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Direct air capture: is it the solution to the CO_2 crisis?

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Abstract

Climate change due to an increasing greenhouse gases concentration in the atmosphere is a challenging issue that humanity will have to address promptly. To limit global warming to 1.5°C, as set out in the Paris agreements during *COP21*, drastic reductions in our emissions by 2030 followed by achieving emissions neutrality in 2050 is recommended. Even if its heat trapping ability is far from being the highest, the abundance of carbon dioxide in the atmosphere makes it the major source of warming. Furthermore, it also has the disadvantage to have a very long lifetime; making past, present and future emissions, long-term contributors to global warming. To counter this, carbon dioxide removal technologies are presented as ways to artificially decreased CO_2 concentration in the atmosphere.

Among them, Direct Air Capture (DAC) is a promising technology at early stage of development. It described the process of extracting carbon dioxide directly from the atmosphere by chemically trapping it. The concentrated stream is then either geologically stored or used in industrial processes. Although the project looks great at first sight, its high energy consumption and other environmental pressures such as land and water use could limit DAC positive impact or even make it detrimental to the climate cause. It is precisely this ambiguity that motivates this work.

Throughout this thesis, the two main DAC technologies, using solid or liquid capture medium, will be discussed by means of a life cycle analysis. After a literature review including a technical description of how the two capture methods work, they are compared on the basis of a reference case. Then, in order to take into account uncertainties related to the choice of the model as well as the limited information available concerning the few plants in operation, a sensitivity analysis is carried out. Based on these results, three location scenarios are established to illustrate them while deepening the analysis by adding the use of the obtained CO_2 in the LCA scope.

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List of Abbreviations

CCS Carbon Capture and Storage.

CDR Carbon Dioxide Removal.

COP Coefficient of performance.

DAC Direct Air Capture.

GHG Greenhouse Gas.

IEA International Energy Agency.

IPCC Intergovernmental Panel on Climate Change.

LCA Life Cycle Assessment.

NZE Net Zero Emission.

PSC Point Source Capture.

RH Relative humidity.

Chapter 1

Introduction

As temperatures continue to rise at a higher rate each year, the measures deployed to mitigate climate change seem insufficient. The concentration of Greenhouse Gases (GHG) in the atmosphere, identified as the main human influence, is reaching new heights every year. Yet, in 2015 the Paris agreements aimed to limit the global temperature increase to 2°C, with a preference for 1.5°C, compared to the pre-industrial period [1]. Given the current trend (Figure 1.1), achieving these ambitions will require rapid changes in a wide range of sectors. Moreover, considering that each climate response brings its own risks, these actions must be taken with great caution.

In order to guide policy decisions, the Intergovernmental Panel on Climate Change (IPCC) regularly publishes reports that bring together the latest knowledge on climate change. In its new report [2], IPCC suggests temperature evolution over 5 scenarios. Among them, only the two scenarios that reach net zero CO_2 emissions before 2100 allow keeping temperature below 2°C. Meeting this ambitious challenge will not only require a drastic decrease in emissions, but also the use of Carbon Dioxide Removal (CDR) methods. Among the potential CDR options, we can mention afforestation, bioenergy with carbon capture and storage and direct air capture (CDR options are presented in Appendix A.2).

Carbon dioxide removal aims to counterbalance residual emissions from hard-to-decarbonize sectors (such as industry, transport and agriculture) by removing CO_2 from the atmosphere to store it. The predominant intention that carbon dioxide receives compared to other greenhouse gases come from two characteristics. First, even if its heat-tapping ability is far from being the highest, CO_2 abundance make it the main cause of global warming. Second, as carbon dioxide does not decompose through atmospheric chemical reactions, its lifetime is particularly long. Thus, each additional emission will affect temperature for centuries [3]. In this regard, CDR allows to artificially reduce its lifetime.

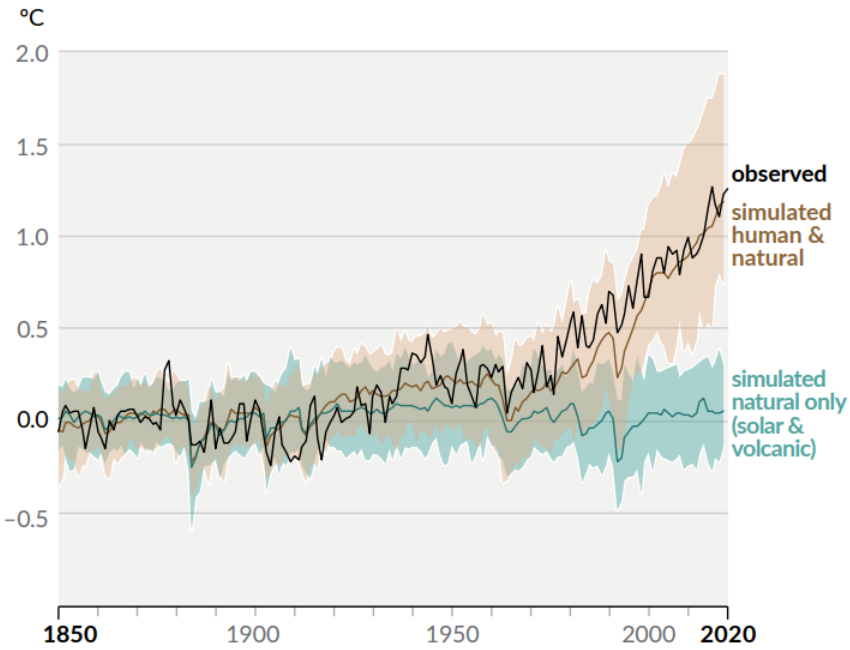

Figure 1.1: Change in global surface temperature between 1850 and 2020 : as observed (black), simulated considering both human and natural influence (brown) and simulated for natural factors only (blue). Figure taken from *Climate Change 2021: The Physical Science Basis* [2]

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1.1 The role of Direct Air Capture

Meeting climate goals will require collective effort to deeply reduce our carbon emissions by: energy sobriety, increase in efficiency and post-combustion capture. Moreover, CDR technologies will have to be deployed on large scale to decrease artificially the GHG concentration in our atmosphere. Among the different approaches for CDR, Direct Air Capture (DAC) is a relatively new process receiving more and more attention.

DAC described the process of extracting carbon dioxide directly from the atmosphere. The ambient air is drawn into a contactor where CO_2 is selectively trapped, and then released as a concentrated stream. DAC is considered as a CDR method when the carbon dioxide thus obtained is permanently stored. The two main DAC technologies use either a liquid solvent or a solid sorbent as capture medium. We will explain and discuss these methods in further details in the next chapter.

Direct air capture derives from a more developed carbon capture technology : Point Source Capture (PSC), also called post-combustion capture. In PSC, carbon dioxide released by large point source such as power generation or industrial facilities is captured before

leaving the chimney. Despite the important role that PSC can play, it will only be able to decrease a portion of the total emissions. Indeed, mobile or small carbon sources such as transport or heating unit are not compatible with PSC. In its report *Net Zero by 2050* [4], the international energy agency proposes a detailed roadmap to achieve zero CO_2 emissions by 2050. Among the various measures outlined, carbon capture with use or storage plays an important role with, in the end, 7.6 Gt of CO_2 captured during the year 2050, of which nearly 1 Gt by DAC (as seen on Figure 1.2). Note that the scale of future DAC deployment is very uncertain and widely vary between sources. For example, the IPCC estimates the capture volume at 0.02 Gt in 2050, with a possible range from 0 to 1.74 Gt per year [5]. In comparison, there are currently 19 DAC plants around the world, capturing together 10 kt_{CO_2} per year [6]. To reach 1 Gt_{CO_2}/year in 2050, the annual capture should increase by 50% each year.

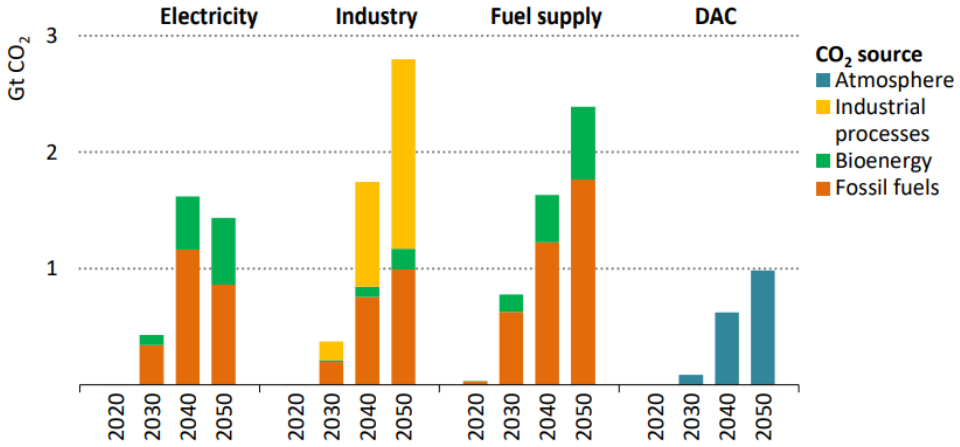

Figure 1.2: Carbon capture with use or storage: by sector and emissions source for the Net Zero emission scenario proposed by the International Energy Agency [4]

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Direct air capture has several advantages that sets it apart from other CDR options. Compared to mitigation options such as afforestation or bioenergy with Carbon Capture and Storage (CCS), DAC require less surface area and is more convenient regarding the type of land [7]. At same scale, it will therefore put a lower pressure on ecosystems and food production systems. Its land type flexibility also allows DAC plant to operate on a large range of locations. Thanks to this characteristic, DAC plant can be located near renewable energy sources and/or near carbon sequestration site, saving the costs and impacts linked to transport [8].

Another asset is the potential use of CO_2 as a by-product [8]. Uses of carbon dioxide can range from the production of synthetic material and fuels to air enrichment in greenhouses. In such cases, direct air capture would not lead to negative emission as it will be re-emitted in a short term. However, the benefits generated could reduce the economic barriers result-

ing from the currently high costs of CO_2 capture. Additionally, production of synthetic fuels could help to decarbonise hard to electrify sectors.

Nevertheless, direct air capture represents a large consumption of energy, around 2000 kWh per ton of CO_2 captured. Generally, the energy demand can be attributed to two processes: moving the air through the contactor (using electricity) and releasing the CO_2 while regenerating the sorbent (using heat). This last step represents around 80 % of the energy requirement making it a key area for improvement. If extended to a capture scenario of 1 Gt_{CO_2} per year, it would require nearly 6 EJ per year (as seen on Figure 1.3). In addition to represent a very massive amount of energy, the origin of this energy is restricted by its GHG emissions and by its operational temperature. As it will be developed in the following chapters, the carbon footprint of the energy source often represents a large share of the DAC emissions and therefore highly impact the capture efficiency, defined by the following equation :

$$\eta_{CO_2,capture} = \frac{m_{CO_2,captured} - m_{CO_2,emitted}}{m_{CO_2,captured}} * 100 \tag{1.1}$$

To have a positive impact, DAC must at least have a positive capture efficiency meaning than more CO_2 is captured than emitted. Moreover, the higher the capture rate, the lower the energy demand of net CO_2 capture.

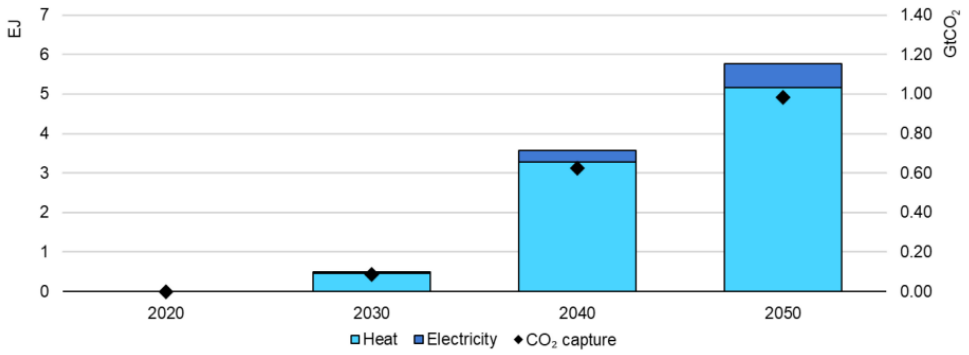


Figure 1.3: Global energy consumption and CO_2 capture from DAC following the Net Zero Emission scenario proposed by the International Energy Agency (IEA). Figure taken from the IEA report on direct air capture [6].

In addition, with high energy requirements comes high cost. Currently, direct air capture is a very expensive way to capture CO_2, much more than PSC for example. According to report [9], the cost of PSC would be around 80\$/t_{CO_2}. Due to the limited number of operating plants, the cost of DAC presented in literature varies widely, from 200 to 700 \$ per ton of CO_2. To be able to develop on a large scale, the price will have to decrease significantly. However, the price is expected to decrease with plant scale expansion and with technology maturation.

1.2 Contribution of this thesis

As mentioned, DAC technologies are in an early stage of development. Many questions about their side-effects, energy consumption and costs are still uncertain and would need further research in order to be deployed on a large scale. To address these concerns, a variety of solutions have been proposed in literature. **Chapter 2** will therefore present the DAC process on the basis of the available information in the literature. At first, the current state of DAC is presented, including operating and under development technologies. After that, DAC using liquid solvent and solid sorbent are discussed in further details. Those two capture methods are the most advanced and therefore the most relevant to represent the DAC process. Hence, the rest of the thesis is exclusively based on these two technologies. Finally, a discussion evaluates and compares the two processes regarding energy consumption, cost and land use.

This thesis is motivated by the lack of information about the relevance of DAC use as a response to climate change. In particular, there is little literature that compares the performance of the two most common technologies and analyses the parameters that influence it. By performance, we mean the ability to be deployed on a large scale while minimising its environmental impact. To characterise this impact, a Life Cycle Analysis (LCA) will be performed. This procedure allows to evaluate the environmental impacts from all the stages of the process. The methodology as well as the life cycle inventory is presented in **Chapter 3**. Through this tool, different research questions will be answered :

- What would be the impacts of DAC deployment at a large scale?
- What are the factors which influence DAC performances?
- How to adapt the process regarding those factors?

The resolution of these questions is divided into three steps. First, in **Chapter 4**, a reference model for each technology is used to make a generic analysis. Their performances are assessed under the same conditions to be able to put them in comparison. However, as these conditions might favour one of the two DAC methods, no definite conclusion is drawn .

Therefore, in the second step (**Chapter 5**), a sensitivity analysis is performed to consider the uncertainties in the data used and to account for the impact of the model variation.

To go further, the reference models are expanded in three scenarios (**Chapter 6**) to assess their performances in real conditions. Each scenario is characterised by a geographic location, thus influencing the energy sources and the environmental conditions. Furthermore, the scope is extended to two CO_2 utilisation : sequestration in geological storage or methanation to produce synthetic fuel.
Finally, the main outcomes and area for improvement are presented in **Chapter 7**.

Chapter 2

Direct air capture technologies

Before evaluating DAC technologies, it is necessary to gain an understanding of how the different existing processes work. But also, to understand the context in which they evolve. In this chapter, the main concepts of direct air capture are developed based on literature review. In the first section, an overview of carbon capture technologies is presented as well as the different outlets for the CO_2 obtained. Among the different ways to operate DAC, two technologies stand out: liquid sorbent absorption and solid sorbent adsorption. The second section will cover them in detail. Finally, the last section put them into perspective through several criteria.

2.1 Current state of direct air capture

The idea of CO_2 capture from air is not new and has in fact been used for the last 70 years in space craft and submarines. However, those were always small-scale processes whose absolute necessity made cost and capture efficiency a low priority. Development of direct air capture on a large scale share different requirements: low cost, good capture efficiency, high CO_2 purity and high rate [10]. The first DAC prototypes were largely inspired by conventional point source capture technologies using an aqueous solution of strong base, making the capture in diluted flow feasible [11].

Carbon dioxide absorption using liquid solvent require temperature around 900°C to regenerate the solvent, restricting the options for heat supply. In the late 2000's, multiple research worked on adapting and improving the NaOH based process in order to reduce cost and energy demand. In 2013, Holmes et all. [12] presented a prototype using KOH instead of NaOH due to its faster kinetic and lower toxicity. This was followed by a series of publications aimed at improving the process. Among the searchers figures David Keith, the founder of Carbon Engineering. To this day, Carbon Engineering is the only company offering a solvent based DAC in the market. Founded in 2009, this Canadian company is currently building a commercial plant in Texas with a CO_2 capacity of 1 Mt_{CO_2}/yr [11, 7].

The other main technique to capture CO_2 from air is using solid sorbent instead of liquid solvent. This process is distinguished by the use of relatively low temperatures, around 100°C. It is the technology with the most operating plants. Those are shared between two companies: Climeworks and Global Thermostat. Climeworks is a Swiss company created in 2009 [13]. They were the first to propose an industrial scale DAC plant, with a capture capacity of 900 t_{CO_2}/yr. The heat is provided by waste heat from incineration and the obtained CO_2 is sold to a nearby greenhouse. Their last project, a DAC plant with a 4000 t_{CO_2}/yr capture capacity based in Iceland started in September 2021. Heat and electricity are provided by geothermal energy and CO_2 is geologically stored on the site.

Global Thermostat was found in 2010 in the United stated and is planning multiple plants USA and Chile [14]. They are using various heat sources : natural gas, waste heat, wind turbines. Their most recent project consists in two containerized units with each a capacity of 2000 t_{CO_2}/yr. Global Thermostat is in close collaboration with ExxonMobil in order to scale-up their capture capacity. Note that none of their plants is currently in operation.

Figure 2.1: DAC plants from the three main companies. Starting from the left : Climeworks (Switzerland), Carbon Engineering (British Columbia) and Global Thermostat (Alabama). Figure taken from [14].

More recently, a new approach to CO_2 desorption has emerged: the moisture swing adsorption. To detach the molecules from the sorbent, this process uses water instead of heat (temperature swing) or mechanical energy (pressure swing). This method is based on the use of sorbents that favour the adsorption of water over carbon dioxide, such as in anionic exchange resins [15]. This way, the sorbent first adsorbs CO_2 under ambient conditions and is then regenerated by introducing water. There are major advantages to this method. First, an important energy reduction induced by the use of water as a desorption switch [16]. Second, a simplification of the infrastructure since heating and cooling units are avoided, leading to cost reduction. Finally, the possibility to modulate the process by adding small thermal and vacuum swing assist depending on the situation. However, moisture swing also has its own disadvantages. Expanded to large scale carbon capture, the massive water

consumption of 10 kg per kg of CO_2 would be a major threat to water resources. Especially as capture performance is highly dependent on environmental conditions, the hot and dry climate desired would put pressure on already threatened water sources. Moreover, the water must be clean in order to avoid sorbent contamination. The necessity of pre-treatment could counterbalance the cost savings from not energy-based desorption swing [17].

Very little documentation exists on the actual results of this process application. The only reported pilot plant was designed by Infinitree with a capture capacity of 100 t_{CO_2}/yr. Founded in 2014, this private company aims to provide CO_2 to greenhouses in order to enhance photosynthetic rate [18] . The little information available dates back to 2018 and since then the company did not give any news about further advancement.

Another company currently developing an innovative way to capture CO_2 is Mechanical Tree [19]. Designed by researchers from Arizona State University, Passive DAC relies on the wind instead of fans to draw in air. They claim that their solution is very energetically efficient and that they could bring the cost of DAC below 100 $ per ton of CO_2. Again, documentation about desorption process and energy consumption is limited but, as a first prototype has been recently installed, we can expect more information to be released. The five discussed companies are not the only one with an interest in DAC but have already or are close to install a DAC facility. They are summarised in Figure 2.2. More details about individual plants can be found in Appendix A.4.

Other innovative concepts are being explored in literature. *Renfrew Sara et al.* [20] and *Sharifian R. et al.* [21] address different options of electrochemical capture which predominantly rely on the concept of pH swing. The capture and regeneration of the solvent is done by switching the pH between acidic and basic using for example electrolysis or reversible redox reactions. The advantage of this process its high efficiency and its heat source independence. However, those technologies are still in their early stage of development and are currently prohibitively expensive. Another concept is cryogenic direct air capture which uses the sublimation of carbon dioxide to extract it from the air [22]. This very promising system has the advantage to produce a high purity stream of CO_2 with only electrical power.

A multitude of companies is emerging, proposing innovative concepts in order to solve the reproaches addressed to current technologies: high energy consumption and cost. This growing interest is coupled with an increase in private investment and government support [6]. As example, the *XPrize Carbon Removal* competition, funded by Elon Musk, offers up to 100 million USD to most promising CDR options [23]. Meanwhile, multiple governments (Canada, US, Europe, UK and so on) support development of DAC [6, 7]

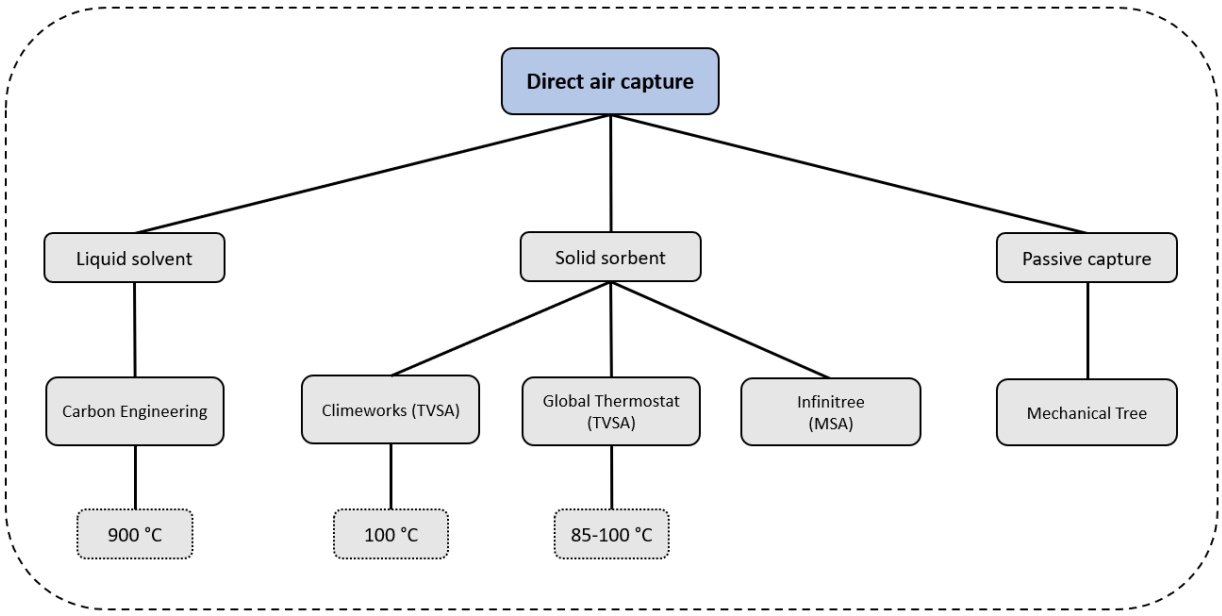


Figure 2.2: Active companies in direct air capture divided by technology types : liquid solvent absorption, solid sorbent adsorption and passive capture. Solid sorbent method is itself divided in two sub categories based on desorption method : temperature-vacuum swing adsorption (TVSA) and moisture swing adsorption (MSA).

