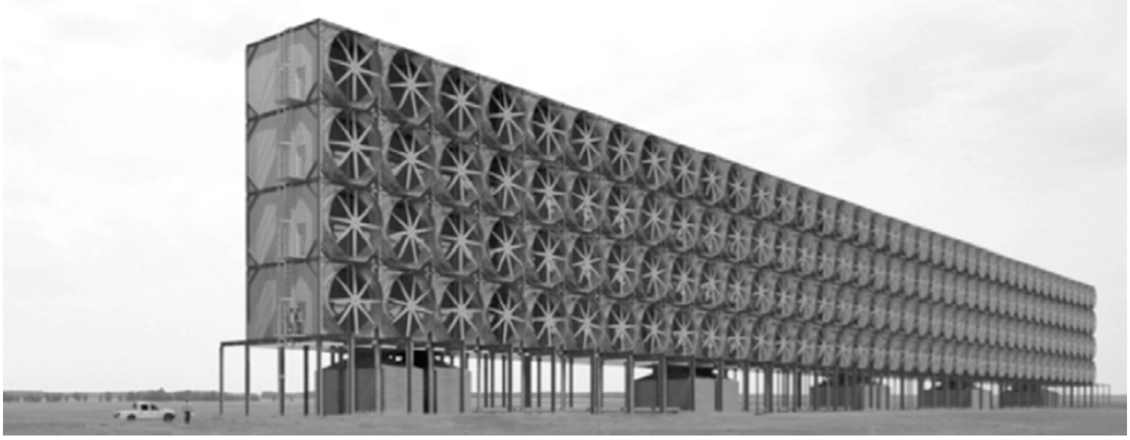

Will solvents present challenges for carbon capture?

Assessing the cost and energy implication of solvent production for carbon capture with an energy system model

Master's thesis in Sustainable energy systems

VINCENT CHANAL AND SAMUEL HUMPAGE

DEPARTMENT OF PHYSICAL RESOURCE THEORY
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2024
www.chalmers.se

MASTER'S THESIS 2024

Will solvents present challenges for carbon capture?

Assessing the cost and energy implication of solvent production for carbon capture with an energy system model

Vincent Chanal and Samuel Humpage

Department of Space, Earth and Environment
Division of Physical Resource Theory
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2024

Will solvents present challenges for carbon capture?
Assessing the cost and energy implication of solvent production for carbon capture with an energy system model
Vincent Chanal and Samuel Humpage

Supervisor: Markus Millinger, Department of Space, Earth, Environment
Examiner: Fredrik Hedenus, Department of Space, Earth, Environment

Master's Thesis 2024
Department of Space, Earth and Environment
Division of Physical Resource Theory
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

Cover: Conceptual drawing of the air contactor for a liquid solvent direct air capture system, Holmes and Keith, 2012 [1].

Typeset in LaTeX
Printed by Chalmers Reproservice
Gothenburg, Sweden 2024

Abstract

Carbon capture technologies have recently received particular interest as a major method for decreasing greenhouse gas emissions, since they are notably part of all modelled IPCC scenarios for reaching climate targets. Carbon dioxide can be captured from a flue gas, with one of the most mature technologies being post-combustion capture, or directly from the atmosphere. Both of these technologies rely on the use of a chemical solvent or sorbent in order to capture the CO_2, with direct air capture being able to use either a solid or a liquid one. Lately, concerns have surfaced about the implications of producing the required amount for large scale deployment. Here, we show that the production of chemical sorbents could have implications in system cost, energy use and material use depending on the amount of which they are consumed in the process. Among the three chemical sorbents investigated, namely monoethanolamine for post-combustion carbon capture, potassium hydroxide for liquid direct air capture and polyethylenimine-silica for solid sorbent direct air capture, we found that the production of the compound for solid sorbent direct air capture would represent the toughest challenges for the system. Although very high uncertainties remain, an optimistic consumption resulted in minimal impacts while a pessimistic sorbent consumption represented a total system cost increase of at most + 6.7% if solid sorbent is chosen for the direct air capture technology, and more limited impacts for the other technologies. Scale-ups in material production capacities may also present challenges. Our results show that implications of sorbent consumption for carbon capture technologies should be considered more thoroughly when modelling energy systems or in IAMs, especially for the case of direct air capture using a solid sorbent.

Keywords: Solvents, Carbon capture, Direct air capture, post-combustion capture, energy system modelling.

Acknowledgements

We would like to thank everyone involved in this project. A special thanks goes to our supervisor Markus Millinger for his guidance, many good discussions and for always being there when we needed advice. We also want to thank our examiner Fredrik Hedenus for thought provoking discussions which helped improve our work. Thanks also to Sina Hoseinpoori, PhD student in the Energy Technology Division at Chalmers, for his clarifications on direct air capture and hints on very relevant literature regarding our topic. We thank Chalmers and more particularly the Physical Resource Theory Division for welcoming us during the semester and enabling us to carry out this work in good conditions. Finally, a big thanks goes to our friends and family who supported us throughout our education and especially during this semester that concludes our master's degree.

Samuel Humpage and Vincent Chanal, Gothenburg, August 2024

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

BECCS	Bioenergy carbon capture and storage
CCS	Carbon capture and storage
CCU	Carbon capture and utilisation
CDR	Carbon dioxide removal
CO_2	Carbon dioxide
DACCS	Direct air capture and storage
EO	Ethylene oxide
HVC	High-value chemical
MEA	Monoethanolamine
PEI	Polyethylenimine
AS sorbent	Amine-silica sorbent

Contents

List of Figures

List of Tables

1

Introduction

Potentially disastrous ramifications caused by climate change such as higher temperature, decrease of biodiversity and ocean acidification are among the issues the world will face if greenhouse gas (GHG) emissions are not curbed [8]. More and more countries, rising to over 140 currently, have therefore set out plans for achieving net zero emissions by the year 2050 [9]. In order to be successful in this endeavour, the first priority is set on abating emissions as much as possible. Electrifying technologies and producing electricity from green and renewable sources are seen as cost-effective options towards this aim [2,10]. Capturing carbon from point sources when it is possible, from fossil fuel power plants, e.g., is also an option that has been increasingly implemented to mitigate emissions. The captured carbon can later be sent to a storage site (CCS) or utilised as a feedstock for another process (CCU) [11].

Nevertheless, certain industries may experience difficulties in this transition, such as for example cement, steel, transports or agriculture [12]. Those "hard-to-abate" emissions are estimated to be between 1,5 and 3,1 $GtCO_{2,eq}/year$ globally by 2100 [3]. In order to compensate for these remaining emissions, the use of so-called carbon dioxide removal technologies (CDR) will be required to limit global warming to 2 ^{o}C as per IPCC scenarios [10]. Besides, should the emission reductions not be achieved in time, these technologies could provide net negative emissions with the aim of reversing the potential overshoot in temperature increase [2, 13]. The CDR technologies that are often discussed in the energy system are Bioenergy carbon capture and storage (BECCS) and direct air carbon capture and storage (DACCS) [2, 14]. In simplified terms, BECCS involves trees and plants absorbing carbon from the atmosphere and then capturing their emissions when the tree is burnt or gasified to produce for example electricity or fuels. BECCS overall achieves negative emissions, taking CO_2 from the atmosphere and sequestering it underground [15]. In a similar fashion, DACCS instead removes carbon straight from the atmosphere [2].

Most scenarios of future trends made by environment experts include these negative emissions technologies in order to reach the expected targets [2,10,16]. One possible scenario is depicted in Figure 1.1 which shows how the carbon removal technologies are used to reach emission targets.

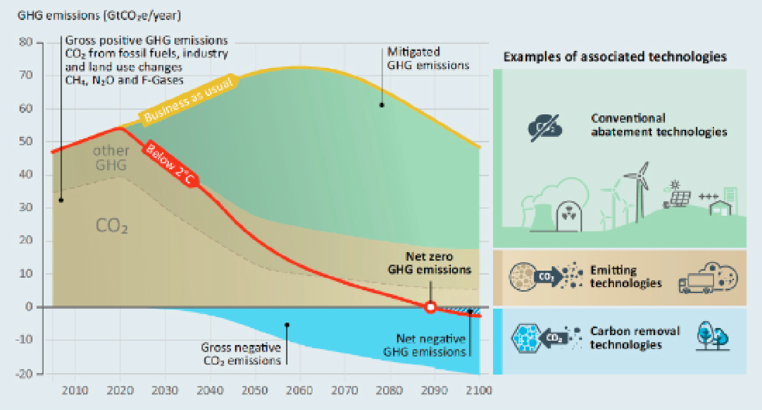

Figure 1.1: The role of carbon dioxide removal in climate change mitigation. Exemplary scenario consistent with an at least 66 percent chance of keeping warming below 2°C relative to pre-industrial levels. Taken from [2].

An aspect regarding carbon capture worth noting is the potential use of solvents or sorbents. These compounds are used in either solid or liquid form to capture the carbon through chemical or physical interactions. DACCS technologies that are currently at the forefront require the use of a solvent or sorbent to capture carbon from the air [17]. On the other hand, carbon capture on point sources, i.e., fossil fuel plants or BECCS, has several choices of mature technological options available. One of them is post-combustion capture which uses chemical solvents [18]. Solvents and sorbents are crucial in the continuous development of CC technologies. During the capture process, those chemicals undergo degradation and need to be replaced frequently. For some of them, this rate of degradation is uncertain and may reach important quantities [19].

The production and usage of solvents and sorbents and their potential consequences have so far not been considered into detail in most major integrated assessment models or energy system models, such as for example PyPSA-Eur, Euro-calliope or LUT [11,20,21]. Yet, certain concerns have recently surfaced regarding the material consumption required to produce the necessary solvents, should there be a heavy reliance on these types of technologies. In a report by Realmonte et al., the potential problems associated with sorbent production for DACCS were discussed [19]. A matters arising by Chatterjee et. al followed this report and considered material and energy requirements required to be unrealistic [22]. They assert that, with their assumptions, the amount of material required for producing the solvents, for any type of DAC technology, would reach around 100 times the current global production based on current global emissions. The energy required for the solvent production and the regeneration necessary for DAC would also be very large and may attain the level of today's global energy supply of a few tens of PWh per year. The question then arises of what would be the impacts of such a CC scale up on the energy system.

The aim of this study is therefore to answer the following question: "What are the implications in terms of cost, energy consumption and material requirements on the energy system associated with the production of solvents?"

2

Theory

2.1 Technology Readiness Level (TRL)

This work presents different technologies for achieving carbon capture. Some are tried-and-tested with real-world applications and some others are novel, still at a laboratory stage. A good indicator for this development level is the Technology Readiness Level indicator (TRL). It has 9 degrees among which the four last are the following [23]:

- TRL 9: “Actual system is proven in an operational environment”
- TRL 8: “System complete and qualified”
- TRL 7: “System prototype demonstration in an operational environment”
- TRL 6: “Technology demonstrated in a relevant environment”

2.2 CO_2 capture pathways

Two of the current most promising technologies when it comes to achieving net negative emissions are direct air carbon capture and storage (DACCS) and bioenergy carbon capture and storage (BECCS). Both of these technological ideas often use solvents as a way of capturing the carbon dioxide from the air or flue gas. Alternatively, solvents can also be used for carbon capture related to waste and fossil use in power plants to reduce emissions. However, this only leads to a reduction in emissions instead of negative emissions, as in the case of DACCS and BECCS.

2.2.1 Point source carbon capture

Point source carbon capture consists in preventing CO_2 from being emitted after a combustion. There exists different ways of doing so, the most common and simplest one being via post-combustion capture. This involves filtering the flue gas that is generated after the fuel combustion. Pre-combustion is another pathway, consisting in preparing the fuel to remove all its carbon before it is burnt. Both technologies have a TRL of 9 [24]. Finally, some innovative pathways currently under research and development are promised as alternatives to conventional technologies. Yet, they are not considered in the present study and will therefore be only introduced briefly.

2.2.1.1 Post-combustion capture

Post-combustion capture takes place after the combustion of a carbon-based fuel (i.e. fossil fuel, biomass or waste, but not hydrogen for example). It is applied to the exhaust gas which contains usually around 10% of CO_2, as well as other impurities like Nitrous oxides (NO_x), Sulphur oxides (SO_x) or fly ashes. These contaminants must be dealt with carefully due to their high toxicity and because they can further degrade the solvents used for carbon capture. For this, a pre-treatment is generally applied beforehand in order to remove the ashes and desulfurise the flue gas. CC is then applied to the flue gas, where a capture of around 90% is generally achieved. Once the solvent has absorbed the carbon, it is regenerated in a so called stripper tower by supplying heat that unbinds the chemicals. The CO_2 thus captured is then compressed and sent to be either stored or utilised [24]. Figure 2.1 illustrates the principle of post-combustion capture.

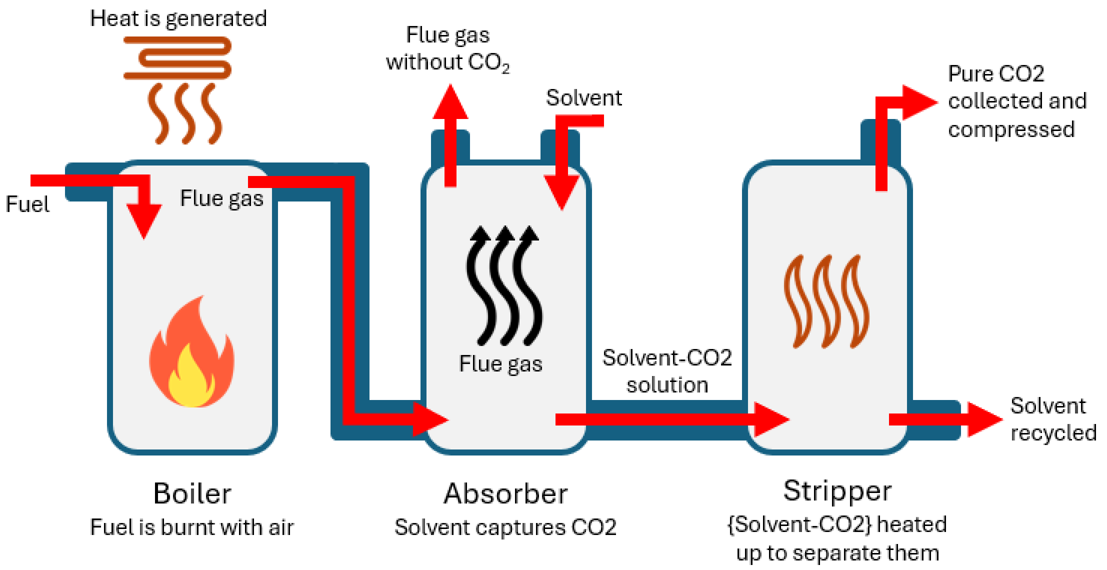

Figure 2.1: Schematic drawing of post-combustion carbon capture with the use of chemical solvents

This capturing method has the main advantage of being applicable to any kind of plant since it takes place at the exhaust, whether it is a power or an industrial plant with any kind of fuel. Another advantage is the possibility to retrofit existing power plants.

Currently, the most common way of capturing CO2 post-combustion is by chemical absorption with the use of an amine-based compound. Several companies have created their proprietary solvents based on the use of amine-based solvents [25]. Many of the current large carbon capture plants such as DRAX, Boundary dam and Petro Nova licence the use of these proprietary solvents [26, 27]. The use of other options aside from amine-based solvents include for example potassium carbonate which is planned to be used by Stockholm Exergi in their BECCS plant [28].

Monoethanolamine, or MEA ($NH_2 - C_2H_5O$), is currently one of the most mature and has been considered the benchmark for solvents in post-combustion carbon capture, with a technological readiness level of 9. This common use is due to its early popularity among industrial companies for the development of the first plants, which then led to having a lot of experimental data available for research to work with. Its main reaction with CO_2 is: $MEA + H_2O + CO_2 \rightleftharpoons MEA^+ + H_2CO_3^-$ [24]. For this reason, this study will exclusively focus on it for post-combustion.

Solvent consumption starts with the initial solvent requirement during the plant start-up. Besides, although most of the solvent is generally recovered after each cycle of absorption and desorbtion, some inevitable losses happen. MEA is degraded mainly by oxidation with oxygen or acid gases present in the flue gas, which is catalysed by the heat of the regeneration. This affects the capture capacity of the solvent as well as creating corrosion issues. The prior removal of NO_x and SO_x from the flue gas can however limit this degradation [24,29,30]. These losses need either way to be compensated by continuously adding a makeup flow. Both initial bulk stock of solvent and replenishment for losses are determined from a literature review. The conclusion of this work is presented in the Data collection section of the Methods 3.1.

2.2.1.2 Pre-combustion

Another CC pathway is pre-combustion capture. It mainly suited for gas power plants since it is either based on steam methane reforming, gasification of solid fuels (e.g., an IGCC process), or biogas upgrading. The two former consist in converting the fuel (methane or a mix of solid fuel and steam) into H_2 and CO_2. This mixture is called syngas and passes then through subsequent processes that separate the CO_2 from the H_2. The actual capture takes place at this stage. H_2 is later used as a carbon-free fuel for gas power generation or any other industrial process. This way, the combustion is done without any emission. CO_2 is treated the same way as in post-combustion capture. Figure 2.2 depicts this principle.

The latter method, biogas upgrading, is a preliminary process of any usage of the fuel which aims at purifying the biogas produced from the digestion of organic matter. This biogas is composed in part of CH_4, and in part of CO_2, as well as some other impurities. Pre-combustion carbon capture can be applied to it to isolate its CO_2 content, while removing some other impurities. The bio-methane thus produced can then be used for a variety of purposes.

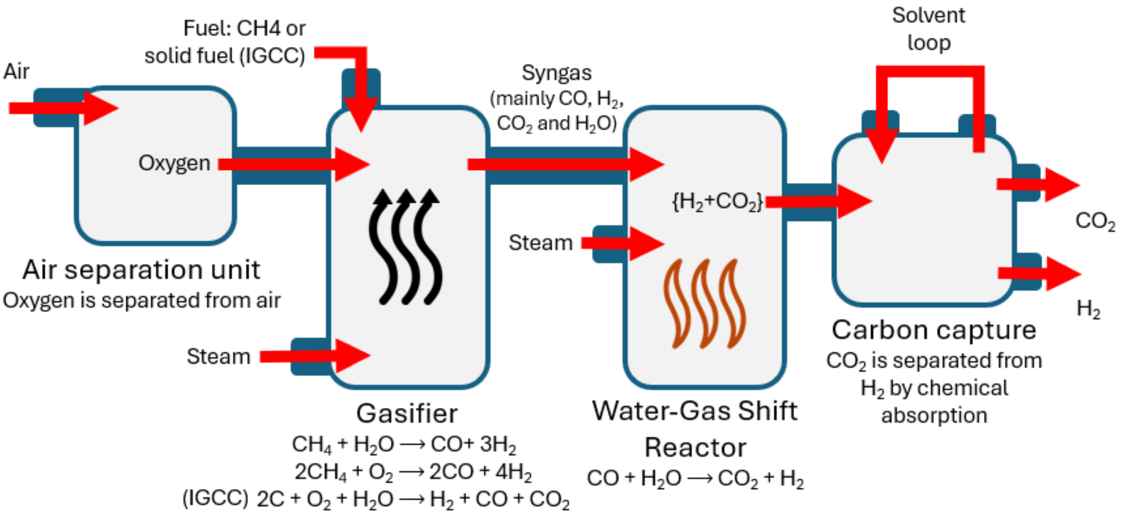

Figure 2.2: Schematic drawing of steam methane reforming and gasification of solid fuels as methods for pre-combustion carbon capture with the use of chemical solvents

The most common way of capturing CO_2 in pre-combustion is via absorption with the use of a solvent, in most cases a physical. Physical solvents mainly at stake are Selexol (dimethyl ether polyethylene glycol) and Rectisol (chilled methanol) [31,32]. Amine scrubbing with the use of for example MEA is also a possible, even though it seems to be less common [24]. A review of LCA studies made by (Duval-Dachary et al., 2023) [33] reported that very little data exists for solvent makeup for pre-combustion. The only article found by the reviewers that talks about it asserts that losses are negligible for Selexol. For all other types of solvents, including Rectisol, no quantitative data was given by any of the reviewed articles. The only solvent consumption is therefore the bulk stock of the plant, the amount that is constantly cycled. However, no data in the literature was found about the size of this bulk stock. It was consequently decided to not include solvents for pre-combustion in the present analysis.

