BABEȘ-BOLYAI UNIVERSITY

Faculty of Chemistry and Chemical Engineering

Summary

Integration of chemical looping technologies in energy-intensive industrial processes to improve energy efficiency and reduce carbon dioxide emissions

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Keywords

carbon dioxide capture and storage; chemical looping; amine-based carbon capture; techno-economic evaluation; life cycle assessment; iron and steel production; hydrogen production; ammonia production.

Introduction

Increased carbon dioxide emissions in the atmosphere caused by human activities have led, over the last decades, to an increase in the average surface temperature, causing unprecedented climate changes with devastating effects on human and natural ecosystems.

The leading CO_2 emitting sector is represented by heat and power, having a share of 41% of the global emissions [1]. According to the International Energy Agency (IEA) [2], 81.3% of the world total primary energy supply and 64.8% of the total electricity generation comes from fossil fuels (i.e. coal, oil and natural gas). Even though in recent years energy generation from renewable sources registered an increase, so did the use of fossil fuels, with coal remaining the major source of energy generation and the main source of energy-related CO_2 emissions [1]. About 37% of the global energy use is attributed to the industrial sector, in particular to energy-intensive industrial activities such as chemicals, iron and steel, cement, pulp and paper and aluminium [3]. As a result, the industrial sector is responsible for about 24% of the global energy-related CO_2 emissions [4]. Besides energy-related emissions (i.e. indirect emissions), the industrial sector brings additional emissions associated with the production process, termed direct emissions. These emissions refer to the CO_2 obtained as by-product or resulting from chemical reactions during the manufacturing process and are often unavoidable (e.g. cement production, iron and steel production). Figure 1 illustrates the carbon and energy intensity of the previously mentioned industrial processes.

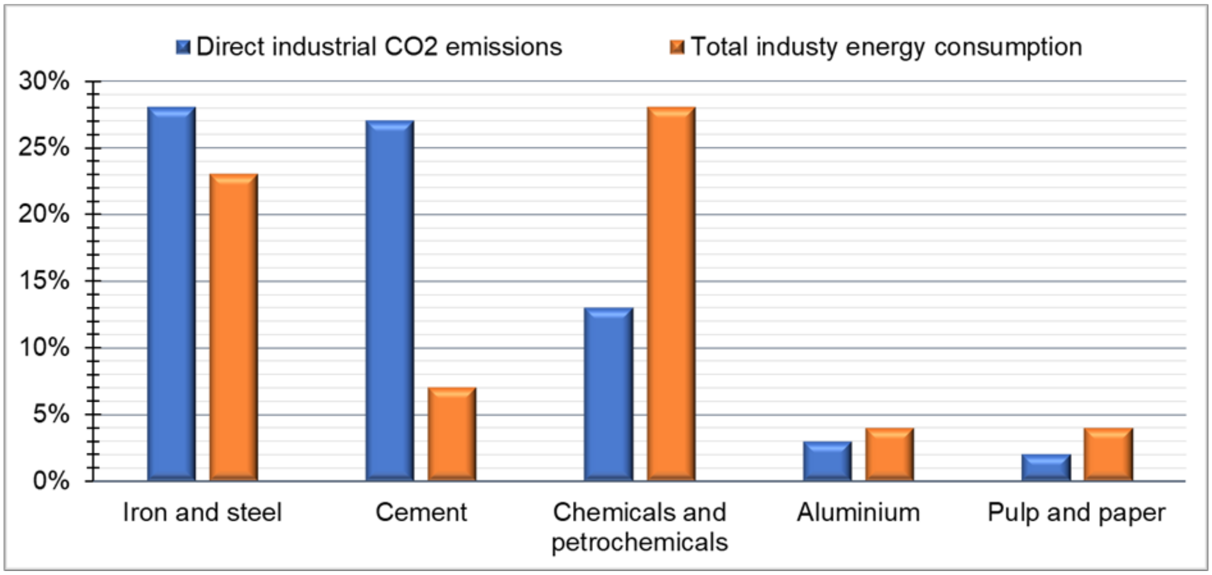


Figure 1. Direct industrial CO_2 emissions and industry energy consumption for the main energy-intensive industrial sectors (reference year 2014 [4])

Steelmaking is the leading industrial contributor to global anthropogenic CO_2 emissions and the second-largest industrial energy consumer with a share of 22% of the total industrial energy use [5]. Cement production follows iron and steel, both in terms of energy consumption and direct CO_2 emissions [4]. The chemical and petrochemical sector is the largest industrial energy consumer accounting for about 28% of the total industrial energy consumption, and the third industrial source of CO_2 emissions as more than 50% of its energy input is used as feedstock and not for electricity generation [4,6]. Aluminium production and the pulp and paper sector are each responsible for about 4% of the total industrial energy consumption, mainly heat and electricity [4]. For aluminium production, electricity is the main source of energy consumption, as well as the main source of CO_2 emissions; energy-related emissions represent about 70% of the total emissions associated with the production of aluminium [7].

Considering both direct and indirect emissions, the industrial sector is responsible for about a quarter of the global CO_2 emissions [8]. Following the current trend of population and economic growth, material requirements are expected to increase in order to meet the demand. As a result, energy requirements will likewise increase, leading to an increase in CO_2 emissions as well. Given that the heat and power sector, as well as all industrial processes, are essential to the growth and development of modern society, effective measures must be taken to reduce these emissions and limit further damage on the environment.

Carbon capture and storage (CCS) technologies offer a viable solution to capture carbon dioxide from large stationary emission points. CCS incorporates the separation of CO_2 from flue gasses, its transport and storage in supercritical conditions in marine or saline aquifers or injection into depleted oil reserves for enhanced oil recovery (EOR). Other option would be to reuse the separated CO_2 as a raw material in other industrial processes such as methanol, urea or synthetic fuels production [9]. Separation or removal of CO_2 is applied at large scale in some industrial processes where technological requirements condition it, such as natural gas processing, hydrogen or ammonia production. However, in most cases, the separated CO_2 is just vented into the atmosphere and very rarely is it used in other processes or sent to storage [10]. Moreover, state-of-the-art technologies come with a significant energy penalty, which leads to high capture costs. As a consequence, new CO_2 capture processes are continuously researched and developed in order to improve energy efficiencies and at the same time, increase the CO_2 capture performance and decrease costs. Chemical looping technologies are an example of such innovative CO_2 capture technologies that have low energy penalty and high carbon capture rates (CCR). The low energy penalty of these technologies is due to the separation of processes and high waste heat recovery potential as the processes take place at elevated temperatures. The basic concept behind the chemical looping technologies is the exploitation of solid materials, in the form of metal oxides, as reaction intermediates. In this way, direct contact between fuel/flue gas and air is avoided, and as a consequence nitrogen dilution of the CO_2 stream is prevented without resorting to an air separation unit (ASU) for O_2 production. Thus, the energy penalty is limited mainly to the CO_2 compression.

The most mature and currently applied capture technology is based on liquid chemical absorption by amine scrubbing. As a result, the amine-based adsorption process can provide a suitable baseline reference for comparison with new emerging technologies.

Description of CO_2 capture technologies

Amine-based CO_2 capture

The process is based on an absorption-desorption cycle in which the solvent chemically absorbs CO_2 in an absorption column followed by regeneration of the rich solvent with low-pressure steam (3-6 bar and 130-160ºC) in a desorption column releasing the absorbed CO_2 [11]. Figure 2 illustrates the amine scrubbing process schematically. The cooled flue gas, at about 40°C, is fed into the bottom section of the absorber where is contacted counter-currently with the lean solvent, which gradually heats up as it absorbs CO_2, yielding a rich solvent. The rich solvent is then heated in a lean/rich heat exchanger by regenerated lean solvent from the stripper before entering the top of the desorber (or stripper) where CO_2 is released from the solvent by heating it to about 120°C-140°C with low-pressure steam. The regenerated solvent is then pumped back to the absorber via the lean/rich heat exchanger to reduce the temperature of the lean solvent. Another heat exchanger is used for further cooling of the lean solvent up to 40°C at the inlet of the absorber unit.

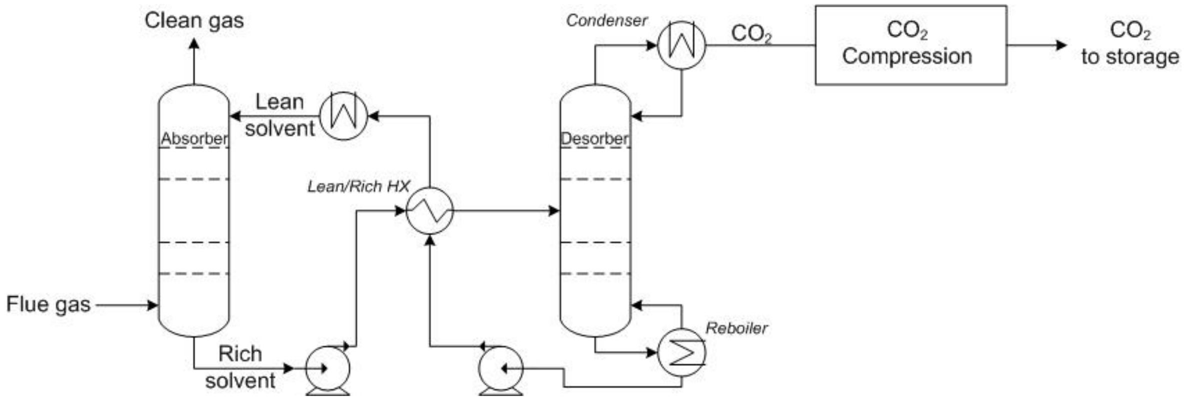


Figure 2. Schematic representation of the amine-based carbon capture process

Chemical looping technologies

Chemical-looping technologies make use of oxygen carriers (OC) or CO_2 sorbents to act as reaction intermediates and inherently separate CO_2 with minimum energy penalty [12]. Oxygen carriers are usually solid metal oxides which are capable of undergoing multiple oxidation-reduction cycles releasing the oxygen (O_2) required for fuel conversion. Replacing the oxygen source, which otherwise would come from air, flue gasses dilution with nitrogen (N_2) or the use of energy-intensive air separation unit (ASU) can be avoided leading to a lower energy penalty compared to other CCS technologies [13]. CO_2 sorbents, usually in the form of calcium oxide (CaO), react chemically with CO_2 forming calcium carbonate ($CaCO_3$) which is decomposed in a separate reactor releasing an almost pure stream of CO_2; this type of chemical looping technology is known in the literature as calcium looping (CaL).

The CaL process is generally applied in a post-combustion configuration; A schematic representation of the CaL process is illustrated in Figure 3. It is based on the reversible carbonation reaction to capture CO_2 in one reactor, called carbonator, and regenerate the sorbent in another reactor, called calciner, according to reaction R1. A stream of pure CO_2 is obtained from the calciner, without additional separation technologies.

$$\mathrm{CO_2 + CaO \rightleftarrows CaCO_3} \qquad \Delta H^0 = \pm 183.04\ \mathrm{kJ/mol} \tag{R1}$$

The direct reaction is exothermic, while the reverse reaction (i.e. decomposition of $CaCO_3$) is endothermic and requires energy input. In most cases, the energy needed for carbonate decomposition is supplied by burning a solid or gaseous fuel in an oxygen atmosphere to avoid the dilution of the CO_2 stream with N_2. Oxygen is obtained from an ASU, which brings unwanted energy penalties; however, the size of the ASU is about a third from that employed in oxy-fuel combustion [12]. Due to the high temperatures employed (i.e. ~650°C in the carbonator and ~950°C in the calciner), there is high energy recovery potential; by generating steam and expanding it in a steam turbine, some of the energy penalty brought by the ASU can be offset.

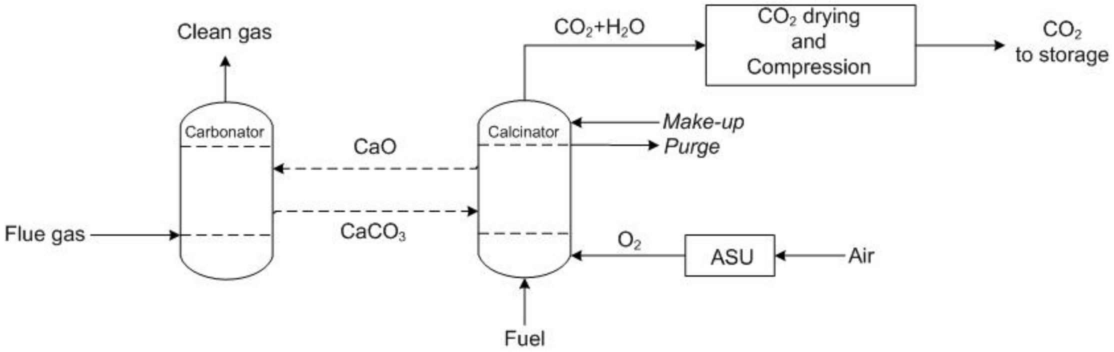


Figure 3. Schematic representation of CaL process

Chemical looping technologies are promising candidates for hydrogen generation with in-situ CO_2 removal, in different configurations that can be classified in two groups: chemical looping reforming (CLR) and chemical looping hydrogen production (CLH). CLR can follow different approaches such as heat supply to conventional reforming technologies, adjusting operating conditions and making use of suitable oxygen carriers in order to partially oxidise the fuel and obtain hydrogen, or integrate CO_2 removal into the reforming technology (i.e. sorption enhanced reforming – SER). The latter is considered for evaluation in the present study for hydrogen generation.

SER is an integrated system which combines in a single unit both hydrogen production and CO_2 removal, reducing the number of process steps as well as reducing the operating temperature due to the new equilibrium balance resulted from the removal of CO_2 in the presence of CaO. Two inter-connected fluidised bed reactors can be used to carry out the process, as illustrated in Figure 4. In the first reactor (i.e. carbonator) H_2 is produced with inherent separation of CO_2 as described by reactions R2 to R4. Since steam reforming of hydrocarbons is an endothermic process, and both carbonation and the water-gas-shift (WGS) reaction are exothermic processes, their coupling leads to an almost autothermal operation of the carbonator.

