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Systematic comparative analysis of carbon dioxide storage and utilization technologies

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Nomenclature

Main symbols

A	activity included in system boundaries,
C	cost,
E	form of energy (chemical or electrical),
e_{CO2}	specific CO_2 emissions,
f	cumulative consumption factor, function,
F	flowrate,
$\dot{m}$	mass flowrate
P	electric power,
r	discount rate,
S	unit capacity,
q	unit energy consumption (requirement),
Q	final energy consumption,
x	extend, conversion,
η	efficiency,

Indexes

$*$	cumulative,
av	avoided
calc	calcination,
carb	carbonation
CCUS	relates to CCUS installation,
ch	chemical,
clk	clinker,
conv	conversion,
dir	direct,
el	electrical,
eq	equivalent,
gross	gross,
in	inlet, input,
indir	indirect,
mol	molar,
net	net
out	outlet, output,
REF	reference,
vol	volumetric,

Abbreviations

AF	alternative fuels,
BAT	best available technology,
BEC	bare erected cost,
BECCS	bioenergy with CCS,
CAC	cost of CO_2 avoided,
CaL	calcium-looping,
CAPEX	capital expenditures,
CCUS	carbon capture and storage or utilization,
CDR	carbon removal technologies,

CEC	cumulative energy consumption,
CEPCI	chemical engineering plant cost index,
CPU	compression and purification unit,
CRF	capital recovery factor,
DAC	direct air capture,
DME	dimethyl ether,
EGS	enhanced geothermal systems,
EF	emission factor,
EOR	enhanced oil recovery,
EPCC	engineering, procurement, and construction cost,
EU ETS	European Union Emissions Trading System,
FOM	fixed, annual operating and maintenance costs,
FU	functional unit,
GHG	greenhouse gas,
HDR	hot dry rock,
LCA	life cycle assessment,
LCI	life cycle inventory,
LHV	lower heating value,
LULUCF	land use, land use change and forestry,
MEA	monoethanolamine,
MSP	minimum selling price,
MTA	methanol-to-aromatics,
MTO	methanol-to-olefins,
NET	negative emission technologies,
NETL	National Energy Technology Laboratory,
NGCC	natural gas combined cycle,
OPEX	operational expenditures,
PC	pulverized coal,
PSA	pressure swing adsorption,
SPECCA	specific primary energy consumption per electricity avoided,
TEG	triethylene glycol,
TOC	total overnight capital,
TPC	total plant cost,
TRL	technology readiness level,
VOM	variable, annual operating and maintenance.

Abstract

In recent years, carbon capture, utilization, and storage (CCUS) technologies have attracted growing attention across power as well as industrial sectors where substantial reductions in carbon dioxide (CO_2) emissions are otherwise technologically unfeasible, unavailable, or economically prohibitive. This trend is primarily driven by the need to cut CO_2 emissions to mitigate global warming and achieve the target of limiting global average temperature rise to below 2°C by 2050. In response, European countries have revised their climate policies, transitioned towards decarbonized economies, and introduced low-emission development strategies. As these technologies scale up, CCUS is expected to play a pivotal role in achieving climate targets and delivering significant environmental benefits. However, a key challenge associated with CCUS deployment lies in the effective storage and utilization pathways for the captured CO_2 within whole technology chain. This doctoral thesis presents a comprehensive assessment of carbon capture, utilization, and storage technological routes under Polish conditions, integrating process modelling, techno-economic assessment (TEA), and life cycle assessment (LCA) by quantifying key performance indicators such as cumulative energy consumption, specific primary energy consumption per CO_2 avoided, cost of CO_2 avoided, and carbon footprint. The main objective is to evaluate the technical, economic, and environmental performance of CCS and CCU chains based on different CO_2 sources, including coal-, natural gas- and biomass-fired power plants, cement production using two representative capture technologies: amine absorption (MEA) and calcium looping (CaL) as well as direct air capture (DAC) system with solid sorbent. The analysis covers key stages of the CCUS chain: capture, conditioning, compression, transport, and either geological storage, or utilization configurations such as chemicals, synthetic fuels, urea production, mineralization, enhanced oil recovery and enhanced geothermal systems to provide a broader overview of identified options. Results indicate that CCS remains the most effective strategy for large-scale and stable emission reductions in Poland, particularly for concentrated CO_2 streams such as from cement production. CaL integrated with cement kilns shows lower specific energy demand and cost compared to MEA, which leads to lower energy penalties when deployed in power generation systems. Based on conducted study, direct air capture technology, due to its high costs and substantial electricity requirements, is currently not a viable option under Polish conditions, as the strongly fossil-based electricity mix undermines their environmental effectiveness and significantly limits their overall climate mitigation potential. Utilization pathways are economically and environmentally viable only under specific conditions, such as low-carbon electricity supply or availability of green hydrogen supply. Utilization of CO_2 without its chemical conversion offers clear advantages over conversion-based pathways, as it is characterized by significantly lower energy demand and unit costs, while also providing a higher potential for permanent carbon storage within the final product.

Streszczenie

W ostatnich latach technologie wychwytu, utylizacji i składowania dwutlenku węgla (CCUS) zyskują na znaczeniu w sektorach energetycznym i przemysłowym, zwłaszcza tam, gdzie głęboka redukcja emisji CO_2 jest technicznie niemożliwa lub ekonomicznie nieopłacalna. Wynika to z potrzeby ograniczenia emisji w celu złagodzenia skutków globalnego ocieplenia i utrzymania wzrostu średniej temperatury poniżej 2°C do 2050 r. W odpowiedzi na te wyzwania kraje europejskie wdrażają działania dekarbonizacyjne, a dalszy rozwój technologii CCUS ma kluczowe znaczenie dla realizacji celów klimatycznych i osiągnięcia istotnych korzyści środowiskowych. Głównym wyzwaniem związanym z wdrożeniem CCUS pozostaje skuteczne składowanie lub gospodarcze wykorzystanie wychwyconego CO_2. Niniejsza praca doktorska przedstawia kompleksową ocenę tych technologii w warunkach polskich, łącząc modelowanie procesowe z analizą techno-ekonomiczną (TEA) i oceną pełnego cyklu życia (LCA) w celu określenia kluczowych wskaźników efektywności, takich jak skumulowane zużycie energii, zużycie energii pierwotnej, koszt uniknięcia emisji CO_2 czy ślad węglowy. Naczelnym celem jest ocena wydajności technicznej, ekonomicznej i środowiskowej łańcuchów CCS i CCU w oparciu o różne źródła CO_2, w tym elektrownie opalane węglem, gazem ziemnym i biomasą oraz cementownię, z wykorzystaniem dwóch technologii wychwytu: absorpcji aminowej (MEA) i pętli wapniowej (CaL), a także wariant bezpośredniego wychwytywania CO_2 z powietrza (DAC) z użyciem stałego sorbentu. Analiza obejmuje kluczowe etapy łańcucha CCUS tj. wychwyt, kondycjonowanie, sprężanie, transport oraz składowanie geologiczne lub różne konfiguracje utylizacji, takie jak produkcja chemikaliów, paliw syntetycznych, mocznika, mineralizacja, wspomagane wydobycie ropy naftowej i wspomagane systemy geotermalne. Wyniki wskazują, że CCS pozostaje najskuteczniejszą strategią dla stabilnej redukcji emisji na dużą skalę w Polsce, szczególnie w przypadku skoncentrowanych strumieni CO_2, takich jak te pochodzące z produkcji cementu. Pętla wapniowa zintegrowana z piecami cementowymi wykazuje niższe zapotrzebowanie na energię i niższe koszty w porównaniu z układem aminowym, który z kolei osiąga mniejsze spadki sprawności wytworzenia energii elektrycznej w przypadku zastosowania w elektrowniach. Na podstawie przeprowadzonych badań stwierdzono, że technologia bezpośredniego wychwytu dwutlenku węgla z powietrza, ze względu na wysokie koszty i znaczne zapotrzebowanie na energię elektryczną, nie jest obecnie opłacalną opcją w warunkach polskich, ponieważ silnie oparty na paliwach kopalnych mix energetyczny podważa jej skuteczność środowiskową i znacznie ogranicza ogólny potencjał w zakresie łagodzenia zmian klimatu. Ponadto, ścieżki gospodarczego wykorzystania CO_2 są ekonomicznie i ekologicznie opłacalne tylko w określonych warunkach, takich jak dostęp do niskoemisyjnej energii elektrycznej lub dostaw zielonego wodoru. Wykorzystanie CO_2 bez jego chemicznej konwersji ma wyraźną przewagę nad ścieżkami opartymi na konwersji, ponieważ charakteryzuje się znacznie niższą energochłonnością i mniejszymi kosztami jednostkowymi, a jednocześnie zapewnia większy potencjał trwałego składowania CO_2 w produkcie końcowym.

1. Introduction

The goal of limiting global warming to no more than 2°C above pre-industrial levels was first recognized under the United Nations Framework Convention on Climate Change (UNFCCC) process and later strengthened and signed in the Paris Agreement in 2015, where Parties further agreed to pursue efforts to limit the global temperature increase to 1.5°C [1]. Polish economy is dependent mainly on coal supply which has the biggest share in terms of electricity production and district heat generation. Coal and other fossil fuels can be characterized with a high intensity of emissions, therefore national energy policy [2] currently emphasizes the need to diversify sources and reduce the reliance on fossil fuels. During the ongoing decarbonization process not only in the energy sector but also in other industry sectors, the authorities prioritize the development of renewable energy, improving the energy security and energy efficiency. Nevertheless, fossil fuels still dominate the energy mix in Poland and thus its greenhouse gas emissions remain at a high level [3]. According to KOBiZE, in 2023 total greenhouse gas (GHG) emissions amounted to approximately 350 $MtCO_{2\text{-}eq}$ (excluding LULUCF - Land use, land use change and forestry) where energy sector had the highest contribution accounted for about 37% of these gross emissions [4].Therefore it is crucial to deploy solutions which will lead to economy decarbonization and reducing the emissions.

Achieving this goal requires rapid reduction in greenhouse gas emissions. The main pathways can be distinguished:

1. Prevention of emissions – by shifting to renewable and nuclear energy, implementing supportive policies, increasing energy efficiency, using low-carbon fuels, and improving material efficiency.
2. Avoidance of emissions at point sources – through carbon capture, utilization, and permanent storage (CCUS).
3. Removal of emissions already in the atmosphere – by developing and deploying carbon dioxide removal (CDR) technologies.

Current analyses show that achieving the 1.5°C target will no longer be possible without significant carbon drawdown and the reduction of GHG emissions will not be enough to fully mitigate climate change therefore, around 1-10Gt of CO_2 should be removed annually by 2050 through negative emission technologies (NET) [5]. Within potential technologies, carbon capture, utilization and storage (CCUS) has gained more and more interest in recent years.

CCUS encompasses a wide set of technologies, including:

1. Capture – of CO_2 either from large point sources or directly from the atmosphere,
2. Transport – moving the captured CO_2 to utilization or storage sites,

3. Utilization – applying CO_2 in industrial processes or converting it into products,
4. Storage – permanent sequestration in geological formations.

It is considered as a solution that can achieve large-scale emission reduction with great significance for energy security and economic stability [6]. Carbon capture refers to CO_2 separation and enrichment and constitutes the beginning of the CCUS chain. What is worth mentioning is that CCUS provides an answer to heavy industries such as steel, cement, oil refineries, which are responsible for approximately 25% of global CO_2 emissions and in which inherent process emissions are hard to avoid or even unavoidable [7].

Given the significant mitigation potential in the hard-to-abate as well as power sectors, understanding the technical, environmental, and economic aspects of CCUS becomes crucial. In particular, assessing costs and carbon footprint across the entire CCUS value chain, from capture to utilization or storage, provides insights into where the greatest opportunities and challenges lie.

CCUS as a way to mitigate CO_2 emissions from the economy sectors are planned to be bridging technologies which should help to meet the required CO_2 emission reduction goals, keeping the fossil fuel based feed to energy and industrial sectors during the transition. Its large-scale deployment is expected mainly between 2030 and 2050, particularly in hard-to-abate industrial sectors, according to the EU Fit-for-55 trajectory and the EU ETS framework [8]. After 2050, CCUS is likely to play a complementary role, focusing on residual process emission and negative emission options. Nevertheless, one of the crucial aspects of CCUS technologies is related to the storage or utilization of captured CO_2. When storage is concerned, there are several options for permanent sequestration of CO_2, i.e. deep saline formations or depleted oil and gas reservoirs. However, one of the ways to improve the cost-effectiveness of CCUS technologies is to utilize the captured CO_2. Among well-established technologies like Enhanced Oil Recovery (EOR), there are some new ones that are of interest for industrial sectors. Therefore, a comprehensive and systematic approach to comparing the options within storage and utilization pathways is urgently needed.

In the context of Poland's urgent need to mitigate greenhouse gas emissions, the development of innovative and economically feasible solutions is essential. CO_2 utilization and geological storage offer promising approaches by either transforming CO_2 into marketable products or securely sequestering it underground, thus preventing atmospheric release. In some scientific papers authors acknowledge the significance of economic viability of different solutions within capturing, transporting and storing the CO_2 [9] as well as the usage for industrial purposes [10], also pointing out the distinction between approaches while calculating costs for different cases [11]. Therefore, this thesis will evaluate selected carbon management technologies not only in terms of their

environmental performance, but also their economic feasibility, required investments and potential market benefits. The assessment combines life cycle analysis (LCA) with economic indicators obtained from process modelling. In doing so, it aims to address current gaps in evaluation methods namely the limited availability of comprehensive data and the lack of consistent approaches for calculating both carbon footprints and economic impacts across the full life cycle of the process chain.

1.1 Structure of the Dissertation

The research was structured in a sequence of interconnected activities, each building on the results of the previous stage as presented in Figure 1.1. At the beginning, the work focused on gathering and analyzing data on various CO_2 sources, including emissions from fossil fuel combustion, bioenergy units, industrial processes and direct air capture. These data were complemented by information on energy balances, raw material requirements, and emissions profiles, forming the basis for classifying CO_2 sources into distinct categories and understanding their potential roles in the CCUS chain. Consecutively, the most suitable CO_2 storage and utilization pathways were identified on the basis of their technological maturity, technical feasibility, and overall potential determined for the profile of Polish economy. Subsequent evaluations analyze these pathways in terms of their life cycle environmental impacts and economic performance and include their role in the economy. Data supporting this evaluation were sourced from mathematical models developed and complemented by information available in the scientific literature. These allow determining the balances of energy and substances for a given system and performing holistic analysis to highlight critical factors influencing the effectiveness of CO_2 utilization and storage in Poland.

Following this, the focus was directed toward collecting and analyzing data on CO_2 utilization technologies. Two main pathways were examined: utilization through chemical conversion such as the production of urea and methanol or carbon mineralization and utilization without conversion, including enhanced oil recovery and enhanced geothermal systems. For each technology, critical technical parameters were identified and data was prepared for the construction of life cycle inventories. The next phase focused on designing the methodology and guidelines for the assessment of CO_2 management pathways under Polish conditions. The analysis involved defining system boundaries, functional units, and allocation rules while identifying the main gaps in environmental and economic evaluation methods. These allowed further data processing, calculations, and simulations, which enabled the comparison of various scenarios and the execution of sensitivity analyses to determine the most influential factors on system performance. These steps were essential to integrate environmental and economic aspects in the assessment.

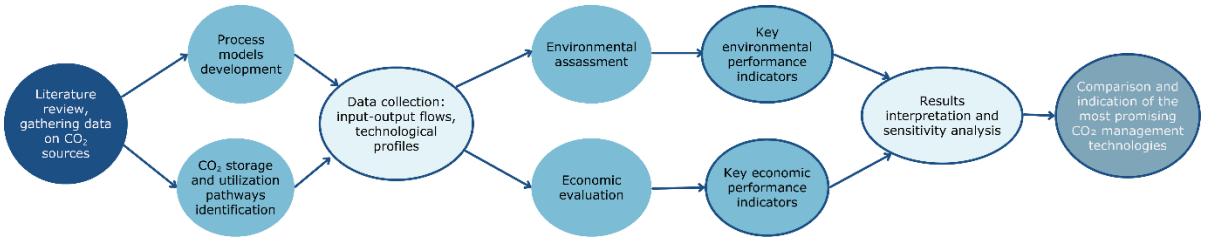

Figure 1.1 Schematic diagram of thesis framework.

Building on the framework developed, subsequent work concentrated on evaluating scenarios for captured CO_2 handling, integrating carbon footprint assessment with economic considerations. The final stage was dedicated to the interpretation of case studies under Polish conditions and the formulation of conclusions. This phase identified the most promising CO_2 utilization and storage pathways, assessed their scalability, and determined the conditions under which these technologies could be implemented without causing adverse impacts on other sectors. The research concluded with a comprehensive comparison of the results, emphasizing the technological configurations that offer the highest potential for sustainable deployment in Poland.

2. Literature review

2.1 Background

The net zero emissions goal is a key challenge in global and domestic climate change policy. It involves a significant reduction in the use of unabated fossil fuels, enhancing the energy efficiency, further development of renewable energy sources, and the deployment of carbon capture, utilization and storage technologies. The motor of this is the willingness to mitigate the carbon dioxide emissions in order to keep the global average temperature increase below 2°C above pre-industrial levels as it was established in the Paris Agreement. With regard to that, countries implement and adjust their climate policies, introduce low-emission strategies, and underline the need of shifting to the decarbonized economy. It is also visible in official Polish documents in the matter of energy policy [2,12]. CCUS expansion and application are expected to be a mitigation tool for achieving this objective along with environmental benefits.

Power and industry dominate in terms of the global amount of CO_2 emitted. In these sectors, CO_2 is released into the atmosphere mainly by combustion of fossil fuels and is emitted from exhaust stacks, which constitute large, stationary point sources which, contrary to mobile sources in the transport or smaller stationary units in the residential sector, represent the potential for CO_2 capture deployment. Large volumes of the flue gas produced in such plants emphasize the role and capability of CCUS implementation to generate a high-purity CO_2 stream that can be subsequently transported and then utilized or stored. Other economy branches such as transport or residential sector contribute with approximately 30% of global CO_2 emissions from diffuse sources. Nevertheless, the volumes associated with these sources tend to be small in comparison with power plants, factories or other industrial plants. Therefore, currently separating CO_2 from such small volumes is highly inefficient and relates to limited near-term potential due to dispersion and low partial pressure [13].

In 2023, most of greenhouse gas emissions came from China, the United States, India, the European Union, Russia, and Brazil. Fossil CO_2 contributed to almost 74% of total GHG emissions, whereas CH_4, N_2O and F-gases accounted for 18.9%, 4.7% and 2.7% respectively. The breakdown of European GHG emissions with their sources is presented in Figure 2.1. Global CO_2 emissions stemming from fossil fuels increased by 72.1% since 1990.

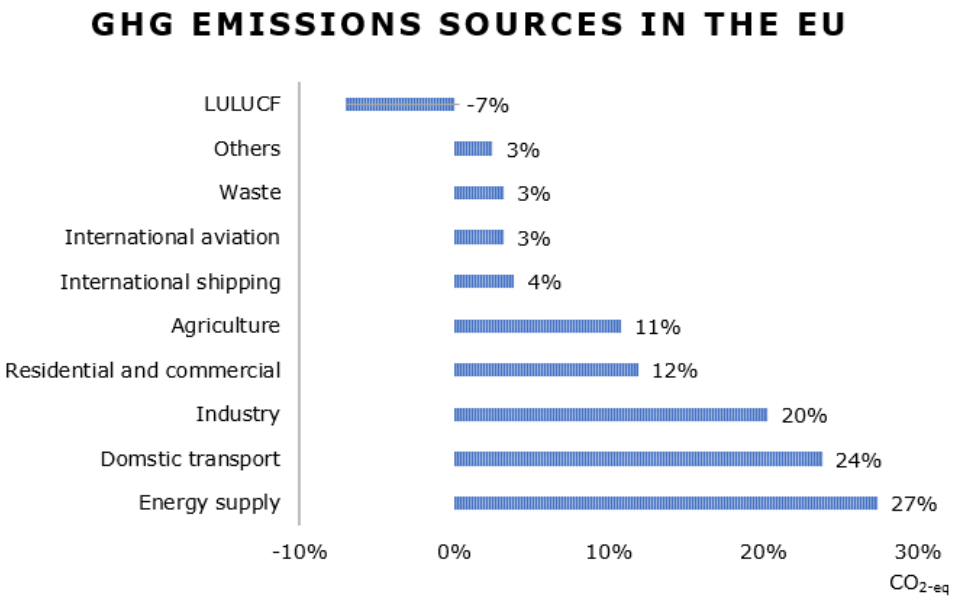

Figure 2.1 GHG emission sources in the EU by sector in 2022 (based on [14]).

In 2023, Poland's net greenhouse gas emissions reached approximately 350 $MtCO_{2\text{-}eq}$, 8.6% less than in previous year and accounting for 10.5% of the EU's total and ranking the country as the third-largest emitter in the Union. In 2023, the fossil fuels combustion for power sector, manufacturing and construction, transport and other sectors was responsible for the vast majority of emissions, contributing 77% (270 $MtCO_2$/yr). Agriculture accounted for 9.8%, industrial processes and product use for 5.6%, and the remaining emissions were contributing for by waste (1.2%) and indirect emissions (0.1%).

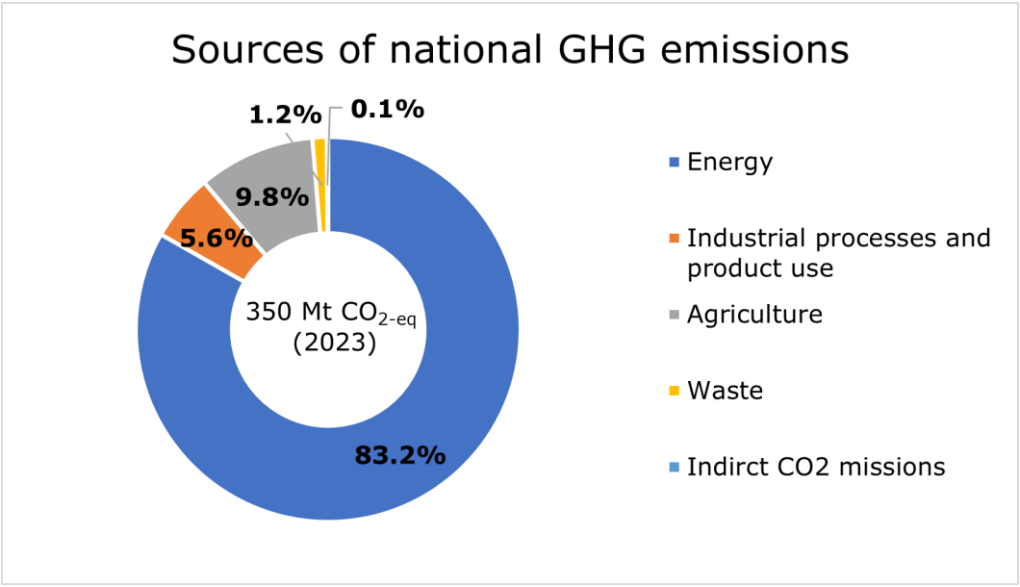

Figure 2.2 Fossil CO_2 emission sources in Poland in 2023, by sector (based on [15]).

This distribution is graphically presented in Figure 2.2. This underscores the dominance of the energy sector alongside significant contributions from energy-intensive industries [15].

Nevertheless, according to European Commission's Climate Action Progress Report 2024, in 2023 European Union noted 8.3% decrease in total GHG emissions compared to the previous year which relates to the continuation of decreasing trend [16]. Almost all countries, excluding Croatia and Cyprus, noted a lower emissions levels compared to 2022. The biggest decrease accounting for 20.1% was experienced in power sector, followed by the industrial sector, falling by 8.1% below 2022 levels. Among EU countries, Germany, France, Italy, Poland and Spain were the largest emitters in 2023 [17]. While these recent reductions highlight progress in lowering emissions, large point sources from the power and industrial sectors remain significant contributors. The characteristics of these emission streams, particularly their CO_2 concentration, strongly influence the choice and cost-effectiveness of capture technologies. The concentration of CO_2 resulting from combustion varies from 3-5%$_{vol}$ in flue gas from natural gas fired boilers to around 12-15%$_{vol}$ from coal fired boilers, while it could be up to 30%$_{vol}$ of CO_2 from cement kiln off-gas [18]. Therefore, the feasibility of CO_2 source for capture and suitable technology depends mainly on its volume, concentration and partial pressure as well as the system aspects and the suitable storage or utilization availability. As already mentioned, CO_2 emissions result from a numerous sources, thus the overall emissions can be grouped in sectors as follows [13]:

a) Transportation – GHG emissions in this sector correspond primarily to direct emissions and come from fossil fuel-based petroleum combustion for cars, trucks, ships, planes and trains, including gasoline and diesel.

b) Electricity and heat production – GHG emissions related to fuel combustion for electricity and heat generation.

c) Industry – GHG emissions from industrial sources are primarily derived from burning fossil fuels to supply the necessary heat, as well as a variety of industrial production processes that transform materials chemically, physically, or biologically from raw feedstock. Such processes include: (i) the use of fuels as feedstocks in petrochemical processes, (ii) the use of carbon as a reducing agent in the commercial production of metals from ores, (iii) the thermal decomposition (calcination) of limestone and dolomite in cement or lime production, and (iv) the fermentation of biomass (e.g., to convert sugar to alcohol). In some applications, these process emissions are a result of a combination with fuel combustion emissions. Within this group, a distinction for emissions related to fossil fuel extraction is made, such as natural gas processing and eventual leakage. For natural gas processing, CO_2 occurs as a common impurity in natural gas and must be removed to improve the heating value of the gas, as well as to meet pipeline requirements [13].

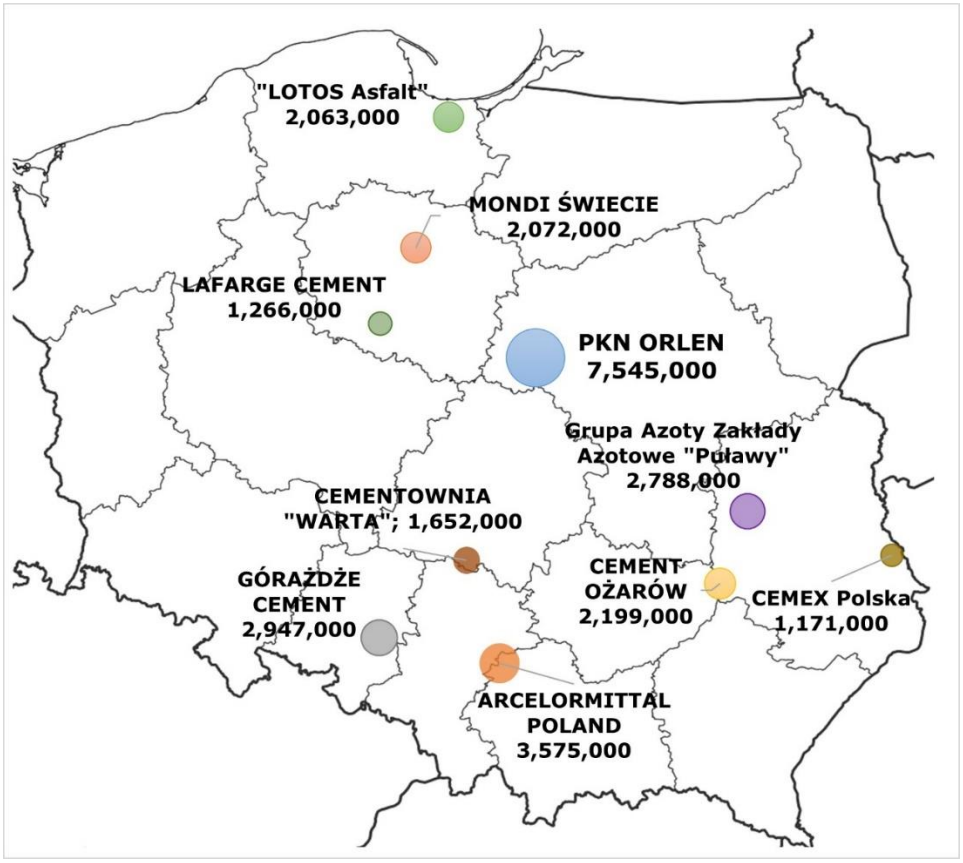

Figure 2.3 The largest industrial emitters with annual emissions in tCO_2 (based on [19]).

The largest industrial CO_2 emitters in Poland are concentrated in the energy-intensive sectors of oil refining, metallurgy, cement, and chemicals (Figure 2.3). The single largest source is PKN Orlen S.A. in Płock, with annual emissions exceeding 7.5 million tonnes of CO_2, followed by ArcelorMittal Poland S.A. in the steel sector (3.6 Mt CO_2) and Górażdże Cement S.A. in the cement industry (2.9 Mt CO_2). Significant emissions also originate from the chemical sector, with Grupa Azoty Zakłady Azotowe "Puławy" S.A. (2.9 Mt CO_2) and LOTOS Asfalt Sp. z o.o. (2.1 Mt CO_2). These facilities represent the core industrial clusters of Polish emissions [19].

d) Commercial and residential sector – GHG emissions in this area results from fossil fuels burned for heating, the use of gases for refrigeration and cooling as well as non-building specific emissions such as waste handling.

e) Agriculture – Greenhouse gas emissions from agriculture come from livestock such as cows, agricultural soils, and rice production.

f) Natural processes – natural sources include decomposition, ocean release, natural-occurring wildfires, land use, and respiration. However, forests and land are a CO_2 sink that absorbs CO_2 from the atmosphere, offsetting overall greenhouse gas emissions [20].

It has to be noted also that in each sector, the electricity use for applications such as ventilation, heating, air conditioning, lighting, equipment power supply results with corresponding indirect emissions as an electricity end-use.

The European Union Emissions Trading System (EU ETS) was introduced in 2005 on the basis of Directive 2003/87/EC of the European Parliament and of the Council of 13 October 2003 [21] establishing a scheme for greenhouse gas emission allowance trading within the Union and amending Council Directive 96/61/EC. This directive constitutes the cornerstone of the EU's climate policy, with the aim of mitigating climate change and reducing greenhouse gas emissions. The EU ETS operates under a "cap-and-trade" principle, whereby a limit is set on the total amount of greenhouse gases that can be emitted by operators covered by the system. This cap is gradually reduced over time, resulting in an overall decline in emissions. Within this cap, operators receive or purchase emission allowances, which they can trade with one another as needed. The limited supply of allowances ensures their market value, while the price signal incentivizes emission reductions and encourages investment in low-carbon and energy-efficient technologies.

At the end of each year, every operator must surrender a number of allowances equal to its verified emissions. If an installation reduces its emissions, the operator may retain surplus allowances for future compliance or sell them to other operators facing a shortage. Revenues from the sale of allowances are largely directed to the budgets of Member States. In addition, allowances are auctioned to support EU-level funds that promote low-carbon innovation and energy efficiency, such as the Innovation Fund and the Modernisation Fund. Poland, like other EU Member States, does not have a national reduction target for 2021–2030 for sources covered by the EU ETS. This is because emission limits are set at the level of the entire Union-wide system and emissions within this framework are monitored and accounted for directly by operators of covered installations [22].

The EU ETS covers the following sectors and greenhouse gases, focusing on emissions that can be measured, reported, and verified with a high level of accuracy:

a) Carbon dioxide (CO_2) from:

- electricity and heat generation;
- energy-intensive industries, including oil refineries, iron and steel production, aluminum and other metals, cement, lime, glass, ceramics, pulp, paper and cardboard, and chemicals;
- aviation within the European Economic Area (EEA) and flights departing from Switzerland and the United Kingdom;
- maritime transport.

b) Nitrous oxide (N_2O) from the production of nitric, adipic, glyoxylic and glyoxal acids.

c) Perfluorocarbons (PFCs) from aluminum production.

The system operates in successive trading phases. It is currently in its fourth phase (2021–2030), and the structure of the EU ETS has undergone several revisions to maintain consistency with the overarching objectives of the EU's climate policy. In 2024, CO_2 emissions in Poland covered by the EU ETS amounted to nearly 154 million tonnes of CO_2 (including the aviation sector). This value is approximately 3% lower compared to 2023. Table 2.1 presents CO_2 emissions in 2023 and 2024 broken down by sector [23].

Table 2.1 Poland's 2023 and 2024 CO_2 emissions by sector (based on [23]).

Sector	**CO_2 emissions [t]**	
	2023	**2024**
Power plants	81 187 491	77 128 977
Combined heat and power plants	20 002 232	18 982 443
Heating plant	4 344 398	3 639 016
Industrial combined heat and power plants	5 014 284	5 176 932
Iron and steel industry	4 160 907	5 034 559
Non-ferrous metals industry	1 883 725	1 927 235
Cement industry	3 553 807	9 432 151
Sugar industry	1 211 567	1 279 838
Chemical industry	7 223 805	7 604 735
Wood-based industry	339 717	196 854
Coke industry	1 806 685	1 753 599
Mineral industry	58 197	73 616
Other industrial branches	1 489 384	1 366 662
Refinery industry	9 775 105	10 020 071
Glass industry	2 019 226	1 994 798
Lime industry	1 199 881	1 317 638
Ceramics industry	717 018	767 305
Paper industry	1 031 921	1 011 751
Sum	**153 019 350**	**148 708 180 (-2.82%)**
Aircraft operators	941 004	1 1190 623
Sum (incl. aviation)	**153 960 354**	**149 898 803 (-2.64%)**

It should also be noted that a share of national greenhouse gas emissions is not covered by the EU ETS. These emissions are referred to as non-ETS, or under the Effort Sharing Regulation (ESR).

The non-ETS domain includes the following sectors:

- the residential and commercial sector, comprising buildings, small combustion sources, households, and services;
- transport;
- industrial emissions outside the EU ETS and product use;
- agriculture;
- waste.

The proportion of emissions not covered by the EU ETS has been gradually increasing as a share of total greenhouse gas emissions. European legislation regulates the level of non-ETS emissions and sets binding reduction targets for Member States for two compliance periods: 2013–2020 and 2021–2030. Moreover, unlike ETS emissions, which are monitored and accounted for at the level of individual installations, the responsibility for non-ETS emissions lies with the Member States. Thus, non-ETS emissions are determined on a national level and settled by governments. In the case of Poland, in 2021 non-ETS emissions represented 52% of total national CO_2 emissions, which amounted to approximately 400 million tonnes $CO_{2\text{-eq}}$. Accordingly, non-ETS emissions reached about 208 million tonnes $CO_{2\text{-eq}}$, while ETS-covered emissions accounted for 192 million tonnes $CO_{2\text{-eq}}$ [4].

A precise classification of emission sources enables improved monitoring, reporting, and management within international mechanisms such as the Emissions Trading System. This categorization also facilitates a better understanding of the role of individual sectors and processes in generating emissions, providing a basis for identifying areas that require further action to minimize environmental impact. In line with the guidelines outlined in the *Strategic Document on Carbon Capture, Utilization, and Storage (CCUS) until 2040 with a Perspective to 2050* [24], this classification supports the implementation of CCUS technologies aimed at reducing greenhouse gas emissions.

Therefore, the identified GHG sources were matched with the corresponding colors and presented as CO_2 emissions on the graph in Figure 2.4. The color-based classification of greenhouse gases proposed in this work is a conceptual framework designed to support discussion and visualization. It is not intended as a formal reporting or accounting standard. The color labels are applied here to highlight different origins, processes, and treatment of emissions, thereby serving as a holistic tool for communication. This representation also includes a distinction between biogenic CO_2 from biomass combustion and CO_2 captured directly from the atmosphere, reflecting the approach promoted in the aforementioned strategic document.

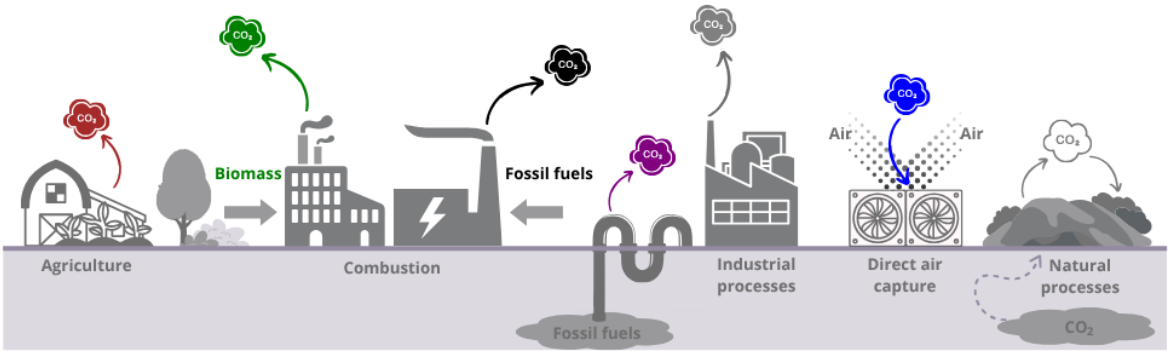

Figure 2.4 The division of GHG emissions into different colors, based on CO_2 emissions.

The distinction of colors for the division of different CO_2 sources is associated with the carbon footprint concept. The colors are used to categorize and communicate the environmental impact of different activities. In the current literature, color-based terms were used to characterize and describe the distribution of organic carbon that contributes to the carbon cycle and therefore broaden conventional classification types (organic or inorganic) [25]. Nevertheless, the proposed division relies on different points in the carbon cycle with the focus on function, location and, characteristics. Thus, the another color-based division was introduced, partially referring to colors established by U.S. Geological Survey [26], which contributes not only to the carbon type but also highlights the CO_2 and other greenhouse gases sources, sectors and processes with the focus on direct emissions released [27]. Each category also includes the information on the accounting for EU ETS and is presented in Table 2.2.

Table 2.2 Proposed color division for different GHG emissions.

Terminology	Source	Related processes	Accounted for EU ETS
Black GHG	Fossil fuels	Combustion	Yes
Grey GHG	Industrial processes	Material decomposition, chemical reactions resulting with CO_2 as a product	Yes
Brown GHG	Agriculture	Decomposition of organic matter including animal waste, fermentation, putrefactive processes	No
Purple GHG	Industry, chemicals, transportation	Direct GHG emissions from fossil fuel extraction incl. natural gas processing CO_2 emissions	Yes
Blue GHG	Atmosphere	Direct air capture	No

Green GHG	Biomass, biofuels	Bioenergy generation via combustion	No
White GHG	Natural	Natural processes including ocean, wetlands, permafrost releases, forest fires, volcanic eruptions, earthquakes [29][28][28] (non-anthropogenic)	No

In the context of different CO_2 sources as well as carbon lifecycle, it is crucial to distinguish three aspects:

- Permanence, which refers to the durability of CO_2 storage or carbon removal. For geological storage, permanence implies long-term retention (thousands of years) with robust monitoring to ensure that the injected CO_2 does not return to the atmosphere. For CO_2 utilization in products (e.g. urea, methanol), permanence is typically low, as most carbon is re-emitted within months to years. Permanence must therefore be assessed on a pathway-specific basis.
- Additionality, which requires that captured and stored (or utilized) CO_2 provides a net climate benefit beyond what would have occurred in a baseline scenario. For instance, CCUS applied to an installation already covered by strict emissions regulation must demonstrate that the captured CO_2 constitutes an additional element to regulatory requirements and that it does not lead to increased emissions elsewhere in the system, such as through shifting production.
- Leakage captures both physical and systemic risks of unintended CO_2 release. Physical leakage refers to the potential escape of CO_2 from pipelines, storage sites, or during product use/end-of-life. Systemic or market leakage arises when the deployment of CCUS indirectly increases emissions elsewhere, for example, by extending the use of fossil assets or displacing low-carbon alternatives. Both types of leakages must be quantified or qualitatively discussed in the assessment to ensure an accurate net climate impact.

The diversity of CO_2 sources directly influences the selection of suitable carbon capture, utilization and storage technologies. Understanding these source-specific factors provides the foundation for discussing the range of CCUS solutions available, from capture methods to downstream utilization and storage options.

2.2 Carbon capture, utilization and storage technologies

Carbon capture, utilization and storage comprises a set of technologies that can substantially reduce emissions from large stationary sources or remove CO_2 directly from the atmosphere (Figure 2.5). Several elements of this chain are commercially proven (e.g. CO_2 pipelines, some capture methods, enhanced oil

recovery), while others continue to scale up. Throughout this thesis, safety, permanence, and additionality are treated as explicit criteria, and costs and carbon impacts are quantified under transparent functional units and system boundaries. CCUS is generally separated into three overarching segments: capture, transport, and storage or utilization. CO_2 capture refers to the process in which CO_2 is separated from a specific gas stream and converted to a purified stream of CO_2. Point source capture involves the separation of CO_2 from discrete individual sources within industrial plants such as cement plants, chemical plants, steel mills, or power plants. Carbon dioxide removal (CDR) involves the capture of CO_2 from the environment, including air with a CO_2 concentration of approximately 420 ppm. CDR related to CCUS encompasses direct air capture (DAC) and bioenergy with CCS (BECCS). The produced CO_2 from a capture plant will be of a high CO_2 purity, often in range of 95-99.9%. This CO_2 is then purified, dehydrated and compressed to the necessary pressure for either liquefaction or injection into transport systems such as pipelines. The next steps involves CO_2 distribution either to storage sites which can be located on-shore or off-shore or to the unit when utilization process takes place [29].

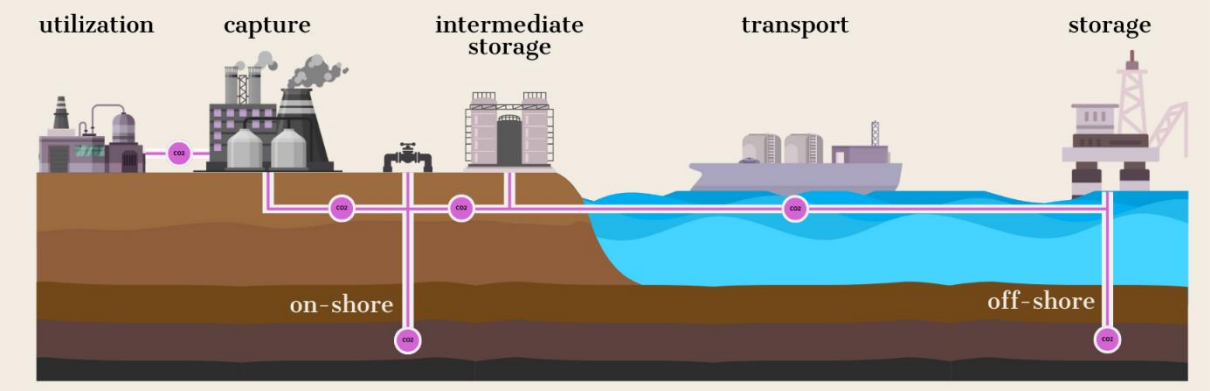

Figure 2.5 Simplified schematic of carbon capture, utilization and storage chain.

2.2.1 CCUS Status

In 2024 CCUS technologies experienced a rapid growth, exceeding 400 $MtCO_2$/year of total sequestration capacity for 628 facilities within CCUS value chain, in different development stages including early and advanced development, under construction or already operating, which is 57% year-on-year increase in CO_2 capacity. Fifty commercial CCUS installations at approximately 51 Mt CO_2 per year, were operating, showing their capabilities and influencing the maturation of carbon market. The majority of these projects are located in the United States and Canada, as well as in Europe, primarily in the United Kingdom, Norway, Denmark, and the Netherlands, where the development of technologies from the CCUS chain is combined in clusters that include entities from all branches of the economy, concentrating their activities on the capture side, expanding the CO_2 transport network, the progression and demonstration of CO_2 utilization methods, and the commercial demonstration of underground geological storage. Another 44 CCUS projects were under

construction and over 500 in development. European decarbonization policies are accelerating the development of a strong CCUS value chain, driven by the EU-wide target of 50 $MtCO_2$ injection capacity by 2030, introduced under the Net-Zero Industry Act in June 2024. It is important to note that this refers to available geological storage capacity and does not directly translate into actual avoided emissions, which depend on capture deployment, utilization rates, and system integration. The UK is also advancing in this area, with government support for clusters capturing 20-30 $MtCO_2$ per year and a funding commitment of £2.17 billion over 25 years for the Teesside and Merseyside projects. Consequently, the number of commercial CCS projects under construction in Europe increased to 10 by July 2024, up from six a year earlier. Building cross-border CO_2 transport infrastructure is crucial to achieving these goals, as demonstrated by milestones such as the completion of the first phase of Northern Lights in Norway and Porthos construction in the Netherlands [30].

Moreover, within the framework of the EU Emissions Trading System, installations covered by the scheme are allowed to deduct the amount of CO_2 that is captured and subsequently transported to a recognized permanent storage site or to another installation for further utilization, provided that monitoring and reporting rules are complied with. This provision is set out in Commission Implementing Regulation (EU) 2018/2066 on the monitoring and reporting of greenhouse gas emissions [31]. In practice, this means that the operator of a point-source installation can report reduced verified emissions equivalent to the amount of CO_2 that has been captured and transferred under a monitoring plan. Consequently, the number of allowances that the emitter must surrender is lowered, creating a direct regulatory incentive for CO_2 capture and storage (CCS) or utilization (CCU) when the latter is recognized under the EU ETS framework.

2.2.1.1 Carbon dioxide removal technologies

Technologies that lead to a negative balance of carbon in the atmosphere are known as carbon dioxide removal or negative emission technologies. Different approaches in range from natural to technological are possible. They include: (i) afforestation and reforestation; (ii) biochar and soil carbon sequestration; (iii) ocean fertilization; (iv) enhanced weathering and carbon mineralization; (v) bioenergy with carbon capture and storage and (vi) direct air capture [2]. These pathways are needed to achieve climate targets. Their graphical interpretation is presented in Figure 2.6 from natural to more technologically advanced approaches.

By 2022, the global capacity of CDR reached 2 $GtCO_2$/year. Most of that was achieved through natural approaches largely through afforestation and reforestation, while engineered solutions such as direct air capture corresponded only to 0.1% of total capacity [32].

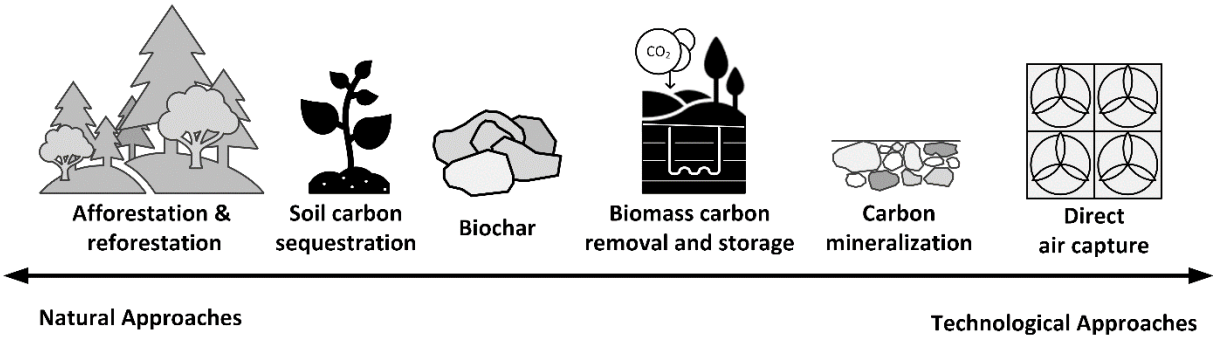

Figure 2.6 Carbon dioxide removal approaches (based on [33]).

The estimated potential for DAC and BECCS development for climate change mitigation is, respectively, up to 5 $GtCO_2$ per year and from up to 5 $GtCO_2$ per year [34] to 11 $GtCO_2$ per year [1]. To keep global warming limited to 1.5°C, carbon removal at the level of 7.9-10.6 $GtCO_2$ for BECCS and 8-32 $GtCO_2$ for DAC by 2100 would be essential [35]. These ranges reflect the outputs of integrated assessment models rather than forecasts, and the feasible scale of deployment will be constrained by resource and system factors, including energy demand, land, water, and other resource availability, as well as supply chains for low-carbon hydrogen.

In terms of BECCS, the possible applications, determined by means of combustion or conversion, are associated with the following:

- bio-chemical biofuels production;
- thermo-chemical production of biofuels and biochemicals;
- biomass combustion for electricity generation and/or heat production [36].

When biomass is combusted for electricity or heat production, CO_2 can be captured directly from the flue gas. In case of biomass conversion through digestion or fermentation, CO_2 is one of the products along with gaseous (biogas) or liquid (biofuel) fuels. [37].

Direct Air Capture is another example of CDR technologies with high development and improvement potential. Within this method, CO_2 is extracted directly from the atmosphere through a contractor using solvents or sorbents that bind it or stick to it. Then, captured CO_2 can be stored or used for other deployments [38]. DAC is characterized with high energy requirements which for such low levels of CO_2 in the flowing stream are considerably higher than those from more concentrated sources. Consequently, many separation processes with CO_2 capture from low concentrated streams are not viable due to economic reasons [5]. It should be noted that carbon dioxide removal does not automatically qualify as an offset. Its net climate benefit depends on permanence, additionality, leakage risks, and broader system-level effects.

2.2.2 CO_2 capture pathways

In terms of CO_2 capture technologies, three main methods can be distinguished (Figure 2.7):

- Post-combustion - carbon dioxide capture from the flue gas after combustion or industrial processes. Post-combustion capture technologies do not require fundamental changes in the reference process and can be adapted to existing plants. Flue gas passes through machinery that separates the majority of CO_2 before being released into the atmosphere. The chemical absorption process is the most common way to separate carbon dioxide from flue gas. Using this process, high-purity gas is obtained and the separation is very efficient.