2.2.1.3 Oxy-fuel combustion

Oxy-fuel combustion consists of using a pure stream of oxygen instead of air for combustion. This leads to a combustion which mainly produces CO_2 and water. This technology is one of the most mature alternative to the conventional post-combustion carbon capture. Despite the additional costs from the air separation unit investment and operation, oxy-fuel brings several benefits. For the combustion, it allows a higher flame temperature and the mitigation of NO_X formation (due to the absence of nitrogen). Besides, it enables an easier capture of the emitted carbon due to the flue gas containing only two compounds. The CO_2 in the flue gas is general captured by physical adsorption with the use of sorbents, or by cooling down the flue gas until the water condensates, also referred to as cryogenic separation [24].

Despite all its promising benefits, this technology is only at a demonstration phase, with a TRL of 7 and a few pilot plants operating [24]. This leads to very little data available about it and for this reason, it will not be included in this work.

2.2.1.4 Innovative and alternative pathways for CCS

Further technologies that show potential for use as carbon capture in the future exist but are currently under development [24]. Due to them not being commercially viable options as of now, they will not be included in this study but some options and their progression are shown below.

Chemical looping, with a TRL of 6, is a sort of oxy-fuel combustion, where oxygen is provided by an "oxygen carrier" instead of an air-separating unit. This carrier is a chemical that oxidises in contact with air, and de-oxidises in the boiler, releasing its oxygen, and that in a closed-loop. Recently, membranes have gained in interest as a novel manner of capturing CO_2 that does not use any solvent. Despite its TRL of 3 to 7, they could be suited for either post- or pre-combustion CC. The Allam cycle has also recently come up as a successful CC pathway, consisting in a sort of oxy-fuel combustion. It has a TRL of 5 to 7.

2.2.2 Direct air capture

Direct air capture is based on the idea of capturing carbon dioxide straight from the air. Fundamentally, this is done by making air pass through a contactor, where the carbon dioxide in the air will subsequently be adsorbed/absorbed by a solvent or a sorbent depending on type of DAC used. The material will then undergo a regeneration process to remove the attached carbon dioxide before being used to capture more carbon dioxide from the air.

Currently, there exists four main proposed ideas for ways of using direct air capture as presented in Figure 2.3, based on (Young et al., 2023) [3]. Out of the four proposed technologies, KOH scrubbing and Ca looping, also know as high temperature aqueous solution [34], and solid sorbents, working with the temperature-vacuum swing adsorption principle, are currently the most developed ones. Both have either operating plants or ones under construction [35]. In this study, they will be referred to as L-DAC and S-DAC respectively. The remaining two technologies are still in an early development stage and will therefore not be considered in this work.

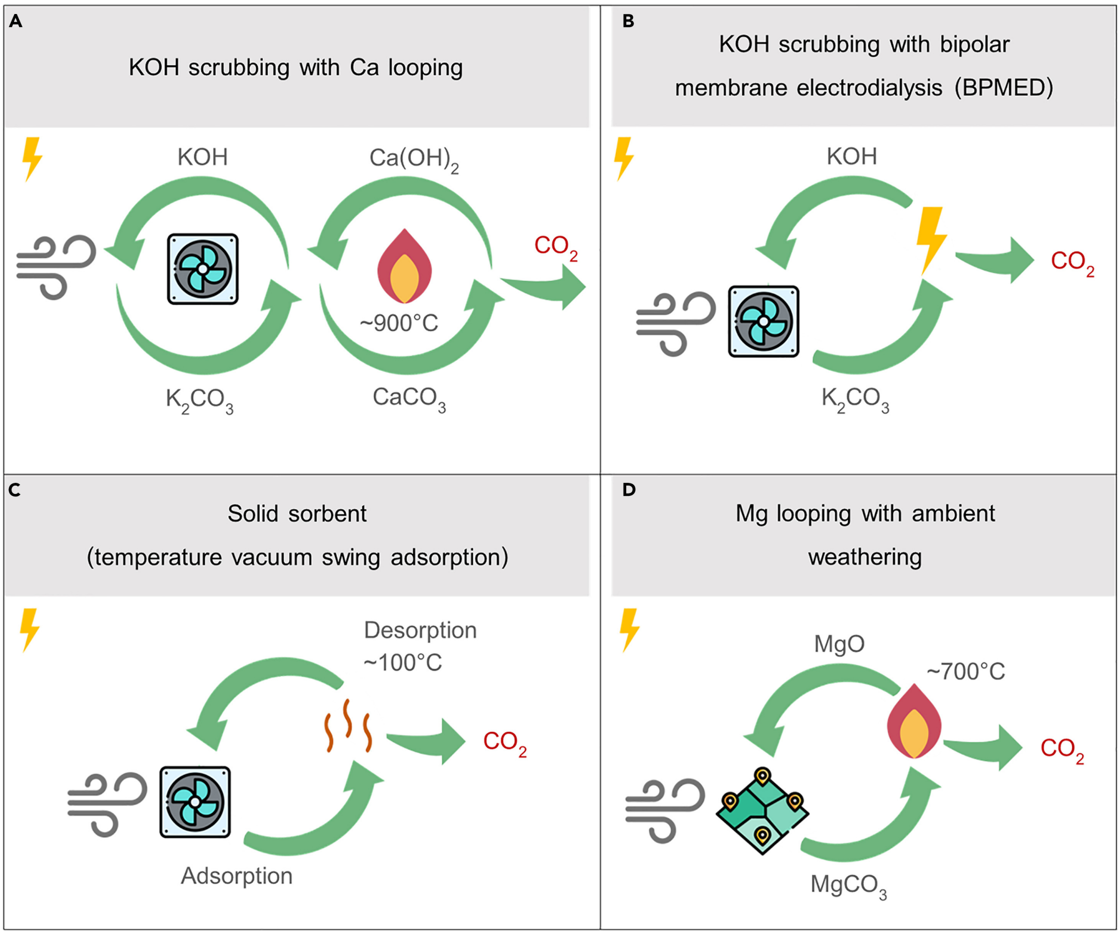

Figure 2.3: Four technologies for DAC. Figure made by Young et. al under CC BY [3].

Direct air capture plants that are currently in operation are few. One of the more renowned direct air capture plants that is in operation is a Solid sorbent plant called Orca, located in Iceland. The plant, developed by Climeworks, has a capture capacity of 4 kt of carbon dioxide per year [36]. Climeworks also has another plant that opened for operation in May 2024 with a expected final carbon capture capacity of 36 kt per year [37]. For liquid direct air capture, Carbon engineering is the main company involved and is currently constructing a plant with an expected capacity of 500 kt of carbon dioxide in the USA [38].

L-DAC

A more detailed explanation of operating process of L-DAC plant can be observed in Figure 2.4. The air is captured in the air contactor by KOH, the solvent Carbon Engineering uses. The CO_2-solvent mixture moves to the pellet reactor where it reacts with calcium hydroxide ($Ca(OH)_2$). It then contains the captured CO_2 in the form of calcium carbonate ($CaCO_3$) after the reaction. The regenerated KOH is returned to the air contactor and the calcium carbonate moves to the calciner to be heated and remove a pure CO_2 stream.

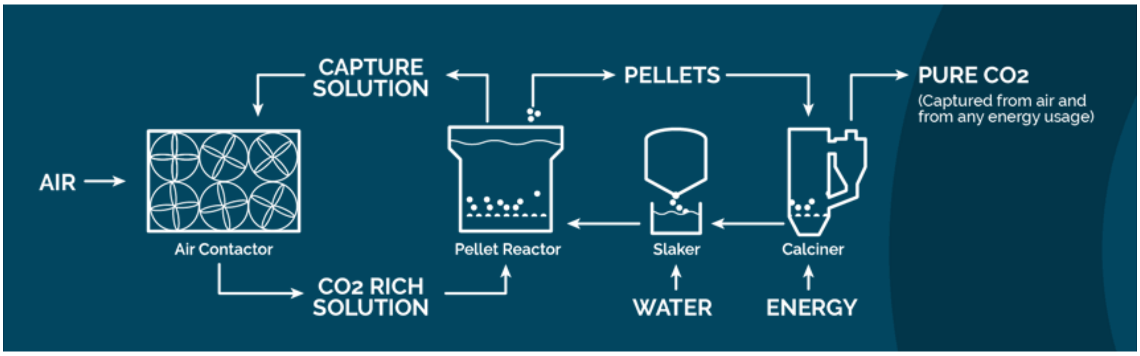

Figure 2.4: Representation of L-DAC operation based on schematic made by Carbon Engineering [4]

The process used is for it to undergo a causticizing reaction which is also used in the pulp and paper industry [39]. This is shown by the chemical reactions occurring in each stage in Figure 2.5 which involves two different loops in order to capture carbon dioxide, using potassium hydroxide to initially capture the carbon dioxide and the calcium carbonate to then in the end creating a pure carbon dioxide outlet stream. Removing the carbon dioxide from the calcium carbonate requires a high temperature of roughly 900 ^{o}C which is one of the main drawbacks of the technology. However, the solvents used are considered simple to produce [34]. Another potential disadvantage for L-DAC is its high water usage required for operation, due to evaporation from the contact of the liquid with the air. Water losses are estimated to be of 5 million m^3 per year and 0.4 km^2 of land is deemed to be required for a 1 Mt/y carbon capture plant [40].

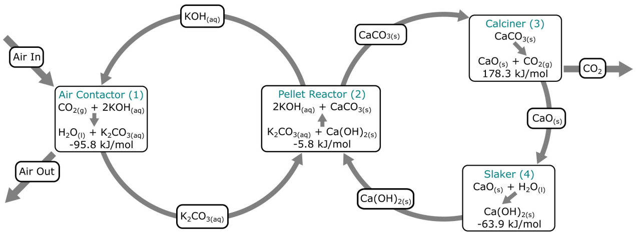

Figure 2.5: Potassium hydroxide and calcium carbonate looping for L-DAC. Figure produced by Keith et al., 2018 under CC BY-NC-ND [1].

Solvents that have been considered for use in L-DAC are sodium hydroxide (NaOH) and potassium hydroxide (KOH). The solvent of main interest is KOH to capture and calcium carbonate ($CaCO_3$) to desorb, as described by 1 $Mt_{CO_2}/year$ capture plant proposed by Keith et al. [1]. Reasoning for using hydroxides instead of an amine such as MEA in DAC is due to it being deemed inefficient at capturing carbon at 400 parts per million (ppm) [41].

Consumption of solvent in an L-DAC system mainly comes from the losses that may happen in the absorber through aerosol formation and spray drift [42]. Those losses are hard to estimate a priori, though, and are likely to change quickly due to research and development. They are therefore usually subject to assumptions [34]. Besides, consumption of solvent should also account for the initial stock that is constantly cycled. A literature review in done in section 3.1 about these aspects.

It is worth noting that Sodium hydroxide (NaOH) can also be used as a carbon capturer for high temperature direct air capture. KOH and NaOH present similar properties and are produced through the same process, Chlor-Alkali (further details provided in Section 2.4). They basically just use a different feedstock for their production, respectively Potassium chloride (KCl) and Sodium chloride (NaCl). While NaOH enables for capture of more CO2 per mass of solvent and is cheaper, KOH presents good kinetics when reacting with CO2 which could prove beneficial for reducing the energy requirement of the process [34]. Overall, both seem equally good candidates for the role of solvent in L-DAC. In this work, KOH was chosen for this role, as this is the same choice that Keith et al. made for the first large scale DAC plant project, construction of which has recently begun in the US [1]. However, most results could also be applied to using NaOH instead.

S-DAC

S-DAC captures carbon with the use of temperature-swing adsorption and a chemical adsorbent. Figure 2.6 presents its working principle. The system works in cycles of accumulation and release of CO_2, while the sorbent stays steady on the filters. The desorption is performed by heating up the sorbent to a temperature of around 100°C. This is much lower than what is required for liquid solvents, and this one of their main advantages [3, 5].

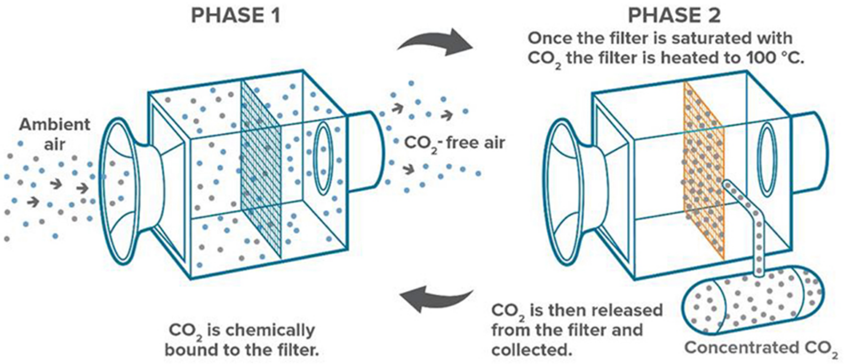

Figure 2.6: Schematic illustration of Climeworks solid sorbent direct air capture process. Figure made by Beuttler et. al under CC BY [5].

An additional benefit is that the sorbents also absorb water from the air [43]. During the regeneration step of the process, an S-DAC plant therefore produces water as a byproduct of the process. On the downsides are that S-DAC will require a larger area of land than L-DAC of around 0.9 km^2 per Mt of CO_2 captured per year [40].

Research into choice of solid sorbent for direct air capture is broad. In a review by Wang et al. [44], companies research a wide range of different sorbents such as chemicals with for example solid-alkali carbonates, amine-functionalized solid sorbents, or physical adsorbents, such as metal-organic frameworks, zeolites or activated carbon. Physical adsorbents are yet deemed less effective for the purpose of capturing CO2 in such a low concentration. On the other hand, amine-based sorbent seem to be promising candidates [45].

One amine-based sorbent that certain literature has considered due to its commercial availability is Lewatit VP OC 1065 [3]. However, with the high complexity of resources needed for production, low data for technical processes and without a clear choice for which sorbent is most suited for use, this study will only focus on one sorbent. Due to available data, it was chosen to select an amine-based solid sorbent using polyethyleneimine (PEI) as the active phase and silica gel as the support, referred to as the amine-silica (AS) sorbent.

In operation, the sorbent is progressively degraded by its exposure to ambient conditions such as sunlight, temperature, humidity or particulate matter, as well as the successions of loadings and unloadings that it undergoes. All sorbents degrade differently and this has still not been fully understood so far [46]. Because of this loss of quality, the sorbent loses in performance and thus needs to be replaced regularly. This replacement frequency is based mostly on economic criteria, that is, the sorbent is renewed when it starts to capture too little compared to the expenses required to run the facility. This typically happens when the sorbent reaches 50 to 80% of its initial capacity. Then, the entire stock of sorbent is removed and replaced by a new one [46, 47].

2.3 CO_2 storage and utilisation

Carbon capture and sequestration is based on the assumption that carbon dioxide can be stored somewhere economically viable and without the potential of leakages occurring. It can be stored naturally in trees, through organic matter or water of the oceans by dissolving into it. The gas may also be stored technologically by compressing and pumping it into deep layers of rock. This technique has been proven to present little leakage over time. The geological sites that are mainly considered for use of carbon storage are depleted oil and gas fields as well as saline aquifers [48]. In order to reach net zero targets by 2050, the European Commission estimates an amount of between 201 and 606 Mt CO_2 is required to be stored per year. They also assert that an estimated 300 Gt of storage reservoirs are available in Europe [49].

Alternatively, green CO_2 can also be utilised as a valuable resource (CCU) in order to increase carbon efficiencies as much as possible. It can be used as a feedstock to produce, e.g., electrofuels through the Fischer-Trospch process, or other chemicals [50].

2.4 Solvents and their production

The research of optimal solvents that have all the necessary properties of long lifetime, good absorption, low energy to regenerate and low toxicity is continuously being carried out. The choice made for this thesis is to focus on solvents that have been the most extensively researched as well as having publicly available data regarding the process. For this reason, the solvents chosen are MEA for post combustion CC, PEI for solid sorbent-DAC and KOH for Liquid-DAC. This section presents the major ways of producing each of these chemicals.

2.4.1 MEA production

MEA is a co-product of ethanolamine production, based on the reaction of ethylene oxide (EO) with ammonia (NH_3): $NH_3 + EO \Rightarrow MEA$. In fact, there exists three types of ethanolamines: monoethanolamine, diethanolamine (DEA) and triethanolamine (TEA), and they are always produced together. To account for this, mass allocation was applied with each product considered of equal value [51]. Their proportions however vary based on the molar ratio of ammonia in the reaction batch, as depicted by Figure 2.7.

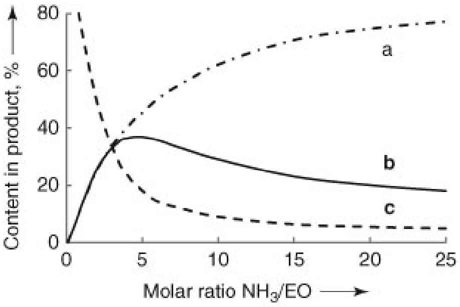

Figure 2.7: EA products selectivity depending on Molar ratio of ammonia and ethylene oxide. Product distribution are as following a) MEA, b) DEA and c) TEA. Figure from Ernst et. al [6].

2.4.2 Ammonia and hydrogen production

Ammonia is a pretty well known chemical and can be produced by the simple combination of nitrogen and hydrogen (also called Haber-Bosch process). Nitrogen can be taken from the air by separation from oxygen in an air separation unit (ASU). Hydrogen can be obtained through two main pathways today. Steam methane reforming is currently the most common process, which separates the atoms of CH_4 and turns it into CO_2 and so-called grey hydrogen (grey refers to using fossil methane). It can also be combined with carbon capture to produce blue hydrogen, as presented in the pre-combustion Section 2.2.1.2. On the other hand, water electrolysis enables for production of green hydrogen, if the electricity used originates from renewable sources [50].

2.4.3 Ethylene production

Ethylene is part of the family of chemicals known as high-value chemicals (HVC) and is used as a base when producing plastics and chemicals [52]. One of the current ways of producing ethylene is through the use of steam cracking naphtha. Naphtha represents 75% of EU's feedstock for ethylene production [53]. Steam cracking breaks down longer chains of hydrocarbons that exist in naphtha into shorter ones such as ethylene and propylene.

Finding ways to produce renewable ethylene is of particular interest in order to aid the transition away from the use of fossil products. Among the options suggested to achieve this is Methanol-to-olefin, which uses methanol instead of for example naphtha [54]. However, due to the uncertainty of what ways will be used to produce ethylene and other HVC products in the future, steam cracking is assumed as the only method to produce ethylene in the model.

2.4.4 Ethylene oxide production

Ethylene oxide is the result of the oxidation of ethylene. The reaction takes place at 200-300 deg and 10-30 bar. It can use oxygen from the air or from a pure oxygen stream [51]. The chemical is used for production of ethylene glycol, among other chemicals. The global annual production was 31 Mt as of 2022 [55].

