BABEȘ-BOLYAI UNIVERSITY
Faculty of Chemistry and Chemical Engineering

Environmental impact assessment of energy intensive industrial processes using Life Cycle Assessment methodology

PhD Candidate: Eng. Ștefan Cristian Galusnyak
Supervisor: Prof. PhD Eng. Călin-Cristian Cormoș

Cluj-Napoca - Romania
2024

Summary table of contents

Thesis table of contents

Keywords

Carbon capture and utilization technologies; Cement production; Bio-methanol production; Biodiesel production; High-value chemicals production; Fertilizer manufacture; Life Cycle Assessment; Process modelling and simulation.

1. Introduction

1.1. Motivation and background

Human activity has been altering the environment for thousands of years, yet these effects have been mostly local. Everything changed more than two centuries ago when the Industrial Revolution sparked with the creation of the steam engine by James Watt [1]. However, all the breakthroughs brought by the Industrial Revolution have been echoed by enormous quantities of carbon dioxide (CO_2) and other greenhouse gases (GHGs) emitted into the atmosphere through the burning of fossil fuels [2]. Even though GHGs are crucial for the existence of life on Earth as the greenhouse effect helps maintaining a proper temperature [3], increased concentration levels in the atmosphere result in additional heat being trapped, thus ultimately leading to global warming and climate change [4].

Each of the GHGs presents an individual effect on warming the Earth. The key distinctions by which the effect of GHGs differ from one another consists of their capacity to absorb energy, which is referred to as radiative efficiency, as well as the period spent in the atmosphere, or so called "lifetime". Global Warming Potential (GWP) serves as a metric that enables comparisons between various GHGs in terms of the effects they have on global warming. To align with the regulations set by the Intergovernmental Panel on Climate Change (IPCC), CO_2 was set as the reference gas thus the GWP score is assigned to 1 regardless of the time period. Table 1.1-1 presents various data related to the main anthropogenic GHGs.

Table 1.1-1. Primary anthropogenic GHGs [5]

GHG	Lifetime in the atmosphere	GWP – 100 years' time frame	Share of total anthropogenic emissions
CO_2	From 200 years up to tens of thousands of years	1	73.11
CH_4 fossil origin	11.8 years	29.8	17.74
CH_4 non fossil origin		27.2	
N_2O	109 years	273	6.58
Fluorinated compounds	From months up to tens of thousands of years	CF_4: 7380 SF_6: 25200	2.57

Carbon dioxide is by far the most significant anthropogenic GHG, with emissions hitting an unprecedented level of 410 parts per million (ppm) in 2019, compared to the 280-ppm registered in the 19th century. In addition, CO_2 accounts for roughly 73% of overall human caused emissions. In 2019, CH_4 and N_2O emissions were 1866 and 332 parts per billion (ppb), respectively. Moreover, based on currently available data, even greater concentrations of the aforementioned GHGs (i.e., 415 ppm CO_2, 1896 ppb CH_4, and 335 ppb N_2O) were recorded in 2021. If considerable worldwide initiatives to diminish CO_2 emissions are not adopted, the IPCC forecasts an increase in global surface temperature of 1.5°C to 4°C during the course of the next century. The majority of the CO_2 emissions are caused by the burning of fossil fuels and industrial operations.

According to the International Energy Agency (IEA), although power generation released 1.3% fewer CO_2 emissions in 2019, it continued to remain the leading contributor, accounting for 41% of global CO_2 emissions with coal as the most commonly used source (i.e., 29%), followed by natural gas (i.e., 9%) and oil (i.e., 2%) [6]. In addition to the GHG emissions that result from thermal and power generation, significant volumes of CO_2 emissions are released as well from the industrial sector. As reported by the IEA, the industrial sector accounts for approximately 37% of total energy consumption in 2022. The sustained rise in production in large energy industrial processes consumers (i.e., iron and steel, cement, pulp and paper, etc.) has been a major factor in the increase in power consumption during the last 10 years [7]. Moreover, in 2022, industry was responsible for 9.0 Gt of CO_2 emissions, thus accounting for almost one-quarter of total GHG releases [7]. The majority of the GHG are directly related to the on-site fossil fuel burning necessary for the power generation. Nevertheless, additional CO_2 emissions occur either as a by-product of the main production process or as a result of chemical transformations that may took place and cannot be mitigated (i.e., mineral decomposition, metallurgical processes, etc.) [8]

In the last 5 years, the iron and steel sector's CO_2 emission intensity has been reasonably consistent, ranging from 1.43 to roughly 1.41 t CO_2 per t of steel. However, in order to meet the targets outlined in the Net-Zero Emissions (NZE) by 2050 Scenario, emission intensity must decrease to 0.7 t CO_2 per t of steel. When it comes to the cement sector, the key problem is lowering GHG emissions while satisfying worldwide demand [7]. As in the case of the iron and steel sector, the direct CO_2 emission intensity of cement manufacturing remained essentially stable over the previous five years, 0.58 t CO_2 per t of cement, and is anticipated to have climbed by 1% in 2022. To achieve the NZE by 2050 Scenario, the CO_2 intensity needs to decrease by 4% every year until 2030, hence is essential to increase energy and material efficiency, adopt renewable energy sources (RESs), substitute clinker with such-other materials and develop new manufacturing methods with almost no emissions [7]. The integration of Carbon Capture and Storage (CCS) systems within cement plants is also considered and this strategy is seen as the best medium-term alternative towards GHG mitigation [9].

During 1990 to 2022, the average yearly growth rate of transportation emissions was 1.7%, which was higher than that of any different sector with the exception of industry, which increased as well at a rate of

1.7%. According to IEA, in 2022, transportation-related GHG emissions increased by 3% (with over 250 Mt of CO_2) over those of 2021 as a result of the resurgence in passenger and freight transport activities following the COVID-19 pandemic. In spite of a projected increase in demand, transportation emissions would need to drop by nearly 25% to close to 6 Gt by 2030 in order to meet the goals of the NZE Scenario [7].

Therefore, for the purpose of preventing new CO_2 emission peaks and stop the ever-increasing GHG releases, it is essential to decarbonize both industry and transportation in addition to the heat and electricity production sector [10]. Several measures such as higher material and energy efficiency, much quicker transition to renewable power sources, as well as much quicker integration of Carbon Capture Utilization and Storage (CCUS) technologies within the production process are required for the industrial sector to curb GHG emission and get on track with the NZE Scenario [7]. In CCUS, CO_2 is usually captured from large stationary sources such for example power plants or industrial processes. CCS entails the transportation of CO_2 to a storage location before it is injected into geologic structures for long-term preservation, whereas Carbon Capture and Utilization (CCU) refers to the use of captured CO_2 as raw material in the manufacturing of valuable chemicals or fuels.

Depending on the characteristics of either the power plant or process, the IPCC [11] defines three primary strategies for integrating CCS systems (Figure 1.1-1):

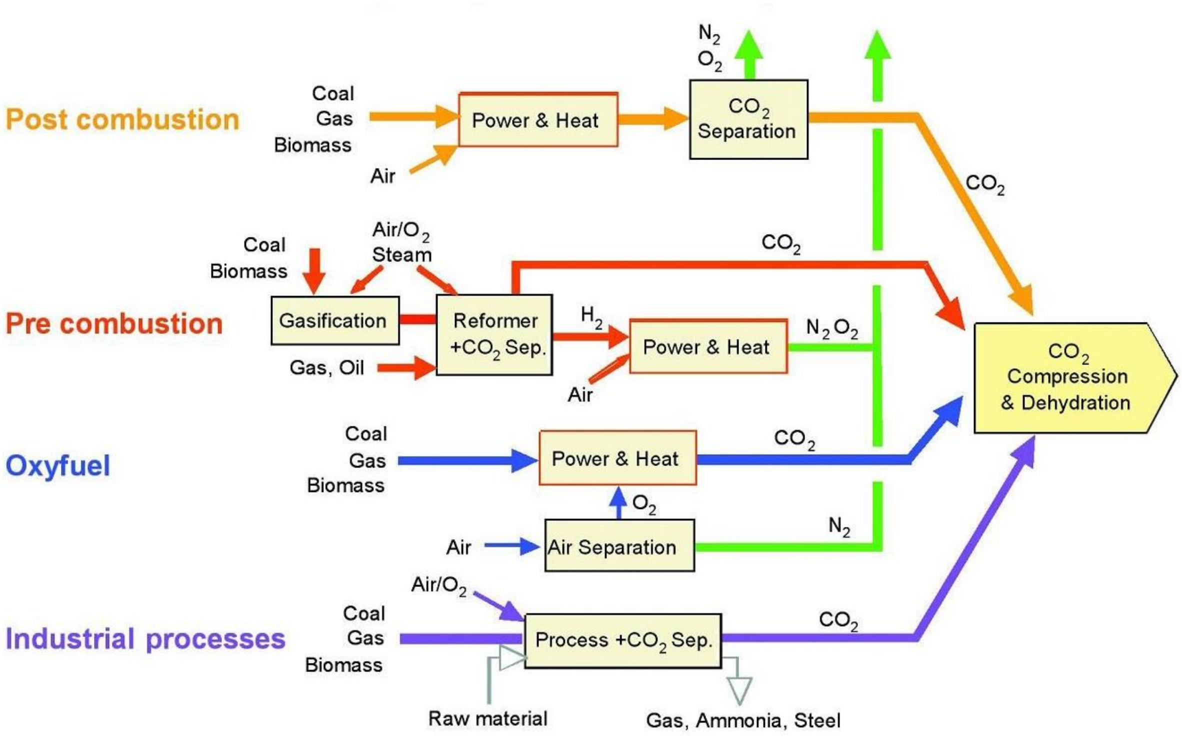


Figure 1.1-1. Overview of CCS configurations [11]

- Post-combustion CO_2 capture systems aim CO_2 separation from the flue gas stream generated by the combustion of fossil fuels in air. Prior to being discharged directly into the environment, the exhaust gases are processed by specific CO_2 removal technology. This type of technology may be used regardless of the type of fuel, however keeping track of impurities is critical in obtaining a cost-effective plant [12].
- Pre-combustion CO_2 capture systems separate the CO_2 from fuel before to its combustion. Following this approach, the primary fuel is reacted with either steam (Eq. (1.1-1)) or air/O_2 (Eq. (1.1-2)) to generate syngas. The first method entails the addition of steam to the main fuel, thus resulting in a process referred to as Steam Methane Reforming (SMR). The second approach involves adding O_2 to the fuel, resulting in a process described as partial oxidation and gasification when performed on liquid and solid fuels, respectively. Then, the water gas shift (WGS) process is employed to transform the syngas into a mixture of CO_2 and H_2.

$$C_xH_y + xH_2O \rightleftarrows xCO + \left(x + \frac{y}{2}\right)H_2 \tag{1.1-1}$$

$$C_xH_y + \frac{x}{2}O_2 \rightleftarrows xCO + \left(\frac{y}{2}\right)H_2 \tag{1.1-2}$$

- Oxy-fuel combustion CO_2 capture refer to the utilization of a pure O_2 stream instead of using air when performing fuel combustion. The exhaust stream in this design mostly consists of large concentrations of CO_2 and water vapor and, therefore, the CO_2 may be removed by condensing the water vapor. Based on the type of fuel burned, a flow consisting of 80% up to 98% CO_2 is produced [13].

The post-combustion capture approach is seen to be the best strategy for large industrial processes, but the power industry can adopt any of the three CO_2 capture technologies. For each of the aforementioned carbon removal technologies, either chemical or physical methods are employed for CO_2 removal.

1.2. Goals and objectives

The main goal of this thesis is to assess and compare the performance of different configurations (integration of a carbon capture system; evaluation of process integration opportunities; or investigation of different energy scenarios) of high pollutant energy intensive industrial processes with the purpose of identifying possibilities to increase the overall efficiency, while reducing the environmental burden. The following is an overview of the objectives that have been set towards achieving the proposed goals:

1. Comprehensive literature review to emphasize the intent and current status of the research;

2. Process modelling and simulation of different configurations and approaches of energy-intensive industrial processes to achieve better technical performance, as well as to gather mass and energy balance data for further performing the environmental impact evaluation;
3. Heat integration by means of the Pinch method to achieve effective energy and materials integration, while reducing emissions and waste generation;
4. Technical assessment of the identified high pollutant energy-intensive industrial processes and comparison with alternative configurations aiming, on the one hand, to reduce the amount of heat and power, as well the primary materials used, and to increase, on the other hand, the environmental performance;
5. Environmental impact evaluation using the Life Cycle Assessment (LCA) methodology of selected industrial processes and a comparison with various alternative configurations that either include a CO_2 removal system or assess different energy scenarios.

The industrial sector accounts for approximately 37% of total energy consumption in 2022, while emitting around 9.0 Gt of CO_2 (quarter of total releases). Of the total share, cement production sector is responsible for nearly 2.5 Gt CO_2 with an emission intensity relatively stable at about 0.6 t CO_2 per t of cement. In addition, it is estimated that the average thermal power of clinker declined by 0.2% per year from 2010 to 2020 before eventually levelling out at around 3.6 GJ per t of clinker. However, the decline paired with a rise in sector’s electricity intensity ending at 100 kWh per t of cement in 2022. Chemical sector ranks first in terms of energy consumption among other industrial sectors, but it is placed third in terms of direct CO_2 emissions. The main products generated by the chemical and petrochemical sector include ammonia, methanol and valuable chemicals such for example ethylene, propylene, benzene, etc. Due to a slowdown in production, the direct CO_2 emissions of primary chemicals manufacturing were roughly steady at 935 Mt in 2022. The largest contributor to emissions from chemical production is ammonia, which accounts for 45% of total releases. Methanol (28%) and high value chemicals (27%) rank second and third, respectively [7]. Ammonia makes a substantial contribution to the agricultural sector since it serves as the first component of all mineral nitrogen fertilizers (70% of total output used in fertilizer production). Currently, ammonia manufacture makes up to 2% of the world’s final electrical consumption. About 40% of the energy intake is used as feedstock contributing to the H_2 in the final product, while the remaining 60% is mostly utilized to produce heat [14]. According to data presented by the IEA, the direct emissions associated to ammonia manufacturing are estimated to be roughly 450 Mt CO_2, which is very similar to the total CO_2 emissions of South Africa’s energy system. Moreover, ammonia produces close to 2.4 t CO_2 per t of product, which is about four times as much as that of cement [14]. Last but not least, CO_2 emissions from transportation continued to increase in 2022, rising by over 250 Mt CO_2 to about 8 Gt CO_2, 3% over the amount recorded in 2021 and almost reaching their 2019 level.

The ever-increasing heat and power demand, as well as the growth in consumption levels owing to the expansion in world's population resulted in unprecedented atmospheric CO_2 levels and extreme climate phenomena. Therefore, the following energy-intensive industrial processes were investigated:

1. Cement production;
2. Biofuel production;
3. High value chemicals production;
4. Fertilizer production.

1.3. Carbon capture, utilization and storage technologies

1.3.1. Reactive gas-liquid absorption system using amine-based solvents

The system operates on an absorption-desorption cycle during which the amine solution chemically reacts with the CO_2 within an absorption column, followed then by solvent regeneration within a desorption unit, thus discharging the absorbed CO_2 [15,16]. The reactive gas-liquid system is presented in Figure 1.3-1. The solvent comes into contact opposite one another with the exhaust gas which progressively warms up while it absorbs CO_2, resulting in a CO_2 rich flow. Further, the CO_2 rich stream is heated through a heat exchanger by using the regenerated solvent stream resulting from the desorption column. Throughout the desorption unit the CO_2 is separated from the solvent stream by rising its temperature to around 120°C to 140°C. In addition, a second heat exchanger is utilized to further reduce the temperature of the amine-based solution before it is recycled into the absorption unit. Alkanolamines are among the most frequent CO_2 capture solvents used. They may be divided as follow: primary (i.e., Mono-Ethanol-Amine – MEA), secondary (i.e., DEA), tertiary (i.e., Methyl-Di-Ethanol-Amine – MDEA), as well as cyclic amines such for example piperazine.