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad \Delta H^0 = +206.10\ kJ/mol \qquad (R2)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \Delta H^0 = -\ 41.16\ kJ/mol \qquad (R3)$$

$$CO_2 + CaO \longrightarrow CaCO_3 \qquad \Delta H^0 = -183.04\ kJ/mol \qquad (R4)$$

In the second reactor (i.e. calcinator) the sorbent is regenerated releasing a pure stream of CO_2 (see reaction R5), ready for compression and storage, same as in the original CaL process.

$$CaCO_3 \longrightarrow CO_2 + CaO \qquad \Delta H^0 = +183.04\ kJ/mol \qquad (R5)$$

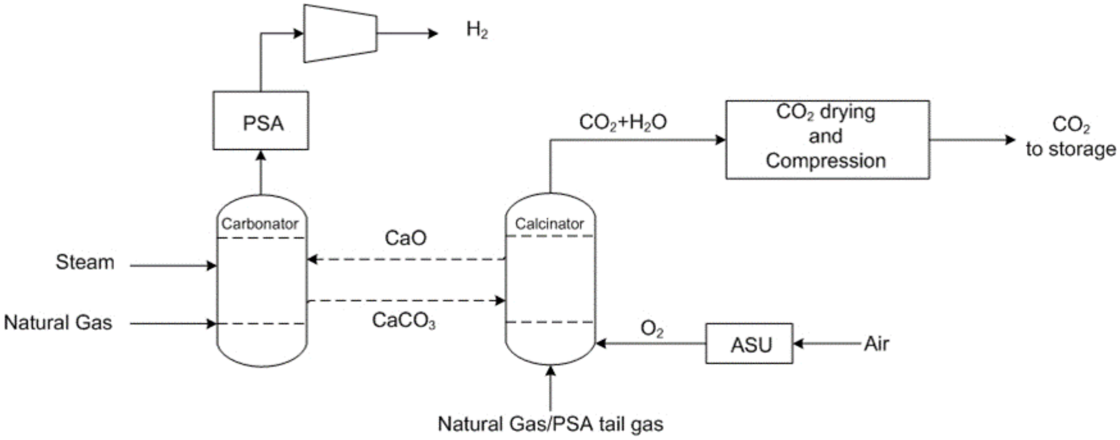


Figure 4. Schematic representation of SER using Ca-based sorbent

In order to avoid additional energy penalties caused by the use of an ASU, a solution would be to couple the SER process with chemical looping (i.e. sorption enhanced chemical looping reforming – SECLR) and take advantage of the heat generated by an exothermic redox cycle to heat the calcinator. In this case, the two-reactor configuration becomes a three-reactor arrangement, as illustrated in Figure 5. The reactions taking place in the carbonator remain the same as described by reactions R2 to R4. A new reactor (i.e. air reactor) is necessary to oxidise the metallic Cu to CuO according to reaction R6. Since this step follows CO_2 separation, air can be used as an oxidising agent without the risk of N_2 dilution, thus eliminating the need for an ASU. However, since Cu oxidation is highly exothermic, proper heat management is required in the air reactor to limit the decomposition of $CaCO_3$, which will lead to a reduction in the CCR. For this reason, part of the oxygen-depleted air is recycled back to the air reactor while the rest can be expanded, generating electricity as depicted in Figure 5.

$$2Cu + O_2 \longrightarrow 2CuO \qquad \Delta H^0 = -322.17\ kJ/mol \qquad (R6)$$

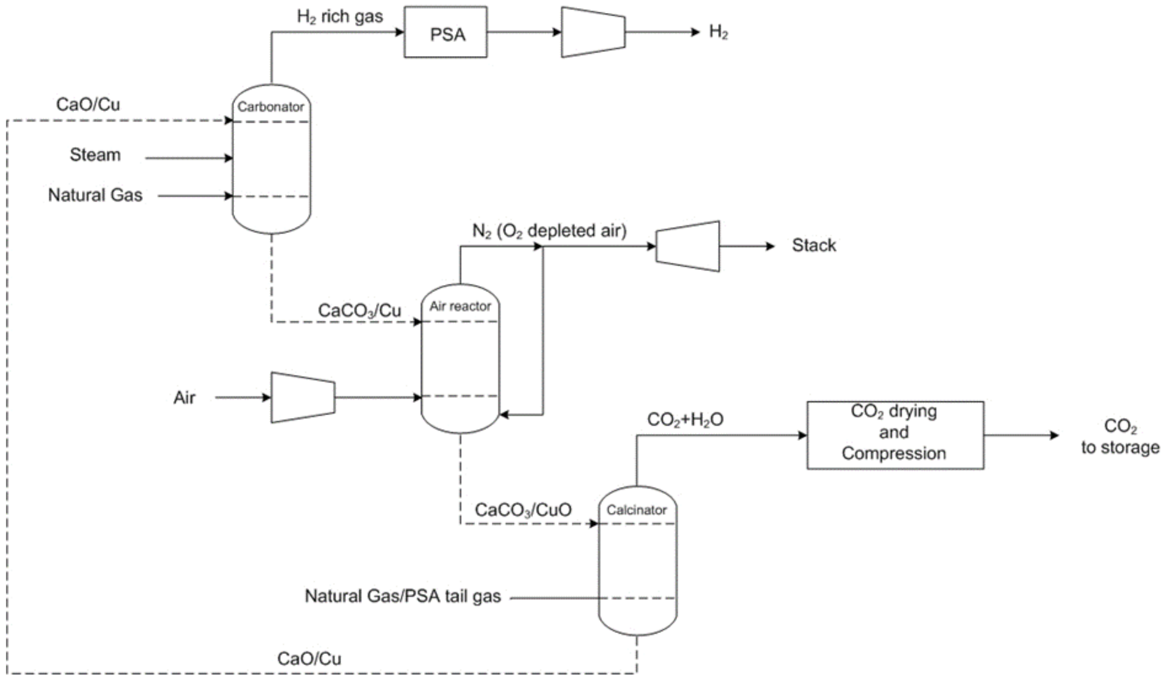


Figure 5. Schematic representation of SECLR using Ca-Cu system

In case of SECLR, the heat required for the endothermic calcination (i.e. reaction R5) can be provided in-situ by the reduction of the metal oxide with a reducing gas (e.g. natural gas, syngas, PSA tail gas). Therefore, the following reactions take place in the calcinator besides the decomposition of $CaCO_3$:

$$CuO + CO \longrightarrow Cu + CO_2 \qquad \Delta H^0 = -121.91\ kJ/mol \qquad (R7)$$

$$4CuO + CH_4 \longrightarrow 4Cu + CO_2 + 2H_2O \qquad \Delta H^0 = -158.03\ kJ/mol \qquad (R8)$$

$$CuO + H_2 \longrightarrow Cu + H_2O \qquad \Delta H^0 = -\ 80.74\ kJ/mol \qquad (R9)$$

CLH takes advantage of the potential of iron-based oxygen carriers to be oxidised by steam and produce hydrogen (via the steam-iron reaction). The process uses a three-reactor configuration [14] as represented schematically in Figure 6. Ultra-high purity hydrogen suitable for fuel cell applications can be obtained without the use of WGS reactors or downstream gas purification (i.e. PSA) as well as inherent CO_2 capture [15]. In the first reactor (i.e. fuel reactor), iron oxide is reduced by the fuel from hematite (Fe_2O_3) to magnetite (Fe_3O_4) to wustite (FeO) or even metallic iron (Fe) [16], according to reactions R10 to R12, resulting in a stream of pure CO_2 after H_2O condensation.

$$12Fe_2O_3 + CH_4 \longrightarrow 8Fe_3O_4 + CO_2 + 2H_2O \qquad \Delta H^0 = +230.24\ kJ/mol \qquad (R10)$$

$$4Fe_3O_4 + CH_4 \longrightarrow 12FeO + CO_2 + 2H_2O \qquad \Delta H^0 = +420.53\ kJ/mol \qquad (R11)$$

$$4FeO + CH_4 \longrightarrow 4Fe + CO_2 + 2H_2O \qquad \Delta H^0 = +278.95\ kJ/mol \qquad (R12)$$

The second step corresponds to hydrogen production by feeding excess steam into the second reactor (i.e. steam reactor) and partially oxidising the oxygen carrier according to reactions R13 and R14.

$$Fe + H_2O \longrightarrow FeO + H_2 \qquad \Delta H^0 = -\ 28.50\ kJ/mol \qquad (R13)$$

$$3FeO + H_2O \longrightarrow Fe_3O_4 + H_2 \qquad \Delta H^0 = -\ 63.90\ kJ/mol \qquad (R14)$$

Complete oxidation is thermodynamically constrained, so a third reactor (i.e. air reactor) is required to completely oxidise Fe_3O_4 to Fe_2O_3 (see reaction R15), as well as to act as thermal balance leading to an overall autothermal system.

$$2Fe_3O_4 + 1/2\ O_2 \longrightarrow 3Fe_2O_3 \qquad \Delta H^0 = -258.15\ kJ/mol \qquad (R15)$$

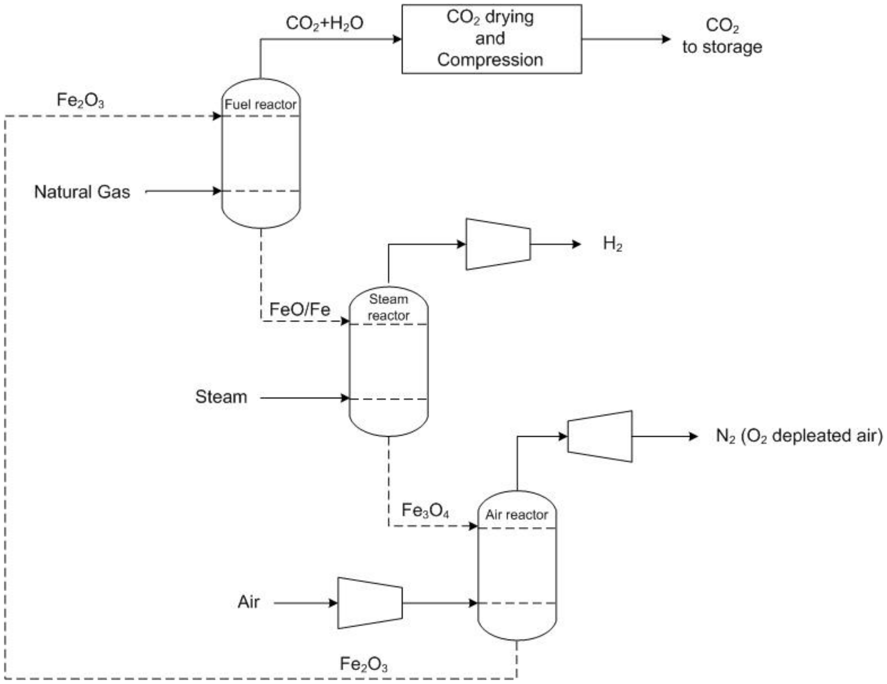


Figure 6. Schematic representation of CLH using ilmenite as the oxygen carrier

Goal and objectives

The goal of the thesis is to evaluate the performance of chemical looping technologies integrated into carbon and energy-intensive industrial processes with the aim of reducing carbon dioxide emissions, improve energy efficiency and reduce costs. The objectives pursued in order to achieve the proposed goal are enumerated below:

1. Extensive literature study to highlight the motivation and current status of research;
2. Modelling and simulation of various chemical looping processes applied for the decarbonisation of major industrial processes in order to obtain mass and energy balances which provide valuable inputs for the economic and environmental assessments;

3. Thermal integration by pinch methodology, in order to determine the minimum cold/hot utility requirements of the studied systems;
4. Techno-economic evaluation of selected industrial processes coupled with chemical looping and their comparison with state-of-the-art technologies with and without carbon capture. Targets for key performance indicators such as CCR and electrical efficiency are set to at least 90% CCR for all CO_2 capture scenarios and between 4 - 6% energy efficiency improvement compared to state-of-the-art scenarios;
5. Environmental impact assessment of the coupling of CO_2 capture technologies with the selected industrial processes and their comparison with the state-of-the-art reference.

Three essential industrial processes are assessed, namely iron and steel production, hydrogen generation and ammonia synthesis. All these processes are indispensable in the growth and development of modern society; however, the current production routes are not sustainable.

As previously presented in Figure 1, the chemical and petrochemical sector, together with iron and steel production, are the leading industrial energy consumers and among the primary industrial CO_2 emissions sources. About 70% of the world steel is produced following the blast furnace – basic oxygen furnace (BF – BOF) route which relies greatly on fossil fuels, especially coal, both as feedstock and fuel. This results in CO_2 emissions between 1.6 and 2.2 tonnes per tonne of steel produced. High-value chemicals (e.g. ethylene, propylene, benzene, toluene, xylene), ammonia and methanol production are the primary products of the chemical and petrochemical sector, as well as the main energy consumers of the sector, having a share of about 73% [4]. Annually, around 880 million tonnes of CO_2 are emitted from the production of chemicals, out of which about 420 million tonnes of CO_2 are emitted during ammonia synthesis [6,17]. Ammonia is mainly used for fertiliser production, particularly urea, accounting for about 85% of the total ammonia production [18]. The current ammonia production route relies significantly on fossil fuels both as an energy source and as feedstock, releasing around 2.5-3 tonnes of CO_2 per tonne of ammonia produced. Hydrogen is a valuable feedstock used in many chemical processes, such as ammonia, methanol, petrochemical, biofuels and food industry, with the potential to play a significant role in decarbonising the transport sector as well [19]. It is produced predominantly from fossil resources, being responsible for about 830 million tonnes of CO_2 emitted annually [20]. Considering the conventional production route by steam methane reforming, between 9-11 kg CO_2 are emitted for the production of one kg of hydrogen.

Each of the three proposed energy and carbon-intensive industrial processes is described and evaluated, covering both techno-economic and environmental aspects to gain a complete overview of the most sustainable alternative.

Assessment methodology

The methodology applied to carry out the evaluation is presented briefly in the following paragraphs.

Modelling and simulation

Process simulators, Aspen Plus and ChemCAD, were utilised to develop the proposed processes and obtain the mass and energy balances, which further act as inputs for the techno-economic and environmental evaluations. To describe the phenomena taking place in the proposed processes, several property methods can be applied in the design of the chemical processes; these methods include appropriate thermodynamics and transport properties and can be defined globally for the entire flowsheet or different flowsheet sections depending on the type of process described. Consequently, in order to model and simulate the desired process, different unit operations are connected and parametrised to describe as accurately as possible the processes taking place in the system.