2.4.5 Potassium Hydroxide (KOH) and Calcium Carbonate ($CaCO_3$) production

Acquiring the chemicals calcium carbonate and potassium hydroxide needed for L-DAC is not a complex procedure. Potassium hydroxide is mainly produced through the use of the chlor-alkali process, which is described with the chemical reaction found in 2.1.

$$2KCl + 2H_2O \rightarrow Cl_2 + H_2 + 2KOH \tag{2.1}$$

The process consists in the electrolysis of brine, a mixture of potassium chloride (KCl) and water. It produces chlorine gas (Cl_2), which is currently the most valuable output of the process, as well as hydrogen gas (H_2) and potassium hydroxide [56]. The majority of the cost associated with the process results from the electricity consumption and investing in the electrolysis unit. Cost of salt, water and steam represents a lower percentage of the total cost [57].

Calcium carbonate was chosen to be neglected in this study as it assumed to be easy to acquire, from limestone mining, and cheap, ten times less expensive than KOH for a similar consumption [40, 58].

2.4.6 Amine-Silica solid sorbent production

The chosen amine-silica sorbent refers to a sorbent based on polyethyleneimine (PEI) as the active phase and silica gel (SiO_2) as the support.

Producing PEI involves two different chemical reaction steps. The first step involves producing Aziridine from ethanolamine. There exists a few different ways of achieving this, but the most common is the Wenker process [59]. The Wenker process involves the reaction between ethanolamine and sulfuric acid in order to create the intermediary step Aziridine.

The second step involves homopolymerization which is achieved by first mixing the Aziridine with hydrochloric acid. It is then mixed with sodium hydroxide and dried. The final two steps are first dissolving the Azirdine in ethanol and filtering. Finally, the polymer is precipitated in diethyl-ether and dried again [46]. Chemicals such as diethyl-ether and sulfuric acid are not able to be 100 % recovered and are therefore needed to be continuously added during production.

3

Method

In this section, the considerations made when deciding parameters to be used are explained. An overview with accounts for material consumption, energy usage and costs associated with each process that were considered is given. The choice of Energy system model used and some of its advantages are also detailed. The different scenarios that are used to determine potential impacts will also be discussed.

3.1 Data collection

This study tries to be as exhaustive as possible on the production of the solvents and sorbents. Therefore, not only the solvent production process per se are included, but also the preliminary production or supply of their feedstocks. This includes the energy needed for the syntheses to happen as well as the capital expenditure (CAPEX) in the chemical facility and the operating expenditure (OPEX). For raw materials inputs, their collection is only accounted for as a cost. This concerns: salt for Chlor-Alkali; oil for Steam cracking (if fossil oil is used, otherwise bio-oil production is accounted for); silica and the other chemicals for PEI production (see Figure 3.2). The section gives the reasoning and the sources behind the choice of parameters used in this study. The complete data collection carried out during this work can be found in Supplementary information.

L-DAC and S-DAC

The original PyPSA model only accounted for the use of S-DAC. Moreover, the source used for its characteristics did not specify whether the cost attributed to sorbents was included. Therefore it was not only required to find a source for the cost and energy consumption used by L-DAC, but also ensure that the capital costs did not already account for cost of sorbent. This is done because in the base model, the solvents and sorbents must be free in terms of cost and energy for production, and in the extended model, those values should be calculated as results from the solver. The CC technologies must therefore be implemented with only the parameters related to everything except solvents and sorbents.

Costs given in analysis of direct air capture typically did not convey the ascertained cost of sorbents of the capital and operational cost expenditures. Therefore the costs associated with L-DAC and S-DAC chosen for this study were based on calculations made by Young and colleagues at a scale of 1 Gt of carbon capture per year. This also accounted for learning rates of components as well as how costs are affected as scale of technology increases [3]. Moreover, it was ensured that cost for solvents and sorbents were removed from capital and variable costs. The CAPEX and OPEX values collected for post-combustion and L-DAC technologies did not include solvents in the first place. However, for S-DAC, costs for the sorbent had to subtracted from both the capital (initial stock) and the variable (periodical replacement) costs for each technology.

Solvent consumption

In order to estimate the impact of solvents, an estimation of the consumption is required. Literature will be used to find a higher and lower consumption estimation needed for the solvents.

MEA for post-combustion

A literature review on MEA consumption for post-combustion capture was carried out. Many studies dealing with this topic were found, but the most exhaustive analysis found was a critical review of life cycle inventories for BECCS performed by Duval-Dachary et al., 2023 [33]. In their work, the authors went through 97 LCAs related to carbon capture applied to bio-energy. Among a lot of technical details, MEA makeup for losses, or consumption, was assessed by 12 studies. The values ranged between 0.27 and 3.98 kg_{MEA}/tCO_2, with an average value of 2.05 $kgMEA/tCO_2$. In this thesis, it was chosen to simulate two cases for solvent consumption: an optimistic scenario and a pessimistic one that will use the lower and the higher bounds, respectively.

Regarding the initial stock of solvent, some insights can be found in the work done by Weir et al., 2023 [60]. Based on their own experimental pilot lignite power plant in Niederaussem with post-combustion CC that uses MEA, they did measurements of solvent degradation and experimented different strategies of managing this degradation. The first of them is feed and bleed (frequent replacement of a part of the solvent) and full solvent replacement after some time. They found that the best way of managing degradation was to replace the solvent after 270 days. This would add 0.460 to their 0.350 $kgMEA/tCO_2$ consumption during this period.

This tells two things. First, the best way of managing the solvent degradation seems to be by replacing the entire stock regularly. Second, the solvent initial stock is very small compared to the losses. Assuming a 20 year lifetime for the plant, this initial stock would represent a levelized $0.460 \cdot 270/365/20 = 0.017$ $kgMEA/tCO_2$ captured. The conclusion is that the initial stock of solvent will be neglected for the MEA consumption considered in this work.

KOH for L-DAC

In their LCA of both DAC technologies, Madhu et al. give a very extensive review of solvent consumption for L-DAC (referred to as HT-Aq DAC in their article), more

precisely in section 2.3 of the supplementary information [34].
They base their low bound estimation on the pulp and paper industry that commonly uses NaOH as a solvent for capturing CO_2 emissions from a much dirtier flue gas, with more impurities, and therefore more harmful. This process generally achieves 97% recovery of the solvent [61]. From that, and due to air being a cleaner gas to treat, they assume a 99% recovery as a their low boundary, leading to a KOH replenishment of 38 kg/tCO_2 captured.

On the other hand, other research has estimated with more details the recovery of solvent for L-DAC. Among them, Madhu et al. cite the National Academies of Sciences, Engineering, and Medicine, 2019 and Solocow et al., 2011, estimating KOH losses to 0.4 kg/t_{CO_2}, equivalent to a 99.984% recovery rate [42, 62].

Other sources were found in the literature for this value, and an extensive literature review is presented in Supplementary information Supplementary information. In this work, Madhu et al.'s boundary values are chosen for optimistic- and pessimistic-case scenarios.

The initial stock of KOH for L-DAC was estimated by a few sources of being between 10 and 72 kt for a 1 MtCO2/y L-DAC plant [40, 63]. For this study, it was chosen to not include the initial stock of KOH as a consumption, because it is assumed that the final stock can be recycled for being used in another application, like in another DAC plant, for example.

Solid sorbent for S-DAC

Estimations for a typical solid sorbent lifetime range between 0.5 - 3 years. Values of consumption calculated by Madhu et al. based on the estimated lifetime and stochiometric ratio of sorbent to CO_2 are between 2.3 - 14 kg/t_{CO_2} [34, 46]. Deutz and Bardow also make estimations of sorbent consumption for S-DAC [46]. Based on data from two commercial plants owned by Climeworks, they estimate it to be of 7.5 kg/tCO_2 in their reference case. Moreover, Climeworks forecasts an improvement of the processes based on an extrapolation of their current measurements enabling a consumption of 3 kg/tCO_2 in the future. The higher and lower consumption used for this study correspond to the higher and lower values obtained by Madhu et al. This range is made to account for uncertainties that exist on sorbents, such as how good the processes will perform in the future, or uncertainties on which sorbent will be used in the future. Perhaps one sorbent will turn out to be easier to produce, or cheaper, or will present better capture, but will degrade faster or slower than the studied PEI.

MEA Production

A few articles have proposed novel ideas for production of ethanolamines and then compared them to a conventional production process [64, 65]. For this study, the inputs showcased by Devaraja et. al were chosen as it was the most recent publication, achieved high selectivity of MEA, simulated energy consumption and gave accounts for both CAPEX and OPEX [65]. In order to be consistent with current production processes the data for the conventional process were used.

It is worth noting that Deveraja et al. has some limitations: the capital cost given only accounts for the equipment costs, lacking the additional expenses for installation, engineering procurement and construction etc., which might significantly increase the value. No operation and maintenance costs other than energy are given either.

Additionally, it was decided to allocate the resources and energy consumption for this process by mass of products. The reasoning is that all three products are considered of similar importance for the industry, as well as for carbon capture since DEA and TEA are also candidates for certain CC technologies. The same allocation choice was made by EcoInvent [51].

Ethylene Oxide production

Energy and material for this process were taken from EcoInvent Life Cycle Inventories of Chemicals, 2008 [51]. Costs estimates were found in (Ghanta et al., 2013), whose authors made a cost analysis of a novel and a conventional process for EO production [66]. Values for the conventional process were used. Good details of capital costs are given including equipment, installation and engineering and procurement are given, as well as production costs containing costs of oxygen (because not included as a variable in the model), other chemicals and cooling utilities. The cost of ethylene is removed from the production cost because it is calculated endogenously in the model.

Ethylene from Steam cracking

Processes involving steam cracking can use naptha as a fuel source and a reactant with split of around 20% fuel to 80% feedstock ratio [53]. It can also be the case that extra steam is used as heat consumption is used to compensate for naptha. In this study a pure naphtha feed was used rather than an ethane one as this process is the most commonly implemented in Europe. Energy requirements were estimated from Ren et al. [53]. Data regarding plant costs was limited and based on data found from DECHEMA [54]. As the steam cracking not only produces ethylene, but also other HVC such as propylene, a mass allocation was used for this process, as suggested by PlasticsEurope [67].

In the model, naphtha is implemented as an oil bus, which can be fossil oil, bio-oil or an electrofuel. This is not completely true since in reality crude oil needs to be refined in order to get products such as naphtha. This assumption amounts then to neglect the crude oil refinery.

KOH from the Chlor-Alkali process

The data of the production process for KOH was estimated from EURO-CHLOR [57]. All necessary inputs regarding materials and energy consumption were accounted for and therefore deemed sufficient for use in this study. The same source all gives insights for variable operational costs. However, the cost of capital investment was estimated using different sources (cf. Supplementary information Supplementary information). For this study, it was chosen to use a CAPEX of 1000 € per kW of electrical input power as a representative value for all the different sources. Besides, no credit is given to chlorine since it is assumed that no extra demand for it has any reason to exist in the future, and it is a toxic gas so potentially complicated to manage. On the other hand, credit was given to hydrogen as is it a valuable product.

Solid sorbent production

The solid sorbent production process was based on values from Deutz and Bardow. They estimated the material and energy consumption required to produce each of the two compounds that compose the AS sorbent, namely PEI and silica gel [46]. The share of each chemical in the sorbent has been subject to a lot of research, and some conclude it is optimal at 50-50, others assert it is for 30% PEI and 70% silica [68, 69]. To be conservative, it was chosen to use a 50% PEI and 50% silica composition in this study. Besides, (Deutz and Bardow) assume that silica can be recovered at a rate of 95% everytime the sorbent needs to be replaced.

Due to PEI being a niche product, with no real industry currently existing, difficulties arose when searching for literary values concerning production costs of this compound. This was therefore estimated based on investment costs for other processes in the model considered similar. Operational costs were considered as the cost of the chemicals involved in the production, consisting mainly of the solvents non-recovered during the reaction. No other operation or maintenance cost was considered.

Final parameters

In table 3.1, the solvent consumption for each technology are shown. They are split into the optimistic and pessimistic consumption values that will be investigated in this study. A summary of literary findings that resulted in these chosen values for solvent consumption can be found in Supplementary information Supplementary information.

Table 3.1: Higher and lower consumptions of solvents chosen in this study

Solvent (Technology)	Optimistic solvent consumption ($kg_{solvent}/t_{CO_2}$)	Pessimistic solvent consumption ($kg_{solvent}/t_{CO_2}$)
KOH (L-DAC)	0.4	38
PEI (S-DAC)	2.3	14
MEA (PCC)	0.27	3.98

A summary of chosen input parameters relating to material consumption, energy input, investment cost and operating cost decided for this study can be found in Table 3.2. The first two columns show the necessary amount of reactant required per ton of output product. The chemical shown in parenthesis is the reactant being consumed for the process.

Table 3.2: Input parameters chosen for this study

Process	Reactant 1 ($t/t_{product}$)	Reactant 2 ($t/t_{product}$)	Heat ($GJ/t_{product}$)	Electricity ($MWh/t_{product}$)	CAPEX (€/($t_{product}$/y))	OPEX (€/$t_{product}$})
Ethylene from steam cracking	Naphtha 80 GJ	-	0	0.15	1200	180
EO production	Ethylene 0.825 t	Oxygen 1.45 t [1]	0	0.33	1100	560
MEA production	EO 0.75 t	NH_3 0.25 t	7.1	0	125	32
Chlor-Alkali	KCl 1.5 t [1]	-	2.7	2.6	291	230
AS sorbent production	MEA 1.0 t	KOH 1.3 t	4.2	0.18	1000	1715

1: Feedstock accounted for as a cost, included in the OPEX.

3.2 Graphical representation

The implementations and changes made to the PyPSA-Eur-Sec model can be visualized in Figures 3.1 and 3.2. In Figure 3.1, the original implementation of carbon capture in the PyPSA model can be observed. It can be observed how the CC technologies only require an input of heat and electricity. These inputs represent the energy required to only operate the CC plant, i.e., to regenerate the solvent. Fuels and other products from these processes are not shown in the figure.

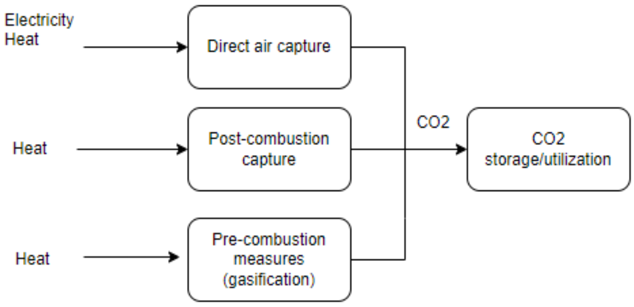

Figure 3.1: Representation of the original PyPSA-Eur-Sec model design for carbon capture

Here, solvents and sorbents are assumed to be free in terms of cost and energy for production, meaning that they are invisible for the system. The aim of this study is in fact to assess what impacts solvent cost and energy required to their production will have on the system. Thus, the base case model will contain CC technologies where only the energy of operating the CC processes are included, i.e., the energy required to regenerate the solvents or sorbents. This base case will be compared to the extended model that includes the marginal cost and energy consumption for the production of one unit of solvent or sorbent consumed by one of the CC technologies.

The addition of solvent and sorbent production to the PyPSA-Eur-Sec model can be observed in Figure 3.2. Arrows represent all necessary inputs that were obtained through a literature review and subsequently implemented into the model.

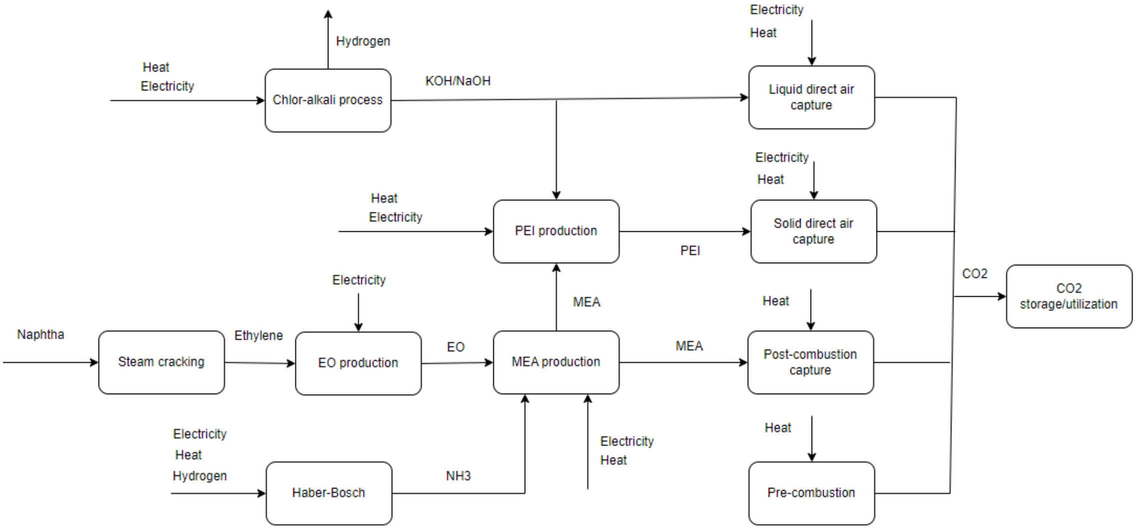

Figure 3.2: Representation of implementations made into PyPSA-Eur-Sec for solvent and sorbent production

3.3 PyPSA-Eur-Sec

PyPSA-Eur-Sec is an open-source energy system model that optimises a sector-coupled European network. The model includes the power sector, transports (including also international shipping and aviation), space and water heating, industry and industrial feedstocks. A summarised image of the interconnection of the model and the main technologies that are included can be found in Figure 3.3.

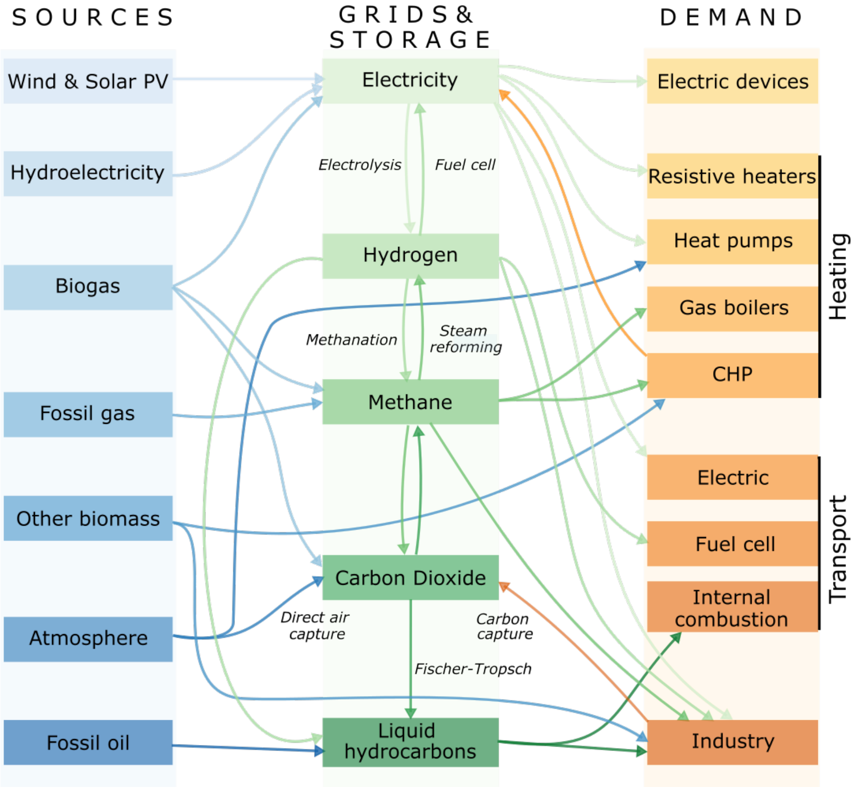

Figure 3.3: Summary graph of PyPSA-Eur-Sec and its different sectors [7].