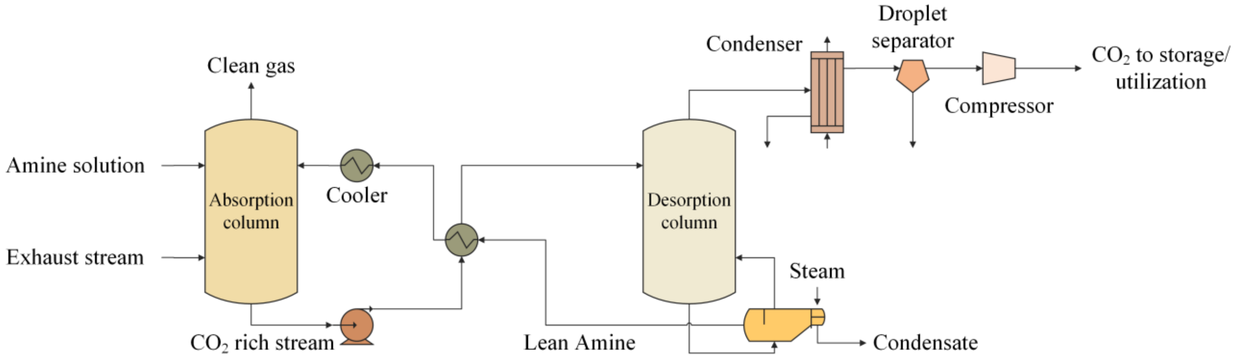


Figure 1.3-1. Schematically representation of the amine-based chemical scrubbing process

1.3.2. Reactive gas-solid adsorption system using calcium looping technology

Chemical-looping methods employ O_2 carriers or CO_2 sorbents as chemical intermediates to naturally remove CO_2 with the least amount of energy [17]. In order to release the O_2 needed for fuel combustion, O_2 carriers are typically solid metal oxides designed to perform repeated oxidation-reduction cycles [18]. This sort of chemical looping technology is referred to by the scientific community as calcium looping (CaL). Herein, sorbents, often in the form of calcium oxide (CaO), react with CO_2 to generate calcium carbonate ($CaCO_3$), which is then decomposed in an entirely separate unit to release an almost pure stream of CO_2. Usually, CaL is employed in post-combustion CO_2 capture applications as it relies upon a reversible carbonation reaction to remove the CO_2 from the flue gas within the first unit (i.e., carbonator) and regenerate the sorbent using a second unit (i.e., calcinator). An almost pure stream of CO_2 is produced by the calciner without the use of any further separation methods.

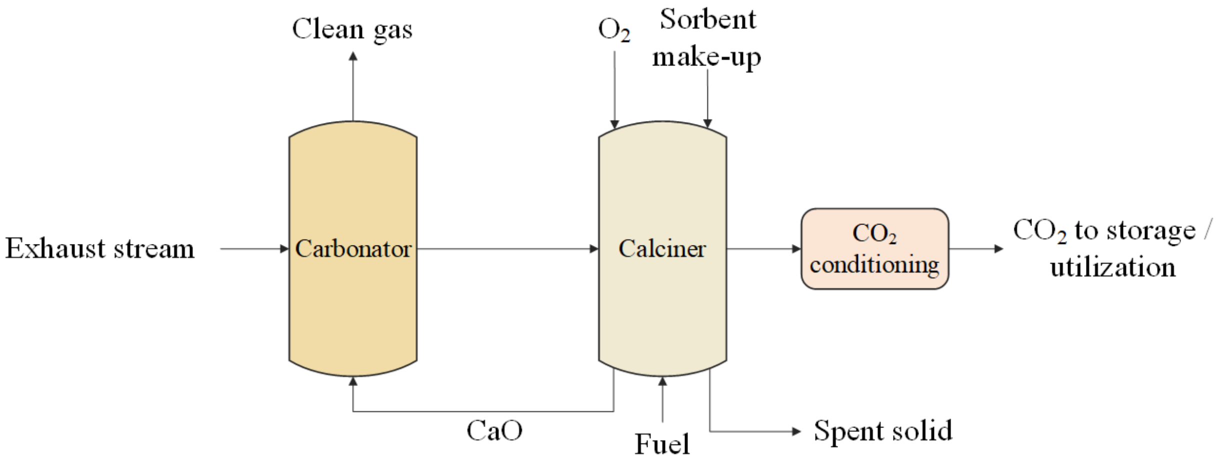


Figure 1.3-2. Schematic diagram of the CaL technology

Figure 1.3-2 illustrates a schematic diagram of the CaL approach for CO_2 capture. As shown, two interconnected reactors are used to carry out the process. CO_2 is removed in the first reactor through the carbonation reaction (i.e., referred as the direct reaction), Eq. (1.3-1), while the sorbent is regenerated in the second unit, discharging the captured CO_2, Eq. (1.3-2).

$$CO_2 + CaO \rightarrow CaCO_3 \qquad \Delta H^0_{298} = -183\ \mathrm{kJ/mol} \qquad (1.3\text{-}1)$$

$$CaCO_3 \rightarrow CO_2 + CaO \qquad \Delta H^0_{298} = +183\ \mathrm{kJ/mol} \qquad (1.3\text{-}2)$$

Given that sorbent regeneration process is highly endothermic, additional fuel must be burned along with O_2 to avoid CO_2 dilution. Therefore, an ASU must be employed, thus causing a decrease in power efficiency. Owing to the fact that high temperatures are employed within this process (i.e., above 600°C in the carbonator and around 950°C in the calciner), there is significant opportunity for energy recovery. Part of the energy loss caused by the ASU might be compensated for by producing steam and expanding it through a steam turbine.

With the exception of having strong CO_2 adsorption capacities rather high O_2 transport ability, CO_2 sorbents should possess similar features such those of the O_2 carriers. Natural ores that have substantial CO_2 adsorption capacities and no health and safety issues are the most researched, for example limestone and dolomite [19,20]. The main drawback when related to sorbents consists of their diminished adsorption ability after performing several cycles [20,21], thus leading to high amounts of sorbent make-up. Nevertheless, it has little impact on the process's viability at large scale because of their low cost and the possibility of reusing the purged material within a different process. Due to this, natural calcium-based materials (i.e., limestone) are utilized as sorbent materials for capturing CO_2 by means of the CaL technology.

1.3.3. Membrane separation processes

Nowadays, membrane separation systems are regarded as one of the most efficient methods because of their numerous advantages, including low energy consumption cheap operating costs, ease of operation, as well as their compatibility with other technologies [22]. Membranes may be utilized in a wide range of applications, such as replacing distillation process by reverse osmosis [23], purifying natural gas using membrane technology instead of the amine scrubbing technology [24], or to capture CO_2 [25].

Membrane separation does not require any phase changes or any chemical solvents, but a membrane must possess a high level of selectivity, high permeance, thinness, and also needs to be physically, chemically, mechanically, as well as thermally stable for industrial use in order to obtain high CO_2 separation yields.

Based on the above consideration, Figure 1.3-3 presents the design of a 3-stage membrane separation system applied for CO_2 capture from cement industrial sector.

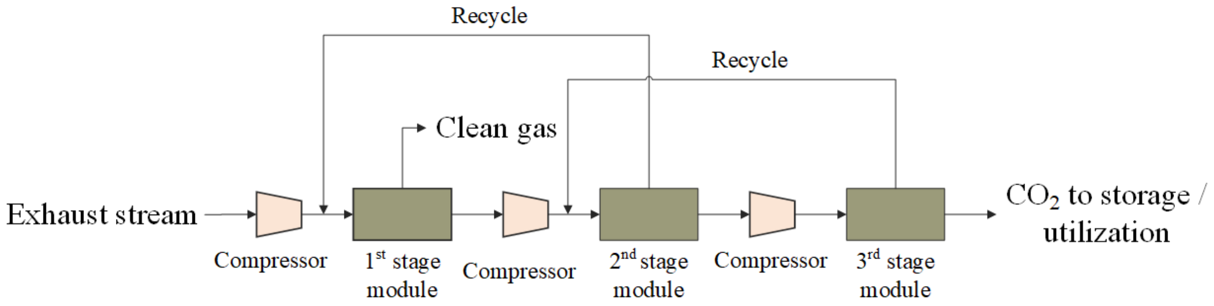


Figure 1.3-3. Membrane separation system applied for post-combustion CO_2 capture

2. Assessment methodology

2.1. Process modelling and simulation

The modelling and simulation aspects of the proposed processes were carried out by means of CHEMCAD process simulation software developed by Chemstations. CHEMCAD, as a chemical process simulator, allows the access to a comprehensive database of chemical components, an extensive library of thermodynamic data, as well to a collection of the most popular unit operations. Because of the numerous benefits it provides, the software is extensively utilized for design, operation, and optimization in many different industries, for example oil and gas production and refining, pharmaceuticals, green fuels, equipment sizing, etc. In addition, CHEMCAD has the ability to simulate both steady-state and dynamic systems, and can perform simulations of batch, semi-batch or continuous processes [26].

2.2. Thermal integration

Heat integration proves crucial for increasing energy efficiency and cutting operating costs in the process industries, for instance carbon capture integration within cement manufacturing sector. In addition, by implementing energy efficiency measures, CO_2 emissions can be decreased [27]. Given that thermal energy significantly impacts the process costs, heat integration has been frequently employed to decrease the consumption of hot and cold utilities. As a result, the deployment of waste heat recovery technology will thus remain an appealing alternative to using excess energy for heating purposes [28].

Pinch analysis (PA) is the first fully viable method for the design of heat exchanger networks. Following this approach, the reduction of energy consumption is tackled from a thermodynamic perspective and it is based on the process flowchart, as well as process' mass and energy balance data [29].

At first, the enthalpy flux change is computed according to Eq. (2.2-1) [30], which takes into consideration the supply and target stream temperatures (i.e., the initial value of the stream temperature and the value of the stream temperature after performing heat integration).

$$\Delta H = m \times C_p \times \Delta T = m \times c_p \times (T_{in} - T_{out}) \qquad (2.2\text{-}1)$$

where m represents the mass flowrate, C_p is specific heat capacity, T_{in} and T_{out} are the supply and target stream temperature, respectively.

Additionally, besides the sensible heat changes, either condensation or evaporation contribute significantly to enthalpy change and this can be computed by means of Eq. (2.2-2):

$$\Delta H = m \times \lambda \tag{2.2-2}$$

where m and λ are the mass flowrate and latent heat of the condensing or evaporating stream.

The composite curves (CCs) are a tool used to provide the energy targets, thus to identify which streams need to be heated or cooled [31]. The Hot Composite Curve (HCC) and the Cold Composite Curve (CCC) express the total heat source and heat demand of a process, respectively, and are obtained merging the hot and cold streams of a process. The latent heat of condensation or vaporization is represented by the horizontal lines in both the hot and cold CCs, respectively.

2.3. Technical evaluation

Technical evaluation is essential to assess both the efficacy and potential of a process or a system, and to determine whether the objectives it was designed to are achieved. Key performance indicators (KPIs) serve as a tool to measure the performance and make it possible to easily compare related processes or of different process configurations. The KPIs that follow can be utilized to ascertain the performance of the proposed processes:

- **Carbon Capture Rate** – quantifies the amount of CO_2 captured by the carbon capture system from the total carbon molar flow from the raw material

$$CCR = \frac{F_{CO_2,captured}}{F_{feedstock\ carbon}} \times 100\% \tag{2.3-1}$$

- **Net power efficiency** – measures the overall electric efficiency of the system and it is computed as the ratio between the net power output and total thermal energy intake

$$\eta_{net} = \frac{P_{net}}{m_f \times LHV} \times 100\% \tag{2.3-2}$$

where P_{net} is the net electric output and m_f and *LHV* are the mass flowrate and low heating value of the fuel, respectively;

- **Gross power efficiency** – can be computed by dividing the gross electric power output to the total thermal input

$$\eta_{gross} = \frac{P_{gross}}{m_f \times LHV} \times 100\% \tag{2.3-3}$$

where P_{gross} represents the gross power output;

- **CO_2 specific emission rate** – total CO_2 specific emission rate is directly related both to the electricity import or export, as well to an average emission factor

$$SE_{CO_2} = \frac{on - site\ CO_2 \pm electricity\ import/export \times emission\ factor}{product\ unit\ (e.g., MW, kg)} \times 100\% \qquad (2.3\text{-}4)$$

2.4. Life Cycle Assessment

Life Cycle Assessment (LCA) was developed with the purpose of promoting the most sustainable alternatives among several options by quantifying the environmental burden of each individual system, thus making LCA a valuable decision-making tool [32]. In addition, the knowledge it offers through tracing and quantifying the inputs and outputs of a system assists in prioritizing the aspects that may be improved, making LCA a complement to technical developments [33].

LCA computes the environmental and human health effect of a specific product or system by considering a particular function and taking into account all life cycle stages. As stated by the International Organization for Standardization (ISO) throughout ISO 14040:2006 (i.e., principles and framework) [34] and ISO 14044:2006 (i.e., requirements and guidelines) [35], an LCA investigation consists of a *Goal and scope definition*, *Life Cycle Inventory (LCI)*, *Life Cycle Impact Assessment (LCIA)*, and Interpretation.

a) ***Goal and scope definition*** – must clearly identify the objectives and purpose of the study, the target group and whether the results will be utilized in comparison assertions meant to be released to the general public [32]. In addition, key elements including system's function, functional unit (FU), system boundaries, allocation between two or more products, limitations etc. must be defined [35].

b) ***Life Cycle Inventory*** – involves creating an inventory of reference flows for a given process or product. It includes accurate recording of all input and output streams, such as raw materials, resources, different types of energy and pollutants to air, water and soil.

c) ***Life Cycle Impact Assessment*** – seeks to establish a connection between the elementary flows of the system to their possible environmental impact, thus it translates the reference flows into environmental impact categories, presented in Table 2.4-1.

d) ***Interpretation*** – delivers a set of conclusions and recommendations based on the results gathered from inventory and impact assessment, respectively. Consists of identification of primary contributors (i.e., hotspots), an examination of the study's comprehensiveness, sensitivity and reliability as well as conclusions, limitations and recommendations [36].

Table 2.4-1. Overview and description of environmental category indicators for ReCiPe impact assessment method

Impact indicator	**Characterization**	**Main contributors**
Global Warming Potential (GWP)	Anthropogenic emissions leading to an increase in surface temperature. Unit: kg of CO_2 equivalents to air	CO_2, CH_4, N_2O, NO_2, CFCs, HCFCs, HFCs
Terrestrial Acidification Potential (TAP)	Increased proton levels in the natural soils due to the impact of acidifying contaminants. Unit: kg of SO_2 equivalents to air	SO_X, NO_X, HCl, HF, HNO_3, H_2SO_4, H_2S
Freshwater Eutrophication Potential (FEP)	Excessive quantities of nutrients detected in the internal water ecosystem. Unit: kg of P equivalents to freshwater	Nitrogen and phosphorus chemicals
Marine Eutrophication Potential (MEP)	Increase in the concentration of dispersed nitrogen-containing nutrients in oceans. Unit: kg of N equivalents to freshwater	Nutrients containing nitrogen
Ozone Depletion Potential (ODP)	Anthropogenic emissions that are causing the stratospheric ozone layer to thin. Unit: kg of CFC-11 equivalents to air	CFCs, HCFCs, halons
Particulate Matter Formation Potential (PMFP)	The ingestion of contaminants in the form of particulate matter by individuals. Unit: kg of PM_{10} equivalents to air	NH_3, NO_X, SO_2
Fossil Depletion Potential (FDP)	Excess energy used for the extraction of one MJ, kg or m^3 of fossil fuel. Unit: kg of oil equivalents (with a lower heating value of 42 MJ)	Extraction of fossil resources
Mineral Depletion Potential (MDP)	Excess energy used for future mineral or ore extraction due to reduced availability. Unit: kg of Fe equivalents	Extraction of mineral resources
Photochemical Oxidant Formation Potential (POFP)	Increase in ozone concentration at the troposphere level Unit: kg of NMVOCs equivalents to air	Particulate matter, NMVOCs, NO_x
Ionising Radiation Potential (IRP)	Reflects the amount of radiation exposure experienced by the world's population. Unit: kg of Uranium 235 equivalents to air	Unstable isotopes, X- and Gamma-rays

Table 2.4-1. continued

Impact category	**Characterization**	**Relevant LCI data**
Human Toxicity Potential (HTP)	Possible damage of toxic chemicals to human health. Unit: kg of 1,4 DCB equivalents to air	Chemical substances toxic to human health
Water Depletion Potential (WDP)	Indicates the amount of freshwater consumption Unit: m^3 of water used	Use of freshwater
Freshwater Ecotoxicity Potential (FETP)	Relates to the possible harm of toxic compounds to the aquatic environment. Unit: kg of 1,4 DCB equivalents to freshwater	Toxic chemicals with a reported lethal concentration to rodents and fish (e.g., Pb, Hg, Cd, halogenated organic compounds, pesticides or sewage sludge)
Marine Ecotoxicity Potential (METP)	Impact on the marine environment due to the increasing amounts of metals in the ocean. Unit: kg of 1,4 DCB equivalents to marine water	
Terrestrial Ecotoxicity Potential (TETP)	Accounts for the potential impact of toxic substances on terrestrial ecosystems. Unit: kg of 1,4 DCB equivalents to industrial soil	
Natural Land Transformation Potential (NLTP)	Refers to the surface of natural land occupied and transformed over a specific timeframe. Unit: m^2 natural land	Area of land used

3. Case studies

3.1. Investigation of cement production industry

The decarbonization of cement industrial sector comes as a crucial challenge due to its large energy consumption and high amounts of anthropogenic GHG releases. The IEA has stated that the cement industry is one of the largest sources of anthropogenic CO_2 emissions, contributing about 7% of the total share, releasing approximately 2.2 Gt of CO_2 per year [9]. Aranda-Usón and co-authors claimed that cement production accounted for between 12% to 15% of total industrial energy consumption [37], while a recent report stated that the cement sector ranked third with a share of around 7% of total energy [38]. Cement related goods are among the most consumed commodities [39], and according to the European Cement Association (CEMBUREAU) [40], global cement production was 3.6 billion tons in 2012, reaching 4.1 billion tons in 2017 [41]. Pacheco-Torgal and collaborators showed that cement demand is closely associated with both economic and industrial development [42], suggesting that cement needs will increase in emerging countries due to rapid expansion of cities and infrastructure [43], while remaining relatively stable in already developed ones. Despite its growing economic strength and extensive urbanisation, China is classified as a developing country, achieving the highest cement production since 1990 [44].