Techno-economic evaluation

As all chemical looping cycles operate at high temperature, waste heat recovery from the process's hot streams or between process streams, whenever possible and practical, it is preferred over the use of hot and cold utilities, leading to emissions and cost reductions. Thermal integration by pinch analysis was applied in order to determine the utility requirements that act as inputs to the economic and environmental assessments.

Key performance indicators (KPI) were calculated to evaluate the technical and economic performance of the evaluated case scenarios, described below:

Carbon Capture Rate (CCR)	$\mathrm{CCR} = \frac{[\mathrm{CO} + \mathrm{CO_2}]_{\mathrm{mols\ in}} - [\mathrm{CO} + \mathrm{CO_2}]_{\mathrm{mols\ out}}}{[\mathrm{CO} + \mathrm{CO_2}]_{\mathrm{mols\ in}}}$	(1)
Net electrical efficiency (η_{el})	$\eta_{\mathrm{el}} = \frac{\mathrm{P}}{\dot{\mathrm{m}}_{\mathrm{f}} \cdot \mathrm{LHV_f}}$	(2)
CO_2 specific emissions rate	$\mathrm{CO_2\ specific\ emission\ rate} = \frac{\dot{\mathrm{m}}_{(\mathrm{CO_2})\mathrm{out}}}{\mathrm{unit\ of\ product\ (e.g.\ MW_e, kg)}}$	(3)
CO_2 avoided	$\mathrm{CO_{2\ avoided}} = \left(1 - \frac{\mathrm{E}}{\mathrm{E_{ref}}}\right)$	(4)
Specific primary energy consumption for avoiding CO_2 (SPECCA)	$\mathrm{SPECCA} = \frac{3600 \cdot \left(\frac{1}{\eta_{\mathrm{el}}} - \frac{1}{\eta_{\mathrm{el\ ref}}}\right)}{\mathrm{E_{ref}} - \mathrm{E}}$	(5)
Specific capital investment cost (SCI)	$\mathrm{SCI} = \frac{\mathrm{Total\ investment\ cost\ [MMeuro]}}{\mathrm{Unit\ of\ finished\ product\ [e.g.\ kg,\ t,\ MW_e]}}$	(6)
CO_2 avoidance cost	$\mathrm{CO_2\ avoidance\ cost} = \frac{\mathrm{LPC_{Capture}} - \mathrm{LPC_{No\ capture}}}{\mathrm{CO_2\ emissions_{No\ capture}} - \mathrm{CO_2\ emissions_{Capture}}}$	(7)
CO_2 removal cost	$\mathrm{Cost\ of\ CO_2\ removal} = \frac{\mathrm{LPC^*_{Capture}} - \mathrm{LPC^*_{No\ capture}}}{\mathrm{CO_2\ captured}}$	(8)

Where:

P is the net electric power output in [MW_e];
$\dot{m}_f$ is the fuel mass flow rate in [kg/s];
LHV_f is the low heating value of the fuel in [MJ/kg_{fuel}];
$\dot{m}_{(CO_2)out}$ is the mass flow rate of CO_2 emissions in [kg/s];
E is the specific CO_2 emission rate of the investigated plant;
E_{ref} is the specific CO_2 emission rate of the reference plant without carbon capture;
$\eta_{el_{ref}}$ is the net electrical efficiency of the reference plant without carbon capture;
LPC is the levelized production cost [currency/unit of valuable product];
LPC* is the levelized production cost excluding the cost of CO_2 transport and storage [currency/unit of valuable product];
CO_2 emissions represent the specific CO_2 emissions of the plant [t_{CO2}/unit of valuable product];
Capture/No capture subscripts refer to the plant with and without CCS.

When looking at different process alternatives, a representative economic indicator is the selling price of the valuable product. This cost is influenced by many factors that are subjected to yearly variations (e.g. the cost of operating materials, the plant's loading factor among others) so in most economic evaluations a levelized production cost (LPC) is calculated, that is "*the uniform annual cost that produces the same NPV as a stream of variable year-to-year costs over a specified plant life*" [21]. The levelized cost is especially useful when comparing different technologies as well as different capital and operating investment costs [22]. It is obtained using the Goal Seek function implemented in Microsoft Excel spreadsheets making the NPV=0. The net present value (NPV), is an economic criterion which measures the profit of a project considering the value of money as a function of time (meaning that money earned earlier on in the project is more valuable than the one obtained later on as it can be reinvested and produce revenue) [23,24]. It can be estimated using equation 9 [25], which expresses the sum of the annual cumulative cash flow covering the entire project's lifetime expressed in years.

$$NPV = \sum_{n=1}^{n=t} \frac{CF_n}{(1+i)^n} \tag{9}$$

Where:

t is the project's lifetime in years;
n represents a specific year in the project's lifetime;
CF_n is the estimated cash flow in year n;
i represents the interest rate.

For case studies which integrate CCS, other economic indicators are calculated as well. The most generally used cost index reported in CCS projects is the cost of CO_2 avoided. It is a measure of "*the average cost of reducing atmospheric CO_2 mass emissions by one unit while providing the same amount of useful product as a reference plant without CCS*" [26]. It should also include the cost of CO_2 transport and storage, as the CO_2 emissions are not considered avoided unless the separated CO_2 is stored [21]. The cost of CO_2 avoided can be evaluated using equation 7. It also coincides with the carbon tax, expressed as the cost per tonne of CO_2 emitted at which the cost of the valuable product in the reference plant without CCS becomes the same with the one with CCS [21].

Another cost measure for CCS projects is the cost of CO_2 capture or removal, quantified by applying equation 8 [21]. The cost of CO_2 removal evaluates the economic feasibility of employing CO_2 capture by comparison with the market price of CO_2, considered as an industrial good [26]. As opposed to the cost of CO_2 avoided, the cost associated with CO_2 transport and storage do not need to be included for the evaluation of the cost of CO_2 removal [21].

Life cycle assessment (LCA)

LCA evaluates the environmental impact of a product, process or service based on a particular function and considering all life cycle stages. According to the definitions provided by the International Organization of Standardization (ISO) standards (i.e. ISO14040 – Principles and Framework [27] and ISO14044 – Requirements and Guidelines [28]), an LCA consists of four phases as follows:

1) Goal and scope definition – states clearly and unambiguously the reason for performing the study and defines the objectives and the scope of the study. A number of crucial elements are determined at this point: the function of the system, the functional unit on which the results will be reported, the system boundaries, assumptions and limitations [27,28].
2) Life cycle inventory (LCI) – quantifies the exchange of materials (e.g. resources and emissions) between the system enclosed within the boundary and the environment [29].
3) Life cycle impact assessment (LCIA) – evaluates the environmental impact of the inventoried emissions. Impact category indicators, corresponding to the two life cycle impact assessment methods applied in the current study (i.e. CML2001 and ReCIPe), are detailed in Table 1.
4) Interpretation – delivers a set of conclusions along with the limitations of the study and recommendations based on the issues identified [27]. The interpretation of the LCA results depends significantly on the accuracy, completeness and consistency of the results [30]. Sensitivity analysis can be applied to pinpoint the major contributors to each impact category.

Table 1. Description of impact category indicators for CML 2001 and ReCIPe environmental impact assessment methods

Impact category	**Characterisation**	**Relevant LCI data**
Global warming/Climate change (GWP)	Increase in the infra-red radiative forcing in the atmosphere, causing the temperature at the Earth's surface to rise. Global area of impact.	CO_2, CH_4, N_2O, CFCs, HCFCs, HFCs, CCl_4
Acidification Potential (AP)	Proton increase in natural soils as a result of acidifying pollutants' impact. Regional or local geographical area of impact.	SO_X, NO_X, HCl, HF, HNO_3, H_2SO_4, H_2S, NH_3
Eutrophication Potential (EP) / Freshwater Eutrophication Potential (FEP)	Excessive levels of macronutrients present in the inland waterways. Regional or local geographical area of impact.	N and P containing nutrients
Ozone Layer Depletion Potential (ODP) / Ozone Depletion Potential (ODP)	Increased UV radiation leading to thinning of the stratospheric ozone layer due to ozone-depleting substances. Global geographical area of impact.	CFCs, HCFCs, halons, CCl_4, CH_3Br
Abiotic Depletion Potential (ADP) fossil / Fossil fuel Depletion Potential (FDP) / Metal Depletion Potential (MDP)	Decrease in fossil resources/ore grade due to excessive exploitation; unavailability for future generations; Global/Regional/Local geographical area of impact.	Extraction of fossil resources / Extraction of mineral resources
Photochemical Ozone Creation Potential (PCOP) / Photochemical Oxidant Formation Potential (POFP)	Refers to the formation of reactive chemical compounds, such as ozone, by the action of sunlight on certain primary air pollutants. Regional or local geographical area of impact.	NO_X, VOCs including CH_4, CO
Human Toxicity Potential (HTP)	Covers the potential impacts on human health of toxic substances present in the environment. Regional/local geographical area of impact.	Toxic substances emitted to the environment due to human activities (e.g. Heavy metals, VOC, PM10, Pesticides, Sewage sludge)
Freshwater Ecotoxicity Potential (FAETP/FETP) / Terrestrial Ecotoxicity Potential (TEP/TETP)	Refers to the potential impacts of toxic substances on aquatic / terrestrial and sediment ecosystems. Regional or local geographical area of impact.	
Marine Aquatic Ecotoxicity Potential (MAETP)	Impact on the marine environment by increased intake of metals to oceans. Regional or local geographical area of impact.	

Case studies

Iron and steel production

The iron and steel industry is one of the most significant drivers of economic and social development, playing a vital role in meeting society's needs as it provides services in vast areas, such as buildings and infrastructure, mechanical and electrical equipment, automotive and other transport systems, metal products and domestic appliances.

Globally, steel is produced following two main routes: blast furnace (BF) – basic oxygen furnace (BOF) also referred to as "integrated steelmaking", and electric arc furnace (EAF) known as "minimill"[31]. In the integrated steelmaking, steel is produced by reducing iron ore in a BF followed by processing in a primary steelmaking plant. The minimill produces steel by melting steel scrap or other scrap substitutes such as direct reduced iron (DRI) or pig iron in an EAF [32]. This steelmaking route is used predominantly in countries with an abundance of natural gas resources, being not so common in Europe [33]. Literature data reports emissions between 1.6 and 2.2 t_{CO2}/t_{steel} using the BF-BOF route, while the EAF route emits between 0.6 and 0.9 t_{CO2}/t_{steel} using scrap metal and between 1.4 and 2 t_{CO2}/t_{steel} when DRI is used in the EAF route [34]. Although the EAF route has lower CO_2 emissions compared to the BF-BOF route, it should be emphasised that the two production routes are not comparable due to differences in feedstock, steel quality and products. The BF-BOF route is the predominant steelmaking route, accounting for about 70% of the world steel production [35].

The production of steel at an integrated steel plant, in the form of hot-rolled coil (HRC), is achieved following a series of associated processes. About 95% of the total direct CO_2 emissions coming from an integrated steel mill have their origin in an on-site power plant (46.98%), the hot stoves (20.80%), sinter production (13.97%), coke oven batteries (9.28%) and the lime kiln (3.42%) [32].

Two main options can be considered in order to mitigate CO_2 emissions from steel plant: increase the energy and process efficiency and/or, adopt CCS technologies. Improving energy efficiencies and focusing on energy-saving or recovering technologies (e.g. dry coke quenching and top pressure recovery turbine) can be regarded as short-term solutions for the reduction of emissions in the iron and steel industry. A cutback of 60% in the energy consumption per tonne of steel produced has already been achieved in the last 50 years, by applying available technologies, making it more challenging for further improvements [5]. Various potential new steelmaking technologies with a lower carbon footprint, including reuse of CO_2, have already been proposed in the literature. In Europe, Hlsarna smelter technology, developed under the Ultra-Low CO_2 Steelmaking (ULCOS) project, has been successfully tested at a pilot plant scale [36]. In Japan, R&D project COURSE50, is currently preceding from a laboratory to a pilot phase [37]. However, in order to significantly reduce CO_2 emissions from the steel industry as to meet the 2°C scenario target by 2050, more advanced long-term approaches have to be adopted, such as increasing the use of renewable energy in steelmaking processes, developing and implementing CCS.

Most literature studies look at post-combustion capture configurations as the most suitable choice for the decarbonisation of the steel industry. Various technologies are considered, with amine-based chemical absorption the most investigated option since it is the most mature CCS technology at present [32].

Currently, there is no literature data on LCA of steelmaking which considers the environmental impact of implementing CCS, assessing the contribution of the CO_2 capture unit and the CO_2 transport and storage step. There are various case studies regarding the environmental evaluation of steel production in different regions of the world such as Poland [38] and Turkey [39] amongst the most recent ones, focusing mainly on the environmental impact of the steel production process as a gate-to-gate LCA. A more extensive research was performed by the World Steel Associations (WSA) [40] which performed a cradle-to-gate LCA, considering upstream processes such as raw-materials supply chain as well.

The scope of this chapter is to investigate from a techno-economic and environmental point of view, two post-combustion carbon capture technologies applied to a Western European integrated steel mill with a capacity of 4 million tonnes of HRC per year. Such a mill is described in detail in an IEAGHG report [32] which will be used as a reference for the mass and energy balances of the steel mill. Calcium-looping is the selected chemical looping technology to be evaluated for the decarbonisation of the iron and steel industry in a post-combustion capture configuration. The performance of the integrated steel mill with CaL carbon capture will be compared with an integrated steel mill without CO_2 capture (i.e. benchmark case) as well as with the more studied and mature CO_2 capture technology based on chemical absorption by amines (i.e. reference case). The main findings of this case study can help choose the more convenient solution for decarbonising the steel industry by evaluating the trade-off between emissions reduction and cost.

Two carbon capture scenarios are investigated, resulting in five case scenarios:

Case 1. Integrated steel mill without CCS (benchmark);

Case 2. Integrated steel mill with CO_2 capture (from two sources) using MEA;

Case 3. Integrated steel mill with CO_2 capture (from four sources) using MEA;

Case 4. Integrated steel mill with CO_2 capture (from two sources) using CaL;

Case 5. Integrated steel mill with CO_2 capture (from four sources) using CaL.

