

Build and Experimental Characterization of a novel continuous Direct Air Capture system

B. A. Gonzalez Aponte

CONFIDENTIAL

Build and Experimental Characterization of a novel continuous Direct Air Capture system

by

B. A. Gonzalez Aponte

To obtain the degree of Master of Science
at the Delft University of Technology,
to be defended publicly on November 24th, 2022 at 10.30 am.

Student Number:	5054613	
Project Duration:	January, 2022 - November, 2022	
Supervisor:	Prof. dr. ir. E. Goetheer	TU Delft
Company Supervisor:	Ir. M. Sinha	ZEF B.V.
Thesis Committee:	Prof. dr. ir. E. Goetheer	TU Delft (Chair)
	Prof. dr. ir. W. de Jong	TU Delft
	Dr. H.B. Eral	TU Delft
	Ir. M. Sinha	ZEF B.V.

This thesis is confidential and cannot be made public until November 24th 2024

An electronic version of this thesis is available at <http://repository.tudelft.nl/>.

Abstract

The unprecedented rise in CO₂ concentration in the atmosphere, and the accompanying rise in global temperature, has created the need for the development of environmentally friendly sources of energy. A very promising line of research focuses in the development of Carbon Capture and Utilisation (CCU) technologies; through which carbon-neutral liquid fuels could be synthesized. A great example of such technologies can be found in Zero Emission Fuels (ZEF), a dutch start-up currently developing a micro-plant capable of producing methanol from solar energy and ambient air. ZEF's process involves the capture of CO₂ and H₂O directly from ambient air, the splitting of the captured H₂O into its constituent elements through electrolysis, and the synthesis of methanol from H₂ and CO₂. The entire process is powered by solar energy, which makes ZEF's methanol a carbon-neutral liquid fuel.

This thesis focuses in the capture of CO₂ and H₂O from ambient air, a process known as Direct Air Capture (DAC). ZEF's DAC unit differs from industry standards by using a novel continuous chemical absorption process through the flow of an amine based sorbent between its absorption and regeneration systems, instead of using a conventional batch process through a supported sorbent. The work of this thesis pertains the build and experimental characterization of ZEF's first full scale DAC prototype, referred to as the 10X DAC prototype.

The built prototype, a fully functional DAC unit working in a continuous process, was experimentally characterized in terms of its performance and energy efficiency for the environmental conditions of the Dutch summer (i.e. hot and wet conditions). The absorption process was found to be limited by the capture of CO₂ when compared to the H₂O capture process, and to be liquid side limited; which aligned with literature sources where CO₂ capture is defined as diffusion limited in the liquid side. Overall, the 10X DAC absorption column has the capacity of capturing 0.52 kgCO₂/m³·hr; which is higher than the reported capture capacity of a very well established company like Carbon Engineering. In the regeneration process, residence times in the stripper column as low as six minutes were enough for the sorbent to reach vapour liquid equilibrium (VLE) loadings for a regeneration temperature of 120°C. The overall 10X DAC process is capable of producing 0.21 kgCO₂/hr with an energy demand of up to 33MJ/kgCO₂; which is up to 6 times higher than the reported most energy efficient DAC unit in industry. Furthermore, the H₂O:CO₂ product ratio was found to vary significantly, with a dependence to absolute humidity in the environment.

Through the experimental results of the characterization process, a chemical absorption model was developed which, assuming a liquid side diffusion limited process, considers the effects of the selected sorbent's characteristics and the environmental conditions in the absorption process. Through this model, and the use of previous developed regeneration models, a DAC cycle is presented through which the effects of varying dynamic conditions (i.e. absolute humidity and ambient air temperature) were determined. Overall, it was noticed that the performance of the absorption process was negatively affected by higher temperatures, while the regeneration process remained unaffected by temperature changes. Absolute humidity variations affected the H₂O loading of the sorbent, which then affected the performance of the regeneration process; lower H₂O loadings in the rich sorbent translated to higher CO₂ lean loadings after regeneration. Furthermore, it was determined that the current sorbent in ZEF's process favors cold and humid environments.

Finally, through the learnings and findings from both experiments and the developed absorption model, an optimized 10X DAC design is presented which focuses in meeting the CO₂ production and energy demand requirements established by ZEF for its process.