Carbon capture, utilisation and storage

To account as CDR, the CO_2 captured must definitely be removed by geologically storing it. For now, most CCS projects inject CO_2 in sedimentary basins where, for an appropriate site, it will stay for thousands of years. The article [24] also proposes the use of reactive rocks, such as basalt. In addition to adding new potential sites, this method would accelerate the mineralization process, thus limiting leakage problems. Maps showing potential sites for both storage methods are present in Appendix A.1.

Although the potential storage sites seem to be able to meet the future demand. The time required to fully characterize the site, i.e., between five and ten years, may limit the storage capacity. Therefore, early actions must be taken to identify and develop CO_2 storage [6].

A combination between storing and using CO_2 is enhanced oil recovery. In order to increase the extractable quantity from an oil field, CO_2 is injected in it. Some of it CO_2 remains stored and some, mixed with oil, can be separated at the surface for reinjection. If the carbon dioxide comes from an anthropogenic source, as in the case of DAC, this could lead to emissions neutral oil [6]. However, the global emissions implied in the process must be carefully taken into account.

Additional usages of CO_2 are possible: enhanced agriculture, food, synthetic fuels [7], chemicals and building materials [13]. As the CO_2 used will ultimately return into the atmosphere, its impact on the environment is difficult to quantify. It could affect positively by reducing the price of capture or by displacing products with higher emissions [6].

The production of synthetic fuels such as: methane, methanol, gasoline and others; is a much discussed topic. The process often consists in the conversion of H_2 and CO_2 into carbon-containing fuel which is easier to handle and use than pure hydrogen. Low carbon hydrogen could be produced from fossil fuel with CCS or from electrolysis with low-carbon electricity [25]. This electricity could be supplied by surplus renewable energy production, leading to chemical storage [26]. An option could be to produce synthetic fuels in remote desert with large solar insolation, allowing to efficiently transport energy from places where photovoltaic power is abundant [27]. However, in these regions, water demand could be a major problem for electrolysis and DAC.

2.2 Technical aspects of direct air capture

2.2.1 Absorption using liquid solvent

Direct air capture based on liquid solvent relies on the chemical reaction between CO_2 and a solvent. Indeed, the system consists of an air contactor where air is brought into contact with the solvent which will absorb carbon dioxide from the air. The solvent need to be regenerated and a pure CO_2 stream at the exit should be obtained. The regeneration of the solvent is based on a variant of the Kraft pulp process. Indeed, direct air capture plants include a causticizer, a calciner and a slacker for the regeneration cycle of the solvent. Energy has to be provided to the DAC plant for the fans, pumps and the regeneration cycle. All steps, solvent and energy requirements are explained in further details below. The simplified absorption process can be seen in Figure 2.3.

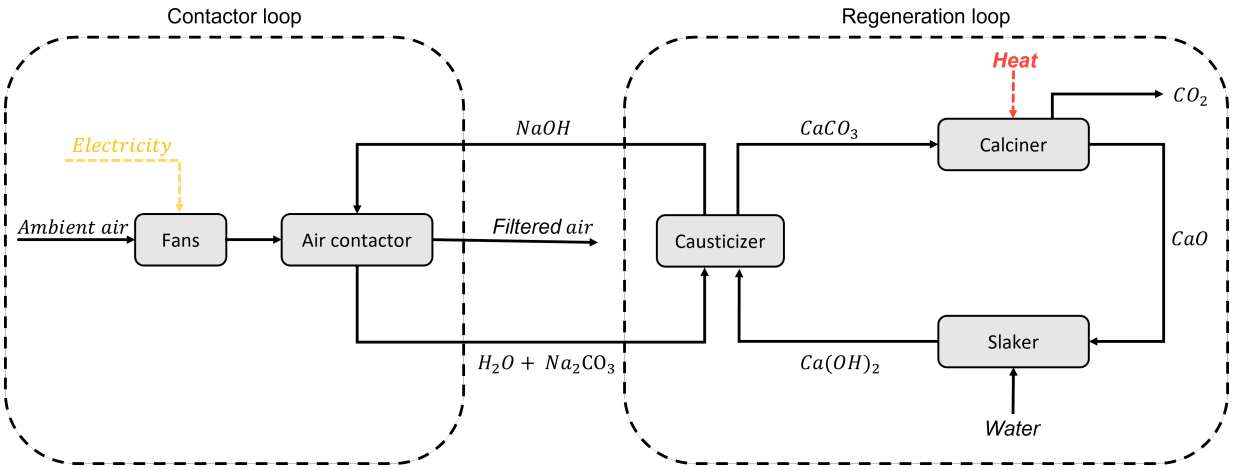


Figure 2.3: Absorption process diagram

Air contactor

The air contactor is assumed to be a horizontal packed tower as shown in Figure 2.4. This type of contactor also called cross-flow tower is based on commercial cooling tower technology and are cheaper than vertical packed tower within the same range of performances [12].

In this design, the liquid solvent flows downward with gravity over a packing material while air flows horizontally into the contactor. The air is blown thanks to fans that create a pressure drop within the contactor. The surface of the packing stack is wetted with the liquid solvent and CO_2 contained in the air, flows over the surfaces of the PVC packing. When the CO_2 molecules encounter the solvent, they are converted to carbonate. The design of the packing area ensure that there is as much as possible contact between the

liquid solvent and air flowing through it by also creating turbulence. Here you can find the chemical reaction between the CO_2 molecules and the liquid solvent:

$$2\,NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(g)} \tag{2.1}$$

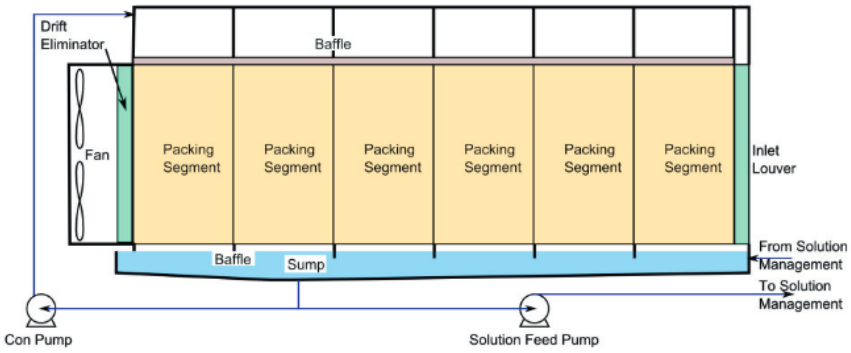


Figure 2.4: Horizontal liquid based packed air contactor

The packing material used is either stainless steel or polyvinyl chloride (PVC) as they have hydrophobic, hydroxide resistant properties. Carbon Engineering has conducted experiments with both materials and concluded that PVC packing material has the same performance as stainless steel in term of CO_2 absorption and reduce the pressure drop across the contactor [28]. Furthermore, the average cost of PVC is around $1\$/m^2$ while stainless steel costs $5\$/m^2$. The PVC packing is shown in Figure 2.5.

Figure 2.5: PVC packing stack

Causticiser

The first step in the regeneration cycle is performed by a causticization process where the carbonate in solution (Na_2CO_3) from the air contactor react with a slurry of calcium hydroxide ($Ca(OH)_2$). This step which regenerates the solvent and produce precipitated calcium carbonate ($CaCO_3$) is performed in a fluidized-bed pellet reactor. The solvent regenerated is pumped back to the air contactor. Calcium carbonate which is forming pellets in the reactor grow and thus sink at the bottom where they are discharged. These pellets will need to be dried with a solid content around 90%. The reaction is shown bellow:

$$Na_2CO_{3(aq)} + Ca(OH)_{2(aq)} \longrightarrow 2\,NaOH_{(aq)} + CaCO_{3(s)} \tag{2.2}$$

Calciner

The pellets are transported to the calciner where they are decomposed into quicklime CaO and pure CO_2 at high temperature (around 900 °C). An important point to mention is that the kiln is generally an oxy-fired circulating fluidized bed. It means that an air separation unit (ASU) is needed to provide pure oxygen to the kiln. It will lead to additional electricity consumption. Using this technology enables to recover pure CO_2 stream from the combustion of natural gas and very low concentration of nitrogen. The CO_2 coming from the combustion of natural gas in the calciner and the decomposition of the pellets are combined in one stream.

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)} \tag{2.3}$$

Slacker

The quicklime coming out of the calciner is hydrated in the slacker resulting in calcium hydroxide $Ca(OH)_2$ for reuse into the causticizer. This chemical reaction releases energy which will be recovered to heat and dry the pellets. Energy requirement and recovered in the process will be explained in further details below.

$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} \tag{2.4}$$

2.2.2 Energy

This system of absorption is also called *High temperature aqueous solution*. Indeed, it require high temperature, around 900°C, in the calciner unit. This is the most energy intensive step and correspond to around 80% of the total energy requirement [29]. The rest of the energy needed is electricity to drive the fans and pumps [9, 30].

Fans

The pressure drop ΔP [Pa] in the air contactor module with a length D [m] and a cross flow area A [m^2] is calculated by the following relation [30] $\Delta P = 7.4DV^{2.14}$ where V is the air velocity [m/s]. The work done by the fans can be expressed as $W_{\text{fans}} = \Delta P\dot{V}$ [J]. Therefore, the mechanical energy requirement for the fans is:

$$W_{\text{fans}} = \frac{7.4DV^{2.14}VA}{\eta_{\text{fans}}} \tag{2.5}$$

Pumps

The mechanical work of the sorbent pump is calculated as $W_{\text{pump}} = \frac{mgh}{\eta_{\text{pump}}}$ [J]. The mass of the solvent is found with the following relation $m = \rho f At$ where ρ is the solvent density [kg/L], f the liquid flow rate [L/m^2s], t [s] the operating time of the plant. The work done by the pumps can be written as:

$$W_{\text{pump}} = \frac{\rho f Atgh}{\eta_{\text{pump}}} \tag{2.6}$$

Solvent

Two major solvents are used in high temperature DAC: Sodium hydroxide (NaOH) and Potassium hydroxide (KOH). As said above, these solvents are used for capturing the carbon dioxide. The summary of all chemical reactions can be found in the tables below.

Table 2.1: Chemical reactions occurring in the absorption process for NaOH solvent

Chemical equation	**Location**	ΔH **[kJ/mol]**
$2\,NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(g)}$	Contactor	-109.4
$Na_2CO_{3(aq)} + Ca(OH)_{2(aq)} \longrightarrow 2\,NaOH_{(aq)} + CaCO_{3(s)}$	Causticiser	-5.3
$CaCO_{3(s)} \xrightarrow{\text{heat}} CaO_{(s)} + CO_{2(g)}$	Calciner	179.2
$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$	Slaker	-64.5

Table 2.2: Chemical reactions occurring in the absorption process for KOH solvent

Chemical equation	**Location**	ΔH **[kJ/mol]**
$2\,KOH_{(aq)} + CO_{2(g)} \longrightarrow K_2CO_{3(aq)} + H_2O_{(g)}$	Contactor	-95.8
$K_2CO_{3(aq)} + Ca(OH)_{2(aq)} \longrightarrow 2\,KOH_{(aq)} + CaCO_{3(s)}$	Causticiser	-5.8
$CaCO_{3(s)} \xrightarrow{\text{heat}} CaO_{(s)} + CO_{2(g)}$	Calciner	179.2
$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$	Slaker	-64.5

2.2.3 Adsorption using solid sorbent

Direct air capture by adsorption is based on the adhesion of CO_2 molecules on a solid sorbent while blowing air through it. Solid sorbent systems are divided in two distinct processes: adsorption and desorption. However, in this case the two phases are not concurrent but sequential. First, an air flow created by fans get into contact with the solid sorbent contained within an air-contactor (Adsorption phase). When the adsorbent is sufficiently saturated with CO_2, the inlet valve is closed and the remaining air is removed. Then the solid sorbent is heated up in order to break the chemical bonds between it and the CO_2 molecules (Desorption phase). This way, a concentrated CO_2 stream is produced and the sorbent is regenerated.

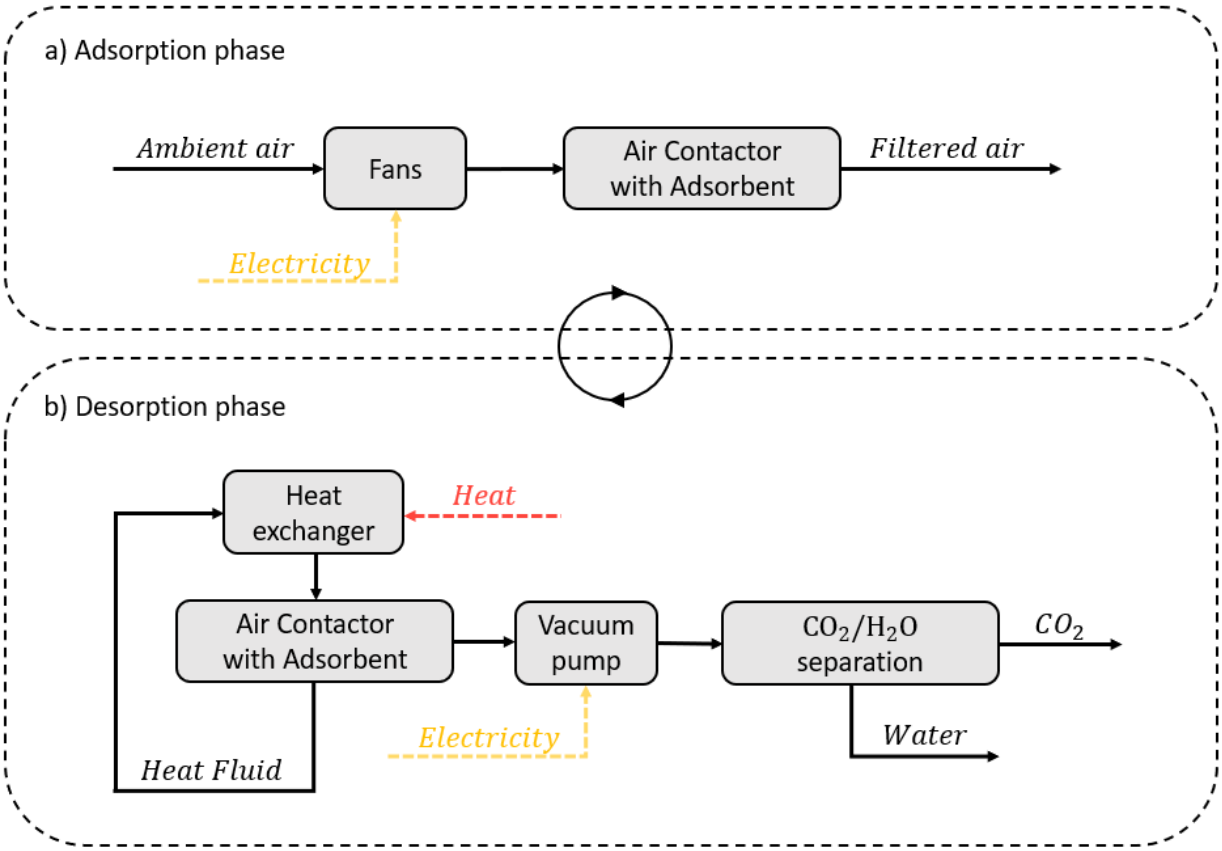


Figure 2.6: Diagram of a cyclic, temperature vacuum swing DAC process. a) Adsorption phase: fans draw air into the sorbent where CO_2 and H_2O are captured. b) Desorption phase: heat fluid and Vacuum pump are used to desorb CO_2 and H_2O, which are further separated.

As previously described, multiple adsorption processes exist. In order to limit its complexity, we will focus our analysis to Temperature-Vacuum Swing (TVS) adsorption (see Figure 2.6). In this system, when the targeted capacity is reached, the inlet flow is closed and a

pressure drop is applied in order to remove residual air. Then a stream of hot gas, e.g., steam, passes through the sorbent. The combination of temperature swing and vacuum has the advantages to reduce the desorption time and temperature, and to increase the output purity [29].

Another major difference with liquid sorbent DAC is the way adsorption deal with air moisture. In this case, water is co-adsorbed from ambient air and can therefore become a valuable byproduct. For a relative humidity of 80%, it represents around 4 moles of water per mole of CO_2 [31]. Nevertheless, some water losses can occur when steam is used as heating fluid. However, if steam is contained in a fully closed system, as shown on Figure 2.6 the water losses can be negligible.

Sorbent

The sorbent choice plays a key role in the performance of adsorption and is therefore much discussed in literature. In general, the assessment of a sorbent material goes through multiple parameters :

- *High CO_2 capacity*: is important to have a good adsorption rate and to avoid frequent regeneration.
- *High CO_2 selectivity* : allows the sorbent to adsorb CO_2 in priority. Consequently avoiding the intervention of other species that could damage the sorbent, decrease its capacity and increase energy consumption.
- *Small heat requirement* : can be associated to a low heat capacity and a low heat of desorption (h_{des}).
- *Minimum pressure drop* : to decrease the electricity linked to the fans.

Other key parameters are price, lifetime and environmental impacts from production and end-of-life. The optimal sorbent results from a balance between these parameters with regard to external factors such as ambient temperature, relative humidity, pressure, product usage and so on [17].

Many sorbents have been proposed to meet these criteria. They can be divided in two main categories depending on the sorption process : physisorption or chemisorption. The difference between the two groups lies in the heat of adsorption (h_{ads}). While physisorption is based on weak intramolecular forces such as van der Waals interaction (h_{ads}< 60 kJ/mol), chemisorption occurs from strong covalent bonding (h_{ads}> 60 kJ/mol) [29]. Although chemisorption works well to selectively capture CO_2, the high chemical binding energy makes the regeneration temperature significant compare to physisorption. The respective advantages and drawbacks of the two sorbents categories are highlighted in the next paragraphs.

As the name suggests, physisorption rely on physical interactions between the sorbent surface and the carbon dioxide [17]. The contact area must therefore be as high as possible, which is done by using materials with high porosity and nanometer dimensions. However, the low sorption heat results in a low sorption capacity for dilute CO_2 concentration. Furthermore, co-adsorption of water strongly affect its capacity and selectivity as CO_2 and H_2O compete for the same physisorption sites. Currently, this sorption process is not the most appropriate to DAC but further progresses (e.g., in pore size control) could enable it to compete with chemisorption.

Chemisorption using amine modified materials is the most used path for CO_2 adsorption . Amine groups are grafted or loaded on porous support and react with carbon dioxide [17]. In dry conditions, primary and secondary amines (equation 2.7 and 2.8) form carbamate whereas in humid condition, secondary and tertiary amines (equation 2.9 and 2.10) form either bicarbonate or carbonate depending on the pH.

$$2\,RNH_2 + CO_2 \longleftrightarrow RNH_3{}^+ + RNHCOO^- \tag{2.7}$$

$$2\,R_1R_2NH + CO_2 \longleftrightarrow R_1R_2NH_2{}^+ + R_1R_2NHCOO^- \tag{2.8}$$

$$R_1R_2NH + CO_2 + H_2O \longleftrightarrow R_1R_2NH_2{}^+HCO_3{}^- \longleftrightarrow R_1R_2NH_2{}^+CO_3{}^{2-} \tag{2.9}$$

$$R_1R_2R_3N + CO_2 + H_2O \longleftrightarrow R_1R_2R_3NH^+HCO_3{}^- \longleftrightarrow R_1R_2R_3NH^+CO_3{}^{2-} \tag{2.10}$$

From these equations, it follows that the molar ratio between CO_2 and N, also called the amine efficiency, is higher in humid condition ($CO_2/N = 1$) than in dry condition ($CO_2/N = 0.5$)[32] . It is important to note that this ratio only concern chemisorption but, in reality, physisorption also occur in small proportion. Overall, chemisorbent present good CO_2 capacity and selectivity with a reasonable desorption energy. However, many challenges remain unsolved and will need to be met. In particularity, sorbent stability and kinetic are often major issues [17].

Energy

Due to the rather low temperature required by the regeneration step, this system is also called in the literature: *Low Temperature (LT) solid sorbent*. Indeed, the temperature varies between 70 and 130°C depending on the model. This particularity has the major advantage to enable the use of low quality heat such as industrial waste heat or geothermal heat. Moreover, this temperature range can be met by industrial heat pump [33] and therefore increase the electricity proportion while decreasing the overall energy consumption. As in absorption process, the heat requirement account for 80% of the total energy supply [29].

The electricity demand can be divided in two provenances : the fans to draw air through the sorbent and the vacuum pump to remove the residual air. Additional requirements

exist but are neglected in this study. To compute the electricity demand, we will consider the work of compression :

$$W_{pump} = \frac{1}{\eta_{pump}} RT_{pump} \ln\left(\frac{p_2}{p_1}\right) \tag{2.11}$$

In the case of fans, the difference between p_2 and p_1 is equivalent to the pressure drop caused by the sorbent while for the vacuum, the difference is between ambient air pressure and desired pressure for desorption.

The energy requirement for desorption can be divided in two factors : the heat necessary to bring sorbent and captured compound to the desorption temperature, i.e., sensible heat (Q_{sens}) and the heat required to desorb the captured species, i.e. desorption heat (Q_{des}) [34].

$$Q_{sens} = \left(\frac{c_{p,sorb}}{q_{CO_2}} + c_{p,CO_2} + \frac{q_{H_2O}}{q_{CO_2}} c_{p,H_2O}\right)(T_{des} - T_{ads}) \tag{2.12}$$

$$Q_{des} = h_{des,CO_2} + \frac{q_{H_2O}}{q_{CO_2}} h_{des,H_2O} \tag{2.13}$$

With $q_{\mathrm{CO_2}}$ and $q_{\mathrm{H_2O}}$, the sorbent capture capacity for carbon dioxide and water. For the values presented in the **Chapter** 4, the sensible heat represents 25% of the total heat requirement.