Scenario 1: CO_2 captured from two sources: hot stoves and steam generation plant for the cases with MEA chemical absorption (Case 2 and Case 3) and hot stoves and power plant for the CaL cases (Case 4 and Case 5);

Scenario 2: CO_2 captured from four sources: besides the source considered in Scenario 1, CO_2 is also captured from the coke oven batteries and lime kiln

A report prepared and published by IEAGHG [32] was used as a basis for the study. Mass and energy balances describing the steel plant without CCS and as well as with CO_2 capture using MEA-based chemical absorption were taken from the specified report. Considering the CaL case scenarios, mass and energy balances were taken from process modelling and simulation results.

The coupling of the amine-based post-combustion capture system (i.e. Case 2 and Case 3) to the benchmark integrated steel mill, brings modifications to the captive power plant. On account of increased energy demand required for solvent regeneration, the presence of a steam turbine is indispensable to meet the steam demand. The off-gasses burned in the benchmark power plant, are used now in the steam plant to generate steam. A natural gas integrated combined cycle (NGCC) power plant, based on an E-Class Gas turbine with natural gas (NG), is now used to satisfy the electricity demand of the steel mill [32].

All other processes relevant to the production of HRC do not undergo any changes compared to the benchmark integrated steel mill without CCS. The same is valid for Case 4 and Case 5 when CaL is used as CO_2 capture technology. A GTCC with duct firing using BFG and basic oxygen furnace gas (BOFG) as fuel was considered as an updated configuration to the power plant used in the benchmark integrated steel mill for improved energy efficiency [32]. Compared to the reference case scenarios (i.e. amine capture), no steam generation plant is necessary; however, pure oxygen is required in the calcinator. The required O_2 can be supplied either from the on-site ASU, either from an additional ASU. Either way, it brings additional energy consumption.

Due to the high-energy recovery potential, in the form of residual heat, implementation of the CaL technology for CO_2 removal in the steel industry, resulted in additional energy generation as seen from the results in Table 2, considered to be exported in the analysed scenarios. This led to favourable outcomes in both economic and environmental aspects. Moreover, considering the natural gas consumption, a reduction of 20.5% was noted for the CaL system in Scenario 1 and a negligible difference of 0.03% in Scenario 2 compared to the reference amine-based capture system as presented in Table 3.

Table 2. Main technical indicators for the evaluated CaL cases

Main Plant Data	Units	Case 4	Case 5
NG to calciner	kg/h	38300.00	63320.21
LHV	MJ/kg	46.49	
NG thermal energy (A)	MW_{th}	494.63	817.76
Gross power production (B)	MW_e	219.17	277.82
Total ancillary power consumption (C)	MW_e	111.41	151.63
ASU	MW_e	29.34	48.34
Pumps	MW_e	4.33	5.12
CO_2 drying & compression	MW_e	77.74	98.18
Net power output (D=B-C)	MW_e	107.76	126.19
CCR	%	95.00	95.00

Low heating Value – LHV

Table 3. Natural gas consumption in auxiliary units excluding steel production units

Natural gas consumption	Unit	Case 1	Case 2	Case 3	Case 4	Case 5
Power Plant	GJ/t_{HRC}	0.85	3.62	3.93	-	-
Steam Generation Plant	GJ/t_{HRC}	-	0.57	1.59	-	-
CaL	GJ/t_{HRC}	-	-	-	3.34	5.52

Looking at the economic aspects, in both evaluated scenarios, reduced capital investments were observed for the CaL cases, by 6.45%, respectively 9.51% compared to the reference CO_2 capture system (see Figure 7). On the other hand, for the operating costs, only Scenario 1 showed a reduction (1.49%), while in Scenario 2 a negligible difference was observed of less than 0.1%.

The profitability analysis presented in Table 4 revealed a higher cost of steel in both scenarios compared to the no capture steel mill. However, this was expected, since the integration of CCS brings additional energy and materials consumption. The smallest increase in the price of steel, of about 22%, was observed for the CaL case in Scenario 1 (i.e. CO_2 capture from 2 sources). In both capture scenarios, the levelized cost of steel showed a reduced value in case of CaL technology, by 4.5% in Scenario 1, respectively 3.8% in Scenario 2, while at the same time avoiding about 15% more CO_2. An interesting observation is that similar costs of steel were obtained for MEA-based capture in Scenarios 1 (544.06 €/t_{HRC}) and CaL in Scenario 2 (545.29 €/t_{HRC}) but with a significant difference in the CO_2 avoidance rate of 50% vs 75%. An important economic indicator, when talking about CCS, is the cost of CO_2 avoided. In both capture scenarios, a reduction in the cost of abating CO_2 was observed for the CaL system by 37.3%, respectively 33.0%. Evaluating all economic KPIs, it can be concluded that applying CCS to an integrated steel mill is more economically attractive than the reference amine-based capture technology.

Table 4. Integrated steel mill profitability analysis

	Unit	Case 1	Case 2	Case 3	Case 4	Case 5
LCOS	€/t_{HRC}	424.96	544.06	566.81	519.58	545.29
CO_2 avoided	%	-	50.00	60.00	63.00	75.00
Cost of CO_2 avoided	€/t_{CO2}	-	115.47	114.13	72.41	76.47
LCOS*	€/t_{HRC}	424.96	428.34	501.05	456.98	475.01
Cost of CO_2 removal	€/t_{CO2}	-	55.64	61.22	24.51	31.81

*without CO_2 transport and storage cost

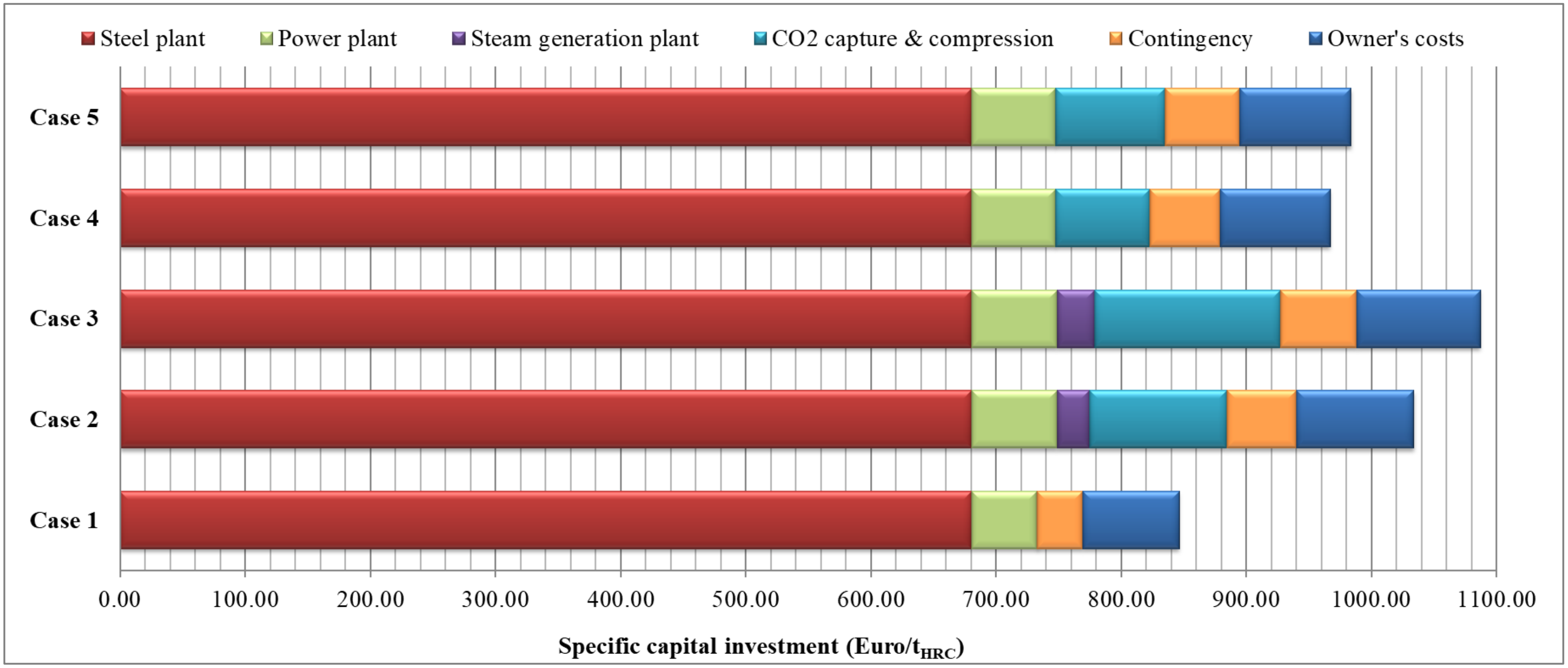


Figure 7. Specific capital investment cost for an integrated steel mill without and with CCS

The goal of the present LCA study is to quantify and analyse the environmental impact of steel production without/with CO_2 capture. The function of the evaluated system is the production of 4 million tonnes of HRC per year; thus, the functional unit proposed is one tonne of HRC. A cradle-to-gate LCA study is intended, covering all the production steps from raw-materials extraction from the earth (i.e. cradle) to the finished product (i.e. HRC) ready to be shipped from the steelworks (i.e. gate) as illustrated in Figure 8.

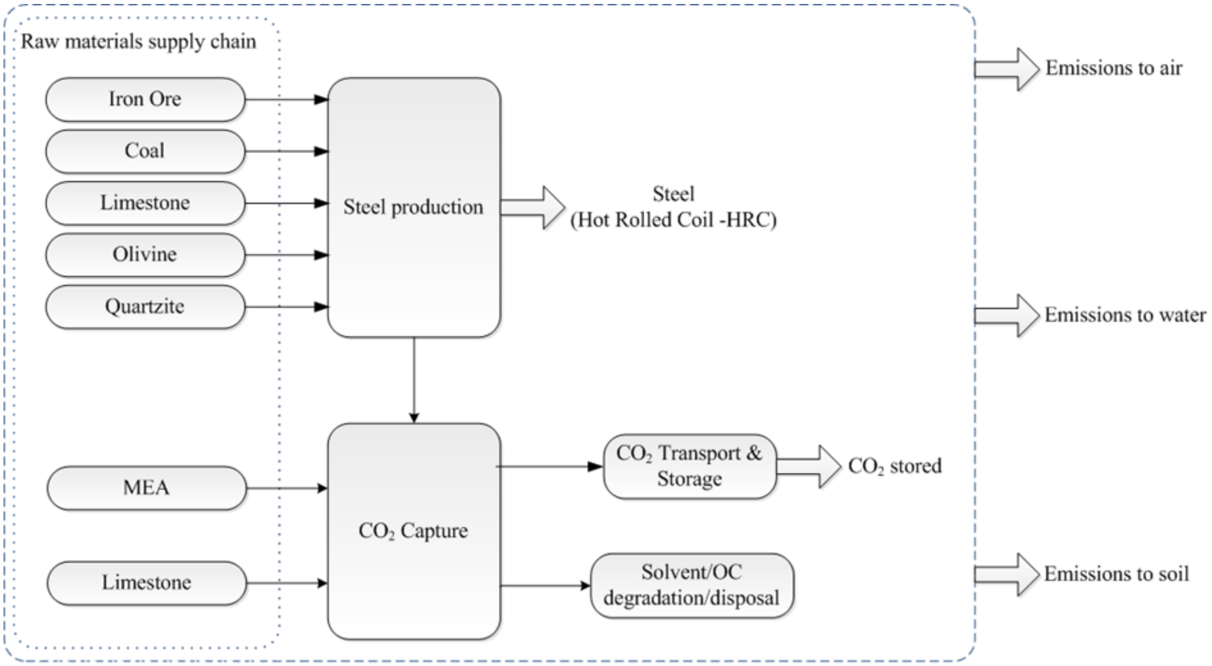


Figure 8. System boundaries

The CML 2001 method assessment implemented in GaBi software [41] was used for the present LCA study. The results of the environmental evaluations for all evaluated cases are summarised in Table 5 [42].

From an environmental point of view, the integration of CCS technologies lead to a significant reduction in GWP of 48.0%-57.8% for the amine-based system, and 64.5%-75.7% in case of CaL technology in the two evaluated capture scenarios. On the other hand, looking at the rest of the environmental impact indicators, a more or less significant increase was observed compared to the benchmark no capture scenario. This increase was caused by processes not present in the benchmark steel mill, such as NGCC power plant in the amine-based cases, additional natural gas and electricity consumption for the CO_2 capture and transport sections.

The influence of solvent/sorbent supply chain and their degradation/disposal was found to have an overall small impact on the environmental results, with the exception of some environmental impact indicators. Figure 9 illustrates the relative difference between the values presented in Table 5 and the values including the up-stream and down-stream processes regarding the solvent/sorbent.

Table 5. LCA results (Cases 1 – 5) according to CML 2001

KPI	Units	Case 1	Case 2	Case 3	Case 4	Case 5
GWP	kg CO_2 eq./t_{HRC}	2127.72	1106.86	897.83	754.34	516.20
AP*10^2	kg SO_2 eq./t_{HRC}	16.00	24.40	25.20	18.30	19.60
EP*10^2	kg PO_4^{3-} eq./t_{HRC}	4.08	5.80	5.96	4.40	4.55
ODP*10^{10}	kg R11 eq./t_{HRC}	12.88	13.03	13.05	13.03	13.08
ADP fossil	MJ/t_{HRC}	5332.39	9269.82	9615.7	7664.03	9633.70
FAETP*10^2	kg 1,4 DCB eq./t_{HRC}	28.80	34.30	34.90	30.60	31.60
HTP	kg 1,4 DCB eq./t_{HRC}	4.43	7.71	8.01	4.77	4.90
PCOP*10^2	kg ethylene eq./t_{HRC}	1.00	2.66	2.80	1.36	1.61
TEP*10^1	kg 1,4 DCB eq./t_{HRC}	1.27	1.38	1.40	1.34	1.37
MAETP	kg 1,4 DCB eq./t_{HRC}	4744.96	5559.04	5690.17	5577.64	5840.75

In case of the MEA-based capture technology, HTP, EP, AP, and to a smaller extent PCOP, were greatly influenced by solvent supply chain and degradation. On the other hand, the possibility to use the spent sorbent resulted from the CaL capture technology in the cement production, lead to additional emissions reduction, especially ADP_{fossil}, GWP, HTP and PCOP environmental impact indicators; at the same time, extraction of additional limestone negatively impacted MAETP, TEP and to a small degree ODP, in particular the electricity used for extraction.