Acknowledgements

It is hard to believe that this journey is coming to an end, in which not only I further developed myself as engineer, but also grew incredibly as a person. These two years at TU Delft have been a success, but I wouldn't be here without the help and support from so many people that one way or another were part of my journey. To all, please allow me to share a quote by Stephen King with you:

"Don't let the sun go down without saying thank you to someone, and without admitting to yourself that absolutely no one gets this far alone."

To Dr. Earl Goetheer, my supervisor and thesis chair, thank you so much for guiding me through this thesis. I know how lucky I was to have you on my side, and to have been able to probe into the vast world of your knowledge. Thank you for never making me feel below you and bringing your enthusiasm to every single meeting; your encouragement was essential for the success of this thesis.

To the ZEF core team: Ulrich, Hessel and Paul. Thank you guys for every talk, joke and word of encouragement when things were not looking so bright; with you guys the future of ZEF is secured. Ulrich a special thanks to you for believing in me over two years ago, and for all our conversations; they brought strength during the hard times.

To Jan and Mrigank, words can't even describe how thankful I am to you and how much I admire you both as engineers and as human beings. Jan, the only thing I am more amazed of than your skills as an engineer is how even while being a human Wikipedia you remain humble and approachable; not once I felt scared nor ashamed of sharing my thoughts and doubts with you, and left every single of our conversations with a learning and feeling motivated. You do still owe me a coffee though!

Mrigank, thank you for taking a risk on me and seeing a potential I couldn't even see myself. The success of this project is as much yours as mine. Thank you for pushing me to convert brass to gold, and lead by example in every single step of this journey. You truly are incredible and it's no surprise the DAC team is the best with you being the one leading the way. Thanks specially for the academy prize worthy motivational speeches when the tough times arrived.

To the rest of the ZEF team, thank you all for allowing ZEF to continue doing its thing and pushing towards new boundaries. A special shot-out to my thesis buddies: Alex, Khaled and Kunal. Thank you my friends for every coffee break, joke, conversation and after-office drinks. You all kept me sane, and I am beyond proud of us for conquering every challenge. The future of the world is bright in the hands of people like you.

To my thesis committee, Dr. Burak Eral and Dr. Wiebren de Jong, thank you for accepting our invitation to be part of this defense and for taking the time to go through this report. I am extremely honored to count with you both in my committee, hope you enjoy this as much as I did.

To my old friends all over the world, thank you for every check-up call, word of motivation and reminding me how long I have come and pushing me. To my new friends in the Netherlands, thank you for making a Venezuelan feel like home and for every conversation, night of heavy drinking, and for being part of the journey.

To my family, the core of who I am and my motivation. Oriana, thank you for everything and taking my role as the support of our parents while I have been away; you are incredible and you are doing an incredible job in such a hard situation. Just know how thankful I am to you, and the immense pride I have of being your brother. Mami, no existen palabras para describirte ni para agradecer tantas cosas; solo mi amor por ti es mayor que la admiracion que te tengo. Te amo inmensamente, ni mil vidas me alcanzarian para pagarte todo lo que me has dado. Dad, I really can't find the words; everything I am is because of you and your example. I admire you, love you and just aim to be a quarter of the man you are. Not even the worst of the situations has taken your smile away and your weird sense of humor. Rest assure that you have raised two great human beings in my sister and me, and that we both are proud to call you our dad. Te amo cabeza, fuiste eres y siempre seras mi modelo a seguir. Que se joda la puta ELA