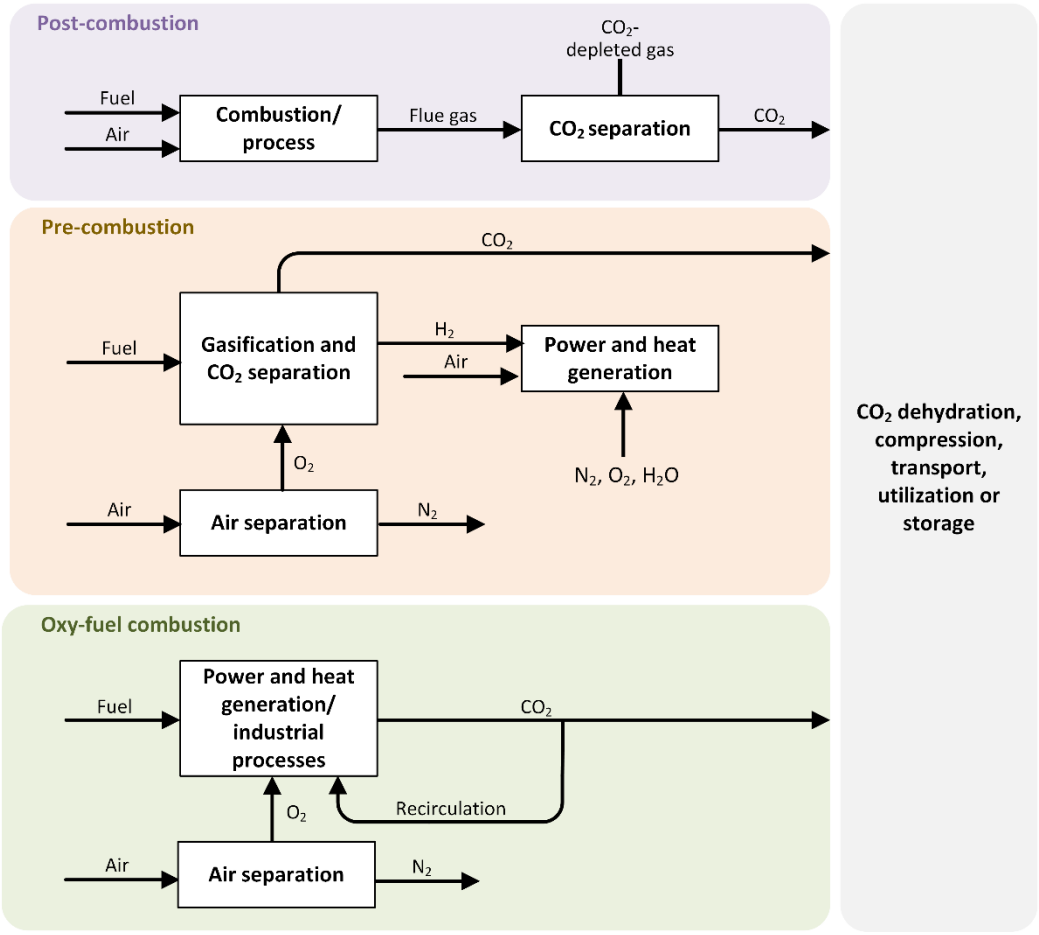

Figure 2.7 Carbon capture post-, pre- and oxy-fuel combustion pathways.

- Pre-combustion - gasification combined with carbon capture via CO_2 separation from produced gas. In pre-combustion capture, a fuel reacts with oxygen, air, and/or steam to produce a synthesis gas (syngas) or another fuel gas that mainly consists of hydrogen and carbon monoxide. Following the separation of CO_2, typically through a physical or chemical absorption process, a hydrogen-rich fuel is produced and can be utilized in a variety of different applications, including fuel cells, boilers, furnaces, gas turbines, and engines.

- Oxy-combustion - oxygen combustion and carbon dioxide separation from flue gas. Once almost pure oxygen is utilized for burning instead of air, the result is a flue gas primarily composed of CO_2 and H_2O. In such process, the flame temperature becomes excessively high when fuel is burned in pure oxygen, however, this can be reduced by recycling CO_2 and/or H_2O-rich flue gas into the combustor. Low temperature (cryogenic) air separation is typically used to produce oxygen, and new methods for supplying oxygen to fuel, such as membranes and chemical looping cycles, are being researched [39].

The primary technologies used for CO_2 capture are absorption, adsorption, membrane, cryogenics, and solid looping, showed in Figure 2.8.

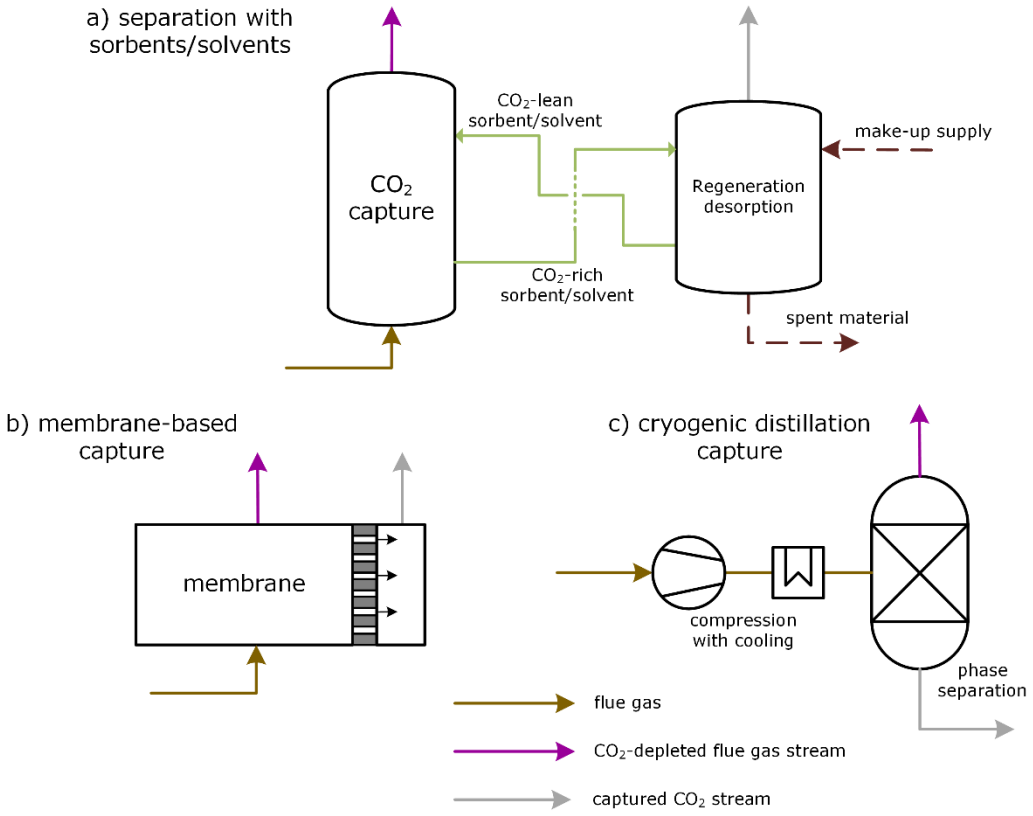

Figure 2.8 Methods of CO_2 capture (based on [39]).

a) absorption/adsorption - methods used for CO_2 separation via intimate contact with a liquid absorbent or solid sorbent that is capable of capturing CO_2. In general, the CO_2-rich sorbent after the first reactor is transported to the second vessel where after being heated and a pressure decrease or any other change of condition CO_2 is released and the sorbent is regenerated to be sent back and close the loop. In an absorption process, CO_2 gas is dissolved in a liquid solvent to form a solution, while adsorbents are solid materials that have binding sites on the surface of the sorbent to remove CO_2 from a gas stream. The materials used for adsorption have either a porous surface or a granular structure that provides a surface area for binding the CO_2 [29]. Absorption and adsorption technologies can be divided into physical and chemical processes. In some, solid sorbent does not circulate between reactors because the sorption and

regeneration processes are performed in cyclic changes in the vessels. In absorption/adsorption methods, a make-up flow of fresh sorbent is required to compensate for the losses or/and natural decay. The need for heat supply, as well as substantial sorbent flows stemming from large amounts of CO_2 that are processed in the system results in a significant equipment size and causes an efficiency penalty with added costs [39].

b) membranes – the separation of CO_2 from a gas mixture using membranes is based on their relative rates of mass transfer through the semi-permeable barrier or medium, which CO_2 would pass faster compared to other molecules in the stream.

c) cryogenic - the process is performed by CO_2 condensation from the other components of the flue gas stream. It is based on different condensation points compared to other components and is pursued by the set of compression, cooling, and condensing processes. The result of the process is liquid CO_2, which is ready for road, rail, or ship transportation.

d) solid-looping - the process includes the use of metal oxide or other solid regenerable compound that can carry CO_2 from the carbonator to the second reactor where the reverse reaction occurs. When sorbent is a solid oxide, in a reactor, a certain amount of fuel has to be burned in order to supply the process of regeneration with heat. Th resulting CO_2 emissions are also captured within the facility [29].

Currently, cryogenics constitute a highly promising approach, especially for industrial CO_2 sources, which potential lies in enabling more efficient capture with enhanced flexibility and adaptation to existing structures and without the need for significant, additional fuel and material supply. At present, this method is being developed in the Kujawy Cement Plant in Poland under the Kujawy Go4ECOPlanet project, which aims to capture all the CO_2 emissions proceeding from clinker production and therefore achieve a net-zero status. The project is financed through the EU Innovation Fund and introduces Air Liquide's Cryocap™ FG technology. The underlying mechanism of Cryocap™ FG combines pressure swing adsorption (PSA) with cryogenic liquefaction, which separates and purifies CO_2 by cooling it to extremely low temperatures. This dual-stage process yields liquified CO_2 of approximately 99.9 % purity, along with valuable by-products such as water and sulphate/nitrate compounds, which can be reused in cement production or even in agriculture [40]. Although cryogenics constitutes a highly promising technological pathway, it has not been incorporated into the analytical framework of the present dissertation mainly because of early stage of technological maturity and lack of resulting data and resources. The financial and infrastructural demands, especially high capital expenditure and dependence on external funding introduce significant uncertainties and contextual dependencies that exceed the scope of the dissertation's methodological structure. In order to preserve analytical consistency, the dissertation is therefore limited to technologies that are either already deployed

at scale or that have reached a higher level of technological readiness. Yet, two methods have been selected for detailed analysis in this thesis. They represent different approaches to capturing CO_2, although remain suitable and promising for large point sources present in Poland. Amine-based absorption is the most mature post-combustion capture method, already demonstrated at commercial scale across various sectors, making it a reliable benchmark for evaluating capture costs, while in contrast, calcium-looping is an emerging technology with high potential for integration in industries such as cement, where it can leverage process synergies and waste heat to reduce costs. Comparing both technologies allows for addressing different industrial contexts.

2.2.2.1 Amine absorption CO_2 capture

The most mature and commercially available technology is amine absorption. The process is conducted in a unit consisting of two columns where the absorption and desorption processes take place, as presented in Figure 2.9. The flue gas before entering the first column is compressed to 1.2 bar and cooled to 40°C in order to perform the process efficiently and reduce the amines damage. In this column, the absorption process occurs using solvent that reacts with the CO_2 from the flue gas stream. Approximately 90% of CO_2 is absorbed into the lean solvent stream. After the absorption, the remaining gas is cooled in water-wash section and then leaves the column via venting to the atmosphere. Rich amine solution is collected at the bottom of the absorption column and pumped through heat exchanger to the second column. The CO_2-rich stream is subsequently fed to the upper section of the stripper. The liquid solvent flows downward whereas steam flows upwards, enabling CO_2 recovery and amine regeneration. The heat needed for this process is provided by low-pressure steam which can be either extracted from the power plant steam cycle or supplied externally e.g. from dedicated boiler. Lean amine solution collected at the bottom of desorption column is cooled in the heat exchanger and transported back to the absorber. CO_2-rich gas separated from solvent leaves from the top of the stripper. The stream is cooled, dried and directed to the compression and purification unit (CPU). The CPU includes between five and eight-stage centrifugal compressor with intercooling and dehydration system applied usually after the fourth stage, although the selection depends on the target pressure and the range of impurities. Moreover, effective operation of amine-based capture requires pre-treatment of the flue gas. Acid gases such as SO_x and NO_2, as well as particulates and aerosols, must be removed to avoid accelerated solvent degradation and corrosion. This necessitates upstream flue-gas desulphurization and de-NO_x systems, particulate control, and, within the capture plant itself, the use of a reclaimer to remove degradation products. Continuous solvent make-up is also required to compensate for losses.

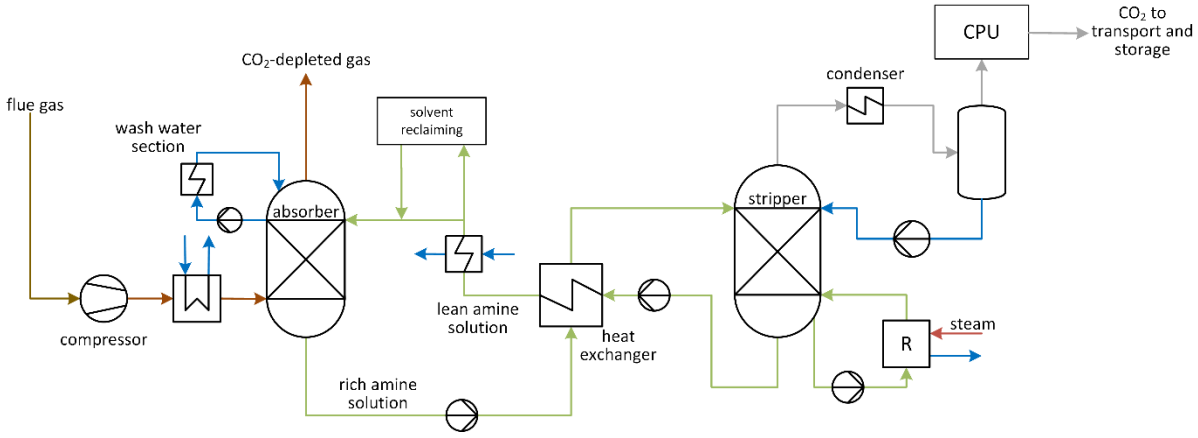

Figure 2.9 Amine absorption CO_2 capture concept.

In general, the capture efficiency for the amine plant can be calculated using Formula 2.1 [41]. It represents the fracture of CO_2 present in the flue gas stream captured in the system. Currently, most reports and studies reflect the capture efficiency in amine units at a minimum of 90%.

$$\eta_{CO2} = \frac{M_{CO2,in} - M_{CO2,out}}{M_{CO2,in}} \ [\%] \tag{2.1}$$

where:

$M_{CO2,in}$ – mass content of CO_2 in flue gas stream, $\%_{mass}$.

Within the amine plant model, several parameters may be introduced. The following formulas 2.2-2.6 present the key performance indicators for amine capture system simulation [41].
Ratio of molar flowrates related to total liquid sorbent requirements per unit of flue gas stream in absorber inlet:

$$\frac{L}{G} = f(y_{CO2}, \varphi_{lean}, \eta_{CO2}, C, T_{fg,in}) \tag{2.2}$$

$$\frac{L}{G} = e^{(-1.4352+0.1239y_{CO2}+3.4863\varphi_{lean}+0.0174\eta_{CO2}-0.0397C+0.0027T_{fg,in})} \tag{2.3}$$

The Q/L ratio estimates the regeneration heat duty per mole of circulating solvent. It decreases with richer feeds and higher lean sorbent loading and increases with higher MEA concentration, thus reflecting the amount of steam needed to be supplied.

$$\frac{Q}{G} = e^{(2.5919-0.0059y_{CO2}-6.3536\varphi_{lean}-0.0159\eta_{CO2}+0.0259C)} \tag{2.4}$$

$T_{fg,out}$ predicts the absorber outlet gas temperature, reflecting the exothermic reaction that occurs in the column.

$$T_{fg,out} = 41.15 + 1.307y_{CO2} - 18.872\varphi_{lean} + 0.270C + 0.062T_{fg,in} \tag{2.5}$$

The molecular weight of the lean solvent is not a fixed physical property but an empirical correlation that is used to approximate the behavior of the amine mixture in process simulations. The correlation reflects a model fitting used to simplify the calculations in process simulation based on experimental or reference data.

$$mw_{lean} = 16.907 + 2.333\varphi_{lean} + 0.204C \quad (2.6)$$

where:

L – total sorbent circulation flowrate, kmol/h,

G – total flue gas inlet flowrate, kmol/h,

Q – total sorbent regeneration heat requirement, GJ/h,

y_{CO2} – CO_2 mole concentration in flue gas stream, $\%_{mol}$,

φ_{lean} – lean sorbent loading, mol_{CO2}/mol_{MEA},

C – MEA concentration in sorbent, wt%,

$T_{fg,in}$, $T_{fg,out}$– temperature of flue gas entering (in) or leaving (out) the column.

2.2.2.2 Calcium-looping CO_2 capture

Less mature but promising solution for CO_2 capture is calcium looping (CaL), a method based on cyclic, reversible calcination and carbonation reactions (Eq. 2.7), usually conducted in dual-interconnected fluidized bed reactors at high temperatures, as presented in Figure 2.10.

$$CO_2 + CaO \leftrightarrow CaCO_3, \qquad \Delta H = -178.2\,\frac{kJ}{mol} \quad (2.7)$$

The flue gas enters the carbonator where CO_2 is removed via exothermic carbonation reaction with CaO. Carbonator temperature is held within the range of 580-650°C, depending on the CO_2 content in flue gas and has to be maintained to ensure the appropriate balance between the equilibrium driving forces and the reaction kinetics [42]. The calcium carbonate resulting from the reaction is thermally decomposed and regenerated in the second reactor - calciner at a temperature of 900-950°C. The endothermic calcination reaction is usually driven by the oxy-fuel combustion which provides the necessary heat. Oxygen for fuel combustion must be supplied. The captured CO_2 leaves the calciner and is cooled before it enters the CPU.

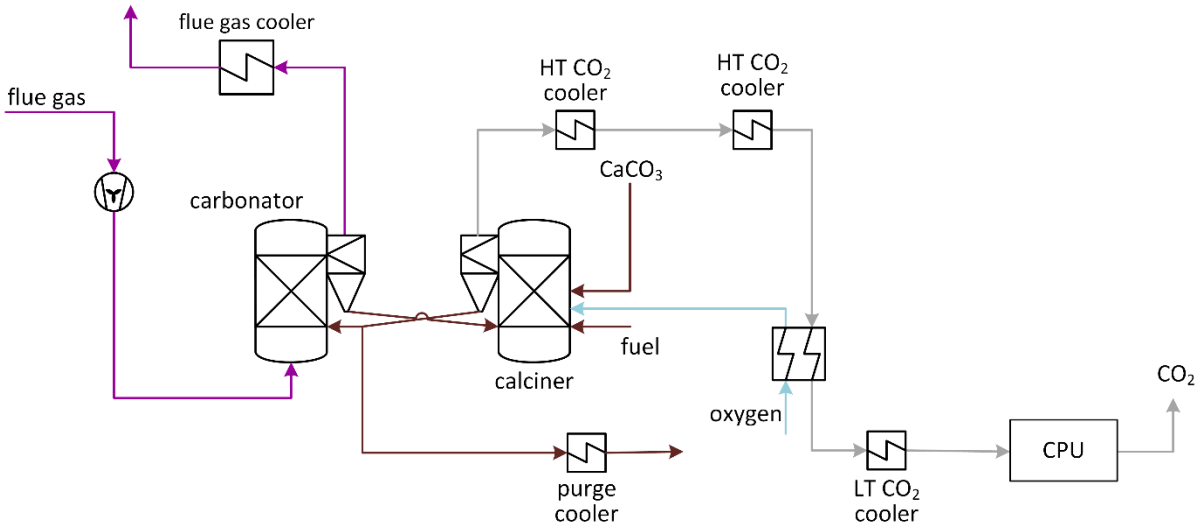

Figure 2.10 Simplified process flowsheet of calcium-looping CO_2 capture.

The main challenge of the CaL process is the deterioration of cyclic sorbent performance. Due to sorbent conversion decrease with the number of carbonation/calcination cycles, the fresh limestone make-up flow (F_0) must be supplied to the calciner while the purge stream containing CaO mixed with ashes or other solids is removed from the system [43]. This is mainly caused by sorbent sintering, attrition, and sulphation that require maintaining the desired average sorbent conversion in the carbonator by the make-up flow [44]. The F_0/F_R ratio, as noted in the current literature [45–47], plays a crucial role in process performance, as it influences the average conversion of the sorbent. The sorbent make-up flowrate should be optimized considering the trade-off between the thermodynamics of the process and the economic performance [10].

Considering sorbent deactivation that occurs with the numerous cycles, the maximum average conversion of the sorbent calculated in this thesis was adapted using the model developed by Rodríguez et al. [43]. The function shown in Eq. 2.8 links the sorbent characteristic (a_1, a_2, b, f_1, f_2) with the degree of carbonation (f_{carb}) and calcination (f_{calc}), the flow rate of make-up $CaCO_3$ (F_0) and the flow rate of recirculating sorbent (F_R).

$$X_{ave} = (F_0 + F_R r_0) f_{calc} \cdot \left[\frac{a_1 {f_1}^2}{F_0 + F_R f_{carb} f_{calc} (1 - f_1)} + \frac{a_2 {f_2}^2}{F_0 + F_R f_{carb} f_{calc} (1 - f_2)} + \frac{b}{F_0} \right] \quad (2.8)$$

where carbonation and calcination extent is calculated as follows:

$$f_{carb} = \frac{X_{carb} - X_{calc}}{X_{ave} - X_{calc}} \quad (2.9)$$

$$f_{calc} = \frac{X_{carb} - X_{calc}}{X_{carb}} \quad (2.10)$$

The mole fraction of CaO circulating in the system which has not undergone any calcination is represented by [43]:

$$r_0 = \frac{F_0(1 - f_{calc})}{F_0 + F_R f_{calc}} \quad (2.11)$$

Moreover, the CO_2 capture efficiency is determined using the following formula:

$$\eta_{CO2} = \frac{F_R \Delta X_{carb}}{F_{CO_2}} \quad (2.12)$$

The maximum carbonation conversion of solids occurs when the reactions are completed, then X_{carb} equals X_{ave} and X_{calc} equals zero. The carbonation conversion for not complete carbonation and calcination reaction is defined as follows [43]:

$$\Delta X_{carb} = X_{carb} - X_{calc} = f_{carb} f_{calc} X_{ave} \quad (2.13)$$

The high-grade waste heat from the process can be extracted, not only from the carbonator, but also from the stream leaving the carbonator and the high temperature CO_2-rich stream from calciner. For that purpose, the additional steam cycle can be applied to generate the electricity and compensate the electric consumption in unit. Although the heat needed for $CaCO_3$ decomposition is higher than that for amine scrubbing, the high-grade heat from the CaL process can be partially recovered through steam generation to lower the energy penalty of the entire process [48].

2.2.2.3 CO_2 capture costs

The costs for CO_2 capture vary widely depending on the source of CO_2 (Figure 2.11). Concentrated streams such as ammonia production or natural gas processing with approx. 95% CO_2 are cheapest, while dilute streams (around 4-15%$_{vol}$ CO_2 in flue gas) are more expensive. In terms of amine scrubbing, fertilizer (ammonia) plants and some hydrogen production units can capture CO_2 for under 90EUR per tonne (including compression for transportation and storage). In contrast, cement plants or waste-to-energy plants which flue gas contains around 10-20%$_{vol}$ CO_2 face capture costs on the order of more than 120EUR per tonne (incl. storage) with today's amine technology [49].

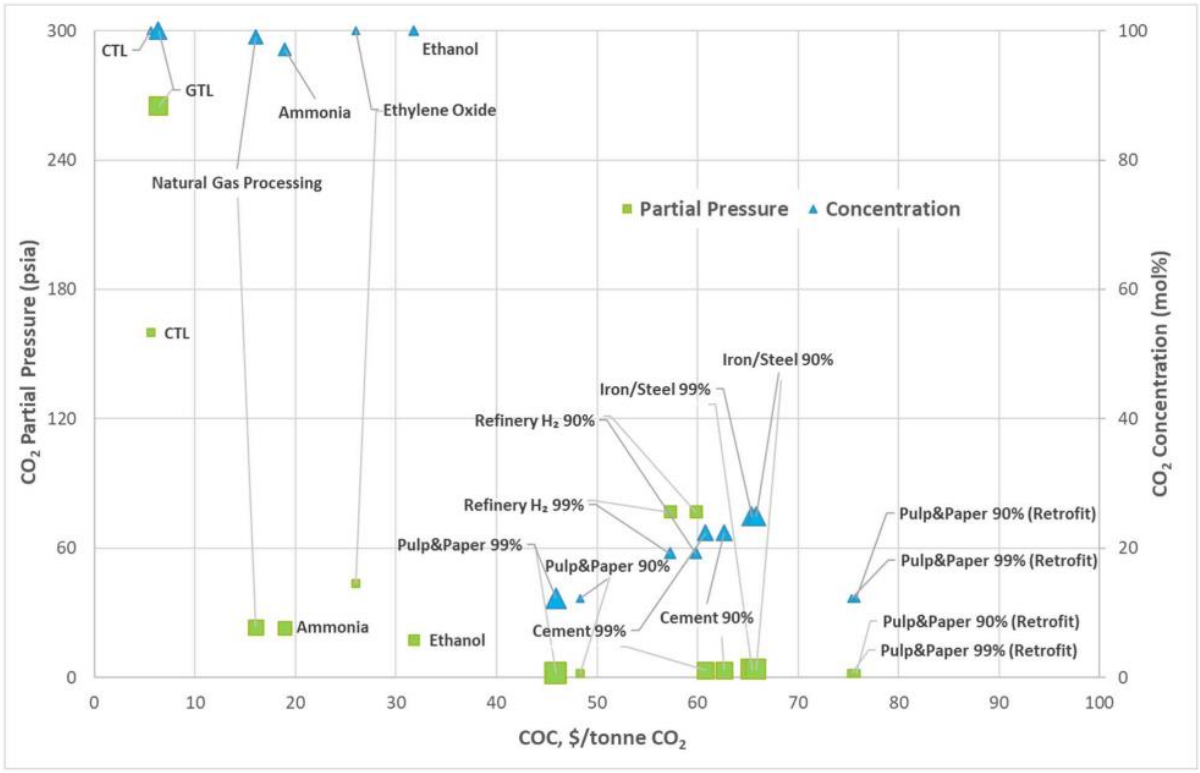

Figure 2.11 Cost of CO_2 capture dependency on CO_2 concentration in flue gas (from [50]).

Depending on the technology, costs for capture varies according to source[1] [50]:

- Ammonia production: 15-28EUR/tCO_2
- Cement production: 42-81EUR/tCO_2
- Power generation: 42-85EUR/tCO_2
- Refineries: 62-83EUR/tCO_2
- Natural gas processing: 16-21EUR/tCO_2
- Standalone hydrogen production: 41-62EUR/tCO_2
- Iron and steel production: 50-90EUR/tCO_2.

A recent European study found that amine capture retrofit in a cement plant would cost about 80EUR per tCO_2 avoided [51]. Likewise, retrofitting a coal power plant with amine capture yields costs roughly in the range of 20–130EUR per tonne of CO_2 (captured basis, varying by technology and assumptions). These figures underscore that amine capture is more economical for high-purity industrial sources, but costs increase above 100EUR/CO_2 for more diluted flue gases such as gas-fired and coal-fired power plants [52]. In case of calcium-looping method for CO_2 capture, techno-economic studies indicate that CaL can achieve CO_2 capture costs comparable to or slightly lower than amines in certain cases. For instance, in a European cement-plant study, the cost of CO_2 avoided with CaL was in the range of 50-70EUR per tonne, while conventional MEA capture costs were estimated at 80EUR/t [51]. This is because, the CaL process

[1]presented costs refers to levelized 2024 unit costs within plant lifetime

can produce excess energy. With a tail-end CaL configuration, electricity can be generated from high-temperature heat, offsetting some costs. The main cost drivers for CaL are the fuel for the calciner and the capital cost of large reactors. If waste heat is available and the cement kiln is integrated with the CaL unit, the effective CO_2 avoidance cost decreases. Therefore, calcium-looping technology shows promise to reduce capture cost (literature suggests 40-60EUR/tCO_2 avoided in optimized scenarios [51]), but it has not yet been proven on a full commercial scale.

2.2.3 Compression and purification unit

After capture, the CO_2-rich stream must be purified and compressed in order to ensure the adequate levels of particular transportation limits. The schematic layout of CPU unit is presented in Figure 2.12. Gas transport is preceded by multi-stage compression, which may be used to achieve supercritical conditions for CO_2. Between each compression stage, separators are installed to remove water. The water content in the gaseous CO_2 stream must comply with the transport specifications required for CO_2 pipelines.

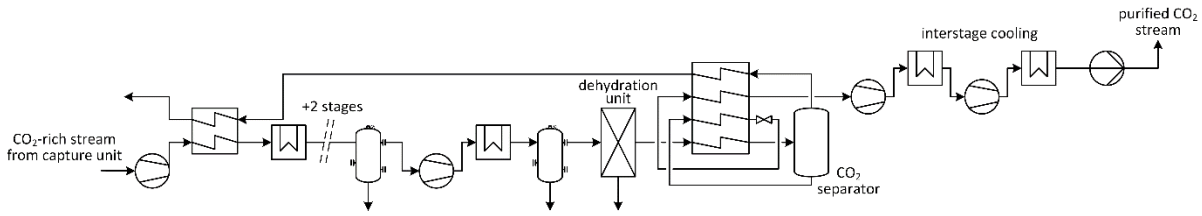

Figure 2.12 Principal layout of CO_2 compression and purification unit (based on [53]).

The main CO_2 drying (dehydration) process is carried out using an absorption system with a triethylene glycol unit (TEG), typically at pressures above 5 MPa, between the 6th and 7th compression stages. The water content in the CO_2 gas stream can be reduced to around 80 to 100 ppmv to meet the pipeline transport specifications for CO_2. This level of water content is accepted in several onshore CO_2 transport projects [53].

A traditional glycol dehydration process is shown in Figure 2.13. Water is absorbed from a gas into a glycol solution in an absorption column. The liquid stream that is a rich glycol is then depressurized in a flash tank to evaporate some of the absorbed CO_2. The liquid is then heated by regenerated glycol in a heat exchanger and sent to a desorber operating as a regenerator. In this column, water is removed from the top and regenerated TEG is removed from the bottom. Heat is added to the reboiler. Regenerated TEG (lean glycol) is pumped through the heat exchanger and a cooler back to the absorber [54]. Moreover, when applying triethylene glycol dehydration to CO_2-based streams, solvent losses, foaming, and potential corrosion have to be taken into account due to significant CO_2 solubility in glycols. For this reason, molecular sieves or other solid desiccants are often preferred as the drying step.

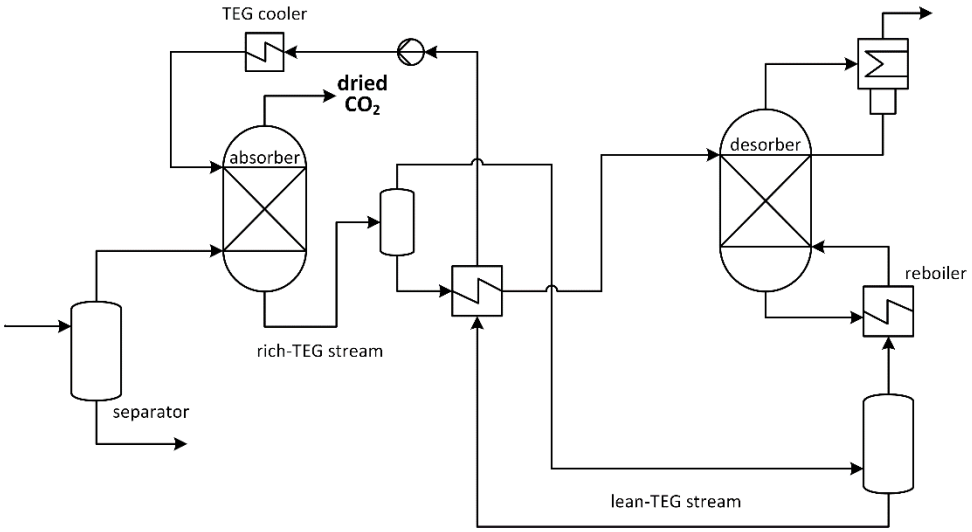

Figure 2.13 Layout of TEG-based dehydration unit (based on [54]).

However, due to the risk of hydrate formation and corrosion, it is recommended to further reduce the water content below 50 ppmv, usually by using adsorption methods. There are three main types of solid adsorbents used for dehydrating gases: silica gel, activated alumina, and molecular sieves. Their relative water vapor adsorption capacity is presented in Figure 2.14. All of them can be regenerated.

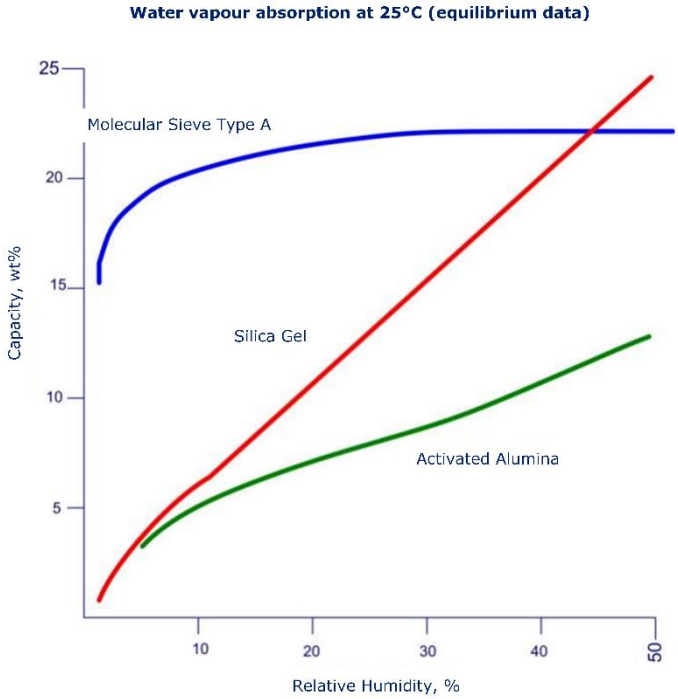

Figure 2.14 Relative water vapor adsorption capacity of solid desiccants at 25°C (from [53]).

- Silica gel is a synthetic material made from silicon dioxide (SiO_2). It is highly porous and can reduce moisture to a dew point of around -50°C under atmospheric pressure. It is easy to regenerate and has a wide pore

size range (1–100 nm), making it effective at capturing a variety of contaminants. Silica gel is acidic and can adsorb acidic gases, but is not suitable for basic substances like ammonia or caustic compounds.

- Activated alumina (Al_2O_3) is a granular, porous substance similar to silica gel. It is a hydrated form of aluminum oxide and can achieve dew points as low as -70°C at atmospheric pressure. It features a wide pore size range (1–1000 nm), although its polar surface is less effective than that of molecular sieves.
- Molecular sieves are synthetic zeolite-based aluminosilicates known for their high surface area, porosity, and ability to achieve dew points as low as -100°C. Their crystalline structure and localized surface charges make them especially effective in adsorbing polar compounds such as water and H_2S. They offer a narrow range of pore sizes, making them highly selective for smaller molecules. These crystals are held together by a binder (commonly clay), which shapes the final product without impeding gas flow. The small size of the binder particles compared to the crystals contributes to the mechanical strength of the adsorbent [53].

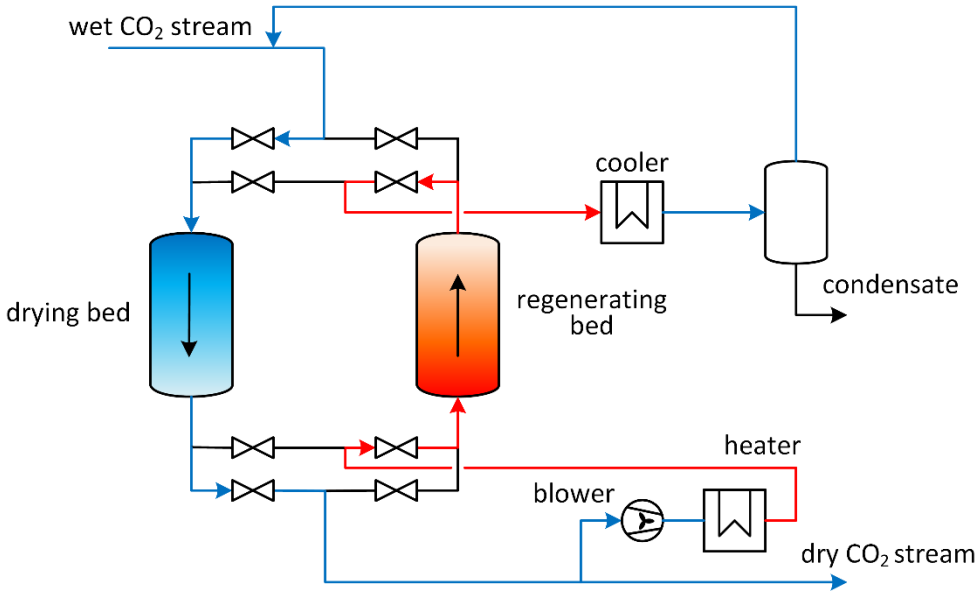

Figure 2.15 Simplified schematic of regeneration with wet gas cycle (based on [53]).

However, triethylene glycol and molecular sieves are the two main dehydration media usually used in CO_2 processing. Acid-resistant molecular sieves, such as type 3A or 4A, are particularly suitable for CO_2 streams containing high levels of impurities such as NO_x, SO_x and H_2S. The required quantity of desiccant depends on the adsorption time, the number of beds in parallel, and the additional capacity needed due to the impurity levels. Low-pressure operations demand larger-diameter beds and higher bed volumes to handle increased gas volumes and moisture content. The regeneration process was schematically presented in Figure 2.15.

The operational lifespan of both molecular sieves and TEG media typically ranges from 2 to 4 years, with 3 years being the average. The maximum train

size for molecular sieve systems varies widely. Design limitations are influenced by factors such as the vessel diameter, capital cost, number of beds in parallel, adsorption time, and regeneration rate. Estimates indicate that a TEG regeneration unit can manage moisture removal from up to 3,500 tonnes per hour of CO_2-rich gas, although achieving this may require multiple contactors. Nevertheless, both TEG and molecular sieve systems offer potential for future capacity expansion, provided the initial design includes space for additional beds [53].

2.2.4 CO_2 transport

CO_2 transport is a key part of the CCUS chain, connecting sources to storage sites or utilization plants. Currently, captured CO_2 is compressed and transported mainly via pipelines and ships, although it can also be derived by truck and rail. Fundamentally, the transportation of gases and liquids via any of these methods is mature, with a technology readiness level of 9. Nevertheless, transportation of CO_2 for large scale associated with CCS units has not yet been achieved using ships or rail. CO_2 pipelines are well-established in countries such as the US and Canada, with decades of experience giving them a high technology readiness level (TRL 8-9). In contrast, liquefied CO_2 shipping is moving rapidly toward industrial scale, with vessels of 7-10 kt capacity already in operation and full port-terminal-injection chains under development. Currently, approximately 3 million tonnes are shipped per year, mainly for the food and beverage industry. Small ships (800-1,800 m^3) are used today, but for economic CCUS operations, ships may be required to carry up to 10,000 tonnes or more. While CO_2 shipping is still developing, the long history of the gas industry with LNG and LPG transport shows that scaling up is technically feasible. The TRL for CO_2 shipping ranges from 3 (offshore injection) to 9 (onshore injection after shipping) [55]. For other types of transport, rail and road transport are generally considered to be pilot- or development-stage options for CCS at scale.

- Pipeline transport

Pipeline CO_2 transport is carried out in two variants: gas-phase transport and liquid-phase transport above saturation pressure. The main elements of the CO_2 pipeline transport system include valve systems, intermediate pump stations (to maintain single-phase flow above saturation pressure), shut-off systems, launch and receiving stations, as well as a monitoring system. The system should ensure pressure control and enable protection against exceeding the maximum allowable pipeline pressure, as well as maintaining the operating pressure within the designated range. Monitoring includes pressure monitoring along the pipeline, temperature monitoring, and air monitoring above the pipeline route. For pipelines, stringent quality specifications must be met to maintain CO_2 in a dense-phase and ensure safety. The water content must typically be below 50 ppmv to prevent hydrates and corrosion, very low levels of H_2S, O_2, and hydrocarbons, and controlled concentrations of inerts such as

N_2 are also required [56]. Pipeline networks also involve booster stations and branching to sustain pressure and flow under supercritical conditions.

- Maritime transport

Maritime transport can enhance the economic flexibility of CO_2 transport, especially when combined with pipeline transport in offshore areas. Carbon dioxide is liquefied upon arrival at the liquefaction facility, either under or without pressure. Then it is stored in temporary storage tanks in liquid form. From these tanks, CO_2 is transferred via a loading system onto a transport ship and subsequently transported to its destination. At the destination port, CO_2 is unloaded from the ship into operational tanks (in liquid phase) using a transfer system similar to that at the departure port. For CCUS technologies, transport ships with a target CO_2 capacity of up to 100,000 m^3 are required. The CO_2, in liquid form, is then compressed and heated to the conditions suitable for pipeline transport to the site of long-term geological storage.

- Rail transport

Since the expansion ratio of liquid to gaseous CO_2 is 1:535, transporting CO_2 in liquid phase is more economical than in gaseous form. The tank cars transporting CO_2 are equipped with three types of pressure protection systems: a pressure relief valve, a rupture disk designed to break at a pressure lower than the tank's test pressure, and two regulating valves. Gas venting from the regulating valve is a normal part of its function. The CO_2 tank cars are filled with chilled liquid under a pressure of 13.8 to 14.8 bar, with CO_2 temperatures between -26.7°C and -28.9°C. The tank cars are insulated with urethane foam, allowing approximately 8 to 10 days of safe transport.

- Road transport

When transporting liquid CO_2 by road using tanker trucks, certain challenges must be considered, particularly the need to stabilize the temperature and, thereby, maintain the saturation pressure of CO_2. Factors such as the size of the tanker and the amount of CO_2 that can be transported are crucial. An important parameter for road transport is the maximum mass of CO_2 that can be carried, which must comply with road traffic regulations. These parameters determine the number and frequency of road trips, directly affecting fuel costs for CO_2 transport, the impact on road wear, and environmental consequences.

Liquefied CO_2 can be transported using trucks with tank trailers and stored in cryogenic tanks. Tankers typically range in size from 2 to 30 tonnes. CO_2 is generally transported at a pressure of 1.7 MPa and a temperature of -30°C. Road tankers offer a flexible and reliable means of transporting smaller amounts of CO_2 over short distances.

Losses in road transport are minimal (approximately 1%), with most occurring during loading and unloading of CO_2. Ambient temperature conditions can affect overall losses. Road transport is a good option for developing CCUS technologies

during pilot project stages, as it requires relatively low financial investment. However, due to road load limits and increased CO_2 emissions associated with road transport, it is unlikely to be suitable for industrial-scale CO_2 transport [57].

2.2.5 CO_2 storage

The choice of a place for an underground geological storage depends on numerous geological, technical, environmental, and economic aspects. The criteria used for the site selection are mainly related to the structure thickness, porosity, permeability, and depth of the layers, as well as water mineralization, an appropriately thick overburden of rocks with poor permeability, the presence of the structure in protected areas and the dimensions of the structure. The captured CO_2 can be stored in:

- saline formations - porous rock formations saturated with brine. These formations are widely distributed and offer by far the largest storage potential. The IPCC estimates that roughly 80% of global theoretical CO_2 storage capacity lies in saline aquifers [58].
- fully or partially depleted oil and gas reservoirs - geological traps that have held hydrocarbons for millions of years can be repurposed to hold injected CO_2. Their geology is well characterized with proven seals and often some existing wells or infrastructure. However, their global capacity is smaller than that of saline aquifers but they still represent an important category for many projects, especially pilot projects.
- coal beds - CO_2 is adsorbed to the coal and releases methane, known as CO_2-ECBM for enhanced coal bed methane recovery.

CO_2 is injected through wells into deep geological formations, typically deeper than 800-1000 m, ensuring a dense supercritical CO_2 state. Once underground, the CO_2 plume is confined beneath impermeable caprock layers and gradually trapped by multiple mechanisms: structural trapping under rock formations, dissolution in brine, residual capillary trapping in pore spaces, and eventual mineralization over decades to centuries. The IPCC AR6 reports the theoretical sequestration potential of roughly 10,000 $GtCO_2$ stored worldwide in geological formations [59]. However, not all sites are accessible or usable due to geologic and engineering limitations. Therefore, the estimations for practical, achievable storage capacity point out 1,000 $GtCO_2$ globally. Therefore, it is essential to distinguish between theoretical capacity (pore space available in principle), practical capacity (technically and economically accessible under current conditions) and matched capacity (linked to identified sources, infrastructure, and demand). In addition, storage capacity is not evenly distributed around the world. Some regions have vast, well-mapped storage resources, while others have less. For instance, North America, Russia, and the Middle East have many large sedimentary basins suitable for CO_2 storage. Europe also has significant capacity, especially offshore. Among others, the North Sea is a prime storage province [58]. When analyzing CO_2 storage and preceding transport, the first

parameterization should be outlined, including modes of transport and indicative distance thresholds. Injection conditions (pressure, purity specifications), as well as frameworks for monitoring, reporting and verification, liability and risk management should be clearly indicated.

Polish structures were recognized and assessed in terms of possible CO_2 storage in many projects and analyses. One of the most comprehensive studies was carried out by a consortium of research and development entities and was led by the Polish Geological Institute - National Research Institute. The potential for CO_2 storage was determined for 46 selected structures occurring in saline formations from the Miocene to Devonian, mainly in the central part of Poland, and for 4 regional aquifers as well as for 38 hydrocarbon deposits with various degrees of depletion and 3 potential options in unexploited coal seams with methane recovery. The storage capacity for Poland was estimated at approximately 15 Gt of CO_2 of which over 90% of potential storage sites are located on land and less than 10% at sea. Moreover, the results show that CO_2 storage potential is primarily aggregated in saline formations (90-93%), while the other storage options amount to 7-10% and ~1% for fully or partially depleted hydrocarbon deposits and deep coal beds, respectively. Suitable sites are typically located at depths greater than 800–1000 m, with sufficient porosity and permeability, an intact caprock seal, and absence of spatial conflicts with groundwater, natural resources or human activities [60]

The CO_2 Storage Atlas developed by the Polish Geological Institute - National Research Institute (PIG-PAN) provides a systematic assessment of geological structures in Poland with the potential for permanent CO_2 storage [61]. Its preparation was based on the collection and integration of geological, hydrogeological and geophysical data, including information from boreholes, seismic surveys, and regional mapping. The analysis focused on identifying formations with sufficient depth to maintain CO_2 in a supercritical state, adequate porosity and permeability to allow injection, and the presence of impermeable cap rocks ensuring long-term containment. Potential storage sites were evaluated in terms of their theoretical and practical storage capacities using volumetric calculations and hydrogeological modelling, while attention was also paid to factors such as structural integrity, sealing efficiency, and proximity to emission clusters and infrastructure.

2.2.6 CO_2 utilization pathways

A promising pathway for captured CO_2 management is CO_2 utilization and conversion, which involve a wide range of industrial processes that transform CO_2 into various useful products. These can be broadly categorized into chemical and durable materials, mineralization, and bio-based routes. Projects around the world, including innovative startups and research centres, are actively exploring these options.

The CO_2 can be utilized for industrial purposes either directly as it occurs in enhanced oil and gas recovery (EOR/EGR) or through out its conversion for synthetic fuels, chemicals production or building materials manufacturing via CO_2 mineralization (Figure 2.16). For methods involving CO_2 conversion, four subgroups can be distinguished: chemical, biochemical, photochemical, and electrochemical. The processes held during conversion require additional energy input with other substrates and feedstocks which leads to the chemicals formulation such as organic and inorganic carbonates, carboxylic acids, carbamic acids, and biodegradable polymers as well as energy carriers such as methane, syngas, methanol, gas hydrates, and biomass fuels [62]

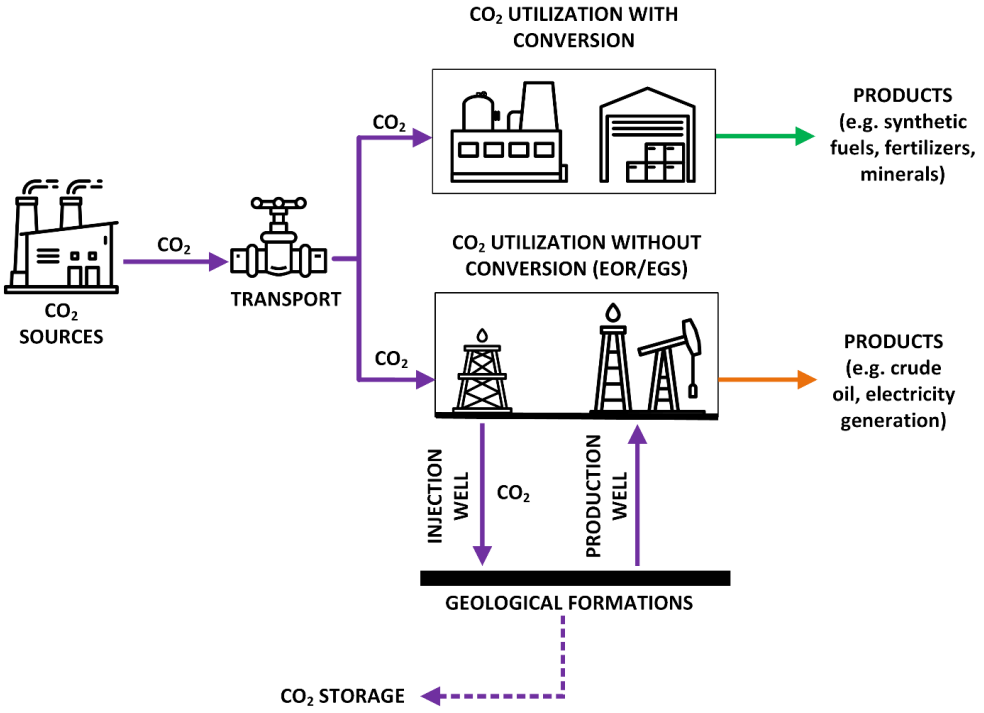

Figure 2.16 Simplified illustration of CCU technological pathways.

In chemical materials, CO_2 is converted into valuable chemicals such as methanol, urea, salicylic acid, polycarbonates, and high-energy liquid fuels. Catalytic hydrogenation of CO_2 is a key method, with methanol production nearing the commercial scale. However, most of these rely on hydrogen derived from fossil fuels, so low-carbon hydrogen sources are essential to make CCU truly sustainable. CO_2 mineralization involves turning CO_2 into stable carbonates, such as calcium carbonate or magnesium carbonate. This process can be performed in situ or ex situ and is considered suitable for permanent storage.

Biological fixation of CO_2 is another promising pathway, using microorganisms, often with renewable energy, to convert CO_2 into fuels and chemicals such as ethanol, butanol, and hexanol. Algae-based systems, in particular, are gaining attention due to their ability to produce biofuels and chemicals. Several pilot and commercial-scale projects are being developed, including facilities from

companies such as Algenol, Dow Chemical, and ENN Group, which are exploring algae-based conversion of CO_2 into fuels and bio-products [63].

