyst types and operating conditions on methanol synthesis efficiency, reactor stability, and by-product formation.

- Conduct scenario-based techno-economic analyses, incorporating future projections for hydrogen prices, methanol market values, and carbon pricing policies.
- Evaluate the role of public incentives and carbon credit mechanisms in improving the economic feasibility of e-methanol production from biogenic CO_2.
- Perform life cycle assessment (LCA) to quantify the environmental benefits and potential trade-offs of the integrated system compared to conventional methanol production.
- Extend the methodology to other biogenic CO_2-emitting sectors, such as bioethanol production or biogas upgrading, to examine broader industrial applicability.
- Investigate multi-product configurations, enabling co-production of methanol and other value-added chemicals or integration with carbon storage for enhanced climate benefits.

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