Clinker, one of the main constituents of cement [45], is produced by the decomposition of calcium carbonate into calcium oxide and high amounts of CO_2, followed by the sintering of calcium oxide with aluminosilicates and the rest of the raw materials [46]. According to Tregambi and co-authors [47], the calcination of limestone accounts for approximately 95% of GHG emissions, while consuming 80% of total energy demands. Throughout limestone decomposition, 50% of the emissions are due to the calcination process, while 40% come from burning fossil fuels [48]. In fact, 1.5 tons of raw materials are used to produce one ton of clinker [49], while each ton of Portland cement generates nearly one ton of CO_2 [50]. Strategies such as: improving energy efficiency, using alternative fuels, clinker substituents, or integrating CCS technologies have been outlined to reduce emissions from the cement sector [51].

The implementation of CCS technologies provides a good opportunity in reducing CO_2 emissions as cement plants are the second biggest stationary source of GHG releases. In addition, CCS system are expected to contribute more than 55% of total GHG reductions [45]. Three different carbon capture approaches are available for CO_2 capture: post-combustion, pre-combustion and oxy-fuel combustion [52]. Since higher amounts of CO_2 emissions are released during the calcination of limestone compared to fuel combustion, pre-combustion is not seen as an attractive approach for the cement sector [45]. The post-combustion capture design, in contrast to oxy-fuel combustion, could be applied in existing clinker production plants without needing significant adjustments [51].

The purpose of this chapter is to evaluate and compare three post-combustion capture technologies for reducing GHG emissions in a conventional cement manufacturing plant. The investigated carbon capture technologies are: amine-based chemical scrubbing using MDEA, reactive gas-solid adsorption by means of CaL technology and membrane separation. Several key performance indices and environmental impact categories are taken into consideration when comparing the benchmark scenario (i.e., cement manufacturing without carbon capture feature) with the three alternative scenarios.

The key novel aspects brought by the current study consists of a thorough technical and environmental assessment by means of modelling and simulation tools, heat integration and LCA methodology of three of the most promising tail-end post-combustion carbon capture systems, thus providing important insights into decarbonisation systems that have potential for application in the cement production sector.

3.1.1. Plant configurations

The potential technical and environmental benefits brought by the integration of different post-combustion carbon capture technologies within cement manufacturing are evaluated. In terms of CO_2 capture systems, amine-based gas-liquid absorption, reactive gas-solid adsorption by means of CaL technology and membrane separation were proposed. The following scenarios are further investigated:

Case 1. Standard cement manufacturing plant without carbon capture feature;

Case 2. Post-combustion capture by means of amine-based chemical scrubbing using MDEA;

Case 3. Post-combustion capture by reactive gas-solid adsorption using CaL technology;

Case 4. Post-combustion capture employing membrane separation.

As a benchmark, a traditional cement production plant without carbon capture is assessed in Case 1. Case 2 considers the reactive gas-liquid post-combustion capture by the use of MDEA as a chemical solvent. The third case (i.e., Case 3) studies the integration of CaL technology as a reactive gas-solid system into a conventional cement manufacturing plant. A more innovative option is explored in Case 4, specifically the integration and utilization of a membrane separation.

3.1.2. Process modelling and simulation and main design assumptions

Process modelling and simulation of the evaluated scenarios was carried out utilizing CHEMCAD, version 7, as a process simulation software [26]. The composition of the exhaust stream exiting the cement production plant, was selected as described by the IEA Greenhouse Gas R&D Programme (IEAGHG) [45]. In addition, an annual production of 1 Mt of cement and a CCR of 90% was set in all investigated scenarios.

Thermal integration is an important step as it significantly enhances the overall energy utilization, while reducing both emission and waste generation. Heat integration by means of PA considering a minimum temperature variation of 10°C was conducted for Case 2 and Case 3.

Following the heat integration, a technical comparison of the three tail-end post-combustion capture methods is shown in Table 3.1-1. As presented, the amount of electricity produced both in Case 2 and Case 3 via the CHP unit and steam generator, respectively, is higher compared to the energy required in the corresponding carbon capture process, thus a small surplus can be utilized in other sections or exported (20.28 MW_e vs. 15.82 MW_e). As opposed to the previous scenarios, since there is no unit to supply the power demand in Case 4 (41.34 MW_e), the power is imported from the grid mix. Given the additional amount of coal supplied to the heat and power unit, approximately 34% less coal is required in the CaL design compared to the reactive gas-liquid separation (33.47 t/h in Case 2 vs. 22.00 t/h in Case 3). No supplementary coal is needed in the membrane separation approach, as no heat and power unit is employed and all the power is imported from the grid. Similar observations can be made when considering the energy consumption in the carbon capture processes (235 MW_e in Case 2 vs. 160 MW_e in Case 3).

Table 3.1-1. Main technical performance indicators of the investigated scenarios

Parameter	Units	Case 2	Case 3	Case 4
Coal flowrate (to heat and power unit)	t/h	33.47	22.00	0
Thermal energy	MW_{th}	234.10	153.80	0
Steam generation output	MW_e	54.42	58.01	0
Total power consumption	MW_e	34.14	42.19	41.34
Net power output	MW_e	20.28	15.82	0
Net power efficiency	%	8.66	10.28	0
Gross power efficiency	%	23.25	37.71	0
Carbon capture rate	%	90.00	90.00	90.00
CO_2 specific emissions (on-site)	kg/t	135.78	120.74	70.63
CO_2 emissions (power import/export)	kg/t	-79.94	-62.36	162.96
CO_2 specific emissions (total)	kg/t	55.83	58.37	233.59
CO_2 captured	kg/t	1,214.15	962.20	635.43

In terms of energy performance, the CaL design provides a higher gross power efficiency compared to both Case 2 (by about 1.6 times), and Case 4. Examining the total specific CO_2 emissions reveals similar results when comparing Case 2 and Case 3 (55.83 kg CO_2/t_{cement} in Case 2 vs. 58.37 kg CO_2/t_{cement} in Case 3), while Case 4 scores much higher (233.59 kg CO_2/t_{cement}), even though on-site specific emissions are the lowest. The results can be explained by the presence of the CHP unit in Case 2 and steam turbine in Case 3, which enable power export due to excess steam.

3.1.3. Environmental evaluation using life cycle assessment methodology

The goal of the present study is to evaluate the environmental burden of a conventional cement plant and analyse the potential benefits of implementing CCS technologies. The function of the system is the production of 1 Mt of cement per year, while one ton of cement was chosen as FU.

The current study represents a cradle-to-gate LCA investigation, therefore the following processes are considered: i) main processes: cement production with and without post-combustion CO_2 capture, ii) upstream processes: limestone supply chain, MDEA production and supply chain, membrane production and supply chain, ASU unit for O_2 generation, CHP unit to provide the required steam and power, iii) downstream processes: MDEA degradation, disposal of wastes, and CO_2 compression, transport and storage. Figure 3.1-1 provides a better representation of the considered system boundaries. The present research was conducted by means of GaBi software [53], while ReCiPe was chosen as the impact assessment method.

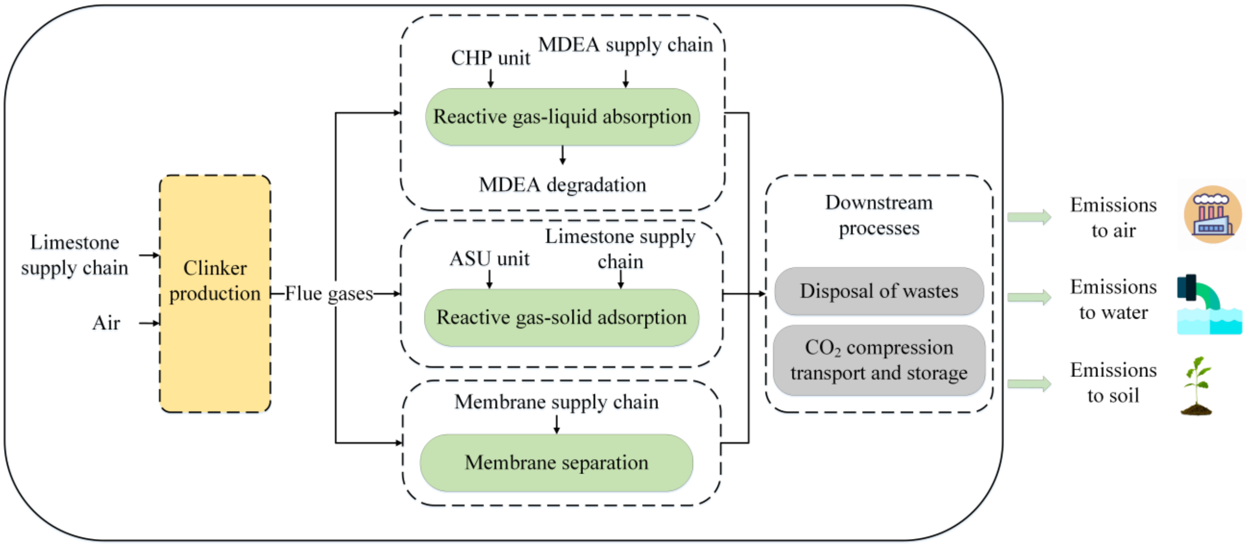


Figure 3.1-1. System boundaries for the environmental evaluation

The assumptions made during an LCA investigation may significantly influence the results, a sensitivity study regarding the power source in Case 4 was performed. Initially, the energy is imported from the electricity grid mix, while wind and PV power were investigated as a more renewable approach.

The outcome of the environmental evaluation considering the previously presented assumptions is summarized in Table 3.1-2. As shown, the base case scenario (i.e., Case 1) exhibits the highest impact for the GWP, POFP and ODP environmental indicators. The implementation of the carbon capture systems has a positive influence on the GWP category, with the reactive gas-liquid system (i.e., Case 2) achieving a 73.63% reduction compared to the benchmark. The utilization of the CaL design leads to even better performances, with a 76.74% decrease. Case 4 leads to a higher GWP score when compared to the other carbon capture methods, but manages to achieve a 69.91% reduction against the benchmark. The higher GWP impact than for the other capture systems can be explained by the fact that the energy is imported from the grid mix (i.e., Case 4a), therefore a large amount of CO_2 emissions come from energy production. A sensitivity analysis is carried out on the energy source with renewable alternatives such as wind and PV power being assessed (i.e., Case 4b and Case 4c, respectively). As the results indicate, the GWP values show a decrease of about 34% in the case of wind power (i.e., Case 4b), and a reduction of about 28% when using PV (i.e., Case 4c) compared to importing energy from the grid mix (i.e., Case 4a).

The integration of the carbon capture technologies, particularly the amine-based chemical scrubbing system, does not result in an overall better environmental performance. Compared to the standard cement plant without CO_2 capture feature (i.e., Case 1), the employment of the CCS in Case 2 leads to higher values for six of the nine impact indicators (i.e., FEP, FDP, FETP, HTP, MDP and TETP), while the other three impact categories present better results (i.e., GWP, ODP and POFP). The largest differences between Cases 1 and 2 are registered in the FDP and FETP impact categories, with an increase of 11.40% and around 7.70%, respectively, for the CCS scenario in Case 2.

The opposite is true when the CaL system is used for the CO_2 capture, with Case 3 showing the best results in terms of GWP, ODP, FDP, MDP, POFP and TETP, while similar values to Case 1 are obtained for FEP, FETP and HTP. Significant differences are found in terms of FDP and POFP, with a 2.2 times lower FDP value and a 3.2 lower score in the POFP impact category for the CCS scenario in Case 3 compared to the conventional cement plant. In addition, comparing the membrane separation system with imported energy from the grid mix (i.e., Case 4a) to the reference case, it can be noticed that lower GWP, ODP and POFP values are obtained, while the FDP impact indicator shows 2.5 times increase for the CCS scenario in Case 4 (14.03 kg oil eq./t_{cement} for Case 1 vs. 34.67 kg oil eq./t_{cement} in Case 4a).

The lowest GWP value, among all investigated cases, is achieved when the electricity is generated by wind power (157.95 kg CO_2 eq./t_{cement} for Case 4b). In addition, the score obtained in the ODP and POFP categories significantly favor the membrane separation system compared to the reference case.

When considering PV power (i.e., Case 4c), the environmental analysis shows lower scores for GWP, ODP and POFP against the base case, while registering a higher value for the MDP impact indicator.

Table 3.1-2. Environmental impact assessment results according to ReCiPe method

KPI	Units	Cases investigated					
		Case 1	**Case 2**	**Case 3**	**Case 4a**	**Case 4b**	**Case 4c**
GWP	kg CO_2 eq./t_{cement}	792.40	208.90	184.30	238.40	157.95	170.94
FEP	kg P eq./t_{cement}	10.50×10^{-3}	11.30×10^{-3}	10.60×10^{-3}	10.90×10^{-3}	10.70×10^{-3}	10.80×10^{-3}
ODP	kg CFC-11 eq./t_{cement}	21.89×10^{-9}	13.03×10^{-9}	12.16×10^{-9}	19.32×10^{-9}	15.69×10^{-9}	15.99×10^{-9}
FDP	kg oil eq./t_{cement}	14.03	15.63	6.78	34.67	14.25	17.79
FETP	kg 1,4-DB eq./t_{cement}	1.19	1.28	1.20	1.24	1.21	1.22
HTP	kg 1,4-DB eq./t_{cement}	103.70	111.50	103.80	107.30	105.50	109.80
MDP	kg Fe eq./t_{cement}	2.15	2.19	1.99	2.77	4.24	9.00
POFP	kg NMVOC/t_{cement}	33.40×10^{-2}	25.10×10^{-2}	10.26×10^{-2}	26.50×10^{-2}	13.30×10^{-2}	17.10×10^{-2}
TETP	kg 1,4-DB eq./t_{cement}	2.11×10^{-2}	2.28×10^{-2}	2.07×10^{-2}	2.27×10^{-2}	2.14×10^{-2}	4.54×10^{-2}

Case 1 – Standard cement plant without carbon capture feature; Case 2 – Reactive gas-liquid separation system; Case 3 – Reactive gas-solid separation; Case 4a – Membrane separation with electricity from grid mix; Case 4b – Membrane separation with electricity from wind power; Case 4c – Membrane separation with electricity from PV power.

3.2. Investigation of biofuels production

In consideration of the increasing energy requirements in domestic and industrial sector [54], fossil energy sources (i.e., natural gas, coal or crude oil) continue to play a significant role in fulfilling the global energy demand [55]. Considering the present energy consumption trends, it is predicted that the limited fossil fuel sources would be exhausted within the next 50 years [56], causing an impact on the economic wealth due to the rising prices of natural energy [57]. In addition, it is well-known that significant amount of GHG emissions is produced by the combustion of fossil fuels. Carbon dioxide comes as the most important GHG released since it is the primary factor contributing to climate change and global warming, resulting in an increase in both global surface temperature and sea levels [58].

The transportation sector depends almost exclusively on gasoline and diesel, accounting for approximately 30% of total GHG releases, thus proving without beyond any doubt that fossil fuels serve a significant role in global energy consumption [59]. To meet this ambitious goal, it is critical to substitute fossil fuels with low-carbon sustainable alternatives [60] in order to diminish the CO_2, CO and NO_x emissions [61]. Several studies have been undertaken to evaluate the potential replacement of fossil energy sources with green alternatives such as wind, hydro, solar or biomass [62]. Despite the fact that all sources offer multiple benefits, biomass is considered to be the best alternative since a variety of biomass is available regardless of the geographical location [63]. Currently, biomass accounts for about 10% of total energy consumption. Moreover, the CO_2 produced during the biofuel combustion is captured in the process of biomass growth, thus potentially reaching carbon neutrality or even negative emissions [64]. Waste biomass may be provided via various forms, from municipal, agricultural and industrial wastes to forest residues [65].