The utilization pathways can be assessed based on their technology readiness level (TRL), CO_2 uptake potential, and market size. Those aspects influence the potential for CO_2 use for CO_2 mitigation. Currently, methane and urea production is characterized by the highest market volume of 180-200 Mt per year but relatively low market prices less than 450 EUR/t. Polycarbonates, polyurethane and acids such as acrylic, salicylic, formic, and acetic are marked by high unit price and low market volume. The market size for products such as methanol, ethanol, sodium, and calcium carbonate is moderate between 60-120 Mt per year with a relatively low unit price below 500 EUR/t [63]. What is worth mentioning, in case of CO_2 utilization, the whole lifecycle assessment is necessary in order to fully evaluate the CO_2 avoidance potential. Especially CO_2-based products, which constitute an alternative for fossil-based products, the use and end-of-life phases result in additional GHG emissions, thereby only delaying the emissions release rather than removing.

To broaden the overview, a technology readiness level was presented in Figure 2.17 to evaluate the maturity of certain technologies. It is a qualitative scale used to classify the progression and development from initial concepts through to laboratory studies, pilot scale, demonstration, and full commercial deployment.

Taking into account all CO_2 conversion processes, the estimated potential for CO_2 utilization is around 500 million tonnes per year (excluding applications involving conversion to methane). Currently, around 130 million tonnes of CO_2 are used annually, primarily in the production of urea, polycarbonates, and salicylic acid, with urea production accounting for the majority of this usage [65]. At the global level, a substantial portion of CO_2 emissions cannot realistically be captured, such as emissions from the transport sector (about 25%), the residential and service sectors (around 30%), and certain other areas like agriculture, forestry, fishing, and non-electric energy industries (roughly 15%). Therefore, studies suggest that only about 10–12% of annual global CO_2 emissions could realistically be utilized [66].

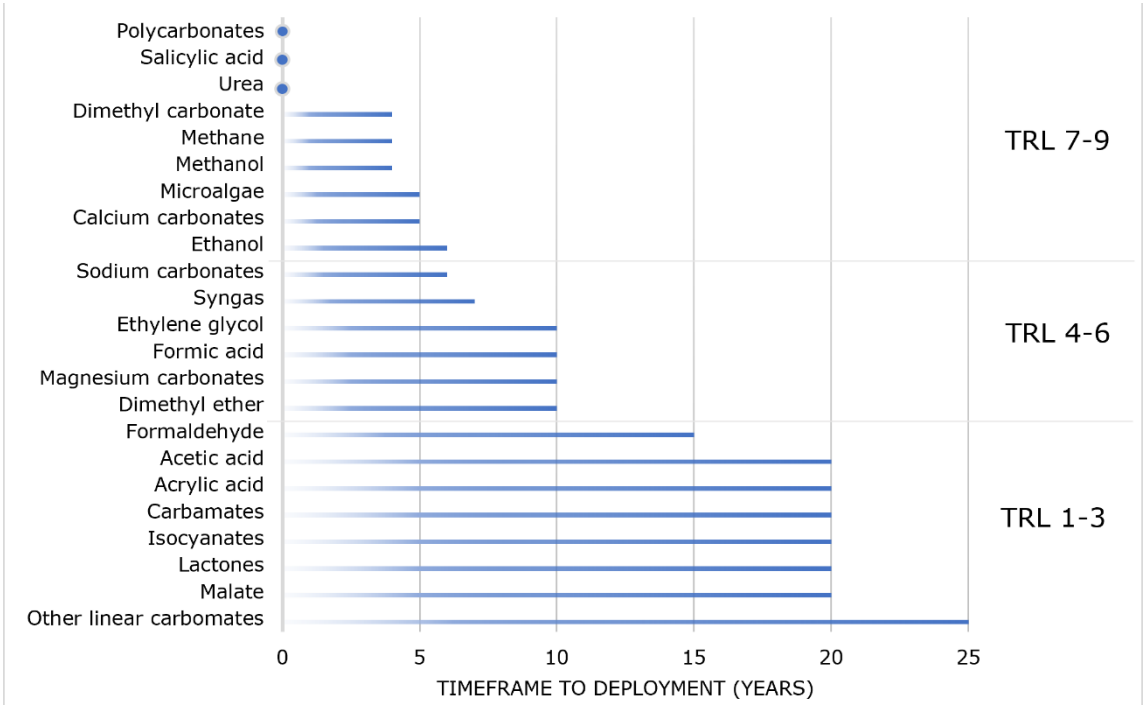

Figure 2.17 TRL and timeframe to deployment for carbon-based chemicals (based on [64])

The next paragraphs discuss several CO_2 utilization pathways selected for a detailed evaluation within the thesis. The cost ranges presented for the utilization pathways and CO_2-derived fuels and chemicals (typically 500 to 2000 EUR per tCO_2 avoided) should be interpreted as scenario-dependent estimates rather than fixed values. They are highly sensitive to assumptions on renewable hydrogen prices, CAPEX, utilization rates, and regional energy markets.

2.2.6.1 Enhanced oil recovery (EOR)

Enhanced oil recovery (EOR) is a well-established technology with a high technology readiness level of 9 [67] that has been in use since the 1970s. Currently, more than 166 commercial projects operate, primarily in the United States [68]. Oil recovery involves three key phases. As for the first one, oil flows naturally to the surface due to its own pressure, although the production rate declines as the reservoir pressure decreases over time. In the secondary phase, water is typically injected into the reservoir to help maintain or raise pressure and displace additional oil. However, due to variations in permeability within the reservoir, the water may flow unevenly, reducing the efficiency of oil extraction [69]. To address this, enhanced oil recovery methods are employed in the tertiary phase, in order to lower oil saturation below its residual level [70]. This operation with captured CO_2 is presented graphically in Figure 2.18.

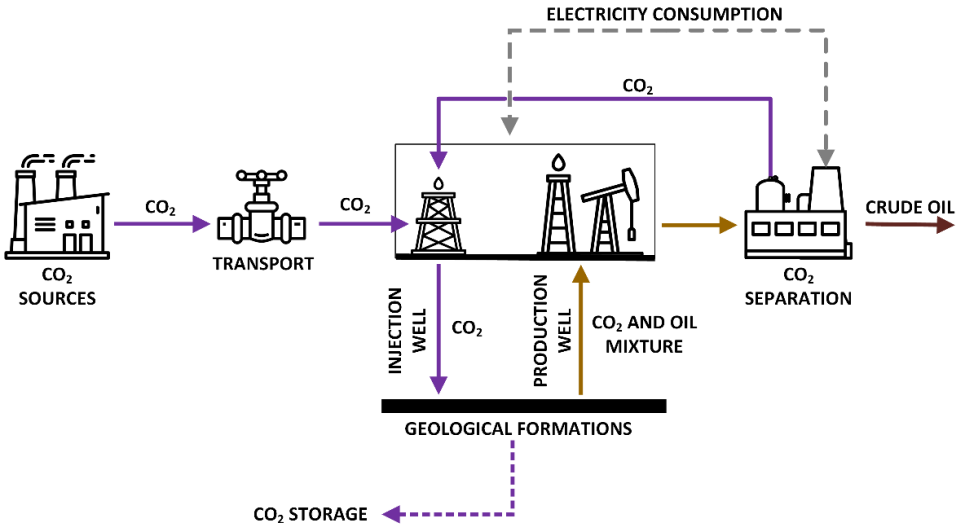

Figure 2.18 Simplified diagram of a CO_2-EOR operation.

EOR techniques can recover an additional 10-20% of oil compared to conventional methods, thus improving extraction efficiency [69]. These techniques include chemical flooding, microbial recovery, thermal recovery, and gas injection, all of which boost oil field productivity. Within the gas injection method, carbon dioxide is used, compressed at the surface, and injected as a liquid into the reservoir, where it acts as a solvent to intensify oil production. As opposed to water, CO_2 can mix with oil and lowers the oil viscosity influencing the ease of flow. Moreover, CO_2 mixed with the oil can be separated and re-injected and thus partially stored in the reservoir. Nevertheless, not every oil field is suitable for CO_2-EOR deployment, depending on reservoir parameters and associated economic or technological aspects [71]. Most of the studies were conducted for United States due to high EOR potential in this region, therefore there is a gap occurring related to environmental research in the European area.

From an economic point of view, EOR provides a revenue stream for CO_2. Oil producers may invest in buying CO_2 for the enhancement of the average oil production. For instance, in the USA, the Texas Permian Basin, the price paid for CO_2 has averaged about 25-35EUR per tonne in recent years. Therefore, the cost per tonne of CO_2 utilized can even be negative in some cases because the sale of CO_2 and the oil revenue (50-60EUR per barrel of oil) offset the capture cost [72]. However, the overall climate benefit of EOR may be questionable, because although some CO_2 is stored in the reservoir, the combustion of the incremental oil produced leads to additional emissions that can offset or even exceed storage gains. Recent studies show that CO_2-EOR can be net-carbon-negative per barrel if a large fraction of CO_2 is retained in the reservoir, but this assumes careful management and does not fully negate emissions from oil use. From a European perspective, CO_2-EOR is not a focus. The EU explicitly excludes EOR-based storage from its climate targets [49]. Currently, no large EOR projects operate in Europe. Hence, CO_2-EOR can offset capture costs by around 25-35EUR per ton via oil revenues, making it a potentially self-financing utilization in regions with suitable

oil fields (primarily North America, China, Middle East), though its alignment with climate goals remains debated [72].

2.2.6.2 Enhanced geothermal systems (EGS)

Another pathway for the utilization of CO_2 without its conversion is enhanced geothermal systems (EGS). Their working principle is based on the hot dry rock (HDR) concept which was studied first in the USA. HDR is underground bedrock, characterized by low permeability, low porosity, and significant geothermal potential [73]. They are usually located at depths of approximately 5 km beneath the surface. They are naturally unsuitable for geothermal energy extraction, therefore, HDR has to be simulated in order to increase its hydraulic performance as well as heat extraction rate. The enhancement of the flow rate of the working fluid can be achieved with several methods, including hydraulic fracturing, chemical stimulation, and thermally induced fracturing [74].

In oil and gas industry, fracturing technologies are commonly known, but in EGS facilities they primarily focus on shear stimulation of pre-existing natural fractures or are adjusted to create new fractures in geothermal fields. Hydraulic stimulation causes fractures to join, expand the contact area, and improve energy exchange efficiency [73]. Heat is collected in the reservoir via injected working fluid, which is subsequently brought to the surface to produce heat and/or electricity, which can be subsequently integrated with a district heating network or other industrial plants. In contrast to hydrothermal, EGS may be suitable in various regions, depending on the viability of the wells and the available source temperature [74].

One of the approaches that improves the overall cost-effectiveness of such an investment is the supercritical CO_2 (sCO_2) cycle that can be applied to EGS [76]. Brown proposed the concept of sCO_2 for EGS as a working fluid and employing reservoir fracturing fluid instead of water, by analyzing the system from a geological perspective [75]. The use of sCO_2 may lead to a thermosyphon effect due to the density gradient between wells. This phenomenon enables direct sCO_2 expansion in a turbine, which significantly simplifies the complexity of a surface plant and performs better operational flexibility [77,78]. In EGS, using sCO_2 as a working fluid can also lead to partial geological storage (Figure 2.19) in the reservoir, which is an additional advantage.

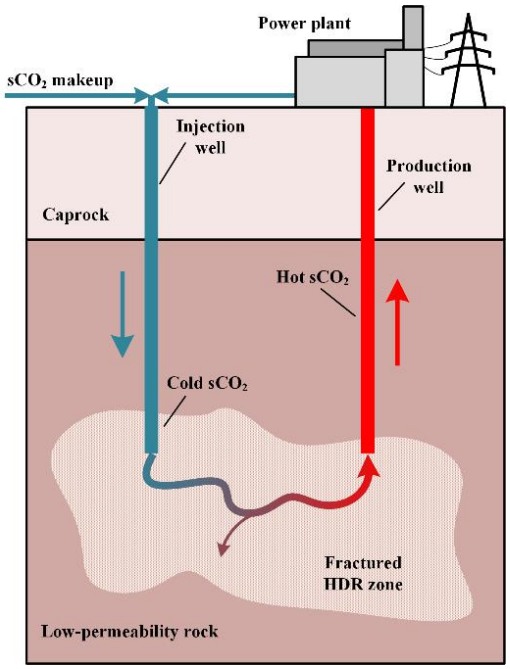

Figure 2.19 Simplified production scheme for enhanced geothermal systems with supercritical CO_2 as a working fluid (based on [75]).

Cost-wise, sCO_2-EGS could potentially offset some carbon capture costs through electricity sales. A study found that, at a CO_2 price of around 90EUR/ton, a hybrid geothermal system could produce electricity at 75EUR/MWh, making it competitive with some renewables [79]. However, in some cases, compensating high capital costs while selling the generated electricity with a levelized price of around 120-170EUR/MWh may financially justify the project deployment [80]. Nevertheless, due to the early-stage of development of such sCO_2-EGS units, there is a lack of comprehensive environmental and economic assessment including limited access to associated data. This option remains at an early technology readiness level, therefore, considerable uncertainty surrounds both its technical feasibility and long-term performance.

2.2.6.3 Chemicals production

a) Methanol

Carbon dioxide in order to be reused as a synthetic fuel, it must be converted to a higher energy form. For this reason, products made from CO_2 should be treated as an energy carrier preferably produced by net-zero or close-zero carbon electricity. The amount of energy required to produce synthetic fuels exceeds the amount of energy recovered, but this can constitute a way to store excess energy in a more useful form. The general class of reactions leading to the production of fuels is known as reforming reactions and includes hydrocarbon and carbon reforming reactions, and hydrogenation reactions.

Methanol (MeOH) is a valuable intermediate for chemical syntheses as well as a fuel, therefore, its use can be considered in two distinct areas. Currently, it is obtained mainly from the synthesis gas produced from the natural gas reforming

or gasification process, but the potential to use hydrogen produced primarily from renewable sources and carbon dioxide from industrial sources opens up new possibilities for its production, while contributing to the reduction of CO_2 emissions into the atmosphere. It can be derived directly from the conversion of CO_2 and hydrogen though hydrogenation process or from hydrogen and carbon monoxide via synthetic methanol process, which is already a commercial technology [81].

Due to the different possible applications, MeOH as a liquid fuel can be considered in two separate directions, offering a feasible solution to contributing to a circular carbon economy. However, CO_2 conversion to a synthetic fuel is an energy-intensive process. The overall conversion efficiency of the methanol production process amount to approximately 50% using hydrogen derived from electrolysis. In such system, approximately 1.37 tCO_2 is used to produce tonne of methanol [81]. Methanol production is considered as highly energy-intensive and is most economically viable where both low-cost renewable energy and CO_2 are available, otherwise conventional MeOH synthesis via using natural gas or coal may increase the GHG emissions [82].

The largest operating unit for renewable methanol production currently is the George Olah facility, which converts around 5600 tCO_2/year using hydrogen from renewable electricity [18].

In the context of CO_2-based methanol production, there are two main catalytic routes for the synthesis of methanol from carbon dioxide: direct hydrogenation of CO_2 from H_2 or conversion of CO_2 to CO and further hydrogenation of CO, according to Formulas 2.13 and 2.14.

$$\mathrm{CO_2 + 3H_2 \rightarrow CH_3OH + H_2O} \tag{2.13}$$

$$\mathrm{CO + 2H_2 \rightarrow CH_3OH} \tag{2.14}$$

Methanol synthesis is a catalytic process, that occurs at high pressure (4-10 MPa) and high temperature (approximately 250°C). The most common catalysts used are copper, zinc, and aluminum. Both reactions described are exothermic with high hydrogen demand.

The production process is schematically presented in Figure 2.20.

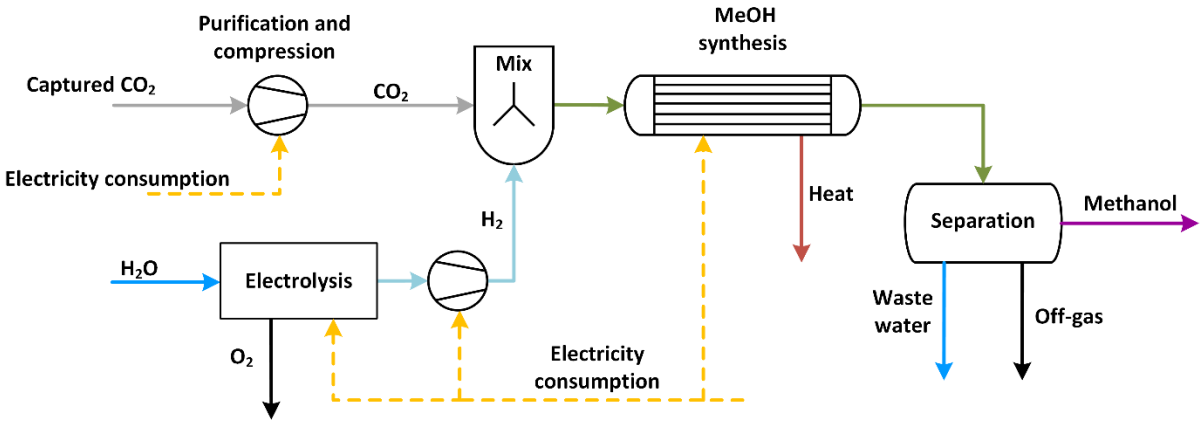

Figure 2.20 Simplified process flowsheet of methanol production (based on [83]).

In the process, carbon dioxide is first purified and compressed. The hydrogen supplied at a pressure of around 30 bar is mixed with CO_2, the mixture is heated and delivered to the methanol rector, where methanol vapor and water are produced. The unreacted synthesis gas is returned to the reactor. After leaving the reactor, the mixture is cooled and separated. The separated gas, consisting primarily of CO_2, is returned to the reactor. Raw methanol contains up to 18% water, as well as ethanol and higher alcohols, and other co-products. Therefore, methanol-rich solution from the separator goes to a distillation column operating at ambient pressure, and is further processed and purified. The overall process requires air, hydrogen, electricity, process heat and cooling, as well as catalysts. Moreover, it is important to distinguish between energy uses of methanol, where the carbon is released again within a short timeframe and chemical or material uses, where the carbon can remain embedded over longer lifetimes.

b) Methane

Thermochemical methanation is a process involving the reaction of carbon dioxide or carbon monoxide with hydrogen in a catalytic reactor. Sabatier reactions, presented in Formulas 2.15-2.17, occurring in the reactor lead to methane production. Both reactions are exothermic.

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (2.15)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2.16)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (2.17)$$

The methanation process steps are presented in Figure 2.21.

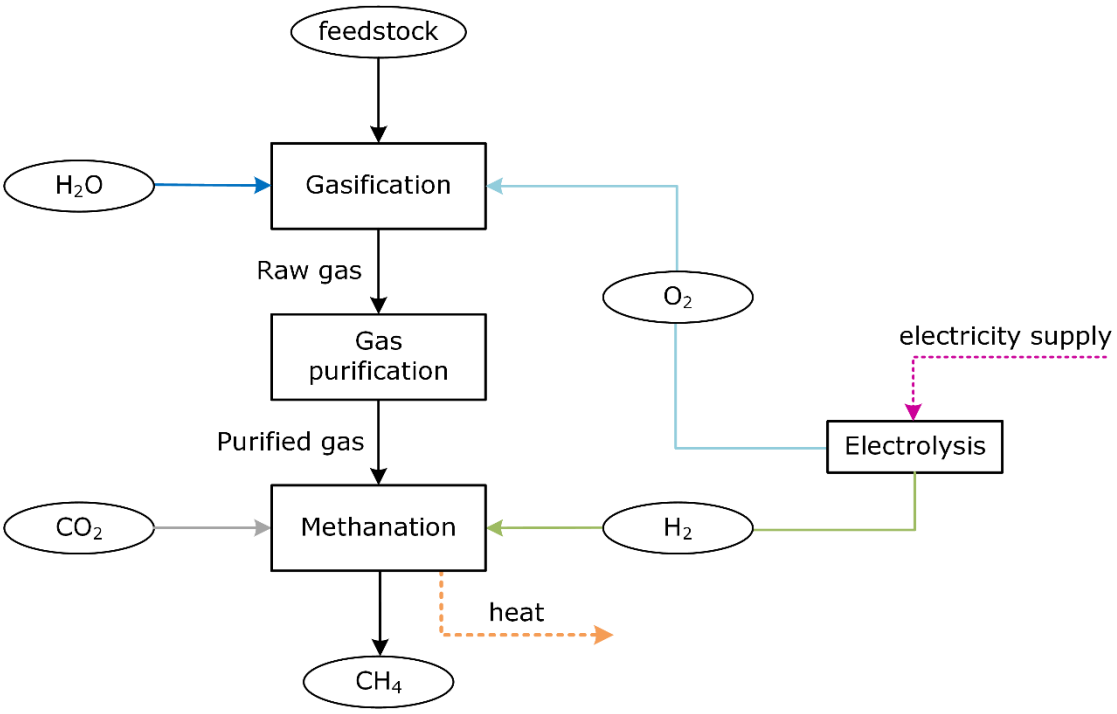

Figure 2.21 Simplified schematic diagram of methanation process (based on [84]).

Reactors are typically operated at temperatures between 300 and 550°C and pressures between 1 and 100 bar. Metals such as nickel, ruthenium, rhodium, and cobalt can be used as catalyst. The most widely used is nickel because of its low price and high activity. In catalytic reactors, large amounts of heat are released as a result of the exothermic methanation reaction, so it is necessary to dissipate it. It is also necessary to control the temperature inside the reactor to prevent its damage. The methanation process can be evaluated primarily in terms of criteria such as achievable methane purity, the reactor volume required for specified purity, and the amount of methane, as well as the maximum achievable process efficiency and energy intensity.

Releasing respectively 206 kJ/mol and 164 kJ/mol. Moreover, reactions are associated with a significant volume concentration of the reacting gases. Methanation using CO_2 is a linear combination of CO methanation and reverse water-gas shift reaction (RWGS), which accompanies the reaction by the use of a nickel catalyst. Theoretically, the reactions may occur as thermodynamically ideal, meaning reversible, with standard conditions, although, to favor the methane production process, high pressures are required. However, high temperatures will limit methane formation, so finding the equilibrium with proper pressures and temperatures is essential [84].

c) Dimethyl ether (DME)

Another valuable product which can be produced from CO_2 is dimethyl ether (DME). It is a well-known propellant and coolant and also constitutes an alternative to fossil fuels used in diesel engines performing high efficiency and low CO, NO_x, and particulate emissions after its combustion. Dimethyl ether is

a volatile compound that burns with a clean, visible blue flame and has properties similar to those of propane and butane, enabling it serve as a substitute for liquefied petroleum gas (LPG).

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (2.18)$$

DME is considered an environmentally friendly and safe fuel due to several factors: it does not form explosive peroxides, it emits lower levels of carbon monoxide and hydrocarbons during combustion because of its oxygen-rich molecular structure, and it releases minimal particulate matter and nitrogen oxides. It also serves as a green alternative in aerosols and refrigerants due to its zero ozone depletion potential and lower global warming impact values. Beyond fuel applications, DME is used in various industrial roles, such as in pesticides, polishing, anti-rust agents, and as a precursor for chemicals such as dimethyl sulphate and light olefins. Traditionally, it is produced from a wide range of feedstocks such as coal, natural gas, or biomass, but can also be derived from the reactions using hydrogen and CO_2. It can be synthesized either indirectly through methanol dehydration (Eq. 2.18) or directly via a more efficient single-stage process using bi-functional catalysts. Purification involves conventional chemical engineering methods such as absorption, flashing, and distillation to remove impurities and recover methanol [85].

d) Urea

One feasible direction for carbon dioxide utilization is urea production. Urea is a nitrogenous fertilizer that originates from the reaction of ammonia and CO_2. The CO_2 utilization reacts with ammonia as follows:

$$CO_2 + 2NH_3 \leftrightarrow NH_2COONH_4 \leftrightarrow NH_2CONH_2 + H_2O \quad (2.19)$$

Urea is one of the most convenient form for fixed nitrogen. It has the highest nitrogen content available in a solid fertilizer, amounting to approximately 46%. It can be produced as prill or granules, which are practical for transportation with no hazard of explosiveness [86]. The final product is used for soil fertilization and nourishing, usually for farmlands due to its high nitrogen content [81]. Besides soil fertilizer, the urea products can be used in other areas of everyday life, either in the form of derivative products or via direct use. The production process is divided into four units corresponding to: urea synthesis, recirculation, evaporation and purification, and waste water treatment [86]. The process flowsheet is illustrated in Figure 2.22. The carbon in urea typically returns quickly to the atmosphere via agricultural application, reflecting a short carbon cycle. This has important implications for life-cycle assessment, as it limits the scope for considering such use as a source of permanent CO_2 removal.

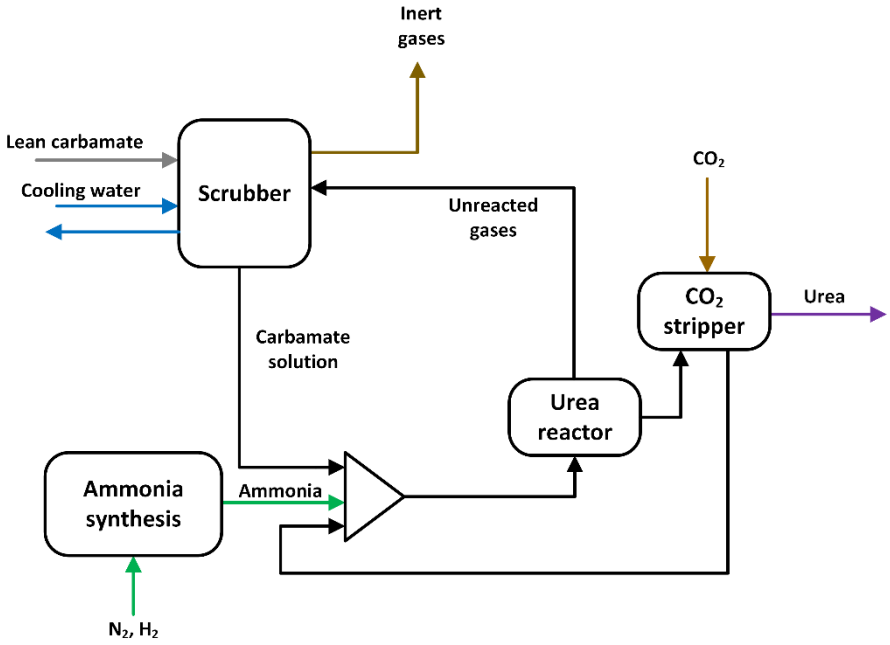

Figure 2.22 Simplified process flowsheet of urea production (based on [87]).

e) Olefins

Another promising application is CO_2 conversion into light olefins such as ethylene and propylene, which play a relevant role in the petrochemical industry. The annual global production capacities of ethylene and propylene together reached 120 Mt and 191.5 Mt in 2018 and 2019, respectively. With steady growth, the numbers are expected to increase to 283 Mt by 2030. They are conventionally derived from fossil fuels, and steam cracking of crude oil and ethane is anticipated to be a leading technology for olefins production, although alternative pathways are more environmentally friendly and accessible.

Methanol-to-olefins (MTO) is one of the approaches that evolved into a stand-alone technology for ethylene and propylene production after the energy crisis in the twentieth century. The reactions occurring in the MTO process, operated at 340-540°C and 1-3 bar, are exothermic themselves, however, the further steps involving the separation and recovery of the products are highly energy-intensive [88].

While the use of renewable hydrogen and captured CO_2 to produce alternative fuels such as methanol and DME has been well evaluated, the application of this approach to light olefins production remains under-researched. Traditional methods such as steam and fluidized catalytic cracking are both energy-intensive with significant carbon emissions, making them environmentally unsustainable for sustainable climate goals, especially given the growing demand for ethylene and propylene. There are two main pathways for converting CO_2 and hydrogen into light olefins: the modified Fischer-Tropsch process and the methanol-mediated route. The former offers higher CO_2 conversion rates and better C_2 product yields with smaller reactor equipment, while the latter provides higher selectivity for C_2–C_4 olefins, reducing

downstream separation costs [88]. Studies show that utilizing 10% of the CO_2 emissions from a cement plant could yield in approximately 591 kg/h of ethylene, 745 kg/h of propylene, and 523 kg/h of butylene, preventing over 28 kt of CO_2 emissions annually and achieving a net negative emission rate of 2.14 kg CO_2 per kg of C_2–C_4 olefins produced (assuming renewable electricity supply for heating, cooling and electric needs and carbon fed to the system counted as avoided emissions from cement plant) [89].

The overall production processes consist of three primary stages: methanol production, methanol-to-olefins conversion, and product purification. If methanol is sourced externally, the first step can be omitted. In the MTO reaction, methanol is initially converted to dimethyl ether and water (Eq. 2.20), followed by the transformation of DME into ethylene (Eq. 2.21) and propylene (Eq. 2.22), with product ratios influenced by catalyst choice, operating conditions, and technology. The UOP/Hydro MTO process achieves nearly complete methanol conversion with up to 80% yield of ethylene and propylene, and eliminates the need for methanol purification which is necessary when crude oil-derived methanol is used. It was developed jointly by Honeywell UOP and Norsk Hydro, as a process with high efficiency and flexibility, allowing for adjustments in the ethylene-to-propylene ratio to meet market demand.

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (2.20)$$

$$CH_3OCH_3 \rightarrow C_2H_4 + H_2O \quad (2.21)$$

$$3CH_3OCH_3 \rightarrow 2C_3H_6 + 3H_2O \quad (2.22)$$

A notable variation is the advanced MTO process, which combines MTO with the Olefin Cracking Process (OCP), which enhances the propylene yield. Reactions are carried out using a SAPO-34 zeolite catalyst in a fluidized-bed reactor [90]. After the reaction, the product stream undergoes multistage compression with interstage cooling, where the condensed water is removed. To avoid dry ice formation, CO_2 must be reduced to below 100 ppm, which is achieved using diglycolamine (DGA) solvent in an absorption-regeneration cycle. The DGA absorbs CO_2 in a counter-current absorber, is regenerated in a stripper, and then recycled. Following CO_2 removal, the hydrocarbon stream is dehydrated to reduce moisture and prevent the formation of hydrates. The dried stream then enters the separation system. The further separation train includes units such as a demethanizer, deethanizer, depropanizer, debutanizer, C_2 splitter, and a pressure swing adsorption (PSA) system for hydrogen recovery. This conversion of methanol to olefins, performed with the SAPO-34 catalyst at 450°C and a pressure of 1.5 bar, produces mainly with 49% of ethylene, 32% of propylene and 9.8% of butene [82].

f) Aromatics

Aromatics such as benzene, toluene, and xylene (BTX) are critical feedstocks in industries such as pharmaceuticals, dyes, paints, and textiles. Their global demand continued to increase over the last years. Conventionally, they are

produced via catalytic reforming and pyrolysis gasoline, but due to the environmental impacts and dependence on fossil feedstocks, alternative production routes are being explored. A promising pathway is the methanol-to-aromatics (MTA) process, particularly when methanol is synthesized from captured CO_2 and renewable hydrogen, offering a sustainable route to aromatic compounds [91].

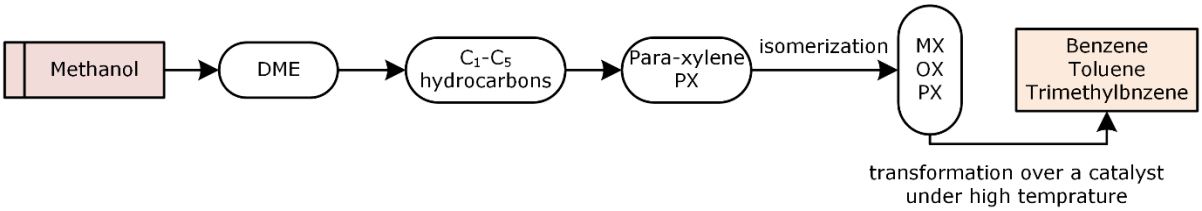

Figure 2.23 Simplified scheme of the production of aromatics from methanol (MX, OX refers to isomers of xylene, based on [92]).

The MTA process involves a series of complex reactions occurring over metal-zeolite catalysts, typically containing elements such as Zn, Ga, or Ag, and using SAPO or ZSM frameworks. Similarly to olefins production, the reaction sequence begins with methanol dehydration to dimethyl ether, followed by a cascade of transformations including hydrogen transfer (from olefins to paraffins), olefin or paraffin dehydrogenation to aromatics, and further reactions such as alkylation, dealkylation, isomerization, and disproportionation (Figure 2.23). The selectivity and yield of aromatics are strongly influenced by catalyst acidity, reaction temperature, and reactor configuration. Operationally, MTA processes are typically designed in multiple stages to optimize each reaction step. The product stream undergoes separation into water, gases (e.g. dry gas, LPG, pentane), and liquid hydrocarbons, from which BTX is extracted by distillation [92].

Environmental assessments indicate that while traditional naphtha-based aromatic production performs well in terms of acidification and toxicity categories, biomass-based and CO_2-based methanol routes significantly reduce global warming potential and ozone depletion. For instance, a pilot MTA facility in Shaanxi, China, has demonstrated industrial viability with a 30,000-tonne annual BTX capacity, showing the potential of CO_2-derived methanol as a clean and scalable feedstock for aromatic production [93].

The costs of CO_2 utilization in chemicals production vary widely by product type. In the near-term scenario (by 2035), the cost per tonne of CO_2 avoided is estimated at 540–1970EUR for methanol, methane and dimethyl ether, reflecting their similar process chains and its high dependence on renewable green hydrogen. For urea, which uses CO_2 as feedstock in a less energy-intensive process, the cost is lower, around 200–1090EUR per tonne of CO_2 avoided. In contrast, olefins and aromatics exhibit particularly high near-term costs, with values ranging from 5060–26,740EUR per ton of CO_2 avoided, especially in regions with high RES costs and where these products require multiple conversion steps and substantial energy input [94]. Compared with

fossil-based production, the same study finds that minimum selling prices (MSPs) for CCU-derived chemicals are typically 2.2–3.0 times higher for methanol, DME, ammonia, urea, and aromatics, and 2.5–3.3 times higher for olefins, while methane remains 6.3–8.9 times more expensive. However, under optimistic scenarios and with favorable electricity price conditions, some CCU-based products could approach costs less than 1.5 times those of their fossil counterparts. This suggests that while current CCU chemical production is not yet economically competitive, ongoing technology advancements and declining renewable energy costs could substantially narrow the gap with fossil-based alternatives in the coming decades [94].

In relation to all chemicals resulting from CO_2 conversion, due to subsequent carbon release, these pathways should be assessed taking into consideration the process characteristic, complexity, and own impacts.

2.2.6.4 Carbon mineralization

Carbon mineralization refers to the process of converting CO_2 into stable solid compounds, typically by bonding it with minerals to form carbonates. In this method, CO_2 is absorbed and stored in inert materials such as concrete or its aggregates, undergoing a natural recarbonation process over time as a result of the reaction with atmospheric CO_2.

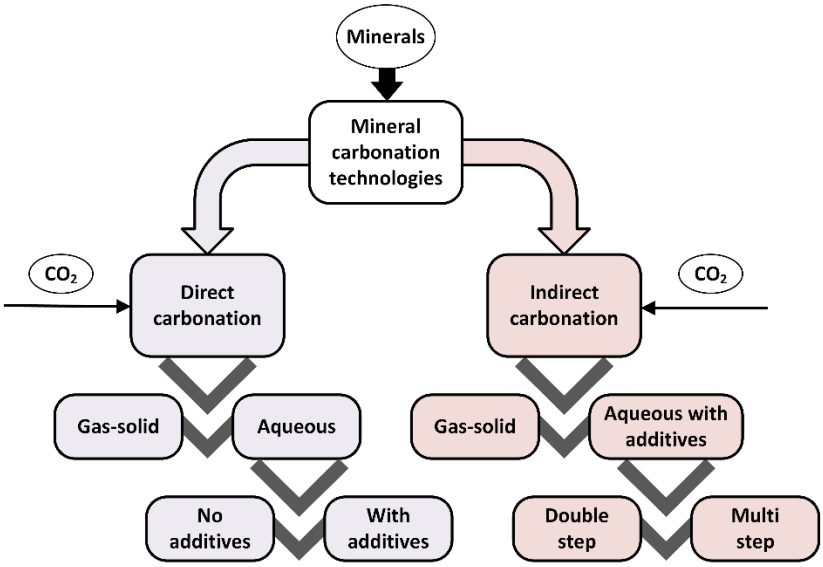

Figure 2.24 Illustration of mineral carbonation pathways (based on [96]).

Various techniques can accelerate this absorption, often using concentrated industrial exhaust streams, as presented in Figure 2.24. During concrete curing, CO_2 enrichment can also enhance strength if moisture and temperature are appropriately controlled [95]. Carbon mineralization technologies often include enhanced chemical weathering of minerals, primarily those rich in calcium or magnesium, which react with CO_2 to form carbonates [96]. The effectiveness of mineralization in reducing emissions and storing CO_2 depends on the specific process and the scale of material demand. Among the available pathways,

carbonate production offers the highest potential for CO_2 utilization. This process involves reacting captured CO_2 with pure minerals or mineral-rich compounds such as olivine, serpentine or wollastonite forming a reaction feedstock. Reactions typically occur in high-pressure, high-temperature reactors and may require additional reagents or heat input depending on the process design [97]. Thus, carbon mineralization can be used for miscellaneous applications in various economic sectors, although the potential for CO_2 emissions reduction and CO_2 stored via mineralization depends on the type of process and total demand for materials.

Mineralization tends to be energy and material-intensive, so costs are currently moderate or high. Reported estimates range widely from 50 up to 400 EUR per tonne of CO_2 for various mineralization methods [98]. In situ mineralization which has been demonstrated on a small scale, reports an injection cost of around 21 to 25EUR per tonne of CO_2 in the Iceland pilot, but that unique geology and cheap renewable power aid the process. A study projects that by 2030, in situ mineralization could cost approximately 100EUR/t or less, while ex situ mineralization cost may lay in range of 150–200EUR/t with technology learning [99].

To conclude the review of CO_2 utilization and storage pathways, Table 2.3 provides a comparative overview of the technologies discussed. The table summarizes their current commercial status and typical requirements for CO_2 purity. It is worth highlighting that, while some options are already commercial with well-established specifications, others remain at an early stage of development and face significant uncertainties.

Table 2.3 Summary of commercial status and CO_2 purity requirements for assessed CO_2 storage and utilization pathways.

Technology	**Commercial status**	**CO_2 purity**	**Reference**
EOR	Commercial	>95%mol	[100]
EGS	Experimental/demonstration	>98%mol	[101]
Methanol production	Pilot/semi-commercial	99%mol	[102]
Methane production	Pilot/early stage	>95%mol	[103]
Urea production	Commercial	>95%mol	[104]
DME production	Pilot/early stage	>99%mol	[105]
Olefins production	Pilot/early stage	>95%mol	[89]
Aromatics production	Pilot/early stage	>95%mol	[93]

Carbon mineralization	Pilot/demonstration	flexible	[106]
CO_2 storage (saline formations)	Commercial	>95%mol	[107,108]

In general, both the literature reviewed here and other publications beyond this state-of-the-art study indicate that CO_2 utilization and storage pathways represent an attractive option for Poland's decarbonization process. This thesis further extends the research by providing additional environmental and economic assessments, while also highlighting the opportunities and challenges associated with deploying CO_2 utilization in Poland's energy transition.

3. Research goal, objectives and scope of the study

The primary objective of this dissertation is to develop an integrated methodology for the evaluation of captured CO_2 management options, encompassing both the utilization and geological storage. This is based on methodology which combines the mathematical modelling findings with a comprehensive framework that simultaneously addresses environmental and economic dimensions. The study specifically targets the comparative analysis of multiple CO_2 sources in combination with two distinct capture methods, with the aim of identifying the most sustainable and efficient pathways for achieving emission reduction targets in Poland while maintaining economic viability.

Research Hypotheses:

a) CCUS technologies can serve as transitional solutions during the energy transformation, enabling the reduction of CO_2 emissions in hard-to-abate sectors by 2050, in line with the EU Fit-for-55 trajectory and the EU ETS system.

b) The decisive factor determining the effectiveness of CCUS is the captured CO_2 management option - permanent underground storage or economically justified use.

c) Evaluation of potential CO_2 management pathways requires a holistic approach integrating environmental (aligned with LCA methodology) and economic (including CAPEX, OPEX, market profitability) analyses.

d) Under Polish conditions, the most promising solutions should balance environmental benefits with economic efficiency, and their implementation must take into account the stage of economic transition in which they deliver the greatest benefits.

Scope of the Dissertation:

- Identification and categorization of CO_2 sources (emissions from fossil fuel combustion, bioenergy units, industrial processes, and direct air capture);
- Selection of CO_2 storage and utilization technologies, taking into account technology maturity, technical feasibility, and potential relevance for the Polish economy;
- Development of methodological frameworks (system boundaries, functional units, allocation rules) and preparation of life cycle inventories for selected technologies;
- Environmental assessment (based on LCA) and economic evaluation (including capital expenditures, operational costs, market benefits) across different CO_2 management scenarios;
- Sensitivity analyses to identify critical factors that influence system performance;

- Interpretation of results in the Polish context, comparison with international experience, and identification of the most promising solutions in terms of scalability and implementation potential.

The dissertation concludes with the formulation of practical guidelines for the evaluation and selection of CO_2 utilization and storage technologies in Poland, as well as an indication of their role within national strategic efforts to reduce greenhouse gas emissions.

4. Methodology for system assessment

The literature review presented in Chapter 2, points out the wide range of possible solutions for captured CO_2 management. Despite that, there is a lack of comprehensive studies embedded in Polish conditions which could provide an answer to some of the crucial questions related to pathway selection, choosing the right moment for the deployment and the scale of their applicability. To address these identified gaps within the broader strategic efforts, this research is designed to build upon previous studies and existing measures related to CO_2 utilization and storage technologies in Poland, integrating them into a comprehensive methodological framework. Building such a framework requires a clear understanding of how emission sources operate and how capture technologies interact with them. This leads to the need for process modelling of energy systems, which serves as the next step in this study.

The energy system is defined by IPCC as a system that comprises all components related to the production, conversion, delivery, and use of energy [109]. It starts with primary energy stored in natural resources such as fossil fuels or renewable sources, which is subsequently harvested, transported, and then converted to transform energy to more usable form throughout employing a wide variety of processes. In addition to serving as a feedstock, primary energy can also be used as process energy. After conversion, usable energy is distributed through the dedicated infrastructure to the final user [110]. The need to comprehend and predict the performance and operation of individual energy system components, as well as the overall system behavior, drives model development. The energy system models focus mainly on the technological characteristics of the system components. Economic, environmental, and social aspects are usually introduced as exogenous parameters or are evaluated based on obtained results, rather than being explicitly modelled. At the process level, operating variables such as flow rates, temperatures, and pressures are modelled directly, while fuel prices, product prices, overall investment costs, as well as environmental impacts are evaluated externally. The following paragraphs elaborate how those three aspects related to the energetic, economic and environmental standpoint were addressed within the framework of the research.

4.1 Process modelling

Model is a representation of reality and modelling is the process of creating a simplified representation of particular concept, physical phenomena, or real-world object with abstract notations including mathematical symbols in order to understand, predict, control or optimize its operation. Modelling is characterized by deriving from physical laws a valid set of mathematical equations which describe the system behavior to quantitatively evaluate the system performance in accordance with a predefined aim [111]. In engineering, modelling refers to

building mathematical models that describe how physical, chemical, or biological processes work. These models use equations based on fundamental principles, primarily mass and energy balances, fluid flow, heat and mass transfer, and reaction kinetics, used to capture the behavior of a system. Depending on the purpose of the model, it can be as follows:

- Forecasting – used to analyze historical trends to evaluate future impacts of certain actions, behaviors, and general patterns.
- Backcasting – unlike forecasting, backcasting starts with a vision of a desired future energy system and works backward to determine the policies, strategies, and actions needed today to achieve that future. It focuses on how to bridge the gap between the present and an idealized outcome.
- Scenario analysis – created to evaluate different possible pathways by comparing multiple alternatives with the reference baseline scenario [112].

It is crucial to point out that described approaches such as these are not modelling structures in the sense of equation types or process representations. Rather, they constitute frameworks that guide how models are used in system analysis. Forecasting extrapolates observed trends into the future, backcasting starts from a desired end-state and works backward to identify feasible pathways, and scenario analysis explores multiple possibilities to test robustness under uncertainty. In this thesis, these approaches are treated as methodological frameworks that complement the process and system models.

The experiment conducted on a model is called simulation. Simulations use a computer-executable version of a model, typically created by compiling it from a computer-based, modelling language. The user must write the model's equations in the modelling language. Based on simulations performed, models provide information about process behavior under different conditions, as well as help to analyze performance, troubleshoot problems, and design new or improved systems. Conventionally, modelling and simulation have been used for strategic, tactical, and operational decision-making at low levels of technological aggregation, for unit operation or at plant level. Higher levels of aggregation involve supply chains, whole sector such as energy sector and entire economy.

Energy system models can be classified according to the modelling approach into three main categories: computational, mathematical, and physical models. Computational models consist of sequences of instructions that can be executed directly by a computer. Unlike mathematical models, which are formulated as sets of equations that describe relationships between variables, computational models are implemented as algorithms that operate autonomously. Such models are frequently applied in areas such as supply chain modelling, electricity market simulations, and process control. In contrast, mathematical

models describe energy systems through formal mathematical relationships and can be subdivided into statistical and mechanistic models. Statistical models employ techniques such as regression and optimization to derive simplified relationships from data, whereas mechanistic models are grounded in first-principle theories such as thermodynamics, fluid mechanics, and mass and energy balances. Depending on the nature of the variables and system dynamics, mathematical models can be further categorized as discrete or continuous, steady-state or dynamic, and deterministic or stochastic. In relation to this, another classification of energy system models can be done along several complementary dimensions. The first distinction concerns the degree of knowledge embedded in the model. White-box models are based on first principles such as thermodynamics, fluid mechanics, mass and energy balances, grey-box models combine mechanistic balances with empirical correlations or regression fits, and black-box models rely purely on statistical or machine-learning relationships derived from data. From an implementation perspective, models can be formulated either in an equation-orientated manner, where all equations are solved simultaneously (usually used in advanced process modelling tools) or in a sequential-modular structure, where unit operations are solved stepwise with information exchange between modules. With respect to system dynamics, models may be steady-state, describing long-term equilibria or design points, or dynamic, capturing transient trajectories and control behavior. Uncertainty analysis further separates deterministic formulations, where all inputs are fixed, from stochastic formulations, which explicitly propagate parameter or scenario variability. Finally, depending on the type of processes represented, models may be continuous, using algebraic, ordinary, or partial differential equations to describe physical and chemical processes or hybrid discrete-event, combining continuous dynamics with discrete transitions such as phase changes, on/off switching, or equipment failures. Physical models differ fundamentally from computational and mathematical models in that they reproduce real-world phenomena on a reduced scale or with lower complexity. For instance, physical prototypes of energy systems, such as solid oxide fuel cells, are constructed to simulate hardware behavior and validate theoretical assumptions [111]. In system analysis, physical modelling is concerned not only with analyzing how a system behaves over time. It can also be applied to calculate operating points, which is known as static modelling. In contrast, dynamic modelling focuses on computing the trajectories of systems as they evolve over time. Static modelling is used primarily during the design phase for system sizing and optimization, while dynamic modelling is typically employed during the operational phase for control design and real-time optimization [111].

Creating mathematical process model involves the following steps (Figure 4.1) [112]:

a) Problem statement

The first step of creating process model includes the definition of the problem and describing of the main goal which provides general concept of the entire system.

b) Model development

The conceptualized problem enables to identify its key features and the following parameters and assumptions that describe the given system. The complexity of the model determines the amount of data needed to develop it. High-quality input data leads to more accurate estimations.

c) Model translation

The next step involves translating the model into computer-readable format based on the chosen modelling language and the type of assessment. That allows for efficient and more effortless data collection and computation of a real-world system models. Within this thesis, models were developed using gPROMS Process engineering software.

d) Verification and validation

Verification step relates to ensuring that model runs without any logical, conceptual, or computational errors. The validation step refers to ensuring that developed model is useful for solving specific problems and satisfies the requirements, and to ensuring that the procedures give sufficient results within a reasonable timeframe to assess if the initial set of searches needs to be adjusted. In addition, validation should be performed to evaluate the model's ability to compare between alternative search methodologies. The verification of gPROMS models involved checking the correct implementation of equations, unit consistency, and robustness of the numerical solution. Convergence was ensured by monitoring the residuals of the mass and energy balances and confirming that iterative solutions reached stable values within predefined numerical tolerances at a level of 10^{-5}. Validation was carried out by comparing model results with experimental and literature data under representative operating conditions.

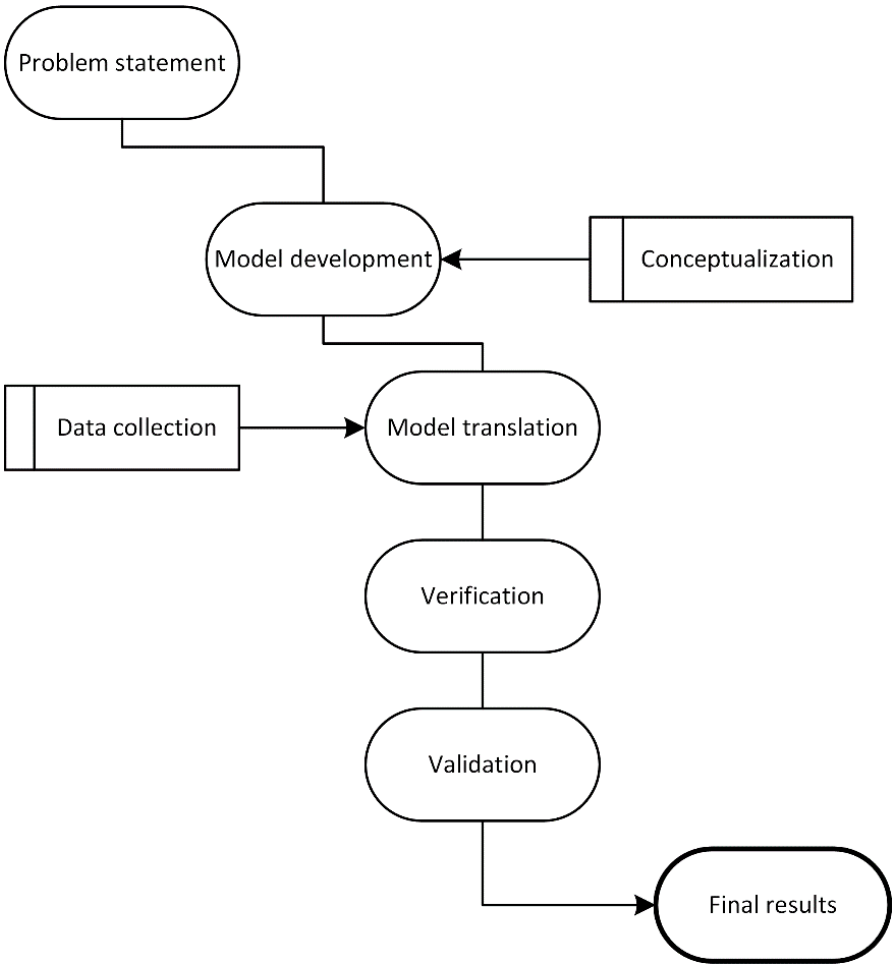

Figure 4.1 Process modelling steps (based on [112]).