2.3 Discussion

The two technologies previously described are technically able to fulfil DAC's functions. Nevertheless, other aspects play roles in evaluation of performances in practical applications: energy and water consumption, size, prices and so on. These criteria will be assessed in this section in order to list the respective advantages and disadvantages of the processes.

Energy use

It is probably the major difference between the two DAC technologies. Even with a relatively similar energy consumption, around 1800 kWh/t_{CO_2}, the required energy qualities differ significantly. While the regeneration temperature of absorption process is around 900°C, the one asked by adsorption usually stays around 100°C. This difference has a significant impact on the available energy sources for the two technologies. In the case of LT solid sorbent, power supply by waste heat from plants or by other lower quality energy sources is appropriate. For example, the active plants developed by Climeworks in Iceland and Switzerland use respectively geothermal energy and heat from municipal waste incineration [7]. In contrast, HT liquid solvent has limited options. Apart from high grade

heat coming from the combustion of natural gas, one possibility would be to use electric furnaces. Currently, electric calcination is in its infancy and may take some time to become commercially available [6]. Other options could be synthetic fuels with low carbon footprint or the co-capture of CO_2 from natural gas combustion.

Land use

Compare to other CDR technologies, the area requirement for direct air capture is considered to be very small [13]. However, this statement is to be taken with caution as the land footprint must include not only the DAC plant but also the facilities providing heat, electricity, water as well as storage site. In [7], Climeworks and Carbon Engineering land use are compared. As a reminder, Climeworks use solid sorbent with geothermal energy while Carbon Engineering uses liquid solvent with natural gas. In both cases, a land area of 0.2 km^2 is necessary to capture one million tones of carbon dioxide. If extended to the capture rate required to keep the temperature rise under 2°C by 2100, the processes would ask just less than 2000 km^2. If the heat was provided by solar energy, the land use would be five to six times that previously estimated. However, it stays far less than the land footprint of reforestation: 862 km^2/Mt_{CO_2}.

Even if absorption and adsorption land use are not fundamentally different, they present disparities regarding modularity. Modularity refers to the ability of a system to be divided in smaller units and is therefore linked to the minimum operational scale [29]. Solid sorbent exhibit greater modularity with smallest unit that can go down to 50 tCO_2/year. This particularity paired with the use of low quality energy could favour the development of decentralised units scaled to available heat sources. In theory, liquid solvent capture could also be divided in small units but the significant cost of the large infrastructure (i.e., calciner and slaker) induce an economical optimum around 1 $MtCO_2$/year. This characteristic could advantage it for large-scale capture plants [29].

Cost

In 2011, a report from MIT [10] addressed the feasibility of DAC and concluded that relying on direct air capture was a very risky mitigation pathway due to its prohibitive cost. They computed an energy related cost of 250 to 1200 $\$/tCO_2$ and warn against optimistic values reported in the literature, i.e., a total cost of 27 to 136 $\$/tCO_2$. Even today, it is difficult not to get lost in the multitude of price estimates as many parameters influence the way process economic is evaluated : technology, boundaries, heat source and so on. But what is certain is that DAC is still far from economic viability, required to be deployed on large scale, estimated to be 100 $\$/tCO_2$ [7]. Nevertheless, considering the rapid progress and the rising interest for direct air capture, the potential in cost reduction is significant.

The total cost can be divided in three sources: the capital cost, the operating cost and

the energy cost. The total cost as well as the share between the sources vary according to technologies, energy sources and utilisation [6]. In particular, the carbon efficiency is a key factor when considering the cost of removal and not only the cost of capture. The combination of techno-economic assessment and LCA could therefore highlight the relationships between economic and environmental impact [35].

Chapter 3

Life cycle assessment

3.1 Introduction to Life Cycle Assessment

Life cycle assessment (LCA) is a methodology that provides and quantifies the environmental impacts of a product throughout its total life cycle. It is used to understand how sustainable a product is by identifying the energy and material uses and releases into the environment. A LCA can take into account the entire life cycle of the product, from extraction of materials, material processing, use and the end of life.

LCA follow standards provided by the International Organisation for Standardization (ISO) which give reliability and transparency. ISO 14040 describes the principles and framework for life cycle assessment and ISO 14044 specifies requirements and provides guidelines for life cycle assessment [36, 37]. This framework is shown in Figure 3.1 and will be discussed in the next section.

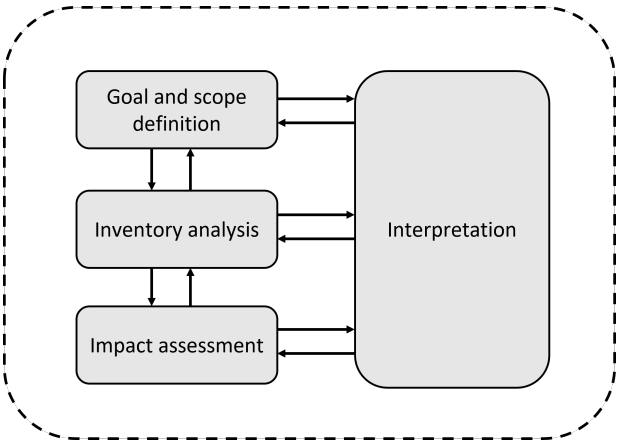


Figure 3.1: Life cycle assessment framework

3.2 Methodology

3.2.1 Goal and scope

The goal and scope ensure that the LCA study is performed consistently. The scope of the LCA has to be set as there are 3 main types of system boundaries (Figure 3.2) [38]:

- **Cradle-to-gate** which is a partial life cycle that takes into account the resource extraction ("cradle") until the product can be used (factory gate).
- **Cradle-to-grave** is a full life cycle assessment from raw material extraction through product use and disposal ("grave").
- **Cradle-to-cradle** or closed loop is a variant of cradle-to-grave where the disposal phase of the product is a recycling process.

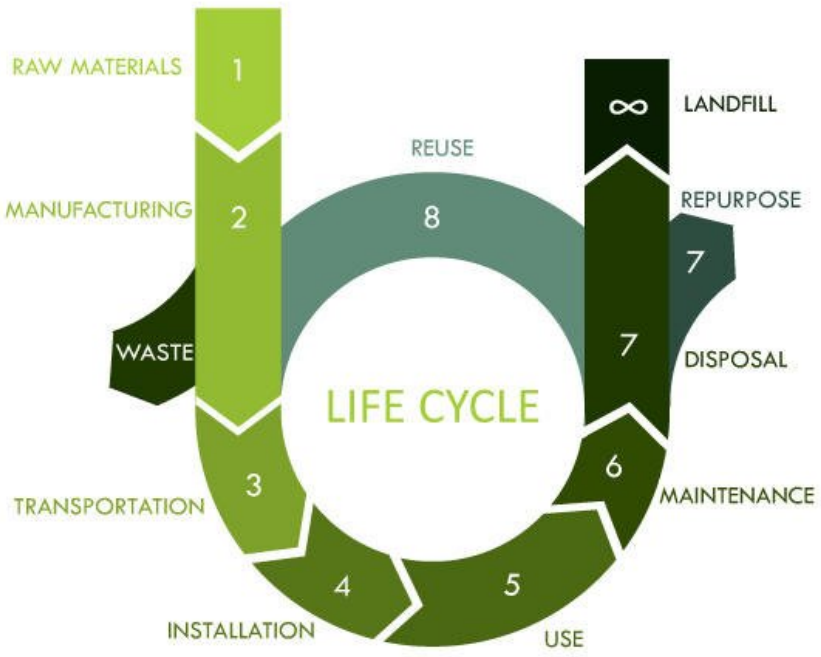


Figure 3.2: Life Cycle Assessment stages of a product life cycle.

As already mentioned, DAC technologies are in an early stage of development. To evaluate and compare their impact, a Life Cycle Assessment is performed from a cradle to grave perspective since we consider the disposal scenario without reuse. Only the end of life of the plant's construction materials and the sorbent is taken into account.
The functional unit for this study is the capture of one kilogram of carbon dioxide using a direct air capture plant. A comparison between two different types of DAC plants will be done:

- An absorption plant based on liquid solvent which is regenerated with high grade heat.
- An adsorption plant based on solid sorbent which is regenerated by Temperature Vacuum Swing process that requires low grade heat.

This functional unit is consistent with the goals of the study, which aim to evaluate the performances and the environmental impact of the plant.
The functional unit is designed with a reference flow of a DAC plant removing 1Mt of CO_2. In addition to the reference case, other scenarios are analysed for different locations such Belgium, Iceland and United Arab Emirates with geological sequestration and use specified in Chapter 6. A sensitivity analysis of the reference case for both technologies is also done in Chapter 5.

For performing the LCA, the DAC plant is subdivided in three main parts:

- **The plant construction** which is assumed to be the same for the low and high temperature DAC technology.
- **The process** that corresponds to the energy needed to run the DAC plant. Basically, heat and electricity.
- **The solvent or sorbent**, it corresponds to the production of the chemical product needed for the low and high temperature DAC technology.

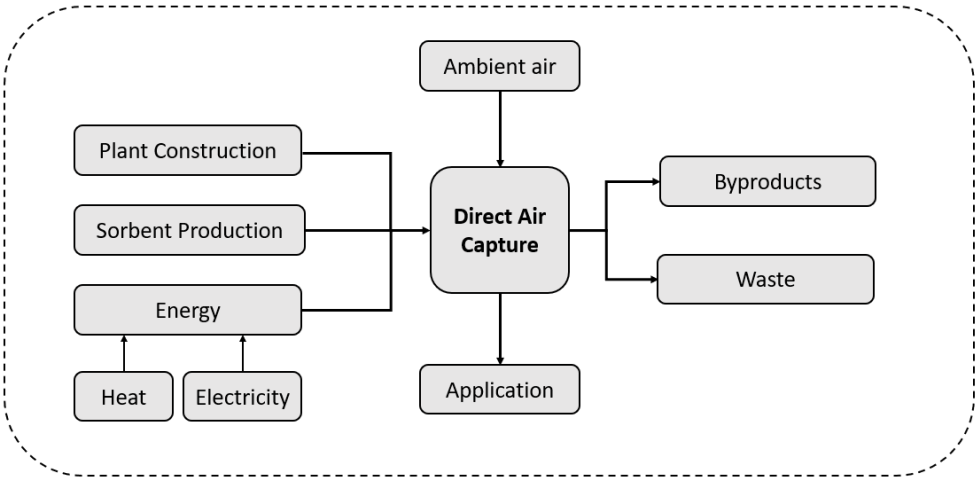


Figure 3.3: Boundary diagram of the DAC product system.

3.2.2 Inventory analysis

This step involve the compilation and quantification of inputs and outputs for a product throughout its life cycle. You will find details of the LCI for the baseline scenario in Chapter 4. There is many data in the literature. The main parameters allowing to characterize the DAC plant have been reviewed. From these parameters, we were able to calculate the amount of energy and chemicals needed for the operation of the DAC plant.

3.2.3 Impact assessment

The impact assessment is the estimation of indicators of the environmental pressures in terms of climate change, resource depletion, acidification, human health effects, etc. attributable to the life-cycle of a product.
There are two indicator levels called midpoint and endpoint in ReciPe methodology (see Figure 3.5. For each methodology, ReciPe includes factors according to the cultural perspectives also called "Archetypes" [39]:

- **Individualist (I)**: based on the short-term interest, impact types that are undisputed, technological optimism as regards human adaptation. It would use the medium time frame e.g., a 20 year time-frame for global warming, GWP20.
- **Hierarchist (H)**: based on the most common policy principles with regards to time-frame and other issues. It would use the medium time frame e.g., a 100 year time-frame for global warming, GWP100.
- **Egalitarian (E)**: is the most precautionary perspective that takes into account the longest time-frame and impact types that are not yet fully established but for which some indication is available. It would use the medium time frame e.g., a 1000 year time-frame for global warming, GWP1000.

	Individualist	**Hierarchist**	**Egalitarian**
Vision on nature	Considers nature robust	Considers nature tolerant	Considers nature vulnerable
Level of knowledge	Only considers certain (proven) effects	Considers likely effects	Considers all known effects
Time horizon	Emphasizes present and short-term effects	Balanced time perspective	Current and future effects are considered equal
Vision on society	Economic output is market driven	Developments within limits of nature	Equality and social driven
Manageability	Adaptive management style	Preventive and comprehensive management style	Controlling and limited management style

Figure 3.4: Overview of the different visions among the individualist, hierarchist and egalitarian perspectives [40].

An overview of the different visions is shown upper in Tab.3.4. In our study, we use the hierarchist perspective which is the method based on most common policy principles [40].

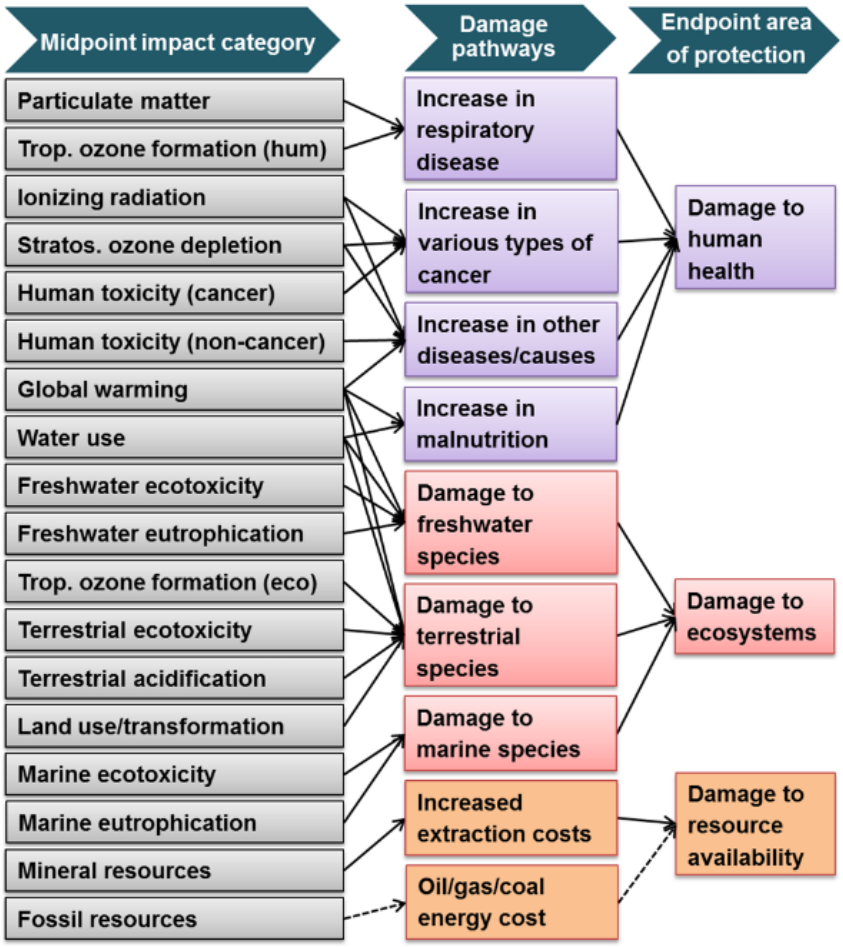


Figure 3.5: Overview of the impact categories that are covered in the ReCiPe2016 methodology and their relation to the areas of protection [41]

3.2.4 Interpretation

Phase of life cycle assessment in which the findings of either the inventory analysis or the impact assessment, or both, are evaluated in relation to the defined goal and scope in order to reach conclusions and recommendations.

3.3 LCA tools

3.3.1 Software

The tool used for the life cycle assessment is *SimaPro*. This software is a worldwide leading tool in LCA for industrial applications. It is trusted and used by industry and academy for more than 25 years and 80 countries. *SimaPro* includes many life cycle inventory databases, e.g., Ecoinvent and impact assessment methods (ReciPe).

3.3.2 Databases/libraries

Ecoinvent database is used worldwide as a background database in LCA and other environmental assessments. *SimaPro* provide Ecoinvent database that we use in this LCA. Ecoinvent has three different system models that we define below[42, 43]:

- **Allocation at point of substitution** (APOS) model uses expansion of product systems to avoid allocation within treatment systems.
- **Allocation cut-off by classification** model is based on the recycled content. This model allocates burdens at the point where a product is sold and applies a cut-off at the point the recyclable material leaves the product system.
- **Consequential, long-term**: All by-products are moved to the input side with a negative sign to maintain the mass balance. As no allocation is applied, the activity is burdened with the impact of all its inputs and emissions. By-products that can substitute other production bring credit to the activity producing them.

Each system model is divided into unit and system processes:

- **Unit process** is the smallest element in the life cycle inventory analysis for which input and output data are quantified. Unit processes describe a distinct part of a life cycle, not a whole life cycle in themselves [44].
- **System process** also known as an aggregated life cycle inventory (LCI) is the result of the compilation and quantification of inputs and outputs for a product throughout its life cycle [44].

In our analyse, we consider the allocation cut-off by classification with the system process model.

Chapter 4

Life cycle analysis of a reference scenario

This chapter will present a life cycle analysis based on a reference case. This reference case consists in a 1 Mt_{CO_2}/yr plant whose operational parameters are computed based on literature. Although an absolute comparison between absorption and adsorption would be biased, the reference case attempts to assess the two technologies under the most similar conditions possible. The scope of this analyse stops after the release of CO_2 and therefore neglect the impact from its compression, transport and use. The impact from DAC is divided into three categories : infrastructure, process and solvent.

The chapter is divided in four sections. First, the infrastructure and the environmental conditions are presented as they are shared by the two processes. Then, the two technologies are individually described through a life cycle inventory and discussed using Simapro results. Finally, a general discussion compare the results and project them following the net zero emission scenario from IEA.

4.1 Introduction to the reference scenario

The analysis is based on a plant with a capture capacity of 1 Mt_{CO_2}/yr. This scaling step is often considered as an essential stage in the cost reduction of the process and some of the main companies are already developing or even building plants with such capacity. Regarding the environmental condition in which the DAC process, the values are presented in Table 4.1. The relative humidity (RH) and temperature don't correspond to a specific location but were arbitrarily chosen.

Table 4.1: Life cycle inventory of the environmental conditions in which CO_2 capture takes place

Parameters	**Value**	**Units**
Environment Conditions		
Relative humidity (RH)	70	[%]
Pressure	1	[bar]
Temperature	20	[°C]
CO_2 air concentration	400	[ppm]

As very little information about infrastructure is present in literature, both absorption and adsorption plant share the same infrastructure inventory (see Table 4.2) taken from an estimation presented in [30]. This article assumes that this inventory underestimates the impact from plant construction but, in view of its relatively small impact, it has very little effect on the results.

Table 4.2: Life cycle inventory of a DAC infrastructure for both absorption and adsorption process. The data are taken from [30].

Inventory	**Value [t]**
Infrastructure	
PVC	14000
Concrete	1.17e+5
Polypropylene	15
Stainless steel	32
Grass fiber reinforced polyurethane	70
Low alloyed steel	5000

The process impact comes from the heat and electricity requirement and strongly depends on their sources. It was decided to use natural gas to provide heat in both cases as it is currently the most used way to provide the 900°C required for solvent based DAC. For the electricity, the global geography of *ecoinvent* was chosen to obtain an average value of electricity carbon footprint around the world. The heat and electricity requirement were independently computed based on chosen characteristic of the DAC facility. More information about this choice as well as solvent and sorbent impact is given in the following sections.

4.2 Absorption case

4.2.1 Life cycle inventory

For first reference model, we will consider a liquid solvent DAC capturing $1Mt_{CO_2}$/yr. High grade heat is therefore needed for the regeneration cycle.

Table 4.3: LCI for a DAC plant based on absorption using liquid solvent

Parameters	**Value**	**Units**	**Range**
DAC specifications			
Capture capacity	1	[Mt_{CO_2}/yr.]	-
Plant lifetime	15	[yr.]	10-30
Capture fraction	0.75	[mole/mole]	0.6-0.9
Product purity	99	[%]	90-99.9
Regeneration temperature	900	[°C]	-

Sodium hydroxide is chosen as the solvent mainly for its low cost compared to potassium hydroxide. Sodium hydroxide is produced in large amount in the world which is around 82 Mt/year due to many other industrial uses such pulp and paper, soap production. The current world production of KOH is very small (around 2 Mt/year) compared to NaOH production [45].

Table 4.4: LCI of the chemical products needed for liquid solvent based on absorption process of 1 kg of CO_2 extracted

Parameters	**Value**	**Units**
Material input		
Sodium hydroxide NaOH	2.5	[g]
Calcium carbonate $CaCO_3$	200	[g]
Water H_2O	3000	[g]

The minimum heat required for the calcination step is around 4.6 MJ/kg_{CO_2}. We assume that we are able to recover heat released during the cooling of the $CO_{2(g)}$ coming out of the kiln and the CaO with a heat transfer efficiency of 90%. Heat is also needed to heat and dry the $CaCO_3$ in the process which represents for more than 2 MJ/kg_{CO_2}. In the reference case, the heat required is provided by combustion of natural gas in an oxyfuel calciner with heat recovery.

The value of recycling efficiency are based on experimental data and other industrial applications using NaOH and $CaCO_3$. As you will see in the sensitivity analysis, the

recycling efficiency has an important impact on the total amount needed of NaOH and $CaCO_3$ to properly run the DAC.

Table 4.5: Energy consumption parameters for electricity, heat and chemicals.

Inventory	**Value**	**Units**
Heat, electricity and chemicals parameters		
Pump efficiency	75	[%]
Heat transfer efficiency	75	[%]
NaOH molarity	2	[M]
$CaCO_3$ Recycling efficiency	90.9	[%]
NaOH Recycling efficiency	99.9	[%]

Table 4.6: Heat required and recovered during the process for 1kg of CO_2 extracted

Inventory	**Value**	**Units**
Heat required		
$CaCO_3$ drying	0.564	[MJ]
$CaCO_3$ heating	2.224	[MJ]
Endothermic reaction in the calciner	3.864	[MJ]
O_2 preheating	0.206	[MJ]
Heat recovered		
Exothermic reaction from the slacker	1.465	[MJ]
$CaO_{(s)}$ cooling from the calciner	0.220	[MJ]
Flue gas $CO_{2(g)}$ cooling	0.627	[MJ]
Flue gas $H_2O_{(g)}$ cooling	0.178	[MJ]

Table 4.7: Life cycle inventory for the energy consumption of 1kg of CO_2 extracted.