Contents

Abstract	i
Acknowledgements	ii
Nomenclature	vi
List of Figures	vii
1 Introduction	1
1.1 Global Warming: our negligence	1
1.2 Avoiding Catastrophe	2
1.2.1 CO ₂ conversion to fuels and chemicals	3
1.3 Zero Emission Fuels	3
1.3.1 ZEF's process	4
1.4 Thesis' focus	4
1.5 Thesis' Scope	5
2 Literature Review	6
2.1 Direct Air Capture	6
2.1.1 Amines based CO ₂ capture	6
2.2 Characterization of DAC Systems	11
2.2.1 Performance	11
2.2.2 Efficiency	13
2.2.3 Lifetime	14
2.3 Factors affecting characterization	15
2.3.1 Sorbent	15
2.3.2 Absorber Column	18
2.3.3 Stripper Column	20
2.3.4 External Parameters	23
2.4 Direct Air Capture at ZEF	24
2.4.1 Major takeaways from ZEF's trajectory	24
2.5 Major Conclusions	25
2.6 Research Objectives and Questions	26
3 Experimental set-up	27
3.1 10X DAC Prototype	27
3.1.1 10X DAC Sorbent	27
3.1.2 Absorber Column	28
3.1.3 Regeneration Section	30
3.1.4 Other Mechanical Components	31
3.1.5 Process Flow and Measurement points	31
3.2 Experimental Plan	34
3.2.1 Absorber Characterization	34
3.2.2 Stripper Characterization	34
3.2.3 Full System Characterization	35
3.2.4 Experimental Plan Summary	35
3.3 Measurements	36
3.3.1 Space Time Yield (STY)	36
3.3.2 Driving Force	37
3.3.3 Viscosity	38
3.3.4 Lean Loading	38
3.3.5 Residence Time	38

3.3.6	CO2 Produced	39
3.3.7	H2O Produced	40
3.3.8	H2O:CO2 Ratio	41
3.3.9	Energy Demand Process	41
3.3.10	Rich-Lean Hex Performance	42
4	Modelling	44
4.1	Absorber Model	44
4.1.1	Mass Transfer Theories and Experimental fit constant	45
4.1.2	Model Assumptions	49
4.1.3	Model Inputs and Outputs	49
4.1.4	Model Description	50
4.2	Stripper Model	51
4.2.1	Model Assumptions	52
4.2.2	Model Inputs and Outputs	52
4.2.3	Model Description	53
4.3	Models Application	53
5	Results and Discussion	55
5.1	Experimental Characterization	55
5.1.1	Absorption Characteristics	55
5.1.2	Desorption Characteristics	58
5.1.3	Full System Characterization	59
5.1.4	Characterization Summary	63
5.2	Environmental Conditions effects	63
5.2.1	Ambient Temperature Effects	64
5.2.2	Absolute Humidity	66
5.2.3	Environmental Conditions Effect Summary	68
5.3	Sorbent Comparison	68
6	Conclusions & Recommendations	71
6.1	Conclusions	71
6.1.1	Built/Commissioning of the 10X DAC	71
6.1.2	System Characteristics	71
6.1.3	Environmental Conditions Effects	72
6.1.4	Optimized 10X DAC System	72
6.2	Recommendations	73
6.2.1	Process Design Recommendations	73
6.2.2	Model Development Recommendations	74
A	Measurement Equipment	75
A.1	Fourier-Transform Infrared Spectroscopy	75
A.2	CO2 Concentration Measurements	76
A.3	Humidity Measurements	77
A.4	Pressure Drop Measurements	77
A.5	Temperature Measurements	78
B	Experimental Results	79
B.1	Absorption Characteristics	79
B.1.1	CO2 vs H2O capture process	79
B.1.2	Air side vs Liquid side limitations	79
B.1.3	Pressure drop in column	81
B.1.4	CO2 Capture Efficiency	82
B.2	Regeneration Characteristics	83
B.2.1	Stripper Pump Characterization	83
B.2.2	Start-up	84
B.2.3	Ratio Sensor	84
B.3	Full system Characteristics	86
B.3.1	Air distribution in column	86

C Building Process	87
D Modelling complimentary Info	88
E Literature complimentary information	89
E.1 Degradation characteristics	89
E.2 Purity	91
E.3 DAC at ZEF.	91
F Intellectual Property Sensitive	92
References	97

Nomenclature

Abbreviations

Abbreviation	Definition
ZEF	Zero Emission Fuels
CCSU	Carbon Capture Storage and Utilisation
DAC	Direct Air Capture
STY	Space Time Yield
TEPA	Tetraethylenepentamine
MEA	Monoethanolamine
PEG	Polyethyleneimine
VLE	Vapor Liquid Equilibrium
Re	Reynold's Number
HEX	Heat Exchanger
PWM	Pulse Width-modulation
FTIR	Fourier-transforminfrared spectroscopy
CapEx	Capital expenditures
NTU	Number of Transfer Units
ppm	parts per million