In the development of an energy model, the modeler inevitably encounters incomplete or unavailable data. To address these gaps, specific assumptions are necessary to compensate for the missing information. These assumptions are inherently integrated into the modelling approach and constitute a critical component of the model itself. They must be carefully formulated and evaluated to ensure that the energy system can be accurately and comprehensively simulated. A fundamental aspect of these assumptions involves the distinction between endogenous and exogenous variables.

- Endogenous variables are those whose values are determined within the model as they are dependent on the relationships and equations that define the system. The technological characteristics of the system components are modelled endogenously.
- Exogenous variables, in contrast, are external to the internal dynamics of the model; their values are assumed to be fixed or provided as input data, unaffected by other variables in the system. The economic, environmental, or social parameters may be modelled exogenously [112].

Process systems modelling traditionally focused on models of chemical conversion processes at the scale of processing plants. In this framework, a system is represented as a network of interconnected subsystems, where the inputs capture the influence of external factors, while the outputs represent the impact of the system on its surroundings. Within a plant, these subsystems correspond to unit operations, and the links between them are described by flows of mass, energy, or information. Physical and chemical mechanisms are mathematically described using differential balance equations. Unit operation models are typically combined with simulation and optimization techniques to support tasks ranging from reaction pathway design to the synthesis of entire process flowsheets and the optimization of networked subsystems. Alternatively, empirical models derived from experimental input-output data can be applied to cover a wider operational range.

For the purpose of creating process models, engineering software programs are used as tools. They allow to develop models based on physical and chemical principles, giving users the flexibility to define custom equations and simulate both steady-state and dynamic behaviors.

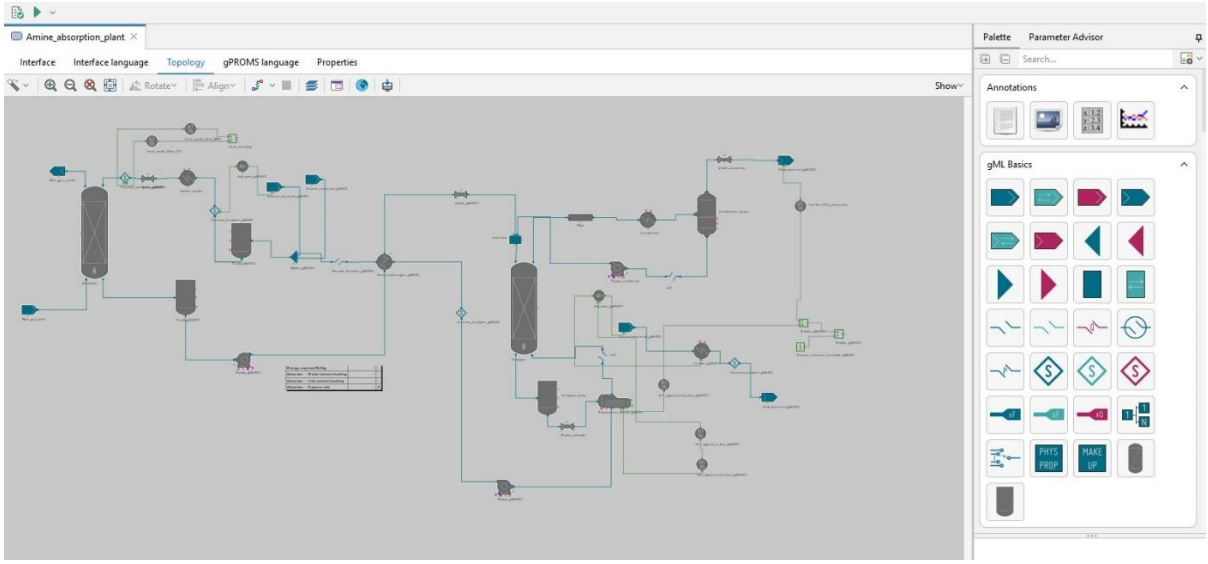

Figure 4.2 User interface of the gPROMS Process environment used for process modelling and simulation.

For further assessment, the process models of selected units were developed using the gPROMS Process engineering software. gPROMS Process is an environment developed by SIEMENS for modelling and optimization for performing both steady-state and dynamic studies of chemical and energy systems. The interface of the modelling environment is presented in Figure 4.2. It supports the entire process design concept through the adaptation of high-fidelity models to achieve optimal design. In contrast to sequential modular simulators, gPROMS represents a process as a coupled set of differential-algebraic equations that are solved simultaneously. This formulation enables the

rigorous treatment of recycle loops, tight mass-energy couplings, and strong nonlinearities. Standard libraries of unit operations and thermodynamic/property packages are available within the software, but the environment is also designed to accommodate custom models when the library scope is insufficient. The models can be written using modelling language, based on conservation laws, constitutive relations, transport correlations, and reaction kinetics [113].

The direct results relate to:

- Mass balance, which allows to evaluate the inlet and outlet flows of materials used in assessed plants and auxiliary facilities such as CO_2, H_2, water, flue gases and other by-products.
- Energy balance, which quantifies overall electricity, heat and cooling needs, as well as allows to evaluate the possible integration of those requirements.

In this thesis, a combination of modelling strategies was employed to represent the various processes under investigation. Several models were developed from the first principles, constructed entirely from scratch on the basis of fundamental governing equations. These models explicitly incorporate the physical and chemical laws describing the system behavior, enabling a mechanistic understanding of the underlying phenomena. Certain models were created by integrating pre-existing components from modelling libraries included in gPROMS Process software. This approach employed validated and computationally efficient modules as building blocks. For selected processes where detailed mechanistic descriptions were either unavailable or unnecessary, an indicator-based modelling approach was applied. This method treats the process as a black-box, relying on empirical correlations, performance indicators, as well as aggregated input-output relationships rather than explicitly modelling internal mechanisms. Indicator-based models are particularly useful for capturing system behavior in cases where data-driven relationships provide sufficient accuracy for simulation or optimization purposes without the computational burden of fully mechanistic modelling.

The modelling work begins by defining the scope and boundaries of the system. Assumptions regarding unit performance, heat losses, pressure drop, and mixing are stated explicitly at the outset to constrain the model space. Consistent with those assumptions, appropriate parameter sets are selected, with property data compiled from reference sources. Subsequently, the flowsheet is assembled using a combination of library units and custom models written in the gPROMS language. Mass and energy balances, rate expressions, or transport relations are formulated within the equipment units. Numerical aspects are addressed in parallel with model assembly. Solver tolerances and discretization choices are tuned to achieve stable convergence. Before simulation run is attempted, the model passed dimensional consistency checks

and the analysis of degrees-of-freedom confirming that the number of specifications matches the number of unknowns. Many corresponding failures are symptoms of under- or over-specification, missing boundary conditions, or inconsistent units. Establishing a consistent set of reference states for enthalpy and entropy, as well as verifying stream compositions and phase declarations, helps eliminate hidden contradictions. Initialization is the next critical step. Equation-oriented solvers are sensitive to the quality of initial guesses, particularly in highly nonlinear flowsheets with recycle and reaction. Feasible starting points are constructed from design calculations, where necessary, subsystems are solved first, and their states used to initialize the full model. These continuation strategies are employed to move from an easy and well-behaved problem to the target problem.

Once prepared, a consistent steady state simulation can be performed. The solver failures or errors can be associated with thermodynamic inconsistency, data and parameter issues, or system runtime, and related warnings. The first ones can be solved by verifying the property-methods selection for particular compositions and stream parameters. The second issue requires its own diagnostics by checking the data set to prevent from structural inadequacy. When the third type of error occurs, usually a minimal reproducible case is extracted by limiting the flowsheet to the smallest subsystem that still exhibits the failure. This reduction accelerates diagnosis by revealing that often an apparently global issue originates from a single unit or correlation. This model verification ensures that simulations are performed without associated failures. The validation step closes the model preparation and its simulation by checking the balances at the unit and flowsheet level. Apart from verification which overlooks if the model is posed correctly and the equations are solved properly, validation aims at confronting with independent data set with pre-defined acceptance criteria ranges. Internally, the model must close mass and energy balances to within stated tolerances and respect thermodynamic constraints and externally, the model is challenged with independent data from scientific publications, experimental data or data from technology providers [114].

4.2 System analysis

The assessment of carbon capture, utilization and storage technologies requires an integrated approach that points out the interactions between technical performance, economic feasibility, and environmental outcomes. Each unit within the chain is characterized with its own requirements, outputs, and resulting emissions (Figure 4.3). Therefore, in the following sections key aspects related to these dimensions are described.

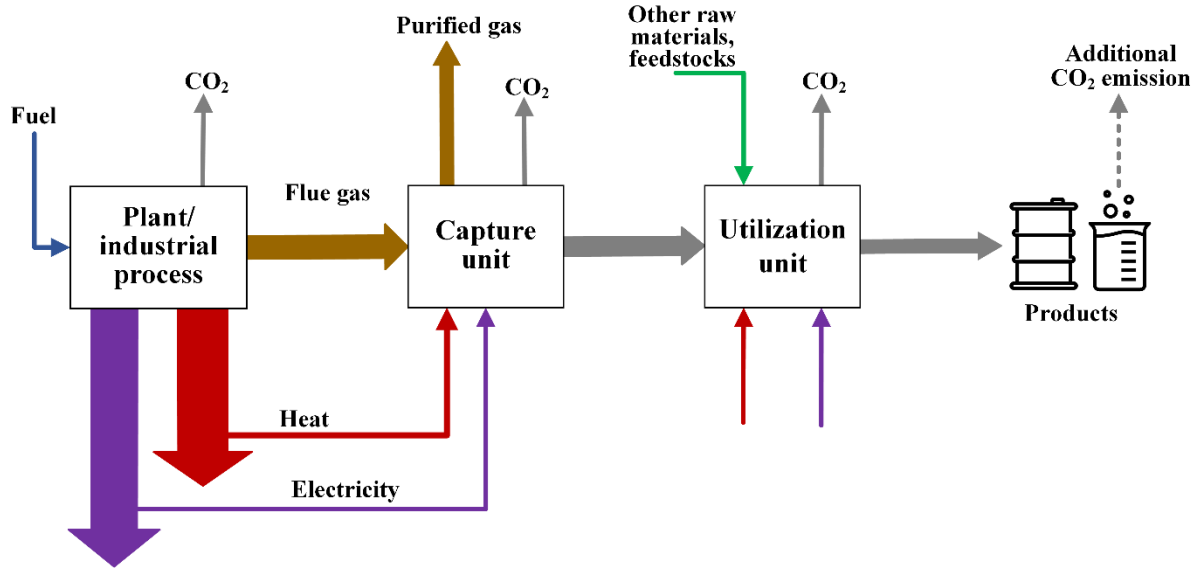

Figure 4.3 Simplified schematic diagram of CCU chain with CO_2 capture from emitter.

4.2.1 Energetic analysis

The overall performance of the analyzed units with capture installations can be calculated using the following formulas:

- net electrical efficiency (η_{net}, %LHV):

$$\eta_{net} = \frac{E_{el}}{\sum_n^i E_{ch,i}} \tag{4.1}$$

- net electrical efficiency penalty ($\Delta\eta_{net}$, %points):

$$\Delta\eta_{net} = \eta_{net,REF} - \eta_{net,CCS} \tag{4.2}$$

- specific primary energy consumption for CO_2 avoided ($SPECCA$, $MJ_{LHV}/kg\ CO_2$):

$$SPECCA = \frac{q_{net,CCUS} - q_{net,REF}}{e_{CO2,REF} - e_{CO2,CCUS}} = \frac{\Delta q_{net}}{e_{CO2,avoideed}} \tag{4.3}$$

$$e_{CO2} = e_{CO2}^{dir} + e_{CO2}^{indir} \tag{4.4}$$

$$SPECCA = \frac{3600 \times \left(\frac{1}{\eta_{net,CCS}} - \frac{1}{\eta_{net,REF}}\right)}{e_{CO2,REF} - e_{CO2,CCUS}} \tag{4.5}$$

where:

E_{el} annual net electricity generation of the system, MWh_{el},

$E_{ch,i}$ annual consumption of the i-th fuel, MWh_{LHV},

q_{net} unit energy requirement per product, MJ_{LHV}/MWh_{el}, $MJ_{LHV}/kg_{product}$,

e_{CO2} amount of specific CO_2 emissions calculated as sum of direct and indirect CO_2 emissions, kg $CO_{2\text{-eq}}$/MWh_{el}. "REF" relates to the reference plant, "CCUS" refers to the plant integrated with the carbon capture installation.

Direct specific primary energy consumption (q_{dir}) is the amount of chemical energy supplied in the form of fuel used per unit of product, while indirect specific primary energy consumption (q_{indir}) is the amount of energy consumed by the generation of power required per unit of product (P_{el}) and for other product supply.

$$q_{net,CCS} = q_{dir} + q_{indir} \tag{4.6}$$

$$q_{dir} = \frac{\dot{m}_{fuel} \cdot LHV}{\dot{m}_{product}} \tag{4.7}$$

$$q_{indir} = \frac{P_{el}}{\eta_{el}} + e^*_j \cdot \dot{m}_j \tag{4.8}$$

where:

η_{el} - electricity generation efficiency, accounting for 41.4% for polish electricity generation,

e^*_j – primary energy consumption index for j-th material flow, MJ^*/MJ, MJ^*/kg,

$\dot{m}_j$ – j-th material mass flow, kg/s.

- CO_2 converted, which refers to the total amount of CO_2 converted in the process, also taking into account the recycling streams. It is expressed as a percentage of the total amount of CO_2 that enters the process unit as a feedstock [115]:

$$CO_{2,conv} = \left(\frac{CO_{2,in} - CO_{2,out}}{CO_{2,in}}\right)_{process} \tag{4.10}$$

where:

$CO_{2,in}$ inlet flowrate of the CO_2 to the system,

$CO_{2,out}$ outlet flowrate of the CO_2 from the system.

- CO_2 utilized, related to the total amount of CO_2 that is converted into the final product (gross) as well as taking into account the indirect emissions e.g. from the use of electricity or heat in the process as well as following CO_2 emissions stemming from the usage of the final product e.g. via combustion (net) [115]:

$$GrossCO_{2,used} = \left(CO_{2,in} - CO_{2,out}\right)_{process} \quad (4.11)$$

$$NetCO_{2,used} = \left(CO_{2,in} - \left(CO_{2,out} + CO_{2,indirect}\right)\right)_{process} \quad (4.12)$$

Moreover, the cumulative energy consumption (CEC) was evaluated to assess the energy requirement for the utilization process as well as for upstream processes that include the energy outcome of the product derived from the CO_2 utilization. Cumulative energy consumption is a life cycle metric that quantifies the total amount of primary energy required by a product system over its entire life cycle. CEC is obtained using Formula 4.14 based on the difference between all input and credits for displaced product or service flows such as electricity, fuels, heat/steam, water, make-up of solvents/sorbents, converted to primary energy via cumulative consumption factor of the i-th or j-th process/product in reference to the amount of CO_2 avoided. The calculation includes also all co-products/services exported by the CCUS system, therefore, Q_j^{out} is the delivered quantity of output j, and f_j^* is the primary-energy intensity of displaced reference supply. For CO_2 management, CEC was calculated as a difference between the amount of energy necessary to utilize or store one tonne of CO_2 and the additional energy originating from developed products. Data related to the cumulative CO_2 emissions in upstream and downstream processes were taken from the literature [116] and LCA databases from SimaPro software, mainly EcoInvent [117].

$$\Delta Q_i = \sum_s \sum_{k \in K_i} f_k^* Q_{s,k} \quad (4.13)$$

$$CEC_{CCUS} = \frac{\sum_s \sum_k f_k^* Q_{s,k}}{\Delta e_{CO2}} - \sum_j \frac{f_j^* Q_j}{\Delta e_{CO2}} = \frac{\sum_i \Delta Q_i - \sum_j f_j^* Q_j}{M_{CO2,avoided}} \quad (4.14)$$

where:

s – life cycle stage (capture, compression and purification, transport, utilization or storage, injection, etc.),

k - final energy carrier,

i - primary (non-renewable) energy form,

j - exported output credited via system expansion (electricity to grid, useful heat, fuels, chemicals, etc.),

$Q_{s,k}$ - final energy consumption of the carrier k in stage s,

f_j^* - cumulative consumption factors of the energy carrier that converts to primary energy,

f_k^* - primary-energy intensity indicator of the displaced reference for output j.

For storage, no exported products occur, thus, CEC is the sum of consumables in capture, conditioning, purification, transport, and injection. In case of utilization, the calculation includes energy outputs such as fuels and/or material products. Credits are the avoided primary energy of the reference pathways these products displace.

4.2.2 Economic assessment

Economic evaluation is divided into calculations of unit costs related to capital investment and operational expenditures and determination of levelized costs of capture, utilization and storage.

- Unit costs (EUR/tCO_2)

Capital expenditures for a carbon capture facility refer to fixed one-time expenses involved in building the facility. In addition to equipment, there are also capital costs associated with engineering, procurement and construction costs, as well as the costs associated with land, ownership of a site, and startup costs, inventory requirements, financing costs [29].

An important factor that influences the capital cost is the size and scale of the capture plant. A preliminary cost estimate for an industrial facility can be made using the factorial method, which relies on scaling from a similar-sized existing plant. The scaling factor (k), typically ranges between 0.6 and 0.8, depending on the specific process and layout of the plant.

$$\mathrm{C} = \mathrm{C_0} \cdot \left(\frac{\mathrm{S}}{\mathrm{S_0}}\right)^{\mathrm{k}} \tag{4.15}$$

where:

C – cost of plant A,

C_0 – cost of plant B,

S – capacity of plant A,

S_0 – capacity of plant B,

k – scaling factor.

The size of the process equipment, as well as the energy requirements of the capture facility and the potential method of CO_2 capture adapted for the reference unit, are determined by the partial pressure of CO_2 in the flue gas. Streams containing more CO_2, with higher CO_2 partial pressures are easier to separate the CO_2, because it will be transferred from the gas to capture the media faster. Therefore, this reduces the equipment size and the subsequent

cost of capture. Furthermore, at low partial CO_2 pressures, chemical solvent-based methods are generally the most suitable, despite their higher capital costs and energy demands for CO_2 separation. As the partial pressure of CO_2 increases, alternative technologies become more practical and economically attractive, often requiring less investment in equipment and lower energy consumption compared to conventional chemical solvent systems [29].

To evaluate the economics of the analyzed investment the levelized cost calculation method was introduced. It depends on capital expenditures (CAPEX), operational expenditures (OPEX), incomes, taxes, and depreciation. The operational costs involve fixed, annual operating and maintenance costs (FOM, EUR/tCO_2) calculated as a sum of labor cost, insurance, tax fees costs, and variable, annual operating and maintenance (VOM, EUR/tCO_2) costs of maintenance and repairing, fuels, and other feedstock as a sum of costs of each medium and material flows. Both are calculated per unit of product.

Levelized cost of storage or utilization (EUR/tCO_2):

$$LCOS\ (LCOU) = LCOC + FOM + VOM \tag{4.16}$$

where levelized cost of capital ($LCOC$, EUR/tCO_2) can be calculated as follows:

$$LCOC = \frac{TOC_{annualized}}{Plant\ size \cdot CF} \tag{4.17}$$

where:

$Plant\ size$ - corresponds to size of unit via amount of CO_2 captured, removed, stored or utilized tCO_2,

CF - capacity factor of a plant, %,

TOC - total overnight cost, total capital requirement, EUR:

$$TOC_{annualized} = TOC \cdot CRF \tag{4.18}$$

$$TOC = C_c + C_i + C_{ep} + C_p + C_o + C_s \tag{4.19}$$

where capital recovery factor (CRF) is derived from:

$$CRF = \frac{r(1+r)^n}{(1+r)^n - 1} \tag{4.20}$$

A bottom-up approach is adopted to evaluate capital investments for CO_2 capture processes. For each equipment item, the direct cost, which is based on the sizes and materials specified by the technical simulation, is estimated using referring published data. The total investment cost is then obtained by summing these direct costs and applying an indirect-cost multiplier to account for installation, engineering, and other overheads. Following this approach, the

Bare Erected Cost (BEC) encompasses the purchase and installation of process equipment along with on-site supporting facilities and infrastructure, including both direct and indirect labor. Adding the engineering, procurement, construction services yields the Engineering, Procurement, and Construction Cost (EPCC). Incorporating process and project contingencies to EPCC gives the Total Plant Cost (TPC). Finally, the Total Overnight Capital (TOC) is obtained by summing TPC with the owner's and other overnight costs. TOC is reported in base-year currency and excludes construction-period escalation and financing charges. The total overnight cost is calculated as a sum of the direct materials cost of the components (C_c), installation cost (C_i), engineering and procurement cost (C_{ep}), process and project contingencies (C_p), owner's costs (C_o), and startup cost (C_s) including pre-production costs and inventory capital, per unit of product.

The cost of CO_2 captured is the total annualized cost of a CO_2 capture plant divided by the total amount of CO_2 captured by the facility. The cost of CO_2 avoided is calculated by dividing the total annualized cost of operating a CO_2 capture plant by the net amount of CO_2 the unit prevents from entering the environment. This net amount is the total CO_2 captured minus the CO_2 emissions generated by the plant itself, such as those from burning fuels and from consuming grid electricity (considered as Scope 1 and 2 emissions in life cycle assessments). Since the avoided CO_2 is always less than the total captured CO_2 due to these operational emissions, the cost of CO_2 avoided is inherently higher than the cost of CO_2 captured, as the total expense is distributed over a smaller effective volume [29].

In terms of operational expenditures, they can be calculated as follows:

$$OPEX = VOM + FOM \tag{4.21}$$

$$VOM = \sum_s C_s = \sum_s c_s M_s \tag{4.22}$$

$$FOM = I + M + O + A \tag{4.23}$$

where VOM represents costs, of total consumables calculated by summing the costs of each material or energy carriers stream (C_s) derived by multiplying cost of each medium (c_s) and its quantity (M_s). FOM includes costs, of insurances and taxes (I), maintenance (M), operating (O) and administration and support (A).

Taking this into account, the cost of CO_2 avoided (CAC) was also introduced. CAC denotes the average cost of CO_2 emissions reduction by unit by adding CCUS to the emitter or building a separate DAC unit. This indicator is used to compare different CCS projects and identify the most economically viable ones.

For power plants the formula can be expressed by:

$$CAC = \frac{LCOE_{CCUS} - LCOE_{REF}}{e_{CO2,REF} - e_{CO2,CCUS}} = \frac{LCOE_{CCUS} - LCOE_{REF}}{(t_{CO2}/MWh)_{REF} - (t_{CO2}/MWh)_{CCUS}} \quad (4.24)$$

where:

$LCOE$ – levelized cost of electricity, EUR/MWh.

In case of CCUS from industrial sources, three different methods are commonly used to calculate the CO_2 avoidance cost, including CO_2 capture, transport, and storage. However, while these three methods aim to calculate the same cost metric, each of these methods relies on different assumptions. The first is based on the power generation calculation method, where the CO_2 avoidance cost is calculated with regard to the cost and CO_2 emission intensity of the product ($LCOP$) of the industrial plant with and without CCUS.

$$CAC = \frac{LCOP_{CCUS} - LCOP_{REF}}{e_{CO2,REF} - e_{CO2,CCUS}} = \frac{LCOP_{CCUS} - LCOP_{REF}}{(t_{CO2}/U_P)_{REF} - (t_{CO2}/U_P)_{CCUS}} \quad (4.25)$$

The second and third methods, referred to as the net present value and annualization approaches, are commonly used to assess production costs, similar to how electricity costs are calculated, as illustrated in Equations 4.26 and 4.28. These methods are based on unit cost calculations derived from the discounted cash flow involved in implementing CCS. Unlike the first method, they do not include the cost of the industrial facility where CCS is applied and are not directly related to the main product or material input of the plant. As a result, these approaches are particularly useful for evaluating CCS in retrofit scenarios, where no changes are made to the plant's production process [11].

$$CAC = \frac{NPV_{CCUS}}{\sum_\tau \delta^\tau (e_{CO2,REF} - e_{CO2,CCUS})} \quad (4.26)$$

$$\delta = \frac{1}{(1+r)^\tau} \quad (4.27)$$

$$CAC = \frac{TOC_{annualized} + FOM_{annual} + VOM_{annual}}{e_{CO2avoided,annual}} \quad (4.28)$$

where:

NPV_{CCUS} - relates to the net present value of the total annual CCUS costs (which may vary annually), EUR.

All costs reported reflect N^{th}-of-a-kind plants and are stated in 2024EUR. Any investment figures not originally in 2024 terms were scaled to 2024 using the Chemical Engineering Plant Cost Index (CEPCI).

Furthermore, considering novel technologies and their future costs, not only scale should be adjusted. The future costs of the project should be evaluated with respect to experience rates for technology components based on their similarities to already mature components in terms of complexity and customization [32]. Based on experience rates, the technology learning rate can be assessed, which influences the cost reduction potential (Figure 4.4) [118].

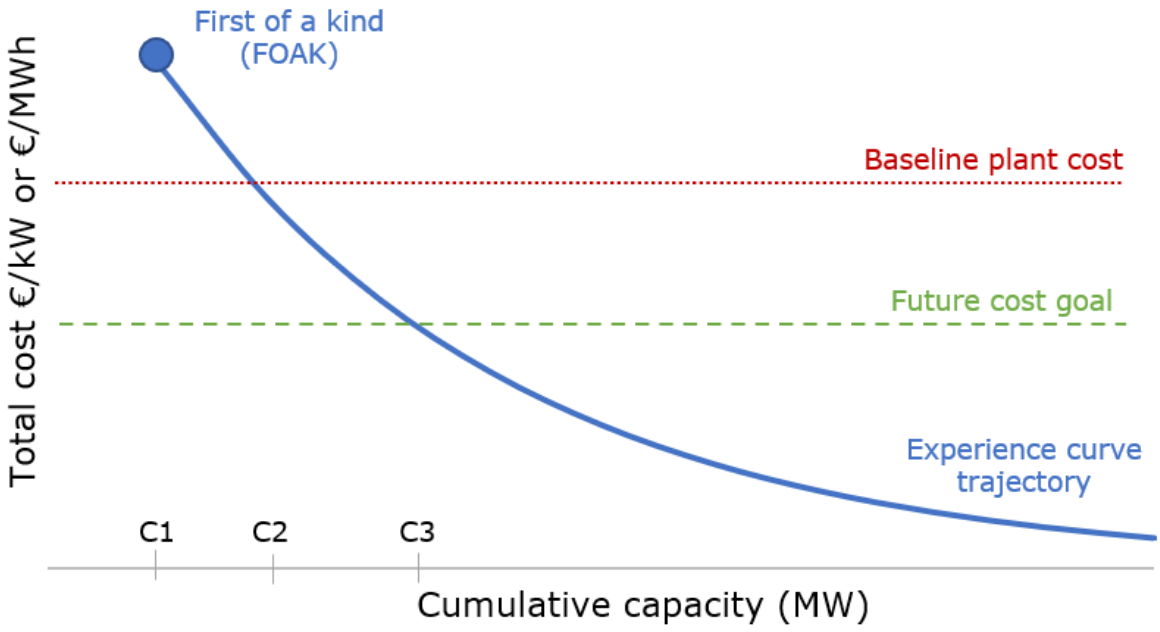

Figure 4.4 Unit cost change with learning rate (based on [118]).

Cost projections for emerging technologies typically rely on two main methods: expert elicitation and model-based approaches, such as experience curves. While experts are effective in describing current conditions, they often struggle with long-term cost forecasting, particularly for new technologies. In contrast, model-based methods, especially those based on historical learning trends, have proven to be more accurate. Experience curves suggest that costs decline as the deployment increases, with Wright's law [119] stating that each doubling of cumulative output leads to a predictable, technology-specific cost reduction, known as the experience rate.

The projections found in literature have assumed experience rates of 10–20% for capital costs and 2–2.5% for variable operating costs. However, these assumptions were often based on analogies with other low-carbon technologies and lacked systematic evaluation, resulting in inconsistent cost forecasts. Recent research emphasizes that a technology's design complexity (number and

interaction of technical components) and need for customization (degree of adaptation to specific environments) are critical factors influencing its actual learning and cost reduction potential. Nevertheless, in this thesis, the costs decrease related to technology maturing was assessed within sensitivity analysis along with framework from [32] to assess how initial capital expenditures impact the final results.

4.2.3 Environmental assessment

In order to evaluate the climate mitigation tools, the life-cycle approach should be introduced while assessing the GHG emissions. It is especially critical when analyzing utilization with hydrogen supply. Potential of hydrogen to limit the negative impact of the emission release. Since hydrogen serves as a secondary energy carrier as well as a feedstock to further processing, its total environmental impact can differ while expanding system boundaries including upstream and downstream processes. Hydrogen production highlights the need for a broader environmental assessment, as well as the products resulting from CO_2 conversion, which usually constitute only a temporary medium for further CO_2 release during combustion.

For the purpose of conducting an environmental assessment based on carbon footprint (CF) analysis, a methodology based on the GHG Protocol guidelines was selected. The GHG Protocol was developed by the World Resources Institute (WRI) and the World Business Council for Sustainable Development (WBCSD) [120]. It is the most widely used framework for estimating greenhouse gas emissions by decision-makers, businesses and governments, providing comprehensive and standardized guidance for inventorying emissions across a wide range of categories, taking into account upstream and downstream supply chains, materials, and operations.

The carbon footprint is a measure of the total greenhouse gas emissions, both direct and indirect, associated with the entire life cycle of a product or technology. It quantifies the GHG emissions generated during an activity, technological process, or the production of a product or service. CF can be used to assess the emission intensity of GHGs or to provide a comprehensive estimate of the total emissions linked to an economic process, service, or operating facility. Despite being part of the broader category of *ecological footprint,* the carbon footprint is not expressed in units of area. Instead, it is measured in mass units, with no conversion to surface area. The result of a CF analysis is expressed as an equivalent amount of carbon dioxide per functional unit, typically in kg of CO_2 equivalent ($CO_{2\text{-eq}}$). Therefore, GHGs other than CO_2 are included in CF by multiplying their actual mass by their Global Warming Potential (GWP). GWP is a relative measure of how much heat a greenhouse gas trap in the atmosphere compared to CO_2. It compares the warming impact of a specific gas with that of the same mass of CO_2 over a given time horizon, usually 100 years (GWP100).

The Intergovernmental Panel on Climate Change (IPCC) periodically publishes GHG Protocol reports that list GWP100 values for all greenhouse gases, providing standardized reference values relative to CO_2 [121]. The formula for calculating the carbon footprint of a product or technology is presented in Eq. 4.29.

$$\mathrm{CF} = \sum_{i=1}^{n} A_i \cdot EF_i \tag{4.29}$$

where:
A_i - i_{th} activity included in product or process system boundaries,

EF_i - emission factor for i_{th} activity.

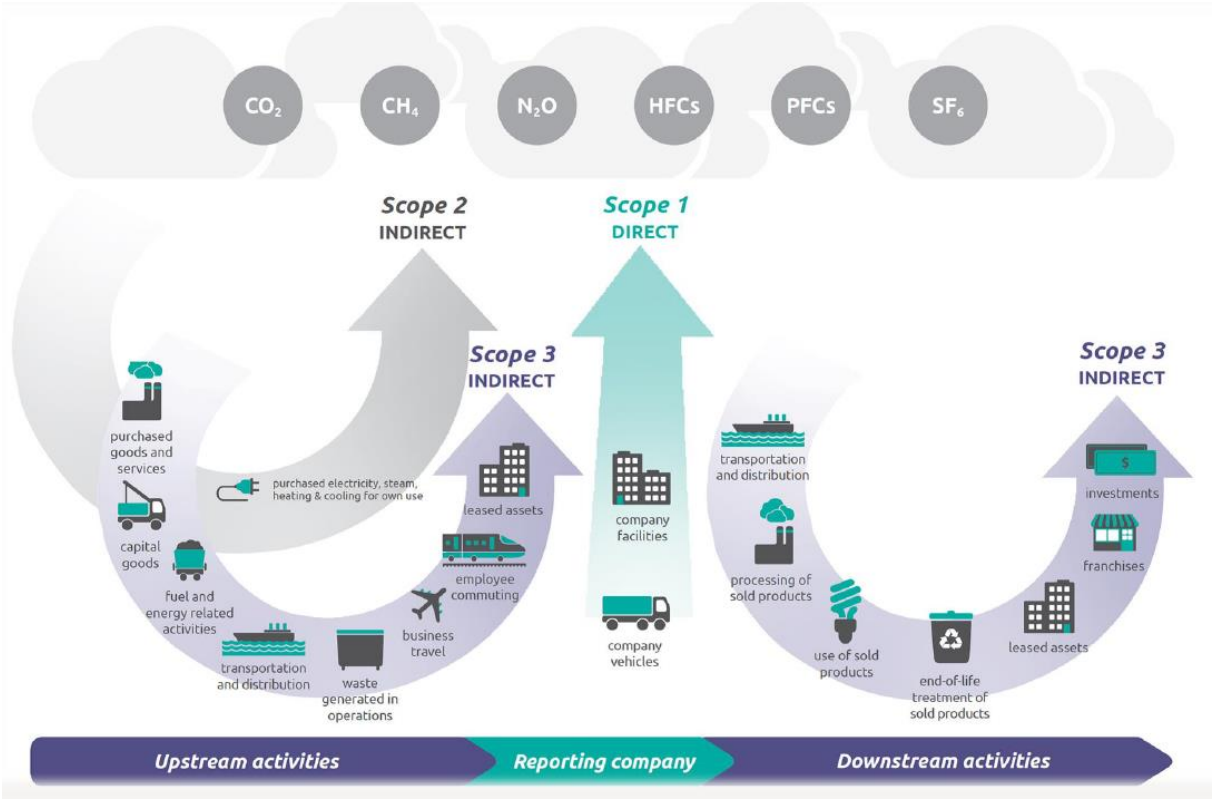

Figure 4.5 Three scopes for GHG accounting (from [120]).

The GHG Protocol classifies emissions into three scopes, as presented in Figure 4.5:

- Scope 1: Direct emissions from facilities (equipment, vehicles, machines, boilers, plants) owned or controlled by the organization.
- Scope 2: Indirect emissions from purchased energy (electricity, heating, cooling).
- Scope 3: Other indirect emissions, resulting from raw material consumption or waste generation and related processes. These cover the remaining emissions across the entire value chain.

For Scope 2, the GHG Protocol indicates two methods for calculations:

- location-based method, based on average GHG emissions per kWh in the country where the energy is consumed,
- market-based value, calculated using the emission data from the specific facilities of the energy supplier.

Moreover, GHG Protocol guidance distinguishes between direct generation emissions and upstream fuel-cycle emissions for purchased energy. Scope 2 covers only the GHG released directly during the generation of purchased energy (electricity, steam, heat, or cooling) consumed by the company. In contrast, the upstream "well-to-tank" (WTT) emissions from extracting, processing, and transporting the fuels used to produce that purchased energy are reported as Scope 3 under Category 3 (fuel- and energy-related activities). This means that fuel supply chain activities such as coal mining, oil refining, and natural gas extraction, which enable the generation of the electricity or heat that the company buys, are accounted for in Scope 3. Likewise, if a company purchases fuels for direct use in its operations, the upstream emissions from producing and delivering those fuels are included in Scope 3, while only the on-site combustion emissions are counted in Scope 1.

In this work, the calculations are based on the location-based approach, taking into account the Polish energy mix.

The GHG analysis methodology, aligned with the GHG Protocol, follows a life cycle assessment (LCA) approach, which includes four key phases, schematically presented in Figure 4.6:

a) Goal and scope definition, including the functional unit and system boundary.

b) Inventory analysis, identifying inputs and outputs.

c) Impact assessment throughout the life cycle.

d) Interpretation of the life cycle.

During the goal and scope definition stage, it is essential to clearly state the relevance of the product or process being analyzed. This includes a description of the product, its intended use, demand forecasting, and how the GHG analysis will inform decisions to prevent or mitigate climate change impacts caused by the facility's operations.

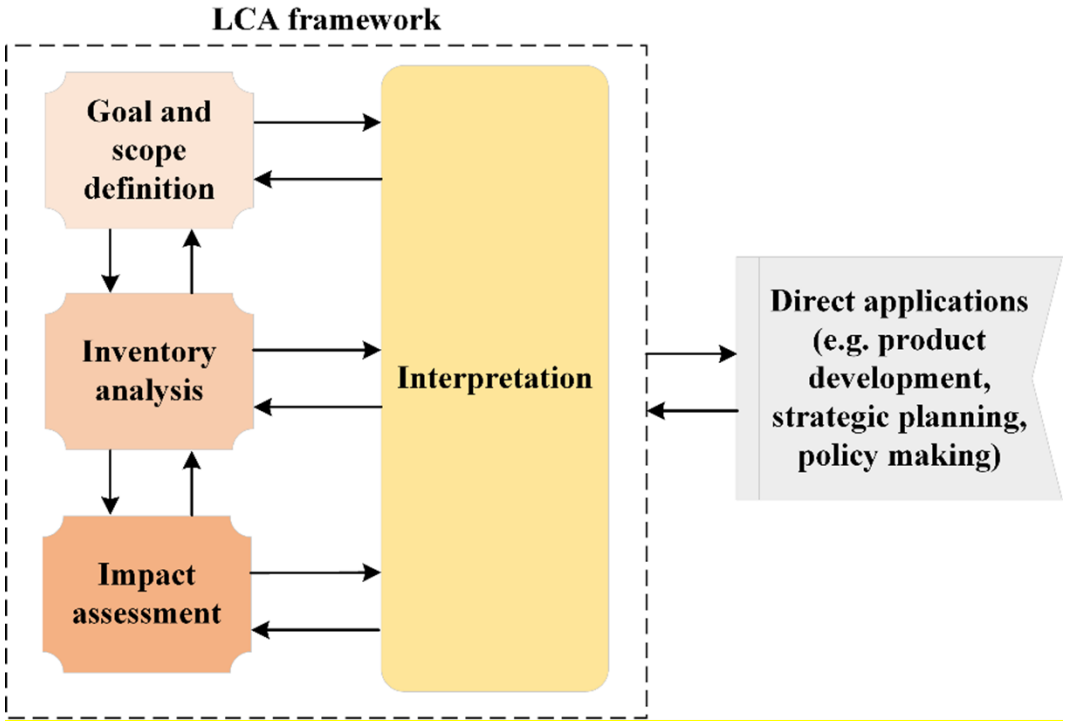

Figure 4.6 Life cycle assessment framework (based on [122]).

The next stage in carbon footprint analysis involves, in accordance with ISO standards, defining the functional unit (FU), the smallest measurable reference unit used in the LCA, for which the CF is calculated and reported. It is based on determining the performance of the assumed system, with the aim of finding the reference unit for life cycle analysis (ISO 14040:2006; ISO 14044:2006; ISO 14067:2018). It must be clearly defined and quantifiable. Using a functional unit is central to the LCA methodology and distinguishes it from other environmental management techniques. The FU can also be based on the functional performance of a process or product, allowing comparison of GHG emissions across different technological options.

The GHG Protocol also requires the definition of system boundaries that determine the processes included in the CF analysis. The most common approaches are as follows:

- Cradle-to-grave, covering all stages from raw material extraction to production and disposal.
- Cradle-to-gate, covering raw material extraction up to the point the product leaves the production facility.

The difference between these two methods for the CCU pathways with the generation of new product is illustrated in Figure 4.7.

Importantly, the GHG Protocol outlines how to choose system boundaries depending on the goals of the CF assessment. In this thesis, the cradle-to-gate

method was used to determine the carbon footprint. This approach is more accurate, has a lower risk of error, and allows for analysis of processes that can realistically be assessed. In contrast, the cradle-to-grave approach involves using average estimates for events that may or may not occur, leading to high uncertainty and a greater risk of error in CF estimation. Since the thesis focuses mainly on the operational phase, supplementary data or processes within plant construction or end-of-life stages are not taken into account. Additionally, any by-products from assessed plants are excluded similarly to solid waste and sludge treatment.

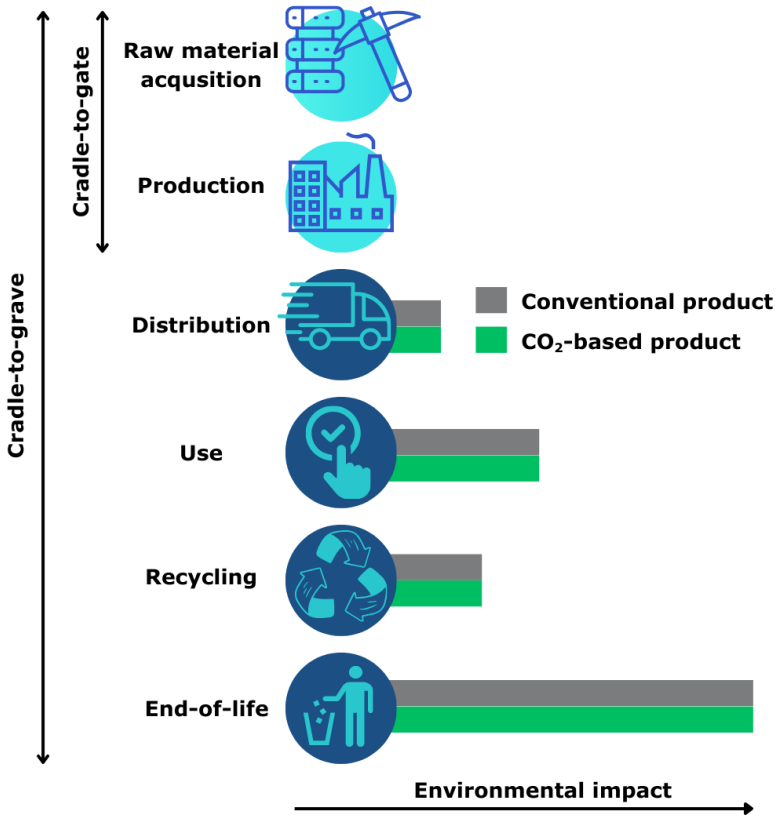

Figure 4.7 The difference between conventional and CO_2-based product environmental impacts in cradle-to-grave and cradle-to-gate approach (based on [123]).

The crucial aspect of LCA studies, especially with multiple system products, is allocation. By ISO definition, allocation is "Partitioning the input or output flows of a process or a product system between the product system under study and one or more other product systems" [124]. It recommends avoiding allocation whenever possible. Although, if allocation cannot be avoided, ISO 14044 urges using physical relationships (e.g. mass or energy) as the basis and resorting to other criteria like economic value only as a last option. The main allocation approaches relevant to the CCUS LCA include mass-based, energy-based, economic allocation, and system expansion (also known as substitution or avoided burden). Each method has a different rationale and is addressed differently by standards such as ISO 14044.

- Mass-based allocation - a physical allocation method, distributes environmental burdens in proportion to the mass of co-products produced. However, a key limitation is that the mass may not correlate with the true drivers of environmental impact. In CCUS contexts, co-products can have very different properties and functions, thus allocating purely by weight can overburden low-value, heavy products or under-allocate impacts to high-impact light products [125].
- Energy-based allocation – a physical allocation method, assigns impacts according to the energy content or energy output associated with each co-product. It is suitable when all co-products are energy carriers or have a defined energy content (e.g. fuels). Energy allocation is less commonly reported in CCUS-specific LCA studies because many CCU processes yield chemicals or materials rather than multiple forms of energy. However, it becomes relevant in scenarios where a CCUS system co-produces energy and material outputs such as in combined power and heat production with CCUS or synthetic fuels production. However, in practice, many CCU fuel studies avoid explicit allocation by instead comparing the CCU fuel to a fossil reference (which may be reported as a system expansion).
- Economic allocation - distributes environmental impacts according to the relative market value (or revenue) of each co-product. The ISO guidelines treat economic allocation as a fallback if no physical basis adequately reflects the causality of impacts. The underling rationale is that the product that generates the most income is considered responsible for most of the inputs and emissions [126].
- System expansion - also known as substitution method, addresses multi-output processes by broadening the system boundaries to include additional functions and products, rather than partitioning impacts. In practice, this means that if a CCUS process yields co-product B in addition to main product A, the production of A and B is accounted together and then the impacts that would have occurred if B were produced via its conventional route are subtracted (or avoided). System expansion is widely applied in CCUS studies [127].

LCA involves all stages of the life of the product and consists in assessing the consequences across all stages of the product or process's life cycle. These consequences include groups such as human health, ecosystem impact, global warming potential, or social equity [122]. While LCA focuses on quantifying environmental impacts such as greenhouse gas emissions, effects on human health, and ecosystem quality, the economic assessment evaluates factors such as capital and operational costs, market competitiveness of CO_2-derived products, and potential financial returns. Therefore, the combination of LCA with economic analysis allows a more complete understanding of CCUS technologies by simultaneously addressing their environmental benefits and economic viability.

Since the main purpose of CO_2 utilization is the emissions mitigation, most LCA and TEA studies in this field aim to quantify the potential of impacts reduction for utilization products relative to existing processes or prospects for improvements. Thus, a conducted assessment can provide the answer to the proposed research question regarding the choice of the most suitable utilization pathway in terms of comparison with conventional products derived from fossil carbon sources used for the same purpose or which technology is preferred considering its environmental and economic hot spots and limitations deployed in particular market, in this case for the Polish economy. LCA gives a wider view on the environmental impacts of the product or process that are often ignored in traditional analyses. Nevertheless, LCA and TEA studies conducted even in the same field often show large variations in their results, therefore, it is essential to develop and fulfil the methodological gaps in order to improve the transparency and comparability for assessing CO_2 storage vs utilization pathways. The literature review presented has already revealed certain areas where methodological gaps exist:

a) data availability and quality – data related to each utilization and storage pathway, including detailed information on energy consumption, raw materials extraction, emissions, and waste generation at various stages of the life cycle. Data refer not only to utilization and storage technologies but also to associated supply chains which cause this a challenging point because data gaps and inconsistencies may introduce uncertainties and limit the accuracy of conducted assessment.

b) CO_2 utilization diversity – a wide range of capture technologies, possible utilization pathways, and storage options, along with their complexity and variability, causes the challenge of developing a consistent and standardized assessment methodology.

c) system boundaries and functional unit – establishing appropriate system boundaries and functional unit specifies which stages will be included and what is the unit of measurement. Due to many different technologies, it has to be carefully considered due to the applied Polish context of assessment and the objective of the study.

d) allocation – multiple products and processes occurring within the possible CO_2 management options make the allocation, so the distribution of impacts among different co-products and processes in system problematic.

This gaps and challenges need to be addressed to ensure accurate and reliable assessment.

4.3 Assumptions and simulation

In this thesis, the calculation and evaluation procedure follows an integrated and systematic approach (Figure 4.8). Based on available data from the literature and predefined assumptions, process models were developed using two complementary strategies. In cases where data were available, detailed process models were built from the first principles, based on fundamental equations of mass and energy balances, as well as thermodynamics and reaction

kinetics. For the remaining cases, indicator-based black-box models were employed, in which process behavior was represented through empirical correlations and aggregated performance indicators. All developed models were subsequently validated against experimental data or established benchmarks to ensure their reliability. Consecutively, the models served as a basis for the calculation of key performance indicators, which were then used to assess the energy, economic, and environmental performance of the analyzed technologies.

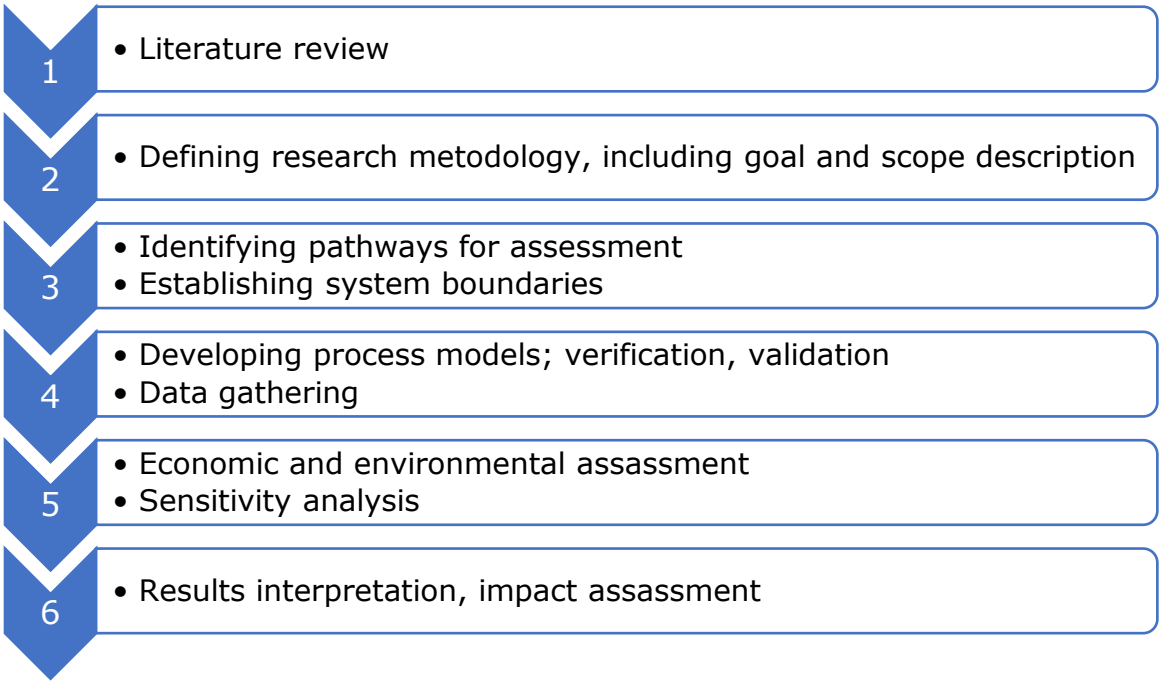

Figure 4.8 Framework of assessment procedure.