Inventory	**Value**	**Units**
Energy Input		
Heat for regeneration	5.82	[MJ]
Electricity	0.73	[MJ]

4.2.2 Network analysis

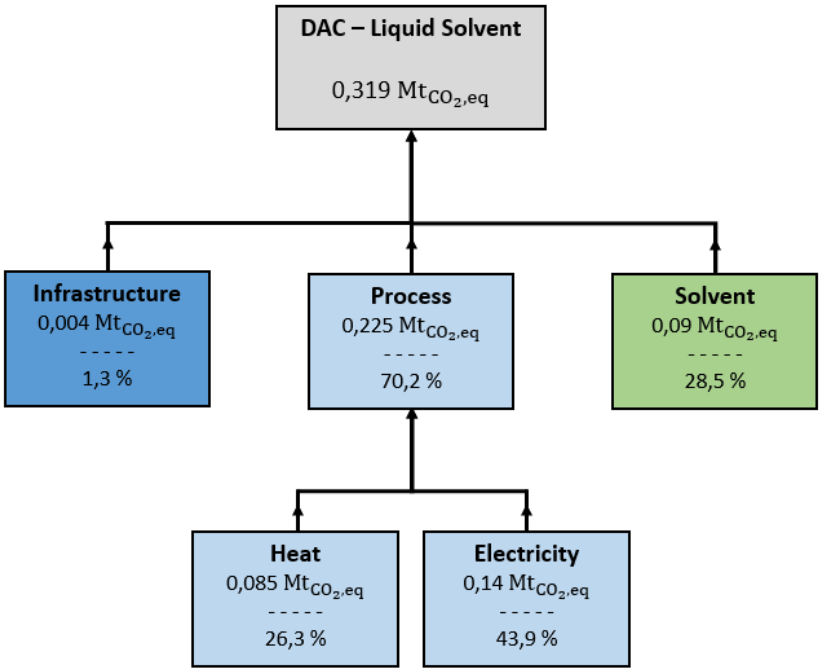


Figure 4.1: Share of the CO_2, eq emissions between the different impact sources of a liquid solvent based DAC facility.

Here you can see in Figure 4.1 the results obtained for the absorption case. When we are looking on the infrastructure side (1.3%), we see that it will be negligible compared to the other parts like the process and the solvent. The plant construction lifetime is assumed to 15 years for the reference case. We know that the lifetime of the plant could be greater and then the impact in terms of equivalent CO_2 emission would be even smaller. The plant construction which includes mainly the foundation and the air contactor is rather based on an optimisation between the performances and its cost.

The major part concerning the CO_2, eq emissions is the process. The process includes the heat and electricity required to run the DAC properly. Details concerning the heat required and recovered during the process is available in Table 4.6. Heat is provided by burning natural gas in an oxyfuel calciner. The exhaust gas containing CO_2 is added to the captured CO_2 flux from the ambient air. Therefore, the CO_2 impact of the heat includes only the quantity of gas and oxygen needed for the heat required as the CO_2 is not emitted in the atmosphere.

The electricity impact is twice than the heat. The energy mix chosen is the global one. The main source that contributes to this mix is the coal and gas which have a huge carbon footprint.

The solvent contributes to 28.5% of the total CO_2, eq emitted. It is mainly due to the fact that the solvent is manufactured by the electrolysis of potassium chloride brine. Therefore the solvent plays an important role in the carbon emission of the DAC. For example, the carbon footprint of KOH is around 4.1 $kg_{CO_2,eq}/kg$ and 0.9 $kg_{CO_2,eq}/kg$ for NaOH.

4.2.3 Impacts

The normalised results of the midpoint impact are shown below in Figure 4.2.

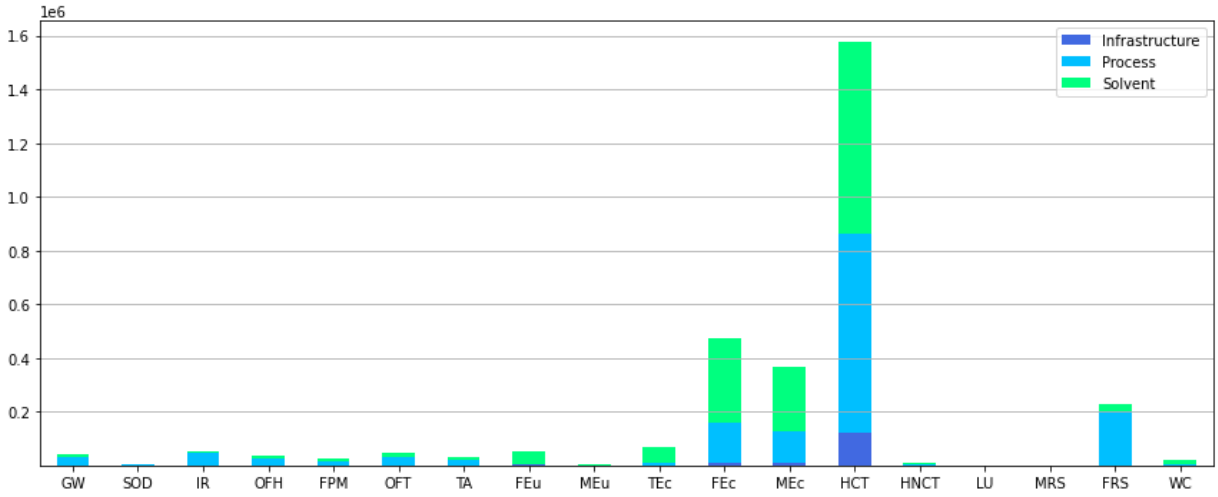


Figure 4.2: Normalised midpoint impact categories from Recipe methodology for a 1 Mt per year liquid solvent based DAC facility. The abbreviations used in the figure are: Global Warming (GW), Stratospheric ozone depletion (SOD), Ionizing radiation (IR), Ozone formation - Human (OFH), Fine particulate matter formation (FPM), Ozone formation - Terrestrial (OFT), Terrestrial acidification (TA), Freshwater eutrophication (FEu), Marine eutrophication (MEu), Terrestrial ecotoxicity (TEc), Freshwater ecotoxicity (FEc), Marine ecotoxicity (MEc), Human carcinogenic toxicity (HCT), Human non-carcinogenic toxicity (HNCT), Land use (LU), Mineral resource scarcity (MRS), Fossil resource scarictiy (FRS), Water consumption (WC).

Looking at the graph, the infrastructure has a very low impact compared to the process and the solvent for each impact categories. Concerning the process, heat is provided by gas and we consider the global electric mix. This mix includes electricity from Asia, a major user of coal. Four impacts stand out from the others and in particular human carcinogenic toxicity which is particularly high. In each case, the process and the solvent represent the biggest part. Coal utilisation in electricity production accounts for a lot concerning freshwater eutrophication and human carcinogenic toxicity impact. The other source concerning these two impacts is the use of a strong base solvent which is manufactured by the electrolysis of potassium chloride brine as seen in *SimaPro*. Regarding freshwater ecotoxicity and marine ecotoxicity, the use of coal is again a significant contributor but additionally, the use of

copper in the transmission network is also an important contribution. The main other contributor is again the solvent which uses potassium chloride brine to be manufactured. Potassium hydroxide could cause the pH level of the surrounding water rising suddenly. Fossil resource scarcity is this time mainly driven by the heat production using natural gas. Natural gas and coal used in electricity production share a part of the impact.

4.3 Reference case for adsorption

4.3.1 Life cycle inventory

For our reference model, we will consider a solid sorbent DAC capturing 1 Mt_{CO_2}/yr. The regeneration of an amine on silica gel sorbent will be done by Temperature Vacuum Swing.

The value choice for plant lifetime, capture fraction and product purity do not differ from the absorption case (see Section 4.2.1) and will not be discussed here. To find the sorbent consumption, the minimum sorbent requirement for a given capture rate is first computed. Then, given the sorbent lifetime, this value is adjusted to the corresponding CO_2 captured. Therefore, the sorbent consumption is directly proportional to sorbent lifetime and inversely proportional to sorbent capacity. The sorbent consumption of 8 g/kg_{CO_2} was found for sorbent lifetime of 1 year and a sorbent capacity of 2 mmol/g of sorbent.

Table 4.8: LCI for a DAC plant based on adsorption and using TVS regeneration process. The values were found in multiple articles: [11, 46] and [47].

Parameters	**Value**	**Units**	**Range**
DAC specifications			
Working capacity	1	[Mt_{CO_2}/yr.]	-
Plant lifetime	15	[yr.]	10 - 30
Capture fraction	0.75	[mole/mole]	0.6 - 0.9
Product purity	99	[%]	90 - 99.9
Sorbent consumption	8	[g/kg_{CO_2}]	-

Sorbent production

The chosen adsorbent is a mesoporous silica support covered by polyethylenimines (PEI), a polymer composed of amine groups connected by ethylene groups (CH_2-CH_2) [17]. Since the proportion between the two components was not found in literature, it was assumed a silica proportion of 70% while PEI represent the last 30%. As PEI is not present in our databases, we consider the LCI from the supplementary notes of [47]. In this study, they consider the production of PEI by homopolymerization of aziridine itself produced by the Wenker process. As they consider a best and a worst-case depending on the energy demand of the processes, we took the average between them. It is important to notice that those multiple assumptions increase the uncertainties linked to the sorbent impact and will therefore be a critical point in further sensitivity analysis.

Table 4.9: Life cycle inventory for the production of 8 g amine on silica sorbent required to capture 1kg of CO_2

Inventory	**Value**	**Units**
Support		
Silica gel	4.8	[g]
Amine (PEI)		
Monoethanolamine	4.8	[g]
Sulfuric acid	10.2	[g]
Ethanol	11.2	[g]
Diethyl ether	1.31	[g]
De-ionised water	44.8	[g]
Sodium hydroxide	8.96	[g]
Hydrochloric acid	0.64	[g]
Energy		
Heat	60	[kJ]
Electricity - medium Voltage	2.8	[kWh]

Energy consumption

The factors driving the energy consumption has been explained in subsection 2.2.3. As a reminder, the electricity consumption comes from the fans which overcome the pressure drop and from the vacuum pump decreasing the pressure from ambient to desorption pressure. Regarding the heat requirement, it is divided in sensible heat to increase temperature of sorbent and captured species, and in desorption heat to detach the species from the sorbent.

Table 4.10: Energy consumption parameters for electricity and heat. The values were found in multiple articles: [29, 48, 34] and [49]

Parameters	**Value**	**Units**	**Range**
Pump			
Electricity (Fans and Pump)	70	[%]	-
Pressure drop	1.4	[mbar]	1-1.4
Vacuum pump temperature	350	[K]	-
Desorption pressure	0.05	[bar]	0.02-1
Heat (Sensible and desorption)			
Desorption temperature	100	[°C]	80-130
CO_2 capacity	2	[mmol/g]	0.5-2.5
H_2O capacity	8	[mmol/g]	-
CO_2 heat capacity	37	[J/mol/K]	-
H_2O heat capacity	74	[J/mol/K]	-
Sorbent heat capacity	1.13	[J/g/K]	1.1-1.7
CO_2 desorption heat	80	[kJ/mol]	-
H_2O desorption heat	43	[kJ/mol]	-

The resulting energy consumption is summarised in Table 4.11. The heat is provided by natural gas and the electricity taken from a global energy mix.

Table 4.11: Life cycle inventory for the energy consumption of 1kg of CO2 extracted.

Inventory	**Value**	**Units**
Energy Input		
Heat for regeneration	7.5	[MJ]
Electricity	1.62	[MJ]

4.3.2 Network analysis

The data previously presented were then entered in the software Simapro to obtain a model of the solid sorbent based facility. To have a first idea of the DAC performances, the capture efficiency was computed using GWP100, meaning that every GHG emissions are taken into account. From cradle-to-grave, each kg captured by the DAC plant during 1 year emits 0,713 kg of $CO_{2,eq}$, resulting in a capture efficiency of 29 %. The distribution between the impact sources is shown in Figure 4.3.

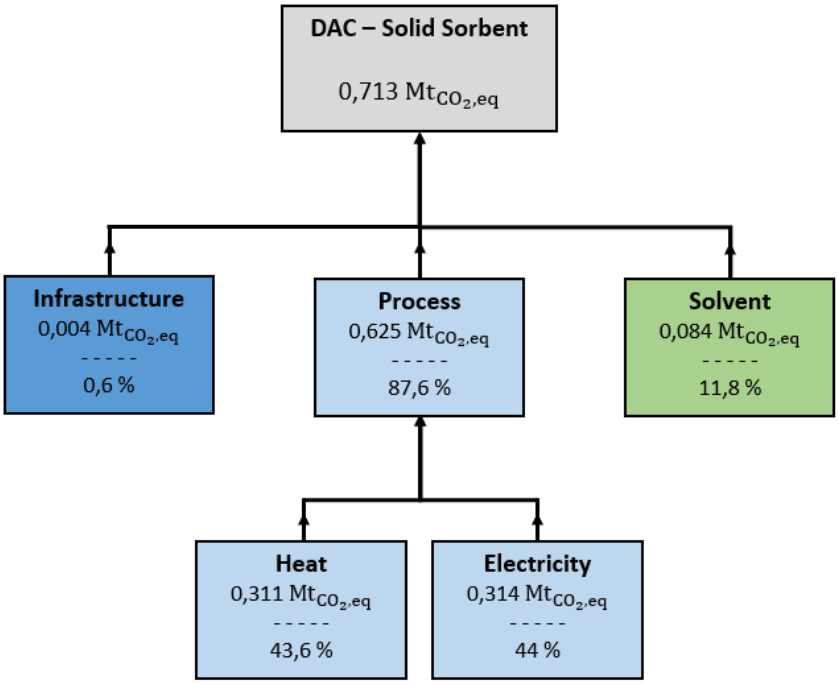


Figure 4.3: Share of the CO_2, eq emissions between the different impact sources of a solid sorbent based DAC facility.

Looking at the share of the infrastructure (0.6 %), it is clear that this component plays a very little role in the total emissions. Even with a short lifetime of 15 years, the distribution of plant construction impact makes it negligible. This low share could also be increased for smaller plants but, as an LCA conducted on the smaller scale Orca plant from Climeworks (4000 t_{CO_2}/yr) also conclude that infrastructure construction was comparatively small [47], we believe that it is a reasonable statement.

It is worth to mention that even if its carbon impact does play a role as big as energy process, the last one is directly linked to infrastructure optimisation. Moreover, the main problem to solve regarding plant construction is its cost. Decreasing its economic impact in exchange for an increase in plant carbon share could be seen as a good trade-off if it allows DAC to be economically sustainable.

Given the high energy consumption, it is not surprising that the process represents the largest share of CO_2, eq emissions with 87,6 % of the total emissions. They are equally dispatched between heat and electricity even though the demand for electricity is four times less than the demand for heat. It can be explained by the very high carbon footprint of the global energy mix from Ecoinvent, mainly due to the large share of coal and oil for electricity generation in Asia. Consequently, the use of less emitting electricity could lead to major improvement of the capture efficiency. In addition, natural gas could also be replaced by greener heat source such as waste heat or geothermal and therefore drastically

improving the process. These configurations will be discussed through a sensitivity analysis in the next chapter.

The sorbent production emits 0,084 $kg_{CO_2,eq}$ which represents 11,8% of the total emissions. This mainly due to production of the amine and in particular to the utilisation of monoethanolamine, ethanol and sodium hydroxide in the PEI production. Together, they represent more than 50% of the sorbent GHG emissions. Regarding the end-of-life, it contributes to 14% and is predominantly caused by the treatment of silica. It is clear that these results are strongly dependent of the sorbent choice; yet, according to [47] which assessed 6 different sorbents, the difference between the sorbents would not be significant. Therefore, the carbon footprint of the sorbent will not be the main environmental impact influencing the sorbent choice but rather: cost, capture performances and other environmental impact that will be discussed in the next section.

4.3.3 Impacts assessment

On figure 4.4 is shown the normalised results for the 18 midpoint impact categories shared between infrastructure, process and sorbent. Note that the results are only an estimation of the potential impact and that due to simplifying assumptions, some impact could be less robust.

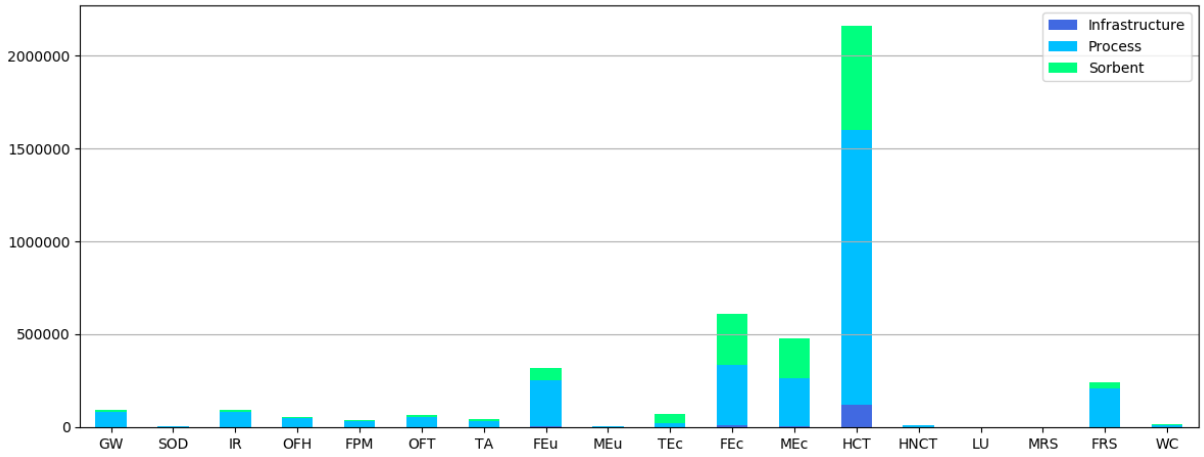


Figure 4.4: Normalised midpoint impact categories from Recipe methodology for a 1 Mt per year solid sorbent based DAC facility. The abbreviations used in the figure are: Global Warming (GW), Stratospheric ozone depletion (SOD), Ionizing radiation (IR), Ozone formation - Human (OFH), Fine particulate matter formation (FPM), Ozone formation - Terrestrial (OFT), Terrestrial acidification (TA), Freshwater eutrophication (FEu), Marine eutrophication (MEu), Terrestrial ecotoxicity (TEc), Freshwater ecotoxicity (FEc), Marine ecotoxicity (MEc), Human carcinogenic toxicity (HCT), Human non-carcinogenic toxicity (HNCT), Land use (LU), Mineral resource scarcity (MRS), Fossil resource scarictiy (FRS), Water consumption (WC).

Looking at the graph, five impacts stand out from the others and in particular human carcinogenic toxicity which is particularly high. In each cases, the process represents the biggest part. For freshwater eutrophication and human carcinogenic toxicity, this impact is mainly from coal utilisation in electricity production. As a reminder, the electricity used is a global mix including electricity from Asia, a major user of coal. Regarding freshwater ecotoxicity and marine ecotoxicity, the use of coal is again a significant contributor but additionally, the use of copper in the transmission network is also an important contribution. Fossil resource scarcity is this time mainly driven by the heat production using natural gas. Natural gas and coal used in electricity production share a part of the impact.

4.4 Discussions

Now that reference models for each technology have been described and analysed individually, this section will put them in parallel. First, in Figure 4.5, the total energy requirement is shown for both absorption and adsorption. It appears clearly that the demand is higher in adsorption case than in absorption case with 7 and 9.1 MJ/kg_{CO_2} captured. The share of electricity is in each case a bit lower than 20%. These result seems consistent with what is found in the literature. It is important to mention that these values represent only one

case, chosen to be in line with what is currently done by DAC companies, but that many variations could be made. Especially for solid sorbent which can provide heat by a large number of means, which often results in an increase in the share of electricity and a decrease in the total energy demand. Moreover, heat recovery system as described in [31] could be integrated. For liquid solvent, the reduction potential is more limited, mainly due to the high temperatures required and the already high energy recovery.

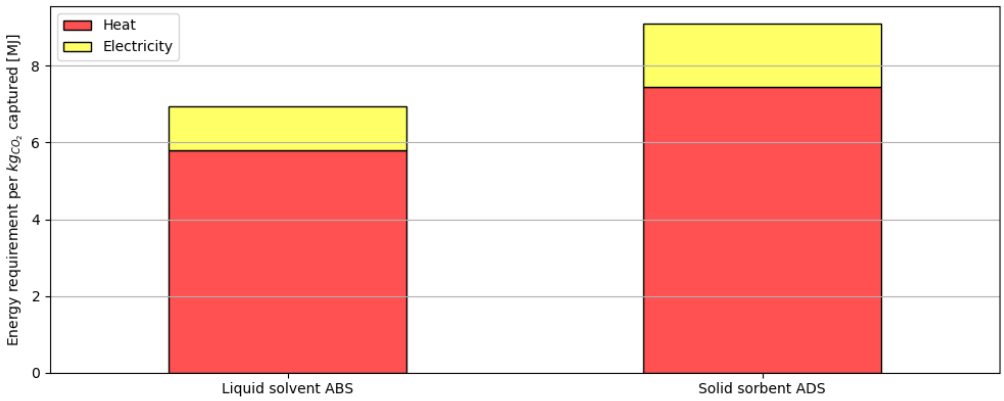


Figure 4.5: Total energy requirement for the capture of 1kg of CO_2 in the atmosphere using absorption or adsorption DAC.

The resulting emissions, divided by sources, are presented in Figure 4.6. Given the major impact of the process on emissions and the fact that, as seen just above, the energy demand is higher in the case of adsorption, it is not surprising that it emits more than absorption. However, the results are particularly distinct with a capture efficiency of 29 and 69% respectively. This difference results from the major influence of the electricity demand in view of the high carbon footprint of the global mix used in *Simapro*. Furthermore, the impact of heat is greatly reduced in the case of absorption considering that the carbon dioxide emitted during gas combustion is incorporated into the total CO_2 output flow. Note that this method leads to a larger amount of CO_2 at the end, hence this benefit will only be retained if it is not directly re-emitted. As this technique has not been found to be associated with adsorption in the literature, it has not been applied.