Molecules

Molecular Structure	Definition
CO ₂	Carbon Dioxide
H ₂	Hydrogen
H ₂ O	Water
CH ₃ OH	Methanol
O ₂	Oxygen
RNH ₂	Primary Amine
R ₂ NH	Secondary Amine
R ₃ N	Tertiary Amine
RNH ₂ ⁺ COO ⁻	Zwitterion
RNHCOO ⁻	Carbamate
HCO ₃ ⁻	Bicarbonate

List of Figures

1.1	CO ₂ atmospheric level through history (reconstruction from ice cores) [42]	1
1.2	Change in global surface temperature in 2081–2100 relative to 1850–1900 [33]	2
1.3	Potential temperature increase [12]	3
1.4	ZEF's microplant overview	4
1.5	Thesis' Overview	5
2.1	Chemical Absorption Process	7
2.2	Chemical Absorption Steps	7
2.3	Concentration gradient for two-film theory (a) film theory (b) more realistic gradients	8
2.4	Stripper Schematics [68]	10
2.5	Characterization categories and indicators	11
2.6	Annual capture capacity of different companies [7] [45]	12
2.7	Volumetric capture capacity of different process [10]	12
2.8	Cost distribution for energy costs for a hypothetical amine sorbent process [10]	14
2.9	Oxidative degradation: Temperature effect in: MEA losses (left), the formation of degradation products in liquid (right) [28]	15
2.10	Sorbent's characteristics and their influence in DAC system characterization	16
2.11	Heat of absorption (kJ/mole of CO ₂) of aqueous amine solution at 313.15 K and atmospheric pressure [15]	17
2.12	Absorber Columns's characteristics and their influence in DAC system characterization	18
2.13	Effect of liquid flow rate on overall mass flow rate [74]	19
2.14	Effect of gas flow rate on overall mass flow rate [20]	19
2.15	Stripper Columns's characteristics and their influence in DAC system characterization	20
2.16	VLE for sorbent ternary mixture at 1 bar and different temperatures [14]	21
2.17	External Parameters' characteristics and their influence in DAC system characterization	23
2.18	ZEF's DAC prototype today	25
3.1	TEPA:PEG 1:2.5 performance [40]	28
3.2	Absorber Header Sections	28
3.3	Absorber Column	30
3.4	Regeneration Section	31
3.5	P&ID diagram of 10X DAC prototype	32
3.6	Example results from sample analysis	37
3.7	CO ₂ Measuring device schematic	40
4.1	DAC Absorber Model	44
4.2	CO ₂ capture capacity versus concentration gradient	45
4.3	Estimation of the Diffusion Coefficient [49]	46
4.4	Schematics of Surface Renewal Theory [36]	47
4.5	Experimental constant A	48
4.6	Absorber Model Description	51
4.7	DAC Stripper Model	52
4.8	DAC Cycle	54
5.1	CO ₂ and H ₂ O capture over time	56
5.2	CO ₂ capture capacity versus concentration gradient	57
5.3	CO ₂ capture capacity comparison	58
5.4	Lean loading as a function of the residence time in the stripper	59
5.5	Heat Exchanger Characteristics at Steady State	61

5.6	Energy Demand Process per molCO ₂ produced	62
5.7	Demand comparison with other companies	63
5.8	DAC Cycle Base Case	64
5.9	Temperature effects in DAC cycle	65
5.10	Temperature Effect in VLE	66
5.11	Absolute humidity effect in water loading	67
5.12	Water Loading Effect in the DAC cycle	68
5.13	Vapor liquid equilibrium loading comparison	69
5.14	STY & Viscosity comparison	70
A.1	Agilent Cary 630 FTIR machine	75
A.2	Working principle of an FTIR machine [61]	76
A.3	K30 10,000ppm CO ₂ sensor	77
A.4	Adafruit Sensiron SHT31-D sensor.	77
A.5	Honeywell Differential Pressure Sensor (26PCAFA6D)	77
A.6	Tegg NTC 3950 100K Thermistors Temperature sensor	78
B.1	Capture capacity of CO ₂ & H ₂ O	80
B.2	Varying air flow rate effects	81
B.3	Pressure drop in the absorption column comparison	82
B.4	CO ₂ Percent removal comparison	83
B.5	fit results	83
B.6	stripper pump characterization	84
B.7	Start-up time and energy demand	85
B.8	Ratio Sensor readings	85
B.9	Absorption vs Regeneration energy demand	86
E.1	Oxidative Degradation rates of the different amines with temperature and air. [30]	89
E.2	Thermal Degradation rates of the different amines with temperature and air. [29]	90
E.3	CO ₂ adsorption-desorption cycles over different adsorbents, (A) under dry conditions, (B) in the presence of moisture (20 °C as dew point) [51]	90
E.4	Vapor Pressure vs Temperature [31]	91