Therefore, the current chapter is at first addressed to the bio-methanol production from secondary biomass via an innovative process that takes advantage of cutting-edge technologies aiming to enhance the environmental performance against the state-of-the-art technology [66]. Secondly, the purpose of the work is to investigate from technical and environmental perspectives the intensified against the conventional biodiesel production methods. The innovative approach consists of the utilization of the reactive distillation (RD), a process intensification method that integrates both reaction and separation into a single unit operation [67].

3.2.1. Plant configuration for bio-methanol production

Owing to residual biomass availability, the share of advanced biofuels manufactured from secondary biomass is forecasted to increase and make a significant contribution in the pursuit of NZE. The CONVERGE system is built on the concept of developing and integrating new technologies such as catalytic cracking of tars (CCT) from an indirectly heated gasifier, recovery of refinery products including aromatics for green Benzene-Toluene-Xylene (BTX) fraction, sorption-enhanced reforming (SER) for excess-carbon removal and H_2 production, highly efficient electrochemical H_2 compression (EHC), and a membrane-based reactor for MeOH synthesis. In this respect, the following CONVERGE technology scenarios are examined in the current chapter:

Table 3.2-1. Definition of evaluated CONVERGE scenarios

Case name	Description
Case 1	Bio-methanol production from wooden biomass baseline;
Case 2	Bio-methanol production from wooden biomass with enhanced CO_2 resistance;
Case 3	Bio-methanol production from exhausted olive pomace with enhanced CO_2 resistance.

3.2.2. Plant configuration for biodiesel production

Sustainable fuels and technologies are expected to substantially contribute towards climate change mitigation since the transport industry generates 23% of the total GHG emissions. Therefore, the following biodiesel production scenarios are further investigated in the present chapter:

Table 3.2-2. Definition of investigated biodiesel production scenarios

Case name	Raw material(s)	Electricity source	Intermediate product	Technology type
Case 1	CO_2 and H_2	Biomass	Methanol	Classic
Case 2	CO_2 and H_2	Natural gas	Methanol	Classic
Case 3	CO_2 and H_2	Biomass	Methanol	Innovative
Case 4	CO_2 and H_2	Natural gas	Methanol	Innovative
Case 5	Natural gas	-	Methanol	Classic
Case 6	Natural gas	-	Methanol	Innovative

Case 1 propose the biodiesel synthesis following the classic pathway, utilizing CO_2 and H_2 for MeOH production and biomass as power source. Case 2 employs the same method as Case 1, the difference consisting of the fact that natural gas is used to provide the required electricity for the water electrolysis process instead of biomass. Case 3 refers to the intensified biodiesel production process by using CO_2 and H_2 as feedstock for the MeOH synthesis. Case 4 utilizes the same approach as in the third case, except that natural gas is used to supply the necessary power for the electrolytic H_2 generation. Case 5 and Case 6 present the biodiesel production both employing natural gas as raw material and following the classic and intensified method, respectively. Water electrolysis process is assessed for H_2 generation with the necessary power being supplied by the use of biomass or natural gas. With respect to the CO_2 source, it is assumed that the much-needed amount of CO_2 is gathered from limestone decomposition, as it generates as well the CaO utilized in the biodiesel manufacture stage.

3.2.3. Process modelling and simulation and main design assumptions for biodiesel production

The process modelling and simulation aspects of the investigated biodiesel scenarios were carried out by means of CHEMCAD simulation software version 7 [26]. All evaluated cases assume an hourly biodiesel production of 13,333.33 kg/h, corresponding to a total of 100,000 tons of biodiesel per year.

Table 3.2-3 presents a technical comparison of investigated cases based on various performance indices. It shows that compared to the water requirements; less natural gas is demanded to produce the same amount of biodiesel. Examining the amount of raw materials, it can be observed that the intensified route requires larger quantities of both H_2 and CO_2 to produce the much-needed MeOH. This is due to the higher amount of fresh MeOH needed in the biodiesel production process. In terms of MeOH consumption, the intensified route described in Cases 3, 4 and 6 requires lower quantities compared to the traditional approach presented in Cases 1, 2 and 5 (i.e., 38,854.51 kg/h in Cases 3, 4 and 6 vs. 36.644.48 kg/h in Cases 1, 2 and 5). The same conclusion can be drawn when looking at the amount of oil and sulfuric acid utilized within the various investigated scenarios. Even though the purity of the main product is over 99% in the conventional route, a slight benefit can be seen when examining the intensified pathway.

Glycerol emerges as an important by-product of the biodiesel production process as on the one side it can be reformed and converted to MeOH which might by recycled and used as raw material in the main process or, on the other side, it can be utilized within the glycerolysis treatment process [68]. The largest quantity of glycerol is generated in the intensified production scenarios (i.e., 41.62 kg/h in Case 6 and 35.17 kg/h in Cases 3 and 4).

In terms of power requirements, a significantly higher consumption can be seen in the cases that assume the integration of water electrolysis process for H_2 supply. Following these cases, the H_2 generation process accounts for over 90% of the total energy demanded, leading to more than ten times higher values.

Table 3.2-3. Technical performance indices of biodiesel production scenarios

Parameter	Unit	Cases investigated					
		Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Natural gas flowrate	kg/h	-	-	-	-	837.92	1,043.75
Water flowrate	kg/h	3,106.75	3,106.75	3,869.77	3,869.77	-	-
Hydrogen flowrate	kg/h	345.20	345.20	430.00	430.00	-	-
Carbon dioxide flowrate	kg/h	2,525.79	2,525.79	3,146.00	3,146.00	-	-
Methanol fresh flowrate	kg/h	1,531.31	1,531.31	1,907.40	1,907.40	1,531.31	1,907.40
Methanol recycled flowrate	kg/h	37,331.21	37,331.21	36,947.11	36,947.11	37,331.21	34,737.08
Total methanol flowrate	kg/h	38,862.52	38,862.52	38,854.51	38,854.51	38,862.52	36,644.48
Oil flowrate	kg/h	21,428.00	21,428.00	20,990.20	20,990.20	21,428.00	20,990.20
Sulfuric acid flowrate	kg/h	3,072.57	3,072.57	3,009.79	3,009.79	3,072.57	3,009.79
Biodiesel flowrate	kg/h	13,333.33	13,333.33	13,333.33	13,333.33	13,333.33	13,333.33
Biodiesel purity	%	99.31	99.31	99.41	99.41	99.31	99.41
Glycerol flowrate	kg/h	18.25	18.25	35.17	35.17	18.25	41.62
Glycerol purity	%	99.77	99.77	99.37	99.37	99.77	99.43
Electricity consumption	$kW_h/t_{biodiesel}$	1.53	1.53	1.90	1.90	0.17	0.14

3.2.4. Environmental evaluation of bio-methanol production using life cycle assessment methodology

The aim of the current work is to quantify, evaluate and compare the environmental impact of the CONVERGE technology for the bio-methanol production against the state-of-the-art technologies for biomass conversion towards bio-methanol manufacture.

The current research is a cradle-to-gate LCA study as it covers stages from raw materials supply chain (i.e., biomass) up to the final product (i.e., bio-methanol). The system boundaries are shown in Figure 3.2-1.

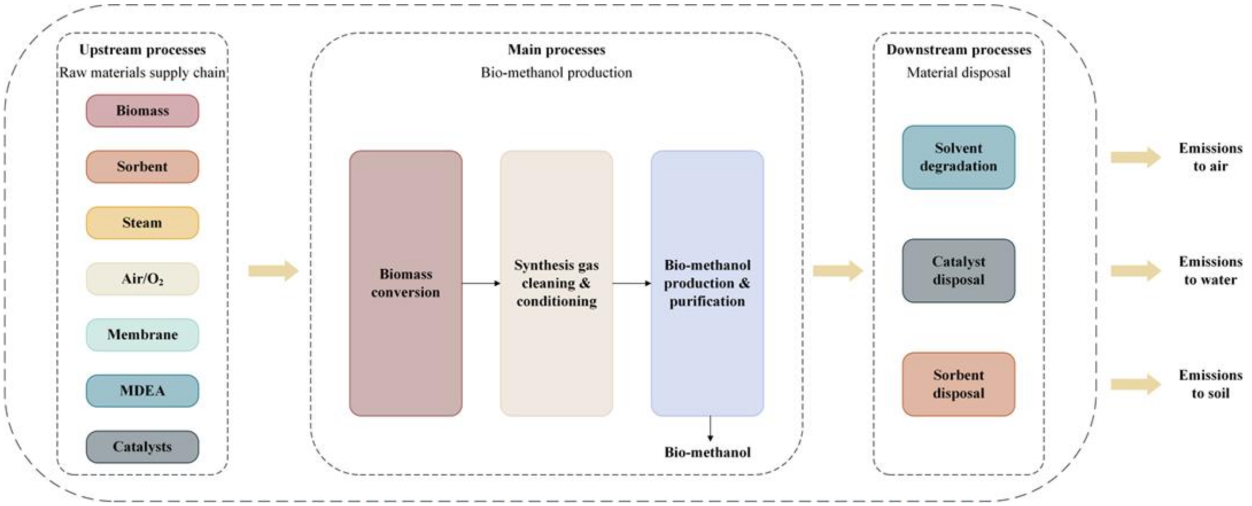


Figure 3.2-1. System boundaries for the CONVERGE technology

In respect to the geographical limitations, Northern Sweden and Italy are assumed as plant locations for the CONVERGE scenarios as it evaluates both the wooden biomass and exhausted olive pomace, respectively. It is assumed that the plant lifetime is 20 years. One ton of bio-methanol was set as FU in the present investigation.

The environmental results for the three bio-methanol manufacture scenarios via the CONVERGE technology are presented in Table 3.2-4. The findings of the LCA study points towards Case 1 as the most sustainable scenario among all evaluated cases. Case 1 exhibits the lowest impact in six out of a total of nine environmental categories (i.e., FEP, ODP, FDP, HTP, MDP and POFP). In addition, Case 1 ranks second in GWP and TETP impact. At the opposite end, Case 3 comes as the worst-case scenario as it records the highest values in seven impact indicators. In Case 3, it is presumed that the main facility is located in Italy and that exhausted olive pomace is employed as biomass source. Therefore, the main reason behind the high environmental score is represented by the electricity generation process, as Italy’s electricity grid mix is for the most part based on fossil resources. Another cause of the increase impact would be the supplementary biomass required as additional fuel within the process.

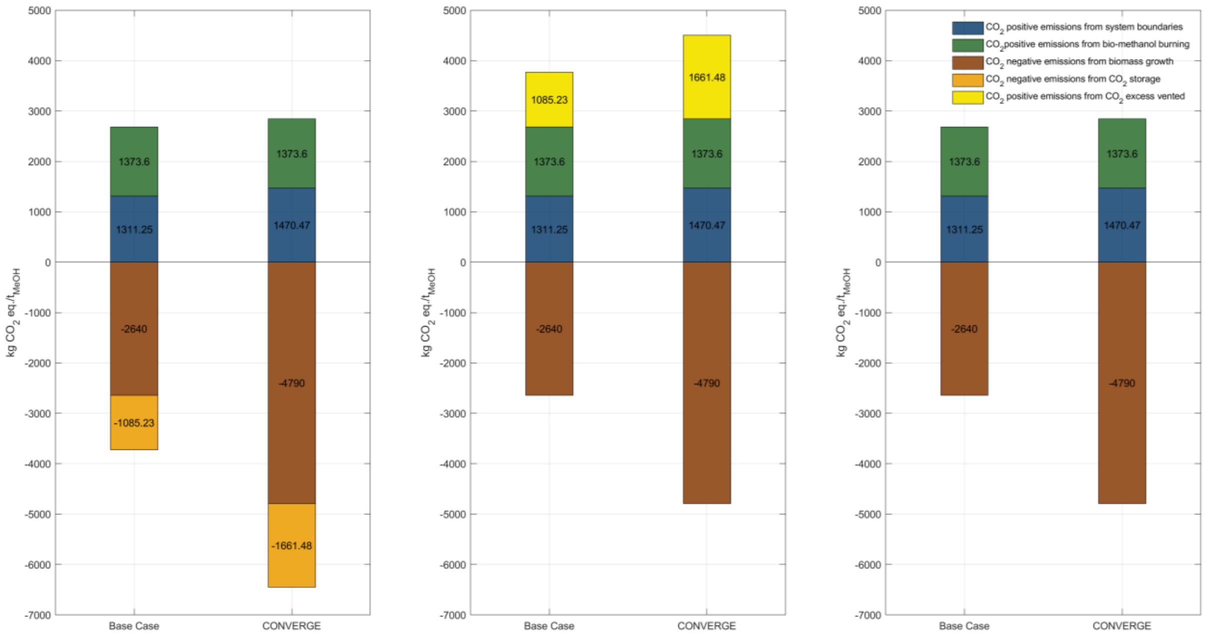
Table 3.2-4. LCA results for the CONVERGE scenarios

KPI	Units	Case 1	Case 2	Case 3
GWP	kg CO_2 eq./t_{MeOH}	1,436.19	1,288.04	2,511.22
FEP×10^3	kg P eq./t_{MeOH}	4.15	7.69	8.73
ODP×10^9	kg CFC-11 eq./t_{MeOH}	2.86	7.09	5.85
FDP	kg oil eq./t_{MeOH}	31.24	32.39	263.86
FETP	kg 1,4-DB eq./t_{MeOH}	0.28	0.26	0.07
HTP	kg 1,4-DB eq./t_{MeOH}	13.58	13.98	22.53
MDP	kg Fe eq./t_{MeOH}	4.95	5.05	10.08
POFP	kg NMVOC/t_{MeOH}	0.28	0.29	1.05
TETP×10^3	kg 1,4-DB eq./t_{MeOH}	7.93	7.69	19.34

However, negative emissions are obtained if all emission sources are taken into account and quantified. The total GWP score after considering the emissions related to the biomass growth, the CO_2 emissions released from processes within the system's boundaries, CO_2 released by the combustion of bio-methanol, and several scenarios regarding the separated CO_2 from AGR (i.e., in the Base Case) and from SER and CO_2 compression stages (i.e., in the CONVERGE process) is displayed in Figure 3.2-2.

The amount of CO_2 removed from AGR, and from SER and CO_2 compression in the Base Case and CONVERGE process, respectively, could be considered as negative emissions if stored. Therefore, an additional amount of 1,085.23 kg CO_2 eq./t_{MeOH} for the Base Case and 1,661.48 kg CO_2 eq./t_{MeOH} in the CONVERGE process might result as negative emissions. The quantity of CO_2 released from the combustion of one ton of bio-methanol is 1,373.60 kg CO_2 eq./t_{MeOH}. The overall amount of CO_2 emissions will reach 1,040.39 kg CO_2 eq./t_{MeOH} and -3,607.72 kg CO_2 eq./t_{MeOH} in the Base Case and CONVERGE technology, respectively. One can observe that the CONVERGE process exhibits a better environmental performance in comparison to the benchmark scenario.

Two additional alternatives may be thought of, depending on the fate of the CO_2 removed from the AGR section, as well from the SER section and CO_2 compression. On the one hand, if the captured CO_2 is discharged into the atmosphere (i.e., see Figure 3.2-2,b), a total of 1,130.08 kg CO_2/t_{MeOH} and -284.45 kg CO_2 eq./t_{MeOH} would be obtained in the Base and CONVERGE case, respectively. The negative score in the CONVERGE scenario are due to a higher quantity of biomass required within the process. On the other hand, the captured CO_2 might be considered as a valuable by-product and, therefore, it can be sold or used as raw material (i.e., see Figure 3.2-2,c). As a consequence, the emissions released from the AGR section or from SER section and CO_2 compression may be deemed as being close to zero. These assumptions result in a total of about 44.85 kg CO_2 eq./t_{MeOH} and -1,945.93 kg CO_2/t_{MeOH} in the benchmark and CONVERGE case, respectively.



a) b) c)

Figure 3.2-2. Detailed GWP impact indicator considering all emission sources: a) excess CO_2 is sent to storage; b) excess CO_2 is released into the atmosphere; c) excess CO_2 is modelled as intermediate component, ready to be utilized as raw material in another process

As an overall conclusion, the CONVERGE system outperforms the Base Case in terms of environmental performance, regardless of whether the captured CO_2 is sent to storage, sold or discharged into the atmosphere.