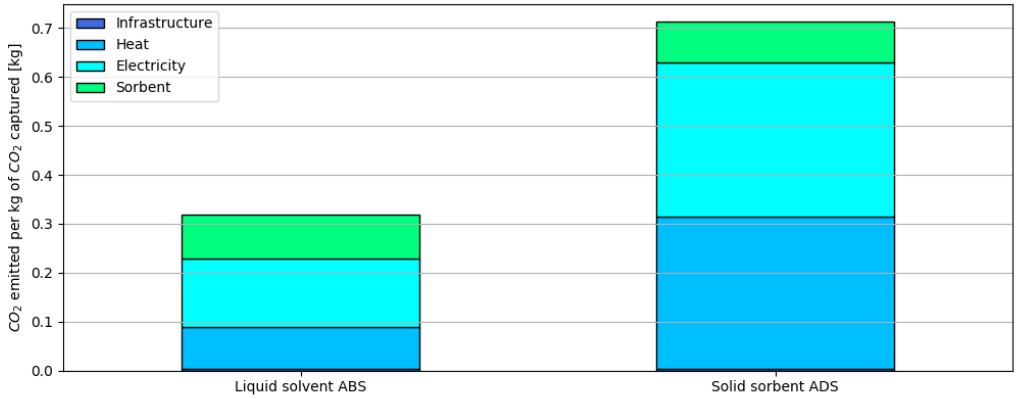


Figure 4.6: Total emissions from the capture of 1kg of CO_2 in the atmosphere using absorption or adsorption DAC.

Regarding the impact categories, the results are once again better, in most of the cases, for absorption than for adsorption. In fact, the only impact where adsorption perform better is in water consumption. For the rest, the same impacts stand out in both cases and were further detailed previously. Contrary to carbon dioxide emissions where the process dominated the impact, here the solvent/sorbent have a large part which underlines the importance of the choice of the latter with regard to its environmental impact. Although solvent seems to have a greater impact than sorbent, the difference is small.

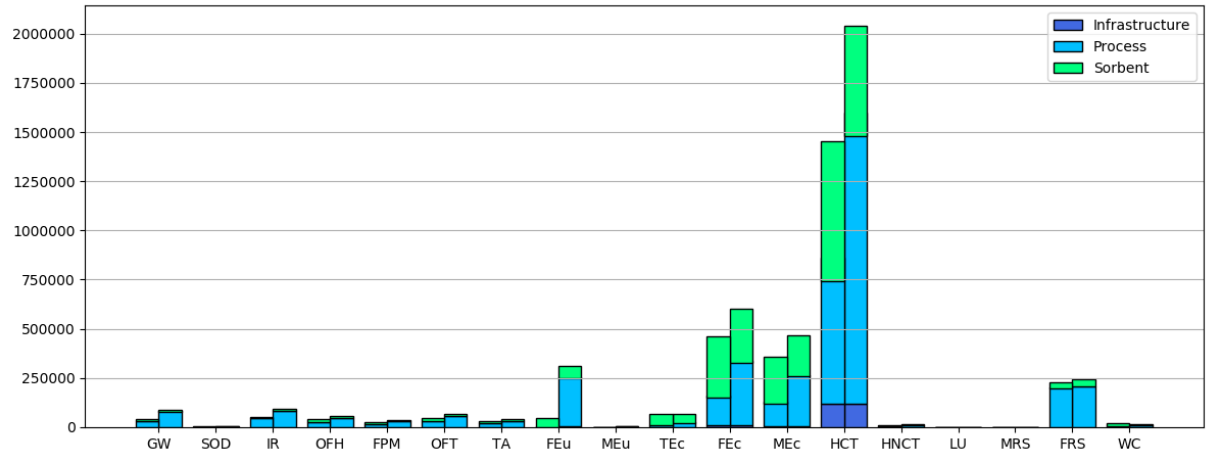


Figure 4.7: Normalised midpoint impact categories from Recipe methodology for a 1 Mt per year DAC facility using liquid solvent (left) or solid sorbent (right). The abbreviations used in the figure are: Global Warming (GW), Stratospheric ozone depletion (SOD), Ionizing radiation (IR), Ozone formation - Human (OFH), Fine particulate matter formation (FPM), Ozone formation - Terrestrial (OFT), Terrestrial acidification (TA), Freshwater eutrophication (FEu), Marine eutrophication (MEu), Terrestrial ecotoxicity (TEc), Freshwater ecotoxicity (FEc), Marine ecotoxicity (MEc), Human carcinogenic toxicity (HCT), Human non-carcinogenic toxicity (HNCT), Land use (LU), Mineral resource scarcity (MRS), Fossil resource scarictiy (FRS), Water consumption (WC).

4.4.1 Net zero emission projection

The temperature limitation goals stated during the COP21 were recently reaffirmed during the COP26 [50]. Moreover, the Glasgow climate pact recognises that limiting global warming by 1.5°C require to reduce CO_2 emissions to net zero around mid-century. In a recent report [4], IEA aims to give guidelines in how to achieve Net Zero Emissions (NZE) by 2050. It highlights the inherent role that CDR plays in the residual emissions balance. Based on their projection of the evolution of CO_2 capture by DAC as well as , the total energy requirement for the given capture rate is shown in Figure 4.8.

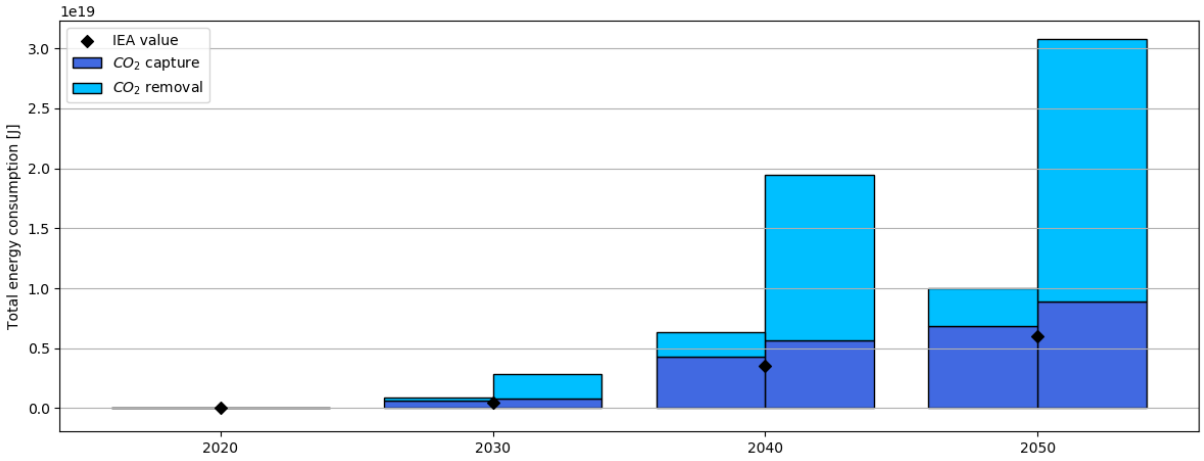


Figure 4.8: Total energy consumption for capturing/removing CO_2 with liquid solvent DAC (left) or solid sorbent DAC (right), following NZE scenario from IEA [4].

In the article [35], the authors emphasize the difference between captured and removed CO_2. The amount of removed subtracts transport and storage losses (not taken into account in this study) as well as overall process emissions from captured CO_2. Hence providing a better vision of its efficiency as a CDR technology. On Figure 4.8, the values shown for energy consumption related to CO_2 capture are quite similar to the one presented by IEA (see Figure 1.3). Not taking into account the emissions related to capture (100% efficiency), these numbers can only be reduced by technological innovations allowing to capture at a lower energy price.

The light blue part of the figure correspond to the additional energy requirement when considering a capture efficiency below 100% (68% for ABS and 29% for ADS). In this case, the values increase drastically to 10 and 30 EJ in 2050 (compared to 6EJ in IEA projections). This highlights the major influence of the capture efficiency, and thus in particular the importance of the carbon footprint of the energy. Note that this reasoning applies to other parameters such as cost and environmental impact.

Chapter 5

Sensitivity Analysis

In this section, we will try to understand how the variation of some parameters affect the performances of direct air capture. To do so, we will perform a sensitivity analysis based on the reference case. This investigation serves several purposes: take into account the uncertainty on the parameters due to large variations in the literature, find the necessary conditions for the successful implementation of a DAC plant and be able to compare absorption and adsorption on a wider level. Since both technologies depend on different factors, we will first assess liquid solvent DAC and then follow with solid sorbent DAC. Finally, a discussion will put them in parallel.

5.1 Absorption sensibility

5.1.1 Water losses

Water losses occur in the air contactor. Indeed, water from the NaOH solution evaporates when air is brought into the solution. These losses represent the difference of moisture content between the air entering in the contactor area and the air leaving it. There are 3 parameters having an effect on these losses. The molarity of the solution and the ambient conditions such as temperature and humidity [51].

$$r_{\mathrm{H_2O/CO_2}} = \frac{P_{\mathrm{v}}(T_{\mathrm{out}})S - P_{\mathrm{v}}(T_{\mathrm{in}})R_{\mathrm{H}}}{\Delta P_{\mathrm{CO_2}}} \tag{5.1}$$

The first parameter which is the molarity of the solution has an effect on the degree of saturation S. The value of the degree of saturation is quite difficult to obtain but can be found thanks to experimental data or by making assumptions. Figure 5.1 shows the degree of saturation in function of the NaOH concentration where we assumed an ideal NaOH solution.
The second and third parameter which corresponds to the atmospheric temperature and relative humidity are linked to the water partial pressure value when air goes into the contactor and leave it.The partial pressure of water is proportional to the vapor pressure of

water. We assume that the inlet T_{in} and outlet temperature T_{out} of the air have the same value. Using the relation upper, you can observe the results for 2M and 5M NaOH solution in Figure 5.2.

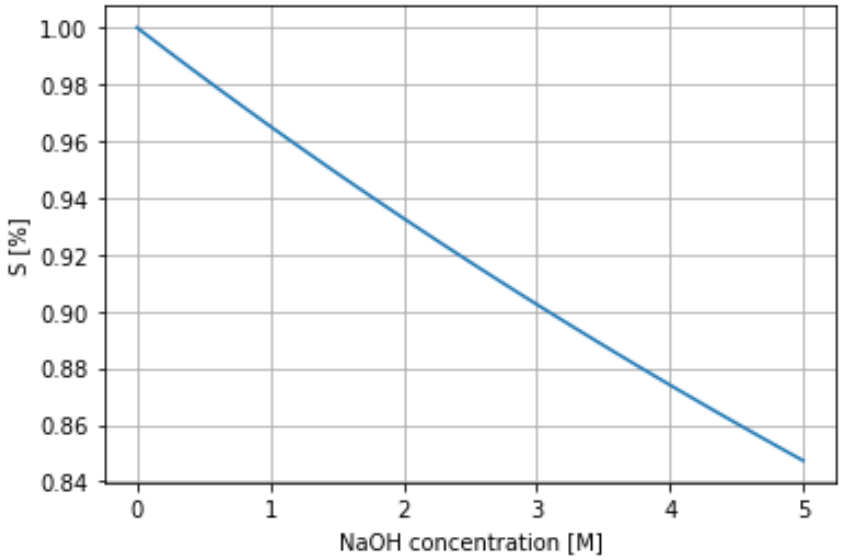
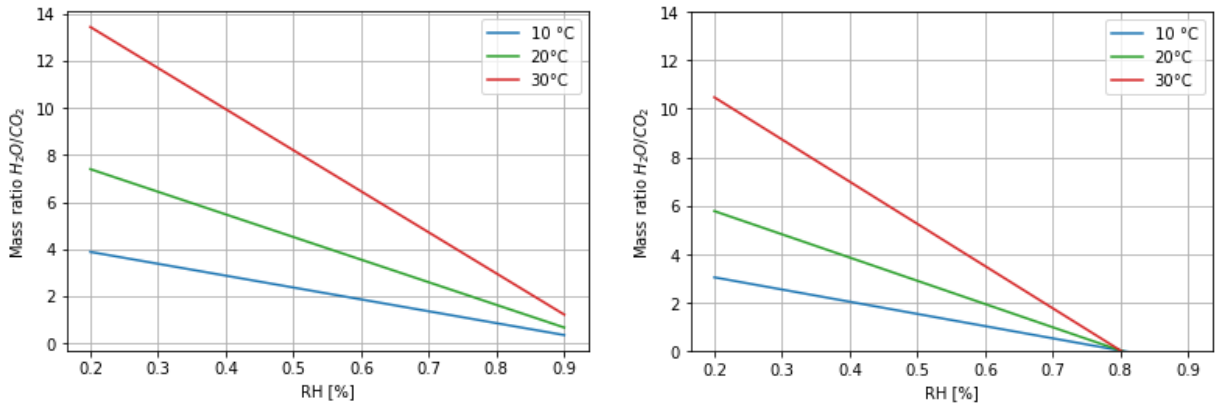


Figure 5.1: Degree of saturation of air in equilibrium with NaOH solution

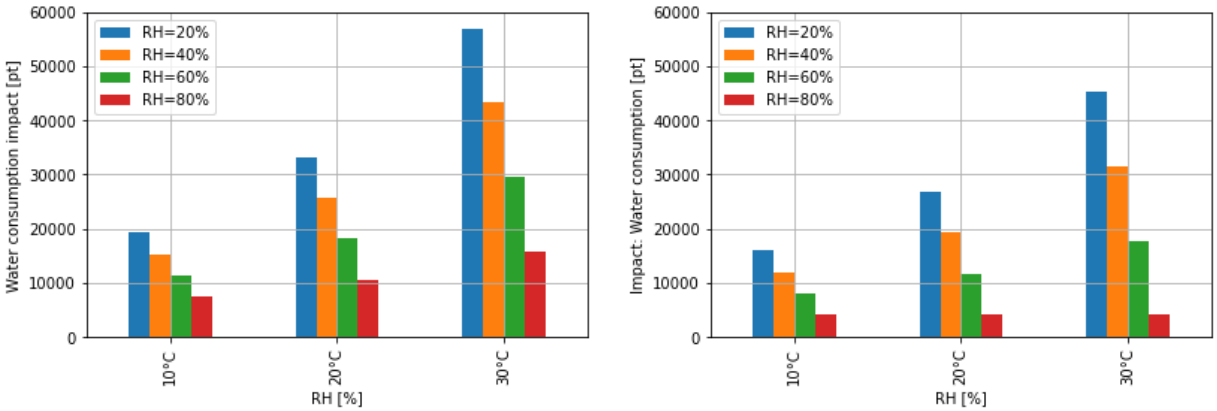


(a) 2M NaOH

(b) 5M NaOH

Figure 5.2: Water losses in terms of mass ratio (H_2O/CO_2)

location and the time where the DAC plant operates change the water consumption as the temperature and relative humidity vary. This variation could be quite huge as you can see in the graph. Having a higher molarity than 2M reduce water losses but doesn't increase by a lot the performances of the DAC. Furthermore, a solution with higher molarity is more difficult to handle [52].

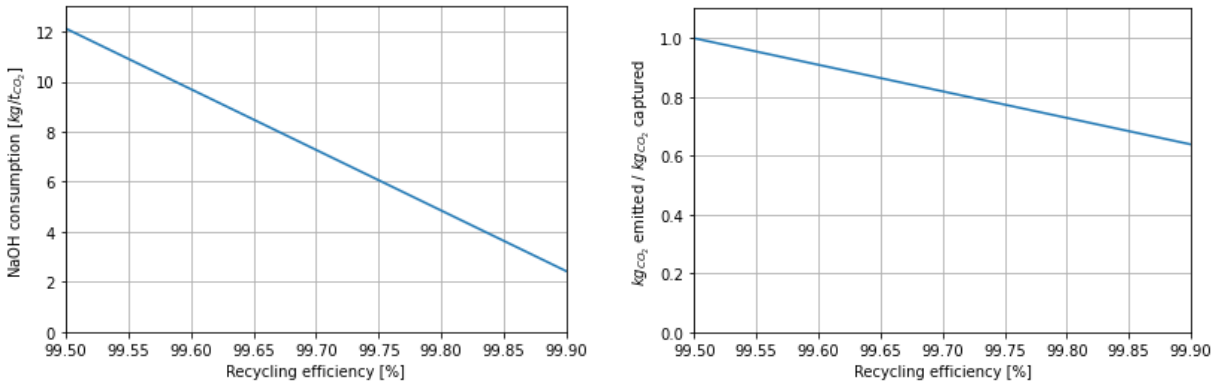


(a) 2M NaOH (b) 5M NaOH

Figure 5.3: Water consumption impact [pt]

5.1.2 Recycling efficiency

Recycling efficiency represents how much the chemical product undergoing through a process will be recovered. In the DAC process, the air contactor and regeneration loop are closed. Chemical losses occur during the cycle and should be accounted as a make-up of NaOH and $CaCO_3$. For example, during the regeneration cycle, calcium carbonate pellets are produced and fines appear which could account for these losses. Fouling could also play a role in the recycling efficiency. The fooling in the air contactor will not appear as the solvent (KOH or NaOH) inhibits biological growth. The results obtained are shown below in Figure 5.4. These results are based on previous experimental study with a mass balances for the process [53].
We observe that the recycling efficiency influence by a lot the quantity of NaOH needed. However, we have seen through the literature that recycling efficiency is well controlled and is assumed to stay around 99.9% for NaOH and 90.9% for $CaCO_3$.



(a) NaOH consumption

(b) GHG impact of the NaOH consumption

Figure 5.4: Recycling efficiency impacts

5.1.3 Electricity carbon footprint

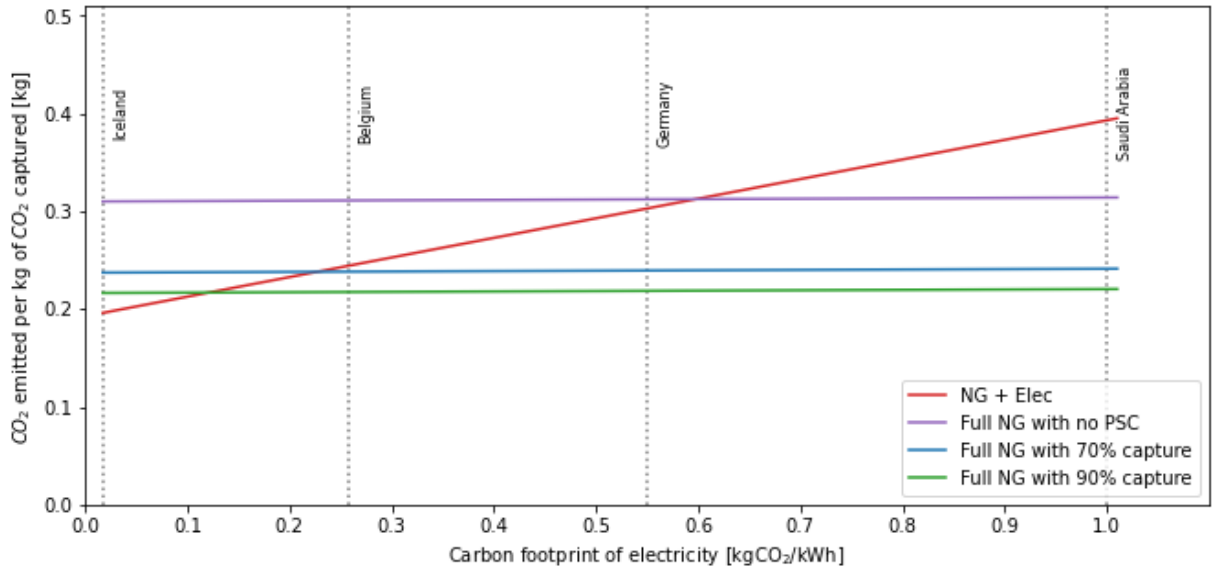


Figure 5.5: Effect of the carbon footprint on the GHG emission of the DAC plant for different energy sources

The *full NG* case consider an oxy-fuelled calciner that burn natural gas for the regeneration cycle and a combined cycle gas turbine plant on site which produces and supply electricity to the DAC. The CCGT is coupled with a point source capture which absorbs 90% of the CO_2 emitted. Therefore, the total gas coming out of the DAC is composed by the 10% of CO_2 remaining after the point source capture of the CCGT, by the CO_2 produced at the oxy-fuel calciner and by the CO_2 captured by the plant itself. To give a rough idea, around

31% of CO_2 is added. The oxy-fuel calciner account for an amount of 24% and the CCGT with point source capture for 7%. This mean that for 1 kg of CO_2 captured by the DAC, we have a total gas flow coming out of the DAC around 1.31 kg_{CO_2} that would be stored or utilised. The same case where the PSC capture 70% of the CO_2 emitted by the CCGT is also shown in Figure 5.5. We observe that having a PSC coupled with the combined cycle plant has a relatively important impact in terms of total CO_2 emission. The point where the cases *Full NG* and *NG+Elec* (red line) intercept could be seen as the carbon footprint of the electricity produced by the CCGT.
For the *NG + Elec* case: we consider an oxy-fuelled calciner for the regeneration cycle but the electricity comes from the country's electricity mix. The carbon footprint of electricity plays a major role in the CO_2 emission as you can see in the figure upper.

5.1.4 Energy recovery

As seen in the reference case, heat is recovered during the process. The recovered energy mainly comes from the flue gas when they are cooled and from the exothermic reaction in the slacker.
It is interesting to compare the case where we recover heat (reference case) and the case where no heat is recovered during the process. Another case is shown in Figure 5.6 where heat is recovered a lower temperature, by the condensation of water in the flue gas.
Recovering energy is not that easy, it will depend on the quality of the heat ,i.e., its exergy and could add some complexities in the process. In the first place, the investment can be higher when systems like heat exchanger, condenser are putted in the process but this cost could be returned.

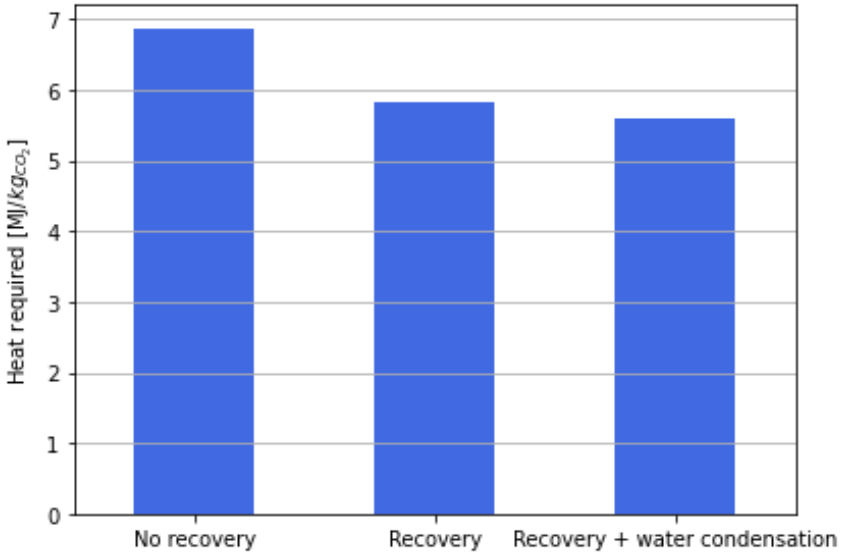


Figure 5.6: Heat required for different cases where energy could be recovered or not.