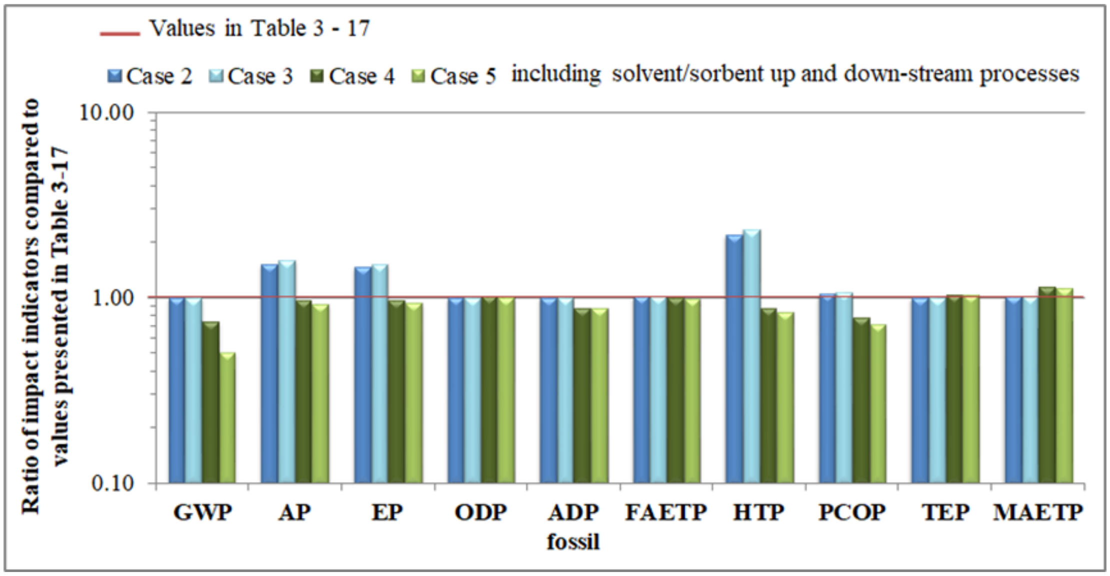


Figure 9. Influence of solvent/sorbent supply chain and degradation/disposal processes compared to the values presented in Table 5 (Table 3 – 17 in the thesis)

Considering all processes included in the boundary limits in comparing the two capture technologies, it was noted that from a total number of ten environmental impact categories, seven of them have lower values when CaL is used for CO_2 capture, in the range of 11.7%-74.9% for Scenario 1, respectively, 12.3%-78.1% for Scenario 2. As a consequence, it can be concluded that adopting CaL as a CO_2 removal technology in an integrated steel mill results in a more environmentally friendly design. Comparing the CaL technology in the two capture scenarios with the benchmark, Scenario 1 leads to smaller variations in the evaluated environmental impact indicators, even though in terms of GWP, Scenario 2 perform better as more CO_2 is avoided (i.e. 63% vs 75%).

Hydrogen generation

The industrial sector is the primary consumer of hydrogen as it is a valuable feedstock in many chemical processes, such as ammonia, methanol, petrochemical, biofuels and food industry [19]. Within the hydrogen economy, it has the potential to play a significant role in decarbonising the transport sector with the development of fuel cells. Moreover, it can act as an energy carrier as it emits only water vapour during its combustion (at the point of usage) and promising storage option for renewable energy [43]. Therefore, in order for the hydrogen economy to thrive, hydrogen must be obtained through energy-efficient, low-carbon and sustainable processes [44]. Moreover, hydrogen production has to be cost-competitive if it is to be considered as an alternative energy carrier to fossil fuels [45].

Hydrogen is obtained mainly from fossil fuels (96%), and only a small share (4%) is produced by electrolysis [46], accounting for about 830 million tonnes of CO_2 emitted annually [20]. Steam methane reforming (SMR) is the most mature and predominantly applied hydrogen production route, being also the most cost-effective compared to the other hydrogen production routes from fossil fuels (e.g. natural gas reforming and coal gasification) and renewables (e.g. electrolysis) [47,48]. However, SMR also yields around 9-11 kg CO_2 for every kg of H_2 produced [49]. As a consequence, hydrogen production has to be coupled with carbon capture if we aim for CO_2 emissions reduction. This option is already operational in various sites around the world such as Port Arthur Project in the USA, Quest Project in Canada and Tomakomai Project in Japan [50]. Currently, hydrogen production with CCS is more cost-effective than hydrogen obtained from renewable sources by electrolysis [51]. Integration of a carbon capture unit in post-combustion configuration is the most suitable way of capturing CO_2 from the reforming process as the stream exiting the shift section is rich in CO_2. However, commercial CCS technologies based on chemical absorption of CO_2 using amine-based solvents are highly energy-intensive, drastically increasing the operating costs and reducing the energy efficiency of the plant. Moreover, current fossil-based hydrogen production plants include endothermic processes which call for additional energy supply, usually provided by burning more fuel (e.g. coal, natural gas). Therefore, in order to reduce the energy penalties associated with carbon capture unit, new technologies need to be developed to make CCS more attractive for future implementation. Chemical looping technologies are able to generate hydrogen in various configurations as described in a previous section.

In the scientific literature, various chemical looping technologies able to generate hydrogen are evaluated and discussed, but no direct comparison between their performance was found. As a result, the present chapter aims to assess from a techno-economic and environmental point of view the most suitable configuration for hydrogen production with CO_2 capture applying three chemical looping systems, such as CLH, SER, SECLR. For comparison reasons, the conventional production route without and with capture by mature technology based on chemical absorption in amines was also evaluated, resulting in five case scenarios:

Case 1a: Steam methane reforming without carbon capture;
Case 1b: Steam methane reforming with MDEA-based CO_2 capture;
Case 2: Chemical-looping hydrogen production using ilmenite as oxygen carrier;
Case 3: Sorption Enhanced Reforming using Ca-based sorbent;
Case 4: Sorption Enhanced Chemical Looping Reforming using Ca-based sorbent and Cu-based oxygen carrier.

Looking at technical KPIs presented in Table 6, such as CCR, specific fossil-energy consumption, hydrogen and electrical efficiency, it was found that CLH has the highest electrical efficiency of all the evaluated case scenarios, including the benchmark no capture scenario, while capturing more than 99% CO_2. Contrarily, SER requires additional electricity import to satisfy its internal demand (especially for the ASU), resulting in more electric-energy consumption than the reference technology coupled with amine-based CO_2 capture by about 3.6 percentage points. However, it compensates by having the highest hydrogen efficiency, 3.4 percentage points above the benchmark/reference scenarios, due to the equilibrium balance resulted from the removal of CO_2. SECLR is considered an update to SER by integrating another redox couple to replace the necessity of the ASU and avoid the corresponding energy penalties. In consequence, SECLR shows an electrical efficiency similar to the benchmark no capture scenarios and about 1.8 percentage points higher than the reference amine-based capture system. On the other hand, by operating at a different pressure, the hydrogen efficiency drops about 7 percentage points compared to SER and 3.6 percentage point compared to the benchmark/reference scenarios. Moreover, compared to SER, the CCR is also reduced in the SECLR scenario as a result of some $CaCO_3$ being decomposed in the air reactor, due to the high exothermicity of copper oxidation. Even so, it still removes about 20% more CO_2 than the reference amine-based scenario. In fact, all looping systems capture around 20%-30% more CO_2 than the amine-based technology. In terms of specific-fossil energy consumption, SER shows a reduction of 4.5% compared to the benchmark/reference scenarios, followed by CLH with 2.4%. SECLR, on the other hand, shows a 5% increase, as additional natural gas is used as reducing gas for the regeneration of the copper-based oxygen carrier and $CaCO_3$ decomposition. Overall, from a technical perspective, CLH was found to give the best results, outperforming in every aspect the benchmark and reference scenarios. Also, compared to the other looping technologies, it gives the lowest SPECCA, meaning that it requires the least energy to avoid the same amount of CO_2.

Table 6. Technical indicators of investigated hydrogen production systems

Main Plant Data	**Units**	**Case 1a**	**Case 1b**	**Case 2**	**Case 3**	**Case 4**
Natural gas flow rate	kg/h	31371.59	31371.58	30632.79	29968.81	32986.66
Natural gas LHV	MJ/kg	46.49				
Thermal energy of the feedstock – LHV (A)	MW_{th}	405.16	405.16	395.61	387.04	426.01
Steam turbine output	MW_e	15.94	11.28	9.34	9.48	19.85
Expander	MW_e	-	-	41.20	-	32.36
Gross power output (B)	MW_e	15.94	11.28	50.54	9.48	52.21
Hydrogen thermal output (C)	MW_{th}	300.00	300.00	300.00	300.00	300.00
Hydrogen compression	MW_e	4.19	4.19	3.98	6.28	2.88
Air separation unit	MW_e	-	-	-	7.16	-
Air compression	MW_e	-	-	33.02	-	30.60
CO_2 compression & drying	MW_e	-	3.92	1.82	7.00	7.56
Total ancillary power consumption (D)	MW_e	4.19	8.10	38.83	20.44	41.05
Net electric power output (E = B - D)	MW_e	11.76	3.18	11.71	-10.96	11.16
Net electrical efficiency (E/A*100)	%	2.90	0.78	2.96	-2.83	2.62
Hydrogen efficiency (C/A*100)	%	74.05	74.05	75.83	77.51	70.42
Cumulative energy efficiency	%	76.95	74.83	78.79	74.68	73.04
SPECCA	MJ/kg_{CO2}	-	0.72	-0.41	0.56	1.04
Carbon capture rate	%	-	70.00	99.19	94.13	90.17
CO_2 specific emissions (hydrogen & power)	kg/MWh	266.54	82.28	1.93	14.20	25.24

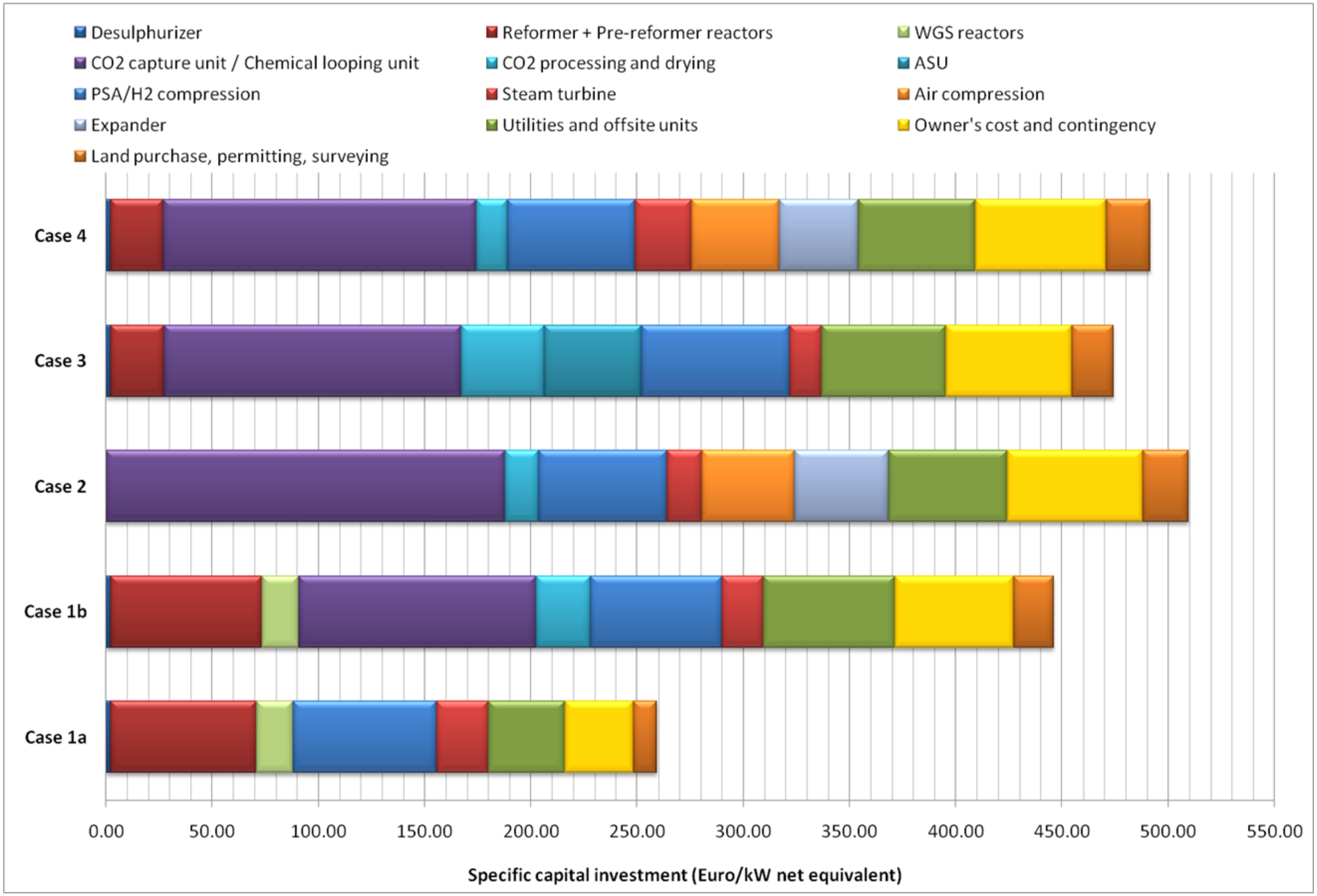


Figure 10. Specific capital investment cost for hydrogen production plants (Cases 1 - 4)

From an economic point of view, looking at Figure 10, it can be noted that all looping technologies require higher capital investments than the reference hydrogen production route based on SMR coupled with MDEA-based post-combustion CO_2 capture in the range 6.4%-14.2%.