3.2.5. Environmental evaluation of biodiesel production using life cycle assessment methodology

The goal of the present study is to assess the environmental impact of several biodiesel production scenarios following both the traditional and the innovative methods. Mass and energy balance data acquired from the modelling and simulation section are used in the LCI stage. The function of the system consists of the manufacture of 13,333.33 kg/h of biodiesel, which represent an annual production of 100,000 tons. One ton of biodiesel was chosen as FU. Regarding the impact assessment method, the present work is addressed to a midpoint level, therefore the ReCiPe method under the hierarchist perspective (H) was utilized.

The current investigation is a cradle-to-gate LCA study since it examines processes from raw materials extraction and supply (i.e., limestone supply chain, oil supply chain, etc.) up to the biodiesel manufacture. The boundaries of the system are displayed in Figure 3.2-3.

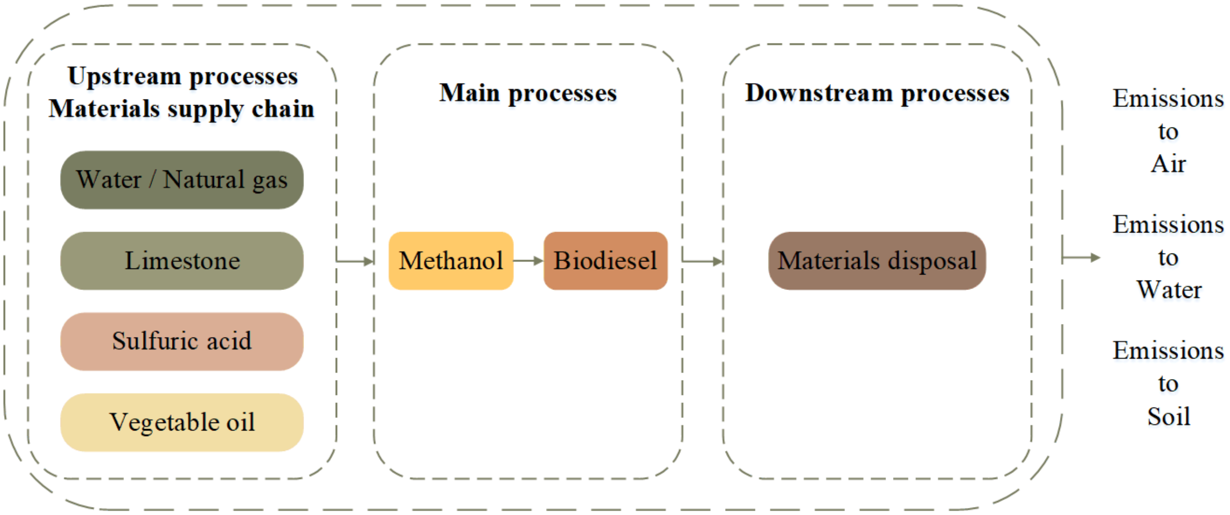


Figure 3.2-3. System boundaries of the investigated scenarios

Since the assumptions made when carrying out an LCA investigation directly impact the outcome, it is recommended to perform a scenario analysis to determine their effect on the performance of the system [32]. A scenario analysis was performed in the current study targeting the power source for the water electrolysis process, therefore, the analysis addresses Cases 1 to 4. In the first case, electricity is generated from solid biomass in either a CHP plant or a biomass-specific power plant. Second, natural gas will serve as the main power source in a CHP plant or a natural gas specific power plant. The supply chain both for solid biomass and natural gas take into account the manufacture of the energy carrier, as well as the processing steps and transport of the fuels to the power plant. The quantity of oil required for biodiesel production is the same for all conventional cases, however it differs from the amount required for the intensified approach.

The outcome of the environmental investigation is reported in Table 3.2-5. By examining the conventional and the intensified methods for the cases employing CO_2 and H_2 as raw materials for biodiesel production and biomass as electricity source for water electrolysis process (i.e., Cases 1 and 3), it can be observed that the innovative approach (i.e., Case 3) leads to higher scores in all evaluated categories. The opposite takes place when natural gas is utilized as feedstock (i.e., Case 5 and Case 6). Six out of nine impact categories (i.e., GWP, FEP, ODP, MDP, POFP and TETP) display lower values in the intensified route compared to the traditional method. Although the difference is not large, there is still a difference in the favor of the intensified path.

Table 3.2-5. LCA results as according to the ReCiPe method

KPI	Units	Cases investigated					
		Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
GWP	kg CO_2 eq./$t_{biodiesel}$	360.40	942.17	390.10	1,114.70	370.55	370.43
FEP×10^3	kg P eq./$t_{biodiesel}$	6.27	4.32	6.72	4.29	4.61	4.58
ODP×10^9	kg CFC-11 eq./$t_{biodiesel}$	7.80	7.05	8.32	7.43	8.77	8.24
FDP	kg oil eq./$t_{biodiesel}$	374.04	610.50	374.10	668.62	439.46	447.61
FETP	kg 1,4-DB eq./$t_{biodiesel}$	0.23	0.20	0.24	0.21	0.24	0.24
HTP	kg 1,4-DB eq./$t_{biodiesel}$	129.75	23.58	156.03	23.79	26.14	26.20
MDP	kg Fe eq./$t_{biodiesel}$	2.25	1.88	2.47	2.01	1.98	1.92
POFP	kg NMVOC/$t_{biodiesel}$	3.18	1.51	3.70	1.61	1.10	1.04
TETP×10^2	kg 1,4-DB eq./$t_{biodiesel}$	4.11	0.90	4.91	0.91	0.97	0.95

In addition, when looking at the conventional pathway (i.e., Case 1 and Case 5), a slight advantage may be observed in the favor of natural gas usage as raw material. Lower impact for FEP, HTP, MDP, POFP and TETP categories can be seen in Case 5, with a large difference for the HTP impact indicator. The same conclusion can be drawn when examining the innovative scenarios (i.e., Case 3 and Case 6). Seven out of a total of nine impact indicators (i.e., GWP, FEP, ODP, HTP, MDP, POFP and TETP) present lower values in Case 6, thus when natural gas is utilized as feedstock. The largest difference is registered in terms of HTP impact category, with the use of CO_2 and H_2 leading to an approximately six times higher impact (i.e., 156.03 kg 1,4-DB eq./$t_{biodiesel}$ in Case 3 vs. 26.20 kg 1,4-DB eq./$t_{biodiesel}$ in Case 6).

As stated before, the use of natural gas as power source for the electrolytic H_2 generation was investigated as well (i.e., Case 2 and Case 4). This approach resulted in the lowest impact scores in five or even six environmental indicators, but significantly affected both the GWP and FDP categories. For instance, Case 1 records 2.6 times lower GWP score in comparison to Case 2 (i.e., 360.40 kg CO_2 eq./$t_{biodiesel}$ in Case 1 vs. 942.17 kg CO_2 eq./$t_{biodiesel}$ in Case 2). The difference is higher when examining Case 3 and Case 4, with 390.10 kg CO_2 eq./$t_{biodiesel}$ generated in Case 3 vs. 1,114.70 kg CO_2 eq./$t_{biodiesel}$ released in Case 4. In regard to the FDP indicator, Case 1 and Case 3 record the smallest values, 374.04 kg oil eq./$t_{biodiesel}$ and 374.10 kg oil eq./$t_{biodiesel}$, while Case 2 and Case 4 come as the scenario with the highest scores, 610.5 kg oil eq./$t_{biodiesel}$ and 668.62 kg oil eq./$t_{biodiesel}$, respectively.

As a general conclusion, the most important sub-processes that exhibit the highest influence on the HTP impact category are the oil supply chain, electricity generation for water electrolysis process and MeOH synthesis, as well the sulfuric acid production and WWTP.

3.3. Investigation of high value chemicals production

The scientific community examined several methods to lessen the environmental implications caused by the ever-increasing power consumption [69]. Improving the energy efficiency, utilization of RESs or the integration of CCUS systems are among the proposed initiatives [70]. The aforementioned approaches can assist in achieving the Paris Agreement’s targets, which aim to keep the increase in global surface temperature below 2°C above the pre-industrial levels [71]. With the purpose of reducing the GHG emissions between 80% to 95% compared to 1990 levels by 2050, CCUS technologies need to be installed in over 50% of the fossil fuel power plants [72]. The implementation of the CCUS systems is regarded as one of the most effective medium-term options for reducing CO_2 emissions [73], given that it not only decreases the CO_2 release but also makes use of the carbon source [74].

As stated by Atsbha and collaborators, CCS and CCU are the two primary CCUS approaches [75]. On the one side, CCS refers to the CO_2 capture, compression, transportation and sequestration to avoid its release into the atmosphere [76]. On the other side, according to Salehi and collaborators [77] and confirmed by Müller and co-authors [78], CCU allows the utilization of captured CO_2 towards the production of high-priced chemicals. Indirect CO_2 emissions are released during the transport and storage steps of the CCS approach, reducing system’s efficiency and affecting process’ costs, hence eventually causing a more challenging implementation of CCS systems [79]. On a broader perspective, the use of the CCU method encourages both GHG mitigation and CO_2 utilization [80], while making valuable contributions in the reduction of energy and raw material consumption [81].

The key novel aspects of the current chapter consist of the techno-environmental comparison between four valuable MeOH derived products (i.e., formalin, DME, MTBE and biodiesel) through modelling and simulation, as well environmental evaluation following the LCA methodology. Technical and environmental impact indexes are considered when comparing the assessed scenarios, thus the purpose of the present work is to evaluate and compare various CO_2 utilization routes.

3.3.1. Plant configurations

In the context of the need for green fuel alternatives and sustainable technologies, the potential technological and environmental advantages of direct CO_2 hydrogenation for MeOH production and its subsequent conversion to high value chemicals are examined. With respect to valuable MeOH derived products, formalin, DME, MTBE and biodiesel production are assessed in the current chapter.

Case 1. MeOH production via direct CO_2 hydrogenation coupled with Formalin production

Case 2. MeOH production via direct CO_2 hydrogenation coupled with DME production

Case 3. MeOH production via direct CO_2 hydrogenation coupled with MTBE production

Case 4. MeOH production via direct CO_2 hydrogenation coupled with alkali Biodiesel production

For green methanol production by direct CO_2 hydrogenation, water electrolysis process is employed for H_2 generation according to the study performed by Tijani and co-authors [82]. Based on the level of development and commercial availability of the amine-based chemical scrubbing system [83], a carbon capture unit using MDEA as solvent was integrated within a cement plant to provide the necessary CO_2.

3.3.2. Process modelling and simulation and main design assumptions

The investigated cases were modelled and simulated by means of CHEMCAD version 7 [26]. The key performance indexes computed to perform the technical evaluation are presented in Table 3.3-1. All evaluated scenarios took into account a CCR of 90%, while targeting a productivity of 1,000 kg/h of MeOH derived product. Case 2 and Case 1 demand the highest amount of MeOH, 1,401.55 kg/h and 1,320.17 kg/h, respectively. Case 3 and Case 4 require three to ten times less MeOH when compared to the first two scenarios (e.g., 440.08 kg/h and 118.41 kg/h in Case 3 and Case 4, respectively).

Table 3.3-1. Technical evaluation of investigated cases

Parameter	Unit	Case 1	Case 2	Case 3	Case 4
CO_2 capture rate	%	90	90	90	90
CO_2 flowrate	kg/h	2176.36	2311.77	725.89	195.32
H_2 flowrate	kg/h	297.44	315.95	99.21	26.70
O_2 flowrate	kg/h	2379.51	2527.56	793.65	213.55
MeOH flowrate	kg/h	1320.17	1401.55	440.08	118.41
Waste water flowrate	kg/h	894.93	1348.74	311.37	99.14
Electricity consumption	MW_e/t	17.74	18.75	5.89	1.72
Product purity	wt.%	32.38	99.44	99.92	99.97
Product rate	kg/h	1000	1000	1000	1000

Direct CO_2 hydrogenation is employed for green sustainable MeOH production, meaning that the quantities of raw materials utilized (i.e., CO_2 and H_2) are directly related to the amount of MeOH produced. As one can observe, Case 2 and Case 1 demand both the largest amount of CO_2 and the largest quantities of H_2. Even though Case 2 and Case 1 demand the largest amount of CO_2 and H_2, it should be noticed that, besides the previously mentioned raw materials, MTBE (Case 3) and biodiesel (Case 4) production also require a mixture of butene and high amount of oil, which exhibits a high influence on the overall biodiesel production cost, contributing with over 70% to the total share [84].

Oxygen comes as a by-product of the water electrolysis process. As the amount of O_2 is directly related to the H_2 requirements, the largest quantities are generated in Case 2 and Case 1, 2,5227.56 kg/h and 2,379.51 kg/h, respectively. On the one hand, the two cases could take advantage of the amount of O_2 produced by further using it in another section or process, while on the other hand, much more power has to be used. Case 2 (i.e., DME production) demands the highest power consumption, 18.75 MW_e/t, followed by Case 1 (i.e., formalin production) with 17.74 MW_e/t. Case 3 and Case 4 need up to ten times less electricity compared to the first two evaluated cases (i.e., 5.89 MW_e/t in Case 3 and 1.72 MW_e/t in Case 4). The electric requirements of the water electrolysis process exhibit the greatest impact on overall power consumption, accounting for at least 85% share (Case 4).

In regard to primary product purity, over 99% purity is achieved in all investigated scenarios, except the 33 wt.% formalin solution obtained in Case 1. In addition, high-purity glycerol (i.e., over 99%) is produced following the biodiesel production process.

3.3.3. Environmental evaluation using life cycle assessment methodology

The present study aims to evaluate the environmental burden of MeOH production via direct CO_2 hydrogenation process and its subsequently conversion to valuable derivatives (i.e., formalin, DME, MTBE and biodiesel). The production of one ton of MeOH derived product was chosen as FU.

The present research represents a cradle-to-gate environmental evaluation as it includes: catalyst supply chain, power production and utilization, input and output of main production processes and waste disposal. Figure 3.3-1 better illustrates the processes considered within the boundaries of the system.

Since the assumptions made during the LCIA stage significantly affect the results, it is best practice to conduct either a sensitivity or scenario analysis to examine and highlight the impact of the primary contributors [85]. The electric source of the water electrolysis process plays a prominent role in the MeOH production, thus a scenario analysis targeting the power supply for H_2 production was conducted. The first scenario assumes that the electricity grid mix provides the required power, while based on scientific literature and aiming to address a more sustainable process, wind and hydro power were considered as well. In addition, the employment of renewable power sources both for the production of H_2 and MeOH was also investigated.

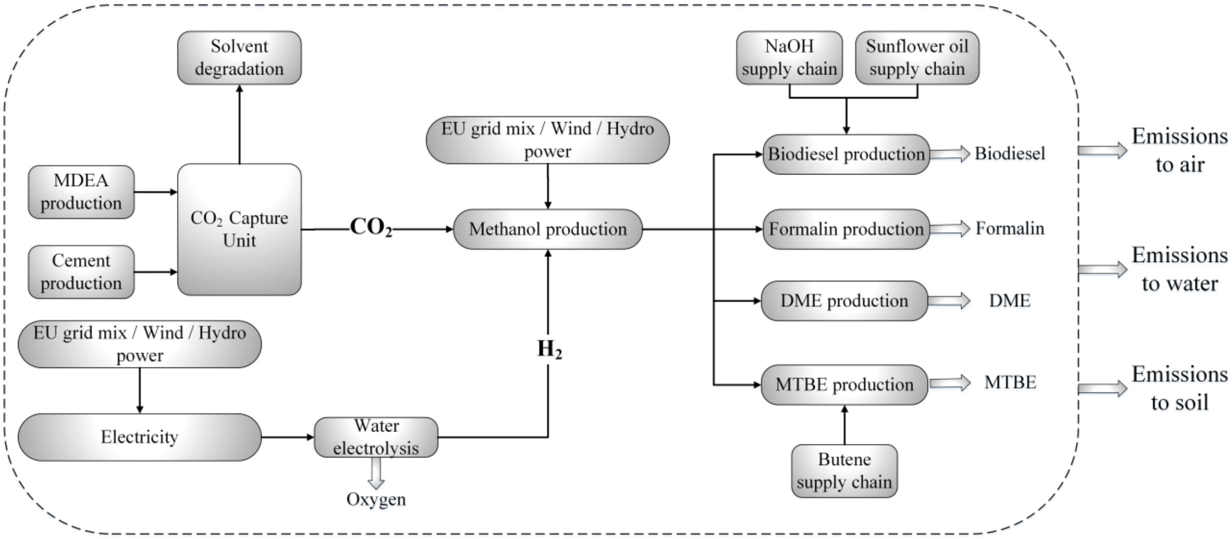


Figure 3.3-1. System boundaries of the LCA investigation

The environmental analysis' findings of the scenario considering the electricity import from the grid mix both for H_2 and MeOH synthesis are presented in Table 3.3-2.