5.2 Adsorption sensibility

This section is dedicated to the sensitivity analysis of a DAC plant using solid sorbent as capture medium. From the analysis of the reference case, we know that the main sources of impact are the energy and sorbent consumption. In each case, the drivers of these parameters are mostly linked to the sorbent choice. In the literature, a multitude of sorbents is analysed on an experimental scale resulting in large uncertainties. Their evaluation involves a wide variety of competing parameters implying trade-offs. While trying to be as general as possible, this analysis is based in particular on the characteristics of a sorbent of the type: amine on silica. Other variation parameters, such as relative humidity and ambient temperature, are rather linked to the localisation of the plant.

5.2.1 Heat of desorption and desorption temperature

In Chapter 2, the energy consumption linked to the sorbent regeneration was discussed. The formula 2.12 express the sensible energy required to heat up the sorbent and adsorbed components to the desorption temperature. The formula 2.13 refers to the energy needed to detach the adsorbed components (water and carbon dioxide) from the sorbent.

Desorption temperature and CO_2 desorption heat are inherently linked to the sorbent design. Having a low desorption temperature decreases the sensible energy but has the major drawback to increase the desorption process time [17]. On the other hand, a too high temperature can deteriorate the sorbent resulting in a degradation of the CO_2 capacity and selectivity over consecutive cycle. Many researches are investigating new type of sorbent and techniques to counter those issues [54]. Regarding desorption heat, [32] highlights that for dilute CO_2 concentration such as in ambient air, higher desorption heat results in a higher separation efficiency. This counter intuitive relation could be explained by the fact that for a sorbent with higher affinity, the desorption is done on a more concentrated feed. To some extent, it explains why chemisorbent are preferred to physisorbent for DAC. Again, this benefit must be balanced with the prohibitive energy consumption of an excessively large affinity.

On Figure 5.7, the evolution of the regeneration heat regarding desorption temperature and heat is shown. According to the formula, a linear relationship is obtained which encourages a temperature and a heat of desorption as small as possible. For a difference of 20°C around the reference desorption temperature (100°C), a variation of 0.4 MJ (5%) is observed. In [54], the temperature interval of 90 to 110°C is considered optimal in order to stay in an acceptable rate range without sorbent degradation. Without being of major importance, the choice of the 90°C temperature seems to be the most relevant in view of the little difference in desorption time between 90°C and 100°C.

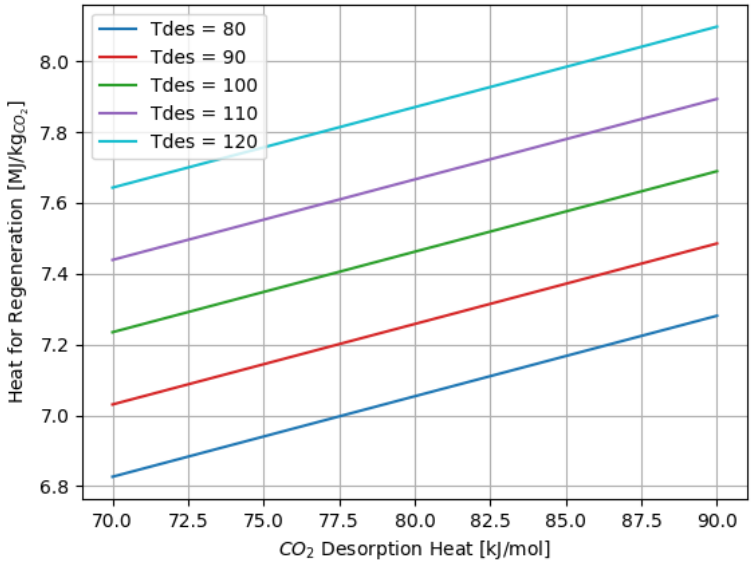


Figure 5.7: Evolution of total heat requirement in function of the CO_2 desorption heat and temperature of desorption

Regarding desorption heat, a variation of nearly 0.25 MJ (3%) occurs for a difference of 10 kJ/mol with the reference (80 kJ/mol). This value should be put in parallel with the benefits of a strong binding linked to a better selectivity. Unfortunately, this will not be done in this thesis due to lack of information about the relationship between desorption heat and capture capacity. It probably exists an optimum specific to each sorbent.
On Figure 5.8, the resulting impact on capture efficiency can be seen. Again the relation is linear. Based on the previous discussion, the desorption temperature of 90°C is chosen as the best candidate.

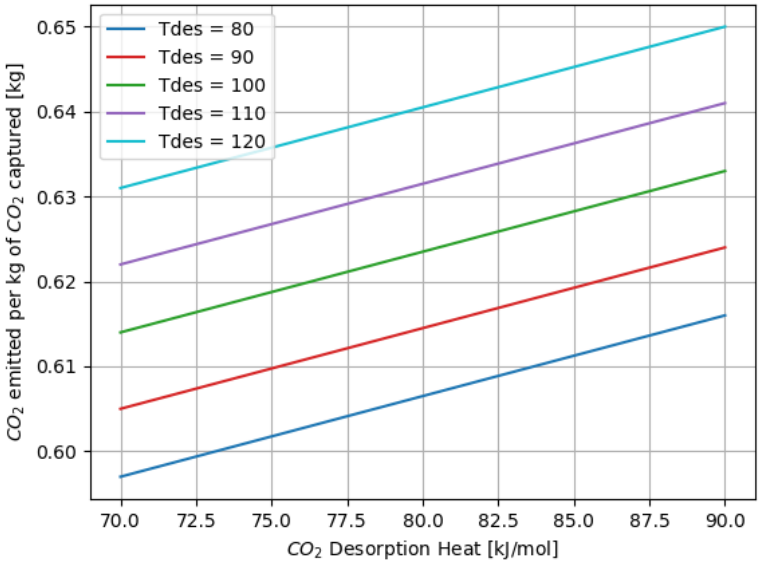


Figure 5.8: Emissions from the process of capturing CO2 using solid sorbent, including heat and electricity requirement, in relation with desorption temperature and heat.

5.2.2 Uptake capacity

The uptake capacity (q) is probably the most determinant sorbent characteristic regarding energy consumption. Indeed, the regeneration heat is strongly linked to q_{CO_2} and q_{H_2O} as seen on formula 2.12 and 2.13. For the reference case, a CO_2 capacity of 2 was assumed for an amine based sorbent [55]. However, knowing the major impact of this parameter as well as the wide variety of values present in the literature, an in-depth measurement of its variation impact is studied below.

First, let's observe how q_{CO_2} is impacted by external conditions (other than sorbent choice). To compute its evolution, Toth isotherm model was used with a parameter set given by [56], slightly modified to fit reference case value. On Figure 5.9, we can observe that CO_2 capacity increases with CO_2 partial pressure and decreases with temperature. For the considered temperature and at for $p_{CO_2} = 40$Pa corresponding to 400 ppm, we obtain CO_2 capacity from 1 to 3. Note that this graph is not intended to predict exact values for other conditions but rather to highlight the behaviour following their variations. Moreover, it is worth to mention that even if Toth model is widely used in literature; other papers suggest a different relationship between adsorption temperature and capture capacity. For example, [32] states that there is an optimum temperature that balances the positive effects of low temperature on sorption and the positive effects of high temperature on diffusion and reaction rate.

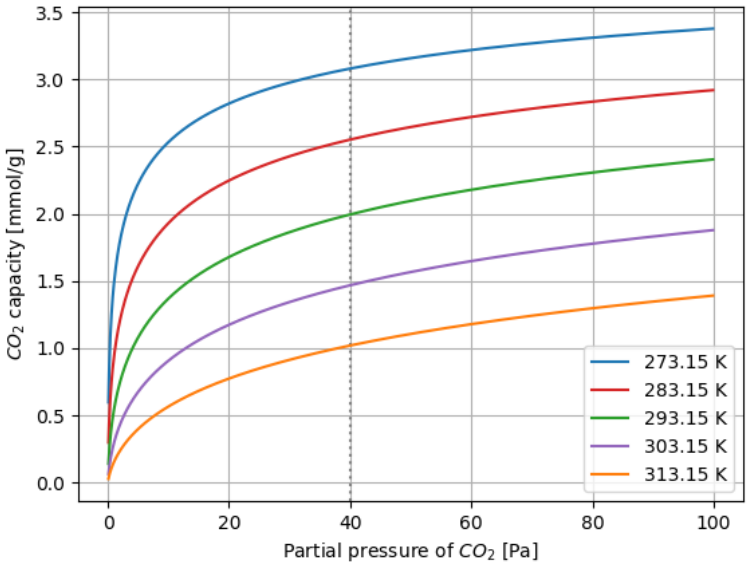


Figure 5.9: Evolution of sorbent CO_2 capacity in relation with change in CO_2 partial pressure and adsorption temperature, as predicted by Toth model.

Regarding co-adsorption of water, we observe on Figure 5.10 a strong relation between q_{H_2O} and the relative humidity as well as a minor impact of adsorption temperature. As the true relationship between uptake capacities and environmental conditions result from very complex relations and for the sake of simplification, major assumptions were made. First, we will consider that q_{H_2O} values are independent from temperature and q_{CO_2} values. Therefore, for a relative humidity of 20, 40, 60 and 80%, we have a water capacity of approximately 2, 4, 6 and 8 mmol/g. In reality, q_{CO_2} and q_{H_2O} are intrinsically linked. In the case of amine sorbents, an increase in water adsorption results in an increase in carbon dioxide adsorption. This counter-intuitive relationship comes from bicarbonate formation instead of carbamate resulting in a stoichiometry favourable to the adsorption of CO_2 [56]. In other sorbent like Zeolites, the CO_2 capacity is decreased by water co-adsorption due to competitive adsorption [48].

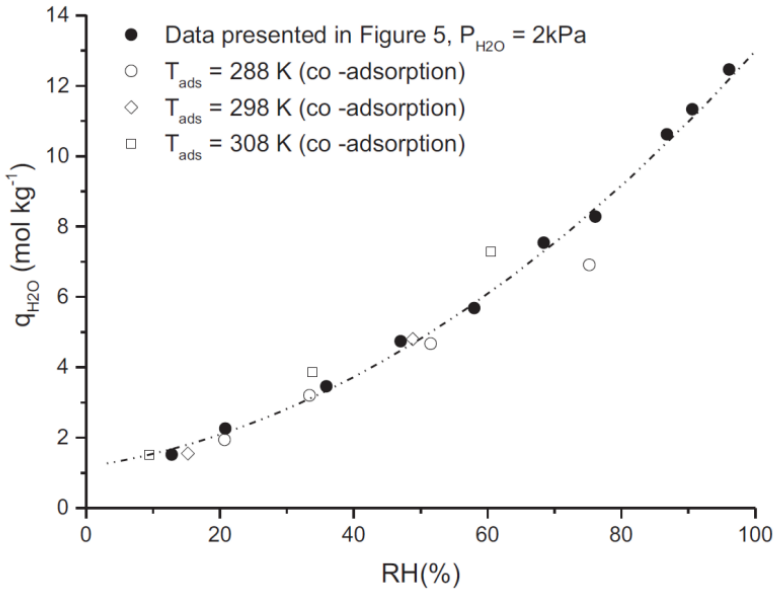


Figure 5.10: Evolution of sorbent water capacity in relation with change in relative humidity and adsorption temperature. Figure taken from [31]

In general, it is very difficult to link capture capacity with environmental conditions. Multiple sorbent exists with different relationships leading to optimal behaviour in hot or cold, humid or dry conditions. The rest of this section therefore focuses less on what influences capture capacity but more on the effects that a certain capacity has on energy consumption. On Figure 5.11, the relation between heat for regeneration and capture capacity depending on relative humidity is shown. Two conclusions can be drawn. First, the energy demand decreases with lower relative humidity. Second, the energy demand decreases with the increase in capture capacity. However, this energy saving becomes less and less significant. It seems that a capture capacity below 1.5 becomes very penalising while a value above 2.5 gives a light contribution compared to the disadvantages (cost and environmental impact) that a higher capacity could generate (notably by increasing the amine loading). The value chosen for the reference case (2 mmol/g) seems to give a middle performance representation.

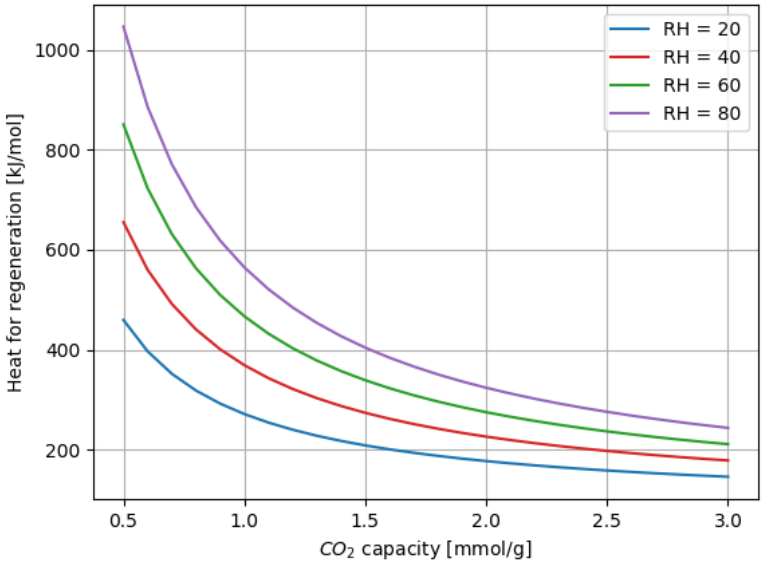


Figure 5.11: Evolution of the regeneration heat in relation with change in CO_2 capacity and relative humidity.

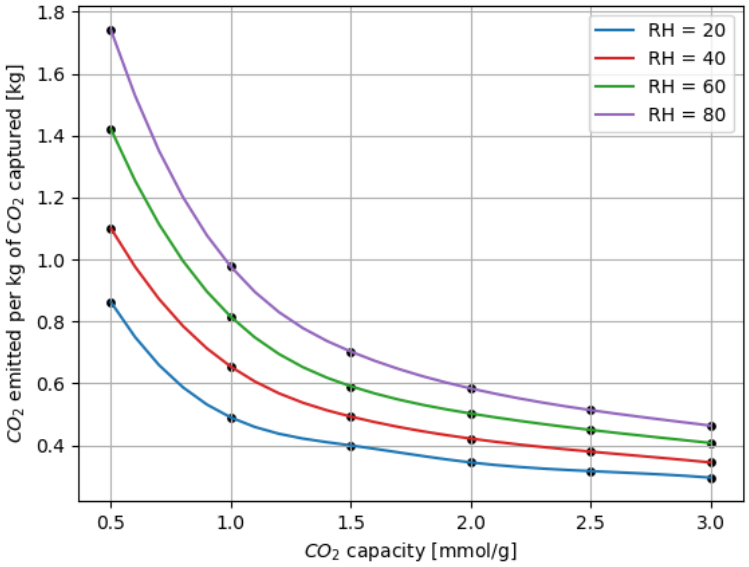


Figure 5.12: Evolution of the $CO_{2,eq}$ in relation with change in CO_2 capacity and relative humidity.

5.2.3 Sorbent consumption

The sorbent consumption can also be linked to the capture capacity as for a fixed capture rate, the sorbent mass required per cycle will decrease with a higher capacity. It can be observed on Figure 5.13 that the consumption decreases exponentially making the benefit from an increase in capture in capacity less and less relevant. The same effect appears for sorbent lifetime.

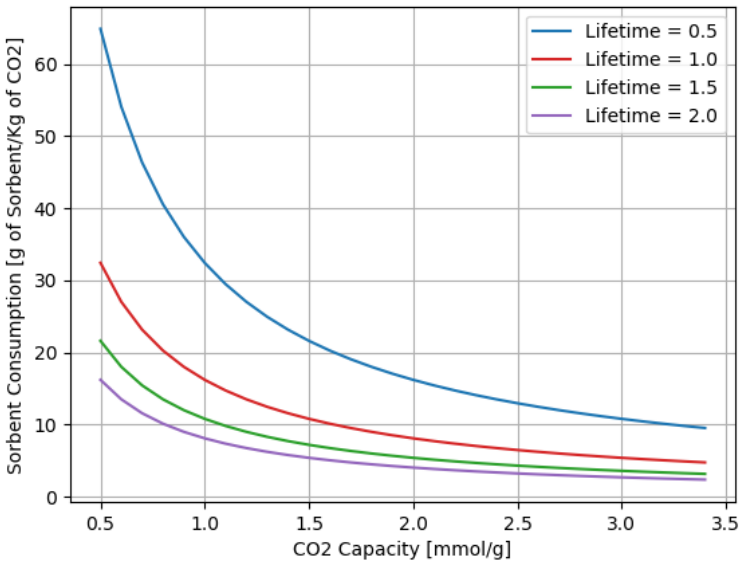


Figure 5.13: Evolution of the sorbent consumption in relation with change in CO_2 capacity and sorbent lifetime.

5.2.4 Electricity carbon footprint

For the reference case, the electricity requirement was met using global electricity mix with a carbon footprint of 0.692 kg_{CO_2}/kWh. For its part, the heat was provided using natural gas. However, depending on the source of the electricity, the carbon footprint of the electricity changes significantly. To illustrate this influence, the Figure 5.14 shows the evolution of the total emissions from a 1Mt/yr DAC plant for different electricity carbon footprints. To illustrate them, countries have been placed on the x-axis corresponding to the carbon footprint of their electricity mix. Additionally, two other heat sources have been added: heat pump and waste heat.

In both cases, the heat requirement is changed into an electrical need but with different Coefficient Of Performance (COP). These were chosen on the basis of the document [33], listing high temperature heat pumps. For a geothermal heat pump rising temperature from 20 to 100°C, a COP of 2 was chosen. In the case of waste heat, exhaust gas temperature

of 70°C was considered resulting in a COP of 4. Please note that this is only a rough estimate to illustrate the consequences of different heat/electricity ratios, but that the real application would require a case-by-case expertise.

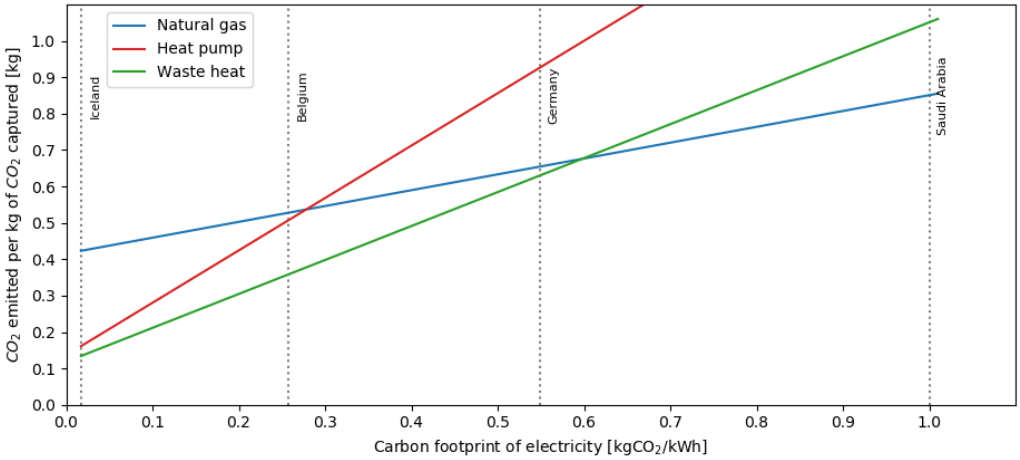


Figure 5.14: Total emissions for a 1Mt DAC plant regarding electricity carbon footprint for three different heat supply.

Depending on the scenario, the curves are impacted in two different ways: the y-intercept and the slope. The intercept corresponds to the emissions for a completely decarbonized electricity. In cases where the heat is from electricity, this only corresponds to the emissions from the sorbent of the plant construction. This is the maximum achievable capture efficiency, just below 90%. In the reference case, using natural gas, this value is much lower with a maximum near 60%.

The slope corresponds to the amount of electricity used. The greater the slope, the greater the impact of the electricity carbon footprint. This is well represented by the curves "Heat pump" and "Waste heat" which, starting from the same y, diverge due to their difference in electricity use. This makes the second case necessarily more interesting but it is to be noted that the use of waste heat is more constraining and could feed other systems such as electricity production. The problematic would deserve more details but is out of the scope of this thesis.

Moreover, the use of waste heat and heat pump is don't always give the best results. In fact, in both cases, their curve crosses that of natural gas, which makes the latter option more attractive. Roughly speaking, the use of natural gas can be considered more interesting when the electricity footprint exceeds that of Belgium and Germany for heat pump and waste heat respectively.

This analysis highlights the predominant impact of energy source choice on DAC performance. Depending on the carbon footprint of the electricity, the heat source used should be chosen carefully. It is important to mention that these considerations do not take into account energy costs but only performance in the sense of capture efficiency. For real applications, the cost of a decarbonized energy could strongly diminish the feasible possibilities.

5.3 Discussion

Various parameters impacting the DAC using liquid solvent were analysed. First of all, we observed that the environmental conditions such as the relative humidity and the temperature has an impact on the water consumption of the DAC plant but don't really influence the energy requirement. Another parameter is the recycling efficiency of the chemical products which could influence the solvent consumption and therefore the GHG emission. However the recycling efficiency is well controlled and should not vary much around their nominal values.

Concerning the GHG emission of the DAC plant, the prevailing parameter influencing it is the carbon footprint of the electricity. The location of the plant play then an important role due to its own environmental condition as said above and the electric mix. It should also be noted that in the case where the plant runs with full natural gas (heat + electricity), the point source capture is an important parameter as it could decrease the total GHG emission up to 10%. The heat recovery management will imply a trade-off between the cost and the GHG emission of the plant as it influences the total energy requirement.