PyPSA-Eur-Sec is based on the Python library PyPSA, an open-source tool for designing and simulating energy systems. In essence, it is a graph-based tool for creating electrical networks. It connects electrical buses together with electrical lines or other types of links. Time-varying loads can attach to them to simulate consumption, and this demand can be met by various types of generators, such as thermal power plants or variable renewable technologies. Storage units are also permitted, and CO2 emissions can be accounted for. Investment costs in the model are all annualised using a discount rate of 7 %. Thanks to a linear programming solver, the problem defined is then optimised by setting the problem variables such that they minimise the total system cost. These variables are the generators and storage dispatch and the capacities investments of generation, storage and transmission. They are the output results of the solver. A detailed description of the original PyPSA-Eur-Sec model can be found in Neumann et. al [70].

In this work, PyPSA-Eur-Sec will be used to analyse the impacts of solvents for carbon capture on the entire energy system. For doing so, a reference model needs to be first decided on.

3.4 Base model definition

To investigate the impacts of solvent and sorbents, the implementations are compared to a base case that is used as a reference. The base model consists of the PyPSA-Eur model with its major assumptions, to which are included the additions made by Millinger et al. in order to account for further details with regards to biomass and direct air capture [11]. Finally, the level of details for direct air capture is extended by introducing L-DAC into the model, as discussed in Section 3.1.

The model forecasts an hypothetical future European energy system. It is designed with a greenfield study, meaning that the whole energy system is being built from scratch. The data for technologies was taken based on 2040 values in the model due to most countries considering net zero being an option at the earliest in 2050. For this study, a 37 nodal and 5-hour time resolution was chosen as a trade-off between accuracy of results and computational power requirement. A representation of the 37 nodal European system can be found in Figure 3.4.

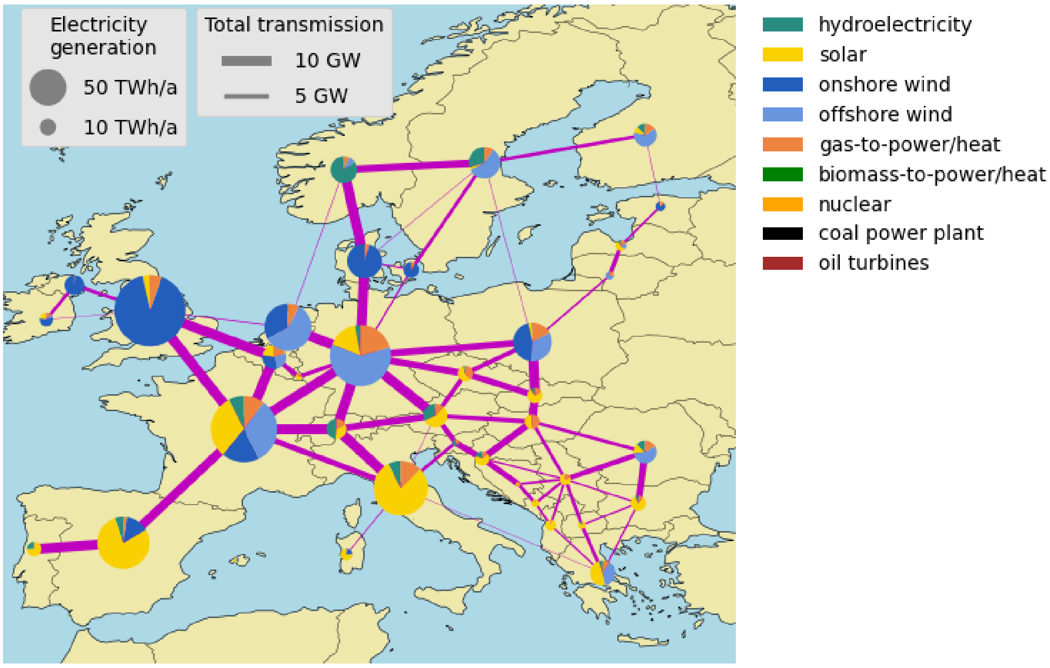

Figure 3.4: European network with 37 nodes used in this thesis and results of electricity generation per country for one of the base case scenarios

3.4.1 Scenarios investigated

In order to investigate the potential ramifications of including solvents in the model, several scenarios are decided based on potential situations that can have an impact in the future. These scenarios include enabling or disabling import of biomass, because it is a crucial resource and brings up sustainability concerns. The second parameter is the potential of CO_2 that can be sequestered each year, this being to date still very uncertain: 600 Mt/y versus 2000 Mt/y. Finally the CO_2 emission target: net zero vs net negative targets. Many countries have in fact already pledged to become net zero by the year 2050. While some of the scenarios may have a lower chance of occurring, they will test the impact of solvents on each potential system.

On top of choosing realistic scenarios, these ones must bring interesting changes to how carbon capture is used in the system. Restricting the import of biomass should make the model more inclined to use DAC as a CDR technology than BECCS, with biomass having more flexibility of use in the energy system and therefore is used where it is most necessary. Increasing the sequestration level will allow the model to become more flexible with the amount of fossil fuels that are used and compensate with the adequate amount of CDR for a cost optimal system. Net-zero versus net-negative carbon targets will push the amount of CDR in the system and give an insight in what the potential amount of CDR could be used in the future.

3.5 Cost assessment

As a method of comparing the effects that implementation of solvent and sorbent production has on the cost of carbon capture systems, their Levelized Cost of Carbon (LCOC) with and without accounting for solvents are compared. This metrics represents the cost of capturing one unit of CO_2. For direct air capture plants, their LCOC is calculated through Equation 3.1.

$$LCOC_{DAC} = \frac{CAPEX + OPEX + E \cdot El_{price} + H \cdot H_{price}}{t_{CO_2}} \tag{3.1}$$

It is calculated as the ratio of the total expenses of the plant over its entire lifetime, divided by the total amount of CO_2 captured during the same period. OPEX stands for the operational expenditures, which doesn't account for cost of energy nor solvent makeup, in , E is the electricity demand (MWh), El_{price} is the electricity price (€/MWh), H is the heat demand (MWh), H_{price} is the cost of producing this heat (€/MWh) and m_{CO_2} is the amount of CO_2 captured by the DAC plant (tCO_2).

Calculating the LCOC for power plants is done according to Equation 3.2 based on work by Garcia et al. [24].

$$LCOC_{powerplant} = \frac{LCOE_{CCS} - LCOE_{NCCS}}{\eta_{captured}} \tag{3.2}$$

$LCOE_{CCS}$ represents the Levelized Cost of Energy when including CCS (€/MWh_{output}), $LCOE_{NCCS}$ is the one for the plant with no CCS and $\eta_{captured}$ represents the specific amount of carbon dioxide captured by the carbon capture module (t_{CO_2}/MWh_{output}). The LCOE of a power plant measures the cost of producing one unit of energy. Its calculation is also taken from the same work [24], and presented in Equation 3.3.

$$LCOE = \frac{CAPEX \cdot (CRF + F_{OM})}{8760 \cdot C_f} + V_{OM} + \frac{C_{fuel}}{\eta_{th}} \tag{3.3}$$

There, CAPEX is the capital cost of the investment in €/MW$_{output}$. It is annualised using a capital recovery factor, the calculation of which is given by Equation 3.4. Then, F$_{OM}$ is the fixed operations and maintenance cost (% of CAPEX /year), 8760 the number of hours per year, C$_f$ is the capacity factor, V$_{OM}$ is the variable operations and maintenance cost in (€/MWh$_{output}$), C$_{fuel}$ is the cost for fuel in €/MW$_{th}$ and η_{th} the efficiency of the plant. For power plants that produce both heat and electricity, it was chosen that the LCOE is calculated per unit of total energy output. Therefore, $\eta_{th} = \eta_{el} + \eta_{heat}$.

$$CRF = \frac{i(1+i)^n}{(1+i)^n - 1} \tag{3.4}$$

where i represents the discount rate (%/year) and n the lifetime of the plant (years).

Details of how the cost calculations were made in this work can be found in the Supplementary information Supplementary information.

4

Results

The results chapter is split into two different sections. The first will assess the energy required to produce the chemicals and assess their impact on the technologies' LCOC. The second will consider their effect on the whole energy system.

4.1 Solvent production impacts on CC technologies

4.1.1 Specific energy requirements for production

Before assessing the impacts of the solvents on the CC technologies, their specific impacts, per ton of product, are determined. The energy requirements for each chemical are expressed as a function of four base energy carrier, namely electricity, heat, oil and hydrogen. Moreover, these energy usages account for the production of all the chemicals in the chain.
Table 4.1 presents the requirements regarding those energy carrier of each chemical considered in this work to produce 1 ton of each compound.

Table 4.1: Total energy required to produce 1 ton of chemical expressed in terms of four energy carriers

Chemical	Electricity ($MWh/t_{product}$)	Heat ($MWh/t_{product}$)	Oil ($MWh/t_{product}$)	H_2 ($MWh/t_{product}$)	Total energy ($MWh/t_{product}$)
NH3	0.25	0	0	1.15	1.40
Ethylene	0.15	0	22.22	0	22.37
EO	0.45	0	18.33	0	18.79
MEA	0.40	1.96	13.82	0.28	16.46
KOH	2.55	0.76	0	-0.83	2.48
AS sorbent	4.13	4.17	13.64	-0.88	21.06

Ethylene is an energy demanding production process due to the amount of naphtha that it requires. The naphtha considered accounts for both the fuel and the feedstock needed, as explained in Section . This thereafter affects the subsequent amount of energy required for the production of EO, MEA and the AS sorbent. Nevertheless, it is worth noting that most of the naphtha consumed to produce ethylene is used as a material, i.e., is converted into mass of ethylene. Production of KOH is an electricity demanding process but requires much less energy overall in comparison to AS sorbent and MEA.

4.1.2 Specific cost of production

The share of different factors per ton of product produced for the different chemicals implemented into the model can be observed in Table 4.2. The levelized cost is divided into cost of energy, cost of necessary reactants, Levelized CAPEX, and OPEX without reactant nor energy costs.

For those calculations, values such as capacity factors for each technology, electricity, heat and fuel prices are required. To account for them a priori, the average of the base model results for these values over the scenarios was used as an estimation.

Table 4.2: Table presenting the levelized cost per ton chemical product produced split into the categories energy, reactants, levelized CAPEX, OPEX (without feedstock nor energy) and current market price.

Chemical product	Energy (€/$t_{product}$)	Reactants (€/$t_{product}$)	Levelized CAPEX (€/$t_{product}$)	OPEX (€/$t_{product}$)	Levelized Cost of Production (€/$t_{product}$)	Market Price (\$/$t_{product}$)
NH_3	91	-	86	32	208	245
Ethylene	1121	-	103	180	1404	800 - 1400 [71]
EO	21	1156	94	560	1834	1500 [72]
MEA	108	1421	11	32	1583	800-1600 [73]
KOH	206	-	25	230	461	1000 [74]
AS sorbent	77	2045	86	1715	4082	7,641 [3,75] [1] 15,000 - 100,000 [42] [2] 25,000 [69] [3]

1: Lewatit VP OC 1065.
2: Generic S-DAC sorbent.
3: Their best sorbent tested, made of 30% PEI and 70% silica.

Some details to note is the high reactant costs required for MEA and AS sorbent production which is a result from the reactant cost associated with the production of ethylene. CAPEX for all processes except for NH_3 production represents a small share of the total levelized cost of production. OPEX represents a high cost for EO and AS sorbent due to chemical replacements required.

4.1.3 Impacts on the technologies

The effects on the technologies energy requirements and LCOC of introducing energy and costs of production for solvents and sorbents are showcased in Figures 4.1 and 4.2. The energy requirement refers here, in the reference case, to the energy to operate the CC plant or post-combustion capture module, i.e., mostly to regenerate the solvents or sorbents, which is compared to the additional energy for producing the chemicals. If one neglects energy requirements for the plant construction, dismantlement, waste disposal and transport to supply the solvents to the plant, the sum of both these consumptions correspond to the CC plant's life-cycle energy requirement. Similarly, the cost assessment was done by comparing the LCOC for each technology excluding cost of solvent or sorbent to the LCOC that includes this consumption. Calculations of LCOC baselines are presented explicitly in the Supplementary information Supplementary information, based on formulas presented in Section 3.5 Cost assessment.

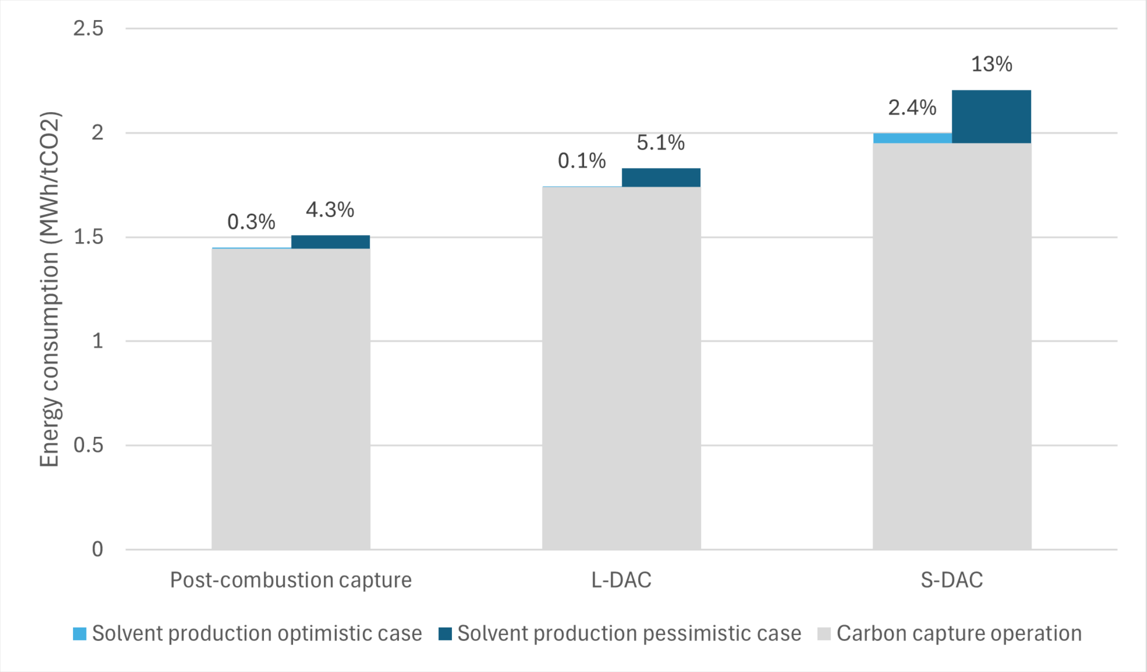

Figure 4.1: Share of the energy for solvents production in the total energy consumption of each CC technology

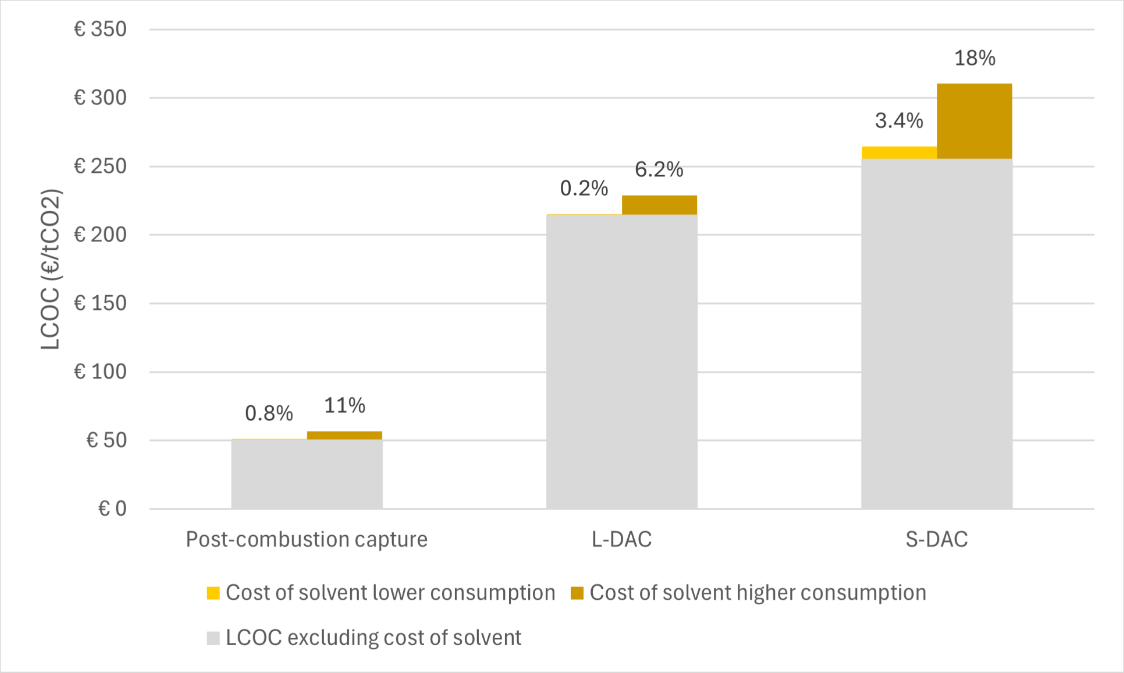

Figure 4.2: Share of the solvents costs of production in the LCOC of each CC technology

With an optimistic consumption, MEA and KOH similarly present very small impacts on post-combustion and L-DAC respectively, both in terms of total life-cycle energy requirements and LCOC. This however becomes more significant with a pessimistic solvent consumption. On the other hand, solid sorbent production leads to more consequent impacts in both cases, and attains 13% of life-cycle energy and 18% of LCOC in the higher consumption case.

4.2 Solvent production impacts on the energy system

After introducing the base system, this section presents the impacts on total system cost, carbon capture methods used and primary energy usage of the increased level of details that implies the production of solvents for carbon capture.

4.2.1 Base case description

This section presents the system of reference through its key results to give an understanding of the energy system investigated for the case of L-DAC being used. Base case for S-DAC can be found in Appendix A as it is very similar.

Figure 4.3 represents the total system cost of the system. It is ordered from least strict requirements on the energy system with the Net zero emission, 2000 Mt sequestration and import of biomass scenario to the most strict Net negative, 600 Mt sequestration and no import of biomass.

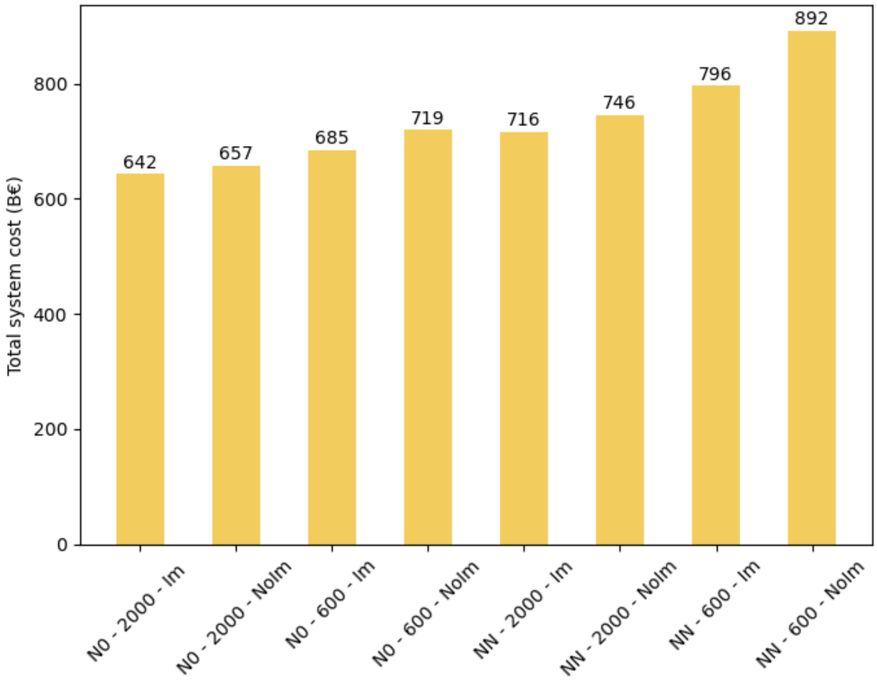

Figure 4.3: Total system cost in the base case

Figure 4.4 shows the amount of total primary energy required per scenario. The primary energy is divided into variable renewable energy, VRE (solar, wind and hydropower), fossil fuels (oil and natural gas) and biomass (solid biomass, digestible biomass and waste).