Energy performance was quantified through specific primary consumption and cumulative energy consumption values that included the efficiency of individual processes and the overall energy demand in the chain within defined system boundaries. The economic evaluation was carried out by determining the cost of CO_2 avoided, which relates the discounted capital and operating costs to the amount of CO_2 emissions mitigated. Environmental performance was assessed using the carbon footprint, expressed as the total greenhouse gas emissions in CO_2-equivalent throughout the process operation. The results of these calculations formed the basis for a comparative analysis of all technologies considered. Described analyses were performed for Polish conditions, meaning that the assumptions for economic and environmental evaluation were taken in the context of Poland. To account for uncertainties and evaluate the robustness of the conclusions, a sensitivity analysis was performed for different scenarios that varied input parameters, most of all, the emissivity of the electricity mix. This corresponds to a local one-at-a-time sensitivity analysis, which is useful for identifying the direct influence of specific assumptions. The scope of this study

is limited to local variations, which should be considered a first-order approximation of the model sensitivity.

Taking the methodology presented into account, the following sections describe each element which was considered within analyzed CCUS chain. It starts with CO_2 sources from power generation, i.e. coal-, natural gas-, and biomass-fired power plants, cement plant, as well as directly from the atmosphere. Then, the flue gas or air stream is treated in the capture unit which was assessed using the amine absorption and calcium-looping method. The captured CO_2 stream is further purified and compressed to meet pipeline transportation requirements, and then delivered either to a geological storage site or a CO_2 utilization unit. All assumptions related to CO_2 management pathways are presented in the following paragraphs.

4.3.1 Reference cases and CO_2 sources

a) Coal-fired power plant

The bituminous coal-fired power plant described in the NETL report [128] as a case B12A constitutes as a reference for CO_2 emissions from conventional coal source. The plant features a supercritical pulverized coal (PC) boiler and a state-of-the-art steam cycle. The boiler operates under supercritical steam conditions (24.1 MPa main steam, 593°C fresh steam and reheat), driving a high-efficiency steam turbine generator (Figure 4.9).

The plant produces approximately 685 MW of net electric power (gross) at roughly 42% net efficiency (LHV basis). Major equipment includes a single train PC boiler, a condensing steam turbine (with a cooling tower heat rejection system), and a comprehensive control systems. Flue gas passes through selective catalytic reduction (SCR) reactors for NO_x control, a fabric filter baghouse for particulate removal, and a wet limestone flue gas desulfurization (FGD) unit (forced oxidation) for SO_2 capture, yielding gypsum by-product. Activated carbon injection (ACI) and dry sorbent injection are also employed ensuring compliance with stringent emission limits.

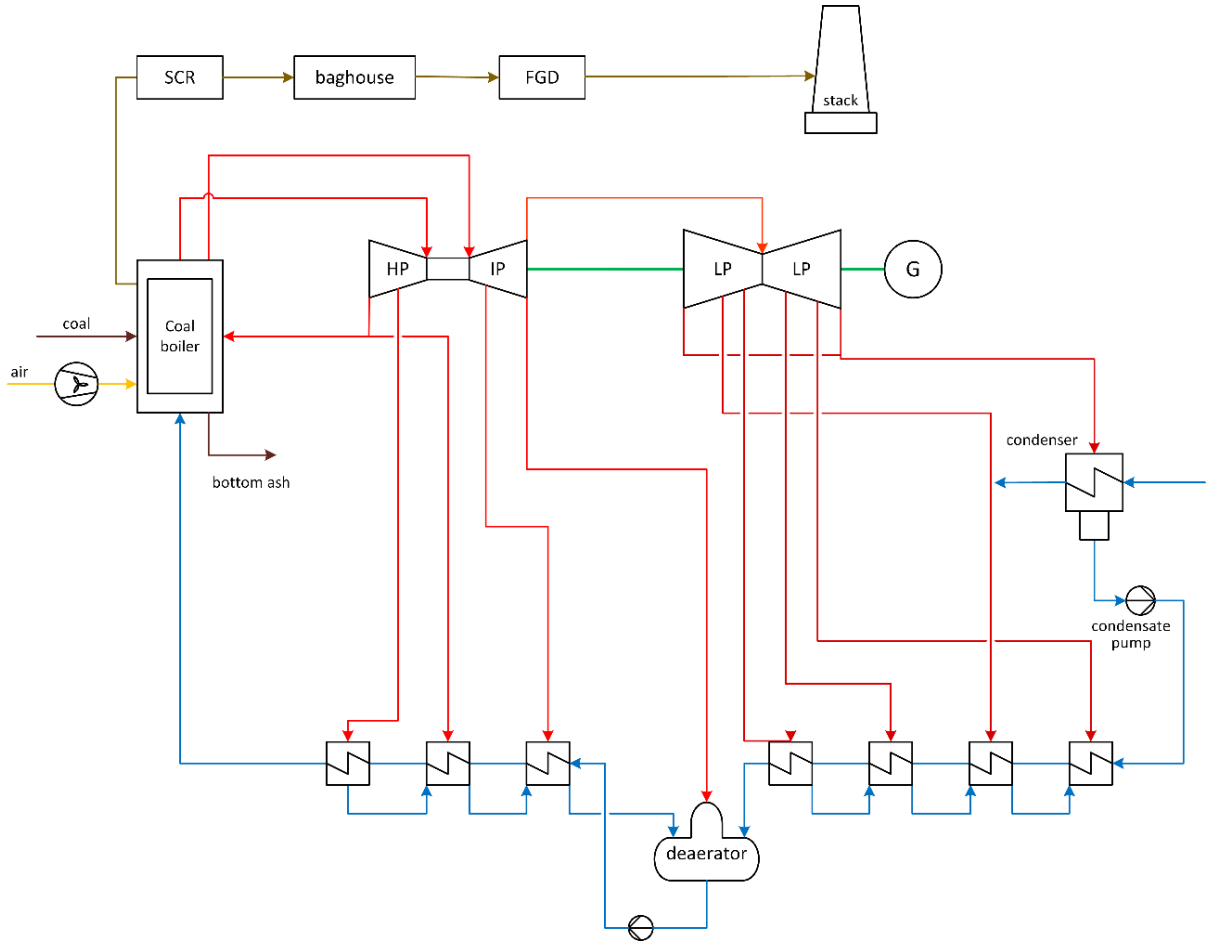

Figure 4.9 Simplified process diagram of coal-fired power plant operation (based on [128]).

A comparison between data from NETL report and values obtained from process model are presented in Table 4.1.

Table 4.1 Comparison between process model and reference key performance parameters of assessed coal-fired power plant.

Parameter	Coal-fired power plant (model)	Coal-fired power plant (reference)
Gross electrical power, MW_e	684.8	685.0
Net electrical power, MW_e	649.2	650.0
LHV gross energy efficiency, %	44.0	44.1
LHV net energy efficiency, %	41.7	41.8
Boiler efficiency, %	88.1	88.1
Coal mass flowrate, kg/s	59.5	59.5
Specific direct CO_2 emission, $kgCO_2/MWh$	771.5	778.0
Annual production, GWh	5 118.4	5 124.6
Flue gas pressure, bar	1.0	1.0

b) Natural gas-fired power plant

In case of natural gas combined cycle (NGCC) power plant without CO_2 capture, the assessment was based on B31A case from NETL report [128]. It is configured in a multi-shaft arrangement with two gas turbines and one steam turbine, presented in Figure 4.10. It employs two advanced F-class combustion turbines whose high-temperature exhaust is sent to heat recovery steam generator (HRSG) which feeds steam to a single steam turbine generator. The HRSG utilize a three-pressure reheat steam cycle (high-pressure steam 16.4 MPa at 585°C, with reheat to 585°C) to maximize energy recovery.

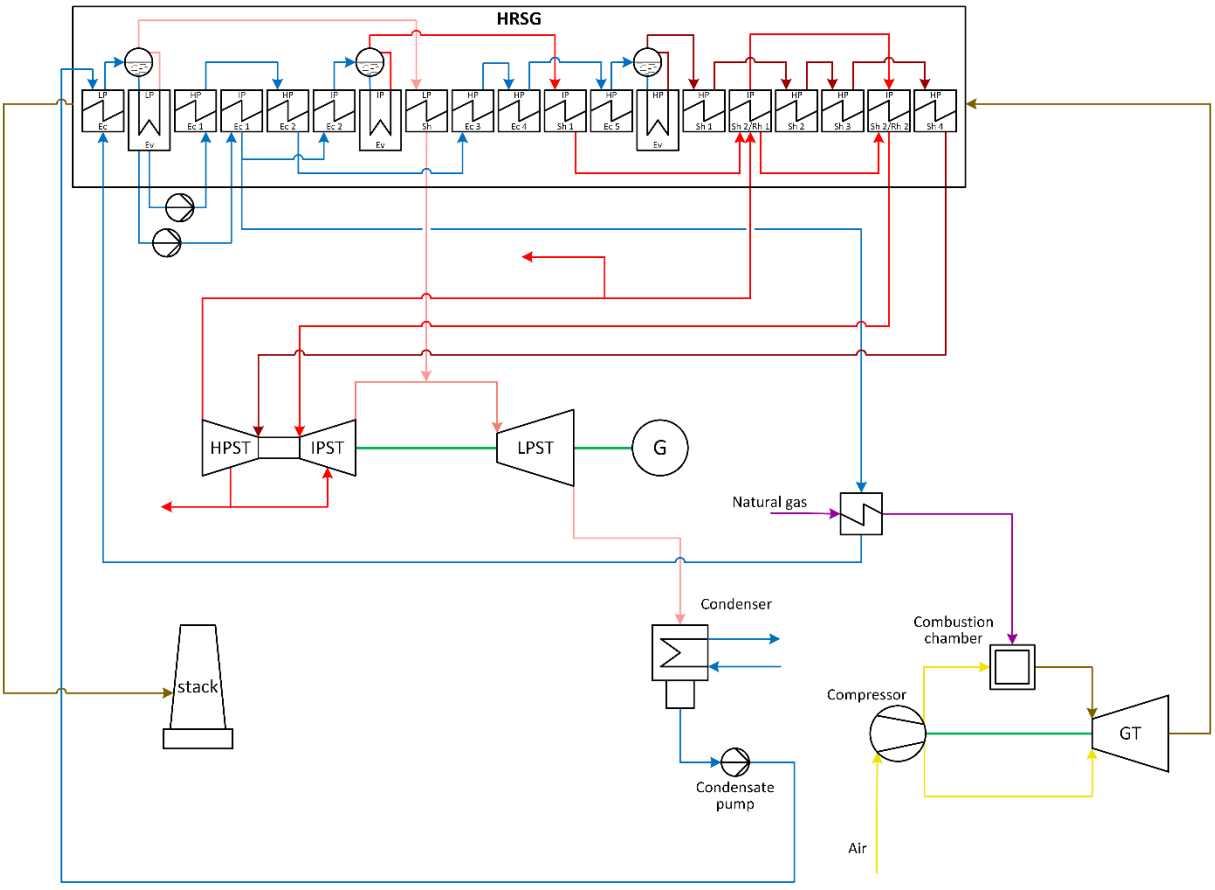

Figure 4.10 Simplified process diagram of natural gas combined cycle operation (based on [128]).

This configuration delivers on the order of 727 MW of net output with a net plant efficiency of roughly 59.4% (LHV), reflecting the high performance of modern NGCC units. Because it combusts clean natural gas, the plant requires minimal pollution control equipment for sulfur, particulates, or mercury (these emissions are negligible from pipeline-quality gas). Dry low-NO_x burners in the turbines limit NO_x formation, and a post-combustion SCR system is included to further reduce NO_x to very low levels. A comparison between data from NETL report and values obtained from process model are presented in Table 4.2.

Table 4.2 Comparison between process model and reference key performance parameters of assessed natural gas combined cycle.

Parameter	NGCC power plant (model)	NGCC power plant (reference)
Gross electrical power, MW_e	739.9	740.0
Net electrical power, MW_e	729.4	727.0
LHV gross energy efficiency, %	60.5	60.5
LHV net energy efficiency, %	59.6	59.4
Combustion turbine efficiency, %	39.0	39.0
Natural gas mass flowrate, kg/s	25.9	25.9
Specific direct CO_2 emission, $kgCO_2/MWh$	347.5	342.0
Annual production, GWh	5 750.3	5 731.7
Flue gas pressure, bar	1.0	1.0

c) Biomass-fired power plant

The reference biomass power plant was based on the Połaniec "Green Unit", which is a 208 MW biomass-fired power plant in Poland [129]. It combusts 100% biomass fuel, utilizing a circulating fluidized-bed (CFB) boiler at subcritical steam conditions (127 bar, 535 °C) [130]. Unit performance is graphically presented in Figure 4.11. The unit's feedstock is predominantly wood residues (approx. 80%) blended with agricultural by-products (approx. 20%) from local forestry and farming sources. Emissions control systems include selective non-catalytic and catalytic reduction (SNCR and SCR) for NO_x abatement and an electrostatic precipitator (ESP) for particulate removal. Additionally, the low sulfur content of the biomass (along with limestone addition in the CFB) enables compliance with SO_2 limits without a flue gas desulfurization unit. A comparison between data from NETL report and values obtained from process model are presented in Table 4.3.

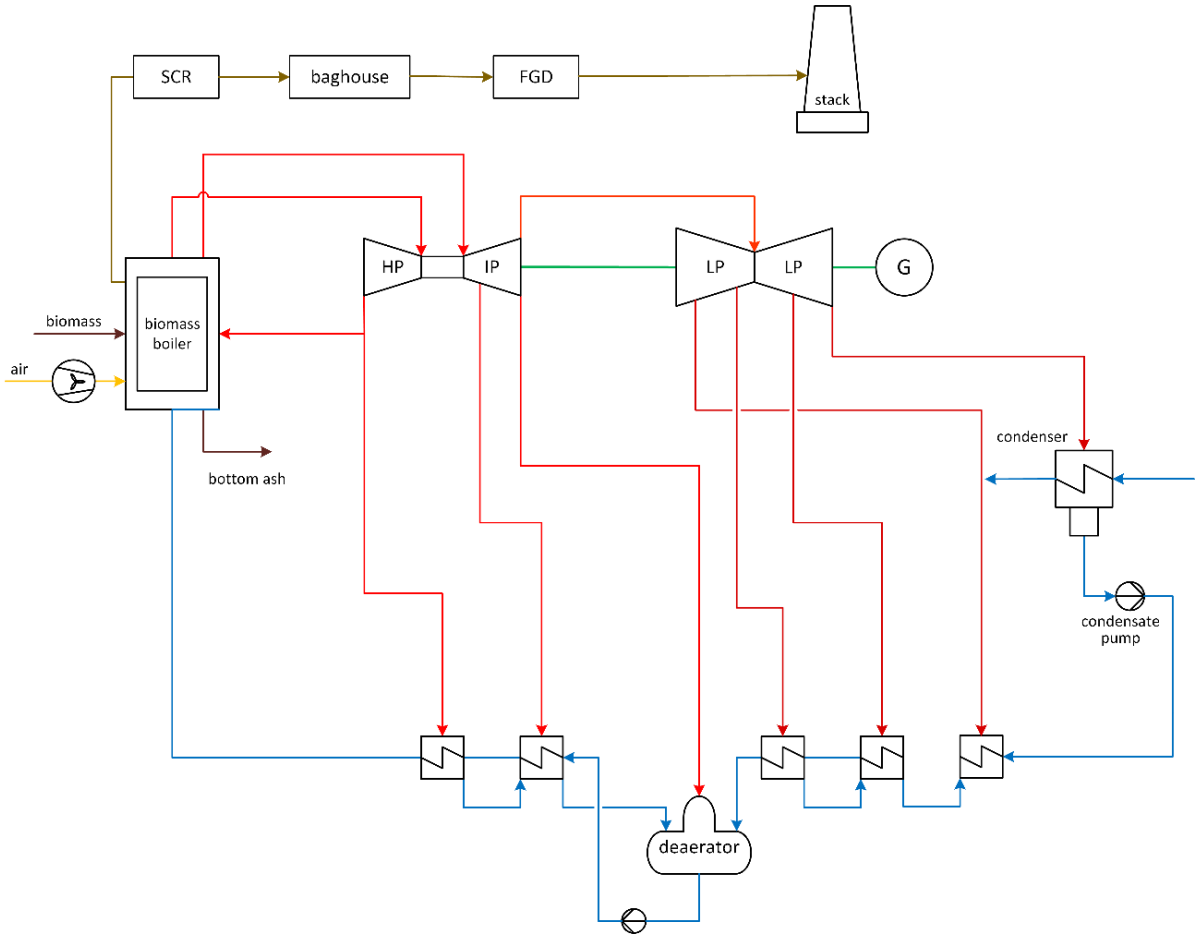

Figure 4.11 Simplified process diagram of coal-fired power plant operation.

The performance of the plant is comparable to that of a conventional coal-fired unit of similar size, while its use of carbon-neutral fuel virtually eliminates net CO_2 emissions of 1.2 million tonnes avoided annually. However, this value in the accounting for CF under the EU ETS convention is the result of reflecting emissions from biomass combustion reported as zero. The overall net climate benefit of large-scale biomass combustion therefore depends strongly on system boundaries, e.g. inclusion of upstream supply-chain emissions from feedstock harvesting, processing and transport as well as other assumptions and inclusion.

Table 4.3 Comparison between process model and reference key performance parameters of assessed biomass-fired power plant [130].

Parameter	Biomass-fired power plant (model)	Biomass-fired power plant (reference)
Gross electrical power, MW_e	225.7	225.0
Net electrical power, MW_e	208.5	208.0
LHV gross energy efficiency, %	39.8	40.1
LHV net energy efficiency, %	36.8	36.5
Boiler efficiency, %	92.0	90.0-95.0

Live steam generation, kg/s	158.3	158.1
Biomass chemical energy MW_{th}	566.6	561.6
Annual production, GWh	1 643.8	1 639.9
Flue gas pressure, bar	1.0	1.0

d) Cement plant

Among industries, the cement industry is recognized as one of the hard-to-abate industries where the major part of carbon dioxide emissions comes from the production process, limestone (calcium carbonate) calcination process in this case. Depending on the fuel mix in the cement plant, the share of process emissions and fuel related emissions varies [131]. Typically, the emissions from the calcination process are 2/3 of the total emissions from the cement plant that are calculated in the Scope 1 emissions [120]. Another aspect that has an impact on process related emissions is the quality of the limestone. Calcination is a heat demanding process in which the previously milled limestone is fed into the preheater tower and after achieving calcination temperature into the calciner. Under high temperature, calcium carbonate decomposes into calcium oxide and carbon dioxide. The theoretical temperature of calcination is 950°C, however, due to imperfect heat transfer, heat losses, imperfect raw material milling and other factors, the typical process temperature is 1000 – 1100°C [132].

The mitigation of greenhouse gas emissions within the sector can be achieved through the implementation of various innovative technologies and optimizations across different stages of the cement production process:

- Introduction of alternative fuels (AF) into the fuel mix, which replaced a large share of fossil fuels. The 2050 industry goal is to achieve the incorporation of 95% AF in the fuel mix, including 50% of biomass.
- A gradual transformation of the clinker production process has been implemented, involving the replacement of wet-process kilns with dry-process kilns, which offer significantly higher energy efficiency.
- Modernization of existing plants and introducing of more energy-efficient equipment in conjunction with automation that regulates the production process.
- Utilization of waste materials from other industries that can be incorporated in cement, such as fly-ash, ground granulated blast-furnace slag, gypsum from desulphurization and others. Reduction of the share of clinker in cement production has a direct effect on CO_2 emissions per tonne of cement produced [133].

Nevertheless, emission reductions can only be achieved to a certain extent without the adoption of new and advanced technologies. In addition to the existing solutions, the industry's current focus is on emerging technologies that

are still under development, offering further potential for decarbonization such as deploying calcined raw clays as partial clinker replacement, recycling concrete particles in the production process [134,135] and enforced carbonation of recycled concrete particles [136].

Achieving net-zero cement production will ultimately require the widespread deployment of carbon capture technologies. According to the BLUE Map scenario, the cement industry is projected to reduce emissions by approximately 500 $MtCO_2$ by 2050 through the construction of CCS facilities [137]. To achieve this target, around 130 projects will need to be developed in the next two decades, marking a substantial increase compared to the current adoption of CCS technologies in the sector. Furthermore, by 2050, an estimated 495 CCS projects will be required worldwide within the cement industry.

As a reference, the cement plant was based on CEMCAP project data [138] which refers to the BAT (Best Available Technique) standards for the cement industry defined in REFBATC document published in 2013. The REFBATC describes the plant that uses the best available technology in production and is used as a reference for existing plants [139].

The cement production process is performed in dry kiln technology, which is the most energy efficient technology available on the market. In the reference plant the pre-heater tower consists of five stage cyclone stacked one above another, the installation is equipped with a tertiary air duct, a rotary kiln and a clinker cooler (Figure 4.12). The plant capacity is 1 Mt of clinker produced per year, which is representative of the average European cement plant. This corresponds to about 2 896 t/d of clinker assuming a run time of 345 days per year. The cement plant was not modelled within the scope of the thesis, as the detailed representation of cement production processes is highly complex. Instead, the CO_2 capture unit was modelled in a tail-end configuration, which means that it operates in the flue gas stream without direct interference in the core cement production process. Therefore, key assumptions concerning the flue gas composition, flow rate and operating conditions (presented in Table 4.4) were adopted for further calculations.

Table 4.4 Main performance indicators for cement plant reference case [138].

Parameter	**Value**
Clinker production	2 896 t_{clk}/d
Working days	345 days
Specific electric power consumption	132 kWh/t_{clk}
Flue gas mass flow	107.8 kg/s
Flue gas temperature	110°C

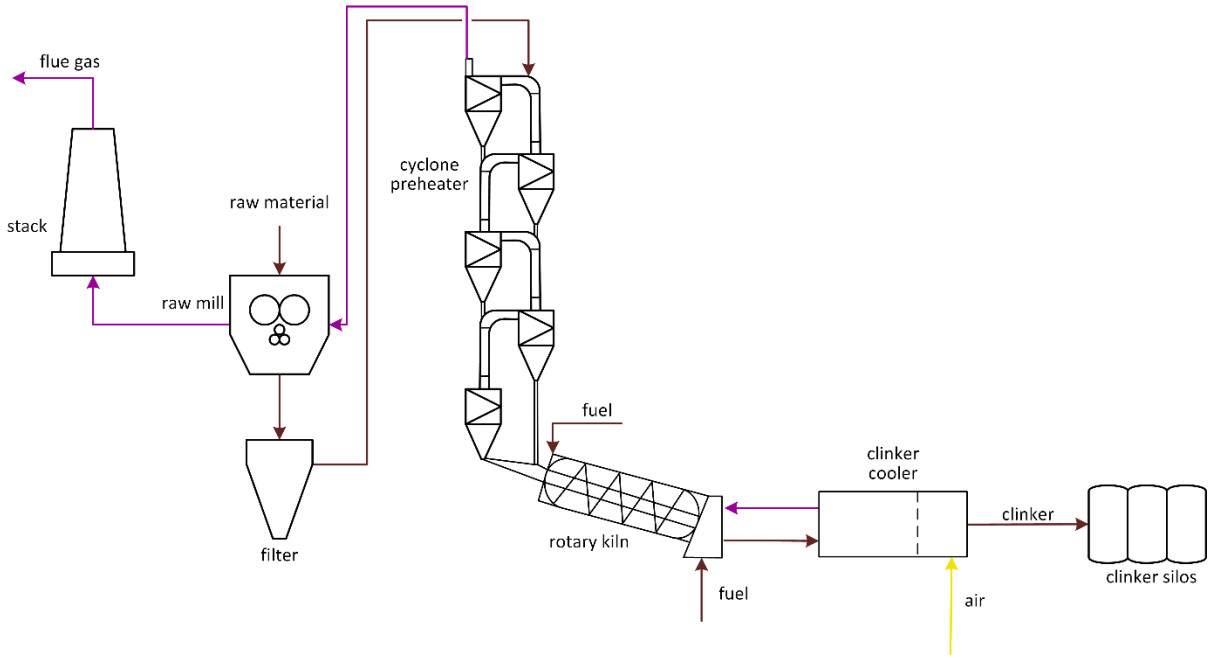

Figure 4.12 Simplified illustration of cement plant operation (based on [138]).

The composition of each stream exiting the power plant or cement plant and the atmospheric air is presented in Table 4.5.

Table 4.5 Flue gas and atmospheric air composition adapted for calculations.

	Coal-fired power plant	Natural gas-fired power plant	Biomass-fired power plant	Cement plant	Atmospheric air
Mass fraction (wet basis), %					
CO_2	20.7	6.4	17.8	26.1	0.04
N_2	72.4	77.2	68.1	58.1	78.08
O_2	1.5	11.2	6.4	10.5	20.95
H_2O	5.4	5.2	7.7	5.3	-
Ar	-	-	-	-	0.93

4.3.2 CO_2 capture units

Table 4.6 outlines the key assumptions adopted for the design and operation of the amine-based CO_2 capture process using monoethanolamine (MEA). It includes parameters related to process efficiencies, flue gas conditions, sorbent properties, and energy requirements for regeneration. These assumptions were based on [41] serve as the basis for evaluating the performance and energy demand of the system, and reflect typical values used in post-combustion

capture applications. Figure 4.13 shows the process flowsheet of a tail-end integration of amine absorption capture within NGCC plant.

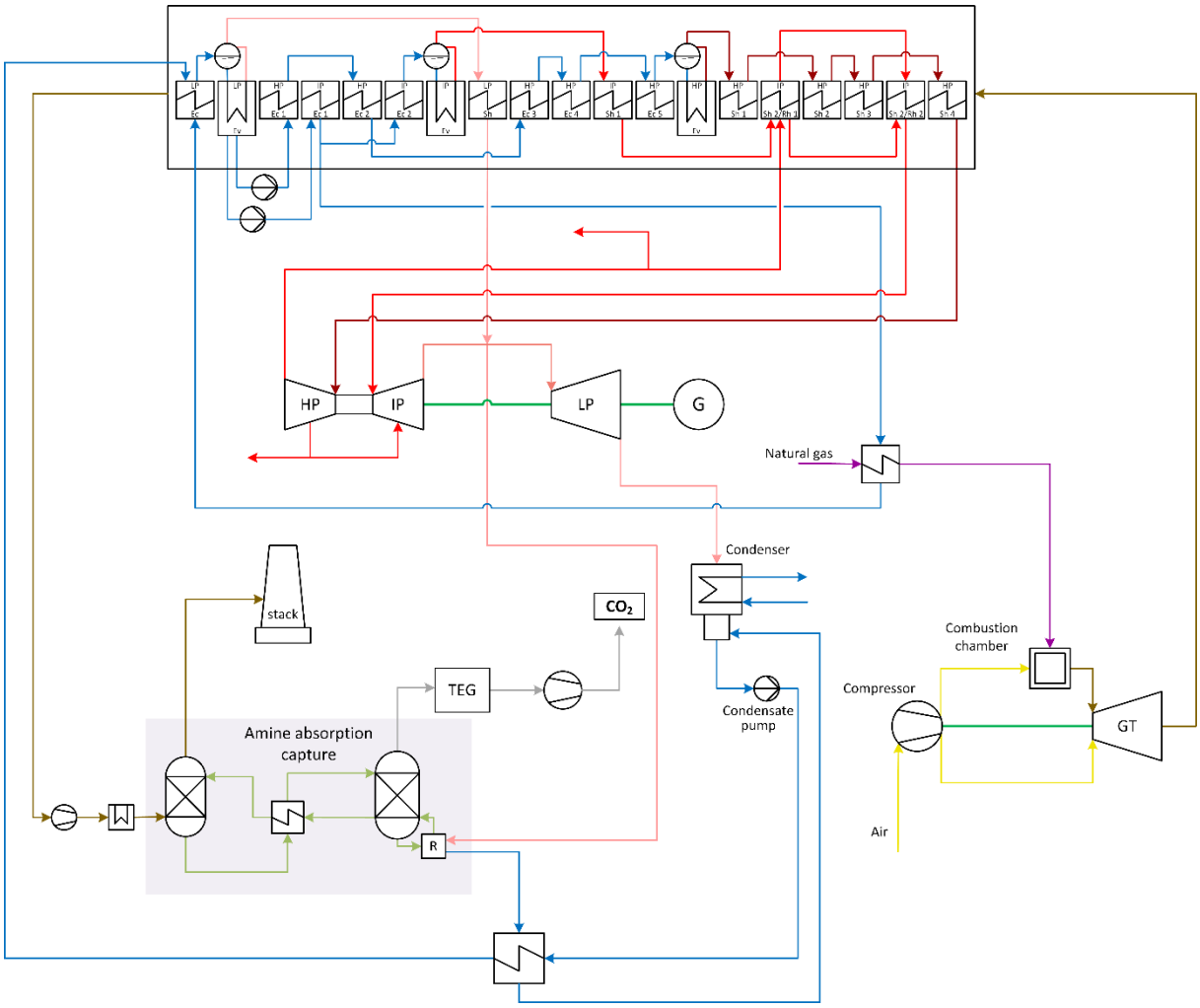

Figure 4.13 Process flowsheet for tail-end amine absorption capture in NGCC case.

Table 4.6 Main amine capture process assumptions (based on [41]).

Parameter	**Value**
Capture efficiency	90%
Flue gas pressure and temperature at absorber inlet	1.2 bar/40°C
MEA concentration	30 wt%
Lean sorbent loading	0.17 $mol_{CO2}/mol_{solvent}$
Rich sorbent loading	0.35 $mol_{CO2}/mol_{solvent}$
Flue gas pressure drop	0.2 bar
Reboiler parameters	1.8 bar/117°C
Circulating pump efficiency	85%
Fan efficiency	85%
Product purity	99 wt%

In the case of calcium-looping, the flue gas parameters and overall process conditions can vary depending on the specific system configuration and integration approach. However, for the purpose of this analysis, it is assumed that the carbonator operates at a temperature of 580-650°C and the calciner at 950°C. This setup also incorporates partial recirculation of the captured CO_2 stream to improve process efficiency and stability. Table 4.7 summarizes the main operational parameters for the calcium-looping process, including reactor conditions, pressure drops, material flow ratios, and auxiliary system requirements, which form the basis for evaluating system performance. In Figure 4.14 the integration of CaL process with clinker line is presented.

Table 4.7 Main calcium-looping process operational parameters[2] (based on [140]).

Parameter	**Value**
Carbonator temperature	580/650°C[3]
Calciner temperature	950°C
Pressure drop in carbonator/calciner	0.15 bar
Temperature drop in calciner	30°C
f_{carb}	0.7
f_{calc}	0.9
f_m (ratio of make-up $CaCO_3$ flow to recirculating sorbent flow)	0.04
a_1	0.1045
a_2	0.7786
b	0.07709
f_1	0.9822
f_2	0.7905
Make-up parameters at calciner inlet	1.03 bar, 20°C, composition: 0.924 mol% $CaCO_3$, 0.076 mol% inert (Al_2O_3, Fe_2O_3, MgO, SiO_2, TiO_2)
Oxygen parameters at calciner inlet	1.3 bar, 150°C, 95mol% O_2
Secondary steam cycle parameters	165 bar/35 bar/5 bar & IP steam reheat

[2]operational parameters relate to formulas presented in section 2.2.2.2

[3]depending on CO_2 content in the flue gas stream

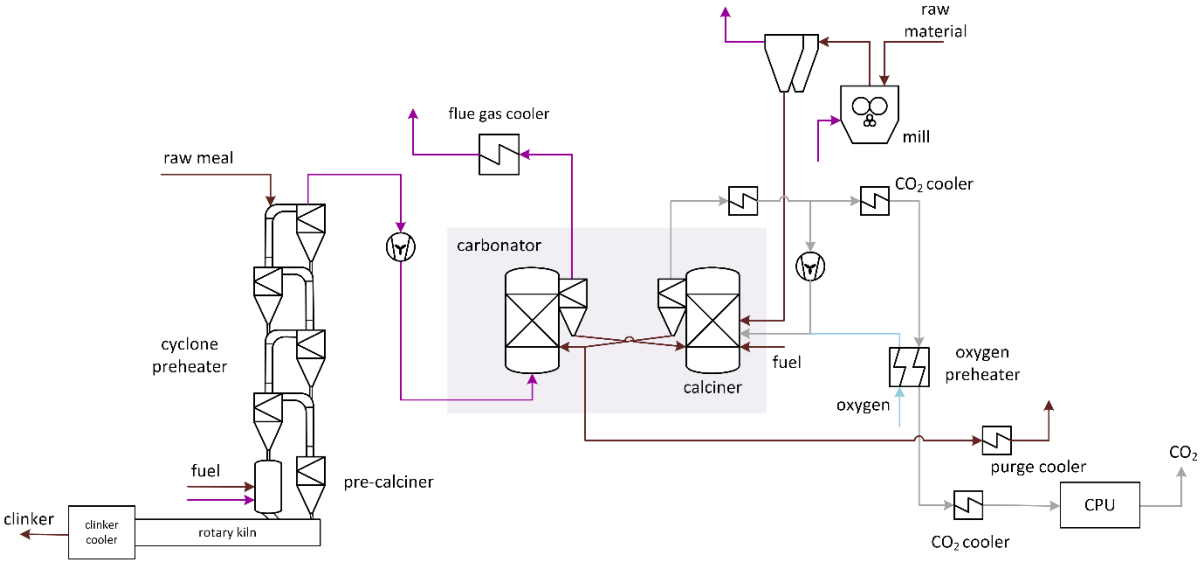

Figure 4.14 Process flowsheet for tail-end calcium-looping capture in clinker production line.

This thesis employs two process models for CO_2 capture developed in gPROMS Process. Calcium-looping model was constructed based on the fundamental conservation laws and constitutive relationships for a reacting gas–solid system. Specifically, mass and energy balances were written for both the carbonator and calciner, with explicit treatment of reactions related to the carbonation and calcination processes, gas–solid heat and mass transfer, pressure-drop correlations, sorbent deactivation and make-up supply, as well as recirculation flows. For transparency and reproducibility, the full set of equations, parameter definitions, and boundary conditions is provided in Appendix A.

By contrast, the amine-based post-combustion capture model was assembled using standard libraries as well as an advanced model library for gas-liquid contactors available in gPROMS, where unit operations such as rate-based absorption and stripping columns, reboiler, condenser, heat exchangers, pumps, and flash vessels are accessible. The process flowsheet, thermodynamic property method, column internals, inter-unit connectivity, and key transfer parameters were configured and calibrated within the bounds of the library components. Because these unit models are pre-defined and documented within the gPROMS libraries rather than coded from first principles in the present work, their internal equation sets are not reproduced within this thesis.

Direct air capture (DAC)

A solid sorbent direct air capture system at the 100,000 tCO₂/year scale was used as a reference case for CO_2 separation from an atmospheric source. It uses an amine-functionalized sorbent to extract CO_2 from ambient air, with regeneration through a low-temperature (approximately 100°C) temperature-vacuum swing adsorption/desorption cycle. Ambient air is drawn through

modular contactors where CO_2 is adsorbed onto the sorbent as presented in Figure 4.15. The loaded sorbent is then heated to 100 °C under reduced pressure to release concentrated CO_2. The captured CO_2 is recovered at high purity (99% CO_2) for compression and storage.

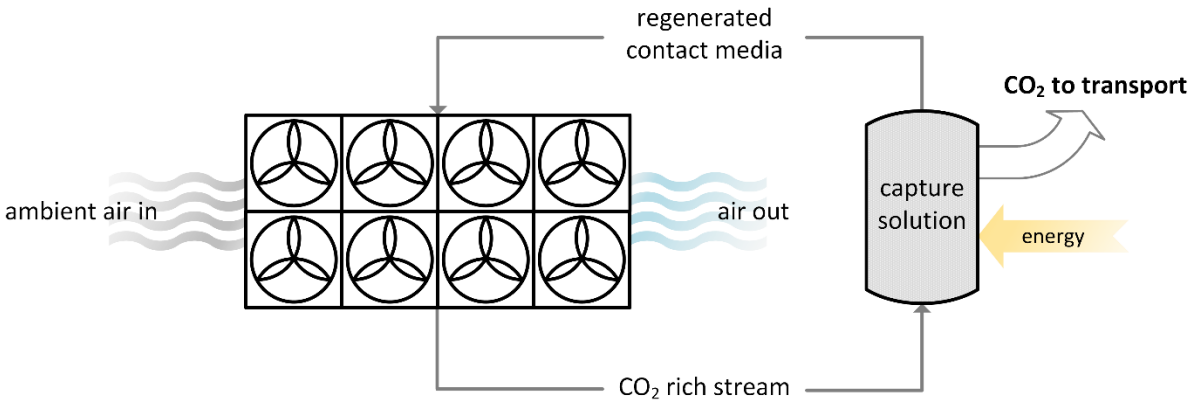

Figure 4.15 Simplified illustration of direct air capture unit.

The operation of DAC system is highly energy-intensive. Almost 0.99 GJ of electricity per tonne of CO_2 is needed to drive fans, blowers, vacuum pumps, and other machinery [32]. In addition, about 9.8 GJ of low-grade heat per tonne of CO_2 is required for sorbent regeneration at temperature of 100°C [32]. This heat demand is supplied through a high-efficiency heat pump (coefficient of performance of 2.1 [141], so about 4.7 GJ of electrical energy yields the 9.8 GJ of thermal energy for desorption. Taking all inputs, the total electricity requirement is on the order of 0.0017 MWh per kg of CO_2 captured. The process also requires a substantial water supply, primarily for the cooling and moisture management in the sorbent cycle [142]. The values presented in Table 4.8 constitute an assumption set for a black-box model prepared for DAC evaluation.

Table 4.8 Key assumptions for direct air capture black-box model.

Assumptions	**Unit**	**Value**
Scale	tpa	100,000
Electricity requirement	GJ/tCO_2	0.99
Heat requirement for heat pump	GJ/tCO_2	9.8
Total electricity requirement	$MWh/kgCO_2$	0.0017
Temperature of heat	°C	100
Water flow requirement	tH_2O/tCO_2	1.5
COP heat pump	-	2.1

4.3.3 CO_2 utilization and storage pathways

Carbon dioxide applications range from geologic sequestration to chemical conversion and mineralization, with each pathway characterized by specific demands for CO_2 purity, storage permanence, and process scale. Energy inputs range from substantial electricity consumption for electrochemical and compression processes to thermal and cooling demands in conversion routes, reflecting differences in thermodynamic efficiency and operational complexity. This variability underscores the importance of evaluating these technologies not only in terms of CO_2 abatement potential but also with regard to their life-cycle energy and resource implications within industrial deployment scenarios. The values presented in Table 4.9 constitute an assumption set for a black-box model prepared for utilization and storage options evaluation. All values relate to 1 tonne of product in case of CO_2 utilization with conversion or 1 tonne of CO_2 utilized/stored for pathways without CO_2 conversion.

Table 4.9 Summary of key parameters related to mass and energy balances for assessed CO_2 storage and utilization pathways.

Technology	Utilization/storage ratio $t_{product}/tCO_{2,in}$[4]	H_2 use $tH_2/tCO_{2,in}$	Electricity requirement $kWh_e/tCO_{2,in}$	Heat requirement $kWh_{th}/tCO_{2,in}$
EOR	1	n/a	20.0	n/a
EGS	1	n/a	10.0	n/a
Methanol production	0.68	0.14	116.4	301
Methane production	0.35	0.17	n/a	n/a
Urea production	1.37	0.14	780.8	822
DME production	0.52	0.13	279.8	n/a
Olefins production	0.26	0.14	255.2	301
Aromatics production	0.27	0.14	159.5	403
Carbon mineralization	1	n/a	317.0	n/a
CO_2 storage (saline formations)	1	n/a	16.0	n/a

Conversion of CO_2 into value-added products often requires the co-utilization of additional feedstocks such as hydrogen or ammonia, depending on the target chemical. The intensity of the material of these processes can be expressed as

[4] In terms of storage and utilization without CO_2 conversion: EOR, EGS, mineralization, the unit refers to tonnes of CO_2 utilized/stored from 1 tonne of CO_2

the mass of CO_2 and auxiliary reactants consumed per unit mass of the product. This characterization enables the evaluation of stoichiometric requirements. In terms of hydrogen, for further environmental and economic calculations it was assumed that it is supplied to corresponding technology with market-based values excluded from system boundaries.

4.3.4 Economic evaluation assumptions

The economic evaluation is based on a comprehensive set of assumptions designed to reflect realistic conditions for large-scale deployment of CO_2 capture, utilization, and storage technologies. Key parameters include capital investment profiles, operational lifetime, and plant utilization rates, as well as financial variables such as discount rate. The analysis accounts for staged capital expenditures during the construction phase. Fixed and variable operating costs are estimated as a function of capital investment and production capacity, including maintenance, insurance, taxes, and labor, as well as a result of materials and energy unit supply costs. Labor costs are calculated using a standardized methodology that scales with plant size and includes allowances for overheads and contingencies. These assumptions, presented in Table 4.10, provide the basis for discounted cash flow analysis, enabling the calculation of CO_2 avoidance costs.

Table 4.10 Main assumptions for economic evaluation.

Parameter	**Unit**	**Value**
lifetime	years	25
capacity factor for power plants	%	90
capacity factor for cement plant, DAC	%	95
investment year 0	-	0.5
investment, year 1	-	0.5
discount rate	%	7
scaling factor	-	0.7
maintenance costs	% of TPC	1.5
labor costs	% of TPC	0.5
administration costs	% of TPC	1.0
local taxes	% of TPC	1.5
insurance cost	% of TPC	1.0
operating supplies	% of maintenance costs	15.0

The economic evaluation was based on an assumed overall plant lifetime of 25 years. In the first year, production was estimated at 30% of total capacity, while in the second year it was raised to 100%. The total investment is allocated as 50% one year before production, and 50% in the first year of production. For

projects on technologies in Europe, the discount rate is usually between 5-8%, therefore 7% discount rate was applied for this thesis [143]. Moreover, Yearly maintenance and repairs costs were assumed to be 1.5% of the total plant cost. Labor cost, general plant overhead and administrative costs, local taxes and insurance cost were assumed to weigh yearly 0.5%, 1%, 1.5% and 1% of the total plant cost, respectively. Operating supplies were assumed to be 15% of maintenance costs [144].

Table 4.11 shows the total capital expenditures breakdown of costs with related shares at each stage of bottom-up calculation approach.

Table 4.11 Capital investment costs breakdown.

BEC (Bare Erected Cost)	
1. EPC services	15% BEC
EPCC (Engineering, Procurement and Construction Cost)	
2.1. Process Contingencies	15% EPCC
2.2. Project Contingencies	10% EPCC + process contingencies
TPC (Total Plant Cost)	
3.1. Pre-production costs	3% TPC
3.2. Inventory capital	1% TPC
3.3. Other owner's costs	6% TPC
TOC (Total Overnight Cost)	

Following the calculation of capital investment, operational expenditures were estimated. Variable OPEX includes the costs associated with each material use and energy supply. The evaluation was performed with constant price values for the entire evaluation period. The market prices adapted for this study are presented in following Table 4.12.

Table 4.12 Prices of key supplies and processes assumed in study.

Parameter	**Unit**	**Price**
Electricity	EUR/MWh	100
Biomass	EUR/GJ	6
Natural gas	EUR/MWh	34
Hydrogen	EUR/kg	3.73
Water	EUR/t	0.04
MEA make-up	EUR/t	1500
NaOH	EUR/t	800
TEG	EUR/t	700
Molecular sieves	EUR/t	18800
Raw sorbent	EUR/t	8

CO_2 transport[5]	EUR/t_{CO2}	7

The values for utilization and storage technologies for capital investments were based on literature and scientific reports and updated accordingly to EUR2024. The values presented in Table 4.13 relate to the 100,000 tCO_2 scale, which corresponds to the scale of an assumed DAC unit. For each case with a higher CO_2 stream, the values were adequately scaled and updated.

Table 4.13 Capital expenditures for associated CO_2 storage and utilization technologies.

Technology	**CAPEX, MEUR$_{2024}$**	**Reference**
EOR	1.7	[145]
EGS	1.8	[80]
Methanol production	65.7	[94]
Methane production	20.1	[94]
Urea production	27.4	[94]
DME production	46.8	[94]
Olefins production	116.0	[94]
Aromatics production	74.7	[94]
Carbon mineralization	15.0	[146]
CO_2 storage (saline formations)	0.7	[147]

The applied methodology for the CCUS chain integrates three complementary dimensions of assessment. Energy analysis is based on process modelling, conducted through both detailed bottom-up simulations and black-box implementations of reference data, with performance expressed by indicators such as SPECCA, CAC, and overall energy efficiency metrics. The environmental analysis evaluates the carbon footprint of each configuration in all three scopes of emissions, ensuring a comprehensive accounting of both direct and indirect impacts. Finally, economic analysis quantifies the cost performance of the systems by calculating the cost of CO_2 avoided, enabling a consistent comparison between capture options and sources. Together, this methodological framework provides a coherent basis for assessing the technical, environmental, and economic implications of CCUS deployment.

4.3.5 Environmental analysis assumptions

The environmental assessment framework applied follows the principles of the GHG Protocol Product Standard, integrating established life cycle assessment (LCA) methodologies. The analysis is grounded in the ISO 14040:2006 and ISO 14044:2006 standards, which define the general principles, framework, and requirements for LCA, as well as PAS 2050, providing additional guidance for

[5]assuming transport distance up to 100 km

product-level greenhouse gas accounting. The inventory of GHG emissions includes direct (Scope 1), indirect (Scope 2), and selected value chain (Scope 3) activities, ensuring comprehensive coverage of the sources of emissions. Environmental impacts are quantified using the IPCC method and the Ecoinvent database, with inventory data derived from detailed process modelling of the technologies examined. Functional units can be defined contextually depending on the process per megawatt-hour (MWh) of electricity for power plants, per tonne of clinker (t_{clk}) for cement production, and per tonne of product ($t_{product}$) for the CO_2 utilization pathways. Nevertheless, to compare all assessed pathways, 1 tonne of CO_2 avoided was introduced as a functional unit. The system boundary is set to a cradle-to-gate perspective, capturing all emissions related to upstream processes. Global warming potential values are assessed over a 100-year horizon in accordance with IPCC guidelines. Reference scenarios and sensitivity analyses are employed to interpret life cycle impacts and evaluate uncertainties in key parameters. The LCA framework is summarized in Table 4.14 and the system boundaries for analysis are presented in Figure 4.16.

Table 4.14 Life cycle assessment framework.

Assumption	GHG Protocol Product Standard
Goal and scope	The scope of the analysis covers all relevant stages of the production and emission chain: (1) extraction and preparation of raw materials, (2) their transport to the processing facility, (3) the core industrial conversion processes in the reference plants considered in the project, and (4) the implementation of carbon capture, utilization and storage (CCUS) technologies. A key element of the study is the assessment of greenhouse gas emissions "before" and "after" the integration of CO_2 capture solutions, accounting for both direct and indirect emissions across all stages of production and operation. The analysis focuses on identifying the principal emission sources within the process chain and quantifying their contribution relative to the declared functional unit. Particular attention is given to CO_2 emissions from fuels combustion, energy supply, process-related emissions from raw material transformation as well as emissions from material and product transport.

	The overall aim is to perform a comprehensive carbon footprint analysis of CCUS technologies across different industrial contexts. The reference scenarios include various emission sources with electricity requirements covered from polish grid and implementation of CCUS into these systems while additional scenarios incorporate low-carbon electricity supply and less emission-intensive solutions (such as green hydrogen).
Scope of applicable standards	The GHG Product Standard is based on the framework and requirements defined in ISO standards for life cycle assessment (ISO 14040:2006, Life Cycle Assessment: Principles and Framework and ISO 14044:2006, Life Cycle Assessment: Requirements and Guidelines) as well as PAS 2050.
Emission inventory scope	Scope 1, Scope 2, and selected activities from Scope 3
Environmental impact assessment method/database	IPCC method/Ecoinvent database
Inventory analysis	Input and output data (material and energy balances) will be obtained from process modelling results for the technologies, aligned with assumptions using data from the EcoInvent databases.
Functional unit, FU	1 t of CO_2 avoided
System boundary	Cradle-to-gate
Time horizon for GWP	GWP100
GWP conversion indicator	According to IPPC guidelines
Impact assessment	GHG emissions inventoried using the GHG Protocol, in compliance with IPCC guidelines
Life cycle interpretation	Reference scenarios and sensitivity analysis

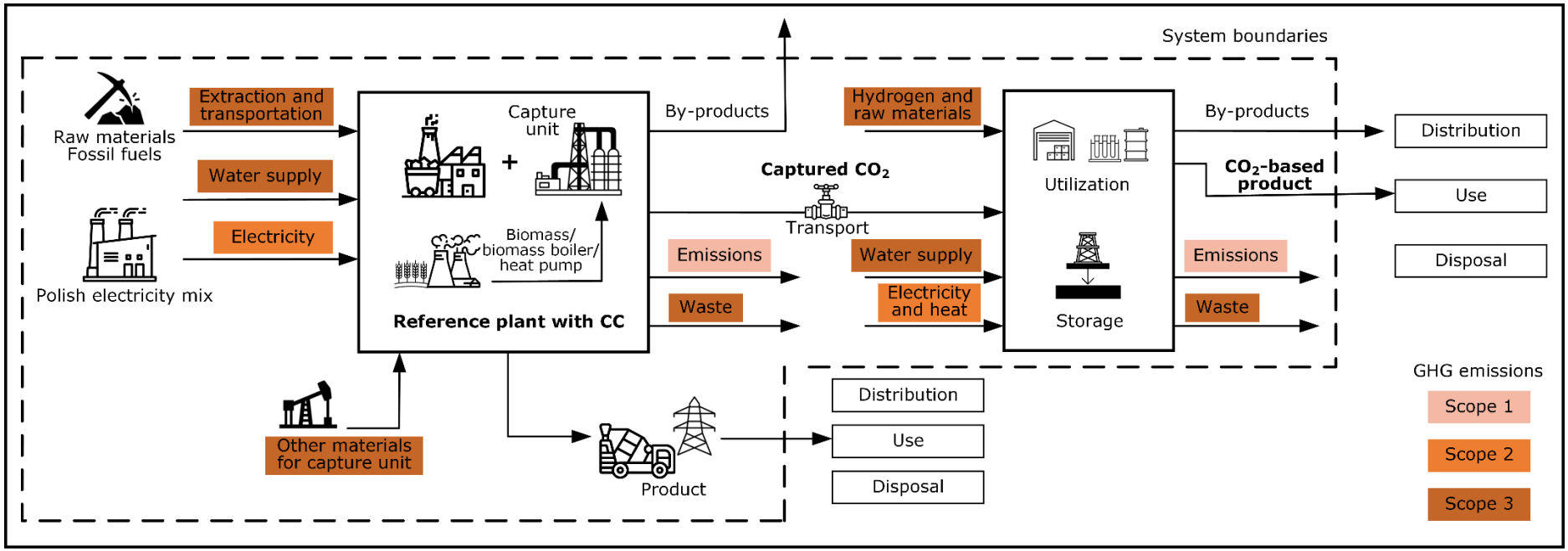

Figure 4.16 Life cycle assessment system boundaries.