In terms of operating cost, CLH shows the lowest OPEX, with about 1% above the benchmark no capture scenario, followed by the amine-based system with 7.6%. The sorption enhanced processes show a much higher increase, of about 15.4 % in case of SER, respectively 26.2% for SECLR, as a result of additional electricity purchase, respectively cost of the copper-based oxygen carrier. Consequently, SECLR results as the least economically favourable scenario, with a cost of hydrogen production 20% higher than the benchmark and 14.3% higher than the amine-based system. SER shows a slight increase in the hydrogen production cost compared to the MDEA-based capture system of 1.3%, at the same time removing about 15% more CO_2. Among the evaluated hydrogen generation looping technologies, CLH is the only technology to show competitive hydrogen production prices with the no capture scenarios at a CO_2 avoidance cost slightly lower than the current carbon tax (i.e. 19.5 vs 20 €/t_{CO2}). Regarding the CO_2 avoidance cost of the other looping technologies, a reduction of 5.5% compared to the amine-based scenarios is observed for the SER technology, while SECLR shows an almost double increase.

Table 7. Cost of hydrogen production and CO_2 avoidance

	Unit	Case 1a	Case 1b	Case 2	Case 3	Case 4
LCOH	€/MWh	42.43	44.58	41.84	45.17	50.96
CO_2 avoided	%	-	69.13	99.28	94.67	90.53
CO_2 avoidance cost	€/t_{CO2}	-	34.32	19.46	32.45	60.35

The goal of the present LCA study is to compare the environmental burden of the proposed hydrogen production routes in order to determine the configuration with the least impact on the environment. As a functional unit, 1 MWh (based on LHV) of hydrogen product is chosen. A cradle-to-gate LCA study is performed. As depicted in Figure 11, system boundaries include i) up-stream processes – catalysts, solvent, sorbent, OC's supply chain, ii) main process – hydrogen production and CO_2 capture, iii) down-stream processes – CO_2 transport and storage, solvent/sorbent/OC's degradation and disposal.

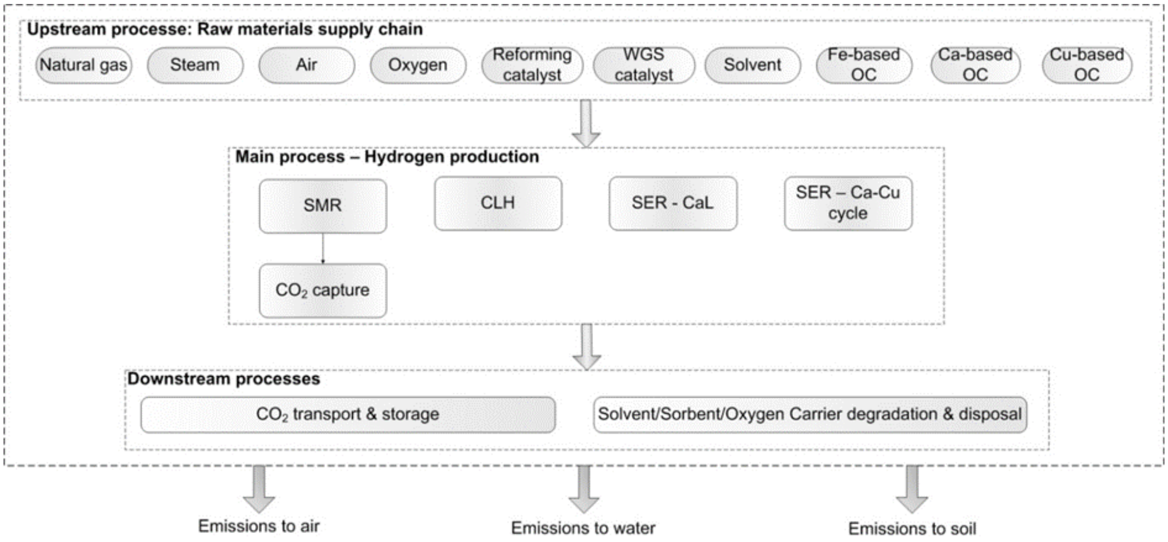


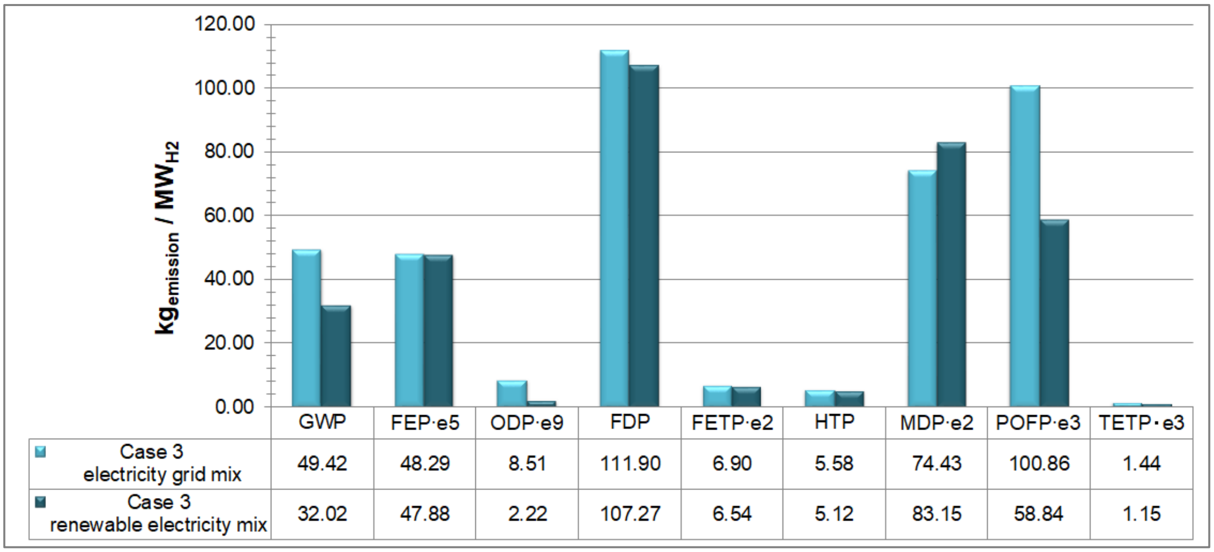
Figure 11. System boundaries

The ReCIPe life cycle impact assessment method was used to calculate impact categories relevant for the cases under study, with the results presented in Table 8.

Table 8. LCA results according to ReCIPe method

	Units	Case 1a	Case 1b	Case 2	Case 3	Case 4
GWP	kg CO_2 eq./MWh H_2	278.47	101.12	5.83	49.42	35.94
FEP*10^5	kg P eq./MWh H_2	39.32	40.27	57.19	48.29	65.89
ODP*10^9	kg CFC-11 eq./MWh H_2	-5.14	0.25	-4.62	8.51	-3.95
FDP	kg oil eq./MWh H_2	108.02	112.54	104.89	111.90	113.17
FETP*10^2	kg 1,4-DB eq./MWh H_2	5.26	5.64	7.26	6.90	8.30
HTP	kg 1,4-DB eq./MWh H_2	3.75	4.22	5.53	5.58	13.14
MDP	kg Fe eq./MWh H_2	0.52	0.62	0.51	0.74	28.46
POFP*10^3	kg NMVOC/MWh H_2	11.40	48.27	13.84	100.86	39.09
TETP*10^3	kg 1,4-DB eq./MWh H_2	0.45	0.79	0.82	1.44	1.04

The life cycle assessment of the evaluated scenarios revealed that all CCS cases show a considerable reduction in GWP, while the majority of the other environmental impact indicators present a smaller or higher increase. Based on these variations of the environmental KPIs compared to the benchmark, it can be established which of the evaluated CCS scenarios has the least impact on the environment. Out of eight environmental impact indicators (excluding GWP), CLH shows smaller values for three indicators (i.e. ODS, FDP and MDP due to reduced natural gas consumption and exported electricity) and an increase between 21.4%-82.8% in the other five indicators. In case of SER, an increase of 3.6% up to 50% is observed in five out of eight environmental impact indicators (excluding GWP), while the remaining three indicators (i.e. TETP, ODP, POFP) show an increase of more than double compared to the values observed in the benchmark. The main process responsible for these increases is the electricity supply chain. As an alternative, reviewable electricity supply was also considered leading to reduction between 0.9%-73.9% in eight out of nine indicators, compared to the case when electricity grid mix was used (see Figure 12). SECLR present the highest variations in the environmental KPIs, with four indicators having a more than double increase in value (i.e. HTP, MDP, POFP, TETP). The process responsible for these high values is the copper oxide OC's supply chain. Compared to the amine-based case scenario, CLH shows smaller values in five out of nine environmental impact indicators. On the other hand, the other two looping technologies present values higher than 20% in more than half of the indicators. Overall, from a techno-economic and environmental perspective, CLH seems to be a more sustainable hydrogen generation alternative than the conventional route based on SMR coupled with MDEA-based CO_2 capture. Also, SER has the potential to outperform the reference technology by finding a cheaper and more environmental electricity supply. In the case of SECLR, there are still some technical issues to overcome, as well as economic and environmental aspect in order to become competitive with the amine-based case scenario.



	GWP	FEP·e5	ODP·e9	FDP	FETP·e2	HTP	MDP·e2	POFP·e3	TETP·e3
Case 3 electricity grid mix	49.42	48.29	8.51	111.90	6.90	5.58	74.43	100.86	1.44
Case 3 renewable electricity mix	32.02	47.88	2.22	107.27	6.54	5.12	83.15	58.84	1.15

Figure 12. Comparison of imported electricity type influence on Case 3 results

Ammonia synthesis

Ammonia is one of the most synthesised chemicals worldwide having widespread use in energy concepts and production of explosives, pharmaceutics, fibres, plastics, paper and other essential chemicals and products. Fertiliser production is the major consumer of ammonia, accounting for about 85% of the total ammonia production [18]. Additional applications of ammonia are in the field of flue gas conditioning by removing and absorbing fly ashes and components like NO_X and CO_2 and in refrigeration applications. Recently, ammonia has received considerable attention as a promising fuel and energy carrier (i.e. indirect hydrogen storage material) due to its characteristics of carbon-free, high energy density, and convenience in transportation and storage [52].

With the continuous growth of the world's population and increasing interest in energy-related ammonia applications, global ammonia production is expected to increase in the following decades. The most common ammonia production methods available in the world are the Haber-Bosch process and solid state ammonia synthesis (SSAS) [53]. Currently, around 90% of the global ammonia production is obtained through the Haber-Bosch process, which combines nitrogen and hydrogen at high pressures and temperatures over an iron-based catalyst [54]. Nitrogen is usually obtained from air by cryogenic ASU; this method is the most mature and developed technology. Hydrogen, on the other hand, can be obtained from various feedstock (e.g. coal, natural gas, biomass, naphtha, heavy fuel oil, coke oven gas, refinery gas, water) and processes (e.g. reforming, pyrolysis, gasification, electrolysis, photocatalysis, biological fermentation). Steam methane reforming is the most mature and generally applied hydrogen production technology for ammonia synthesis [53]. Even though electrochemical production of hydrogen is a mature and commercially applied technology, the fluctuating nature of renewable energy sources and the higher production cost make fossil-based hydrogen production the dominant production route [55]. Solid state ammonia synthesis, still a developing technology, is an electrochemical process that can operate in a broad temperature range (i.e. 100 - 400ºC) at atmospheric pressure using solid state H^+ cells. Gaseous H_2 and N_2 are introduced into the system, with H_2 being converted into protons at the anode and transferred electrochemically to the cathode where they react with N_2 to obtain NH_3 [56].

Globally, ammonia production is accountable for over 1% of the total energy-related CO_2 emissions, together with about 420 million tonnes of CO_2 being emitted into the atmosphere during its synthesis [17]. In order to limit the impact on the environment caused by the current ammonia production routes which rely significantly on fossil fuels both as an energy source and as feedstock, other greener and sustainable production pathways need to be implemented.

In the scientific literature, several studies focus on the technological and economic aspects of ammonia production, while environmental aspects are investigated less. The potential techno-economic and environmental benefits of integrating chemical looping technologies into ammonia production were not yet investigated to the authors' best knowledge. Likewise, LCA of chemical looping for hydrogen production is scarcely investigated. The reviewed literature, environmental aspects of ammonia production cover mainly renewable production routes. However, considering the economic criteria, fossil-based ammonia production will remain a significant production pathway in the following decades. Thus, the present chapter aims to evaluate and compare the performance of an ammonia plant with a capacity of 2500 tonnes per day, located in Germany (as most of the European chemical industry is concentrated here). As the hydrogen supply chain is the primary emissions source in the ammonia synthesis route, the present case study aimed at finding a cleaner ammonia production route by evaluating and comparing alternative hydrogen supply chains. Four case scenarios are subjected to evaluation defined in Table 9 for better understanding.

Table 9. Definition of evaluated case scenarios

	N_2 production	H_2 production	AGR	NH_3 production	Electricity supply
Case 1	ASU	SMR	Absorption by MDEA	Haber-Bosch	Electricity grid mix*
Case 2	ASU	SMR	Absorption by Chilled Ammonia	Haber-Bosch	Electricity grid mix*
Case 3	CLH	CLH	CLH	Haber-Bosch	Electricity grid mix*
Case 4a	ASU	Water electrolysis	-	Haber-Bosch	Electricity grid mix*
Case 4b	ASU	Water electrolysis	-	Haber-Bosch	Renewable electricity mix†

*Electricity is modelled according to Germany's specific grid mix taking as the reference year 2019 [57]. It consists of 23.59% wind energy, 20.05% lignite, 13.70% nuclear energy, 10.53% natural gas, 9.80% solar PV, 9.47% hard coal, 8.62% biomass, 3.82% hydropower, 0.29% oil and the rest waste. †The renewable electricity mix follows the same distribution as the original electricity grid mix. It is composed of 8.34% hydropower, 18.81% biomass, 51.46% wind energy and 21.39% solar PV

From the technical assessment results presented in Table 10, it was observed that integrating CLH in the ammonia synthesis route leads to a reduction in both specific fossil and electric-energy consumption by 15%, respectively 63% compared to the reference case with amine-based CO_2 removal. The reduction in electricity consumption is obtained due to the high heat recovery potential as well as the elimination of the ASU. Comparing the specific fossil energy consumption (natural gas used as raw material), there is no significant difference between Case 1 and Case 2, as they both employ the same H_2 production technology. Similar results are obtained in case of the specific electric power consumption as well. Even if the energy for solvent regeneration is reduced in Case 2 compared to Case 1 by 27%, additional energy is required in Case 2 to cool down the gas stream and the solvent to the required temperature for the chilled ammonia process (i.e. 5ºC). Among the evaluated case scenarios, Case 4 has the highest specific energy consumption, mainly due to the electrolyser (i.e. 95.69%), nitrogen production having only a small share of less than 1%.