Introduction

Humanity is facing what may be its biggest challenge ever: climate change. This is a problem that affects every single person regardless of race, gender, social status or nationality; so it is a problem we must all solve together. Since the industrial revolution, human activities have created an increase in atmospheric concentration of greenhouse gases, out of which the most worrying increase is the one of carbon dioxide (CO_2). This gas, which is the main driver of climate change, has increased from 280ppm in pre industrial times to 419ppm in 2022 [21]. This unprecedented increase in CO_2 atmospheric concentration has caused a mean global surface temperature increase of roughly 1°C [41]. It is clear then that something must be done if severe consequences to our planet are to be avoided, and that's the main motivation of this thesis, to contribute in our fight against climate change.

1.1. Global Warming: our negligence

There is no doubt at all that human activities are the responsible for the raise in temperature in our atmosphere, land and oceans [33]. The concentration of CO_2 in the atmosphere has never been as high as it is today in the last 2 million years. Since 1750, the increase in CO_2 concentration far exceeds the natural multi-millennial changes between glacial and interglacial periods over at least the past 800,000 year [33]. It, of course, is no crazy coincidence that this sudden change in CO_2 atmospheric concentration aligns with the beginning of the industrial revolution [62].

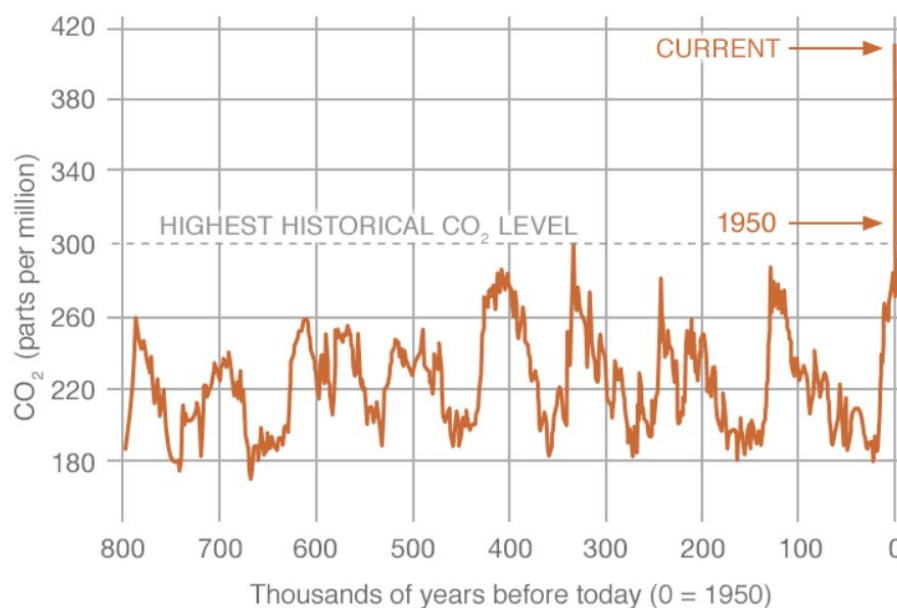


Figure 1.1: CO_2 atmospheric level through history (reconstruction from ice cores) [42]

These levels in atmospheric CO₂ concentration, along with other greenhouse gases, have caused an increase in the average temperature of our planet which is unprecedented in the last 2,000 years. The consequences of this increase in temperature are both many and severe: hot extremes (including heatwaves) have become more frequent and more intense across most land regions, the frequency and intensity of heavy precipitation events have increased since the 1950s over most land area, annual average Arctic sea ice area reached its lowest level since at least 1850, global mean sea level increased by 0.20m [0.15 to 0.25] between 1901 and 2018, amongst many others [33].