Data on specific CO_2 emissions for each product or process were extracted from the Ecoinvent database [148] and KOBiZE [149] and are presented in Table 4.15

Table 4.15 Emission factors for activities [148].

Activity	**Input value**	**Unit**
Emission factor for electricity production[6]	597.0	kg CO_2/MWh
Emission factor for natural gas	0.833	kg $CO_{2\text{-eq}}/m^3$
Emission factor for combustion of certified biomass	0.000	kg $CO_{2\text{-eq}}$/Mg
Emission factor for biomass production	0.003	kg $CO_{2\text{-eq}}$/MJ
Emission factor for limestone	2.140	kg $CO_{2\text{-eq}}$ /Mg
Emission factor for liquid oxygen (cryogenic method)	0.550	kg $CO_{2\text{-eq}}$/kg
Emission factor for hydrogen (electrolysis)	35.150	kg $CO_{2\text{-eq}}$/kg
Emission factor for MEA	3.180	kg $CO_{2\text{-eq}}$/kg
Emission factor for MEA waste treatment	1.970	kg $CO_{2\text{-eq}}$/kg
Emission factor for zeolite	5.080	kg $CO_{2\text{-eq}}$/kg
Emission factor for zeolite waste treatment	0.005	kg $CO_{2\text{-eq}}$/kg
Emission factor for TEG	1.160	kg $CO_{2\text{-eq}}$/kg
Emission factor for TEG waste treatment	2.420	kg $CO_{2\text{-eq}}$/kg
Emission factor for ammonia	2.730	kg $CO_{2\text{-eq}}$/kg
Emission factor for NaOH	1.280	kg $CO_{2\text{-eq}}$/kg
Emission factor for waste water treatment	0.486	kg $CO_{2\text{-eq}}$/Mg
Emission factor for sand	0.012	kg $CO_{2\text{-eq}}$/kg
Emission factor for CO_2 pipeline transport[7]	0.000	kg $CO_{2\text{-eq}}$/kg

In Poland, the official greenhouse gas emission factor for electricity used in carbon footprint calculations is defined by the national regulation issued by the Minister of Climate and Environment. According to the Regulation of 26 October 2023 (Journal of Laws 2023, item 2370), the emission factor for electricity for the year 2024 is 178.9 g $CO_{2\text{-eq}}$/MJ, which corresponds to approximately 644 kg $CO_{2\text{-eq}}$/MWh. This factor represents the total life-cycle greenhouse gas emissions associated with electricity generation, covering both the direct emissions from fuel combustion in power plants ("Tank-to-Wheel", TTW) and the upstream emissions related to the extraction, processing, and transport of fuels ("Well-

[6] The total electricity indicator value includes not only direct emissions associated with the production of 1 MWh of electricity, but also indirect emissions related to transport via the transmission network, i.e., overhead lines and cables. This indicator includes the emission intensity of electricity produced in accordance with the country's energy mix, including imports, and the transmission network, direct air emissions, and electricity losses during transmission.

[7] It was assumed that no CO_2 leakage occurs during the pipeline transportation. Possible additional emissions related to transport were calculated based on electricity usage.

to-Tank", WTT). As such, it reflects the full "Well-to-Wheel" (WTW) emissions of the Polish electricity mix, in line with the requirements of the EU Renewable Energy Directive (RED II). In thesis, direct emissions factors for electricity supply (Scope 2) were adopted in accordance with the national electricity emission factor published by KOBiZE (597 kg CO_2/MWh). For the purpose of estimating upstream emissions (Scope 3, category 3), the difference between the total carbon footprint of electricity in Poland and the direct emissions value was used.

Similarly, in Table 4.16 the indicators for cumulative energy consumption are presented [148].

Table 4.16 Cumulative energy consumption for activities [148].

Activity	**Input value**	**Unit**
Cumulative energy consumption for electricity generation	3.51	MJ*/MJ
Cumulative energy consumption for heat generation	1.17	MJ*/MJ
Cumulative energy consumption for coal	1.05	MJ*/MJ
Cumulative energy consumption for natural gas	1.16	MJ*/MJ
Cumulative energy consumption for biomass	0.03	MJ*/MJ
Cumulative energy consumption for limestone	0.03	MJ*/kg
Cumulative energy consumption for oxygen	14.45	MJ*/kg
Cumulative energy consumption for hydrogen	78.34	MJ*/kg
Cumulative energy consumption for MEA	72.99	MJ*/kg
Cumulative energy consumption for MEA waste treatment	3.21	MJ*/kg
Cumulative energy consumption for zeolite	71.92	MJ*/kg
Cumulative energy consumption for zeolite waste treatment	0.16	MJ*/kg
Cumulative energy consumption for TEG	39.50	MJ*/kg
Cumulative energy consumption for TEG waste treatment	12.64	MJ*/kg
Cumulative energy consumption for ammonia	48.15	MJ*/kg
Cumulative energy consumption for NaOH	19.46	MJ*/kg
Cumulative energy consumption for cooling water	0.80	MJ*/m^3
Cumulative energy consumption for process water	6.60	MJ*/m^3
Cumulative energy consumption for waste water treatment	6.50	MJ*/m^3
Cumulative energy consumption for sand	0.18	MJ*/kg

As part of the modelling assumptions, biomass was represented by forest chips with LHV of 10.8 MJ/kg. For this type of fuel, a zero direct CO_2 emission factor from combustion was adopted, in accordance with the accounting convention applied under the EU Emissions Trading System.

However, since 2023, the regulatory framework for classifying biomass as "zero-emission" has been significantly strengthened. In accordance with Article 29, paragraphs 2–7 and 10 of Directive (EU) 2018/2001 of the European Parliament and Council (RED II), only biofuels, bioliquids, and biomass fuels that meet the sustainability and greenhouse gas emissions reduction criteria may contribute to the EU-wide renewable energy target for 2030 and qualify for financial support. From that point onwards, the absence of certification confirming compliance with these criteria means that such fuels cannot be treated as zero-emission. In Poland, the provisions of RED II have already been transposed, as reflected in the unified text of the Act on Bio-components and Liquid Biofuels published on 7 December 2023.

In the context of the present study, the critical condition is sustainable biomass procurement. The obligation to demonstrate compliance with sustainability and GHG reduction criteria under the EU ETS arises directly from EU law, specifically Article 38, paragraphs 2 and 5 of Commission Implementing Regulation (EU) 2018/2066 on the monitoring and reporting of GHG emissions. This requirement has applied since 2022, independently of RED II and its implementing acts. Only biomass certified as sustainable may be reported with an emission factor of zero in annual emissions reports submitted to the National Centre for Emissions Management, thereby reducing the number of allowances required under the EU ETS. To date, the European Commission has approved 13 certification schemes, including those commonly used in the Polish market such as ISCC EU, KZR iNiG, REDcert EU, and SURE. These schemes differ in certain details but are each recognized as valid for certifying biomass supply chains. Certification is the responsibility of producers and suppliers, who must ensure compliance in order to maintain the zero-emission status of biomass in reporting. In this context, the Oil and Gas Institute - National Research Institute conducted a risk assessment within the framework of the KZR iNiG scheme. The assessment concluded that RED II sustainability requirements for forest biomass harvested in Poland are met and that the risk of unsustainable biomass procurement is low.

However, for this thesis, it should be emphasized that although combustion is reported as zero-emission, the upstream supply chain of forest biomass is associated with a non-negligible carbon footprint. Based on life cycle inventory data, it was assumed that forest chips the production and logistics were responsible for approximately 0.0036 kg of $CO_{2\text{-eq}}$ per kg of biomass.

5. Results

5.1 Energy assessment

In this section, the results of the energy assessment are presented, with a particular focus on the overall energy demand of the considered CCUS configurations. The analysis covers the energy balance of each system, quantifying both the input requirements and the useful energy output. Key performance indicators such as the specific primary energy consumption per CO_2 avoided and the cumulative energy consumption are evaluated to provide a consistent basis for comparison between different capture options and emission sources. By examining these metrics, it is possible to identify the relative efficiency of each pathway and highlight the trade-offs between energy demand and CO_2 mitigation potential. The results are divided according to the CO_2 sources: power generation (Table 5.1), cement production (Table 5.2), and direct air capture (Table 5.3).

Table 5.1 Results of energy assessment, power generation cases.

Case	**Coal-fired power plant with CC**		**Natural gas-fired power plant with CC**		**Biomass-fired power plant with CC**	
Capture method	**MEA**	**CaL**	**MEA**	**CaL**	**MEA**	**CaL**
Capture efficiency, %	90	90	90	90	90	90
Net power, MW_{el}	524.6	768.8	639.6	929.0	164.0	297.5
Gross power, MW_{el}	617.8	1009.2	694.4	1128.3	193.6	408.0
• Gas turbine	n/a	n/a	486.8	486.8	n/a	n/a
• Existing steam cycle	617.8	684.8	207.6	253.0	193.6	225.6
• New steam cycle	n/a	324.4	n/a	388.5	n/a	182.4
Capture unit auxiliaries, MW_{el}	57.6	204.9	44.3	188.8	12.5	93.4
Total chemical energy input (LHV), MW_{ch}	1557.1	2579.8	1223.0	2106.0	566.6	1011.1
Additional chemical energy input (LHV) related to CO_2 capture, MW_{ch}	n/a	1,022.6	n/a	883.0	n/a	444.5
Total energy consumption per CO_2 captured, $MJ/kgCO_2$	2.4	4.1	2.8	3.9	2.4	4.1

Gross plant electrical efficiency (LHV), %	39.7	39.1	56.8	53.6	34.2	40.4
Net plant electrical efficiency (LHV), %	33.7	29.8	52.3	44.1	28.9	29.4
Net electrical efficiency penalty, %points	**8.0**	**11.9**	**7.4**	**15.5**	**7.9**	**7.4**
Annual net electricity production, GWh	4136.1	6060.8	5042.7	7324.4	1292.8	2345.1
CO_2 captured for sequestration, Mtpa	3550.8	7174.2	1832.4	6004.6	1492.4	3038.6
SPECCA, MJ/kg$_{CO2,av}$	**3.04**	**4.88**	**2.75**	**6.63**	**3.02**	**2.62**
CEC, MJ*/kgCO$_{2,captured}$	**1.72**	**2.56**	**2.55**	**1.04**	**0.93**	**1.41**
CEC, MJ*/kgCO$_{2,av}$	**1.74**	**3.01**	**2.59**	**1.56**	**0.48**	**0.59**

The graph in Figure 5.1 illustrates the electricity requirements associated with CO_2 capture technologies applied to three types of power plants divided into components of the system.

For all assessed types of plants, CaL exhibits a significantly higher total electrical requirement compared to MEA, primarily driven by the compression unit power demand, which dominates the total load in CaL systems. Calcium-looping process also requires substantial power for the air separation unit. The contribution from dehydration and auxiliary systems is relatively minor in all cases, but their share is slightly larger in CaL configurations because of the higher outlet stream which results from additional capture from biomass combustion in the calciner.

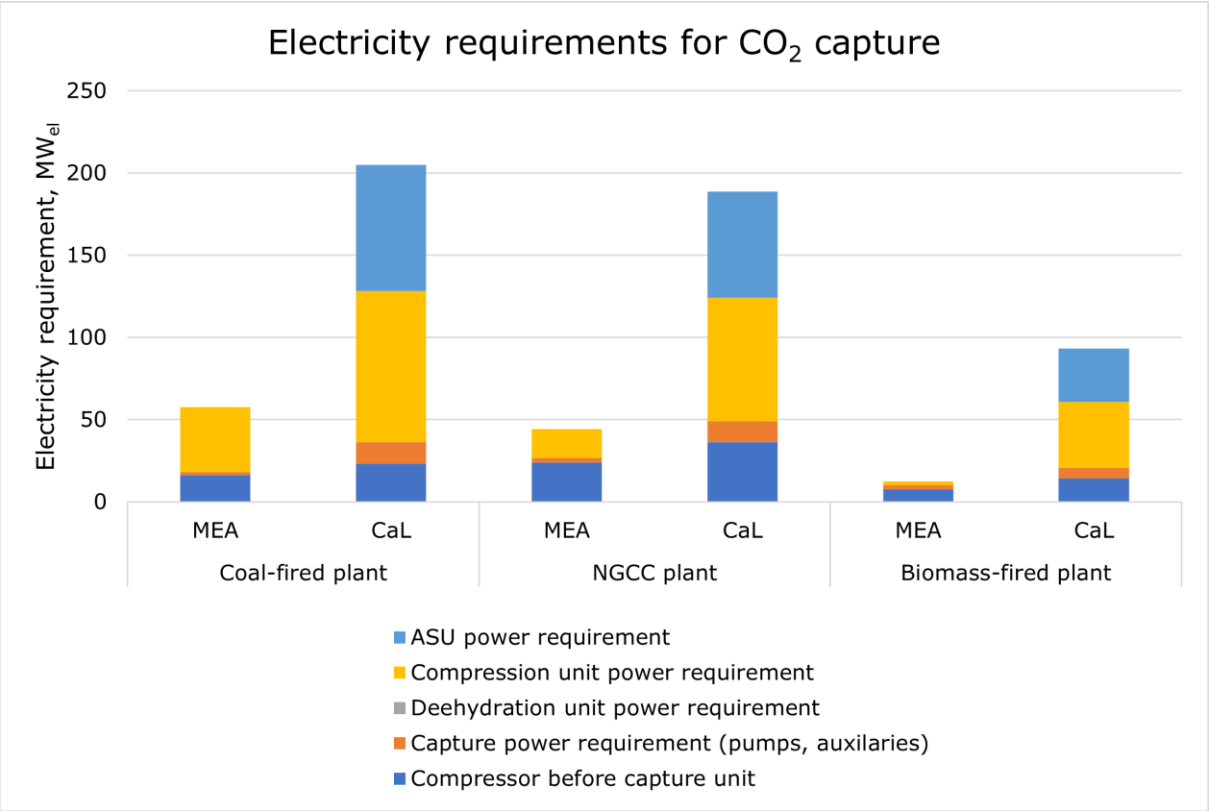

Figure 5.1 Electricity requirements for corresponding CO_2 capture units.

Table 5.2 Results of energy assessment, cement plant case.

Parameter	**Cement plant**	
	MEA	**CaL**
Heat duty, MJ/kg_{CO2}	2.3	4.1
Total added equivalent specific primary energy consumption, MJ/t_{clk}	3061.6	3903.3
Added equivalent specific primary energy consumption, MJ/t_{clk}		
• biomass consumption	1703.5	6324.7
• electric power consumption	1302.5	3032.5
• electric power generation	n/a	-5641.9
• others	55.6	188.6
Equivalent specific CO_2 avoided, kg_{CO2}/t_{clk}	601.6	1,212.9
SPECCA, $MJ/kg_{CO2,av}$	**4.76**	**3.03**
CEC, $MJ^*/kgCO_{2,captured}$	**5.51**	**1.94**
CEC, $MJ^*/kgCO_{2,av}$	**5.70**	**2.16**

A comparison between the results obtained and those from previous studies conducted within the CEMCAP project reveals that the SPECCA values for MEA

are lower (4.8 vs. 7.1 MJ/kgCO_2). This reduction is primarily attributed to the use of biomass (as a net-zero fuel) instead of natural gas for steam generation. In the CaL scenario, the SPECCA value is also lower (3.0 vs. 4.1 MJ/kgCO_2) compared to the CEMCAP results due to biomass supply and also lower than that of MEA because of additional electricity generation.

Table 5.3 Results of energy assessment, DAC case.

Parameter	**Direct air capture (solid sorbent)**
Scale, tCO_2	100000.0
Capture unit auxiliaries, MW_{el}	17.9
• unit operation auxiliaries, MW_{el}	3.1
• heat pump, MW_{el}	14.8
Total energy consumption per CO_2 captured, MJ/kgCO_2	9.8
CO_2 captured for sequestration, Mtpa	100000.0
SPECCA, MJ/kg$_{CO2,av}$	**113.73**
CEC, MJ*/kg$CO_{2,captured}$	**18.79**
CEC, MJ*/kg$CO_{2,av}$	**462.54**

Due to the high heat demand in the capture process for DAC systems, which is covered by heat pumps, there is a high demand for electricity, which is covered by the Polish power grid and generates additional emissions in Scope 2 of GHG emissions. This contributes to the fact that this system achieve only limited effect of avoided emissions. CEC value related to amount of CO_2 captured is around 10 times higher than in power plants and around 3.5 times higher compared to cement plant.

Based on established assumptions for electricity and heat demands associated with each CO_2 utilization and storage pathway, the cumulative energy consumption of the processes was quantified and presented for each case in Table 5.4 - Table 5.8. This assessment captures both the direct energy requirements for operating the individual technologies and the additional energy burden introduced by integrating these processes.

Table 5.4 Results of energy assessment for CO_2 storage and utilization pathways with CO_2 source from coal-fired power plant.

Case	**Coal-fired power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Unit	MJ*/kg$CO_{2,in}$	MJ*/kg$CO_{2,av}$	MJ*/kg$CO_{2,in}$	MJ*/kg$CO_{2,av}$
Storage	1.92	1.95	2.76	3.21
EOR	1.97	2.00	2.81	3.26
EGS	1.93	2.02	2.77	3.28
Methanol	15.29	-	16.13	-

Methane	15.27	-	16.11	-
Urea	26.04	-	26.88	-
DME	15.81	-	16.65	-
Olefins	16.92	-	17.76	-
Aromatics	17.08	-	17.92	-
Mineralization	9.75	12.44	10.59	13.70

Table 5.5 Results of energy assessment for CO_2 storage and utilization pathways with CO_2 source from natural gas combined cycle.

Case	**Natural gas-fired power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Unit	$MJ^*/kgCO_{2,in}$	$MJ^*/kgCO_{2,av}$	$MJ^*/kgCO_{2,in}$	$MJ^*/kgCO_{2,av}$
Storage	2.75	2.79	1.24	1.76
EOR	2.81	2.84	1.29	1.81
EGS	2.77	2.86	1.25	1.83
Methanol	16.12	-	14.61	-
Methane	16.11	-	14.59	-
Urea	26.88	-	25.36	-
DME	16.64	-	15.13	-
Olefins	17.76	-	16.24	-
Aromatics	17.92	-	16.40	-
Mineralization	10.58	13.28	9.07	12.25

Table 5.6 Results of energy assessment for CO_2 storage and utilization pathways with CO_2 source from biomass-fired power plant.

Case	**Biomass-fired power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Unit	$MJ^*/kgCO_{2,in}$	$MJ^*/kgCO_{2,av}$	$MJ^*/kgCO_{2,in}$	$MJ^*/kgCO_{2,av}$
Storage	1.13	0.68	1.62	0.79
EOR	1.18	0.73	1.67	0.84
EGS	1.14	0.75	1.63	0.86
Methanol	14.50	-	14.98	-
Methane	14.48	-	14.97	-
Urea	25.25	-	25.74	-
DME	15.02	-	15.50	-
Olefins	16.13	-	16.62	-
Aromatics	16.29	-	16.78	-
Mineralization	8.95	11.17	9.44	11.28

Table 5.7 Results of energy assessment for CO_2 storage and utilization pathways with CO_2 source from cement plant.

Case	**Cement plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Unit	$MJ^*/kgCO_{2,in}$	$MJ^*/kgCO_{2,av}$	$MJ^*/kgCO_{2,in}$	$MJ^*/kgCO_{2,av}$
Storage	5.71	5.90	2.14	2.36
EOR	5.76	5.95	2.19	2.41
EGS	5.72	5.97	2.15	2.43
Methanol	19.08	-	15.51	-
Methane	19.06	-	15.49	-
Urea	29.83	-	26.26	-
DME	19.60	-	16.03	-
Olefins	20.71	-	17.14	-
Aromatics	20.87	-	17.30	-
Mineralization	13.53	16.39	9.96	12.85

Table 5.8 Results of energy assessment for CO_2 storage and utilization pathways with CO_2 source from atmosphere.

Case	**DAC**	
Capture method	**Solid sorbent**	
Unit	$MJ^*/kgCO_{2,in}$	$MJ^*/kgCO_{2,av}$
Storage	18.99	462.74
EOR	19.04	462.79
EGS	19.00	462.81
Methanol	32.36	-
Methane	32.34	-
Urea	43.11	-
DME	32.88	-
Olefins	33.99	-
Aromatics	34.15	-
Mineralization	26.82	473.23

The cumulative energy consumption analysis indicates clear differences between storage- and utilization-based pathways. Storage options are associated with a relatively low additional energy demand, while utilization routes exhibit a much wider range of results. Energy-intensive conversion pathways, particularly those producing synthetic fuels and chemicals, significantly increase the overall CEC as a result of the high requirements for hydrogen and electricity. For each CO_2 source assessed chemicals production leads to additional emissions which make the avoidance effect impossible. Small or no avoidance effect occurs also in every DAC-based pathway with CO_2 conversion. Mineralization shows intermediate results, reflecting moderate

additional energy inputs combined with relatively stable permanence of CO_2. Overall, the trends highlight a trade-off between permanence of storage and the energetic cost of utilization. CCS offers lower energy penalties while CCU pathways results in higher variability depending on the product and boundary conditions assumed.

Furthermore, considering the embodied energy incorporated into the resulting products within system expansion, reflects the share of energy that is effectively transferred from the utilization process to the end product. For this case only the pathways leading to generation of new energy product can be assessed. Additional amount of energy is calculated based on heating value or amount of electricity generated from 1 tonne of CO_2 utilized. Remaining chemicals, DME, urea, olefins and aromatics are assumed to constitute a feedstock to a subsequent chemical reaction or used not in the form of energy, since resulting products such as plastics, polymers or rubbers are not destined to be burnt for energy generation. The results indicate that the total value of cumulative energy consumption decreases by approximately 60 times for EOR, and by 1.3-, 1.8-, 1.5-fold for EGS, methanol and methane production respectively. Results for the example of cement plant are presented in Table 5.9.

Table 5.9 Results of energy assessment for utilization pathways with CO_2 source from cement plant, system expansion variant.

Case	**Cement plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Unit	$MJ^*/kgCO_{2,in}$	$MJ^*/kgCO_{2,av}$	$MJ^*/kgCO_{2,in}$	$MJ^*/kgCO_{2,av}$
EOR	-13.11	-11.70	-12.27	-10.44
EGS	-0.14	1.66	0.70	2.92
Methanol	-8.70	-	-7.86	-
Methane	-4.70	-21.66	-3.86	-20.39

Based on obtained results, it is visible that some utilization options, such as enhanced oil recovery, appear to reduce the system-level CEC when applying system expansion, as the produced oil displaces conventional extraction and provides additional energy related to product. It translates to negative CEC values meaning the overall amount of energy produced is higher than the process requirements.

5.2 Economic evaluation

This chapter presents the results of the economic evaluation of the investigated CO_2 capture, utilization, and storage pathways, with a particular emphasis on the cost of CO_2 avoided. The analysis was carried out within the techno-economic assessment framework, using consistent assumptions regarding

capital and operating expenditures, discount rates, capacity factors, and market conditions defined in the methodology chapter.

The primary objective is to quantify the costs of alternative technologies and value-chain configurations in terms of their ability to reduce greenhouse gas emissions. Results are reported as levelized metrics, including the levelized cost of CO_2 captured, cost of CO_2 avoided, and other relevant economic indicators, expressed in EUR per tonne of CO_2.

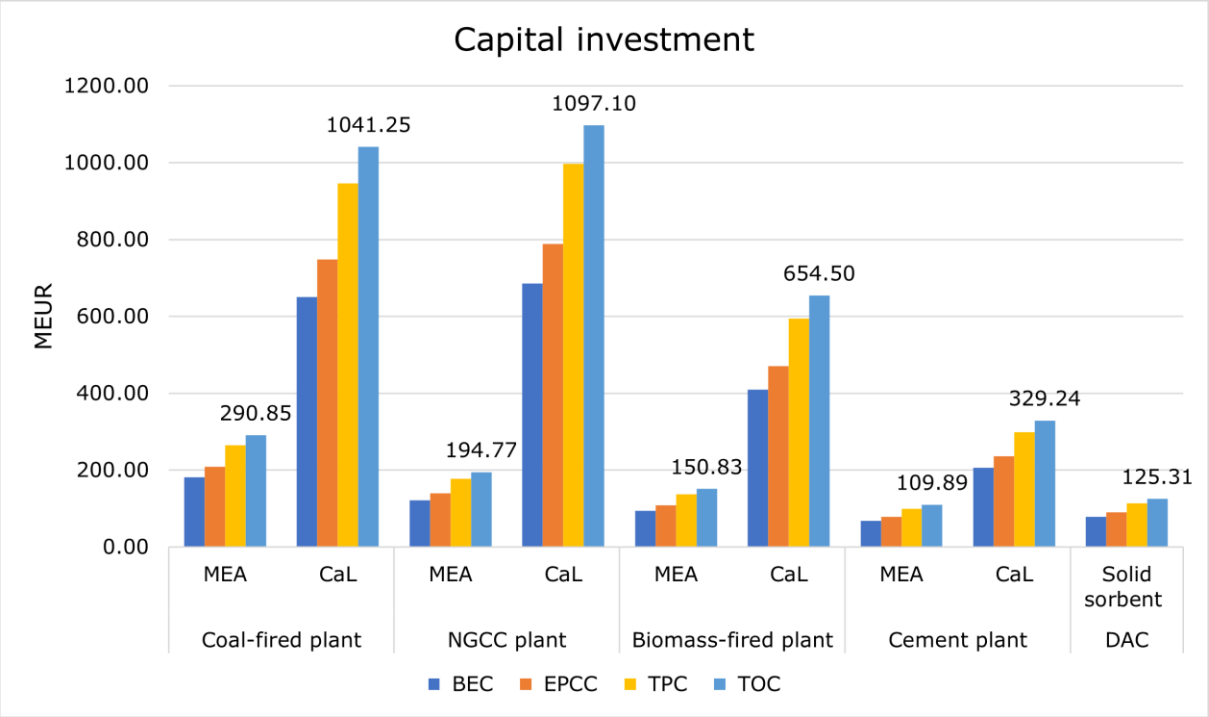

Figure 5.2 Values for each category in capital cost estimates for analyzed cases.

Coal- and natural gas power plants are associated with the highest total capital investments, while biomass fired power plant and cement plants as well as DAC units display lower overall investment requirements due to lower flue gas stream or capture capacity in assumed scenarios (Figure 5.2). In terms of capture methods, as presented in Figure 5.3 and Figure 5.4, calcium looping generally shows significantly higher CAPEX compared to conventional amine scrubbing, primarily due to additional investment for the steam cycle and air separation unit. Due to material exchange and fuel combustion in the calciner in the CaL unit, the reactors need to be designed for high temperatures and large volumes, which corresponds to high initial costs.

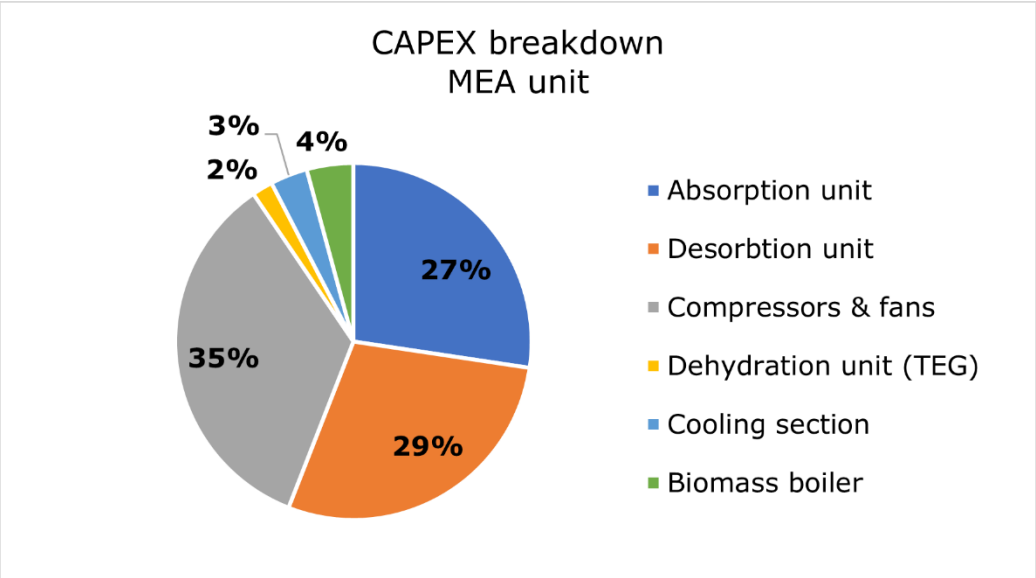

Figure 5.3 Capital expenditures unit shares, amine absorption method.

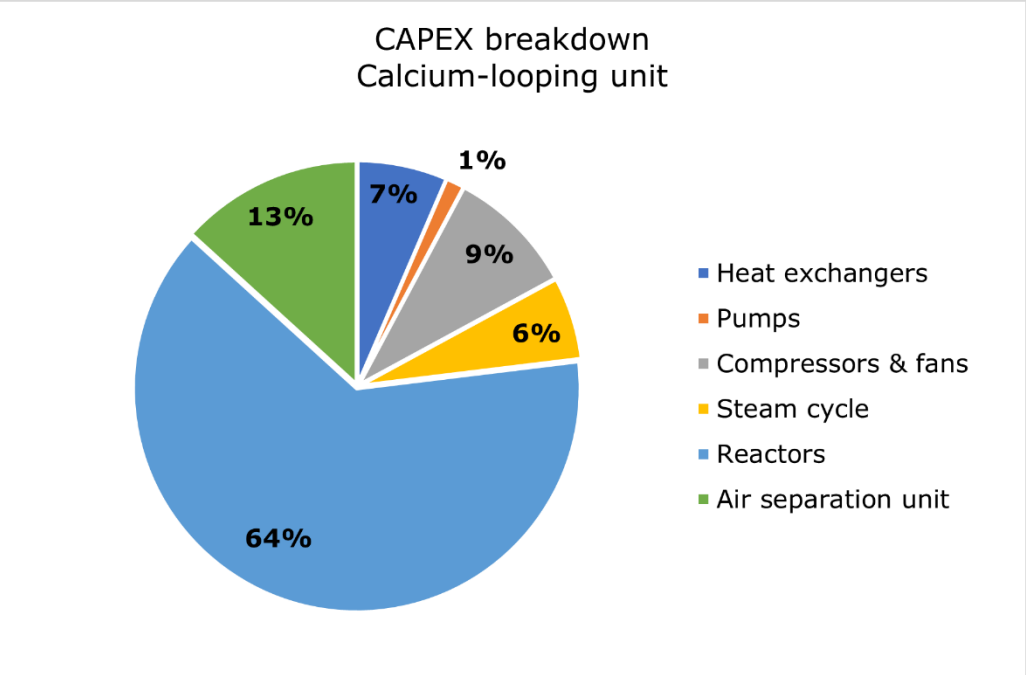

Figure 5.4 Capital expenditures unit shares, calcium-looping method.

Analyzing the obtained COC and CAC results (Table 5.10), trends indicate that capture from point sources with high CO_2 concentrations, such as cement plants and coal-based facilities, is more economically favorable than low-concentration sources.

Solid sorbent-based direct air capture technologies are characterized by clearly lower capital intensity per unit of installed capacity, but remain constrained by higher capture costs per tonne of captured CO_2.

Table 5.10 Results of economic evaluation for CO_2 capture cases.

CO_2 source	**Capture method**	**COC, EUR/$tCO_{2,captured}$**	**CAC, EUR/$tCO_{2,av}$**
Coal-fired power plant	MEA	51.02	51.73
	CaL	41.58	48.90
NGCC plant	MEA	67.35	68.27
	CaL	37.12	55.54
Biomass-fired power plant	MEA	48.65	24.98
	CaL	44.63	18.58
Cement plant	MEA	57.76	59.76
	CaL	46.96	52.34
DAC	Solid sorbent	268.84	6618.17

Table 5.11 - Table 5.15 present the results for the CO_2 avoided costs as well as levelized cost of capture and storage (LCOS) and levelized cost of capture and utilization (LCOU) for assessed cases. The tables show values for each CO_2 source and two capture methods.

Table 5.11 Results of economic evaluation for CO_2 storage and utilization pathways with CO_2 source from coal-fired power plant.

Case	**Coal-fired power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Parameter	CAC	LCOU/LCOS	CAC	LCOU/LCOS
Unit	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$
Storage	58.49	57.08	58.62	49.25
EOR	63.60	61.90	63.14	52.88
EGS	59.25	58.05	61.64	52.03
Methanol	-	619.45	-	605.08
Methane	-	709.67	-	699.53
Urea	-	684.88	-	674.06
DME	-	604.87	-	595.24
Olefins	-	620.00	-	607.05
Aromatics	-	694.38	-	608.54
Mineralization	151.34	111.50	175.52	105.49

Table 5.12 Results of economic evaluation for CO_2 storage and utilization pathways with CO_2 source from natural gas combined cycle.

Case	**Natural gas-fired power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Parameter	CAC	LCOU/LCOS	CAC	LCOU/LCOS
Unit	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$
Storage	78.04	76.18	69.83	45.95
EOR	80.03	77.93	72.77	47.70
EGS	78.72	77.15	70.89	46.92
Methanol	-	641.89	-	602.64
Methane	-	727.10	-	696.10
Urea	-	703.11	-	670.79
DME	-	628.23	-	592.39
Olefins	-	640.75	-	604.28
Aromatics	-	641.54	-	605.70
Mineralization	171.34	126.30	229.33	96.07

Table 5.13 Results of economic evaluation for CO_2 storage and utilization pathways with CO_2 source from biomass-fired power plant.

Case	**Biomass-fired power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Parameter	CAC	LCOU/LCOS	CAC	LCOU/LCOS
Unit	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$
Storage	29.67	57.48	22.35	53.46
EOR	30.61	59.23	23.11	55.20
EGS	30.11	58.45	22.72	54.43
Methanol	-	626.93	-	637.14
Methane	-	710.54	-	705.13
Urea	-	686.80	-	680.51
DME	-	612.60	-	603.95
Olefins	-	625.25	-	616.17
Aromatics	-	625.91	-	617.25
Mineralization	63.36	107.60	48.11	103.57

Table 5.14 Results of economic evaluation for CO_2 storage and utilization pathways with CO_2 source from cement plant.

Case	**Cement plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Parameter	CAC	LCOU/LCOS	CAC	LCOU/LCOS
Unit	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$
Storage	69.64	66.59	62.90	55.79
EOR	71.66	68.34	65.06	57.54
EGS	70.37	67.56	63.72	56.76
Methanol	-	645.39	-	625.72
Methane	-	722.23	-	709.60
Urea	-	699.57	-	685.82
DME	-	628.26	-	611.50
Olefins	-	641.43	-	624.13
Aromatics	-	641.57	-	624.81
Mineralization	162.75	116.70	163.48	105.90

Table 5.15 Results of economic evaluation for CO_2 storage and utilization pathways with CO_2 source from the atmosphere.

Case	**DAC**	
Capture method	**Solid sorbent**	
Parameter	CAC	LCOU/LCOS
Unit	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$
Storage	9158.83	277.67
EOR	10072.21	279.42
EGS	8152.35	278.64
Methanol	-	855.88
Methane	-	896.56
Urea	-	880.50
DME	-	827.72
Olefins	-	932.61
Aromatics	-	878.27
Mineralization	-	327.79

The financial analysis also highlights the clear differences between CO_2 storage and utilization. For non-conversion pathways, geological storage, EOR, and EGS are associated with moderate costs of CO_2 avoidance. Mineralization is characterized by 2-3 times higher values. However, accounting the revenues from the sale of additional product such as oil in the case of EOR and from

mineral products in the case of mineralization, may offset the associated costs and make these options appear economically favorable.

In case of pathways involving chemical conversion of CO_2 into fuels or chemicals, the options are characterized by very high costs per tonne of CO_2 utilized, approximately 5-10 times higher compared to non-conversion variants. For these products, the calculation of the CO_2 avoided cost is not applicable, only the utilization cost is reported. DAC variant pathways remain the most expensive for deployment.

Results recalculated per tonne of product give a value of minimum selling price which for 100,000 tCO_2 scale are shown in Table 5.16 and compared with current market prices for oil [150], renewable electricity [151], methanol [152], methane [151], urea [153], DME [94], olefins [94], aromatics [94], and mineralization (based on precipitated calcium carbonate price) [154]. Because hydrogen is the dominant cost driver in CO_2 conversion pathways, calculation included the break-even price to assess whether cost parity with fossil-based alternatives is achievable.

Table 5.16 Comparison between prices for assessed products resulting from CO_2 utilization and corresponding break even price for hydrogen.

Scale	**100 000 tCO_2**		
Parameter	**MSP (own results)**	**MSP (market average value)**	**BEP (hydrogen price)**
Unit	EUR/$t_{product}$ (EUR/MWh[8])	EUR/$t_{product}$ (EUR/MWh[8])	EUR/kg
EOR	219	488	n/a
EGS	1843	150	n/a
Methanol	1007	510	1.24
Methane	2128	480	0.44
Urea	524	350	1.99
DME	1274	477	0.66
Olefins	2960	1048	0.05
Aromatics	2641	811	0.04
Mineralization	119	180	n/a

[8] refers to EGS system generating electricity as a product

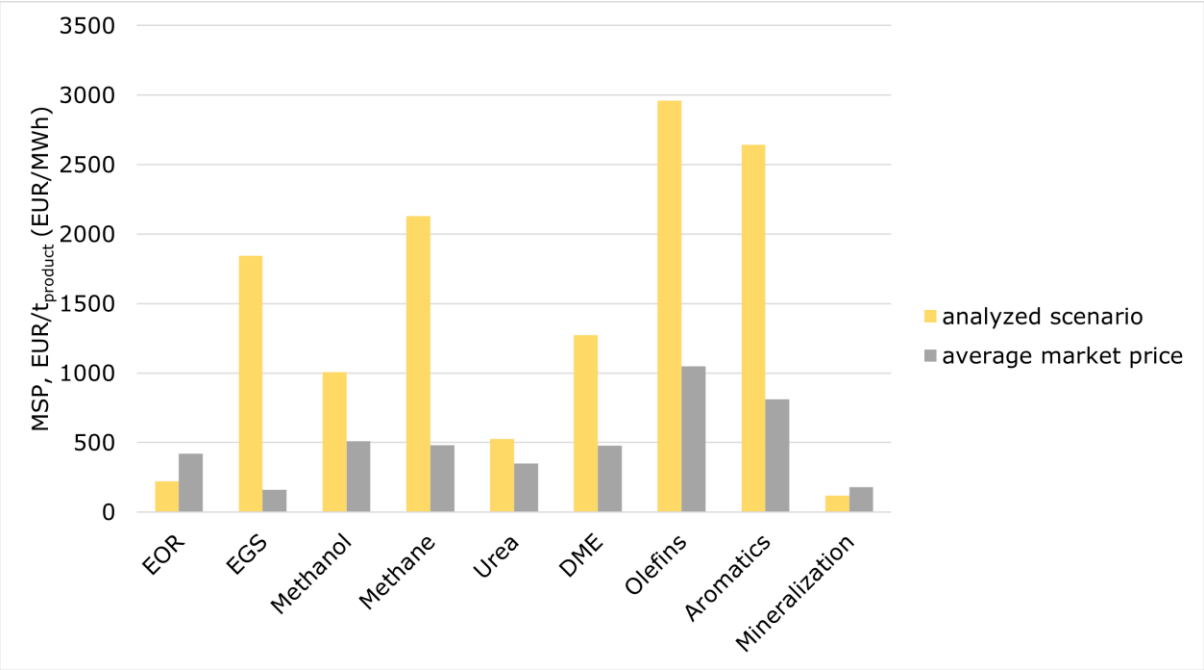

Figure 5.5 Comparison between prices for assessed products resulting from CO_2 utilization.

Even when revenues from product sales would be included, options with CO_2 conversion remain substantially more expensive than geological storage, reflecting their strong dependence on electricity and hydrogen. Under the assumptions adopted in this study, only the CO_2-EOR and mineralization pathways yield minimum selling prices below prevailing market benchmarks (Figure 5.5). However, these MSP estimates exclude downstream and commercial cost elements such as distribution and transportation, field services, merchant margins, and additional infrastructure, which would increase the effective price. A detailed, project-specific assessment should be performed, although both options exhibit credible potential for economic viability. For EGS-derived electricity, when only the utilization stage is considered, the implied MSP falls below €300/MWh. While still high, this level is comparatively more attainable, particularly if incentives or credits associated with CO_2 sequestration can be realized.

5.3 Environmental impact assessment

This chapter presents the results of the environmental assessment of the investigated CO_2 capture, utilization and storage pathways, with a particular focus on their carbon footprint. The analysis was carried out using the life-cycle assessment methodology in accordance with ISO 14040/44 standards and the GHG Protocol, ensuring consistency and comparability of results. Functional units, system boundaries, allocation rules, and impact categories were defined in the methodology chapter and are applied here to quantify greenhouse gas emissions expressed as CO_2 equivalent (GWP100, IPCC).

The primary objective of this chapter is to quantify the net climate impact of the modelled systems, and identify the main emission hotspots along the process chains. The results are first presented at the level of individual steps related to CO_2 capture, followed by integrated value-chain results. Special attention is given to the role of the energy supply mix, and the carbon intensity of auxiliary materials, as these parameters strongly influence the overall footprint.

Obtained results are presented in Table 5.17 - Table 5.23. They are divided according to primary functional unit which is tonne of CO_2 avoided, but in order to give a better overview of each case, the results were also presented for production unit, so 1 MWh in case of power plants and 1 tonne of clinker for cement plant.

Table 5.17 Carbon footprint results per unit of production for fossil-based power generation.

Case	**Coal-fired power plant with CC**			**Natural gas-fired power plant with CC**		
Capture method	**REF**	**MEA**	**CaL**	**REF**	**MEA**	**CaL**
Scope 1, $kgCO_{2\text{-}eq}$/MWh	771.5	106.9	72.4	347.5	42.8	30.3
Scope 2, $kgCO_{2\text{-}eq}$/MWh	0.0	0.0	0.0	0.0	0.0	0.0
Scope 3, $kgCO_{2\text{-}eq}$/MWh	115.1	143.6	115.1	106.5	121.9	96.4
Total CF, $kgCO_{2\text{-}eq}$/MWh	886.6	250.5	187.5	454.0	164.8	126.7

Table 5.18 Carbon footprint results per CO_2 avoided for fossil-based power generation.

Case	**Coal-fired power plant with CC**		**Natural gas-fired power plant with CC**	
Capture method	**MEA**	**CaL**	**MEA**	**CaL**
Total amount of CO_2 avoided, $ktCO_2$	3501.9	6101.3	1811.3	4013.1
Scope 1, $kgCO_{2\text{-}eq}/tCO_{2,av}$	126.3	71.9	121.4	55.3
Scope 2, $kgCO_{2\text{-}eq}/tCO_{2,av}$	0.0	0.0	0.0	0.0
Scope 3, $kgCO_{2\text{-}eq}/tCO_{2,av}$	169.7	114.3	345.5	176.0
Total CF, $kgCO_{2\text{-}eq}/tCO_{2,av}$	295.9	186.2	466.9	231.3
Total CF, $kgCO_{2\text{-}eq}$ /$tCO_{2,captured}$	291.8	158.4	460.6	154.6

The values for Scope 1 in the reference unit confirm the dominant role of direct combustion emissions in power plants, while the addition of carbon capture

substantially reduces this category. No Scope 2 emissions are reported, as the indirect electricity supply was not included in the system boundary. The steam required for the capture processes is directly extracted from the plant cycle. Scope 3 contributions, mainly associated with upstream fuel supply chains, remain present in all cases and vary depending on the fuel type and capture method.

The total carbon footprint per unit of electricity generated decreases significantly when capture is applied, and CaL generally provides lower residual emissions than MEA in both coal- and gas-based plants. On a per tonne of CO_2 avoided basis, the indicators show that the avoidance effect from coal-fired plants is greater due to higher CO_2 content in the flue gas.

Table 5.19 Carbon footprint results per unit of production for biomass-fired power generation.

Case	**Biomass-fired power plant with CC**		
Capture method	**REF**	**MEA**	**CaL**
Scope 1, $kgCO_{2\text{-}eq}$/MWh	0.0	-1140.1	-1361.1
Scope 2, $kgCO_{2\text{-}eq}$/MWh	0.0	0.0	0.0
Scope 3, $kgCO_{2\text{-}eq}$/MWh	35.0	46.1	44.8
Total CF, $kgCO_{2\text{-}eq}$/MWh	35.0	-1094.0	-1316.3

Table 5.20 Carbon footprint results per CO_2 avoided for biomass-fired power generation.

Case	**Biomass-fired power plant with CC**	
Capture method	**MEA**	**CaL**
Total amount of CO_2 avoided, $ktCO_2$	2906.7	7298.8
Scope 1, $kgCO_{2\text{-}eq}/tCO_{2,av}$	-507.1	-437.3
Scope 2, $kgCO_{2\text{-}eq}/tCO_{2,av}$	0.0	0.0
Scope 3, $kgCO_{2\text{-}eq}/tCO_{2,av}$	20.5	14.4
Total CF, $kgCO_{2\text{-}eq}/tCO_{2,av}$	-486.6	-422.9
Total CF, $kgCO_{2\text{-}eq}$ /$tCO_{2,captured}$	-947.7	-1015.9

Assessment of biomass-fired power plants equipped with CO_2 capture reveals a different profile compared to fossil-based cases. Since the combustion of sustainably sourced biomass is treated as carbon neutral at the point of release, the addition of CO_2 capture leads to net negative emissions. This effect is evident in the Scope 1 results, where the values fall below zero. Scope 3 contributions, linked to upstream supply chains, remain positive but relatively small in comparison, and thus do not offset the negative balance. The total carbon footprint becomes strongly negative for both MEA and CaL, with the latter

yielding a slightly higher avoidance potential. Negative values for Scope 1 confirm the role of biomass as a carbon dioxide removal option.

Figure 5.6 presents the comparison between all CO_2 sources from power generation.

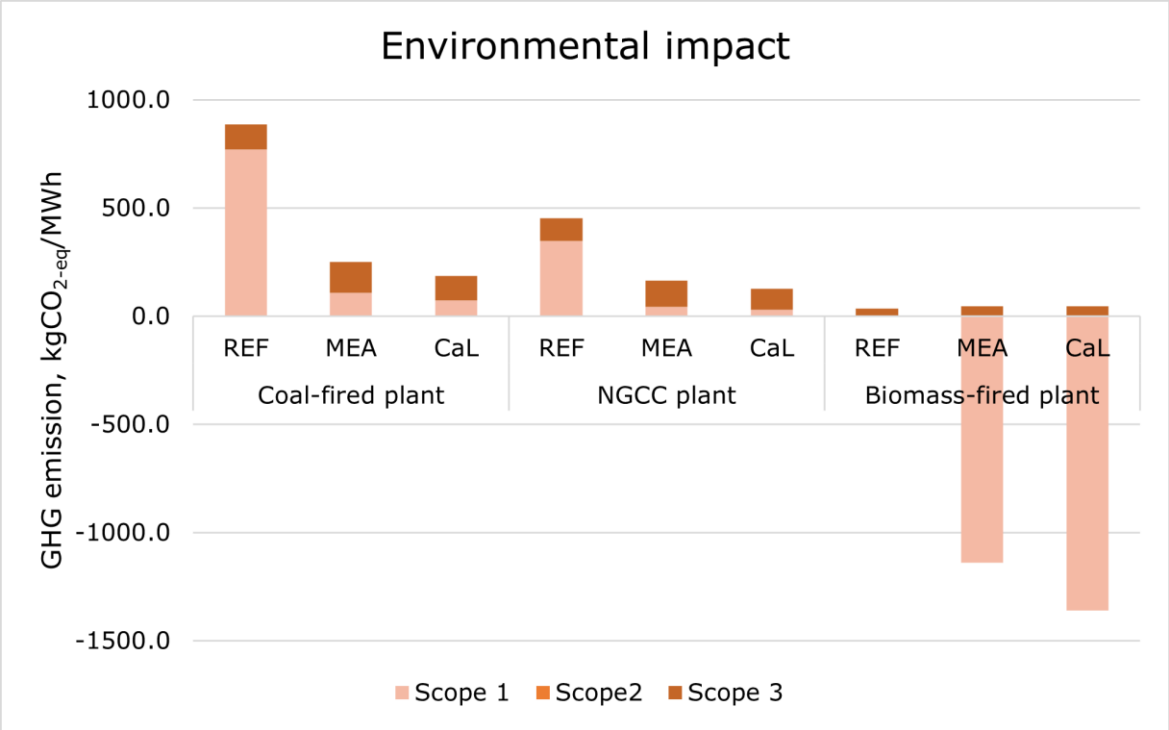

Figure 5.6 Environmental impact among analyzed technologies for power generation cases.

For the cement plant, the deployment of CO_2 capture technologies leads to a substantial reduction in direct (Scope 1) emissions, decreasing the carbon footprint to 88.7 $kgCO_{2\text{-eq}}/t_{clk}$ for both MEA and CaL, corresponding to an approximate reduction of 90% relative to the reference unit. The contribution of Scope 2 emissions increases for the MEA process due to additional electricity demand (89.4 $kgCO_{2\text{-eq}}/t_{clk}$), while in the CaL case Scope 2 is negligible. Scope 3 emissions remain comparatively minor, though slightly higher for CaL (Figure 5.7).

Table 5.21 Carbon footprint results per unit of production for cement plant.

Case	**Cement plant with CC**		
Capture method	**REF**	**MEA**	**CaL**
Scope 1, $kgCO_{2\text{-eq}}/t_{clk}$	838.1	88.7	88.7
Scope 2, $kgCO_{2\text{-eq}}/t_{clk}$	58.1	89.4	0.0
Scope 3, $kgCO_{2\text{-eq}}/t_{clk}$	14.6	17.6	23.6
Total CF, $kgCO_{2\text{-eq}}/t_{clk}$	910.8	195.7	112.3

In terms of avoided emissions per tonne of CO_2, CaL achieves lower intensities (81.2 $kgCO_{2\text{-eq}}/tCO_{2,av}$) compared to MEA (273.7 $kgCO_{2\text{-eq}}/tCO_{2,av}$), reflecting the

advantage of process integration in the CaL configuration with additional CO_2 capture from biomass combustion.

Table 5.22 Carbon footprint results per CO_2 avoided for cement plant.