Table 3.3-2. LCA results corresponding to grid mix import for H_2 and MeOH production

Parameter	Unit	Case 1	Case 2	Case 3	Case 4
GWP	kg CO_2 eq./t	8,529.72	9,021.31	7,273.83	884.47
FEP×10^2	kg P eq./t	2.04	2.21	1.60	0.45
ODP×10^7	kg CFC-11 eq./t	3.51	3.72	1.18	0.34
FDP	kg oil eq./t	2,017.05	2,132.40	3,739.19	368.54
FETP	kg 1,4-DB eq./t	2.79	2.98	2.14	0.35
HTP	kg 1,4-DB eq./t	302.60	220.34	239.32	30.50
MDP	kg Fe eq./t	55.84	59.12	25.34	5.80
POFP	kg NMVOC/t	70.99	14.88	47.22	2.08
TETP×10^2	kg 1,4-DB eq./t	20.90	14.50	8.31	1.72

Case 2 (i.e., DME production) shows the highest impact in five out of nine impact indicators (i.e., GWP, FEP, ODP, FETP and MDP). Case 1 (i.e., formalin manufacture) registers the highest score in regards to HTP, POFP and TETP, while Case 3 (i.e., MTBE production) shows the highest FDP impact. From the technical evaluation (see Table 3.3-1) and previously reported LCA results (see Table 3.3-2) one can observe that the GWP value is directly related to the H_2 demand. DME synthesis requires the largest quantity of MeOH, demanding as well the highest energy consumption. Formalin production displays similar energy requirements as DME manufacture, thus justifying the increased GWP impact. For the production of MTBE, even though the energy demand is not as high as in the previous cases, the butene supply chain comes as the main contributor to the total GWP score (over 60% share of the overall score). Case 4 (i.e., biodiesel production) shows the lowest impact in all nine evaluated impact categories, registering approximately ten times lower score with respect to GWP, FDP and HTP when compared to the worst-case scenario (i.e., 9,021.31 kg CO_2 eq./t vs. 884.47 kg CO_2 eq./t, 3,739.19 kg oil eq./t vs. 368.54 kg oil eq./t and 302.60 kg 1,4-DB eq./t vs. 30.50 kg 1,4-DB eq./t, respectively). When comparing either Case 1, Case 2 or Case 3 to Case 4, the power needs for H_2 generation and the butene supply chain in Case 3 explain for the drastically different GWP, FDP and HTP scores achieved.

Renewable energy is growing popularity, therefore, based on relevant scientific literature [86–89], the integration of wind power within the water electrolysis process was investigated. The outcome of the LCA study is summarized in Table 3.3-3.

Table 3.3-3. LCA results corresponding to wind-powered H_2 production

Parameter	Unit	Case 1	Case 2	Case 3	Case 4
GWP	kg CO_2 eq./t	1,309.95	1,352.31	4,865.82	236.54
FEP×10^3	kg P eq./t	2.79	3.37	10.10	2.91
ODP×10^8	kg CFC-11 eq./t	2.48	2.51	0.91	0.51
FDP	kg oil eq./t	183.37	184.62	3,127.60	203.98
FETP	kg 1,4-DB eq./t	0.37	0.41	1.33	0.13
HTP	kg 1,4-DB eq./t	144.70	52.62	186.65	16.33
MDP	kg Fe eq./t	188.02	199.53	69.43	17.66
POFP	kg NMVOC/t	59.10	2.25	43.25	1.02
TETP×10^2	kg 1,4-DB eq./t	9.34	2.14	4.44	0.68

All four evaluated cases achieve a significantly better environmental performance when employing wind power instead of grid mix for the water electrolysis process. Case 1 and Case 2 register over six times lower GWP effect (i.e., 8,529.72 kg CO_2 eq./t vs. 1,309.95 kg CO_2 eq./t in Case 1 and 9,021.31 kg CO_2 eq./t vs. 1,352.31 kg CO_2 eq./t in Case 2), while Case 4 shows three times decreased impact (i.e., 884. 47 CO_2 eq. vs. 236.54 CO_2 eq.). In the case of MTBE manufacture, the butene supply chain brings a considerable contribution to the overall GWP score, but the utilization of wind power sources decreased the GWP score by 1.5 times. Apart from the GWP impact, significant reductions (i.e., about one order of magnitude) are registered as well in the FEP, ODP and FDP impact categories. For example, in the EU grid mix scenario, the FDP score registered either in Case 1 or Case 2 is about 2,000 kg oil eq./t, while in the wind-power scenario the impact score drops to 184 kg oil eq./t. The increased FDP impact in Case 3 is due to the butene supply chain, while the oil supply chain, in addition to the electricity requirements, plays an important role in Case 4.

In the light of the fact that a large number of countries target between 40% to 50% reduction in the carbon footprint [90], and current policy initiatives aim towards a 48% share of RESs by 2050 [72], the authors examined the integration of wind power sources both for H_2 and MeOH manufacture (see Table 3.3-4).

Table 3.3-4. LCA results corresponding to wind power use for H_2 and MeOH production

Parameter	Unit	Case 1	Case 2	Case 3	Case 4
GWP	kg CO_2 eq./t	858.20	872.45	4715.15	195.98
FEP×10^3	kg P eq./t	1.69	2.20	9.76	2.81
ODP×10^9	kg CFC-11 eq./t	4.42	3.45	2.29	3.28
FDP	kg oil eq./t	68.63	62.75	3089.33	193.68
FETP	kg 1,4-DB eq./t	0.22	0.25	1.28	0.12
HTP	kg 1,4-DB eq./t	134.82	42.13	183.36	15.44
MDP	kg Fe eq./t	196.30	208.32	72.19	18.40
POFP	kg NMVOC/t	58.36	1.46	43.00	0.95
TETP×10^2	kg 1,4-DB eq./t	8.61	1.37	4.20	0.61

The outcome of this scenario analysis shows a decrease score in all investigated impact categories in either of the four evaluated cases. Case 4 (i.e., biodiesel production) provides the best results in six out of nine impact indicators (i.e., GWP, FETP, HTP, MDP, POFP and TETP). Case 1 and Case 2 (i.e., formalin and DME production, respectively) show a GWP reduction from over 1,300 kg CO_2 eq./t to roughly 860 kg CO_2 eq./t. In the third case scenario (i.e., MTBE production), the butene supply chain continues to provide the largest impact in regard to either GWP or FDP impact. The ODP indicator shows ten times decreased impact in either of the four examined cases. Case 3 displays the best results and it is followed by Case 4 and Case 2, respectively (i.e., 2.29×10^{-9} kg CFC-11 eq./t in Case 3 vs. 3.28×10^{-9} kg CFC-11 eq./t in Case 4 vs. 3.45×10^{-9} kg CFC-11 eq./t in Case 2). Compared to previously examined scenarios (i.e., electricity import from grid mix and wind-powered H_2 generation), the employment of wind power sources both for H_2 and MeOH manufacture led to an increase MDP score in all cases due to the installation of the wind turbines (e.g., for the best-case scenario, Case 4, 5.80 kg Fe eq./t vs. 17.66 kg Fe eq./t vs. 18.40 kg Fe eq./t).

According to previously presented results, Case 1 outperforms Case 2 in terms of GWP, FEP, ODP, FDP, FETP and MDP, if wind power sources are used just for H_2 production. The opposite occurs when employing wind power sources both for H_2 and MeOH manufacture. Case 2 (i.e., DME production) comes as second best-case scenario, outperforming Case 1 in five of a total of nine impact indicators studied (i.e., ODP, FDP, HTP, POFP and TETP). The high differences in the POFP category may be attributed to the formalin impact (i.e., 58.36 kg NMVOC/t in Case 1 vs. 1.46 kg NMVOC/t in Case 2).

The type of RESs that can be leveraged to achieved carbon neutrality and cut GHG emissions substantially depend upon the geographical context. Considering a prior investigation conducted by the authors [91], the current research addresses as well to the use of hydro power for H_2 and MeOH production.

Table 3.3-5. LCA results corresponding to hydro power use for H_2 production

Parameter	Unit	Case 1	Case 2	Case 3	Case 4
GWP	kg CO_2 eq./t	1267.37	1307.08	4851.62	232.72
FEP×10^3	kg P eq./t	2.55	3.11	10.08	2.89
ODP×10^8	kg CFC-11 eq./t	2.38	2.41	0.88	0.50
FDP	kg oil eq./t	151.77	151.06	3117.06	201.15
FETP	kg 1,4-DB eq./t	0.34	0.38	1.32	0.13
HTP	kg 1,4-DB eq./t	129.92	36.92	181.73	15.01
MDP	kg Fe eq./t	95.89	101.67	38.70	9.39
POFP	kg NMVOC/t	58.95	2.09	43.19	1.00
TETP×10^2	kg 1,4-DB eq./t	8.63	1.39	4.20	0.61

The findings of the environmental analysis when employing hydro power sources to supply the electricity requirements for the water electrolysis process are slightly better compared to those obtained following the wind-powered scenario. The highest reduction is observed in the MDP indicator, with about 50% lower score achieved in either of the four investigated cases. Case 4 performs best in seven out of nine impact categories studied (i.e., GWP, ODP, FETP, HTP, MDP, POFP and TETP). At the opposite side, Case 3 comes as the worst-case scenario leading to the highest impact in GWP, FEP, FDP, FETP and HTP. The butene supply chain is the primary cause of the higher GWP, FDP and HTP score. Case 1 and Case 2 display similar results, however, a slightly better performance in terms of GWP, FEP, ODP, FETP and MDP is achieved in Case 1.

The scenario accounting for the integration of hydro power sources both for H_2 and MeOH manufacture was investigated as well. The environmental results obtained in this scenario are reported in Table 3.3-6.

Table 3.3-6. LCA results corresponding to hydro power use for H_2 and MeOH production

Parameter	Unit	Case 1	Case 2	Case 3	Case 4
GWP	kg CO_2 eq./t	812.96	824.40	4700.06	191.93
FEP×10^3	kg P eq./t	1.43	1.92	9.68	2.79
ODP×10^9	kg CFC-11 eq./t	3.34	2.30	1.93	3.18
FDP	kg oil eq./t	35.06	27.09	3078.13	190.67
FETP	kg 1,4-DB eq./t	0.19	0.22	1.27	0.12
HTP	kg 1,4-DB eq./t	119.12	25.45	178.12	14.04
MDP	kg Fe eq./t	98.40	104.33	39.54	9.62
POFP	kg NMVOC/t	58.20	1.29	42.95	0.94
TETP×10^2	kg 1,4-DB eq./t	7.86	0.57	3.95	0.55

The utilization of hydro power both for water electrolysis, as well for MeOH production resulted in the best environmental performance for each of the examined cases. Compared to the use of wind power for H_2 and MeOH synthesis, the MDP score is approximately two times lower when using hydro sources. As previously noted, the butene supply chain is the key contributor to the increased GWP, FDP and HTP impact scores in Case 3. The increased HTP and POFP effect in Case 1 is mostly attributed to formalin emissions.

As in the previously assessed scenario (i.e., wind power both for H_2 and MeOH synthesis), the best environmental performance is obtained in Case 4, while Case 3 comes as the worst-case scenario with the highest impact in terms of GWP, FEP, FDP, FETP and HTP. Case 1 and Case 2 present similar environmental performance, except the TETP impact score (i.e., 7.86 kg 1,4-DB eq./t in Case 1 vs. 0.57 kg 1,4-DB eq./t in Case 2).

3.4. Investigation of fertilizer production

Ammonia (NH_3) is amongst the most widely produced chemicals worldwide [92], having a variety of applications in sectors such as fertilizer production, explosives, plastics and pharmaceuticals [93]. In 2021, global NH_3 production reached 168 million tons, with 2% yearly growth projected [94] owing to the ever-increasing worldwide population and food production, which will drive up demand for fertilizer [95]. China is the largest ammonia producer, accounting for 31.4% of total production, followed by Russia (i.e., 10%), the United States (i.e., 8.9%) and India (i.e., 7.8%) [96]. Ammonia has recently attracted interest as a possible energy carrier or H_2 storage medium due to its three times higher volumetric energy density compared to H_2 [97], as well as its advantageous transportation and storage characteristics [98]. However, the main utilization of NH_3 (i.e., over 80% of global output) consists of fertilizer production [99], particularly in the production of urea, ammonium nitrate and ammonium phosphate [100]. As stated by Walling and Vaneeckhaute, urea and ammonium nitrate supply nearly 75% of the nitrogen fertilizers consumed worldwide [101].

Therefore, fertilizer production is of paramount importance to modern society and, with the increasing adoption of renewable resources, it has the potential to play a crucial role in mitigating climate change. The current study aims to evaluate and determine the potential environmental benefits of utilizing green ammonia coupled with the production of both urea and ammonium nitrate compared to conventional process technologies. As stated before, there have been limited studies regarding fertilizer production from an LCA perspective. The key novelty aspects brought by the present study consist of a technical and environmental performance comparison between green and blue ammonia production, both paths coupled with urea and ammonium nitrate manufacture.

3.4.1. Plant configuration for urea and ammonium nitrate production

In an effort to support the rising global food demand and help achieve the Net Zero Emissions scenario by 2050, green sustainable ammonia production routes for urea and ammonium nitrate fertilizers are explored. Therefore, the following pathways are investigated in the current chapter:

Case 1. Traditional ammonia manufacture coupled with either urea or ammonium nitrate production;

Case 2. Wind-powered H_2 generation for green ammonia production coupled with either urea or ammonium nitrate production processes;

Case 3. Hydro-powered H_2 generation for green ammonia production coupled with either urea or ammonium nitrate production processes;

Case 4. Photovoltaic-powered H_2 generation for green ammonia production coupled with either urea or ammonium nitrate production processes;

Case 5. Nuclear-powered H_2 generation for green ammonia production coupled with either urea or ammonium nitrate production processes.

Considering that the SMR process with the employment of the reactive gas-liquid carbon capture system is the most popular method for H_2 manufacture for ammonia production through the Haber-Bosch process, Case 1 is regarded as the benchmark. In Cases 2 through 5, green ammonia is produced via water electrolysis using a variety of RESs, including wind (i.e., Case 2), hydro (i.e., Case 3), PV (i.e., Case 4) and nuclear (i.e., Case 5). All scenarios take into account an ASU for N_2 production, and the synthesized ammonia is further used for either urea or ammonium nitrate production processes.

3.4.2. Process modelling and simulation and main design assumptions

The key technical performance indexes for urea and ammonium nitrate manufacture under the evaluated cases are displayed in Table 3.4-1. All examined sustainable urea production cases show lower raw materials specific consumption when compared to the traditional approach which employs SMR for H_2 synthesis (i.e., 1.71 times less water and 5.43 times lower air quantities). It should be noted that Case 1 requires a supplementary 517.76 kg of natural gas to generate the much-needed H_2 for the ammonia synthesis, while demand for intermediate materials remained consistent throughout all scenarios. With regard to the power consumption in Case 1, 186.12 kW out of the total required power of 436.85 kW is produced by the SMR section and approximately 250 kW is imported from the grid mix. On the other hand, each alternative urea manufacture scenario (i.e., Cases 2 to 5) demands more electricity than the traditional pathway, primarily because of the water electrolysis process.

For ammonium nitrate production, roughly 93% of the total natural gas needed in Case 1 is utilized within the SMR process, while the rest is demanded in the main ammonium nitrate production process. A small amount of natural gas is as well required in the sustainable ammonium nitrate production scenarios. In regards to the specific water consumption, Case 1 shows a demand of 2,975.81 kg, half being employed within the SMR process and the rest for nitric acid production. In contrast, Cases 2 to 5 demand about 900 kg within the water electrolysis process and an identical amount as in Case 1 for the production of nitric acid. Air requirement is 1.43 times higher in Case 1 compared to all green ammonium nitrate scenarios. In terms of specific energy consumption, approximately 126 kW out of the total required 480 kW is internally supplied within the SMR section, while the remaining is imported from the grid. Similar to green urea synthesis, over 90% of electricity utilized in the alternative ammonium nitrate production cases is consumed for water electrolysis, resulting in an energy requirement significantly larger than the traditional pathway.