For DAC using solid sorbent, the parameters influencing the GHG emissions were also analysed. It was concluded that the main drivers are the capture capacity of the sorbent and the electricity carbon footprint. The capture capacity has indeed a major influence, in terms of energy and sorbent consumption. The sorbent capacity depends on many parameters and the relation between them is specific to each kind of sorbent. This way, different environmental conditions will require different capture medium. Obtaining sorbents with good capture capacity seems to be a preferred way to improve the performances.

Note that relative humidity also has a major impact on energy consumption. However, obtaining water could be of great interest in some application. Therefore, the choice of the DAC location would change depending on the application.

In Figure 5.15, you can observe the total CO_2 emission of both technologies. For low carbon footprint of electricity, the adsorption system seems better than the absorption technology in terms of CO_2 emission. As the adsorption technology consume more electricity, its slope is much higher.

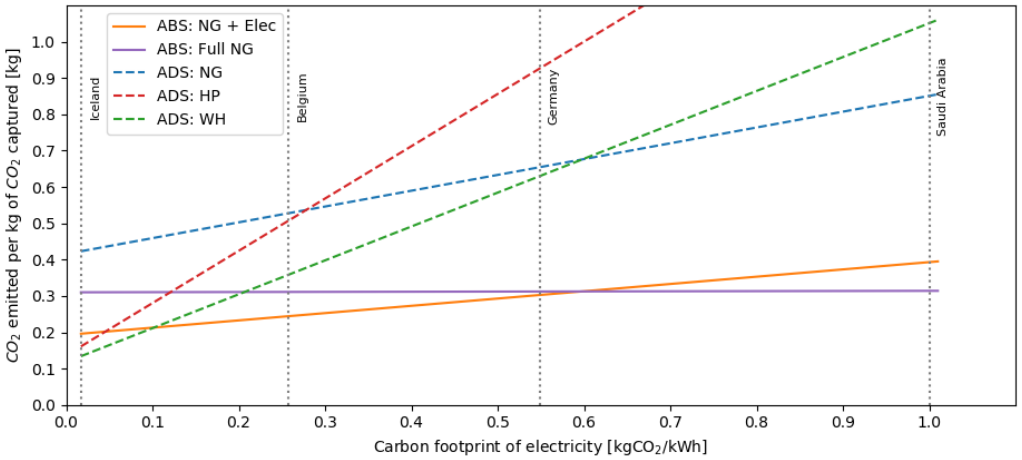


Figure 5.15: Total emissions for a 1Mt DAC plant regarding electricity carbon footprint for both absorption (ABS) and adsorption (ADS) technologies.

Chapter 6

Analysis of further scenarios

This chapter aims to extend the reference case to more practical scenarios which highlight the factors that favour or disfavour direct air capture. The last two chapters have already partly answered the second and third research questions but this one provides a more detailed analysis. To do so, three scenarios based on different geographical locations are presented.

The three locations are characterised by specific environmental conditions. An average annual value was chosen for the temperature and relative humidity. This simplification represents a major field of improvement but is reasonable in order to observe the global impact of the location on water and energy requirements. Another aspect influenced by the country choice is the carbon footprint of the electricity. Depending on the electricity share, this factor will have a greater or lesser impact on capture efficiency.

For each scenario, CO_2 is captured by absorption or adsorption process and is either geologically sequestered or used to feed a methanation plant. Moreover, each technology exists in two different configurations. For absorption using liquid solvent, the electricity requirement is met either by on site production using natural gas turbine or by the electricity grid. For adsorption using solid sorbent, the heat requirement is met using heat pump with different temperature source corresponding to different coefficient of performance.

6.1 Introduction to the scenarios

6.1.1 Carbon dioxide storage

Carbon dioxide storage combined with DAC aims to remove CO_2 from the atmosphere and then to store it in underground geological formation for millennia. Compared to carbon capture and storage (CCS) from post-combustion capture, DAC with CCS can be located directly above the suitable rock formation, hence avoiding cost and leakage linked to the transport.

Multiple methods exist to store CO_2 [24]. The most common approach consists in the injection of carbon dioxide in underground reservoirs, such as sedimentary basins, where it is trapped into porous rock and isolated under an impermeable cap rock. This technique strongly relies on the impermeable layer to prevent CO_2 from rising to the surface. Another option is mineral carbonation; consisting in the reaction between water containing CO_2 and mafic rock to form carbonate minerals. This way, the risk of carbon leakage over time is strongly decreased. It is this technique that was chosen by Climeworks in collaboration with the company Carbfix and this technique that is modelled in the following scenarios.

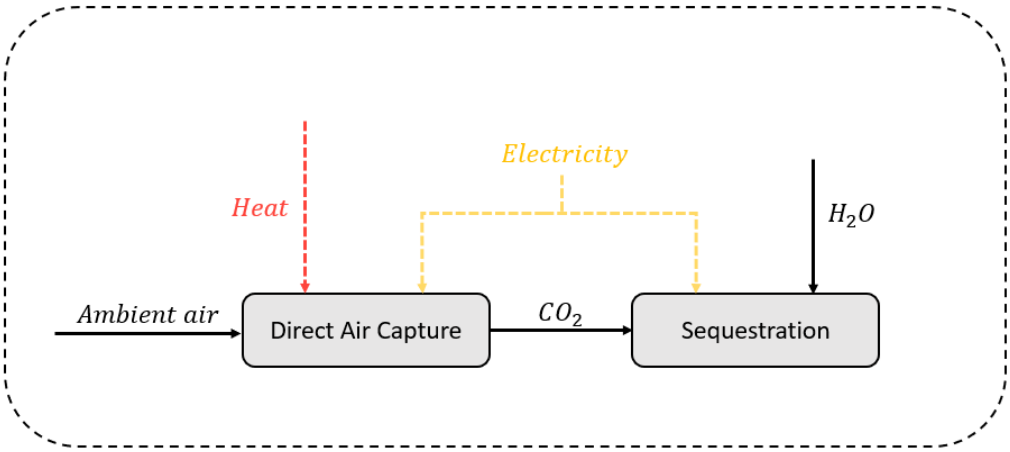


Figure 6.1: Geological sequestration combined with direct air capture

As it is not the central topic of this thesis, the modelling of the sequestration process is simplified in two requirements: water and electricity (Figure 6.1). The amount of water needed to dissolve CO_2 depends on its partial pressure. In the case of Carbfix, around 25 tonnes of water per tonne of carbon dioxide was used to fully dissolve it [24]. Regarding electricity consumption, [47] indicates a consumption of 100 kWh to raise 1 tonne of CO_2 from 1 to 150 bar. In order to take into account additional electricity requirements for transport and injection, 50 kWh is added to this number.

Table 6.1: Input and output related to the sequestration of 1kg of CO_2 in geological storage

Inventory	**Value**	**Units**
Geological sequestration		
Water	-25	[kg]
Electricity	-0.15	[kWh]

6.1.2 Carbon dioxide usage

Another way to use the captured CO_2 is to produce synthetic fuel. This way, DAC does not act as a Negative Emission Technology anymore but could allow to produce low carbon fuels for hard to decarbonise sectors such as transport and in particular aviation. In this thesis, the production of methane using Sabatier reaction (Equation 6.1) is considered. The required H_2 would be produced by electrolysis. You can observe the interactions between the different production components on the Figure 6.2.

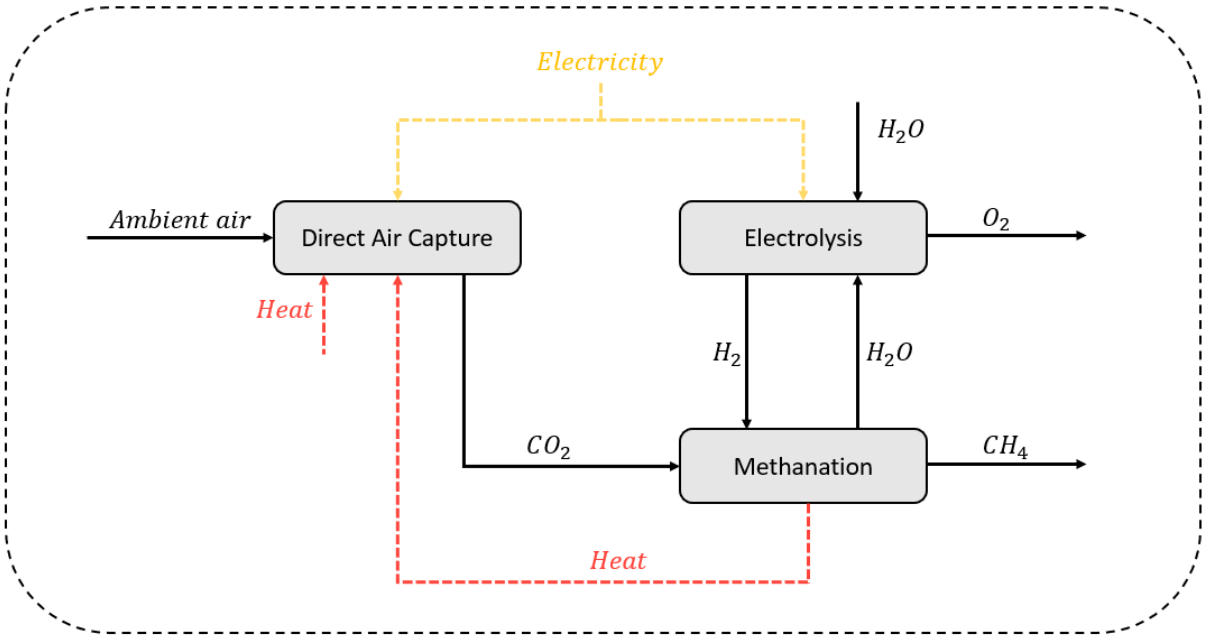


Figure 6.2: Synthetic methane production combined with direct air capture

To perform a complete methanation reaction, 4 moles of H_2 are required. This can be obtained using electrolysis with 4 moles of H_2O and an electrical supply of 110 kWh per mole of H_2 produced. It is equivalent to 10 kWh per kg of CO_2. Regarding the water consumption, 11 liters per kg of H_2 is considered [57], which is equivalent to 2 kg of water per kg of CO_2. This value only considers the electrolysis process itself without considering the additional water related to the demineralisation process. Therefore, the results might underestimate this criteria. Finally, we obtain 1 mole of CH_4, 1 mole of O_2 and 2 moles of H_2O.

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O \tag{6.1}$$

$$2\,H_2O \rightarrow O_2 + 2\,H_2 \tag{6.2}$$

Additionally, the methanation process is exothermic and typically perform at a temperature between 300 and 400°C [58]. Hence, accounting 165 kJ/mol of CO_2 consumed, around 2.8

MJ/kg_{CO_2} is assumed to be recovered with 75% recovery efficiency. The different inputs and outputs discussed previously are shown in Table 6.2.

Table 6.2: Input and output related to the transformation of 1kg of CO_2 in CH_4 using Sabatier process

Inventory	**Value**	**Units**
Electrolysis		
Water	-2	[kg]
Electricity	-10	[kWh]
O_2	+1.45	[kg]
Methanation		
CO_2	-1	[kg]
H_2	-0.18	[kg]
CH_4	+0.36	[kg]
H_2O	+0.8	[kg]
Heat	+2.8	[MJ]

It is important to note that depending on the technology associated with it, the species and energy equilibrium will not be the same. In particular, the heat recovery from methanation is considered lower in the case of absorption as the minimum energy requirement correspond to higher temperature. Further research should be done regarding exergy in order to give a really accurate energy balance.

6.1.3 Location

The choice of countries was made according to two main criteria: the carbon footprint of electricity and the climate conditions. In each case, the goal was to find countries that stand out while remaining within a credible range based on the results of the sensitivity analysis. In addition, attention was paid to consider countries for which CO_2 storage was feasible. To do so, [59, 6] and [24] were used to identify the potential storage sites.

6.2 Results

6.2.1 Scenario 1 - Belgium

In the first scenario, a 1 Mt/yr DAC plant, corresponding to the one described in the reference case, is based in Belgium. An average temperature of 10°C and a relative humidity of 80% is considered. Among the three scenarios, the carbon footprint of the Belgium electricity mix is an intermediate value with 258 $g_{CO_{2,eq}}/kWh$.

The obtained results for carbon dioxide equivalent emissions are shown in Figure 6.5 with, in the left box, emissions for scenarios using geological sequestration and in the right box, emissions for scenarios associated with CH_4 production. In each case, the process is found to be the major impact, followed by the sorbent/solvent production and by the infrastructure construction. Regarding the technologies, absorption using liquid solvent give better results than adsorption which is not surprising since ADS has a higher energy requirement and in particular a higher electricity demand. It can be seen by looking at Figure 4.5.
Similarly, Belgium's relatively high carbon footprint favours the stand-alone process using only natural gas with capture compared to the one relying on country electricity mix. Regarding adsorption using waste heat and heat pump, the first option will always be better but can be considered as an optimistic solution while the second is more realistic.

Focusing on CO_2 storage, the values vary between 0.22 ($\eta_{Capture}$ = 78%) and 0.51 ($\eta_{Capture}$ = 49%) kg_{CO_2} emitted per kg_{CO_2} captured. Although these results can all be considered to be within an acceptable range of capture efficiency, the adsorption results are of concern. Indeed, the lower the capture efficiency, the greater the resources, costs, environmental impacts such as water and land use for the same net amount captured. In this respect, the deployment of DAC using solid sorbent as a capture medium does not seem appropriate in regions with similar electricity carbon footprint as Belgium. Unless the electricity comes directly from a low-emission electricity sources such as nuclear, wind and solar power. However, it seems unwise to attribute low-carbon energy to direct air capture in a country where electricity is more carbon intensive than the latter.

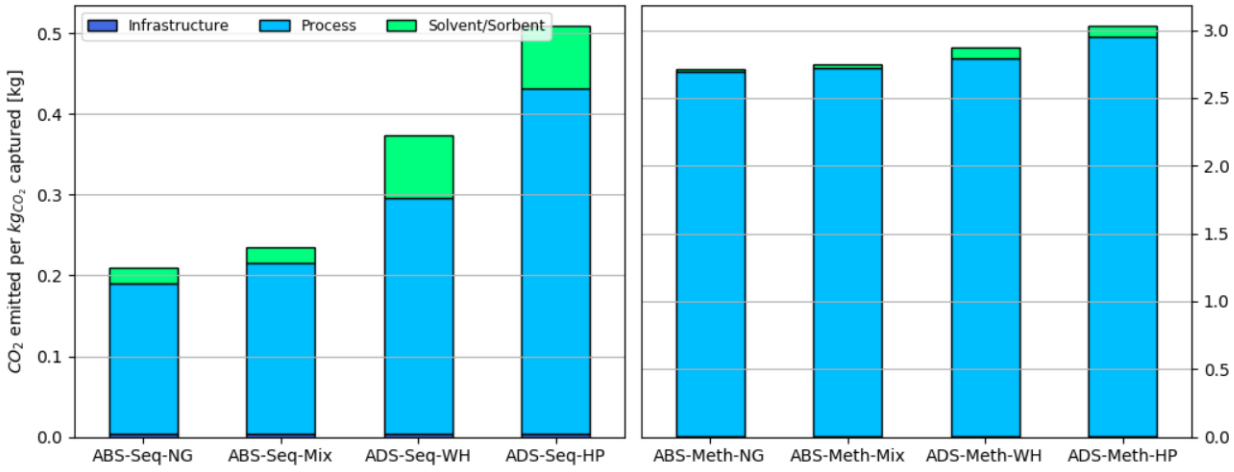


Figure 6.3: Total CO_2 emissions for a DAC plant based in Belgium according to different capture technologies and CO_2 utilisation. The abbreviations used: Abs (Absorption DAC), Ads (Adsorption DAC), seq (with sequestration), meth (with methanation), NG (using only natural gas), Mix (using natural gas and country electricity mix), WH (using waste heat) and HP (using heat pump).

Regarding methanation process, the results range from 2.7 to 3 kg_{CO_2} emitted per kg_{CO_2} captured which is equivalent to 7.5 and 8.3 kg_{CO_2} emitted per kg_{CH_4} produced. Considering methane combustion emission of 2.75 kg_{CO_2}, the results obtained are strongly unfavourable. This is mainly due to the large amount of energy required for electrolysis which is around 75% of the total energy requirement. In defence of the methanation process, multiple improvements could be made to our model. For example, the use of low-carbon energy for hydrogen production, in particular from surplus renewable energy production. Or the optimisation of the synergy between the electrolysis process and direct air capture, which could lead to a drastic reduction in energy demand [60].

6.2.2 Scenario 2 - Iceland

In the second scenario, a 1 Mt/yr DAC plant corresponding to the one described in the reference case is based in Iceland. An average temperature of 5°C and a relative humidity of 80% is considered. As the environmental conditions are quite similar to those in scenario 1, the demand for water and energy differs little. The main difference is the very low carbon footprint of Iceland electricity with 50 $gCO_{2,eq}$/kWh.

This low-carbon electricity favours the scenarios that use it, in particular adsorption now gets the best result with a capture efficiency reaching 86% when combined to geological storage. Unlike the other two scenarios, the case ABS-seq-Mix obtain better results which suggest that a full electrification, if possible, would obtain better results. However, differences between the two technologies are so small that they can be considered to have equivalent performances. In the same scenario (ADS-Seq-WH), the share of sorbent emissions is greater than from process. It shows that the lower the impact from energy use, the higher the relative impact from the other emitters. Therefore, the choice of sorbent is no longer limited to capture performance, it must also have a low production impact.

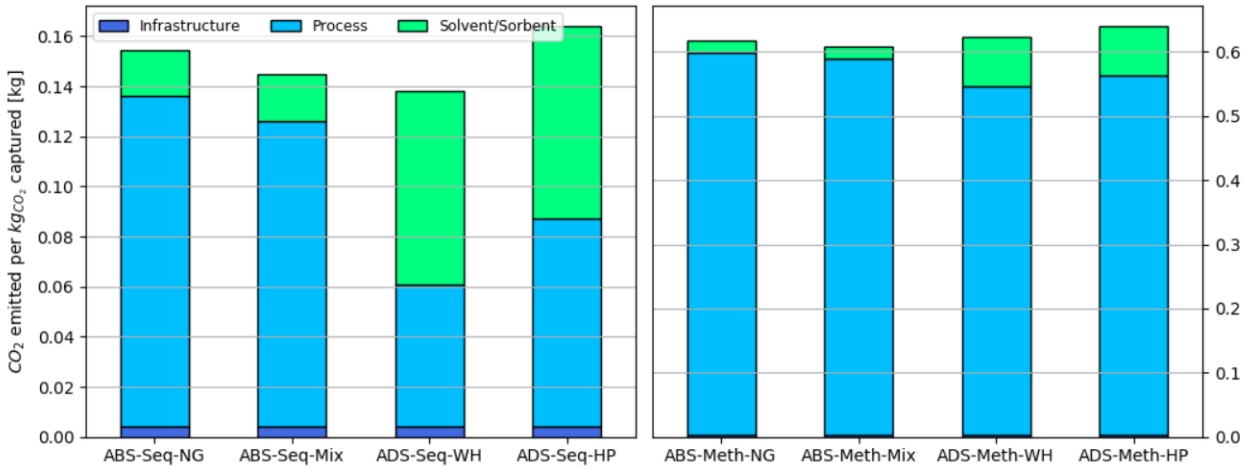


Figure 6.4: Total CO_2 emissions for a DAC plant based in Iceland according to different capture technologies and CO_2 utilisation. The abbreviations used: Abs (Absorption DAC), Ads (Adsorption DAC), seq (with sequestration), meth (with methanation), NG (using only natural gas), Mix (using natural gas and country electricity mix), WH (using waste heat) and HP (using heat pump).

The results are also much better for methane production, with emissions around 0.6 kg_{CO_2} emitted per kg_{CO_2} captured which gives 1.7 kg_{CO_2} emitted per kg_{CH_4} produced. The methane produced in this way emits at least 40% less than its fossil counterpart, and thus becomes a viable alternative. Once again, the few differences between the different scenarios do not favour one over the others. Hence, they should be weighed against their costs and other environmental impacts.

6.2.3 Scenario 3 - United Arab Emirates (UAE)

In the third scenario, a 1 Mt/yr DAC plant corresponding to the one described in the reference case is based in United Arab Emirates. An average temperature of 30°C and a relative humidity of 40% is considered. Here the environmental conditions are very different from the two previous scenarios. In particular, the low RH avoid energy related to water desorption in solid sorbent DAC. On the other hand, the plant is no longer self-sufficient in water, which is problematic in a country where water is a rare commodity. The required water was considered to come from a desalination plant, of which there are many in this country. Among the three scenarios, the carbon footprint of the UAE electricity mix is the highest with 530 $gCO_{2,eq}$/kWh.

In this case, the difference between absorption and adsorption DAC is very pronounced. While ABS obtain capture efficiency around 65%, ADS goes down to 36 or even 4%. These values can be considered as not applicable. Of course, this does not mean that this technology could not be implemented in this country. But, as we have seen in scenario

1, the use of renewable energy, such as solar energy in this case, should be favoured for emission reduction.

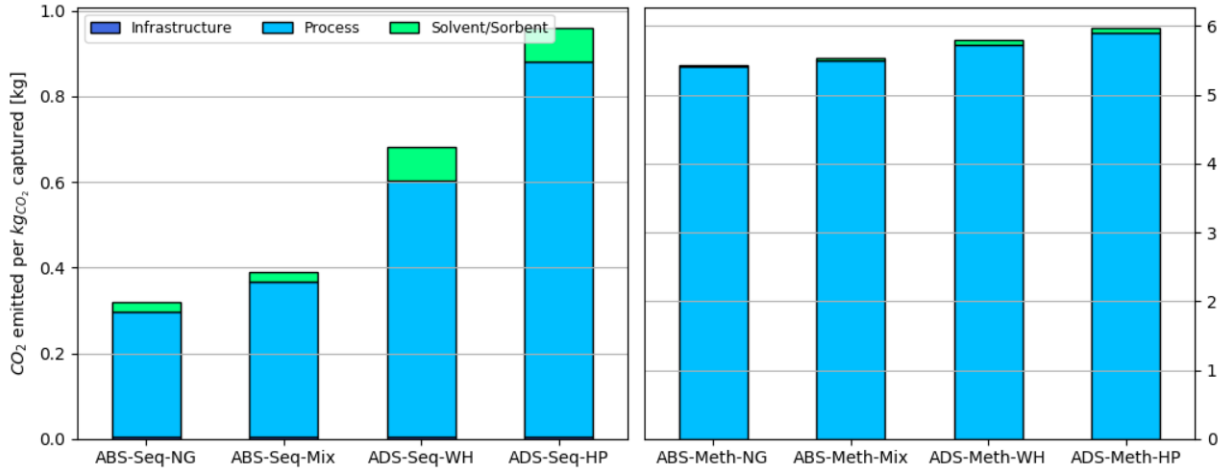


Figure 6.5: Total CO_2 emissions for a DAC plant based in United Arab Emirates according to different capture technologies and CO_2 utilisation. The abbreviations used: Abs (Absorption DAC), Ads (Adsorption DAC), seq (with sequestration), meth (with methanation), NG (using only natural gas), Mix (using natural gas and country electricity mix), WH (using waste heat) and HP (using heat pump).