The fact that CLH (Case 3) is able to produce both hydrogen and nitrogen suitable for ammonia synthesis, eliminating the need for an ASU, has positive effects on the economic KPIs. As observed from Figure 13 a reduction in specific capital investment costs of 24% is obtained for this production route. Replacing the amine-based CO_2 capture with chilled ammonia technology leads to a reduction in the SCI cost of about 8%. Even though additional equipment, such as chillers, are required, the materials used in construction are less expensive due to reduced corrosion of the solvent. Ammonia synthesis route integrated with hydrogen obtained from water electrolysis was found to have the highest SCI cost. In this case, the electrolyser has the most significant influence on the capital cost, leading to an increase of 54% compared to the benchmark case (i.e. Case 1) and requiring about double the capital investment of Case 3.

Table 10. Technical indicators of the proposed ammonia production routes

Main Plant Data	Unit	Case 1	Case 2	Case 3	Case 4
NH_3 output	t/day	2500.00	2500.00	2500.00	2500.00
Fuel thermal energy input (NG)	MW_{th}	1017.43	1016.13	864.96	-
LHV_{NG}	MJ/kg		46.49		-
N_2 production (ASU)	**MW_e**	**-10.59**	**-10.57**	**-**	**-10.22**
H_2 production	**MW_e**	**27.50**	**23.73**	**16.06**	**-1098.28**
ST	MW_e	30.52	30.48	24.02	-
N_2 expander	MW_e	-	-	36.71	-
Electrolyser	MW_e	-	-	-	-1098.28
Ancillary (pumps)	MW_e	-0.36	-0.36	-0.34	-
CO_2 capture	MW_e	-2.66	-6.40	-	-
Air compression	MW_e	-	-	-44.33	-
H_2 & N_2 compression	**MW_e**	**-37.97**	**-37.94**	**-35.17**	**-66.86**
NH_3 synthesis	**MW_e**	**7.46**	**7.45**	**16.31**	**17.41**
Reactor cooling	MW_e	9.41	9.40	18.02	18.23
Recycle compression	MW_e	-1.96	-1.96	-1.72	-0.82
CO_2 transport & storage	**MW_e**	**-8.91**	**-6.92**	**-5.45**	**-**
CO_2 compression	MW_e	-7.92	-5.93	-3.99	-
Re-compression	MW_e	-0.16	-0.16	-0.24	-
Injection	MW_e	-0.82	-0.83	-1.22	-
Net electric energy consumption	**MWe**	**22.51**	**24.26**	**8.26**	**1157.95**
Specific fossil energy consumption	MW_{th}/t_{NH3}	9.77	9.75	8.30	-
Specific electric energy consumption	MW_e/t_{NH3}	0.22	0.23	0.08	11.12
CCR	%	99.88	99.88	100.00	-
CO_2 captured	t/h	118.40	118.11	174.00	-
O_2 product	t/h	25.80	25.80	-	183.12

*Refers to both Case 4a and Case 4b;

”-” sign in front of a value signifies consumption;

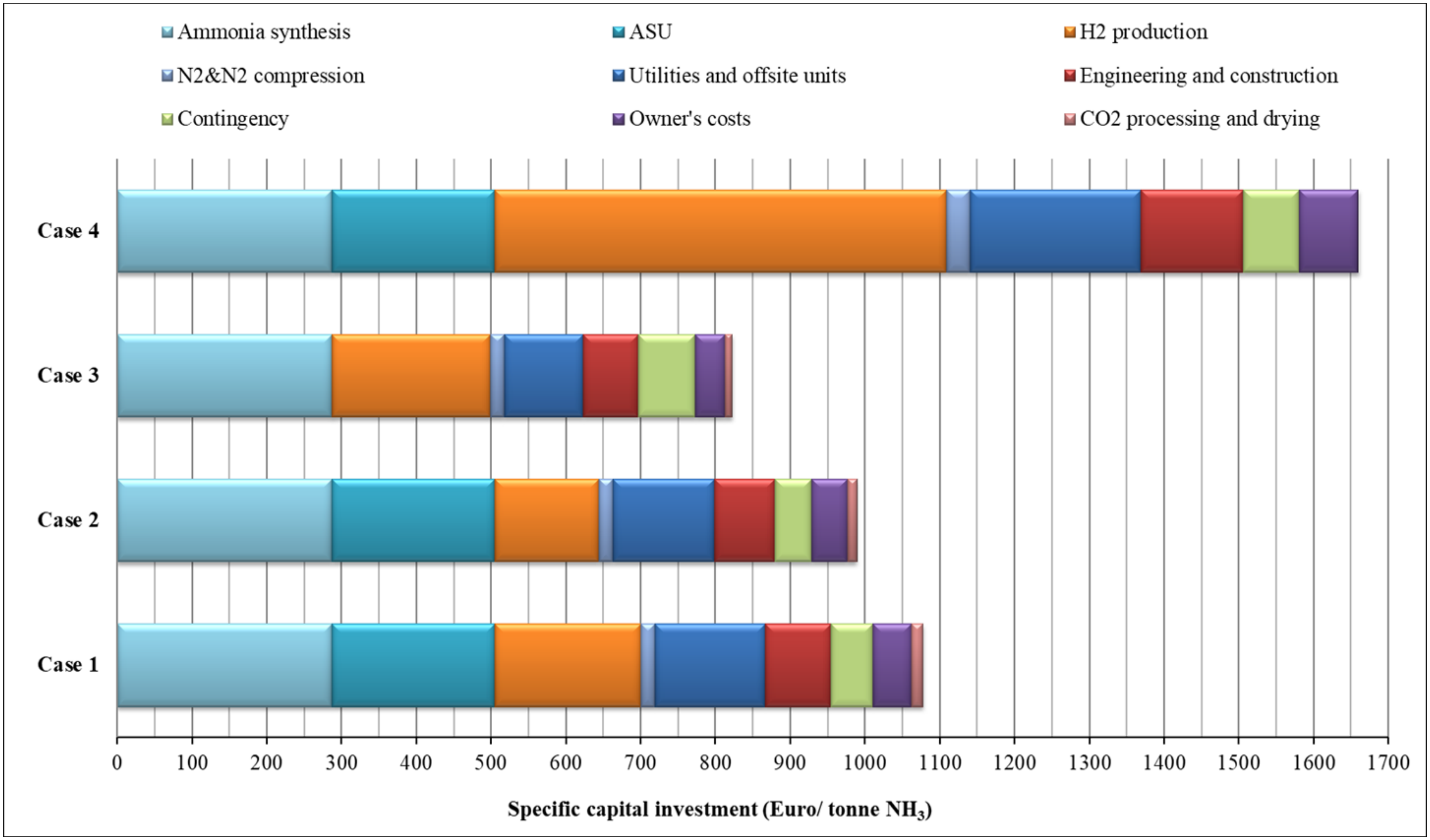


Figure 13. Specific capital investment cost for ammonia production considering various hydrogen production routes

Similar to the SCI cost, Case 3 shows a reduction in the O&M costs by about 20% compared to the benchmark case, due to lower natural gas and electricity consumption. Between Case 1 and Case 2, a difference of less than 2% is observed in favour of Case 2, as a result of reduced solvent cost. In Case 4, electricity consumption is the major contributor to the O&M cost representing about 99% of the variable O&M costs.

Two scenarios were investigated concerning the fate of the separated $CO_2$with the results presented in Table 11. Scenario 1 considers CO_2 to be sent to storage while in Scenario 2 the removed CO_2 is sold as a product. Comparing Case 1 and Case 2, a reduction in the production cost of ammonia is observed of around 4% for Case 2 in both CO_2 capture scenarios. Likewise, Case 3 shows lower production prices compared to Case 1 by 18% in Scenario 1 and 9% in Scenario 2. In comparison, the LCOA estimated for Case 4 shows the highest values with an increase of 60-77% compared to cases in Scenario 1, and 84-124% compared to cases in Scenario 2.

For the calculations of the CO_2 avoidance and CO_2 removal costs, the reference no capture case considers all separated CO_2 to be released into the atmosphere. As a result, any cost related to CO_2 compression and CO_2 transport and storage are eliminated. Looking at the results presented in Table 11, a negative value for the cost of CO_2 avoided in Case 3 is observed, which means that this production route is profitable even at a carbon tax of up to 52 €/t_{CO2}. The overall techno-economic results showed that the integration of CLH in the ammonia synthesis leads to significant energy consumptions and cost, making it a more economically attractive alternative.

Table 11. Profitability assessment of ammonia production case scenarios

	Unit	No capture	Case 1	Case 2	Case 3	Case 4
LCOA (S1)	€/t_{NH3}	342.08	368.09	354.23	333.24	588.86
CO_2 avoided	%	-	63.00	63.00	99.65	-
Cost of CO_2 avoided	€/t_{CO2}		22.88	10.68	-52.47	-
LCOA*	€/t_{NH3}	342.08	349.45	335.63	305.79	588.86
Cost of CO_2 removal	€/t_{CO2}		6.48	-5.69	-26.14	-
LCOA* (S2)	€/t_{NH3}		320.55	306.80	263.32	588.86

*without CO_2 transport and storage cost; S1-Scenario 1; S2-Scenario 2

The goal of the life cycle assessment is to compare the environmental burden of four ammonia production scenarios considering hydrogen production from natural gas coupled with CO_2 capture by conventional/state-of-the-art gas-liquid absorption, iron-based chemical looping and water electrolysis in order to find a more environmentally benign ammonia production route. All the environmental indicators are reported to one tonne of ammonia produced, as the chosen functional unit for the investigated case scenarios. A "cradle-to-gate" LCA study covering all the production steps from raw-materials extraction from the earth (i.e. the cradle) to the finished product (i.e. ammonia) ready to be shipped (i.e. the gate) is considered as illustrated in Figure 14.

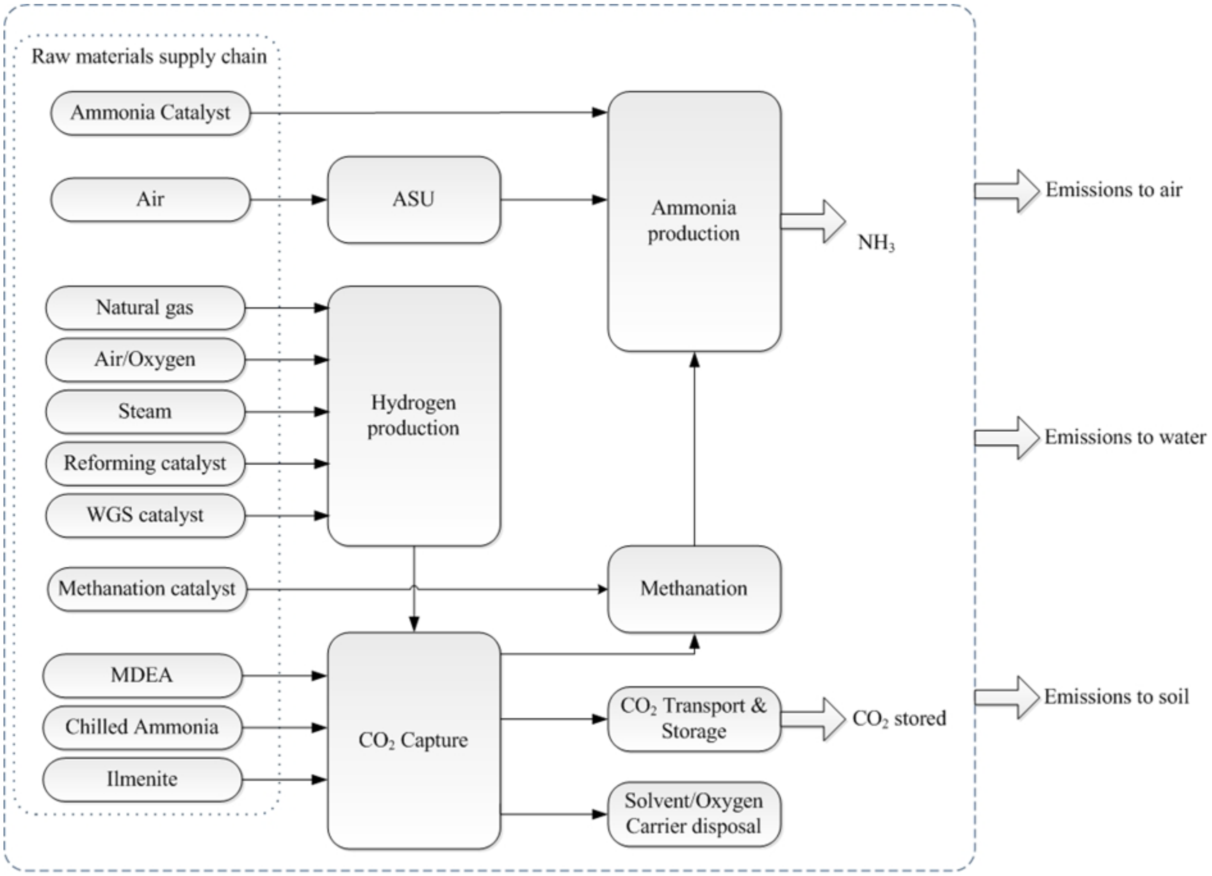


Figure 14. System boundaries

Focusing on the results of the environmental assessment presented in Table 12, it was noted that the integrated CLH case scenario shows reduced environmental impact, in the range 17.0%-86.6%, in four out of nine environmental indicators, with an increase between 27.7%-57.8% in the rest of the indicators (i.e. FEP, ODP, FETP, HTP). These emissions are attributed mainly to the wastewater treatment section of the process/cooling water used in the system. Due to the high energy recovery potential from the process' hot streams, a higher water input is required in the CLH process. The ammonia synthesis route integrated with hydrogen obtained from electrolysis results in the highest overall environmental impact unless the electricity for electrolysis is supplied by renewable sources. In this latter case, five out of nine environmental impact indicators register smaller values than the proposed chemical looping technology in the range 7.5%-93.9%. On the other hand, two environmental indicators, in particular, TETP and MDP, show values more than 10, respectively 20 times higher than the CLH case scenario. Between the two scenarios with chemical absorption CO_2 capture technologies, no significant difference was observed in term of environmental impact. Analysing the overall results, it can be concluded that emissions and material's consumptions in ammonia synthesis can be reduced by integrating CLH for both hydrogen and nitrogen production, making it a more sustainable production alternative. Even though from an environmental perspective renewable hydrogen obtained from electrolysis has a lower impact, the economic evaluation revealed that it leads to the highest production costs.