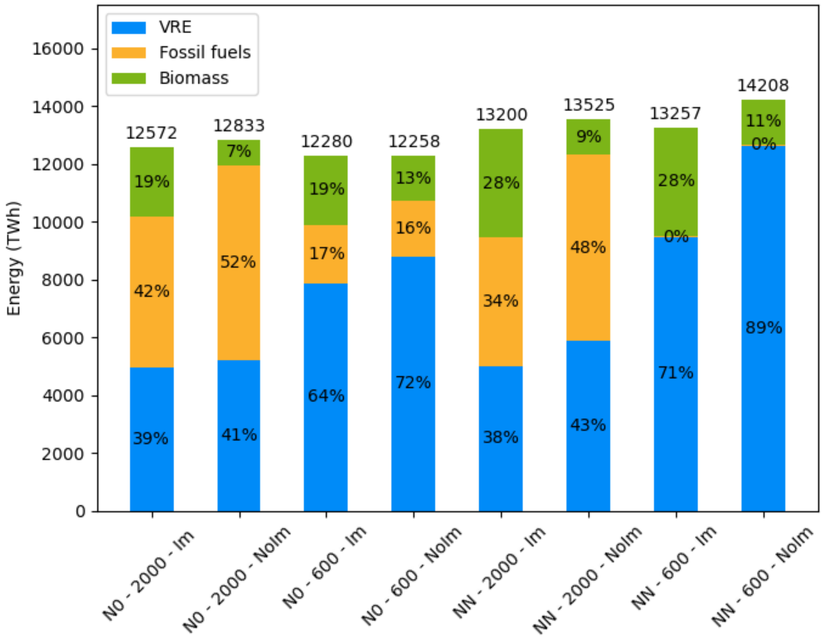

Figure 4.4: Primary energy usage in the base case

As can be observed, the scenarios allow for a variable amount of fossil fuel usage. The high sequestration enables the system to use more fossil fuels before having to use more expensive CCU options. If fossil fuels can't be used, their absence is usually compensated by a higher share of renewables. Biomass usage remains fairly consistent, yet increases most when net negative and import of biomass is the case scenario.

Figure 4.5 presents the amount of carbon that is captured in each scenario, as well as its distribution between each four types of CCS technologies.

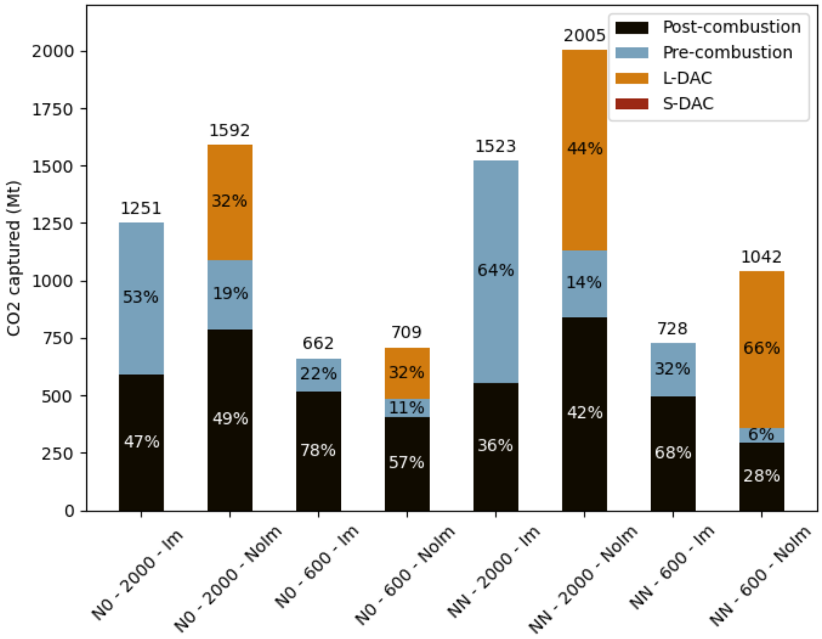

Figure 4.5: Carbon captured by each technology in the base case

It can be observed that, in general, a large carbon capture usage occurs when a lot of fossil fuels is consumed, which makes sense because the fossil emissions need to be captured in order to achieve the emission goal. Besides, the more storage available, the more carbon capture is used. This graph also shows which CC technology is on the margin, i.e., which is the least expensive at the end of the simulation. It can be seen that DAC is in this case in four of the scenarios because in the remaining ones, if it is not used, it is necessarily because it is more costly. Moreover, the results show that DAC is never used when a lot of biomass is available, because the latter is more cost-effective, as the LCOC calculations show.

In some cases, the total carbon captured in the year is greater than the amount that can be sequestered in the storage, especially in the the 600Mt cases. This is because some of the captured carbon is utilised by the model to produce electrofuels.

An important note on this model is that under these configurations, S-DAC is never used. In fact, since L-DAC and S-DAC provide the exact same service of solely capturing carbon, they are in direct competition. Moreover, they roughly have the same OPEX over time which leads to L-DAC being consistently cheaper than S-DAC because it has a lower CAPEX. Therefore, and since there is no limit on how much capacity of each technology can be installed, S-DAC is never invested in in this base model, to the benefit of L-DAC. To cope with this, all the scenarios were duplicated to analyse a system where only S-DAC is available, instead of an only L-DAC system in the base case. The base model for this system presents little variation from the L-DAC base model and is therefore not included in this section for the purpose of clarity. It is however depicted in Appendix A.

Total system cost

Pessimistic consumption of solvents and sorbents

Figure 4.6 and 4.7 depict the total system cost increase and the variations in carbon captured by each technology for an only-L-DAC system and for each scenario.

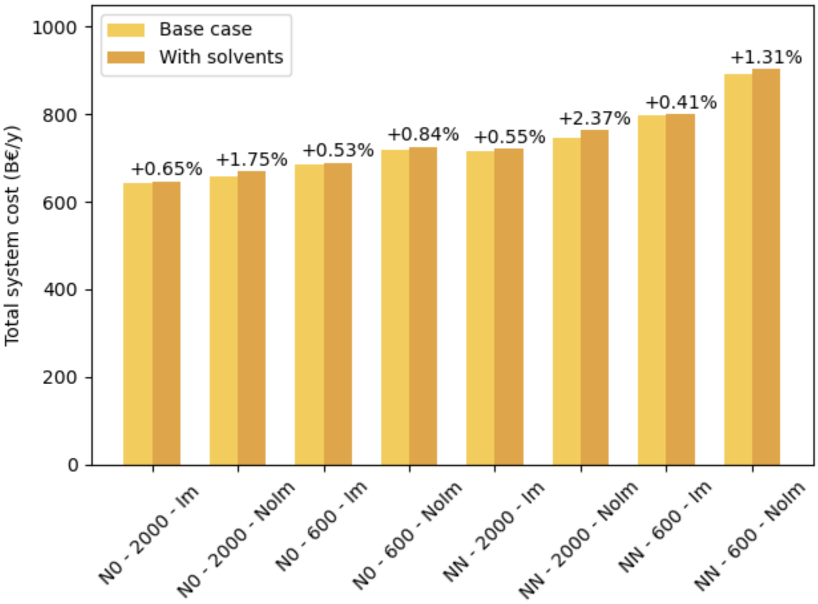

Figure 4.6: Total system cost variations for higher consumption of solvent with L-DAC

Three scenarios in Figure 4.6 result in a total system cost above 1%, namely N0-2000-NoIm with 1.8%, NN-2000-NoIm with 2.4% and NN-600-NoIm with 1.3%. All three scenarios include some DAC usage.

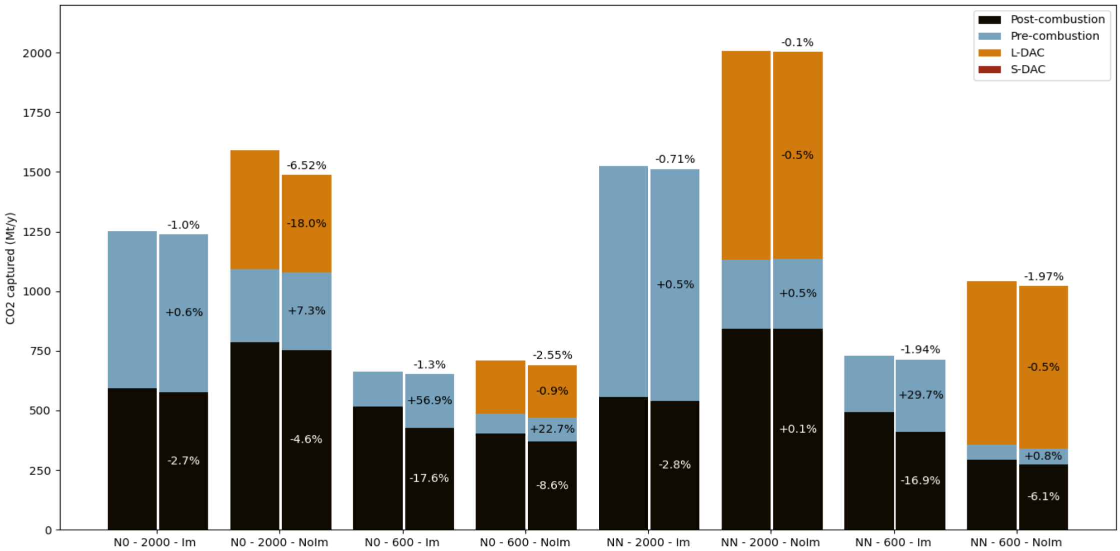

Figure 4.7: Carbon capture usage variation for different scenarios using L-DAC and higher consumption

The general trend in Figure 4.7 is that CC technologies are used less when accounting for production of solvents, as a result of their increased cost. The impact of solvent production is most clearly observed in the scenario No-2000-NoIm where the use of L-DAC decreases by 18%. Pre-combustion being more favourable to post-combustion can also be observed in N0-600-Im and NN-600-Im. The system cost increase is therefore explained by the use of other solutions that become less expensive than keeping CC running as much as in the base case. One of them is notably pre-combustion, since this set of technologies is not affected by the changes related to solvents production. Some scenarios observe less changes, though, as in the NN-2000-NoIm one. This means that no cheaper solution than keeping the same extent of CC technologies exist (they remain on the margin), and in this case the cost increase on the system is directly proportional to the cost increase on each technology, weighted by their respective usages.

Figure 4.8 and 4.9 represent the total system cost and the carbon captured by each technology respectively when S-DAC is used as the only DAC technology instead of L-DAC.

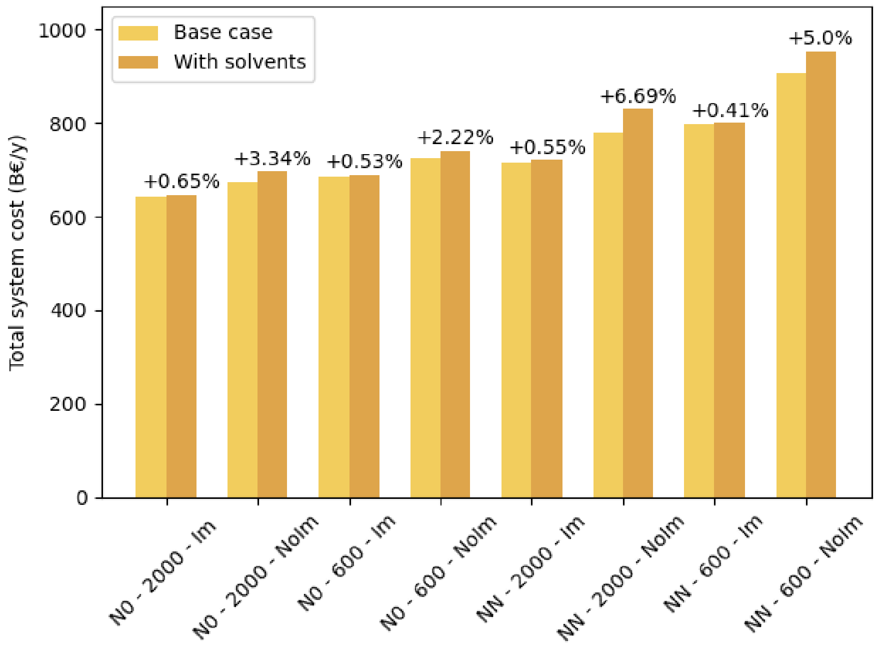

Figure 4.8: Total system cost variations for higher consumption of solvent with S-DAC

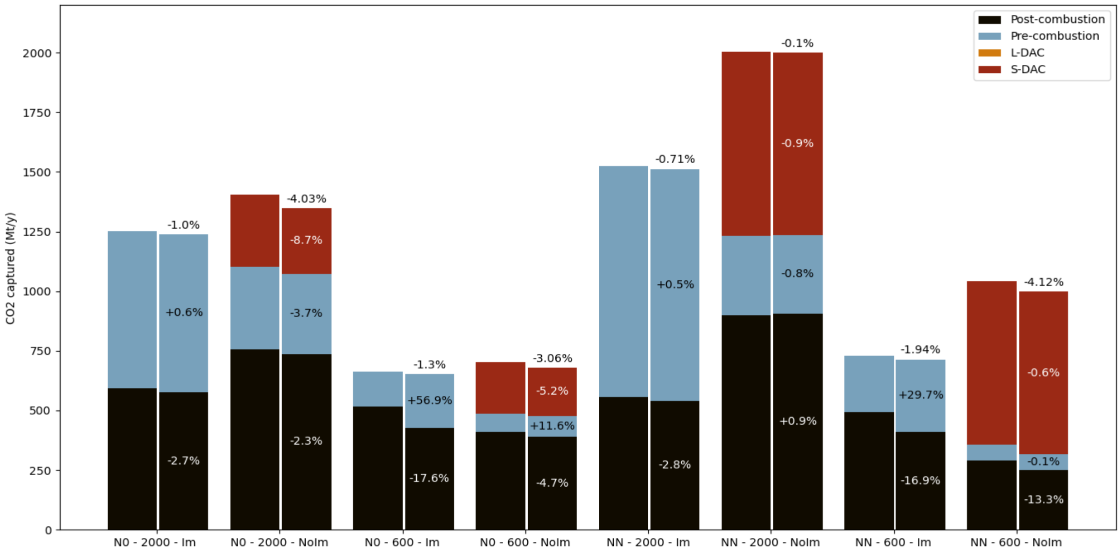

Figure 4.9: Carbon capture usage variation for different scenarios using S-DAC and higher consumption

Similar trends can be seen in these figures as in the only-L-DAC case. Cost increases for all scenarios without import of biomass are above 2%, with the highest being 6.7% in the NN-2000-NoIm scenario.

The L-DAC and S-DAC cases reach a maximum cost increase of 2.4% and 6.7% respectively. Both maxima happen in the NN-2000-NoIm scenario, which is has the highest amount of carbon captured (roughly 2000 Mt/y), and this results in the highest solvent requirements.

Optimistic consumption of solvents and sorbents

In the case of lower consumption, the total system cost effects for the only-L-DAC and only-S-DAC systems are shown in Figure 4.10.

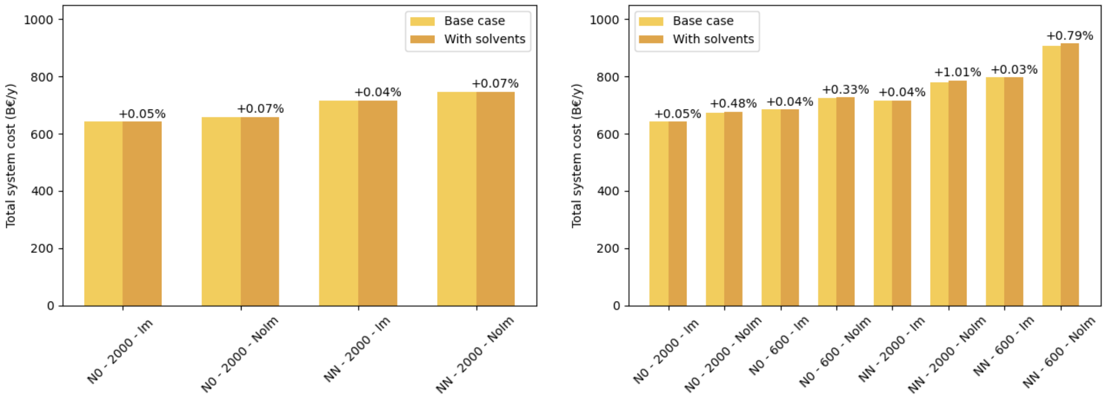

Figure 4.10: Total system cost variations for lower consumption of solvent with L-DAC (left) and S-DAC (right)

Both represent minimal effects to the system cost with the highest increase being 1.0 % in the NN-2000-NoIm scenario for S-DAC. The corresponding carbon capture graphs associated with the costs are included in Appendix B as they show similar effects to that of the pessimistic consumption case but to a lesser extent.

Primary energy consumption

Since the effects in the optimistic case are small, as observed in the system cost analysis section, only the results for the pessimistic case are presented here. The impacts of solvents and sorbents production on the use of primary energy in the system are represented in Figures 4.11 and 4.12 for the cases when only L-DAC and only S-DAC are present in the system, respectively.