The reality is that the consequences of our negligence are both undeniable and unavoidable. Several scenarios have been developed to understand what will happen in the future for different trends in global emissions: scenarios with high and very high GHG emissions (SSP3-7.0 and SSP5-8.5), scenarios with intermediate GHG emissions (SSP2-4.5), and scenarios with very low and low GHG emissions and CO₂ emissions declining to net zero around or after 2050, followed by varying levels of net negative CO₂ emissions²³ (SSP1-1.9 and SSP1-2.6) [33]. Even in the most optimistic scenarios (SSP1-2.6 and SSP1-1.9) the planet would still suffer an increase in global surface temperature; which means we are committed to some level of climate change no matter what.

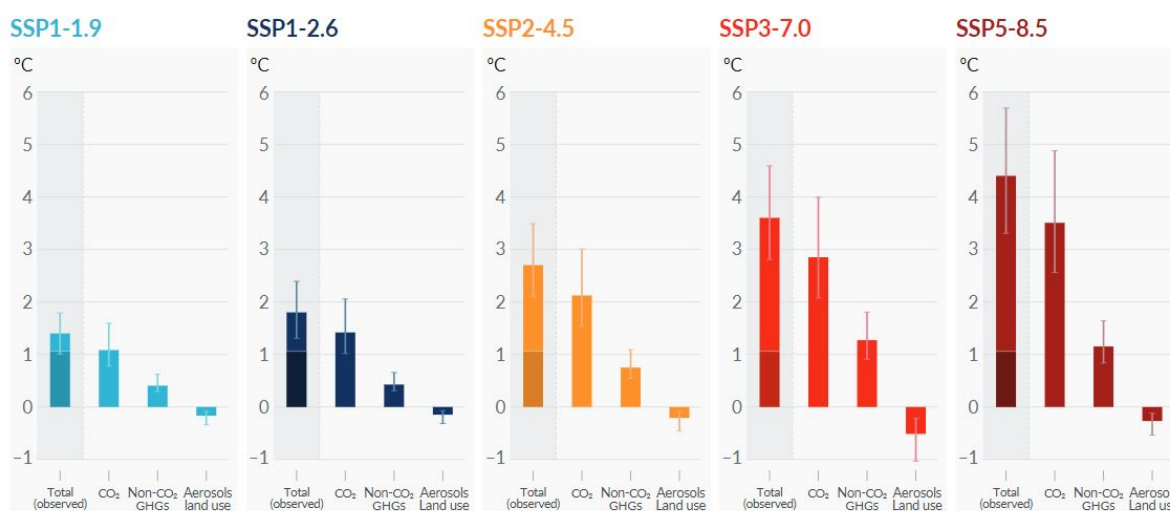


Figure 1.2: Change in global surface temperature in 2081–2100 relative to 1850–1900 [33]

1.2. Avoiding Catastrophe

If the worst scenarios, and consequences, are to be avoided we need to act now. In 2015, the Paris Agreement was signed with the goal of "holding the increase in the global average temperature to well below 2°C above pre-industrial levels and pursuing efforts to limit the temperature increase to 1.5°C" [65]. In 2020, this agreement was revisited during COP26 in Glasgow. It was recognized that the commitments acquired in the Paris Agreement put the world in the path of a temperature increase of 2.7°– 3.7°C [12]. However, it was also recognized that the hope for limiting the temperature increase to 1.5° was still alive; so new pledges were made in order to reach this goal.