Table 3.4-1. Technical performance indices for the investigated scenarios

Parameter	**Unit of measure**	**Case 1**	**Case 2**	**Case 3**	**Case 4**	**Case 5**
Product name		Urea				
Product quantity	kg	1,000	1,000	1,000	1,000	1,000
Product purity	%	99.90	99.90	99.90	99.90	99.90
Raw materials						
Natural gas	kg	517.76	-	-	-	-
Water	kg	2,294.09	1,340.67	1,340.67	1,340.67	1,340.67
Air	kg	4,959.53	912.17	912.17	912.17	912.17
Intermediate materials						
N_2	kg	689.27	689.27	689.27	689.27	689.27
H_2	kg	148.90	148.90	148.90	148.90	148.90
NH_3	kg	810.20	810.20	810.20	810.20	810.20
CO_2	kg	1,127.78	1,127.78	1,127.78	1,127.78	1,127.78
Total electricity consumption	kW	436.84	8,421.59	8,421.59	8,421.59	8,421.59
Internal electric power	kW	186.12	-	-	-	-
External electric power	kW	250.72	8,421.59	8,421.59	8,421.59	8,421.59

Table 3.4-1. continued

Parameter	Unit of measure	Case 1	Case 2	Case 3	Case 4	Case 5
Product name				Ammonium nitrate		
Product quantity	kg	1,000	1,000	1,000	1,000	1,000
Product purity	%	98.58	98.58	98.58	98.58	98.58
Raw materials						
Natural gas	kg	372.55	25.03	25.03	25.03	25.03
Water	kg	2,975.81	2,335.81	2,335.81	2,335.81	2,335.81
Air	kg	8,960.66	6,244.41	6,244.41	6,244.41	6,244.41
Steam	kg	50.43	50.43	50.43	50.43	50.43
Intermediate materials						
N_2	kg	462.77	462.77	462.77	462.77	462.77
H_2	kg	99.97	99.97	99.97	99.97	99.97
NH_3	kg	543.97	543.97	543.97	543.97	543.97
CO_2 captured	kg	644.24	644.24	644.24	644.24	644.24
Total Electricity consumption	kW	480.14	5,930.11	5,930.11	5,930.11	5,930.11
Internal electric power	kW	125.93	-	-	-	-
External electric power	kW	354.21	5,930.11	5,930.11	5,930.11	5,930.11

3.4.3. Environmental evaluation using life cycle assessment methodology

The current research aims to evaluate and compare the environmental burden of several green ammonia production pathways that are coupled with green urea and ammonium nitrate production processes against traditional technologies. The function of the system consists of an annual production of 450,000 tons of urea and ammonium nitrate, respectively, representing an hourly production of 57 tons of product. One ton of urea and ammonium nitrate, respectively, is considered as FU. The present study represents a cradle-to-gate LCA since the following processes are considered within the system boundaries: i) upstream processes: N_2 supply through ASU, H_2 generation by water electrolysis and SMR process, electricity supply chain; ii) main processes: ammonia manufacture and subsequent utilization for urea and ammonium nitrate production, respectively; iii) downstream processes: waste disposal and waste water treatment.

The environmental results of the study regarding the urea production are displayed in Table 3.4-2.

Table 3.4-2. LCA results for urea production according to ReCiPe 2016 method

KPI	**Units**	**Cases investigated**				
		Case 1	**Case 2**	**Case 3**	**Case 4**	**Case 5**
GWP	kg CO_2 eq./ t_{urea}	681.84	159.14	134.83	654.16	123.36
FEP×10^3	kg P eq./ t_{urea}	3.20	1.20	1.09	1.96	1.37
ODP×10^5	kg CFC-11 eq./ t_{urea}	5.45	4.37	3.15	15.04	3.77
FDP	kg oil eq./ t_{urea}	628.91	56.32	38.79	204.12	1,854.79
FETP×10^2	kg 1,4-DB eq./ t_{urea}	11.50	2.63	1.45	12.90	34.70
HTP_{cancer}	kg 1,4-DB eq./ t_{urea}	0.18	4.32	2.78	0.44	0.23
$HTP_{non\text{-}cancer}$	kg 1,4-DB eq./ t_{urea}	8.47	13.87	3.58	187.93	34.35
MDP	kg Cu eq./ t_{urea}	0.56	2.75	1.02	17.55	0.25
$PCOF_{ecosystem}$	kg NO_x eq./ t_{urea}	0.37	0.26	0.15	1.26	0.29
$PCOF_{human\ health}$	kg NO_x eq./ t_{urea}	0.37	0.26	0.15	1.21	0.28

All sustainable ammonia production coupled with urea manufacture scenarios (i.e., Cases 2 to 5) present a lower GWP score compared to the benchmark (i.e., Case 1), which registers the highest score (i.e., 681.84 kg CO_2 eq./t_{urea}). By embedding water electrolysis process with RESs, the wind power scenario (i.e., Case 2) results in 4.3 times lower GWP impact, while the utilization of hydro sources (i.e., Case 3) provides a reduction by 5 times. The utilization of nuclear power sources (i.e., Case 5) led to the lowest GWP indicator, with 5.5 times decrease compared to the traditional process. Unlike the other renewable sources scenarios, the use of PVs for power generation does not lead to a substantial reduction in GWP, by and large as a result of the large amount of electricity required for electrolysis-based H_2 synthesis. As a result, the GWP indicator for Case 4 was only slightly less than that of the benchmark scenario (i.e., 654.16 kg CO_2 eq./t_{urea} vs. 681.84 kg CO_2 eq./t_{urea}).

Overall, the environmental performance of the green H_2 manufacture methods is heavily reliant on the choice of renewable power source. Wind, hydro and nuclear power provided considerably better performance compared to the benchmark case. The integration of hydro power as an electric source for the water electrolysis process proves to be the most favourable option among all investigated routes, achieving the best environmental performance in seven out of the total of ten impact categories. However, the utilization of PV panels to provide the electricity for electrolysis displays the worst results in certain impact indicators among all examined cases, scoring the highest values in five out of ten impact categories investigated.

The findings of the environmental investigation of the ammonium nitrate manufacture scenarios are presented in Table 3.4-3. The scenario involving the use of hydro power for sustainable ammonia production coupled with ammonium nitrate manufacture yields the lowest impact scores of all scenarios in six out of the ten impact categories. Compared to Case 1, the use of wind or nuclear power sources provide considerably better environmental performance, with lower impact scores on seven categories, suggesting the potential application of these renewable or carbon free sources for green H_2 generation, wherever feasible.

Table 3.4-3. LCA results for ammonium nitrate production according to ReCiPe 2016 method

KPI	Units	Cases investigated				
		Case 1	Case 2	Case 3	Case 4	Case 5
GWP	kg CO_2 eq./ $t_{ammonium\ nitrate}$	636.13	285.29	268.98	617.52	261.28
FEP×10^4	kg P eq./ $t_{ammonium\ nitrate}$	18.78	5.38	4.66	10.46	6.54
ODP×10^5	kg CFC-11 eq./ $t_{ammonium\ nitrate}$	7.11	6.39	5.57	13.55	5.98
FDP	kg oil eq./ $t_{ammonium\ nitrate}$	467.19	82.87	71.11	182.07	1,289.89
FETP×10^2	kg 1,4-DB eq./ $t_{ammonium\ nitrate}$	8.10	2.15	1.36	9.06	0.24
HTP_{cancer}	kg 1,4-DB eq./ $t_{ammonium\ nitrate}$	0.14	2.92	1.89	0.32	0.18
$HTP_{non-cancer}$	kg 1,4-DB eq./ $t_{ammonium\ nitrate}$	8.01	11.63	4.73	128.45	25.38
MDP	kg Cu eq./ $t_{ammonium\ nitrate}$	0.55	2.02	0.86	11.95	0.34
$PCOF_{ecosystem}$	kg NO_x eq./ $t_{ammonium\ nitrate}$	0.43	0.36	0.29	1.03	0.38
$PCOF_{human\ health}$	kg NO_x eq./ $t_{ammonium\ nitrate}$	0.43	0.36	0.28	0.99	0.37

The largest GWP impact is associated with traditional ammonia and ammonium nitrate synthesis, closely followed by the use of PV panels as the power source (i.e., 636.13 kg CO_2 eq./$t_{ammonium\ nitrate}$ vs. 617.52 kg CO_2 eq./$t_{ammonium\ nitrate}$). Employing wind or hydro power as the renewable electricity sources within the water electrolysis process results in a considerable reduction in GWP score, reaching values 2.3 times lower than Case 1. The lowest impact is achieved when integrating nuclear power as a carbon free energy source for green H_2 production (i.e., 261.28 kg CO_2 eq./$t_{ammonium\ nitrate}$). In Cases 2,3 and 5, a higher GWP score is observed for the green ammonium nitrate manufacture in comparison to the GWP values for sustainable urea synthesis. This can be explained by the fact that additional emissions stem from nitric acid manufacture.

Renewable energy sources such as wind and hydro are highly dependent on geographical location, and not all areas have access to these better-performing options. Therefore, to account for the limited availability of these RESs, PVs are evaluated as an alternative in this analysis. The environmental evaluation proves that the use of PV panels leads in the poorest performance for six out of ten impact categories.

4. Concluding remarks

Key industrial sectors with high energy needs and large amounts of GHG emissions were examined throughout the current thesis. Studies were performed in order to determine whether combining CCUS technologies with different RESs, that rely upon the geographical context, may lower the environmental burden and contribute towards net zero CO_2 emissions. The four investigated industries are cement manufacturing, biofuel production (including bio-methanol and biodiesel), high value chemicals production, as well as fertilizer manufacturing.

To have a thorough understanding of the potential effects of combining carbon capture and utilization methods with the integration of RESs towards decoupling the industry from CO_2 emissions, all case scenarios were examined from technical and environmental perspectives. In addition, the investigated case scenarios were compared against the current production approaches.

The analysis of the available scientific studies revealed that there were few investigations on the topic, particularly in regard to the environmental benefits brought by the integration of membrane separation systems within cement manufacture, use of RD as means of process intensification for biodiesel production, as well from the employment of renewable power sources within fertilizer manufacture. Therefore, the focus of the present study was to evaluate the performance of carbon capture methods along with green power sources based on key technical and environmental performance parameters.

The findings suggested that when comparing the CaL technology against the reactive gas-liquid CO_2 capture (which is currently the state-of-the-art given its technological maturity) and membrane separation, despite being in earlier stages of development and not as commercially available, CaL is proving to be a better alternative. In addition, the integration of RESs in the production of high value chemicals resulted in an overall better environmental performance, particularly when hydro power sources are used.

When taking into account the technological and environmental components of each case scenario that was investigated, integrating carbon capture technology with green power mostly generated a much cleaner and a more sustainable production pathway.

References

[1] Shakhashiri BZ, Bell JA. Climate change and our responsibilities as chemists. Arab J Chem 2014;7:5–9. https://doi.org/10.1016/j.arabjc.2013.10.004.

[2] Wilberforce T, Olabi AG, Sayed ET, Elsaid K, Abdelkareem MA. Progress in carbon capture technologies. Sci Total Environ 2021;761:143203. https://doi.org/10.1016/j.scitotenv.2020.143203.

[3] Yoro KO, Daramola MO. CO_2 emission sources, greenhouse gases, and the global warming effect. Adv. Carbon Capture Methods, Technol. Appl., Woodhead Publishing; 2020, p. 3–28. https://doi.org/10.1016/B978-0-12-819657-1.00001-3.

[4] Li J, Sun S, Sharma D, Ho MS, Liu H. Tracking the drivers of global greenhouse gas emissions with spillover effects in the post-financial crisis era. Energy Policy 2023;174:113464. https://doi.org/10.1016/j.enpol.2023.113464.

[5] IPCC. Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. Geneva: 2023. https://doi.org/10.59327/IPCC/AR6-9789291691647.

[6] IEA - International Energy Agency. The role of CCUS in low-carbon power systems 2020.

[7] IEA - International Energy Agency. Tracking Clean Energy Progress 2023 2023.

[8] IPCC. Climate Change 2014. Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. 2014.

[9] IEA - International Energy Agency. Direct CO_2 Intensity of Cement in the Sustainable Development Scenario, 2014-2030 - Charts - Data & Statistics 2020.

[10] IEA - International Energy Agency. Global Energy Review 2021 2021.

[11] IPCC. Carbon Dioxide Capture and Storage. Contribution of Working Group III of the Intergovernmental Panel on Climate Change. 2005.

[12] Meuleman E, Cottrell A, Ghayur A. Treatment of flue-gas impurities for liquid absorbent-based post-combustion CO_2 capture processes. Absorption-Based Post-combustion Capture of Carbon Dioxide, Elsevier; 2016, p. 519–51. https://doi.org/10.1016/B978-0-08-100514-9.00022-6.

[13] Espatolero S, Romeo LM. Optimization of Oxygen-based CFBC Technology with CO_2 Capture. Energy Procedia 2017;114:581–8. https://doi.org/10.1016/j.egypro.2017.03.1200.

[14] IEA - International Energy Agency. Ammonia Technology Roadmap – Analysis. 2019.

[15] Wang M, Lawal A, Stephenson P, Sidders J, Ramshaw C. Post-combustion CO_2 capture with chemical absorption: A state-of-the-art review. Chem Eng Res Des 2011;89:1609–24. https://doi.org/10.1016/J.CHERD.2010.11.005.

[16] Petrescu L, Chisalita DA, Cormos C-C, Manzolini G, Cobden P, van Dijk HAJ. Life Cycle Assessment of SEWGS Technology Applied to Integrated Steel Plants. Sustainability 2019;11:1825. https://doi.org/10.3390/SU11071825.

[17] Fennell P. Calcium and chemical looping technology: An introduction. Calcium Chem. Looping Technol. Power Gener. Carbon Dioxide Capture, Woodhead Publishing; 2015, p. 3–14. https://doi.org/10.1016/B978-0-85709-243-4.00001-X.

[18] Abad A. Chemical looping for hydrogen production. Calcium Chem. Looping Technol. Power Gener. Carbon Dioxide Capture, Woodhead Publishing; 2015, p. 327–74. https://doi.org/10.1016/B978-0-85709-243-4.00015-X.

[19] Ströhle J, Hilz J, Epple B. Performance of the carbonator and calciner during long-term carbonate looping tests in a 1 MWth pilot plant. J Environ Chem Eng 2020;8:103578. https://doi.org/10.1016/J.JECE.2019.103578.

[20] Chou Y-C, Liu W-H, Hsu H-W. Calcium Looping Carbon Capture Process. Handb. Chem. Looping Technol., John Wiley & Sons, Ltd; 2018, p. 397–433. https://doi.org/10.1002/9783527809332.CH13.

[21] Broda M, Kierzkowska AM, Müller CR. Synthetic calcium oxide-based carbon dioxide sorbents for calcium looping processes. Calcium Chem. Looping Technol. Power Gener. Carbon Dioxide Capture, Woodhead Publishing; 2015, p. 51–72. https://doi.org/10.1016/B978-0-85709-243-4.00004-5.

[22] Vakharia V, Salim W, Wu D, Han Y, Chen Y, Zhao L, et al. Scale-up of amine-containing thin-film composite membranes for CO_2 capture from flue gas. J Memb Sci 2018;555:379–87. https://doi.org/10.1016/j.memsci.2018.03.074.

[23] Bruggen B Van Der. Desalination by distillation and by reverse osmosis — trends towards the future. Membr Technol 2003;2003:6–9. https://doi.org/10.1016/S0958-2118(03)02018-4.

[24] Baker RW, Freeman B, Kniep J, Wei X, Merkel T. CO_2 capture from natural gas power plants using selective exhaust gas recycle membrane designs. Int J Greenh Gas Control 2017;66:35–47. https://doi.org/10.1016/J.IJGGC.2017.08.016.

[25] Leung DYC, Caramanna G, Maroto-Valer MM. An overview of current status of carbon dioxide capture and storage technologies. Renew Sustain Energy Rev 2014;39:426–43. https://doi.org/10.1016/J.RSER.2014.07.093.

[26] Chemstations. CHEMCAD, Chemical Process Simulation Software 2022. https://www.chemstations.com/.

[27] Marton S, Svensson E, Harvey S. Operability and Technical Implementation Issues Related to Heat Integration Measures — Interview Study at an Oil Refinery in Sweden. Energies

2020;13:3478.

[28] Yu H, Vikse M, Anantharaman R, Gundersen T. Model reformulations for Work and Heat Exchange Network (WHEN) synthesis problems. Comput Chem Eng 2019;125:89–97. https://doi.org/10.1016/j.compchemeng.2019.02.018.

[29] Roetzel W, Luo X, Chen D. Chapter 6 – Optimal design of heat exchanger networks. Des. Oper. Heat Exch. their Networks, Elsevier Inc.; 2020, p. 231–317. https://doi.org/10.1016/B978-0-12-817894-2.00006-6.

[30] Zoughaib A. 1– Energy Integration of Continuous Processes : From Pinch Analysis to Hybrid Exergy/Pinch Analysis. From Pinch Methodol. to Pinch-Energy Integr. Flex. Syst., Elsevier Inc.; 2017, p. 1–53. https://doi.org/10.1016/B978-1-78548-194-9.50001-6.