Case	**Cement plant with CC**	
Capture method	**MEA**	**CaL**
Total amount of CO_2 avoided, $ktCO_2$	714.4	1381.9
Scope 1, $kgCO_{2\text{-eq}}/tCO_{2,av}$	124.0	64.1
Scope 2, $kgCO_{2\text{-eq}}/tCO_{2,av}$	125.1	0.0
Scope 3, $kgCO_{2\text{-eq}}/tCO_{2,av}$	24.6	17.1
Total CF, $kgCO_{2\text{-eq}}/tCO_{2,av}$	273.7	81.2
Total CF, $kgCO_{2\text{-eq}}/tCO_{2,captured}$	264.5	72.8

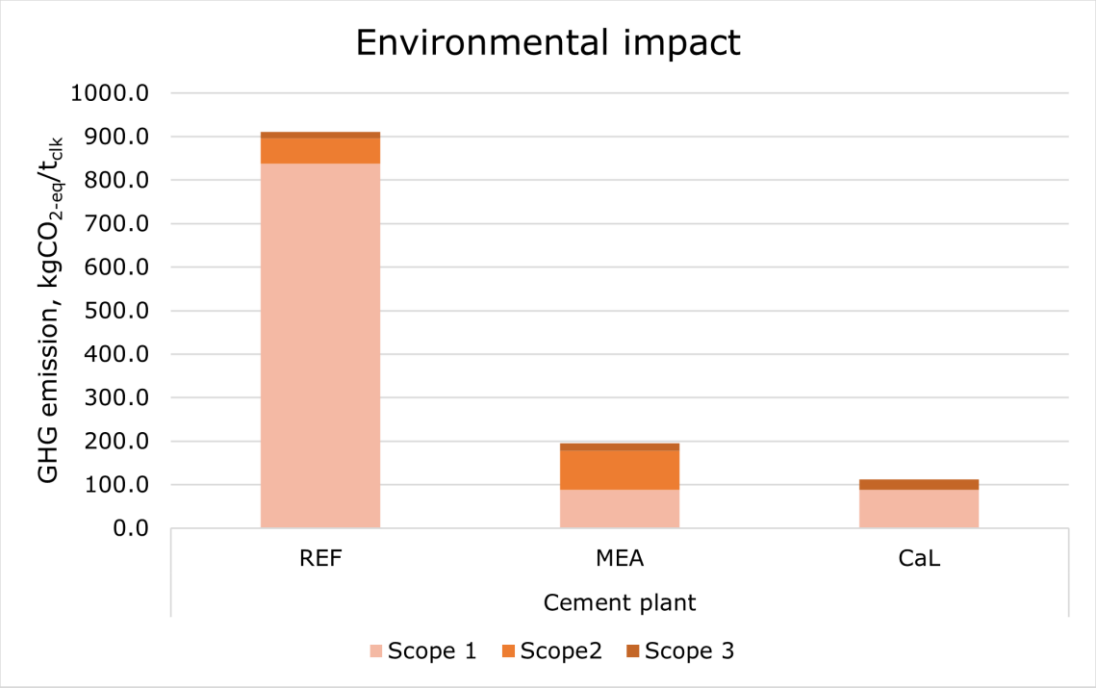

Figure 5.7 Environmental impact results comparison for cement plant.

In the case of direct air capture with solid sorbents, the life-cycle results highlight both the potential and the current limitations of the technology. Scope 1 emissions are reported as strongly negative, reflecting the removal of CO_2 directly from the atmosphere at a rate of 1000 kt annually. However, this benefit is offset by very high Scope 2 emissions (886.5 $kgCO_{2\text{-eq}}/tCO_{2,captured}$), which arise from the substantial electricity demand of the capture process. Scope 3 contributions associated with materials supply are minor. As a result, the net balance amounts to a total carbon footprint of -40.6 $kgCO_{2\text{-eq}}/tCO_{2,captured}$. This indicates that the process achieves a gross removal of atmospheric CO_2, but also underlines the overall effectiveness which is highly dependent on the carbon intensity of the electricity supply. When powered by high-emission grids,

DAC may provide only limited net benefits or, even yield negative avoidance values. However, in this case, slightly positive climate effect is achieved.

Table 5.23 Carbon footprint results per unit of production for direct air capture.

Case	**DAC**
Capture method	**Solid sorbent**
Total amount of CO_2 avoided, $ktCO_2$	4.1
Scope 1, $kgCO_{2\text{-eq}}/tCO_{2,captured}$	-1000.0
Scope 2, $kgCO_{2\text{-eq}}/tCO_{2,captured}$	886.5
Scope 3, $kgCO_{2\text{-eq}}/tCO_{2,captured}$	72.9
Total CF, $kgCO_{2\text{-eq}}/tCO_{2,captured}$	-40.6

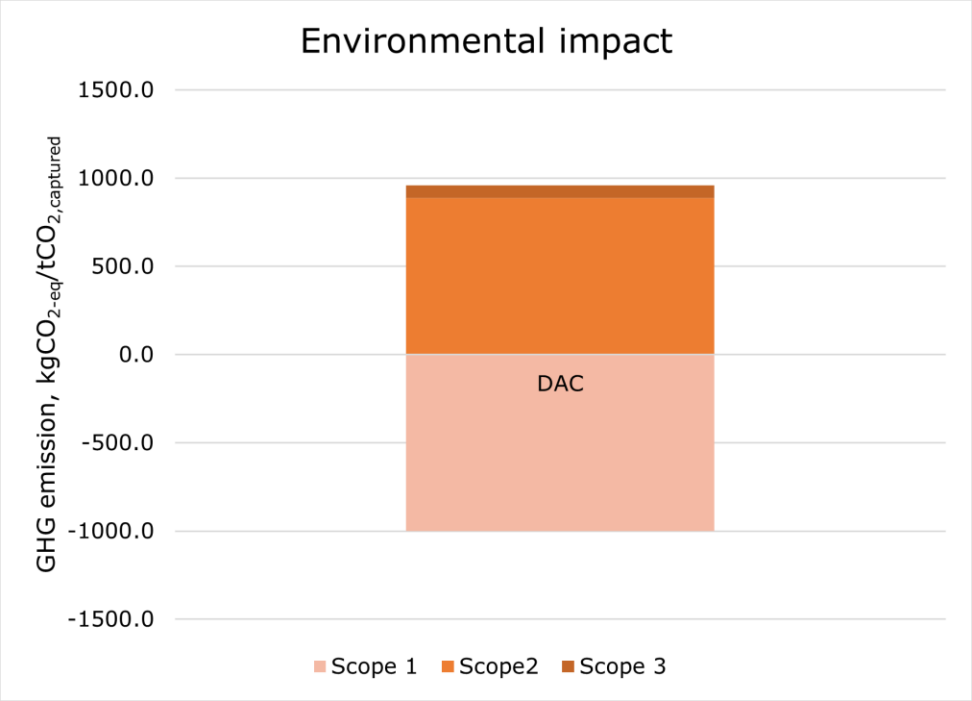

Figure 5.8 Environmental impact results comparison for direct air capture.

The carbon intensity of electricity generation has a decisive influence on the overall environmental performance of direct air capture systems. As shown in Figure 5.8 and Figure 5.9, the net carbon footprint of DAC per unit of CO_2 captured is highly sensitive to the emission factor of the electricity supply.

When the emission intensity is low, DAC achieves significant net negative emissions, effectively removing CO_2 from the atmosphere. However, as the carbon intensity of electricity increases, the benefits of DAC diminish, and beyond a certain threshold the process can result in net positive emissions. For Poland, where the current average emission factor for electricity generation is approximately 600 kg $CO_{2\text{-eq}}$/MWh, the performance of DAC is substantially reduced compared to systems powered by low-carbon or renewable electricity.

At such emission intensities, a considerable fraction of the CO_2 captured is offset by emissions associated with the energy required to operate the DAC process.

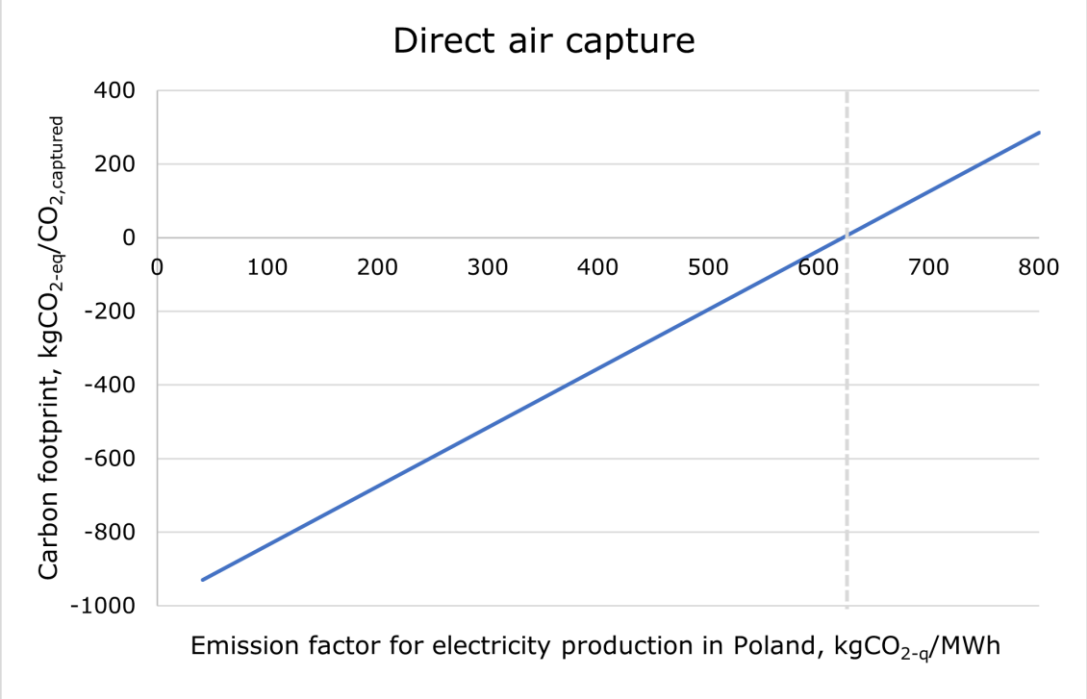

Figure 5.9 Change in carbon footprint value for DAC (solid sorbent) unit with different emission factors for Polish electricity mix.

Figure 5.10 presents the comparison among all CO_2 sources assessed indicating negative emissions obtained within Scope 1 in biomass-fired power plant and DAC cases. These results emphasize that, while capture reduces stack emissions efficiently, the choice of fuel and capture method strongly influences the balance of upstream and residual life-cycle emissions. In terms of CO_2 utilization and storage pathways, all substantial inlet and outlet flows were considered. Because system boundaries initially ends with product, the additional emissions stemming from product use where not taken into account. Moreover, when system expansion (substitution) is adopted, use-phase emissions that are identical for the studied product and the displaced fossil-based alternative cancel out. The net balance therefore credits the life-cycle burdens of the substituted product over the function replaced, primarily its upstream production and supply, rather than double-counting equal use-phase emissions.

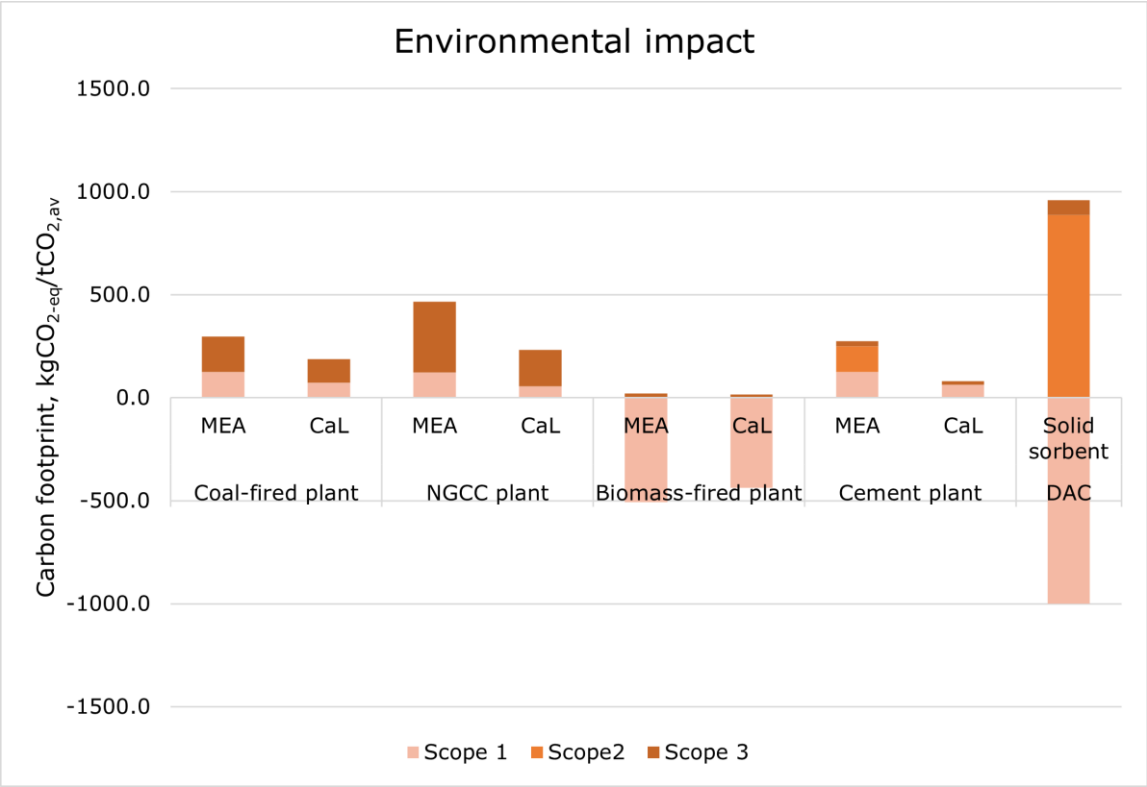

Figure 5.10 Environmental impact results comparison for assessed CO_2 sources.

Table 5.24 shows the results obtained for each technology. Geological storage in saline formations yields the lowest impacts, with values on the order of 10 $kgCO_{2\text{-}eq}/tCO_2$, reflecting only the energy and infrastructure requirements of injection and monitoring. Enhanced oil recovery and enhanced geothermal systems show similar footprints on a per tonne of CO_2 basis, although the values per unit of product differ, with EGS achieving very low intensities due to electricity production as the main unit purpose.

Table 5.24 Carbon footprint results for CO_2 storage and utilization technologies.

	Total, $kgCO_{2eq}/tCO_{2,in}$	**Total, $kgCO_{2\text{-}eq}/t_{product}$ ($kgCO_{2\text{-}eq}/kWh$[9])**
Storage (saline formations)	10.3	10.3
EOR	12.9	42.6
EGS	6.4	0.2
Methanol	4910.1	7168.7
Methane	6081.3	17575.0
Urea	5372.6	3922.0
DME	4915.4	9486.8
Olefins	4944.3	18986.2
Aromatics	4974.5	18405.6
Mineralization	249.5	249.5

[9]refers to EGS generating electricity as a product

However, impacts of chemical utilization pathways are significantly higher, especially when expressed per tonne of product. This is primarily a result of the large energy demand associated with hydrogen production and synthesis processes. Mineralization presents relatively modest carbon footprints that reflect both the permanence of CO_2 binding and the comparatively lower process energy requirements.

Figure 5.11 and Figure 5.12 present carbon footprint breakdown within the scopes of GHG emissions for pathways with and without CO_2 conversion.

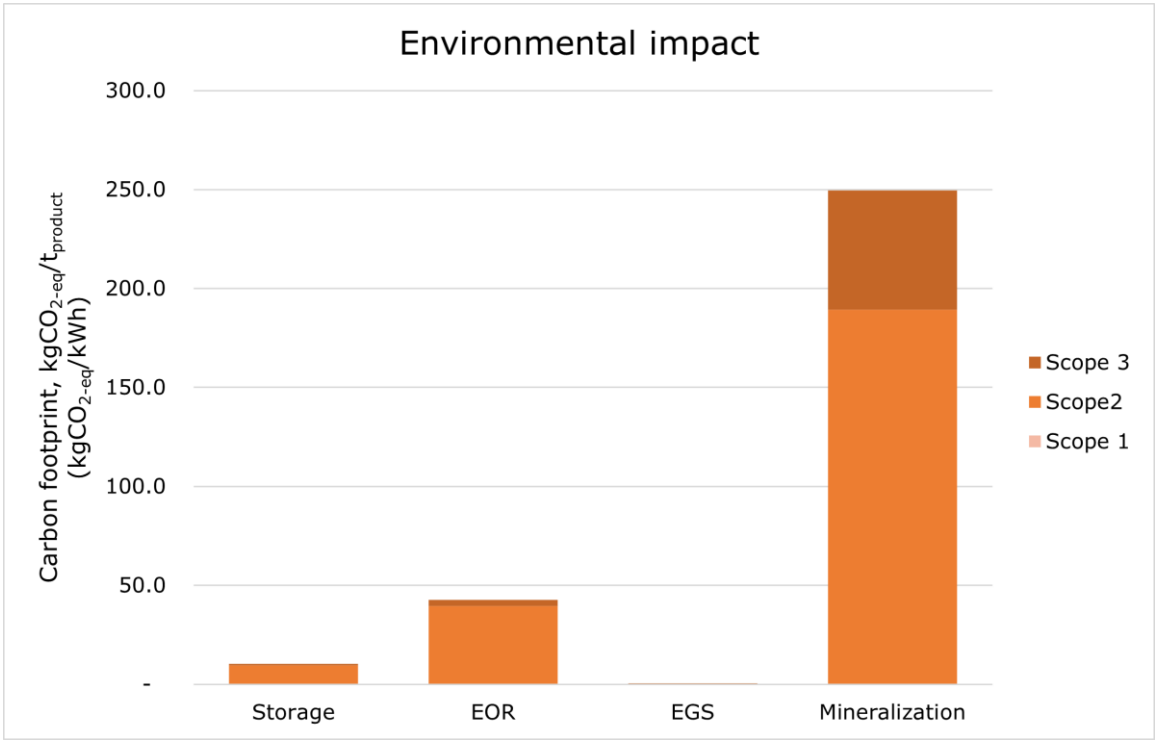

Figure 5.11 Environmental impact of CO_2 storage and CO_2 utilization without conversion.

It should be noted that a carbon footprint expressed per 1 t of product or per 1 kWh of electricity reflects the environmental intensity of the delivered output but is not directly comparable across all CO_2 utilization pathways. In the EGS case, the quantity of CO_2 that can be utilized is constrained by the system's sequestration capacity, which limits the total CO_2 avoided and thus influences output-based indicators derived from that total. By contrast, normalizing impacts per tonne of CO_2 utilized provides a more level basis that is largely independent of system throughput or capacity. On this basis, EGS, as a renewable source, exhibits the lowest CF values.

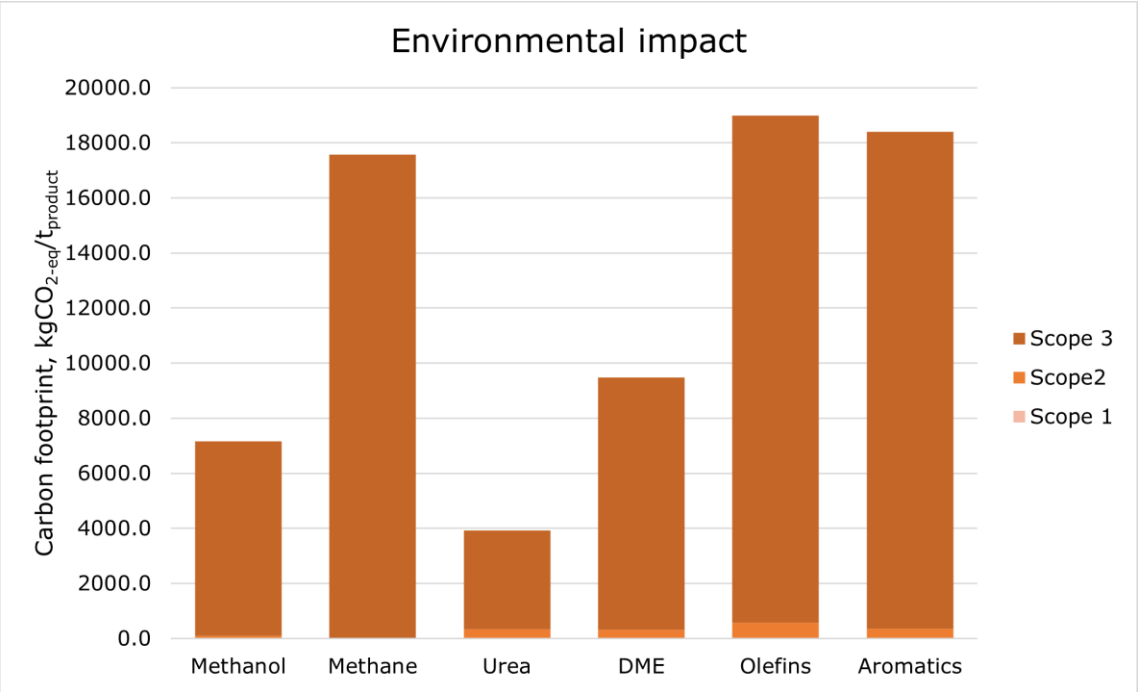

Figure 5.12 Environmental impact of CO_2 utilization with conversion.

Table 5.25 - Table 5.29 present results obtained within the environmental assessment for combined processes and whole CCS or CCU chains with analyzed pathways.

Table 5.25 Results of environmental assessment for CO_2 storage and utilization pathways with CO_2 source from coal-fired power plant.

Case	**Coal-fired power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Unit	CF, $kgCO_{2\text{-eq}}/kg_{CO2,av}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,in}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,av}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,in}$
Storage	309.6	302.1	200.8	168.7
EOR	310.2	304.7	202.3	171.2
EGS	393.3	298.3	264.6	164.8
Methanol	-	5201.9	-	5068.5
Methane	-	6373.2	-	6239.7
Urea	-	5664.4	-	5530.9
DME	-	5207.3	-	5073.8
Olefins	-	5236.2	-	5102.7
Aromatics	-	5266.3	-	5132.8
Mineralization	734.7	541.3	678.6	407.8

Table 5.26 Results of environmental assessment for CO_2 storage and utilization pathways with CO_2 source from natural gas combined cycle.

Case	**NGCC power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Unit	CF, $kgCO_{2\text{-eq}}/kg_{CO2,av}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,in}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,av}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,in}$
Storage	482.3	470.9	250.6	164.9
EOR	481.8	473.5	252.1	167.5
EGS	615.4	467.0	365.5	161.0
Methanol	-	5370.7	-	5064.7
Methane	-	6541.9	-	6235.9
Urea	-	5833.1	-	5527.2
DME	-	5376.0	-	5070.0
Olefins	-	5404.9	-	5098.9
Aromatics	-	5435.1	-	5129.1
Mineralization	963.3	710.0	964.6	404.1

Table 5.27 Results of environmental assessment for CO_2 storage and utilization pathways with CO_2 source from biomass-fired power plant.

Case	**Biomass-fired power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Unit	CF, $kgCO_{2\text{-eq}}/kg_{CO2,av}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,in}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,av}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,in}$
Storage	-480.9	-934.8	-420.4	-1005.6
EOR	-480.9	-934.8	-418.2	-1003.0
EGS	-547.2	-941.2	-464.3	-1009.5
Methanol	-	3962.4	-	3894.2
Methane	-	5133.6	-	3894.2
Urea	-	4424.9	-	4356.7
DME	-	3967.7	-	3899.5
Olefins	-	3996.6	-	3928.4
Aromatics	-	4026.8	-	3958.6
Mineralization	-411.2	-698.2	-356.1	-766.4

Table 5.28 Results of environmental assessment for CO_2 storage and utilization pathways with CO_2 source from cement plant.

Case	**Cement plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Unit	CF, $kgCO_{2\text{-eq}}/kg_{CO2,av}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,in}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,av}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,in}$
Storage	287.4	274.8	93.7	83.2
EOR	288.2	277.4	96.0	85.7
EGS	366.7	271.0	118.4	79.3
Methanol	-	5174.6	-	4982.9
Methane	-	6345.8	-	6154.2
Urea	-	5637.1	-	5445.4
DME	-	5179.9	-	4988.3
Olefins	-	5208.8	-	5017.2
Aromatics	-	5239.0	-	5047.3
Mineralization	716.8	514.0	497.5	322.3

Table 5.29 Results of environmental assessment for CO_2 storage and utilization pathways with CO_2 source from atmosphere.

Case	**DAC**	
Capture method	**Solid sorbent**	
Unit	CF, $kgCO_{2\text{-eq}}/kg_{CO2,av}$	CF, $kgCO_{2\text{-eq}}/kg_{CO2,in}$
Storage	-	-30.3
EOR	-	-27.7
EGS	-	-34.2
Methanol	-	4869.5
Methane	-	6040.7
Urea	-	5331.9
DME	-	4874.8
Olefins	-	4903.7
Aromatics	-	4933.9
Mineralization	-	208.8

As noted earlier, adopting system expansion credits the analysis with the life-cycle emissions of the conventional product that is displaced. Under this accounting, the apparent CO_2 avoidance increases because the emissions that would otherwise arise from producing the substituted product are avoided. For the cement-plant case study, the system-expanded results are reported in Table

5.30. Nevertheless, even with system expansion, the CO_2-conversion pathways evaluated do not achieve net CO_2 avoidance, meaning they remain net-emitting.

Table 5.30 Results of environmental assessment for CO_2 storage and utilization pathways with CO_2 source from cement plant, system expansion scenario.

Case	**Cement plant**	
Capture method	**MEA**	**CaL**
Unit	CF, $kgCO_{2\text{-}eq}$/ $kg_{CO2,av}$	CF, $kgCO_{2\text{-}eq}$/ $kg_{CO2,av}$
Storage	n/a	n/a
EOR	278.8	92.6
EGS	0.4	0.1
Methanol	-	-
Methane	-	-
Urea	-	-
DME	-	-
Olefins	-	-
Aromatics	-	-
Mineralization	292.5	191.0

5.4 Sensitivity analysis

Due to the inherent uncertainty and time-place dependency of some assumptions, the sensitivities of the economic key performance indicators to the following factors are evaluated by performing a parameter variation within the indicated ranges:

- CAPEX for CO_2 capture technologies: +50/-50% of base case estimates,
- electricity price is +/- 50% of the reference cost,
- biomass price is +/- 50% of the reference cost,
- CO_2 transportation cost is +/- 50% of the reference cost,
- Hydrogen price is +/- 50% of the reference cost.

Furthermore, two case studies are conducted to investigate the influence of the electricity mix on SPECCA, CEC, economic factors, and environmental impacts as well as carbon footprint differences when non-sustainable biomass is used. In latter one, the emissions resulting from biomass combustion are not treated neutrally and taken into account.

5.4.1 Parameter variation

In this section, parameter variation was applied to evaluate how the change in capital expenditures as well as prices of key energy and material supplies influence the total cost of capture and storage, or utilization. The assessment

was evaluated for three cases, storage in saline formations (Figure 5.13), CO_2 utilization without conversion in enhanced geothermal systems (Figure 5.14), and CO_2 utilization with conversion into methanol (Figure 5.15). In the latter one, the hydrogen price change was also assessed to examine its impact on economic viability as presented in Figure 5.16.

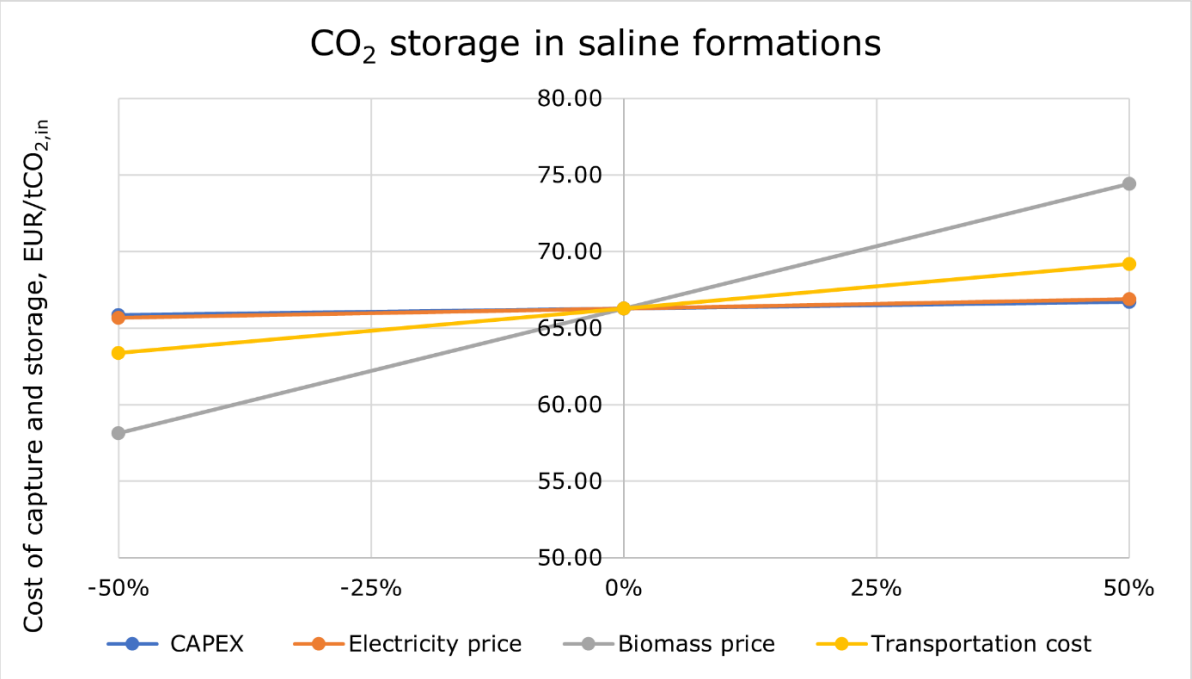

Figure 5.13 Parameter variation evaluation for CO_2 storage in saline formation.

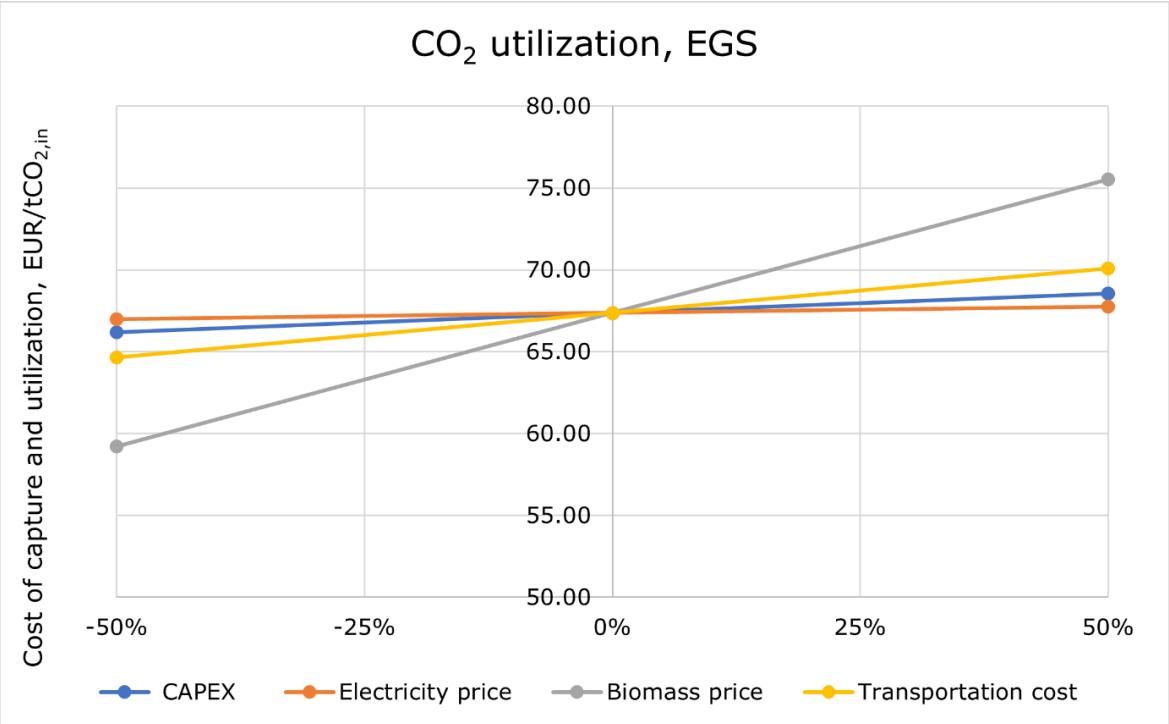

Figure 5.14 Parameter variation evaluation for CO_2 utilization in EGS.

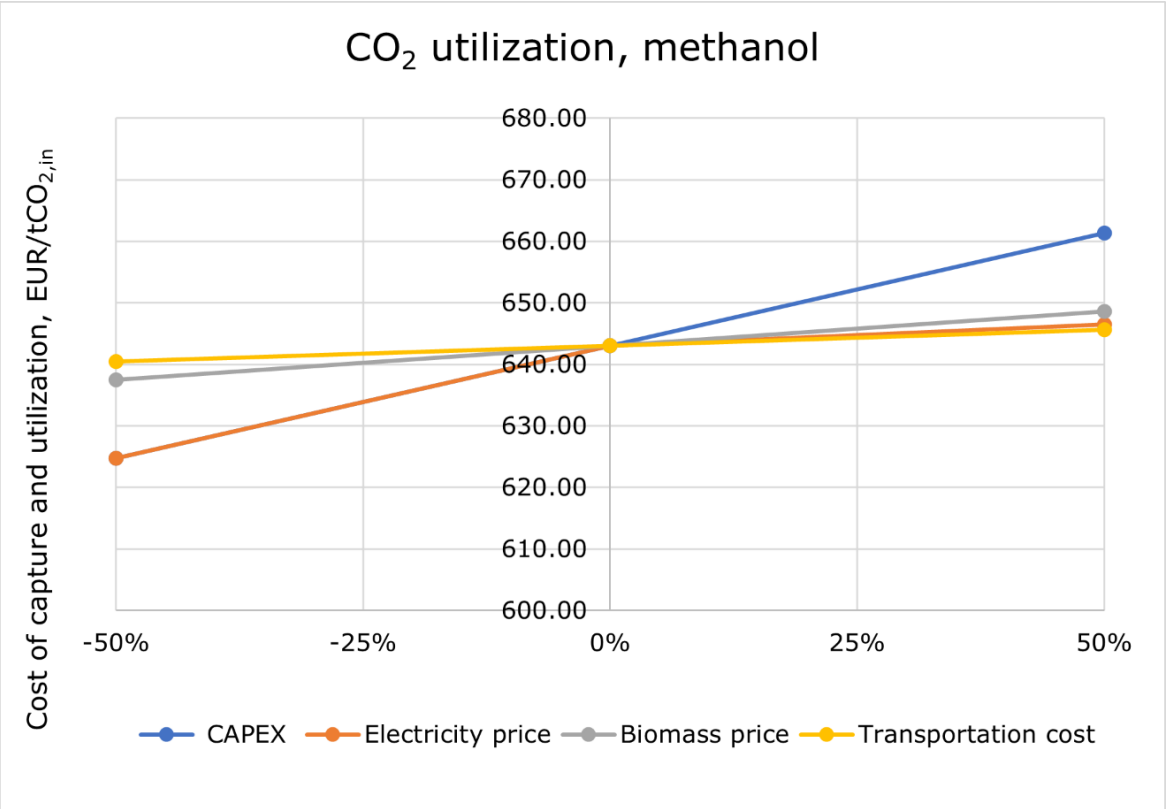

Figure 5.15 Parameter variation evaluation for CO_2 utilization in methanol production.

Based on the results obtained, it is visible that investment cost plays the most influential role in determining the cost of the carbon management pathway in each case. The price of biomass is also impactful in case of total costs, while electricity and transportation costs remain on a similar level.

In addition to CAPEX, electricity, biomass and transportation prices variation, for the methanol case, the change in hydrogen price was also assessed. A 50% change in the price of hydrogen results in an increase or decrease of over 50% in the total utilization costs, which means that this parameter determines the overall profitability of such a solution.

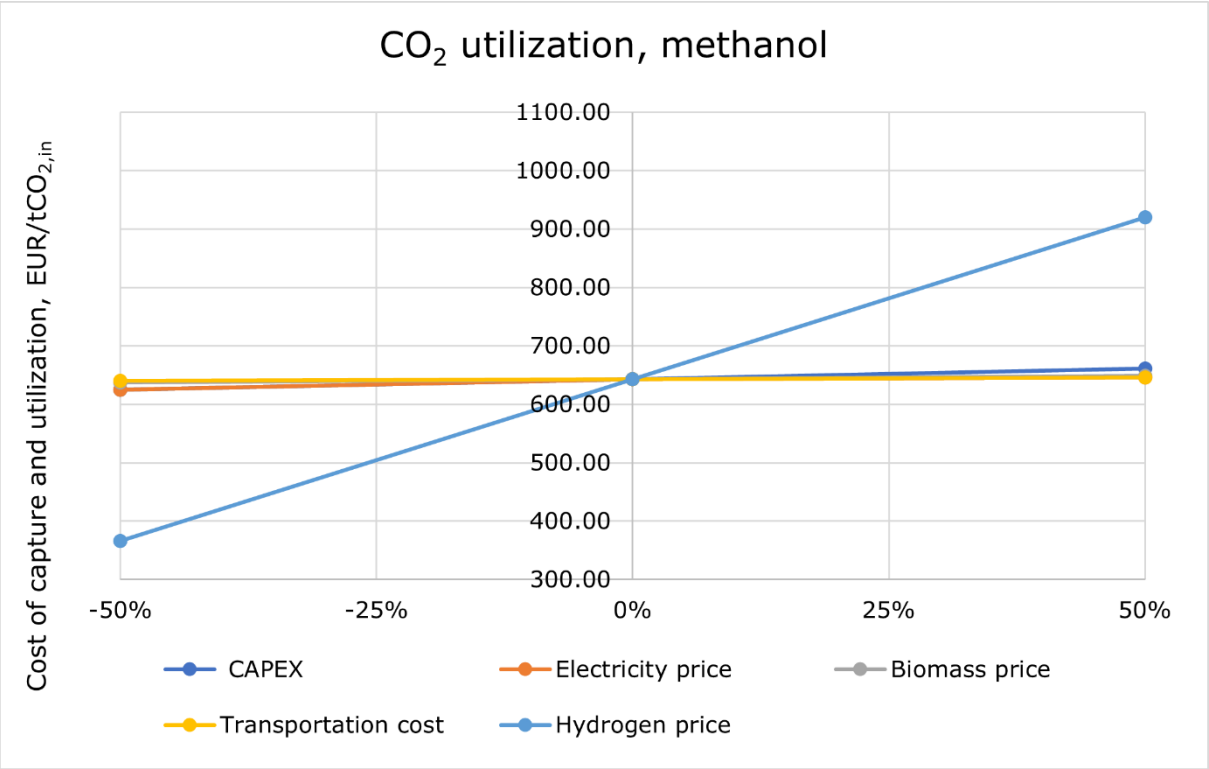

Figure 5.16 Parameter variation evaluation for CO_2 utilization in methanol production, incl. hydrogen price change.

5.4.2 Low-carbon electricity supply case study

The characteristics of the power generation system in terms of electricity generation efficiency and the specific CO_2 emissions of the energy mix have an impact on the SPECCA, CEC, and the cost of CO_2 avoided as well as carbon footprint. Generation efficiency and specific CO_2 emissions are directly linked to the power generation technology that is assumed to provide the electricity required by the processes. In reference scenario, current, polish electricity mix was assumed, while in sensitivity analysis, low-carbon electricity supply constitutes basis for the assessment. Low-carbon electricity values were based on Swedish electricity mix from EcoInvent database. Moreover, hydrogen generation through electrolysis is highly dependent on electricity supply, therefore, its environmental impact factors were also changed to align with low-carbon scenario. The values assumed for this scenario are summarized in Table 5.31.

Table 5.31 Key assumptions for sensitivity analysis performance.

Parameter	**Unit**	**Value**
Emission factor for electricity production	kg $CO_{2\text{-eq}}$/MWh	41.50
Emission factor for hydrogen (electrolysis)	kg $CO_{2\text{-eq}}$/kg	3.38
Cumulative energy consumption for electricity generation	MJ*/MJ	2.36

In this scenario, the amount of CO_2 avoided does not change in power generation cases, because electricity requirements for the capture process are covered internally. In the cement plant, SPECCA value decreases by approximately 15% for both capture methods compared to base scenario, which is visible in Figure 5.17. In terms of DAC, the avoidance effect is more visible, but obtained results highlight substantial dependence on electricity supply with SPECCA values above 13 MJ/kg$CO_{2,av}$.

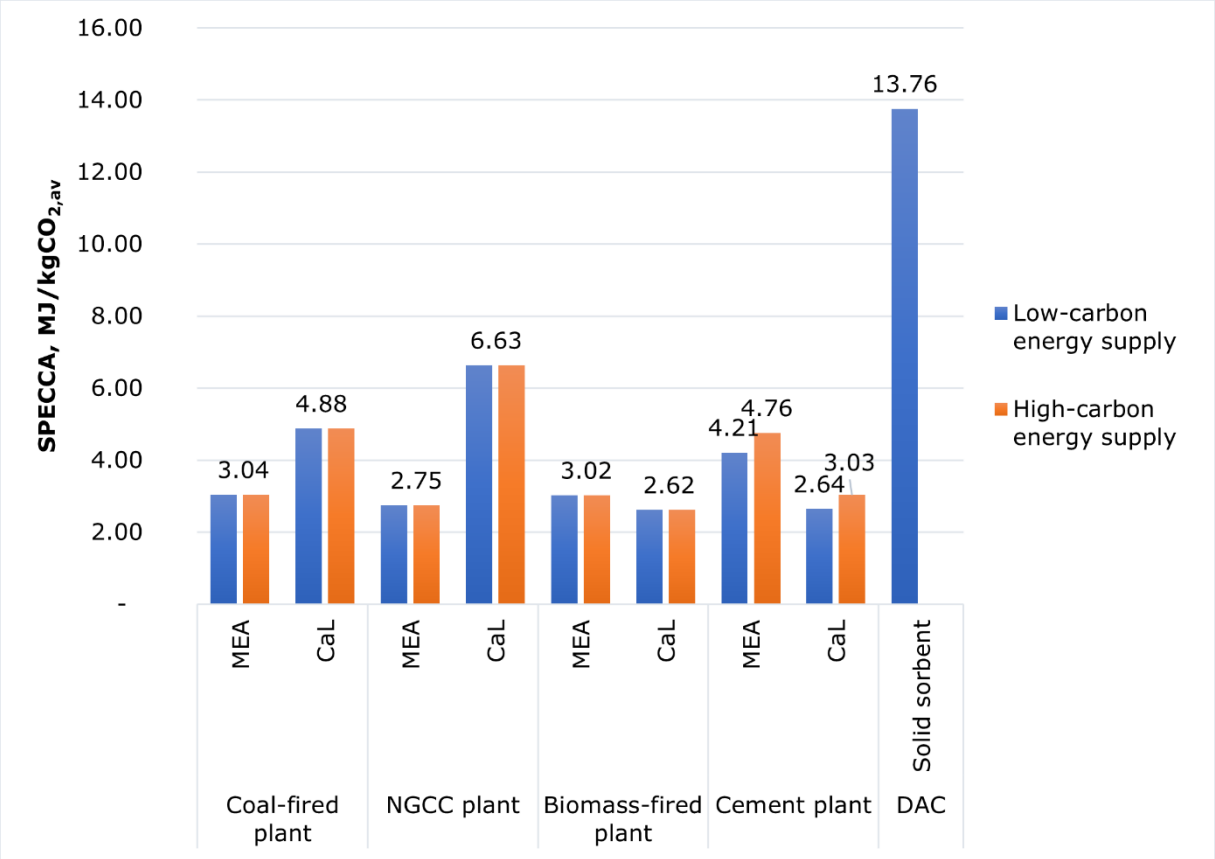

Figure 5.17 Comparison of SPECCA values for analyzed CO_2 sources (excl. DAC for high-carbon case, 113.73 MJ/kg$CO_{2,av}$).

The cumulative energy demand associated with electricity generation is not a fixed value because it is strongly dependent on the composition of the power generation mix. In fossil-fuel-based systems, the CED per kilowatt-hour is relatively high, since a large amount of primary energy must be consumed to produce a unit of final electricity, with overall conversion efficiencies in power plants typically between 30 and 45%. In contrast, electricity from renewable sources such as wind and solar has a much lower CED, because no continuous input of fossil fuels is required and the primary energy demand is mainly attributed to the construction, materials, and maintenance of the installations. Nuclear power also exhibits relatively low CED values, as the fuel requirements are modest compared to the large output of electricity, although mining and enrichment of uranium are taken into account. Consequently, as the grid mix becomes "greener" through the increasing share of renewables and nuclear

power and the declining role of fossil fuels, the CED of electricity decreases, reflecting the lower consumption of primary energy resources per unit of delivered electricity. Therefore, in this scenario cumulative energy consumption factor for Swedish electricity mix was also assumed with value of 2.36 MJ*/MJ. This impacts results of CEC analysis, which are presented in Figure 5.18.

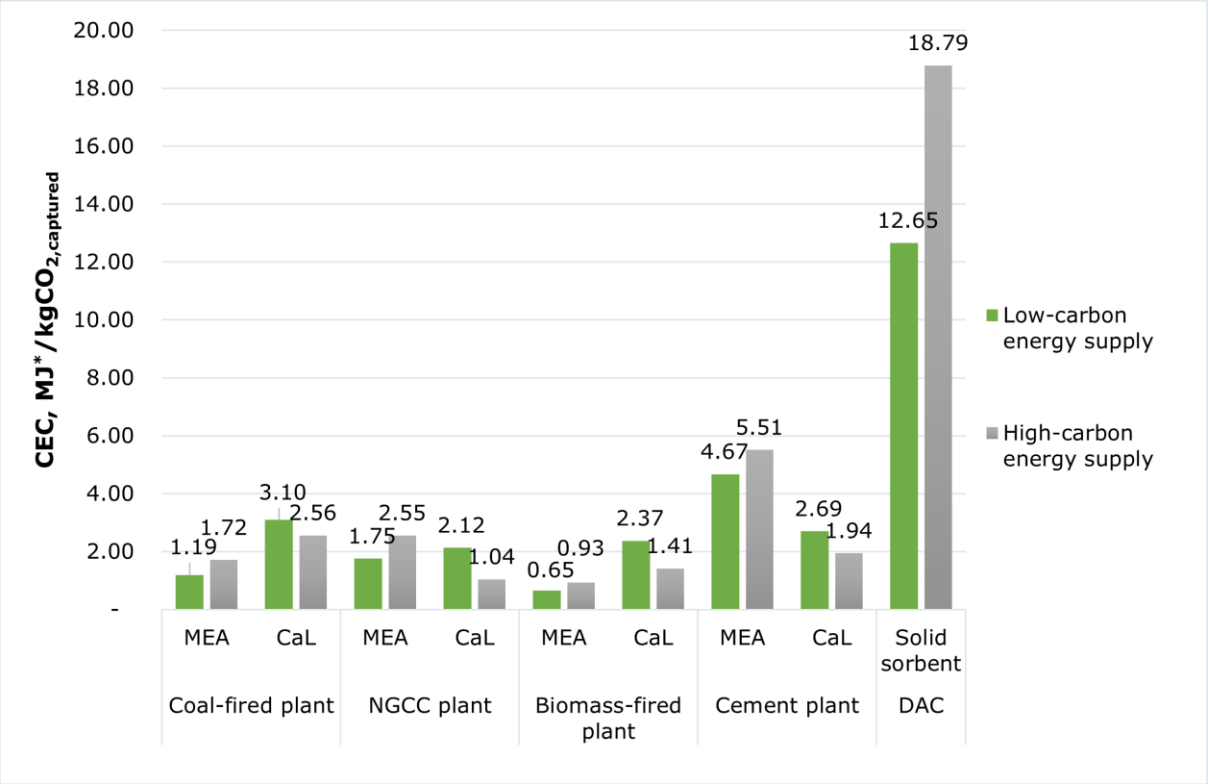

Figure 5.18 Comparison of CEC values for analyzed CO_2 sources.

In all MEA and solid sorbent DAC cases, CEC values decrease within assessed second scenario. Nevertheless, in calcium-looping cases, CEC values are higher than in the reference scenario. This is because in CaL integrated with a cement kiln or power plant, the process generates additional high-temperature heat that can drive a steam cycle and produce electricity. This was assumed as selling excess electricity to the grid, the flows are counted within the system boundary. Thus, although electricity generation does not change, the related cumulative energy consumption decreases, increasing the total CEC value.

In Table 5.32 and Table 5.33 economic and environmental results for the low-carbon electricity supply scenario are presented for each technology assesses within a coal-fired power plant and DAC.

Table 5.32 Sensitivity analysis results of economic evaluation for CO_2 storage and utilization pathways with CO_2 source from coal-fired power plant.

Case	**Coal-fired power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Parameter	CAC	COU/COS	CAC	COU/COS
Unit	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$	EUR/$tCO_{2,in}$	EUR/$tCO_{2,in}$
Storage	57.92	57.08	57.95	49.25
EOR	62.82	61.90	62.25	52.88
EGS	58.89	58.05	61.21	52.03
Methanol	1244.00	619.45	1670.59	605.08
Methane	1767.82	709.67	2632.98	699.53
Urea	1579.52	684.88	2263.16	674.06
DME	1166.91	604.87	1555.80	595.24
Olefins	1247.49	620.00	1680.47	607.05
Aromatics	1427.61	694.38	1735.55	608.54
Mineralization	120.32	111.50	133.37	105.49

Table 5.33 Sensitivity analysis results of economic evaluation for CO_2 storage and utilization pathways with CO_2 source from atmosphere.

Case	**DAC**	
Capture method	**Solid sorbent**	
Parameter	CAC	COU/COS
Unit	EUR/$tCO_{2,av}$	EUR/$tCO_{2,in}$
Storage	298.67	277.67
EOR	300.61	279.42
EGS	299.63	278.64
Methanol	1935.75	855.88
Methane	2593.96	896.56
Urea	2330.64	880.50
DME	1789.49	827.72
Olefins	2113.86	932.61
Aromatics	2039.71	878.27
Mineralization	376.37	327.79

In all cases, the effect of low-carbon electricity supply is present, especially in conversion routes such as methanol, methane, DME, and olefins exhibit avoidance effect. The results underscore the high costs per tonne of CO_2.

In terms of environmental assessment, each case indicates a significant decrease in emissions in Scope 2, which is noticeable in Figure 5.19. Scope 3 becomes dominant in fossil-based power plants. BECCS and DAC cases point out obtained negative emissions which corresponds to negative carbon footprint values.