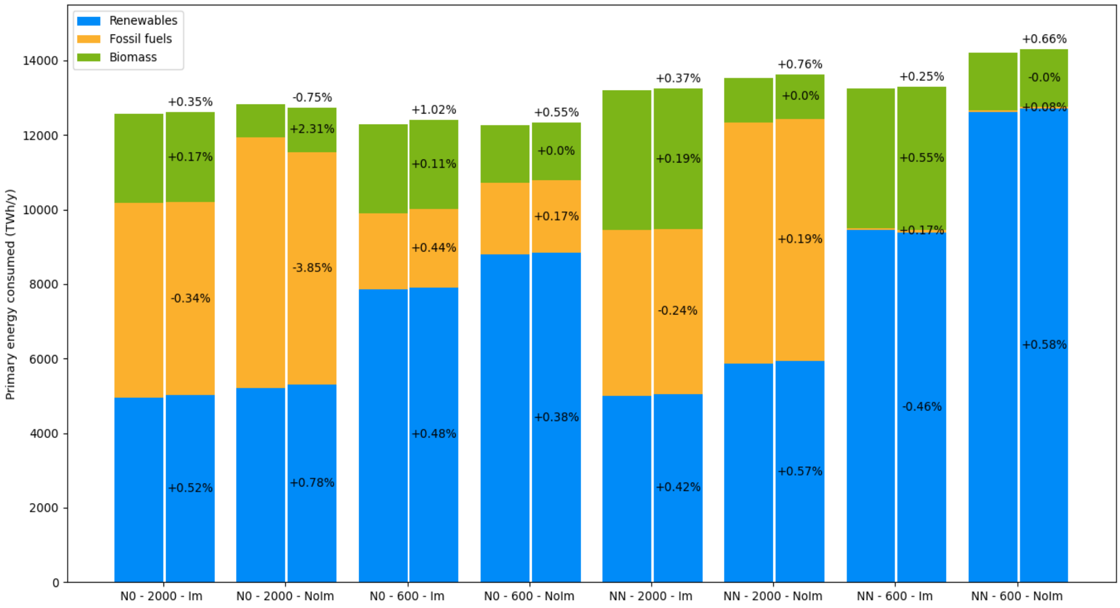

Figure 4.11: Primary energy variations due to solvents implementation compared to the base case, with the higher solvent consumption and only L-DAC

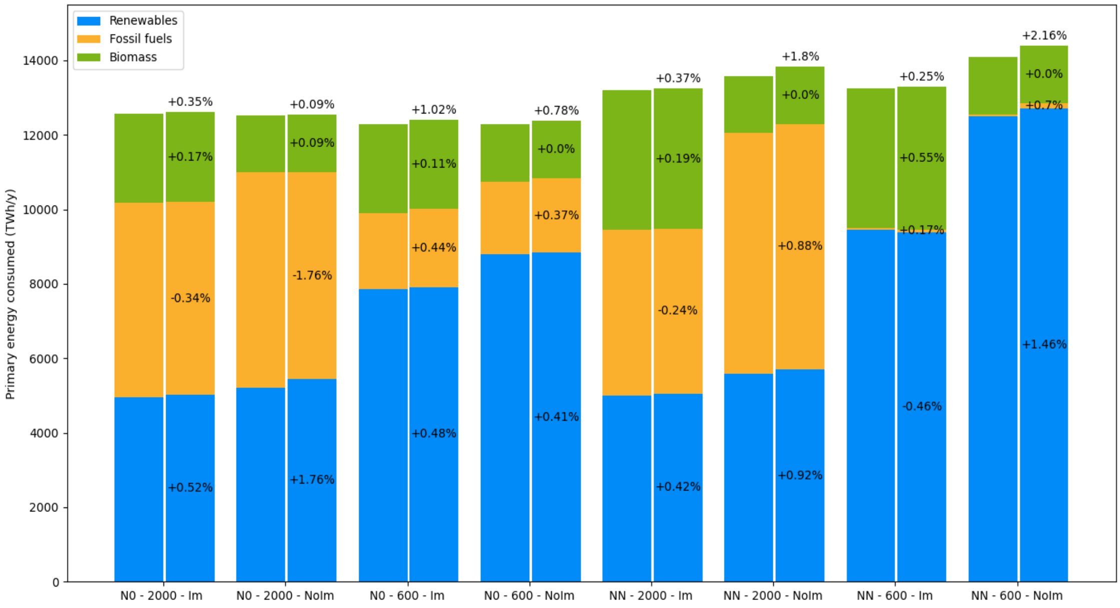

Figure 4.12: Primary energy variations due to solvents implementation compared to the base case, with the higher sorbent consumption and only S-DAC

For both cases, the general trend is an increase in use of primary energy, this being more pronounced in the only-S-DAC case similarly as for the cost impacts. The primary energy increase presents different variations in each of the three primary energies in the system, showing that different technologies are on the margin in each case. However in most scenarios, fossil fuels are phased out in favour of greener energies, this being more cost-effective than keeping more expensive CC technologies.

The variations are the largest in the case N0-600-Im for the only-L-DAC system of + 1.0% and in the NN-600-Im scenario for the only-S-DAC system of + 2.2%.

To summarise, an optimistic consumption of solvent results in minimal impacts on the system, whereas a pessimistic consumption implies a total system cost increase of at most + 6.7% and primary energy consumption increase of + 2.2% if solid sorbent is chosen as the dominating DAC technology. Impacts are more limited for the other technologies (L-DAC and post-combustion CC). These variations observed in these figures are due in some cases to part of these technologies being replaced by cheaper alternatives (e.g., pre-combustion or phasing out fossil fuel usage) and in some other cases to the direct additional cost and energy requirements for solvent production when no other alternative exist.

Material requirement

Material requirements and understanding the necessary increases in production based on current supply are also investigated. The chemical requirements for the optimistic and pessimistic cases are shown in Table 4.3. It is also compared to the current global production. The optimistic and pessimistic cases being referred to are those with most and least direct air capture involved with the lower and higher consumption, respectively.

Table 4.3: Material requirement for the lower and the higher solvent consumption. The values are the highest material usage of all 8 scenarios and of either the S-DAC or L-DAC system.

Material requirement (Mt/y)	MEA	KOH	PEI	EO	Ethylene	NH_3
Optimistic case	2	2,1	0,9	1,5	1,3	2,6
Pessimistic case	14,4	27,5	5,4	10,8	8,9	18,6
Current global production	2,46[1] [46]	9[2] [40]	0,014 [46]	31 [76]	225 [77]	240 [78]

1: Global production of all three EAs.
2: For NaOH, the global production is of 82 Mt/y [79]

Compared to Realmonte et al. and Chatterjee and Huang [19, 22], the results obtained turn out to be much lower than what feared, as Figure 4.13 depicts.

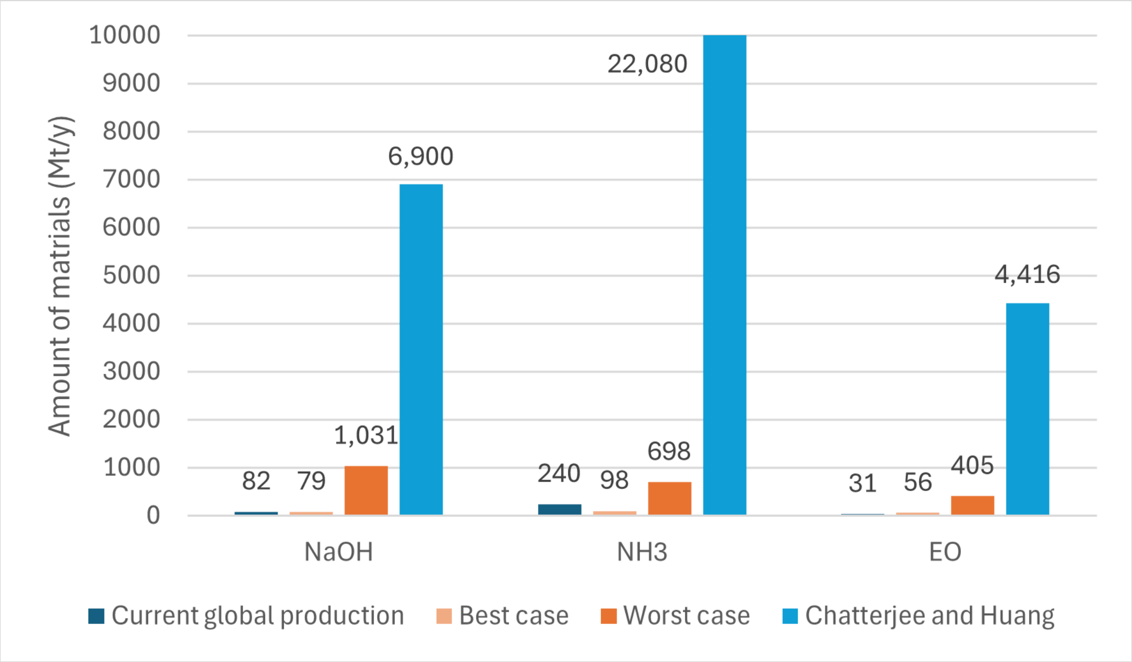

Figure 4.13: Material consumption with this study's assumptions for a DAC scale-up to 30 $GtCO_2$/y

The reasons for these differences are a combination of several factors. First, a much lower solvent consumption for both DAC technologies, from 170-290 t/tCO_2 estimated by Realmonte and co-workers to 0.4-38 and 2.3-14 for L- and S-DAC respectively in this study. Second, for MEA production, a lower consumption of ammonia, from 3.2 to 0.25 t/tMEA. Finally, Realmonte and colleagues assumed a deployment of DAC being at the scale of a 30 Gt of CO_2 captured per year, whereas this study accounts for a much lower need of this technology of at most 0.9 Gt/y (in the NN-2000-NoIm scenario) and for Europe only.

5

Discussion

5.1 Results analysis

Based on the results obtained, it can be observed that the extent of the implications heavily depends on the solvent consumption. If the consumption of solvents are towards the lower ranges as chosen in this study, the impact will be minimal for both cost and energy. Should the solvents require a higher replacement rate, they may have an impact on the cost and energy requirements of the CC technologies. This particularly concerning for S-DAC, where the cost and energy requirement for solvent production results to represent up to 18% and 13% of the total LCOC and life-cycle energy requirement of the technology.

Those implications on the technologies subsequently have repercussions on the whole energy system, especially in terms of cost, with results showing a maximum increase of + 6.7% of the total system cost if S-DAC becomes the main DAC technological choice and + 2.4% if it is L-DAC, compared to neglecting to cost of providing the solvents. The energy requirements for producing those solvents may also need to be taken into account and are estimated to increase the system energy usage by + 2.2% and + 1.0% in the most pessimistic case.

The highest increase in total system cost occurs in the NN-2000-NoIm scenario, regardless whether L-DAC or S-DAC is chosen as the main DAC technology. This is due to the scenario having restricted biomass availability, leaving DAC as the only scalable CDR option in order to meet a constraining carbon emissions target (-10% compared to pre-industrial levels, -461 MtCO2/y). The amount of DAC used after solvent production implementation in fact barely changes (-0.9%). DAC being the most expensive technology, as LCOC calculations proved, the system cost rises consequently. Besides, this scenario, while being constraining, is probable to happen in the future which comforts in the relevance of the concern regarding solvents production.
In the net zero scenarios, it was observed that the DAC decreased by as much as 18% for L-DAC and 8.7 % for S-DAC. The decrease in fossil fuel use seen in scenario N0-2000-NoIm also shows that fossil fuel together with DAC was the more cost-optimal option before solvent were accounted for. The increase in direct air capture being used with higher sequestration follows findings by Millinger et. al [11].

This shows that solvents and sorbents production therefore affects the cost-effectiveness of CCS for mitigating GHG emissions and would deserve more attention to details by energy system models.

With most energy system models currently choosing S-DAC as their preferred DAC technology, it may be of interest to assess the impact that solid sorbents could have on its cost. While a lower consumption has minimal effects, it can also be observed the consequences of a higher consumption increases the LCOC from 3.7% to 22.7% compared to the base case. The trade-off between the higher regeneration temperature required for L-DAC versus a more complex solvent is interesting for modellers to assess when choosing type of DAC to implement.

5.2 Uncertainties of future technologies

Assessing the cost and development of new technologies such as DAC gives way for a large amount of uncertainty regarding input parameters. Solid sorbents may have a big breakthrough during this time or the disadvantages with L-DAC's high temperature for regeneration may have been simplified. The effect on ways of producing the necessary solvents may also change from those assumed in this study based on current available technology.

First of all, a lot of uncertainty remain on the consumption of solvent or sorbent that will be required to operate the CC technologies. Although this is less the case for the well-established post-combustion capture, high differences remain for both DAC technologies. As aforementioned, this consumption of solvent or sorbent comes from how it degrades during operation, and this has still not been fully understood today. DAC being a fairly novel technology, with so far a TRL of 6-7, and the candidate chemicals having still a lot of research on them, it is hard to estimate how they will perform when the CDR technology is deployed at a large scale. This will, nonetheless, greatly affect the operational costs for S-DAC, as this study highlights.

Similarly, the choice of CCS technology used in power plants and process industry might change drastically in the future. Technologies such as oxy-fuel combustion continuously develop and with technologies such as chemical-looping combustion emerging, the problems of solvents may not affect the power production industry to the extent assumed in this study. One of the biggest advantages of using post combustion capture is the ease to introduce it in already existing processes. However, modelling this far future, as done in this work, allows for newer technological usages, since most current production capacities will have reached their end of life by then. Besides, the effect of MEA for use in PCC did not present a significant impact on the energy system and mostly affected its competitiveness compared to pre-combustion technologies.

The choice of solvents studied in this model were dependent on available data. Many different sorbents are proposed for use. Some proprietary sorbents may perform much better than PEI and MEA that were considered in this study. Without the necessary production data, this was not possible to be considered.

Finally, uncertainties exist for how production of certain chemicals such as HVC. Renewable options such as the use of ethanol and Methanol-to-olefin may become more of interest instead of the conventional steam cracking done today. As these renewable methods continuously develop, they may become more efficient and cheaper than the use of oil. An alternative is the introduction of electric steam cracking which would lower the required amount of naphtha needed in the process.

Comparing chemical prices calculated with market prices show similarities gave an indication of how realistic results obtained were. Although some simplifications were made, such as no profit margin or engineering and procurement costs for some processes were included in the cost of production, the costs estimated were overall comparable to market prices. The biggest differences were observed for KOH and PEI. Due to the low amount of PEI currently available on market, it was instead compared to another commercial solid sorbent, Lewatit VP OC 1065. The solid sorbent cost is on the lower end that was estimated by Sievert et. al [75]. It was also lower than costs attributed by the National Encyclopedic of Science, Engineering and Medicine [42].

Other limitations in this study are that considerations were not taken into account for learning rates of the chemical processes. This resulted in a potentially higher cost of solid sorbent than what will be achieved in the future despite it being on the cheaper side based on literature. As the society moves away from fossil fuels, considerations may also need to consider renewable alternatives instead of for example steam cracking being used.

Another aspect that was not considered in this study is the potential advantages and disadvantages of geographical placements between L-DAC and S-DAC. Factors such as climate can have an impact on direct air capture performance. Factors such as humidity and temperature have an effect on the energy consumption and water usage required for the direct air capture. This could also potentially allow for having both L-DAC and S-DAC in the energy system instead of one or the other as this study required. In the case of solid sorbents, a colder and more humid climate seem preferential [80]. For liquid direct air capture it also prefers high humidity but instead a higher ambient temperature [81].

This study used 3 different parameters in our scenarios to investigate the different impacts that could happen. Net zero is the current aim but net negative may be required if the net zero target is not reached quick enough therefore makes them potential futures. Restriction of biomass was considered due to its potentially high importance for other sectors. While there is high potential for biomass, it being considered as a main CDR technology user would likely not make the scenario as drastic as chosen here. Direct air capture currently exists as a more expensive option but could find other opportunities with for example policy. The last parameter chosen was sequestration available per year. While Europe has access to a large amount of potential storage, big efforts are needed to realise them into usable storage.

5.3 Future challenges of CCS

Material requirements and scale up of chemicals production

In terms of material requirement, the largest increase in production would be needed for PEI that would have to increase to industrial scale from its current smaller scale production based on the choice of solid sorbent used in this study. However, this remains feasible as PEI is part of the well-known family of polymeric materials [46]. If ethanolamines were to be used in both post combustion and as part of solid sorbents, they would also demand an increased amount of investment to meet necessary needs. Ethylene, ammonia and ethylene oxide all show a smaller percentage of total current supply and may therefore be considered simpler to meet demands even in the worst case scenario. However, increasing production capacity of, for example, ethylene could benefit from more renewable pathways being pursued instead of the conventional steam cracking. Finally, KOH and NaOH should be fairly easy to scale-up, as supported by literacy findings [34]. This is because they come from KCl and NaCl salts that are very abundant on Earth, and rely on the Chlor-Alkali process which is a common industrial process, an electrolysis of brine.

There exists many different companies investigating the potential of S-DAC which could also shift the burden of production among more processes. This would decrease the required capacity of production that could be required each year to achieve the necessary GHG emission goals. Increased production of KOH is easier to achieve with only the chlor-alkali process being required. On the other hand it may be more difficult for MEA and AS sorbent as it requires increased production of more chemicals. Benefits with regards to H_2 production is also an additional advantage of increasing its production.

The L-DAC / S-DAC trade-off

Based on results, S-DAC has a larger disadvantage when it comes to solvent production compared to L-DAC, as was shown in Section 4.1.3. On the other hand, the main disadvantage of using L-DAC is its high temperature required for regeneration. The heat required may therefore need its own heat source based on either natural/bio gas (as assumed in this study), hydrogen or, more hardly, electricity. Conversely, S-DAC could use existing waste heat from industry with the addition of a heat pump if required. Papapetrou et. al. estimated the waste heat potential in the European Union to be 100 TWh of low temperature ($< 200\ ^oC$) [82]. This was estimated to account for 37 Mt of S-DAC capture in the best case scenario [3]. Each scenario using S-DAC includes between 100 and 900 Mt of CO_2 capture based on the results obtained meaning further investments would be required to account for this extra heat required.

The use of S-DAC was estimated to be cheaper comparatively to L-DAC by Fasihi et. al [83]. However, based on cost breakdown assessed by Ozkan et. al, the adsorbent cost can have a large impact on this and results in L-DAC being a cheaper alternative in some instances [84]. Young et al. similarly estimate that L-DAC could less costly if implemented at a large scale, although high uncertainties remain [3]. Finally, from an life-cycle perspective, Madhu et al. came to the conclusion that L-DAC has a higher environmental footprint than S-DAC due mainly to this high-temperature heat requirements and the displacement of substantial mass flows in the process. L-DAC would also consume significant amounts of water and require large areas of land for being implemented, unlike S-DAC [43]. These trade-off are worth further consideration for energy system models which have mainly used S-DAC.

Another consideration is investigating the potential of L-DAC and S-DAC coexisting. This will decrease any potential burden placed on production of chemicals and requirements on the energy system. Factors such as climate, water usage (in the case of L-DAC) and decrease in fossil fuel use could all add increased dimensions to the choice between the two technologies and preferable geographical placements. Utilizing potential waste heat in smaller scale could also benefit S-DAC. This would be of interest to further investigate.

6

Conclusion

To summarize, this study investigated the potential impacts concerning costs and energy that solvent production can have on the energy system. The solvents considered were MEA for post-combustion capture, KOH for L-DAC and a PEI-Silica solid sorbent for S-DAC. Results showed that the sorbent was the most expensive to produce and KOH the cheapest, which agrees with literary findings. The extent to which this affects the energy system is strongly determined by the consumption of solvents and sorbents. The comparison is made between a system where solvent and sorbent production is outside of the system boundaries, meaning that they are provided at no additional cost,and a system where this is accounted for. With a pessimistic value of consumption, the system cost increased by a maximum of 2.3% if L-DAC is chosen as the only DAC technology and 6.7% if S-DAC takes this role. Both are used at a capacity of 880 and 800 Mt/y, respectively. Simultaneously, the system primary energy consumption rose up to a maximum of 2.2% due to production of said solvents in a scenario including post-combustion CC and S-DAC. Should the efficiency of the solvents continuously improve, the production will likely not be considered an issue for cost and energy based on results obtained, since an optimistic solvent consumption led to system cost increasing by a maximum amount of 0.1 % for an only-L-DAC system and 1.0% for an only-S-DAC one.

Besides, should carbon capture be deployed at a large scale, the production capacities required to supply solvents and sorbents will have to scale up. Our results show that if post-combustion CC is used at a capacity of 900 Mt/y, this capacity will have to increase by up to seven times compared to current global production for MEA, and that is just considering Europe. For novel chemicals such as PEI, a new industry will have to be created since this chemical compound does not have any industrial production facility to date. Nonetheless, capacity scale-up and supplying the precursor material for production of the chemicals considered in this work should present little challenge based on previous history with similar materials.

Consequently, if a high consumption is required, especially concerning solid sorbents, it will need further research to assess the extent of its effects on the energy system. Despite this, S-DAC may have advantages compared to L-DAC with the possibility for smaller scale capture as shown with operating plants made by Climeworks. The lower temperature heat required to regenerate solid sorbents is also much easier to produce and may create more opportunities to use with waste heat for regeneration. This could make S-DAC more appealing despite potentially having a higher capital cost.