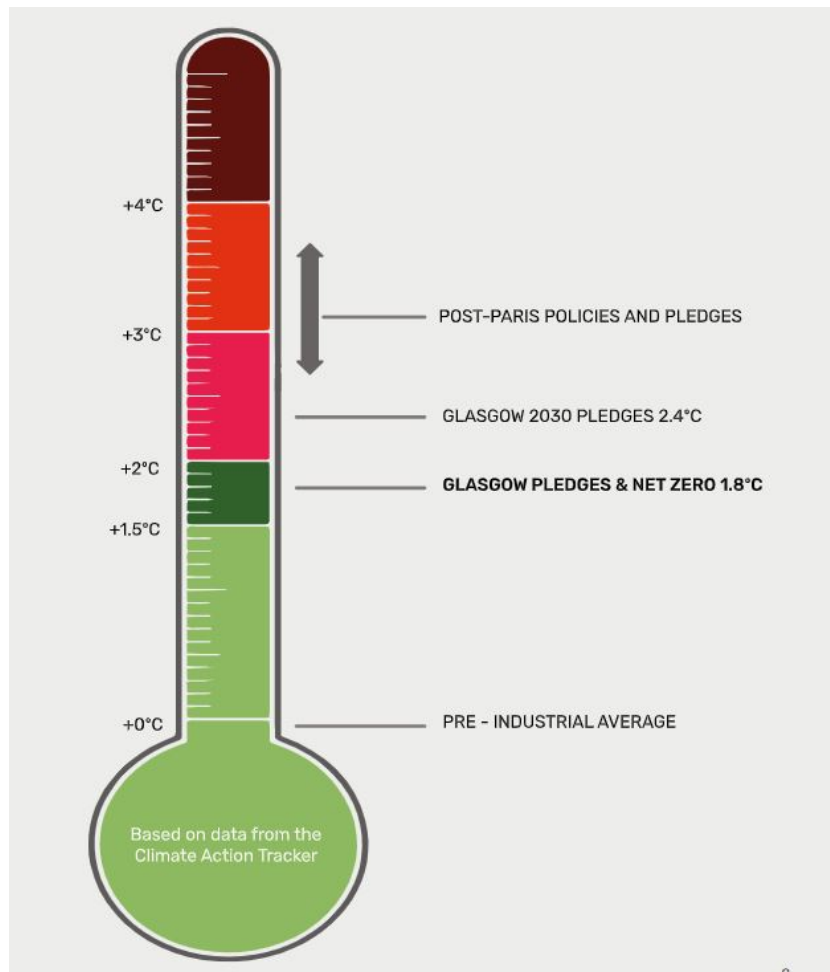


Figure 1.3: Potential temperature increase [12]

According to the 2020 Emission Gap Report [66], the projected global greenhouse emissions under the implementation on nationally determined contributions (NDCs) are way above the allowable emissions required to meet the limits of 2°C. In fact, current policies trends will result in an emission gap of 15 GtCO₂.

Clearly, what we are doing is not enough, and new measures need to be implemented. In this regard, the implementation of Carbon Capture Storage and Utilisation (CCSU) technologies is one of the best options we have to reach the Paris Agreement's goals. According to the Intergovernmental Panel on Climate Change (IPCC), carbon capture technologies are necessary to achieve the acquired targets in limiting global warming at the lowest cost [17].

1.2.1. CO₂ conversion to fuels and chemicals

One very promising pathway to follow in the fight against climate change is the production of e-fuels from renewable energies [66]. One such potential e-fuel is methanol, which can be produced through syngas (a mixture of CO₂ and H₂) synthesis. If the required CO₂ is captured directly from the atmosphere, and the required H₂ is produced via electrolysis powered by renewable energy, methanol production has the potential of being a net zero process and thus aid in a transition away from fossil fuels. Green Methanol could be directly implemented in the shipping industry, which is projected to consume between 60-220% of allowable CO₂ emissions with the current policies [66].

1.3. Zero Emission Fuels

Zero Emission Fuels B.V. (ZEF) is a dutch start-up currently developing a micro-plant capable of producing net zero methanol using energy from the sun and raw materials obtained directly from ambient

air. ZEF has successfully proven the concept of each of its subsystems in small scale prototypes, and is moving towards the design, build, and characterization of their full scale system.