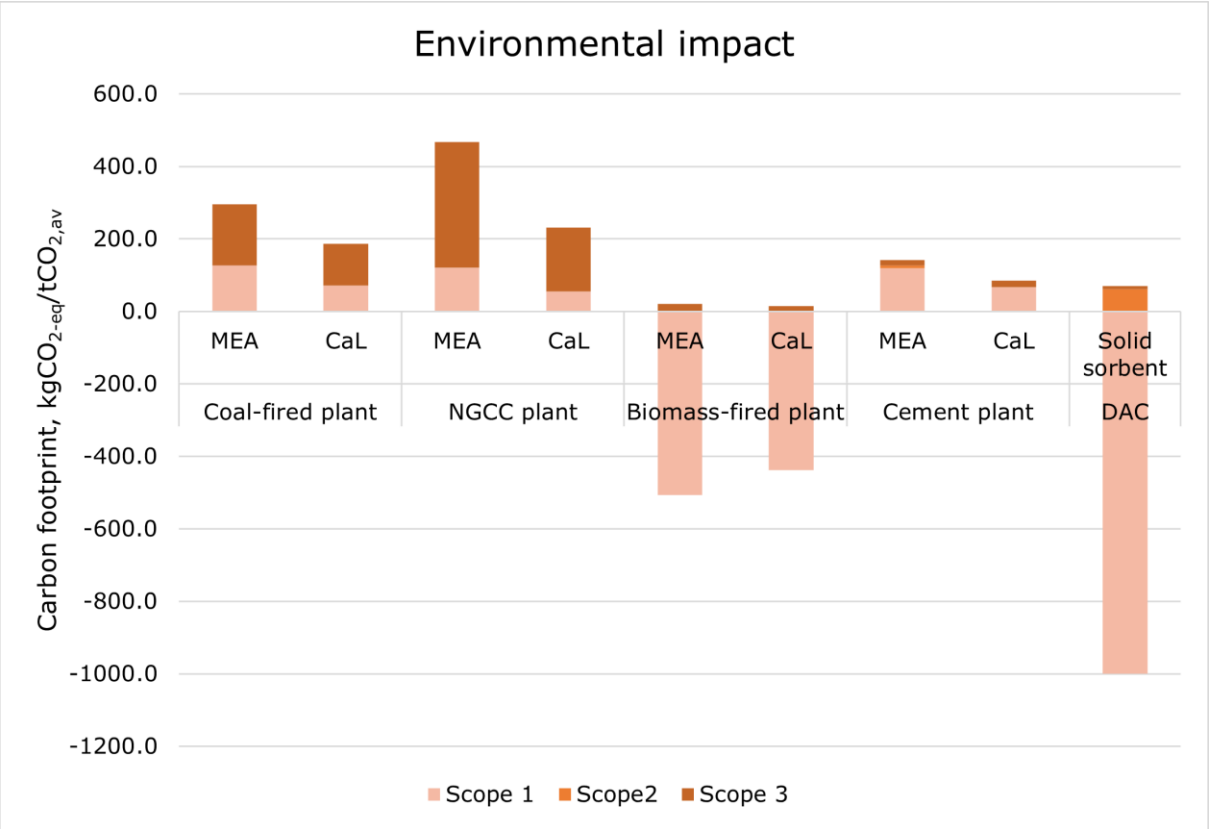

Figure 5.19 Environmental impact for analyzed cases in low-carbon electricity scenario.

Table 5.34 Results of environmental assessment for CO_2 storage and utilization pathways with CO_2 source from coal-fired power plant, low-carbon electricity scenario.

Case	**Coal-fired power plant with CCS/CCU**			
Capture method	**MEA**		**CaL**	
Unit	CF, $kgCO_{2\text{-}eq}/kg_{CO2,av}$	CF, $kgCO_{2\text{-}eq}/kg_{CO2,in}$	CF, $kgCO_{2\text{-}eq}/kg_{CO2,av}$	CF, $kgCO_{2\text{-}eq}/kg_{CO2,in}$
Storage	296.9	292.6	187.2	159.1
EOR	296.9	292.7	187.3	159.3
EGS	301.2	292.3	190.3	158.8
Methanol	1196.9	780.1	1253.1	646.6
Methane	1118.3	876.6	1146.6	743.1
Urea	3684.2	844.5	7608.0	711.0
DME	1021.4	759.7	1029.9	626.2
Olefins	909.5	781.1	895.6	647.6
Aromatics	930.1	791.7	920.1	658.2
Mineralization	379.1	351.3	275.4	217.9

In case of DAC, all pathways show CO_2 avoided values that influence total carbon footprint values below zero.

Table 5.35 Results of environmental assessment for CO_2 storage and utilization pathways with CO_2 source from atmosphere, low-carbon electricity scenario.

Case	**DAC**	
Capture method	**Solid sorbent**	
Unit	CF, $kgCO_{2\text{-}eq}$/ $kg_{CO2,av}$	CF, $kgCO_{2\text{-}eq}$/ $kg_{CO2,in}$
Storage	-1000.0	-929.7
EOR	-3310.0	-929.5
EGS	-28.3	-930.0
Methanol	-1460.0	-442.1
Methane	-2890.0	-345.6
Urea	-730.0	-377.8
DME	-1930.0	-462.5
Olefins	-3840.0	-441.2
Aromatics	-3700.0	-430.6
Mineralization	-1000.0	-870.9

5.4.3 Non-sustainable biomass supply case study

Sustainability is crucial aspect in the carbon footprint of biomass energy in industrial systems. The climate benefit of bioenergy hinges on sustainable land use and feedstock sourcing practices that avoid deforestation and preserve carbon-rich ecosystems. If biomass is harvested in ways that diminish forest carbon stocks or involve high land-use change emissions, the resulting "carbon debt" can negate or even outweigh the emissions savings from replacing fossil fuels. Recognizing this variability, regulators and industry have instituted sustainability criteria and certification schemes to ensure genuine climate performance. Jurisdictions like the EU and UK require that biomass fuels meet strict sustainability standards, feedstocks must not come from high-biodiversity or high-carbon lands, and life-cycle GHG emissions must fall below set thresholds to guarantee significant emissions reductions compared to fossil benchmarks. Therefore, for sensitivity analysis, a case with emissions stemming from biomass combustion is also assessed to examine how they influence overall system performance.

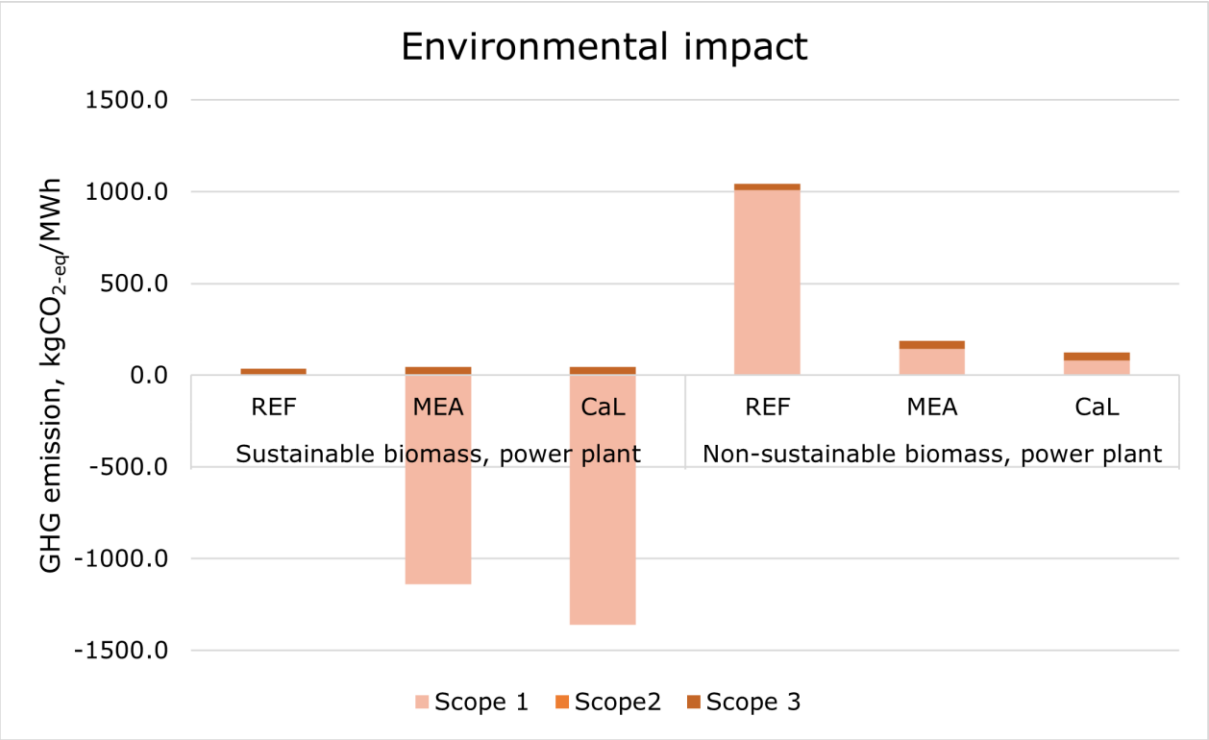

Figure 5.20 Carbon footprint comparison between the use of sustainable and non-sustainable biomass feedstock.

In Figure 5.20 it is visible that without sustainable biomass supply, industrial bioenergy systems do not deliver net carbon benefits. Obtained results are similar to fossil-based cases, with carbon footprint values of 189 $kgCO_{2\text{-}eq}$/MWh for MEA and 123 $kgCO_{2\text{-}eq}$/MWh for CaL. Thus, it is essential to underline that only sustainably sourced biomass can meet climate neutrality goals and serve as an effective mitigation tool.

6. Summary

This chapter re-examine the research goals and hypotheses formulated in the introduction and evaluates how they have been addressed in the course of the study. The following sections summarize the key findings and provide the final conclusions.

The aim of this dissertation is to develop an integrated methodology for assessing captured CO_2 management pathways, contrasting utilization and geological storage, under Polish conditions. This objective has been successfully achieved by establishing and applying the proposed methodology, allowing for a comprehensive comparison of different pathways. The approach combines process modelling with techno-economic assessment and life-cycle assessment, applied to representative CO_2 sources and two capture technologies: amine absorption and calcium looping. The main finding is that, in Poland, the most stable and cost-effective emission reductions can be achieved through CCS chains based on high-concentration sources (e.g. cement plant) and further process integration, while CCU pathways become climatically competitive only when powered by low-carbon energy and when products substitute carbon-intensive counterparts with sufficient permanence. The study covers capture (MEA and CaL), conditioning and compression, transport by pipeline, storage in saline aquifers or selected CCU pathways including variants with and without CO_2 conversion.

a) Research hypotheses:

- CCUS technologies are bridging solutions in the energy transition, essential for hard-to-abate sectors in Poland, with large-scale deployment foreseen by 2030–2050 in line with EU Fit-for-55 and ETS trajectories.
- The effectiveness of CCUS depends critically on the choice of CO_2 destination:
  - geological storage provides secure and permanent abatement,
  - utilization pathways are climatically competitive only when based on low-carbon energy and when products substitute carbon-intensive counterparts with sufficient permanence.
- Comparative evaluation requires the integration of life cycle assessment with techno-economic analysis, ensuring consistency in functional units, system boundaries and performance indicators.
- National deployment of CCUS must guarantee scalability, cost-effectiveness, and system-level benefits, without shifting emissions or costs to other sectors.

The scope of this research encompassed several complementary steps that were gradually undertaken and brought together in a consistent framework.

- Identification and classification of CO_2 sources relevant for Poland were identified and classified, including fossil fuel combustion, bioenergy units, industrial processes, direct air capture.

- CO_2 storage and utilization technologies were selected according to technological maturity, feasibility, and potential role in the Polish economy.
- Methodological guidelines were established, defining system boundaries, functional units, allocation rules, and construction of life cycle inventories for selected technologies.
- Comparative environmental and economic assessment of capture, storage and utilization pathways, integrating LCA with TEA was performed.
- Scenario analyses within sensitivity analyses supported the results in order to identify the most influential technical and economic factors affecting system performance.
- The results were interpreted in the context of Polish conditions, including scalability, viability, and benchmarking against international references.

The expected contribution of this research lies in providing practical guidelines for assessing and selecting CO_2 storage and utilization pathways under national conditions. In doing so, it helps to address methodological gaps in the combined environmental and economic evaluation of CCUS chains. At the same time, the study delivers new knowledge on sustainable carbon management by highlighting pathways that offer the most favorable balance between environmental performance and economic feasibility, and that could be viably implemented within Poland's decarbonization strategy.

6.1 SWOT analysis

In following Table 6.1, Table 6.2, Table 6.3 SWOT analysis is presented for CO_2 storage and CO_2 conversion pathways with and without its conversion.

a) CO_2 storage in saline formations

Table 6.1 SWOT analysis for CO_2 storage in saline formations.

Strengths: – The highest potential in CO_2 reduction doe to permanent sequestration; – High technological readiness level, many commercial projects around the world; – Regulatory incentives in EU ETS, captured and stored CO_2 reduces verified emissions; – Relatively low unit costs compare to other CO_2 management pathways.	**Weaknesses**: – Lack of direct product stemming from CO_2 usage; – Social risks associated with public perception of CO_2 storage – The need to build transport and injection infrastructure, which involves obtaining the necessary consents and meeting the requirements in this regard; – The necessity of transport and sites monitoring.

Opportunities: – EU regulatory support; – Opportunities to create industrial joint clusters; – Development of cross-border CO_2 networks.	**Threats**: - Low public acceptance of underground, onshore storage; – Uncertainty regarding long-term costs and liability for monitoring or possible leakages; – Risk of dependence on cross-border infrastructure and the policies of neighbors.

b) CO_2 utilization with conversion

Table 6.2 SWOT analysis for CO_2 utilization with conversion.

Strengths: – Creating valuable products which give market revenue potential; – Possibility of partial decarbonization of transportation sector (by deploying CO_2-based synthetic fuels); – Synergy with RES and green hydrogen production via Power-to-X.	**Weaknesses**: – Very high unit costs; – High electricity and hydrogen requirements; – Permanent sequestration durability is low (CO_2 is usually released during product use phase); – Dependence on electricity and hydrogen prices which results in strong economic sensitivity.
Opportunities: – Development of the e-fuels market in transport sector, especially SAF; – Possibility of substituting fossil-based chemicals; – Potential subsidies for new products.	**Threats**: – Market competition with cheaper fossil fuels and biofuels; – Lack of sustainable emission reduction due to short life cycle of energy products.

c) CO_2 utilization without conversion

Table 6.3 SWOT analysis for CO_2 utilization without conversion.

Strengths: – High sequestration durability, especially in mineralization processes, partial permanent storage via EOR and EGS – Potential additional revenues – Possibility of utilizing existing infrastructure.	**Weaknesses**: – Limited scale for mineralization and dependency on geological sites for EOR and EGS; – Lack of mass market for mineralization products – Lower net climate effect in EOR due to additional emissions from oil combustion.
Opportunities: – Local markets creation; – Support for EOR as CCUS demonstration method; – Development of sustainability certification for mineralized materials.	**Threats**: – Logistical and environmental barriers for large-scale deployment; – Low acceptance for EOR projects in the EU.

6.2 Conclusions and remarks

This chapter summarizes the key findings derived from the conducted analyses of selected CO_2 utilization and storage technologies within the CCUS chain, considering various CO_2 sources. The conclusions are structured around three main perspectives: energy performance, economic feasibility, and environmental impact.

a) Conclusions from energy assessment:

- Power generation cases:
  - Amine absorption (MEA) consistently exhibits lower auxiliary power demand and lower overall electricity requirements compared to calcium looping.
  - The CaL process, despite higher gross output in some configurations, characterizes with substantial penalties mainly due to higher compression and air separation units electrical demands, leading to net efficiency reductions up to 15 percentage points.
  - Biomass-fired plant with CO_2 capture achieve relatively favorable avoidance-specific energy consumption, indicating potential synergy between biogenic feed and CCS in negative-emission strategies.
- Cement plant case:
  - Both MEA and CaL show lower specific primary energy consumption compared to earlier CEMCAP benchmarks, primarily due to biomass integration.

  - CaL demonstrates a clear energy advantage over MEA in this sector, with lower SPECCA and CEC values, largely because of additional electricity generation within the process.
  - The cement sector therefore emerges as one of the most promising contexts for CaL deployment, also with potential integration with clinker production process.
- Direct air capture:
  - DAC shows an order-of-magnitude higher energy requirement compared to point-source capture, dominated by electricity demand for heat requirements covered by heat pumps.
  - Under the assumed Polish electricity mix, DAC configurations do not deliver avoided emissions or only to a limited extend, highlighting the dependency of DAC viability on access to abundant low-carbon power.
- Storage vs. utilization pathways:
  - Geological storage consistently represents the lowest additional energy demand per tonne of CO_2 managed across all sources.
  - Enhanced oil recovery can lead to net reductions in cumulative energy consumption under system expansion assumptions, as produced oil substitutes conventional extraction.
  - Mineralization provides moderate additional energy demand and high permanence, representing a balanced though not highly efficient option.
  - Synthetic fuel and chemicals production routes (methanol, methane, DME, urea, olefins, aromatics) are highly energy intensive due to hydrogen requirements, often offsetting any avoidance effect under current boundary conditions.

CCS pathways have generally lower and more predictable energy costs, but CCU pathways can only achieve favorable balances under certain situations (low-carbon electricity, replacement of high-emission products, or co-benefits such as electricity generation).

From a systemic standpoint, deployment priority should align with high-concentration sources (cement, biomass plants) with the best capture efficiency and mild energy penalties.

b) Conclusions from economic evaluation:

- Capital intensity:
  - Coal- and natural gas-based power plants require the highest overall capital expenditures, reflecting large-scale capacity and complex capture unit integration.
  - Biomass plants, cement plants, and DAC units are associated with lower total investments, primarily due to smaller flue gas streams or assumed capture scales.

  - Calcium looping demonstrates higher initial CAPEX than MEA absorption, driven by the need for large, high-temperature reactors, air separation units, and additional steam cycle integration.
- Cost of capture and avoidance:
  - CaL achieves lower capture costs per tonne of CO_2 captured compared to MEA, due to larger mass flowrates of captured CO_2 (including calciner flue gas streams). However, when expressed as cost of CO_2 avoided, MEA often performs comparably or better, as efficiency penalties are smaller.
  - Capture from point sources with high CO_2 concentrations (coal and cement) is more economically favorable than from low-concentration sources (NGCC, DAC).
  - Biomass-fired cases display particularly low avoidance costs in some scenarios, underlining the advantages of potential negative emissions.
  - DAC pathways are by far the most expensive, with CAC and COS values an order of magnitude higher than for point-source capture, underscoring their reliance on abundant, low-cost, low-carbon electricity to become viable.
  - Geological storage and enhanced geothermal systems show moderate avoidance costs, positioning them as the most straightforward and scalable options under Polish conditions.
  - Enhanced oil recovery and mineralization may result in negative CAC values, as system expansion credits (from oil sales or mineral products) offset capture costs. While these results appear favorable, they are sensitive to boundary assumptions and market factors.
  - Conversion pathways to fuels and chemicals are consistently associated with very high utilization costs, driven by hydrogen and electricity demand. Even when revenues are considered, these technologies remain significantly more expensive than geological storage.

c) Conclusions from environmental impact assessment

- Fossil-based power generation:
  - Both MEA and CaL substantially reduce direct (Scope 1) emissions compared to reference plants.
  - CaL generally achieves lower residual footprints per unit of electricity generated and per tonne of CO_2 avoided, reflecting the potential of covering electricity needs through new steam cycle as well as lower emissions related to upstream supplies.
  - Avoided-emission effectiveness is greater in coal plants (due to higher flue gas CO_2 content) than in NGCC, confirming the advantage of targeting high-concentration sources.
- Biomass-fired power plants:
  - When combined with capture, biomass systems deliver strong net-negative emissions, with Scope 1 values falling well below zero.

  - Both MEA and CaL achieve negative carbon footprints per unit of production and per tonne of CO_2 avoided. CaL provides slightly stronger avoidance potential.
- Cement plants:
  - CO_2 capture reduces emissions by approximately 90% relative to the reference plant, with total footprints dropping to approx. 165 $kgCO_{2\text{-}eq}/t_{clk}$ (MEA) and 130 $kgCO_{2\text{-}eq}/t_{clk}$ (CaL).
  - CaL achieves lower intensities per tonne avoided (81 vs. 274 $kgCO_{2\text{-}eq}/tCO_{2,av}$), reflecting the benefits of process integration.
  - Scope 2 emissions increase for MEA (due to electricity demand), but are negligible in CaL, further improving its performance profile.
- Direct air capture (DAC):
  - DAC achieves gross CO_2 removal (Scope 1 strongly negative), but high electricity demand results in very large Scope 2 emissions when powered by the Polish grid mix.
  - Net footprints remain slightly negative (-41 $kgCO_{2\text{-}eq}/tCO_{2,captured}$), showing that DAC is not effective without abundant low-carbon electricity.
  - This confirms DAC as a long-term option dependent on deep decarbonization of the power sector.
- Storage vs. utilization pathways:
  - Geological storage (saline formations) consistently provides the lowest life-cycle impacts (around 10 $kgCO_{2\text{-}eq}/tCO_{2,in}$), reflecting only injection and monitoring requirements.
  - EOR and EGS deliver similar footprints per tonne of CO_2 managed, but EGS offers particularly favorable results when expressed per unit of electricity produced.
  - Mineralization yields moderate footprints, balancing permanence with manageable energy inputs.
  - Chemical conversion pathways are associated with extremely high life-cycle impacts, largely due to hydrogen production and energy-intensive synthesis. These pathways do not achieve avoided emissions and are environmentally unfavorable under current conditions.

At the system level, CCS emerges as the most predictable, scalable, and cost-effective pathway for Poland through 2050, delivering robust benefits across energy, economic, and environmental dimensions. The most promising opportunities are found in high-concentration sources such as cement and biomass, which provide the most favorable balance of efficiency, cost, and environmental performance. Within these, BECCS stands out as the strongest candidate for carbon dioxide removal under Polish conditions. By comparison, DAC and chemical conversion-based CCU should be considered as complementary or long-term options, contingent upon deep decarbonization of the electricity mix. Table 6.4 summarizes findings of the study, while Figure 6.1 and Figure 6.2 provide graphs showing the key factors of assessed technologies

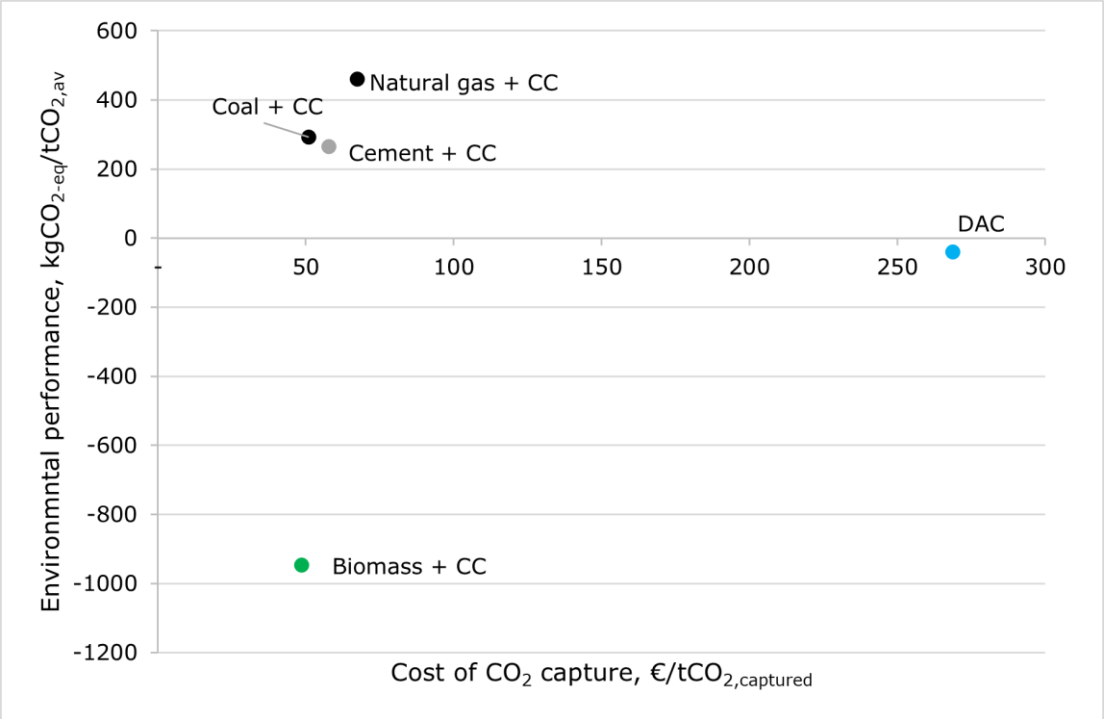

Figure 6.1 Comparison between assessed carbon capture variants.

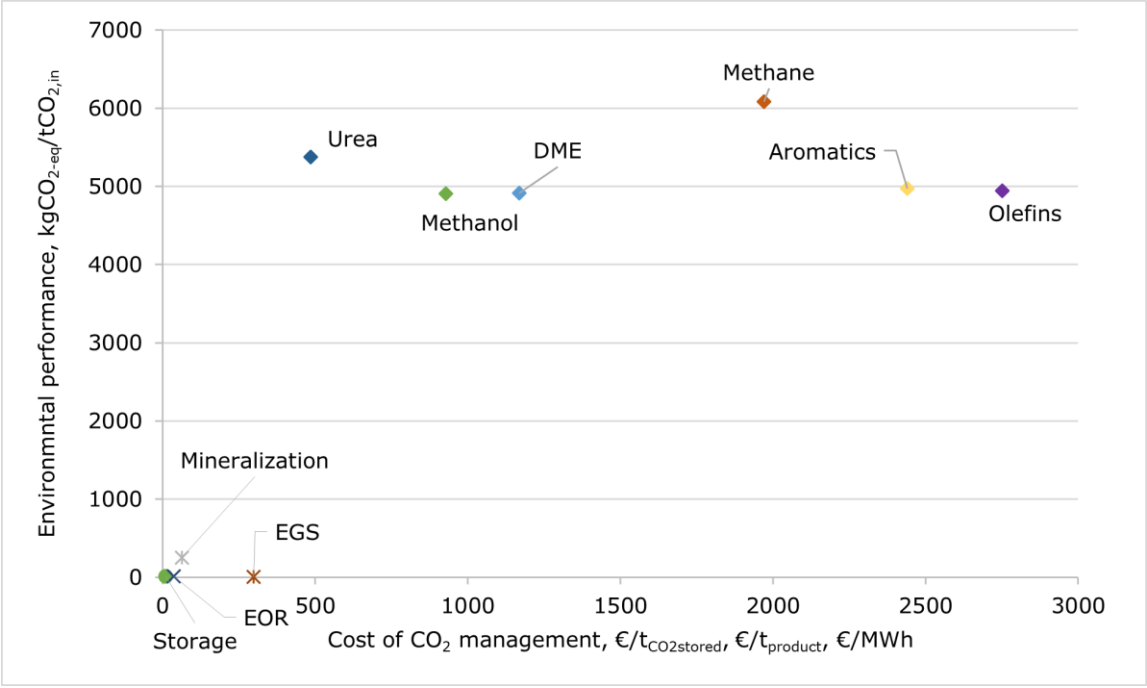

Figure 6.2 Comparison between assessed carbon management variants.

Table 6.4 Summary of the assessment.

Sector/ Pathway	Energy performance	Economic performance	Environmental performance	Overall assessment
Coal-fired power plant with CC	Moderate electrical efficiency penalty (8 to 12 %points); CaL higher energy demand than MEA	CAC ~50–175 €/$tCO_{2,av}$; moderate costs; storage most viable	CF ~190–300 $kgCO_{2\text{-}eq}/tCO_{2,av}$; large absolute reductions	Feasible but less attractive than cement/biomass; best with storage
NGCC with CC	Significant electrical efficiency penalty; MEA more efficient than CaL	CAC ~70–230 €/$tCO_{2,av}$; relatively high due to low CO_2 concentration	CF ~230-470 $kgCO_{2\text{-}eq}/tCO_{2,av}$	Limited near-term attractiveness; less favorable economics
Biomass-fired power plant with CC	Moderate penalty; CaL yields higher capture mass flowrates	Very low CAC of 22–63 €/$tCO_{2,av}$)	Net-negative carbon footprint (–400 to –500 $kgCO_{2\text{-}eq}/tCO_{2,av}$)	Strong CDR option; highly strategic for Poland
Cement plant with CC	CaL highly efficient, lower SPECCA values; ~90% emission reduction	CAC ~60–160 €/$tCO_{2,av}$ (CaL lower than MEA)	CF ~80–270 $kgCO_{2\text{-}eq}/tCO_{2,av}$; 90% emission reduction	Best sector for CaL; highly favorable energy balance
Direct Air Capture	Very high electricity demand (approx. 10 $MJ/kgCO_2$)	>270 €/$tCO_{2,av}$; currently prohibitive	Net-positive carbon footprint on fossil grid; negative avoidance	Long-term option; dependent on abundant low-carbon electricity
Geological storage	Lowest energy demand	COS ~50-60 €/$tCO_{2,in}$	CF ~10 $kgCO_{2\text{-}eq}/tCO_{2,in}$	Backbone of CCS deployment

EOR	Moderate energy use	COU ~50-70 €/$tCO_{2,in}$; Possible negative CAC due to oil revenues	CF ~13 $kgCO_{2\text{-}eq}/tCO_{2,in}$; sensitive to assumptions	Attractive only with stable oil market and system expansion
EGS	Moderate energy use; adds power output	Moderate CAC	CF <10 $kgCO_{2\text{-}eq}/tCO_{2,in}$; comparable to some RES	Promising niche with co-benefit of renewable energy
Mineralization	Moderate energy demand	Low to negative CAC depending on products	CF ~250 $kgCO_{2\text{-}eq}/tCO_{2,in}$	Balanced option: permanent storage, moderate costs
CO_2-based chemicals	Very high electricity demand and hydrogen requirements	COS >600 €/$tCO_{2,in}$; uncompetitive;	CF >4000 $kgCO_{2\text{-}eq}/tCO_{2,in}$	Environmentally and economically unfavorable today

Building on the current thesis, future research should extend CCUS applications beyond the cement and power industries to other major CO_2-emitting sectors. In heavy industrial processes such as steel production, chemicals manufacturing, and waste-to-energy incineration, CCUS provides a crucial solution to mitigate process-related CO_2 emissions that alternative measures, such as fuel switching or electrification, cannot easily eliminate. These sectors collectively account for a significant share of global CO_2 output and thus CCUS is essential for achieving deep emissions cuts in these "hard-to-abate" industries. Addressing these diverse sectors in future CCUS research will involve tailoring capture technologies to different flue gas conditions and may explore integrated industrial clusters where multiple co-located facilities share CO_2 transport and storage infrastructure.

Another important direction is to evaluate and analyze next-generation CO_2 capture technologies beyond the conventional amine-based absorption or calcium-looping methods used within the thesis. Membrane separation, chemical looping, and high-temperature solid sorbent adsorption have each shown promise in reducing energy penalties and expanding CCUS applicability. Each of these emerging technologies brings distinct advantages. For instance, membranes eliminate solvent handling and can be modular, while looping processes can drastically reduce the energy penalty by integrating with the host process. Future work should include comparative assessment of these methods under realistic conditions to determine their performance and cost relative to benchmark amine scrubbing. To support the development of new capture technologies and their deployment in various industries, future research should employ advanced, dynamic process modelling tools to simulate the performance of capture units and their integration with reference unit. This allows to evaluate, for instance, how fluctuations in a power plant's load might impact CO_2 capture efficiency and what buffering or storage capacity is needed to handle intermittent operation. Future work should incorporate dynamic simulation and control strategy development as well, ensuring that integrated CCUS systems can respond to transient operating conditions.

Looking beyond individual technologies and plants, future CCUS research should also address the strategic deployment of capture, utilization, and storage on a regional scale. Scenario analysis could entail constructing a set of plausible future scenarios including varying future carbon prices, energy costs, technology advancements, and policy support by evaluating CCUS deployment in each case. Simulating these scenarios can show how sensitive CCUS outcomes are to key uncertainties like fuel prices or regulatory incentives. It also enables the exploration of how significant reductions in renewable electricity costs could influence the competitiveness of direct air capture, as well as how different CO_2 utilization markets, such as synthetic fuel production or concrete curing, may shape future demand for captured CO_2.

Finally, a comprehensive research plan should adopt a broader EU-wide perspective on CCUS deployment, taking into account the diverse energy mixes,

infrastructure readiness levels, and policy frameworks across European countries. The existing thesis work can be expanded by contextualizing its findings within the wider European perspective and varying national circumstances. The differences between member states influence where CCUS would be most impactful and what form it should take. Therefore, future research should evaluate CCUS deployment strategies under a range of European scenarios, examining, for example, how a country with a renewables-dominated grid might use CCUS primarily for industrial process emissions and negative emissions (e.g. through BECCS), whereas a country with fossil-dependent power might focus on retrofitting gas or coal plants with capture to meet climate targets.

By evaluating CCUS options in an EU-wide context, including identification of optimal deployment pathways can also help to foresee and address Europe-specific challenges, such as public acceptance issues in different countries or the need for harmonized standards for CO_2 quality and measurement. In summary, broadening the research ensures that the proposed future CCUS solutions are applicable under particular energy and industrial landscape. Integrating this perspective into the research plan will make the conclusions and recommendations of the work more robust and relevant to CCUS deployment in the coming decades.

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Appendix A

This appendix presents detailed description of calcium-looping model which was built based on IECM Technical Documentation [155] and adapted in gPROMS Process as presented in Figure A.1.

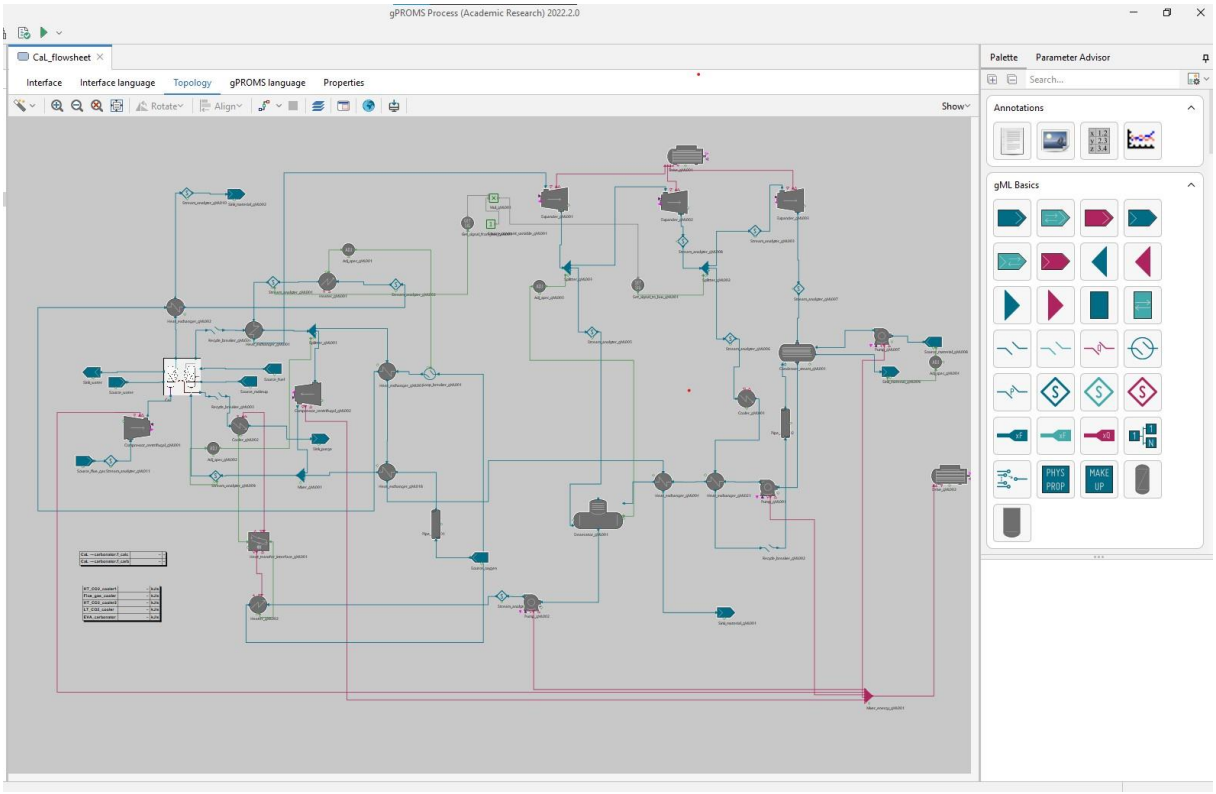

Figure A.1 Calcium-looping model flowsheet in gPROMS Process.

Process environment to develop calcium-looping process model from the first principles. All calculations shown are based on molar flowrates.

The stream entering the carbonator comprises CaO, uncalcined $CaCO_3$, sorbent impurities from limestone stream together with $CaSO_4$ and ash.

Initially, SO_2 reacts with CaO resulting in less amount of CaO available for the carbonation process. Consequently, the amount of CaO available can be expressed as:

$$F_{CaO,1,available} = F_{CaO,1} - F_{SO_2,fg} \tag{A.1}$$

Since one mole of CaO reacts with one mole of CO_2 to form one mole of $CaCO_3$, the amount of $CaCO_3$ formed in the carbonator is equal to the amount of CO_2 captured. Thus, the $CaCO_3$ formed can be obtained using following equation:

$$F_{CaCO_3,formed} = E_{CO_2} \cdot F_{CO_2,fg} = X_{carb}\left(F_{CaO,1} - F_{SO_2,fg}\right) \tag{A.2}$$

X_{carb} describes the fraction of CaO converted to $CaCO_3$ in the carbonator, therefore, the amount of CaO in the carbonator inlet can be rewritten as:

$$F_{CaO,1} = \frac{E_{CO_2} \cdot F_{CO_2,fg}}{X_{carb}} + F_{SO_2,fg} \quad \text{(A.3)}$$

X_{calc} is defined as the fraction of $CaCO_3$ in the solids inlet flow and can be expressed as follows:

$$F_{CaCO_3,1} = \frac{X_{calc}}{1 - X_{calc}} F_{CaO,1} \quad \text{(A.4)}$$

Consecutively, the formulas A.5-A.7 can be used to determine the makeup streams in the calciner such as total makeup flowrate, $CaCO_3$ in the makeup flowrate and the flowrate of the impurities in limestone (inert).

$$F_{CaCO_3,m} = f_m\left(F_{CaO,1} + F_{CaCO_3,1}\right) \quad \text{(A.5)}$$

$$F_{sorbent,m} = \frac{1}{a_{sorbent}} F_{CaCO_3,m} \quad \text{(A.6)}$$

$$F_{inert,m} = F_{sorbent,m} - F_{CaCO_3,m} \quad \text{(A.7)}$$

Therefore $CaSO_4$, inert and ash flowrate in the carbonator inlet can be calculated using expressions A.8-A.10.

$$F_{CaSO_4,1} = \frac{F_{CaO,1}}{1 - X_{calc}} \frac{F_{SO_2,fg}}{F_{CaCO_3,m} - F_{SO_2,fg}} \quad \text{(A.8)}$$

$$F_{inert,1} = \frac{F_{CaO,1}}{1 - X_{calc}} \frac{F_{inert,m}}{F_{CaCO_3,m} - F_{SO_2,fg}} \quad \text{(A.9)}$$

$$F_{ash,1} = \frac{F_{CaO,1}}{1 - X_{calc}} \frac{F_{ash,oxy}}{F_{CaCO_3,m} - F_{SO_2,fg}} \quad \text{(A.10)}$$

In the top of the carbonator, gases released from process are vented to the atmosphere. This is the CO_2-depleted stream containing gaseous products which flowrates from the carbonator can be described using following formulas:

$$F_{CO_2,pg} = \left(1 - E_{CO_2}\right) F_{CO_2,fg} \quad \text{(A.11)}$$

$$F_{O_2,pg} = F_{O_2,fg} - F_{SO_2,fg} \quad \text{(A.12)}$$

$$F_{i,pg} = F_{i,fg} \quad \text{(A.13)}$$

The solids stream leaving the carbonator is the stream entering the calciner.

$$F_{CaCO_3,2} = F_{CaCO_3,1} + F_{CaCO_3,formed} \quad \text{(A.14)}$$

$$F_{CaO,2} = F_{CaO,1} - F_{CaCO_3,formed} - F_{SO_2,fg} \quad \text{(A.15)}$$

$$F_{i,pg} = F_{i,fg} \tag{A.16}$$

Since one mole of SO_2 forms one mole of $CaSO_4$, the calculation of $CaSO_4$ in the carbonator outlet takes into account the $CaSO_4$ inlet flow and the amount of SO_2 in the flue gas:

$$F_{CaSO_4,2} = F_{CaSO_4,1} + F_{SO_2,fg} \tag{A.17}$$

The amount of inert and ash do not change during the process.

$$F_{inert,2} = F_{inert,1} \tag{A.18}$$

$$F_{ash,2} = F_{ash,1} \tag{A.19}$$

The amount of $CaCO_3$ calcined can be estimated as a difference between the sum of $CaCO_3$ in the calciner, which is the amount from the carbonator, and the amount in make-up and $CaCO_3$ in the calciner outlet.

$$F_{CaCO_3,calcined} = F_{CaCO_3,2} + F_{CaCO_3,m} - F_{CaCO_3,3} \tag{A.20}$$

Assuming that there is no SO_2 in oxy-stream, the CaO formed in the calciner can be expressed as:

$$F_{CaO,3} = F_{CaO,2} + F_{CaCO_3,calcined} \tag{A.21}$$

From the X_{calc} definition the amount of $CaCO_3$ left can be written as:

$$F_{CaCO_3,3} = \frac{X_{calc}}{1 - X_{calc}} F_{CaO,3} \tag{A.22}$$

Based on this equation, the CaO amount can be rewritten.

$$F_{CaO,3} = F_{CaO,1} + (1 - X_{calc})\left(F_{CaCO_3,m} - F_{SO_2,fg}\right) \tag{A.23}$$

Assuming no SO_2 in ox-stream, the amount of $CaSO_4$ will not change.

$$F_{CaSO_4,3} = F_{CaSO_4,2} \tag{A.24}$$

Finally, the remaining components can be calculated as:

$$F_{inert,3} = F_{inert,2} + F_{inert,m} \tag{A.25}$$

$$F_{ash,3} = F_{ash,2} + F_{ash,oxy} \tag{A.26}$$

The heat needed for the calcination process is provided by oxy-combustion of fuel, thus:

$$Q_{calc} = \dot{m}_{fuel} \cdot LHV_{fuel} \cdot \eta_{comb} \tag{A.27}$$

Mass flowrate of a given fuel depend on component inlet molar flowrate F_i, molecular weight MW_i and weight fraction w_i.

$$\dot{m}_{fuel} = F_i \left(\frac{MW_i}{w_i}\right) \tag{A.28}$$

The following reactions take place in calciner:

$$CaCO_3 \leftrightarrow CaO + CO_2 \tag{A.29}$$

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \tag{A.30}$$

The combustion process depends on a type of fuel supplied to the system. Therefore, the equations should be adjusted in terms of:
a) solid fuel:

$$C + O_2 \rightarrow CO_2 \tag{A.31}$$

$$S + O_2 \rightarrow SO_2 \tag{A.32}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{A.33}$$

The amount of O_2 from the oxy-stream required:

$$F_{O2,in} = \lambda(F_{C,in} + F_{S,in} + \frac{1}{2}F_{H2,in}) \tag{A.34}$$

where λ is the excess air coefficient.

b) gaseous fuels:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{A.35}$$

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 \rightarrow nCO_2 + \left(\frac{m}{2}\right)H_2O \tag{A.36}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{A.37}$$

$$S + O_2 \rightarrow SO_2 \tag{A.38}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{A.39}$$

The amount of oxygen required is expressed as:

$$F_{O2,in} = \lambda\left[\frac{1}{2}\left(F_{H2,in} + F_{CO,in}\right) + 2F_{CH4,in} + \left(n + \frac{m}{4}\right)F_{CnHm,in}\right] \tag{A.40}$$

The gaseous products from the calciner can be calculated using following formulas:
a) for solid fuels:

$$F_{CO_2,out} = F_{CaCO_3,calcined} + F_{C,in} \tag{A.41}$$

$$F_{H_2O,out} = F_{H_2,in} \tag{A.42}$$

$$F_{SO_2,out} = 0 \tag{A.43}$$

$$F_{O_2,out} = F_{O2,in} - \left(F_{C,in} + \frac{3}{2}F_{S,in} + \frac{1}{2}F_{H2,in}\right) \quad \text{(A.44)}$$

b) for gaseous fuels:

$$F_{CO_2,out} = F_{CaCO_3,calcined} + F_{CH4,in} + nF_{CnHm,in} + F_{CO_2,in} \quad \text{(A.45)}$$

$$F_{H_2O,out} = 2F_{CH4,in} + \left(\frac{m}{2}\right)F_{CnHm,in} + F_{H_2,in} \quad \text{(A.46)}$$

$$F_{SO_2,out} = 0 \quad \text{(A.47)}$$

$$F_{Ar,out} = F_{Ar,in} \quad \text{(A.48)}$$

$$F_{O_2,out} = F_{O2,in} - \left[\frac{1}{2}\left(F_{H2,in} + F_{CO,in}\right) + 2F_{CH4,in} + \left(n + \frac{m}{4}\right)F_{CnHm,in}\right] \quad \text{(A.49)}$$

Assuming no NO_x are generated:

$$F_{N_2,out} = F_{N_2,in} \quad \text{(A.50)}$$

Since additional heat is required to raise the temperature of recirculating stream to match the calciner temperature, the recirculation of the gaseous stream back to the calciner should be considered in the system design. Thus, the components flowrates can be written as:

$$F_{CO_2,rec} = \frac{x_{rec}}{1 - x_{rec}}F_{CO_2,out} \quad \text{(A.51)}$$

$$F_{H_2O,rec} = \frac{x_{rec}}{1 - x_{rec}}F_{H_2O,out} \quad \text{(A.52)}$$

$$F_{O_2,rec} = \frac{x_{rec}}{1 - x_{rec}}F_{O_2,out} \quad \text{(A.53)}$$

$$F_{N_2,rec} = \frac{x_{rec}}{1 - x_{rec}}F_{N_2,out} \quad \text{(A.54)}$$

where, x_{rec} describes the fraction of recycled gases.
The purge stream is assumed to be extracted between the calciner outlet and the carbonator inlet, therefore the flowrates can be obtained from the difference between these stages.

$$F_{CaO,P} = F_{CaO,3} - F_{CaO,1} \quad \text{(A.55)}$$

$$F_{CaCO_3,P} = F_{CaCO_3,3} - F_{CaCO_3,1} \quad \text{(A.56)}$$

$$F_{CaSO_4,P} = F_{CaSO_4,3} - F_{CaSO_4,1} \quad \text{(A.57)}$$

$$F_{inert,P} = F_{inert,m} \quad \text{(A.58)}$$

$$F_{ash,P} = F_{ash,3} - F_{ash,1} = F_{ash,oxy} \quad \text{(A.59)}$$

Both, ash and sulphur present in the system are taken out in purge stream.

Since all of the mass balances are provided the heat requirement in the calciner can be expressed using formula A.60.

$$\begin{aligned} Q_{calc} = {} & F_{CaCO_3,calcined}\Delta H_{carb} \\ & + \left(F_{CaO,2}C_{p,CaO} + \left(F_{CaCO_3,2} + F_{inert,2}\right)C_{p,CaCO_3}\right. \\ & \left. + F_{CaSO_4,2}C_{p,CaSO_4}\right)\Delta T_{calc} + F_{sorbent,m}C_{p,CaCO_3}\Delta T_m \\ & + \sum F_{i,r}C_{p,i}\Delta T_r \end{aligned} \tag{A.60}$$

where:

$$\Delta T_{calc} = T_{calc} - T_{carb} \tag{A.61}$$

$$\Delta T_m = T_{calc} - T_m \tag{A.62}$$

$$\Delta T_r = T_{calc} - T_r \tag{A.63}$$

It can also be obtained from energy balance:

$$\begin{aligned} F_{solids,2} \cdot h_{solids,2} + F_{makeup} \cdot \Delta h_{makeup} + F_{oxy} \cdot \Delta h_{oxy} + F_{rec} \cdot \Delta h_{rec} + F_{fuel} \\ \cdot (\Delta h_{fuel} + LHV) \\ = F_{solids,3} \cdot h_{solids,3} + F_{gas_{out}} \cdot \Delta h_{gas_{out}} + F_{purge} \cdot h_{purge} + Q_{calc} \end{aligned} \tag{A.64}$$

where:

$$Q_{calc} = F_{CaCO_3,calcined}\Delta H_{carb} \tag{A.65}$$

The heat generated in the carbonator can be expressed as:

$$\begin{aligned} Q_{carb} = {} & \left(F_{CO_2,2} - F_{CO_2,fg}\right)H_{f,CO_2} + \left(F_{CaO,2} - F_{CaO,1}\right)H_{f,CaO} \\ & + \left(F_{CaCO_3,2} - F_{CaCO_3,1}\right)H_{f,CaCO_2} \\ & + \left(F_{N_2,fg}C_{pN_2} + F_{O_2,fg}C_{pO_2} + F_{H_2O,fg}C_{pH_2O} + F_{CO_2,fg}C_{pCO_2}\right)(25 \\ & - T_{fg}) \\ & + \left(F_{CaO,1}C_{pCaO} + F_{CaCO_3,1}C_{pCaCO_3} + F_{CaSO_4,1}C_{pCaSO_4}\right. \\ & \left. + F_{ash,1}C_{p,ash}\right)(25 - T_{calc}) \\ & + \left(F_{N_2,2}C_{pN_2} + F_{O_2,2}C_{pO_2} + F_{H_2O,2}C_{pH_2O} + F_{CO_2,2}C_{pCO_2}\right. \\ & + F_{CaO,2}C_{p,CaO} + F_{CaCO_3,2}C_{pCaCO_3} + F_{CaSO_4,2}C_{pCaSO_4} \\ & \left. + F_{ash,2}C_{p,ash}\right)(T_{carb} - 25) \end{aligned} \tag{A.66}$$

The following formulas can be used to determine the temperatures and pressures of the solids streams that are part of the process model:

$$T_1 = T_{calc} = T_3 \tag{A.67}$$

$$T_2 = T_{carb} \tag{A.68}$$

$$p_2 = p_1 - p_{loss,carb} \tag{A.69}$$

$$p_3 = p_2 - p_{loss,calc} \tag{A.70}$$