For energy system modellers, understanding parameters of solvents in deciding sources used may be valuable, especially as most energy system models currently assume the use of S-DAC that shows to be the most affected by sorbents. For example, lifetime of sorbent can contribute to large differences in costs and may therefore need further consideration. Certain literature explicitly state the share that sorbents will have on the CAPEX while some make it unclear. Cost estimations of solid sorbents also vary significantly based on assumptions used. As a result of these very high uncertainties that lie in carbon capture technologies, especially direct air capture, it is also hard to accurately assess what consequences these technologies will have on the energy system.

Bibliography

[1] D. W. Keith, G. Holmes, D. St. Angelo, and K. Heidel, “A process for capturing co2 from the atmosphere,” *Joule*, vol. 2, no. 8, pp. 1573–1594, 2018. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S2542435118302253

[2] United Nations Environment Programme (UNEP), *The Emissions Gap Report 2017*. Nairobi: United Nations Environment Programme (UNEP), 2017.

[3] J. Young, N. McQueen, C. Charalambous, S. Foteinis, O. Hawrot, M. Ojeda, H. Pilorgé, J. Andresen, P. Psarras, P. Renforth *et al.*, “The cost of direct air capture and storage can be reduced via strategic deployment but is unlikely to fall below stated cost targets,” *One Earth*, vol. 6, no. 7, pp. 899–917, 2023.

[4] Carbon Engineering, “Our technology,” 2024, accessed: 2024-06-05. [Online]. Available: https://carbonengineering.com/our-technology/

[5] C. Beuttler, L. Charles, and J. Wurzbacher, “The role of direct air capture in mitigation of anthropogenic greenhouse gas emissions,” *Frontiers in Climate*, vol. 1, Nov 2019.

[6] M. Ernst, J.-P. Melder, F. I. Berger, and C. Koch, *Ethanolamines and Propanolamines*. John Wiley & Sons, Ltd, 2022, pp. 1–30. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/14356007.a10_001.pub2

[7] T. Brown, L. Zeyen, M. Victoria, F. Hoffmann, and J. Hoersch, “Eur: A sector-coupled open optimisation model of the european energy system.” [Online]. Available: https://pypsa-eur.readthedocs.io/en/latest/

[8] European Commission, “Consequences of climate change.” [Online]. Available: https://climate.ec.europa.eu/climate-change/consequences-climate-change_en

[9] United Nations, “Net zero coalition.” [Online]. Available: https://www.un.org/en/climatechange/net-zero-coalition#:~:text=Yes%2C%20a%20growing%20coalition%20of,about%2088%25%20of%20global%20emissions.

[10] IPCC, “Carbon dioxide removal.” [Online]. Available: https://www.ipcc.ch/report/ar6/wg3/downloads/outreach/IPCC_AR6_WGIII_Factsheet_CDR.pdf

[11] M. Millinger, F. Hedenus, L. Reichenberg, E. Zeyen, F. Neumann, and G. Berndes, “Diversity of biomass usage pathways to achieve emissions targets in the european energy system,” July 2023. [Online]. Available: http://dx.doi.org/10.21203/rs.3.rs-3097648/v1

[12] IRENA, “Decarbonising hard-to-abate sectors with renewables: Perspectives for the g7,” Apr 2024. [Online]. Available: https://www.irena.org/Publications/2024/Apr/Decarbonising-hard-to-abate-sectors-with-renewables-Perspecti

ves-for-the-G7#:~:text=Sectors%20that%20are%20particularly%20hard,fifth%20of%20total%20CO2%20emissions.

[13] J. Bednar, R. Hoglund, K. Mollersten, M. Obersteiner, and E. Tamme, *The role of carbon dioxide removal in contributing to the long-term goal of the Paris Agreement*, 12 2023.

[14] Reverse Carbon, "Carbon dioxde removal." [Online]. Available: https://www.reversecarbon.com/carbon-dioxide-removal

[15] Beccs Stockholm, "Carbon dioxide removal." [Online]. Available: https://beccs.se/cdr-carbon-dioxide-removal/#:~:text=When%20forest%20residues%20are%20used,released%20back%20to%20the%20atmosphere.

[16] IEA, "Ccus – analysis." [Online]. Available: https://www.iea.org/reports/ccus

[17] Carbonfuture. [Online]. Available: https://www.carbonfuture.earth/cdr-insight-technologies/direct-air-carbon-capture-and-storage-daccs

[18] M. Shahbaz, A. AlNouss, I. Ghiat, G. Mckay, H. Mackey, S. Elkhalifa, and T. Al-Ansari, "A comprehensive review of biomass based thermochemical conversion technologies integrated with co2 capture and utilisation within beccs networks," *Resources, Conservation and Recycling*, vol. 173, p. 105734, 2021. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0921344921003438

[19] G. Realmonte, L. Drouet, A. Gambhir, J. Glynn, A. Hawkes, A. C. Köberle, and M. Tavoni, "An inter-model assessment of the role of direct air capture in deep mitigation pathways," *Nature communications*, vol. 10, no. 1, p. 3277, 2019.

[20] B. Pickering, F. Lombardi, and S. Pfenninger, "Diversity of options to eliminate fossil fuels and reach carbon neutrality across the entire european energy system," *Joule*, vol. 6, no. 6, pp. 1253–1276, 2022. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S2542435122002367

[21] M. Ram, D. Bogdanov, A. Aghahosseini, A. Gulagi, O. Solomon, M. Child, U. Caldera, K. Sadovskaia, F. Farfan Orozco, L. Noel, M. Fasihi, S. Khalili, and H.-J. Fell, "Global energy system based on 100% renewable energy: Energy transition in europe across power, heat, transport and desalination sectors," 12 2018.

[22] S. Chatterjee and K.-W. Huang, "Unrealistic energy and materials requirement for direct air capture in deep mitigation pathways," *Nature communications*, vol. 11, no. 1, p. 3287, 2020.

[23] P. Raffaini and L. Manfredi, "Chapter 15 - project management," in *Endorobotics*, L. Manfredi, Ed. Academic Press, 2022, pp. 337–358. [Online]. Available: https://www.sciencedirect.com/science/article/pii/B9780128217504000153

[24] J. A. Garcia, M. Villen-Guzman, J. M. Rodriguez-Maroto, and J. M. Paz-Garcia, "Technical analysis of co2 capture pathways and technologies," *Journal of Environmental Chemical Engineering*, vol. 10, no. 5, p. 108470, 2022. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S2213343722013434

[25] Global CCS Institute, "Co2 capture technologies: Post combustion capture (pcc)," 2012, accessed: 2024-06-13. [Online]. Available: https:

//www.globalccsinstitute.com/archive/hub/publications/29721/co2-capture-technologies-pcc.pdf

[26] D. Group. (2021, June) Drax and mitsubishi heavy industries sign pioneering deal to deliver the world's largest carbon capture power project. Accessed: 2024-06-13. [Online]. Available: https://www.drax.com/press_release/drax-and-mitsubishi-heavy-industries-sign-pioneering-deal-to-deliver-the-worlds-largest-carbon-capture-power-project/

[27] S. Yun, S.-Y. Oh, and J.-K. Kim, "Techno-economic assessment of absorption-based co2 capture process based on novel solvent for coal-fired power plant," *Applied Energy*, vol. 268, p. 114933, 2020. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0306261920304451

[28] CATACARB, "Catacarb technology to help stockholm exergi combat climate change," 2023, accessed: 2024-06-13. [Online]. Available: https://catacarb.com/about/stockholm-exergi/

[29] V. Buvik, K. K. Høisæter, S. J. Vevelstad, and H. K. Knuutila, "A review of degradation and emissions in post-combustion co2 capture pilot plants," *International Journal of Greenhouse Gas Control*, vol. 106, p. 103246, 2021. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S175058362030671X

[30] B. R. Strazisar, R. R. Anderson, and C. M. White, "Degradation pathways for monoethanolamine in a co2 capture facility," *Energy & Fuels*, vol. 17, no. 4, pp. 1034–1039, 2003. [Online]. Available: https://doi.org/10.1021/ef020272i

[31] J. Davison, P. Freund, and A. Smith, "Putting carbon back into the ground," IEA Greenhouse Gas R&D Programme, Cheltenham, Technical Report, 2001.

[32] S. Yang, Y. Qian, and S. Yang, "Development of a full co2 capture process based on the rectisol wash technology," *Industrial & Engineering Chemistry Research*, vol. 55, no. 21, pp. 6186–6193, 2016. [Online]. Available: https://doi.org/10.1021/acs.iecr.6b00747

[33] S. Duval-Dachary, S. Beauchet, D. Lorne, T. Salou, A. Helias, and A. Pastor, "Life cycle assessment of bioenergy with carbon capture and storage systems: Critical review of life cycle inventories," *Renewable and Sustainable Energy Reviews*, vol. 183, p. 113415, 2023. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S1364032123002721

[34] K. Madhu, S. Pauliuk, S. Dhathri, and F. Creutzig, "Understanding environmental trade-offs and resource demand of direct air capture technologies through comparative life-cycle assessment," *Nature Energy*, vol. 6, no. 11, pp. 1035–1044, 2021.

[35] K. Lebling, H. Leslie-Bole, Z. Byrum, and L. Bridgwater, "6 things to know about direct air capture," May 2022. [Online]. Available: https://www.wri.org/insights/direct-air-capture-resource-considerations-and-costs-carbon-removal

[36] Climeworks, "Orca the first large-scale plant." [Online]. Available: https://climeworks.com/plant-orca

[37] "Mammoth: our newest facility." [Online]. Available: https://climeworks.com/plant-mammoth

[38] “History in the making: experience the ground-breaking moment for world’s largest direct air capture facility,” Jun 2023. [Online]. Available: https://carbonengineering.com/news-updates/direct-air-capture-groundbreaking/

[39] M. Mostafa, C. Antonicelli, C. Varela, D. Barletta, and E. Zondervan, “Capturing co2 from the atmosphere: Design and analysis of a large-scale dac facility,” *Carbon Capture Science & Technology*, vol. 4, p. 100060, 2022. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S2772656822000318

[40] P. Webb, H. Muslemani, M. Fulton, and N. Curson, Dec 2023. [Online]. Available: https://www.oxfordenergy.org/wpcms/wp-content/uploads/2023/12/CM07-Scaling-Direct-Air-Capture-DAC-technology.pdf

[41] A. Sodiq, Y. Abdullatif, B. Aissa, A. Ostovar, N. Nassar, M. El-Naas, and A. Amhamed, “A review on progress made in direct air capture of co2,” *Environmental Technology & Innovation*, vol. 29, p. 102991, 2023. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S235218642200414X

[42] N. A. of Sciences Engineering and Medicine, *Negative Emissions Technologies and Reliable Sequestration: A Research Agenda.* Washington DC: The National Academies Press, 2019. [Online]. Available: https://nap.nationalacademies.org/catalog/25259/negative-emissions-technologies-and-reliable-sequestration-a-research-agenda

[43] A. Bergman and A. Rinberg, “The case for carbon dioxide removal: From science to justice,” in *CDR Primer*, J. Wilcox, B. Kolosz, and J. Freeman, Eds. CDR Primer, 2021.

[44] E. Wang, R. Navik, Y. Miao, Q. Gao, D. Izikowitz, L. Chen, and J. Li, “Reviewing direct air capture startups and emerging technologies,” *Cell Reports Physical Science*, vol. 5, no. 2, p. 101791, 2024. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S2666386424000110

[45] E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas, and C. W. Jones, “Direct capture of co2 from ambient air,” *Chemical Reviews*, vol. 116, no. 19, pp. 11 840–11 876, 2016, pMID: 27560307. [Online]. Available: https://doi.org/10.1021/acs.chemrev.6b00173

[46] S. Deutz and A. Bardow, “Life-cycle assessment of an industrial direct air capture process based on temperature–vacuum swing adsorption,” *Nat Energy*, vol. 6, pp. 203–213, 2021. [Online]. Available: https://doi.org/10.1038/s41560-020-00771-9

[47] H. Azarabadi and K. S. Lackner, “A sorbent-focused techno-economic analysis of direct air capture,” *Applied Energy*, vol. 250, pp. 959–975, 2019. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0306261919306385

[48] M. Albertz, S. A. Stewart, and R. Goteti, “Perspectives on geologic carbon storage,” *Frontiers in Energy Research*, vol. 10, 2023. [Online]. Available: https://www.frontiersin.org/articles/10.3389/fenrg.2022.1071735

[49] European Commission, “Why do we need carbon capture, use and storage?” Dec 2021. [Online]. Available: https://climate.ec.europa.eu/eu-action/carbon

-capture-use-and-storage/overview_en#ensuring-safe-and-environmentally-sound-ccs-and-ccu

[50] D. E. Agency, “Technology data for renewable fuels, or energy carrier generation and conversion,” Danish Energy Agency, Tech. Rep., first publication 2017, lastest update 2024.

[51] A. H.-J. et al., “Life cycle inventories of chemicals. ecoinvent report no. 8, v2.0.” EMPA Dübendorf, Swiss Centre for Life Cycle Inventories, Dübendorf, CH, from www.ecoinvent.org., Tech. Rep., 2007.

[52] S. W. Kim, Y. T. Kim, Y. F. Tsang, and J. Lee, “Sustainable ethylene production: Recovery from plastic waste via thermochemical processes,” *Science of The Total Environment*, vol. 903, p. 166789, 2023. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0048969723054141

[53] T. Ren, M. Patel, and K. Blok, “Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes,” *Energy*, vol. 31, no. 4, pp. 425–451, 2006. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0360544205000745

[54] D. A. M. Bazzanella, D. F. Ausfelder, and DECHEMA, Jun 2017. [Online]. Available: https://dechema.de/dechema_media/Downloads/Positionspapiere/Technology_study_Low_carbon_energy_and_feedstock_for_the_European_chemical_industry.pdf

[55] Statista, “Ethylene oxide market volume worldwide 2022-2030,” 2024, accessed: 2024-06-05. [Online]. Available: https://www.statista.com/statistics/1245260/ethylene-oxide-market-volume-worldwide/

[56] J. L. Pellegrino, L. Sousa, and H. Kenchington, “Energy and environmental profile of the u.s. chemical ...” May 2000. [Online]. Available: https://www1.eere.energy.gov/manufacturing/resources/chemicals/pdfs/profile_full.pdf

[57] Euro-Chlor, “Electrolysis and production costs,” Nov 2023. [Online]. Available: https://www.eurochlor.org/wp-content/uploads/2018/06/12-Electrolysis-production-costs-November-2023.pdf

[58] Intratec, “Calcum carbonate price.” [Online]. Available: https://www.intratec.us/chemical-markets/calcium-carbonate-price

[59] U. Steuerle and R. Feuerhake, *Aziridines.* John Wiley & Sons, Ltd, 2006. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/14356007.a03_239.pub2

[60] H. Weir, E. Sanchez-Fernandez, C. Charalambous, J. Ros, J. G. M.-S. Monteiro, E. Skylogianni, G. Wiechers, P. Moser, M. van der Spek, and S. Garcia, “Impact of high capture rates and solvent and emission management strategies on the costs of full-scale post-combustion co2 capture plants using long-term pilot plant data,” *International Journal of Greenhouse Gas Control*, vol. 126, p. 103914, 2023. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S1750583623000841

[61] H. Tran and E. Vakkilainen, “The kraft chemcial recovery process,” 02 2016.

[62] R. Socolow, M. Desmond, R. Aines, J. Blackstock, O. Bolland, T. Kaarsberg, N. Lewis, M. Mazzotti, A. Pfeffer, K. Sawyer, J. Siirola, B. Smit, and J. Wilcox, *Direct Air Capture of CO2 with Chemicals: A Technology Assessment for the APS Panel on Public Affairs*, 01 2011.

[63] L.-P. D. V. e. a. Qiu, Y., “Environmental trade-offs of direct air capture technologies in climate change mitigation toward 2100,” *Nature Communications*, vol. 13, p. 3635, 2022.

[64] D. Liu, Z. Lin, W. An, R. An, and H. Bie, “Simulation and energy consumption evaluation of reactive distillation process for ethanolamine production,” *Chemical Engineering and Processing - Process Intensification*, vol. 153, p. 107930, 2020. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0255270120303871

[65] D. Devaraja and A. A. Kiss, “Novel intensified process for ethanolamines production using reactive distillation and dividing-wall column technologies,” *Chemical Engineering and Processing - Process Intensification*, vol. 179, p. 109073, 2022. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0255270122002835

[66] M. Ghanta, T. Ruddy, D. Fahey, D. Busch, and B. Subramaniam, “Is the liquid-phase h2o2-based ethylene oxide process more economical and greener than the gas-phase o2-based silver-catalyzed process?” *Industrial & Engineering Chemistry Research*, vol. 52, no. 1, pp. 18–29, 2013. [Online]. Available: https://doi.org/10.1021/ie301601y

[67] PlasticsEurope, “Plasticseurope recommendation on steam cracker allocation,” Sep 2017. [Online]. Available: https://plasticseurope.org/wp-content/uploads/2021/12/PlasticsEurope_recommendation_on_Steam_Cracker_allocation-_Juillet_2018.pdf

[68] K. Li, J. Jianguo, S. Tian, F. Yan, and X. Chen, “Polyethyleneimine–nano silica composites: A low-cost and promising adsorbent for co2 capture,” *Journal of Materials Chemistry A*, vol. 3, p. 2166–2175, 11 2014.

[69] K. Wang, H. Shang, L. Li, X. Yan, Z. Yan, C. Liu, and Q. Zha, “Efficient co2 capture on low-cost silica gel modified by polyethyleneimine,” *Journal of Natural Gas Chemistry*, vol. 21, no. 3, pp. 319–323, 2012. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S100399531160371X

[70] F. Neumann, E. Zeyen, M. Victoria, and T. Brown, “The potential role of a hydrogen network in europe,” pp. 1–25, 2023.

[71] Statista, “Monthly price of ethylene worldwide from january 2020 to october 2022,” 2023, accessed: 2024-06-06. [Online]. Available: https://www.statista.com/statistics/1318102/monthly-price-ethylene-worldwide/

[72] Intratec, “Ethylene oxide prices,” 2019, accessed: 2024-06-06. [Online]. Available: https://www.intratec.us/chemical-markets/ethylene-oxide-price

[73] ——, “Monoethanolamine price,” 2019, accessed: 2024-06-06. [Online]. Available: https://www.intratec.us/chemical-markets/monoethanolamine-price

[74] ——, “Potassium hydroxide prices,” 2019, accessed: 2024-06-06. [Online]. Available: https://www.intratec.us/chemical-markets/potassium-hydroxide-price

[75] K. Sievert, T. S. Schmidt, and B. Steffen, “Considering technology characteristics to project future costs of direct air capture,” *Joule*, vol. 8, no. 4, pp. 979–999, 2024. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S2542435124000606

[76] Statista, "Ethylene oxide market volume worldwide 2022-2030," 2023, accessed: 2024-06-06. [Online]. Available: https://www.statista.com/statistics/1245260/ethylene-oxide-market-volume-worldwide/

[77] ——, "Global ethylene production capacity 2018-2023," 2023, accessed: 2024-06-06. [Online]. Available: https://www.statista.com/statistics/1067372/global-ethylene-production-capacity/

[78] G. Data, "Ammonia market analysis," 2023, accessed: 2024-06-06. [Online]. Available: https://www.globaldata.com/store/report/ammonia-market-analysis/

[79] T. Brinkmann, G. Giner-Santonja, F. Schorcht, S. Roudier, and L. Sancho, "Best available techniques (bat) reference document for the production of chlor-alkali," 12 2014.