[31] Thollander P, Karlsson M, Rohdin P, Wollin J, Rosenqvist J. 13 – Energy management. Introd. to Ind. Energy Effic., Elsevier Inc.; 2020, p. 239–57. https://doi.org/10.1016/B978-0-12-817247-6.00013-4.

[32] Jolliet O, Saade-Sbeih M, Shaked S, Jolliet A, Crettaz P. Environmental Life Cycle Assessment 2016. https://doi.org/10.1201/B19138.

[33] Schenck R, White P. Environmental Life Cycle Assessment: Measuring the Environmental Performance of Products. Washington, United States of America: American Center for Life Cycle Assessment; 2014.

[34] ISO - ISO 14040:2006 - Environmental management — Life cycle assessment — Principles and framework 2006.

[35] ISO - ISO 14044:2006 - Environmental management — Life cycle assessment — Requirements and guidelines 2006.

[36] Klöpffer W, Grahl B. Life Cycle Assessment (LCA): A Guide to Best Practice. Weinheim: Wiley-VCH; 2014. https://doi.org/10.1002/9783527655625.

[37] Aranda-Usón A, Ferreira G, Sabirón AML, Sastresa EL, Guinoa AS De. Characterisation and Environmental Analysis of Sewage Sludge as Secondary Fuel for Cement Manufacturing. Chem Eng Trans 2012;29:457–62. https://doi.org/10.3303/CET1229077.

[38] IEA - International Energy Agency. World Energy Outlook 2014 – Analysis - IEA 2014.

[39] Alex J, Dhanalakshmi J, Ambedkar B. Experimental investigation on rice husk ash as cement replacement on concrete production. Constr Build Mater 2016;127:353–62. https://doi.org/10.1016/j.conbuildmat.2016.09.150.

[40] CEMBUREAU. The Cement Sector: A Strategic Contributor to Europe’s Future. 2013.

[41] CEMBUREAU. Built in concrete, Made with Cement. 2019.

[42] Pacheco-Torgal F, Cabeza LF, Labrincha J, de Magalhaes AG. Eco-efficient construction and

building materials: life cycle assessment (LCA), eco-labelling and case studies. Woodhead Publishing; 2014.

[43] Chen W, Hong J, Xu C. Pollutants generated by cement production in China, their impacts, and the potential for environmental improvement. J Clean Prod 2015;103:61–9. https://doi.org/10.1016/j.jclepro.2014.04.048.

[44] Zheng C, Zhang H, Cai X, Chen L, Liu M, Lin H, et al. Characteristics of CO_2 and atmospheric pollutant emissions from China's cement industry: A life-cycle perspective. J Clean Prod 2021;282:124533. https://doi.org/10.1016/j.jclepro.2020.124533.

[45] IEA - International Energy Agency - Greenhouse Gas R&D Programme. CO_2 capture in the cement industry (Technical study No. 2008/3). 2008.

[46] Galvez-Martos J-L, Schoenberger H. An analysis of the use of life cycle assessment for waste co-incineration in cement kilns. Resour Conserv Recycl 2014;86:118–31. https://doi.org/10.1016/j.resconrec.2014.02.009.

[47] Tregambi C, Solimene R, Montagnaro F, Salatino P, Marroccoli M, Ibris N, et al. Solar-driven production of lime for ordinary Portland cement formulation. Sol Energy 2018;173:759–68. https://doi.org/10.1016/j.solener.2018.08.018.

[48] Benhelal E, Zahedi G, Hashim H. A novel design for green and economical cement manufacturing. J Clean Prod 2012;22:60–6. https://doi.org/10.1016/j.jclepro.2011.09.019.

[49] Georgiopoulou M, Lyberatos G. Life cycle assessment of the use of alternative fuels in cement kilns: A case study. J Environ Manage 2018;216:224–34. https://doi.org/10.1016/j.jenvman.2017.07.017.

[50] Meyer C. The greening of the concrete industry. Cem Concr Compos 2009;31:601–5. https://doi.org/10.1016/j.cemconcomp.2008.12.010.

[51] García-Gusano D, Garraín D, Herrera I, Cabal H, Lechón Y. Life Cycle Assessment of applying CO_2 post-combustion capture to the Spanish cement production. J Clean Prod 2015;104:328–38. https://doi.org/10.1016/j.jclepro.2013.11.056.

[52] Cormos A-M, Cormos C-C. Reducing the carbon footprint of cement industry by post-combustion CO_2 capture: Techno-economic and environmental assessment of a CCS project in Romania. Chem Eng Res Des 2017;123:230–9. https://doi.org/10.1016/j.cherd.2017.05.013.

[53] Sphera. GaBi Software 2021. https://gabi.sphera.com/international/software/gabi-software/.

[54] Kumar R, Kumar A, Pal P. Synergy of biofuel production with waste remediation along with value- added co-products recovery through microalgae cultivation : A review of membrane-integrated green approach. Sci Total Environ 2020;698:134169. https://doi.org/10.1016/j.scitotenv.2019.134169.

[55] Gebremariam SN, Marchetti JM. Economics of biodiesel production : Review. Energy Convers Manag 2018;168:74–84. https://doi.org/10.1016/j.enconman.2018.05.002.

[56] Zabed H, Sahu JN, Suely A, Boyce AN, Faruq G. Bioethanol production from renewable sources : Current perspectives and technological progress. Renew Sustain Energy Rev 2017;71:475–501. https://doi.org/10.1016/j.rser.2016.12.076.

[57] Khan E, Ozaltin K, Spagnuolo D, Bernal-ballen A, Piskunov M V, Martino A Di. Biodiesel from Rapeseed and Sunflower Oil : Effect of the Transesterification Conditions and Oxidation Stability. Energies 2023;16:657.

[58] Garba MD, Usman M, Khan S, Shehzad F, Galadima A, Fahad M, et al. CO_2 towards fuels : A review of catalytic conversion of carbon dioxide to hydrocarbons. J Environ Chem Eng 2021;9:104756. https://doi.org/10.1016/j.jece.2020.104756.

[59] Awad OI, Mamat R, Ibrahim TK, Hammid AT, Yusri IM, Hamidi MA, et al. Overview of the oxygenated fuels in spark ignition engine : Environmental and performance. Renew Sustain Energy Rev 2018;91:394–408. https://doi.org/10.1016/j.rser.2018.03.107.

[60] Eggemann L, Escobar N, Peters R, Burauel P, Stolten D. Life cycle assessment of a small-scale methanol production system : A Power-to-Fuel strategy for biogas plants. J Clean Prod 2020;271:122476. https://doi.org/10.1016/j.jclepro.2020.122476.

[61] Thakur AK, Kaviti AK, Mehra R, Mer KKS. Progress in performance analysis of ethanol-gasoline blends on SI engine. Renew Sustain Energy Rev 2017;69:324–40. https://doi.org/10.1016/j.rser.2016.11.056.

[62] Gautam P, Upadhyay SN, Dubey SK. Bio-methanol as a renewable fuel from waste biomass : Current trends and future perspective. Fuel 2020;273:117783. https://doi.org/10.1016/j.fuel.2020.117783.

[63] Singh V, Zhao M, Fennell PS, Shah N, Anthony EJ. Progress in biofuel production from gasification. Prog Energy Combust Sci 2017;61:189–248. https://doi.org/10.1016/j.pecs.2017.04.001.

[64] Zhang Z, Delcroix B, Rezazgui O, Mangin P. Simulation and techno-economic assessment of bio-methanol production from pine biomass, biochar and pyrolysis oil. Sustain Energy Technol Assessments 2021;44:101002. https://doi.org/10.1016/j.seta.2021.101002.

[65] Zhou C, Wang Y. Recent progress in the conversion of biomass wastes into functional materials for value-added applications. Sci Technol Adv Mater 2020;21:787–804. https://doi.org/10.1080/14686996.2020.1848213.

[66] CONVERGE H2020 Project. CONVERGE H2020 Project n.d. https://www.converge-h2020.eu/.

[67] Im-orb K, Arpornwichanop A, Simasatitkul L. Process intensification approach for design and

optimization of biodiesel production from palm fatty acid distillate. Biotechnol Reports 2021;30:e00622. https://doi.org/10.1016/j.btre.2021.e00622.

[68] Elgharbawy AS, Sadik WA, Sadek OM, Kasaby MA. Glycerolysis treatment to enhance biodiesel production from low-quality feedstocks. Fuel 2021;284:118970. https://doi.org/10.1016/j.fuel.2020.118970.

[69] Jin Y, Scherer L, Sutanudjaja EH, Tukker A, Behrens P. Climate change and CCS increase the water vulnerability of China's thermoelectric power fleet. Energy 2022;245:123339. https://doi.org/10.1016/j.energy.2022.123339.

[70] Bramstoft R, Pizarro-alonso A, Græsted I, Ravn H, Münster M. Modelling of renewable gas and renewable liquid fuels in future integrated energy systems. Appl Energy 2020;268:114869. https://doi.org/10.1016/j.apenergy.2020.114869.

[71] Battaglia P, Buffo G, Ferrero D, Santarelli M, Lanzini A. Methanol synthesis through CO_2capture and hydrogenation: Thermal integration, energy performance and techno-economic assessment. J CO_2 Util 2021;44:101407. https://doi.org/10.1016/j.jcou.2020.101407.

[72] Decker M, Vasakova L. Energy Roadmap 2050. Impact assessment and scenario analysis. Brussels: Commission staff working paper. European Commission (EC); 2011.

[73] Chen X, Wu X, Lee KY. The mutual benefits of renewables and carbon capture: Achieved by an artificial intelligent scheduling strategy. Energy Convers Manag 2021;233:113856. https://doi.org/10.1016/j.enconman.2021.113856.

[74] Quarton CJ, Samsatli S. The value of hydrogen and carbon capture, storage and utilisation in decarbonising energy: Insights from integrated value chain optimisation. Appl Energy 2020;257:113936. https://doi.org/10.1016/j.apenergy.2019.113936.

[75] Atsbha AT, Yoon T, Seongho P, Lee C. A review on the catalytic conversion of CO_2 using H_2 for synthesis of CO, methanol , and hydrocarbons. J CO_2 Util 2021;44:101413. https://doi.org/10.1016/j.jcou.2020.101413.

[76] Cormos C-C, Dinca C. Techno-economic and environmental implications of decarbonization process applied for Romanian fossil-based power generation sector. Energy 2021;220:119734. https://doi.org/10.1016/j.energy.2020.119734.

[77] Salehi MS, Askarishahi M, Gallucci F, Godini HR. Selective CO_2-Hydrogenation using a membrane reactor. Chem Eng Process - Process Intensif 2021;160:108264. https://doi.org/10.1016/j.cep.2020.108264.

[78] Müller LJ, Kätelhön A, Bringezu S, McCoy S, Suh S, Edwards R, et al. The carbon footprint of the carbon feedstock CO_2. Energy Environ Sci 2020;13:2979–92. https://doi.org/10.1039/d0ee01530j.

[79] Dongliang W, Wenliang M, Huairong Z, Guixian L, Yong Y, Hongwei L. Green hydrogen coupling with CO_2 utilization of coal-to-methanol for high methanol productivity and low CO_2 emission. Energy 2021;231:120970. https://doi.org/10.1016/j.energy.2021.120970.

[80] Ma Q, Chang Y, Yuan B, Song Z, Xue J, Jiang Q. Utilizing carbon dioxide from refinery flue gas for methanol production : System design and assessment. Energy 2022;249:123602. https://doi.org/10.1016/j.energy.2022.123602.

[81] Chauvy R, Meunier N, Thomas D, Weireld G De. Selecting emerging CO_2 utilization products for short- to mid-term deployment. Appl Energy 2019;236:662–80. https://doi.org/10.1016/j.apenergy.2018.11.096.

[82] Tijani AS, Yusup NAB, Rahim AHA. Mathematical modelling and simulation analysis of advanced alkaline electrolyzer system for hydrogen production. Procedia Technol 2014;15:798–806. https://doi.org/10.1016/j.protcy.2014.09.053.

[83] Cristea V-M, Burca MI, Ilea FM, Cormos A-M. Efficient decentralized control of the post combustion CO_2 capture plant for flexible operation against influent flue gas disturbances. Energy 2020;205:117960. https://doi.org/10.1016/j.energy.2020.117960.

[84] Jamil F, Al-Muhtaseb A, Myint MTZ, Al-Hinai M, Al-Haj L, Baawain M, et al. Biodiesel production by valorizing waste Phoenix dactylifera L. Kernel oil in the presence of synthesized heterogeneous metallic oxide catalyst (Mn@MgO-ZrO2). Energy Convers Manag 2018;155:128–37. https://doi.org/10.1016/j.enconman.2017.10.064.

[85] Tomatis M, Parvez AM, Afzal MT, Mareta S, Wu T, He J, et al. Utilization of CO_2 in renewable DME fuel production : A life cycle analysis (LCA) - based case study in China. Fuel 2019;254:115627. https://doi.org/10.1016/j.fuel.2019.115627.

[86] Meunier N, Chauvy R, Mouhoubi S, Thomas D, De Weireld G. Alternative production of methanol from industrial CO_2. Renew Energy 2020;146:1192–203. https://doi.org/10.1016/j.renene.2019.07.010.

[87] Ryoo SG, Jung HS, Kim M, Kang YT. Bridge to zero-emission : Life cycle assessment of CO_2-methanol conversion process and energy optimization. Energy 2021;229:120626. https://doi.org/10.1016/j.energy.2021.120626.

[88] Al-Kalbani H, Xuan J, García S, Wang H. Comparative energetic assessment of methanol production from CO_2 : Chemical versus electrochemical process. Appl Energy 2016;165:1–13. https://doi.org/10.1016/j.apenergy.2015.12.027.

[89] Matzen M, Demirel Y. Methanol and dimethyl ether from renewable hydrogen and carbon dioxide : Alternative fuels production and life-cycle assessment. J Clean Prod 2016;139:1068–77. https://doi.org/10.1016/j.jclepro.2016.08.163.

[90] Liu W-Y, Chiang Y-H, Lin C-C. Adopting renewable energies to meet the carbon reduction target : Is forest carbon sequestration cheaper? Energy 2022;246:123328. https://doi.org/10.1016/j.energy.2022.123328.

[91] Galusnyak SC, Petrescu L, Chisalita DA, Cormos CC. Life Cycle Assessment of Bio-methanol Derived from Various Raw-materials. Chem Eng Trans 2021;86:667–72. https://doi.org/10.3303/CET2186112.

[92] Bicer Y, Dincer I. Life cycle assessment of ammonia utilization in city transportation and power generation. J Clean Prod 2018;170:1594–601. https://doi.org/10.1016/j.jclepro.2017.09.243.

[93] Khasani, Prasidha W, Widyatama A, Aziz M. Energy-saving and environmentally-benign integrated ammonia production system. Energy 2021;235:121400. https://doi.org/10.1016/j.energy.2021.121400.

[94] Klaas L, Guban D, Roeb M, Sattler C. Recent progress towards solar energy integration into low-pressure green ammonia production technologies. Int J Hydrogen Energy 2021;46:25121–36. https://doi.org/10.1016/j.ijhydene.2021.05.063.

[95] Ghavam S, Taylor CM, Styring P. The life cycle environmental impacts of a novel sustainable ammonia production process from food waste and brown water. J Clean Prod 2021;320:128776. https://doi.org/10.1016/j.jclepro.2021.128776.

[96] Zhang H, Wang L, Van herle J, Maréchal F, Desideri U. Techno-economic comparison of green ammonia production processes. Appl Energy 2020;259:114135. https://doi.org/10.1016/j.apenergy.2019.114135.

[97] Pawar ND, Heinrichs HU, Winkler C, Heuser P-M, Ryberg SD, Robinius M, et al. Potential of green ammonia production in India. Int J Hydrogen Energy 2021;46:27247–67. https://doi.org/10.1016/j.ijhydene.2021.05.203.

[98] Ghavam S, Vahdati M, Wilson IAG, Styring P. Sustainable Ammonia Production Processes. Front Energy Res 2021;9:1–19. https://doi.org/10.3389/fenrg.2021.580808.

[99] Lim J, Fernández CA, Lee SW, Hatzell MC. Ammonia and nitric acid demands for fertilizer use in 2050. ACS Energy Lett 2021;6:3676–85. https://doi.org/10.1021/acsenergylett.1c01614.

[100] Khademi MH, Lotfi-Varnoosfaderani M. Sustainable ammonia production from steam reforming of biomass-derived glycerol in a heat-integrated intensified process : Modeling and feasibility study. J Clean Prod 2021;324:129241. https://doi.org/10.1016/j.jclepro.2021.129241.

[101] Walling E, Vaneeckhaute C. Greenhouse gas emissions from inorganic and organic fertilizer production and use : A review of emission factors and their variability. J Environ Manage 2020;276:111211. https://doi.org/10.1016/j.jenvman.2020.111211.