For methane production, the results are unequivocal. With emissions above 5.4 kg_{CO_2} emitted per kg_{CO_2} captured which gives 15 kg_{CO_2} emitted per kg_{CH_4} produced, the methane thus obtained release far more CO_2 than normal.

6.3 Discussion

After analyzing each scenario individually, this section brings together the different results and compares them. On Figure 6.6, the scenarios combined with CO_2 storage are gathered. Two major behaviours can be observed. First, as already said, the carbon footprint of the electricity plays a predominant role in the capture efficiency. Secondly, the greater the proportion of electricity in the process, the more influential this role is. Across the different scenarios, the variation in efficiency is thus much greater in the case of adsorption. This therefore suggests less flexibility on location than absorption. The location of the latter would more likely be chosen according to the price of natural gas.

In both cases, DAC could obviously free itself from the country's electricity mix and be powered by a renewable source of electricity. This is even more the case for adsorption whose modularity would allow to adapt the size of the DAC to the available source of electricity. This possibility raises a concern about the total energy demand that a large-scale deployment would require. The use of renewable energy by DAC in a country where the

electricity mix could benefit from it to reduce its overall emissions seems inappropriate. In addition to having a relatively high energy demand compared to other mitigation options, e.g., point combustion capture, priority should be given to reducing upstream emissions.

One could also consider using excess renewable energy when production exceeds demand, but this would require further study of the ability of DAC plant to quickly adapt their capture rate.

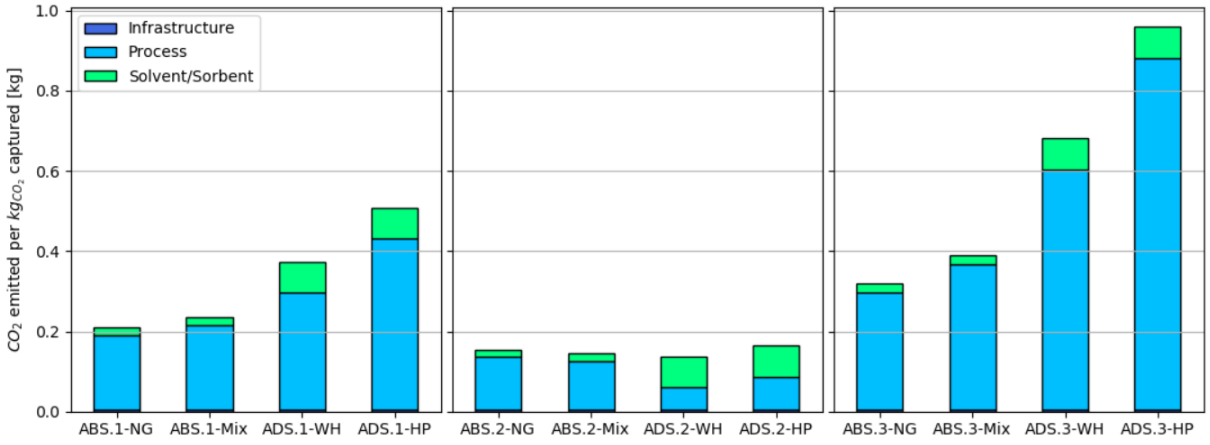


Figure 6.6: Total CO_2 emissions for a DAC plant with CO_2 storage according to different capture technologies and scenarios. The abbreviations used: Abs (Absorption DAC), Ads (Adsorption DAC), NG (using only natural gas), Mix (using natural gas and country electricity mix), WH (using waste heat) and HP (using heat pump).

Production of synthetic methane for the three scenarios is shown in Figure 6.7. The conclusions drawn in the case of CO_2 storage are exacerbated in this case. Indeed, the production of H_2 by electrolysis drastically increases the power consumption (10 kWh/kg_{CO_2} compared to 318-480 kWh/kg_{CO_2} for DAC). It is only when this electricity has a very low carbon footprint, as in Iceland, that the synthetic fuel obtained is less emissive than its fossil counterpart. On the whole, these results correspond rather well to those found by the article [35]. Considering 55.5 MJ/kg_{CH_4}, the three scenarios release 0.13-0.15, 0.3 and 0.27-0.30 kg_{CO_2}/MJ compared to just over 0.1 kg_{CO_2}/MJ for conventional diesel. For comparison, the figure from [35] is shown in Appendix A.3.

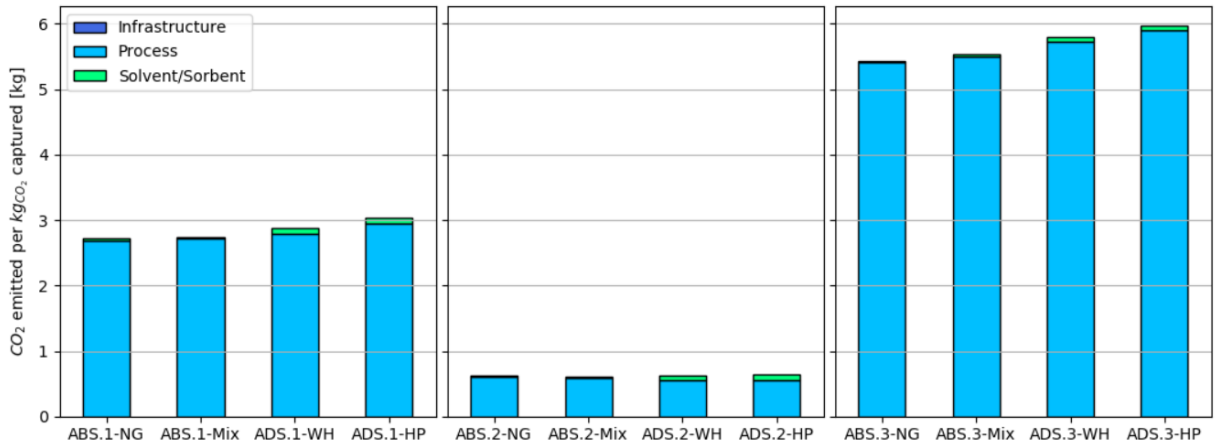


Figure 6.7: Total CO_2 emissions for a DAC plant with CH_4 production according to different capture technologies and scenarios. The abbreviations used: Abs (Absorption DAC), Ads (Adsorption DAC), NG (using only natural gas), Mix (using natural gas and country electricity mix), WH (using waste heat) and HP (using heat pump).

Chapter 7

Conclusion

To limit global warming to 1.5°C, drastic reductions in anthropogenic greenhouse gases emissions are necessary. Among the portfolio of solutions discussed in literature, direct capture of carbon dioxide from the air is a promising option at early stage of development. Direct air capture (DAC) describe the process of extracting carbon dioxide directly from the atmosphere by chemically trapping it. The process shows many advantages such as: low surface requirements, high location flexibility and a potential use of the obtained CO_2 in the industry. On the other hand, it is reproached with excessive costs, high energy consumption and an environmental impact when extended to large scale. This thesis aims to shed light on these different points in order to determine if their balance is in favour of a large-scale deployment.

Direct air capture is an emerging concept with few operational plants in activity. For now, three companies share the majority of them : Climeworks, Carbon Engineering and Global Thermostat. Even if many DAC technologies are proposed in literature, these companies only focus on two: absorption using liquid solvent and adsorption using solid sorbent. Besides the state of their capture medium, they stand out from each other by their very different temperature requirements. The 900°C required for absorption makes the process less flexible with respect to its energy supply, severely limiting it to the use of fossil fuels, the CO_2 emitted of which will be directly incorporated into the final flow. Regarding adsorption, the necessary temperature is around 100 degrees which gives it a much greater field of possibilities in terms of energy supply, particularly in terms of low-carbon energies.

To assess the two technologies in more detail, a life cycle analysis was performed on them using *Simapro* software. To model the direct air capture plants, the database *ecoinvent* was chosen. Through it, the various bricks allowing to model the construction of the factory, the production of the solvent or sorbent as well as the energy necessary for the operation were found. In view of the very diverse information in the literature, the collection of various information in order to obtain a coherent model has required substantial work.

The resulting models were called the reference cases as they point out the results on which the rest of the analysis will be built. Although these only represent the specific cases

resulting from assumptions taken during the models design, it turns out that the obtained results corroborate rather well with the literature. The energy requirement for absorption and adsorption were 7 and 9 MJ per kg_{CO_2} captured, leading respectively to emissions of 0.31 and 0.71 $kg_{CO_{2,eq}}$ per kg_{CO_2} captured. The main emitter being by far the energy consumption of the process, followed by the production of solvent/sorbent.The impact of the plant construction stay negligible.

These results, obtained using GWP100 method, highlight the better performances of the liquid solvent absorption technology. However, this last present fewer improvement options compared to adsorption which could be coupled with low carbon energy. Moreover, the modularity of the adsorption technology allows it to work at a wide range of scale when the absorption method requires large scale plants to be operational. This way, the adsorption plant could benefit of a larger availability of applications. In addition to greenhouse gas emissions, other environmental impacts were evaluated using *ReCipe* model. Once again, absorption shows better results except in water consumption.

As mentioned, the reference cases are only specific models. It is therefore necessary to study the impact from the variation of certain parameters. From one technology to another, these parameters change. But in each case, the main influence appears to come from the energy source carbon footprint and in particular the electricity. In function of the energy supply, the capture efficiency will differently vary with electricity carbon footprint. If the electricity is considered to come from the country electricity mix, the plant location becomes a major parameter in DAC performances.

To extend the scope of the references cases, three main scenarios were created including multiple variations. Among them, the CO_2 could be either geologically stored or used to produce synthetic methane. In the first case, the goal is to directly decrease the atmosphere concentration when the second case aims to provide alternatives to hard-to-decarbonize sectors. Of course, other options could be applied to DAC and would be interesting to study in a future work. These scenarios take place in different countries characterised by their own environmental condition and electricity mix. As pointed out during the sensitivity analysis, the carbon footprint of the electricity is decisive in the performance results.

Following this statement, the results of countries such as Iceland (50 $g_{CO_{2,eq}}$/kWh) are far better than Belgium (258 $g_{CO_{2,eq}}$/kWh) or United Arab Emirates (530 $g_{CO_{2,eq}}$/kWh). In the light of its smaller electricity demand, the absorption technology is less sensitive to this parameter, leading to far better results in case of highly carbonated electricity. In the case of Iceland, the performances for both technology are similar, with a capture efficiency of 85% for geological sequestration. Regarding methanation, the production of a synthetic methane with a lower carbon footprint than its fossil equivalent require highly favourable conditions. Only the Iceland scenario was able to provide low carbon CH_4 with 40% less emissions than its fossil counterpart. An alternative could be to directly use electricity from low carbon sources such as solar or wind energy, but it would be unwise to devote this

energy to direct CO_2 capture where it could prevent its emission by reducing the country's electricity carbon footprint.

Through this study, we conclude that direct air capture is theoretically feasible in favourable conditions, including low carbon footprint energy. In addition, considering its early stage of development, these limitations are expected to become less constraining. However, direct air capture should not be taken as a way to avoid major decrease in greenhouse gases emissions. If DAC allows to retrieve previously emitted emissions, priority should be given to the avoidance of them. Therefore, the scenarios presented in literature where direct air capture compensate the entire anthropogenic emissions seem to be a distraction to avoid sobriety as the resources associated would be considerable. Nevertheless, the use of direct air capture could remain interesting on a relatively small scale.

Appendix A

complementary information

A.1 CO_2 geological storage

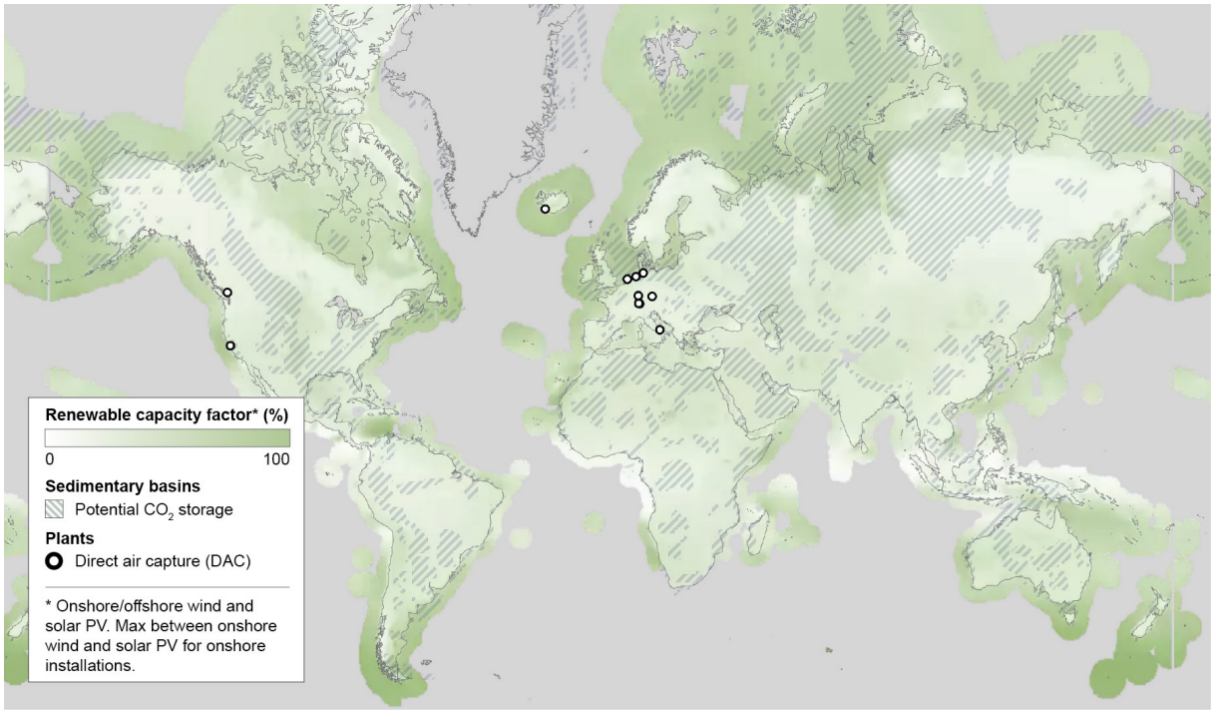


Figure A.1: CO_2 geological storage, taken from IEA special report on DAC [6].

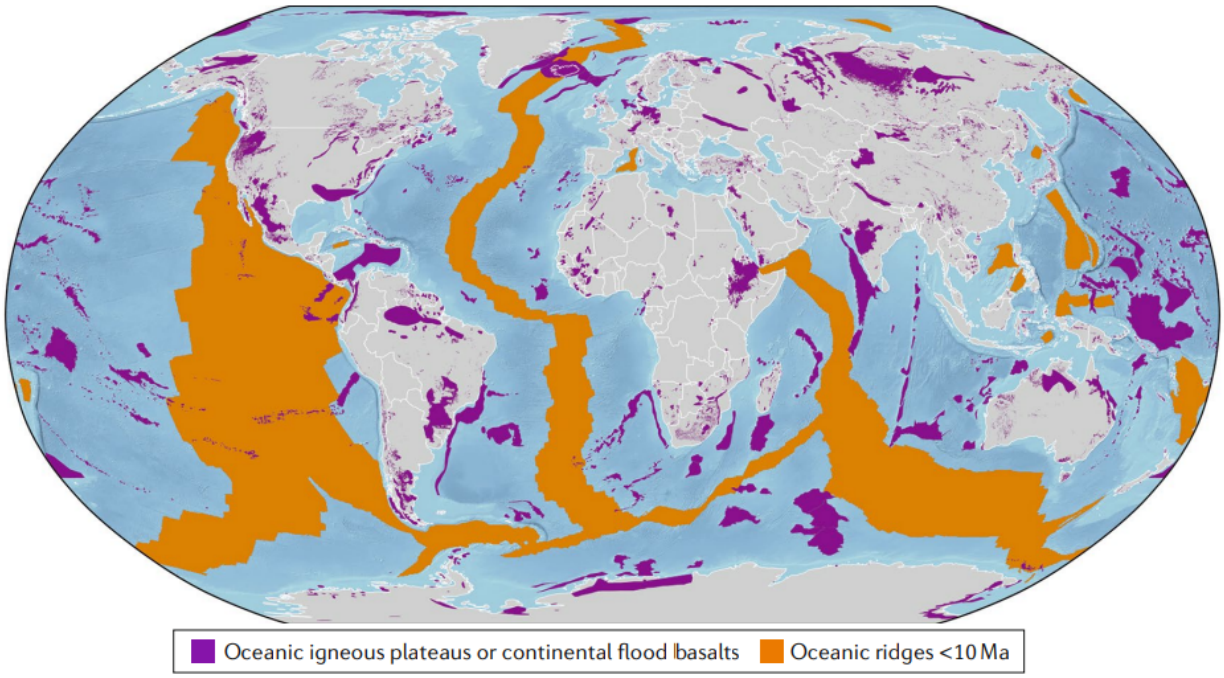


Figure A.2: CO_2 geological storage, taken from [24].

A.2 CDR technologies

Table A.1: Summary of CDR methods adapted from Table 12.6 of IPCC report [5].

CDR option	**Status (TRL)**	**Cost [USD/ t_{CO_2}]**	**Mitigation potential [Gt_{CO_2}/yr]**	**Risk**	**Co-benefits**
DAC with CCS	6	100-300	5-40	Increased energy and water use.	Water produced for ADS.
Enhanced weathering	3-4	50-200	2-4	Mining and air quality impacts	Enhanced plant growth and soil carbon, reduced pH.
Ocean alkalinity enhancement	1-2	40-260	1-100	Increase seawater PH, release of toxic compounds and mining impact.	Limiting ocean acidification.
Ocean fertilisation	1-2	50-500	1-3	Potential for decadal-to-millennial-scale return to the atmosphere of nearly all the extra carbon.	Increased productivity and fisheries, reduced upper ocean acidification.
BECCS	5-6	15-400	0.5-11	Land competition, loss in biodiversity.	Fuel security, reduction of air pollutants, additional income.

A.3 Comparative results for synthetic fuel production

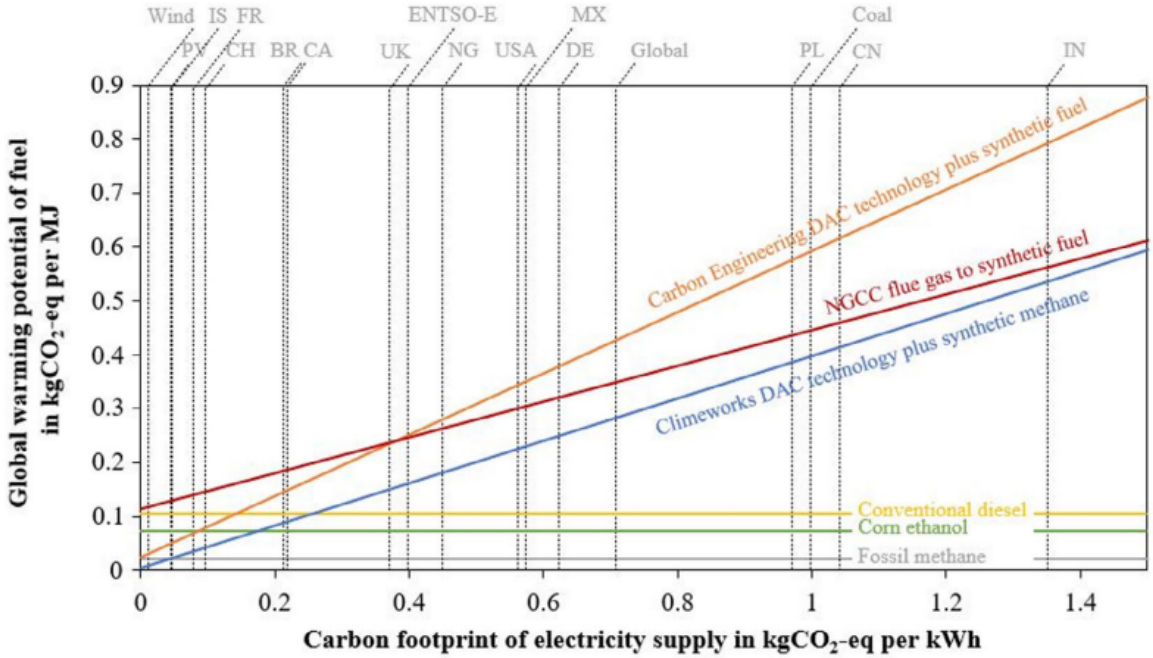


Figure A.3: Global warming potential of diverse transportation fuel production pathways according to the carbon footprint of the electricity supply. Taken from article [35].

A.4 Pilot and operational DAC plants

Table A.2: Current state of pilot and operational DAC plants. This table is adapted from Table 1 of [7].

Location	**Status**	**Capacity**	**Technology**	**Utilisation**	**Year**[1]
Climeworks					
Europe (operating)	Pilot/Commercial	2000 (14 plants)	TVSA	Geothermal/Waste	2015
Switzerland (operating)	Pilot	900	TVSA	Waste	2017
Iceland (operating)	Pilot	4000	TVSA	Geothermal	2021
Carbon Engineering					
Canada (operating)	Pilot	350	Liquid solvent	Natural gas	2015
Canada (construction)	Innovation	1500	Liquid solvent	Natural gas	2022
Texas (construction)	Commercial	1e6	Liquid solvent	Natural Gas	2025
Global Thermostat					
USA (non-operating)	Pilot	10000	TVSA	Waste	2013
USA (non-operating)	Pilot	4000	TVSA	Waste	2019
USA (construction)	Commercial	4000 (2 plants)	TVSA	Natural gas	2021
Chile (planned)	Pilot	250 kg/h	TVSA	Wind	2022
Mechanical tree					
USA (construction)	Pilot	30/tree	Passive capture	-	2023
Not known (planned)	Commercial	4e6	Passive capture	-	2030
Infinitree					
USA (operating)	Pilot	100	Moisture swing	-	2014

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