[80] J. F. Wiegner, A. Grimm, L. Weimann, and M. Gazzani, "Optimal design and operation of solid sorbent direct air capture processes at varying ambient conditions," *Industrial & Engineering Chemistry Research*, vol. 61, no. 34, pp. 12 649–12 667, 2022. [Online]. Available: https://doi.org/10.1021/acs.iecr.2c00681

[81] K. An, A. Farooqui, and S. T. McCoy, "The impact of climate on solvent-based direct air capture systems," *Applied Energy*, vol. 325, p. 119895, 2022. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0306261922011588

[82] M. Papapetrou, G. Kosmadakis, A. Cipollina, U. La Commare, and G. Micale, "Industrial waste heat: Estimation of the technically available resource in the eu per industrial sector, temperature level and country," *Applied Thermal Engineering*, vol. 138, pp. 207–216, 2018. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S1359431117347919

[83] M. Fasihi and O. Efimova, "Techno-economic assessment of co2 direct air capture plants," *Journal of Cleaner Production*, vol. 224, pp. 957–980, 07 2019.

[84] M. Ozkan, S. P. Nayak, A. D. Ruiz, and W. Jiang, "Current status and pillars of direct air capture technologies," *iScience*, vol. 25, no. 4, p. 103990, 2022. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S2589004222002607

7

Supplementary information

Supplementary information consisting of a spreadsheet that contains the entire data collection carried out in this work as well as some of the main calculations about the impacts on the technologies. Can be found at this web address:

`https://zenodo.org/records/13312324?token=eyJhbGciOiJIUzUxMiJ9.eyJpZCI6ImZjMDIyY2Q1LThiMTEtNGI2ZC04ZDNhLTYwZWJmNjU3NGM3YyIsImRhdGEiOnt9LCJyYW5kb20iOiJhNzY5ZTFkOWRlNjJiNTZlNjQzNTE5MjE5ZTM0YmJjNCJ9.fd0ruh6xrBIkCpDcZvr8fo_8gARrbFJ-RkcqXYSDttEp_tBjoqIoR6NqAgq3P-LhwLKixJZP9iXd7TGruPwElw`

A

Appendix 1: S-DAC base model

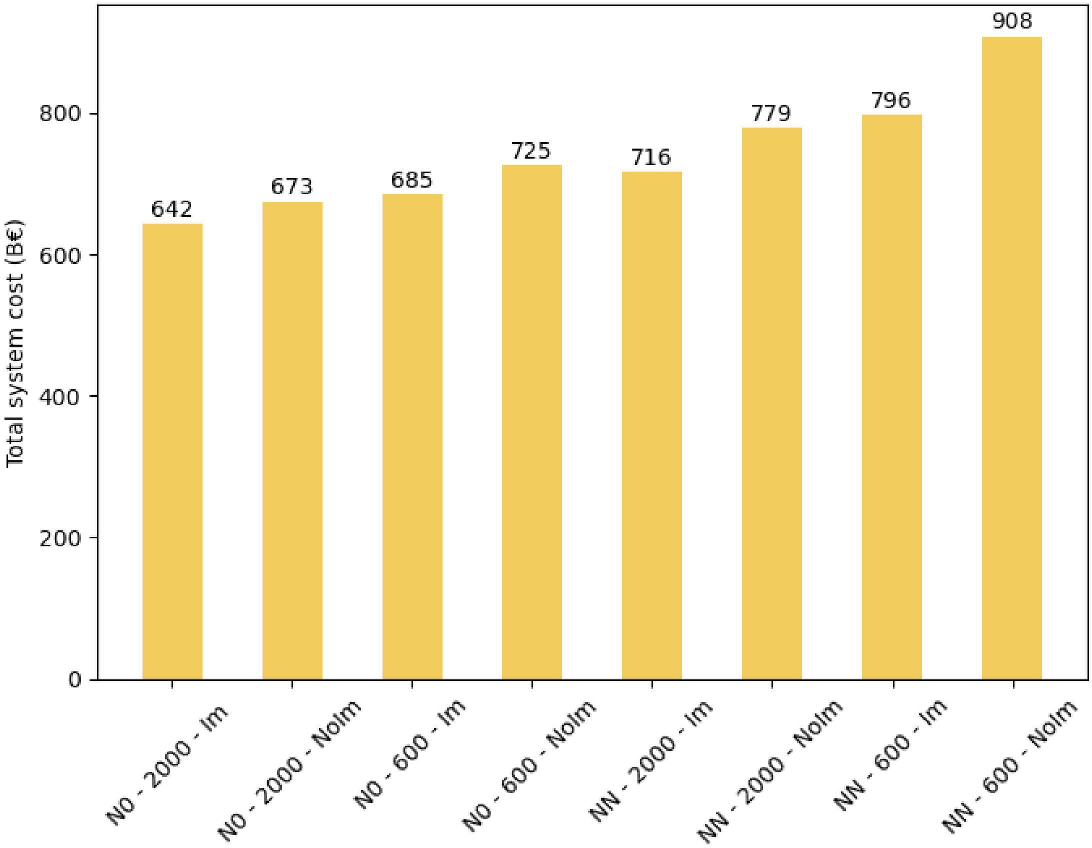

Figure A.1: Total system cost in the base case with only S-DAC

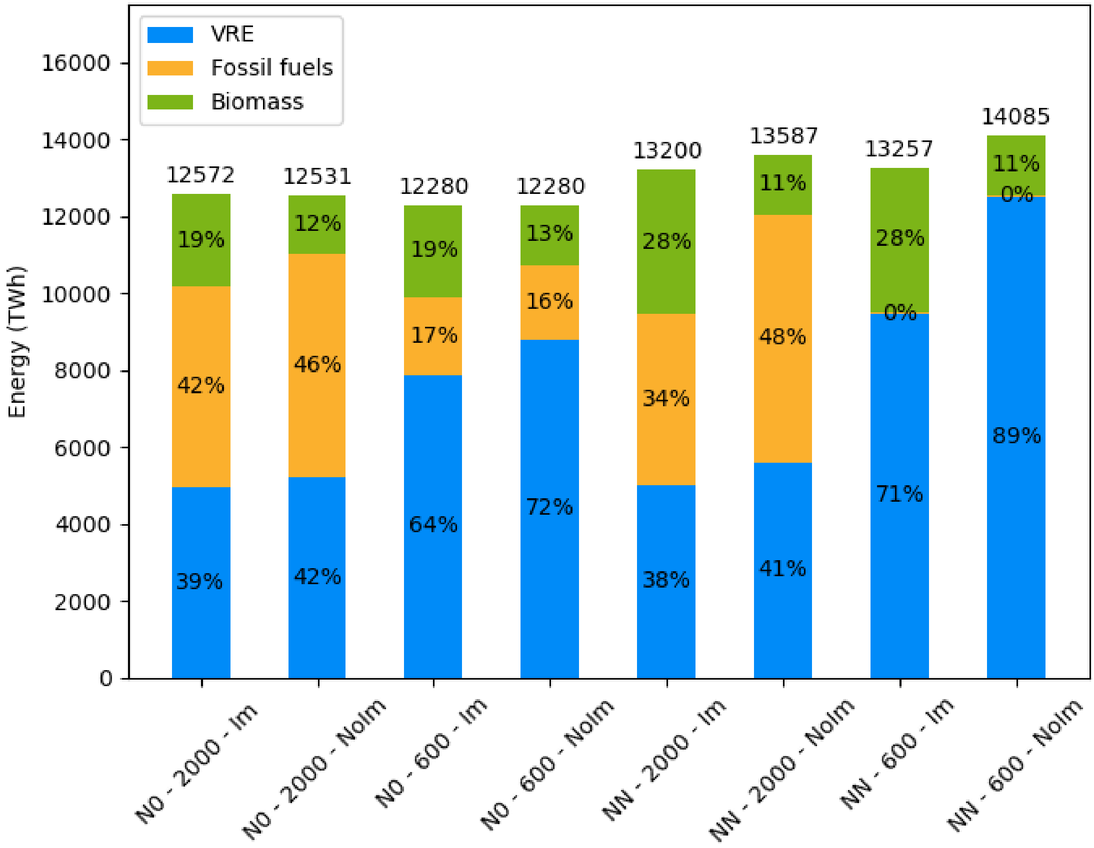

Figure A.2: Primary energy usage in the base case with only S-DAC

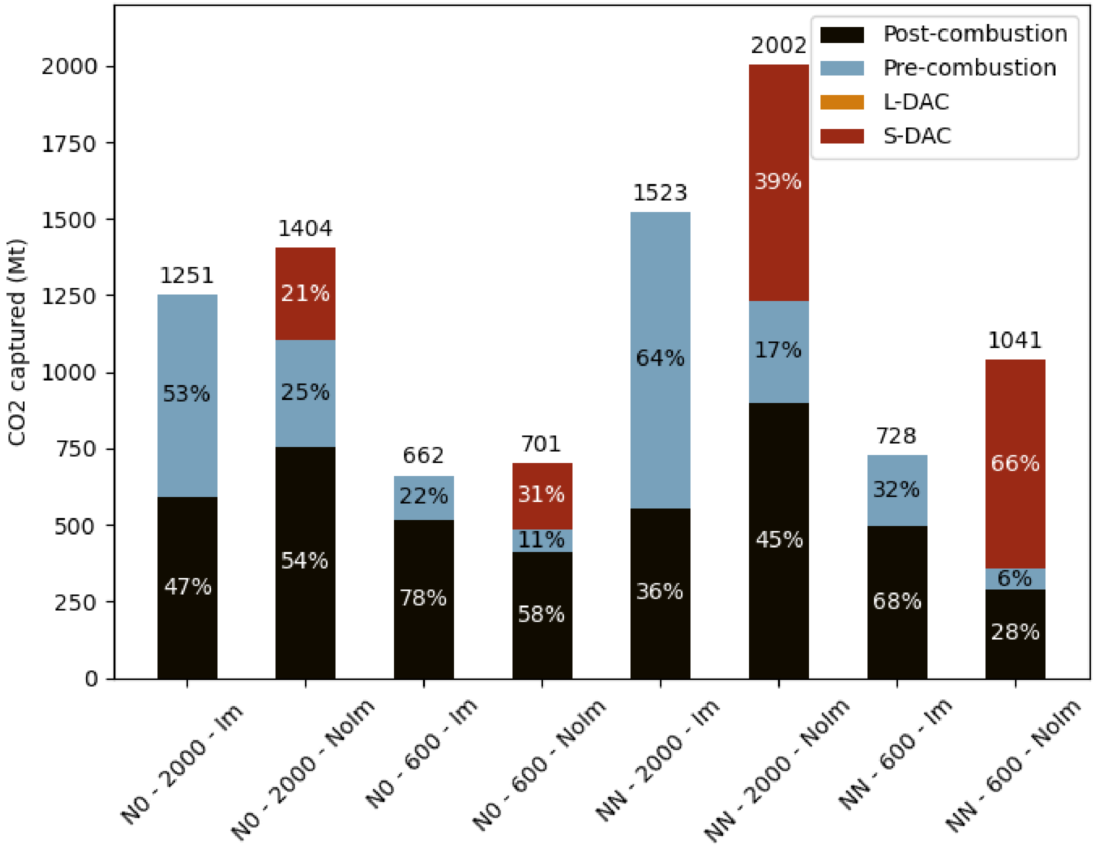

Figure A.3: Carbon captured by each technology in the base case with only S-DAC

B

Appendix 2: Additional graphs from lower consumption of solvents

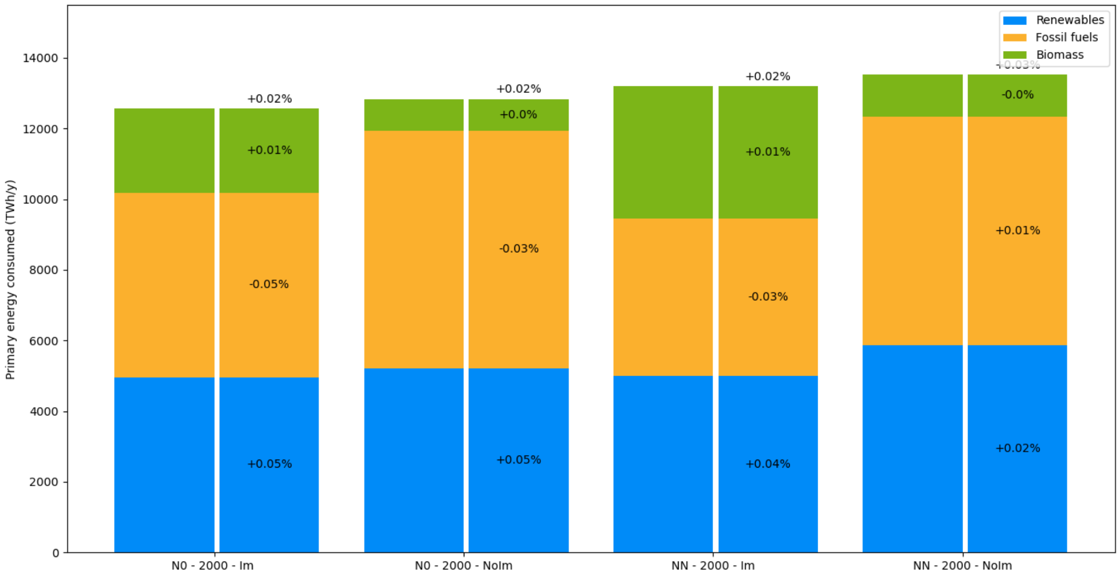

Figure B.1: Energy variations due to solvents implementation compared to the base case, with the lower sorbent consumption and L-DAC

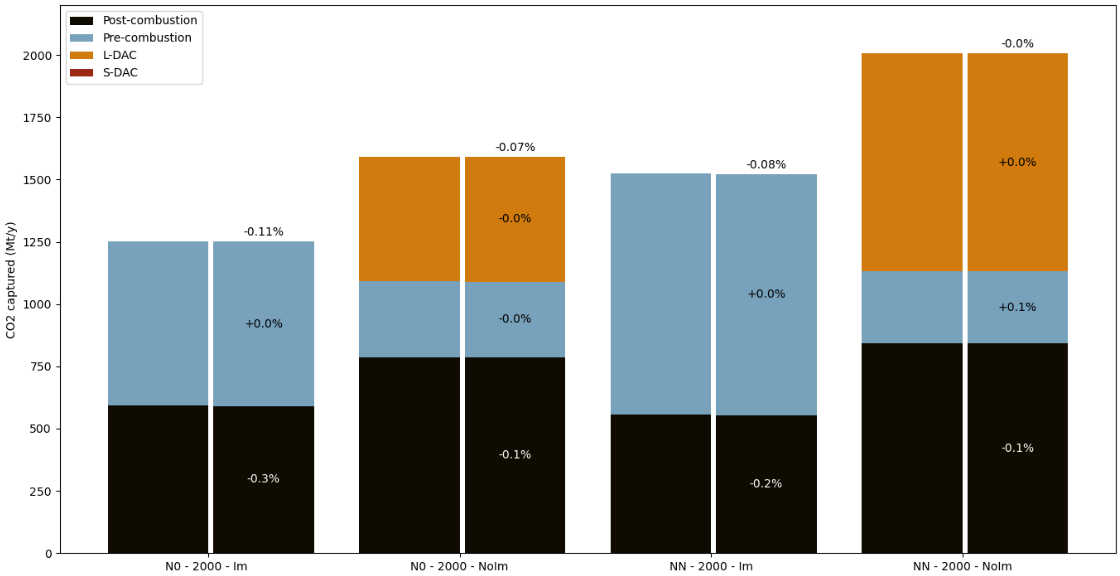

Figure B.2: Carbon capture usage for different scenarios using L-DAC lower consumption

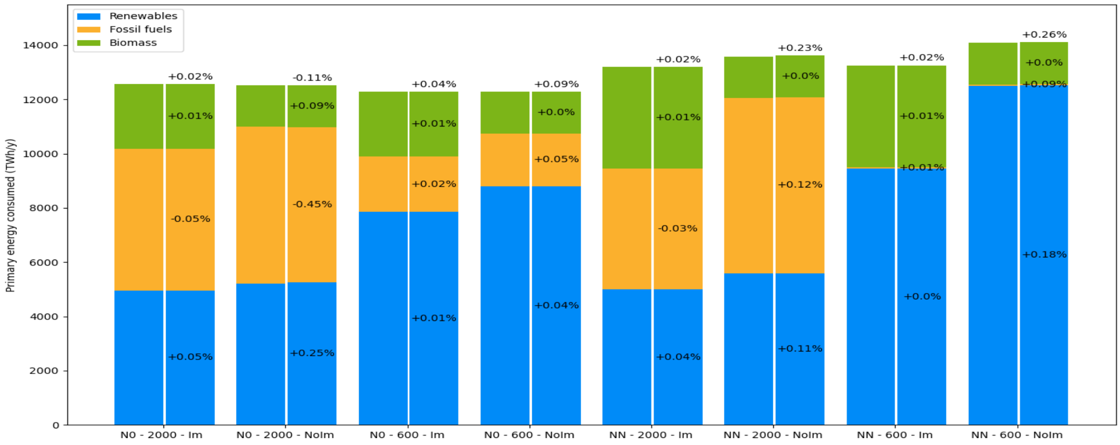

Figure B.3: Energy variations due to solvents implementation compared to the base case, with the lower sorbent consumption and S-DAC

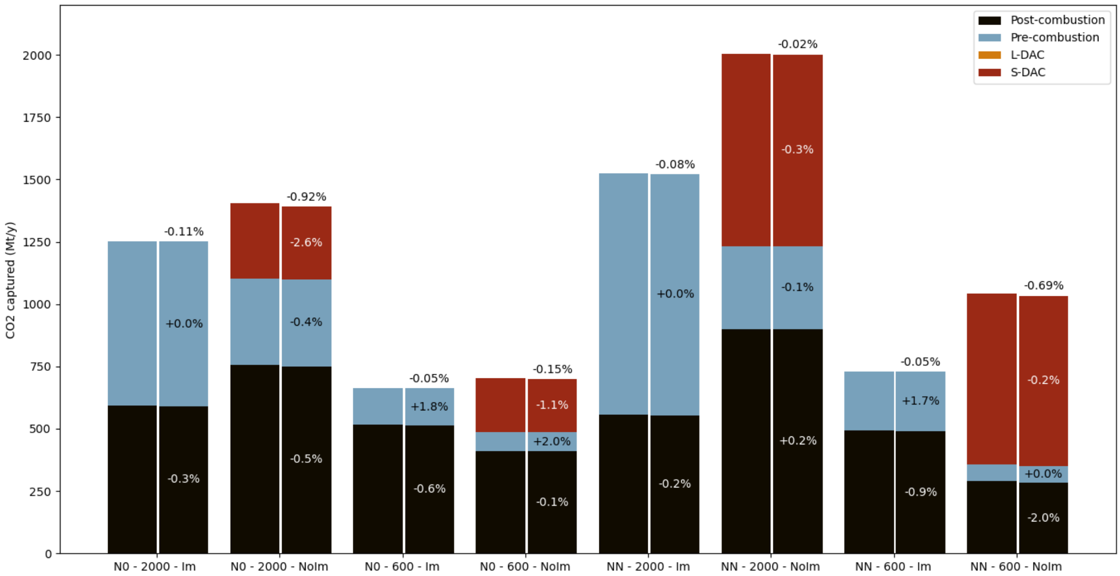

Figure B.4: Carbon capture usage for different scenarios using S-DAC lower consumption

DEPARTMENT OF SOME SUBJECT OR TECHNOLOGY
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden
www.chalmers.se

AVANCEZ
1829

CHALMERS
UNIVERSITY OF TECHNOLOGY