Table 12. LCA results according to ReCIPe method

	Units	Case 1	Case 2	Case 3	Case 4a	Case 4b
GWP	kg CO_2 eq./t_{NH3}	2794.82	2804.69	373.54	6718.84	149.14
FEP*10^3	kg P eq./t_{NH3}	3.00	3.00	4.67	4.75	4.13
ODP*10^9	kg CFC-11 eq./t_{NH3}	3.47	3.48	5.38	10.64	2.62
FDP	kg oil eq./t_{NH3}	913.90	915.04	758.89	1570.74	36.06
FETP	kg 1,4-DB eq./t_{NH3}	0.35	0.35	0.55	0.97	0.19
HTP	kg 1,4-DB eq./t_{NH3}	29.77	29.86	46.97	117.80	31.61
MDP	kg Fe eq./t_{NH3}	3.29	3.18	2.64	38.79	36.75
POFP	kg NMVOC/t_{NH3}	1.55	1.56	0.69	6.68	0.48
TETP*10^3	kg 1,4-DB eq./t_{NH3}	7.91	8.08	10.10	123.00	74.10

Conclusions

As part of the research carried out in this thesis, key industrial sectors with large energy requirements and CO_2 emissions were evaluated for the potential benefits of applying chemical looping technologies. Three main carbon and energy-intensive industrial applications were examined, steel production, hydrogen generation and ammonia synthesis.

All case studies were evaluated from a technical, economic and environmental perspective to gain a complete overview of the impact of integrating chemical looping technologies for the decarbonisation of these important industrial sectors. For comparison reasons, the state-of-the-art in the evaluated case scenarios was considered without and with carbon capture by mature and industrially applied CO_2 capture technologies such as liquid absorption in amines.

From the literature review, it was observed that limited studies were conducted on the subject, in particular, when it comes to the environmental impact of chemical looping technologies as well as the direct comparison of various looping technologies that have the same application (i.e. hydrogen production). As a result, this work aimed to assess the performance of chemical looping technologies looking at key techno-economic and environmental performance indicators.

The main findings of the evaluated case scenarios revealed that in each industrial sector, there is the possibility to reduce emissions and energy consumption by the integration of a suitable chemical looping technology. As a result, reductions of 2%-20% in specific fossil-energy consumption, respectively, more than 50% cutback in specific electric-energy consumption were obtained for the evaluated chemical looping technologies. This led to cost reductions compared to the reference amine-based technology in the range 3.8%-9.5% while avoiding between 15%-30% more CO_2. From an environmental perspective, the carbon intensity of the evaluated industrial activities was reduced to 0.26-0.56 tonnes of CO_2 per tonne of steel produced, 0.19-

1.65 kg CO_2 per kg of hydrogen generated, respectively 0.37 tonnes of CO_2 per tonne of ammonia produced. Overall, the performance of the chemical looping-integrated case studies outperformed those based on chemical absorption by amines.

References

[1] IEA (International Energy Agency). Tracking Power 2020. Paris: 2020.

[2] IEA (International Energy Agency). Key world energy statistics. Paris: 2019.

[3] IEA (International Energy Agency). Tracking Industry 2020. Paris: 2020.

[4] IEA (International Energy Agency). Energy Technology Perspectives 2017: Catalysing Energy Technology Transformations. Paris: 2017.

[5] World Steel Association. Steel's contribution to a low carbon future and climate resilient societies - worldsteel position paper. 2017.

[6] IEA (International Energy Agency). Tracking Industry 2020: Chemicals. Paris: 2020.

[7] IEA (International Energy Agency). Tracking Industry 2020: Aluminium. Paris: 2020.

[8] Markewitz P, Bongartz R. Carbon Capture Technologies. In: Kuckshinrichs W, Jurgen-Friedrich H, editors. Carbon capture, storage use, Springer International; 2015.

[9] Maroto-Valer MM. Developments and innovation in carbon dioxide (CO_2) capture and storage technology. Volume 2, Carbon dioxide (CO_2) storage and utilisation. CRC Press; 2010.

[10] Reddy PJ. Clean coal technologies for power generation. CRC Press; 2013.

[11] Wang M, Lawal A, Stephenson P, Sidders J, Ramshaw C. Post-combustion CO2 capture with chemical absorption: A state-of-the-art review. Chem Eng Res Des 2011;89:1609–24. doi:10.1016/J.CHERD.2010.11.005.

[12] Fennell P. Chapter 1 – Calcium and chemical looping technology: An introduction. Calcium Chem. Looping Technol. Power Gener. Carbon Dioxide Capture, 2015, p. 3–14. doi:10.1016/B978-0-85709-243-4.00001-X.

[13] Abad A. Chapter 15 – Chemical looping for hydrogen production. Calcium Chem. Looping Technol. Power Gener. Carbon Dioxide Capture, 2015, p. 327–74. doi:10.1016/B978-0-85709-243-4.00015-X.

[14] Chiesa P, Lozza G, Malandrino A, Romano M, Piccolo V. Three-reactors chemical looping process for hydrogen production. Int J Hydrogen Energy 2008;33:2233–45. doi:10.1016/J.IJHYDENE.2008.02.032.

[15] Bohn CD, Müller CR, Cleeton JP, Hayhurst AN, Davidson JF, Scott SA, et al. Production of Very Pure Hydrogen with Simultaneous Capture of Carbon Dioxide using the Redox Reactions of Iron Oxides in Packed Beds. Ind Eng Chem Res 2008;47:7623–30. doi:10.1021/ie800335j.

[16] Rydén M, Arjmand M. Continuous hydrogen production via the steam–iron reaction by chemical

looping in a circulating fluidised-bed reactor. Int J Hydrogen Energy 2012;37:4843–54. doi:10.1016/J.IJHYDENE.2011.12.037.

[17] Philibert C. Producing ammonia and fertilisers: new opportunities from renewables. Power to Ammon Conf 2017. https://www.ee.co.za/wp-content/uploads/2017/06/Producing-ammonia-and-fertilizers-new-opportunities-from-renewables.pdf (accessed April 10, 2020).

[18] Rossetti I. Reactor Design, Modelling and Process Intensification for Ammonia Synthesis. Sustain. Ammon. Prod. Green Energy Technol., Springer, Cham; 2020. doi:https://doi.org/10.1007/978-3-030-35106-9_2.

[19] Dean CC, Blamey J, Florin NH, Al-Jeboori MJ, Fennell PS. The calcium looping cycle for CO2 capture from power generation, cement manufacture and hydrogen production. Chem Eng Res Des 2011;89:836–55. doi:10.1016/J.CHERD.2010.10.013.

[20] IEA (International Energy Agency). The Future of Hydrogen. Paris: 2019.

[21] Rubin ES. Understanding the pitfalls of CCS cost estimates. Int J Greenh Gas Control 2012;10:181–90. doi:10.1016/J.IJGGC.2012.06.004.

[22] Rubin ES, Booras G, Davison J, Ekstrom C, Matuszewski M, McCoy S, et al. Toward a common method of cost estimation for CO2 capture and storage at fossil fuel power plants. Glob CCS Inst 2013.

[23] Smith R. Chapter 2 - Process Economics. Chem. Process Des. Integr., John Wiley & Sons; 2005, p. 17–34.

[24] Sinnott RK. Chapter 6 - Costing and Project Evaluation. Chem. Eng. Des. Vol. 6. Forth Edit, Elsevier; 2005, p. 243–83.

[25] Towler G, Sinnott RK. Chapter 9 - Economic Evaluation of Projects. Chem. Eng. Des. - Princ. Pract. Econ. Plant Process Des. Second Edi, Oxford, UK: Butterworth-Heinemann; 2013, p. 289–429.

[26] IPCC. IPCC special report on carbon dioxide capture and storage. Cambridge University Press; 2005.

[27] ISO. ISO14040 Environmental management - Life Cycle Assessment - Principles and Framework. International Organization for Standardization. Geneva: 2006.

[28] ISO. ISO14044 Environmental Management - Life Cycle Assessment - Requirments and Guidelines. International Organization for Standardization. Geneva: 2006.

[29] Hauschild MZ, Huijbregts MAJ, editors. Introducing Life Cycle Impact Assessment. Life Cycle Impact Assessment. LCA Compend. - Complet. World Life Cycle Assess., Dordrecht: Springer; 2015. doi:https://doi.org/10.1007/978-94-017-9744-3_1.

[30] Curran MA, editor. Goal and scope definition in life cycle assessment. LCA Compend. – Complet. World Life Cycle Assess., Dordrecht: Springer; 2017. doi:https://doi.org/10.1007/978-94-024-0855-3.

[31] Hasanbeigi A, Price LK, McKane AT. The State–of-the-Art Clean Technologies (SOACT) for Steelmaking Handbook 2010.

[32] IEAGHG. Iron and Steel CCS Study (Techno-Economics Integrated Steel Mill), 2013/04. 2013.

[33] Pardo N, Moya JA, Vatopoulos K. Prospective scenarios on energy efficiency and CO 2 emissions in the EU Iron & Steel Industry. Publications Office of the European Union; 2012.

[34] IEAGHG. Challenges and opportunities of CO2 capture and storage for the iron and steel industry, 2011/17. 2011.

[35] IEA (International Energy Agency). Tracking Clean Energy Progress 2017. International Energy Agency. Paris: 2017.

[36] Abdul Quader M, Ahmed S, Dawal SZ, Nukman Y. Present needs, recent progress and future trends of energy-efficient Ultra-Low Carbon Dioxide (CO2) Steelmaking (ULCOS) program. Renew Sustain Energy Rev 2016;55:537–49. doi:10.1016/J.RSER.2015.10.101.

[37] Tonomura S. Outline of Course 50. Energy Procedia 2013;37:7160–7. doi:10.1016/J.EGYPRO.2013.06.653.

[38] Burchart-Korol D. Life cycle assessment of steel production in Poland: a case study. J Clean Prod 2013;54:235–43. doi:10.1016/J.JCLEPRO.2013.04.031.

[39] Olmez GM, Dilek FB, Karanfil T, Yetis U. The environmental impacts of iron and steel industry: a life cycle assessment study. J Clean Prod 2016;130:195–201. doi:10.1016/J.JCLEPRO.2015.09.139.

[40] World Steel Association. Life Cycle Assessment Methodology Report. World Steel Association. 2011.

[41] PE International. GaBi ts 2018.

[42] Chisalita D-A, Petrescu L, Cobden P, van Dijk H, Cormos A-M, Cormos C-C. Assessing the environmental impact of an integrated steel mill with post-combustion CO2 capture and storage using the LCA methodology. J Clean Prod 2019;211:1015–25. doi:10.1016/J.JCLEPRO.2018.11.256.

[43] IEA (International Energy Agency). Technology Roadmap - Hydrogen and Fuel Cells. Paris: 2015.

[44] Luo M, Yi Y, Wang S, Wang Z, Du M, Pan J, et al. Review of hydrogen production using chemical-looping technology. Renew Sustain Energy Rev 2018;81:3186–214. doi:10.1016/J.RSER.2017.07.007.

[45] Dincer I, Acar C. Innovation in hydrogen production. Int J Hydrogen Energy 2017;42:14843–64. doi:10.1016/J.IJHYDENE.2017.04.107.

[46] Coutanceau C, Baranton S, Audichon T. Hydrogen Electrochemical Production. Hydrog. Electrochem. Prod., Elsevier; 2018, p. 1–6. doi:10.1016/B978-0-12-811250-2.00001-7.

[47] Simbeck DR, Chang E. Hydrogen supply: Cost Estimate for Hydrogen Pathways - Scoping Analysis. Bolden, Colorado: 2002.

[48] Mueller-Langer F, Tzimas E, Kaltschmitt M, Peteves S. Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term. Int J Hydrogen Energy 2007;32:3797–810. doi:10.1016/J.IJHYDENE.2007.05.027.

[49] Khojasteh Salkuyeh Y, Saville BA, MacLean HL. Techno-economic analysis and life cycle assessment of hydrogen production from natural gas using current and emerging technologies. Int J Hydrogen Energy 2017;42:18894–909. doi:10.1016/J.IJHYDENE.2017.05.219.

[50] IEAGHG. Techo-Economic Evaluation of SMR Based Standalone (Merchant) Plant with CCS. 2017.

[51] Global CCS Institute. The Global Status of CCS: 2018. Australia: 2018.

[52] Lan R, Irvine JTS, Tao S. Ammonia and related chemicals as potential indirect hydrogen storage materials. Int J Hydrogen Energy 2012;37:1482–94. doi:https://doi.org/10.1016/j.ijhydene.2011.10.004.

[53] Bicer Y. Chapter 3.2: Ammonia Production. Compr. Energy Syst., Oxford: Elsevier; 2018, p. 41–94. doi:10.1016/B978-0-12-809597-3.00305-9.

[54] Dincer I, Bicer Y. Chapter 2.1: Ammonia. Compr. Energy Syst., Oxford: Elsevier; 2018, p. 1–39. doi:https://doi.org/10.1016/B978-0-12-809597-3.00201-7.

[55] Abdin Z, Zafaranloo A, Rafiee A, Mérida W, Lipiński W, Khalilpour KR. Hydrogen as an energy vector. Renew Sustain Energy Rev 2020;120:109620. doi:10.1016/J.RSER.2019.109620.

[56] Garagounis I, Vourros A, Stoukides D, Dasopoulos D, Stoukides M. Electrochemical Synthesis of Ammonia: Recent Efforts and Future Outlook. Membranes (Basel) 2019;9:112. doi:10.3390/membranes9090112.

[57] Fraunhofer-Gesellschaft. ENERGY CHARTS 2019. https://www.energy-charts.de/energy_pie.htm?year=2019 (accessed November 25, 2019).