1.3.1. ZEF's process

The ZEF process can be divided into six subsystems: Direct Air Capture (DAC), Fluid Machinery (FM), Alkaline Electrolysis Cell (AEC), Methanol Synthesis Reactor (MSR), Distillation (DS) and Photovoltaic Energy (PV). The DAC system is in charge of capturing both CO₂ and H₂O directly from ambient air. This process is divided in two parts: absorption and desorption. In the absorption step, ambient air is directed towards the absorption column, where it is brought into contact counter-currently with a flowing sorbent, and the present CO₂ and H₂O are captured through chemical and physical mechanisms. The loaded sorbent is then taken into the desorption column, where the captured CO₂ and H₂O are released through a temperature swing process. The lean sorbent is then recirculated back to the absorption column, while the released CO₂ and H₂O are sent to the FM and AEC systems respectively.

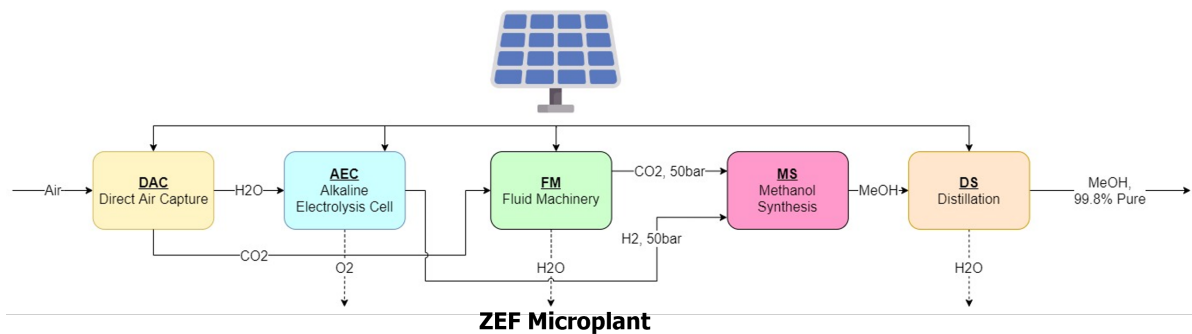


Figure 1.4: ZEF's microplant overview

The CO₂ stream leaving the DAC system is first dried and then compressed to 50 bar by the FM system. The H₂O stream is taken to the AEC system, where it undergoes electrolysis at 50 bar and is split into H₂ and O₂. H₂ and CO₂ are taken to the MSR system, where methanol synthesis takes place through the following reaction:



Finally, the product stream is taken to the DS system, where the methanol and water are separated to give a final methanol product stream that is 99.8% pure.

1.4. Thesis' focus

The focus of this thesis lies around ZEF's DAC system. In the past years, ZEF has done great advancements in their DAC process, developing both incredible knowledge as well as small scale working prototypes. Through these prototypes, ZEF has been able to proof their DAC concept, and characterize it. ZEF's DAC process consists of a continuous absorption/desorption cycle, using an liquid aqueous amine based sorbent that is distributed in the absorption column in an extremely innovative manner; which successfully overcomes the many challenges faced in industry when trying to use this type of sorbent.

Now, ZEF has embarked in the challenge of designing, building, and characterizing a full scale prototype of its DAC system, which has been named the 10X DAC Prototype. That's where the work developed in this thesis comes into play, which can be divided in the following parts:

1. Design & Build: the design of the 10X DAC system, based in the knowledge developed by previous teams, will be explained. Said design will then be assembled and commissioned.
2. Experimental Characterization and Validation: through experiments, the 10X DAC system will be characterized regarding several performance indicators. The experimental results will be used to validate ZEF's existing models, and optimise them in case of any deviations.
3. Design Optimization: through the experimental findings, an optimized design of ZEF 10X DAC system will be proposed to better fulfill ZEF's requirements.

1.5. Thesis' Scope

The main goal of this thesis is the experimental characterization of the 10X DAC System. The design of said system has been performed by previous ZEF's teams, so this thesis will limit to explain the design decisions and give some insights into the reasons behind them. The build process is also a major part of this thesis. The characterization process can be divided in four main categories:

- Performance.
- Efficiency.
- Lifetime.
- Cost.

This thesis will neither cover the lifetime category of the characterization process nor the cost category. The results of the characterization experiments will be used to develop an experimental model of the absorption process. The rest of the DAC process models will be from previous work done at ZEF, and the results of this thesis will be used to validate them/draw conclusions. An overview of this thesis is presented in figure 1.5.

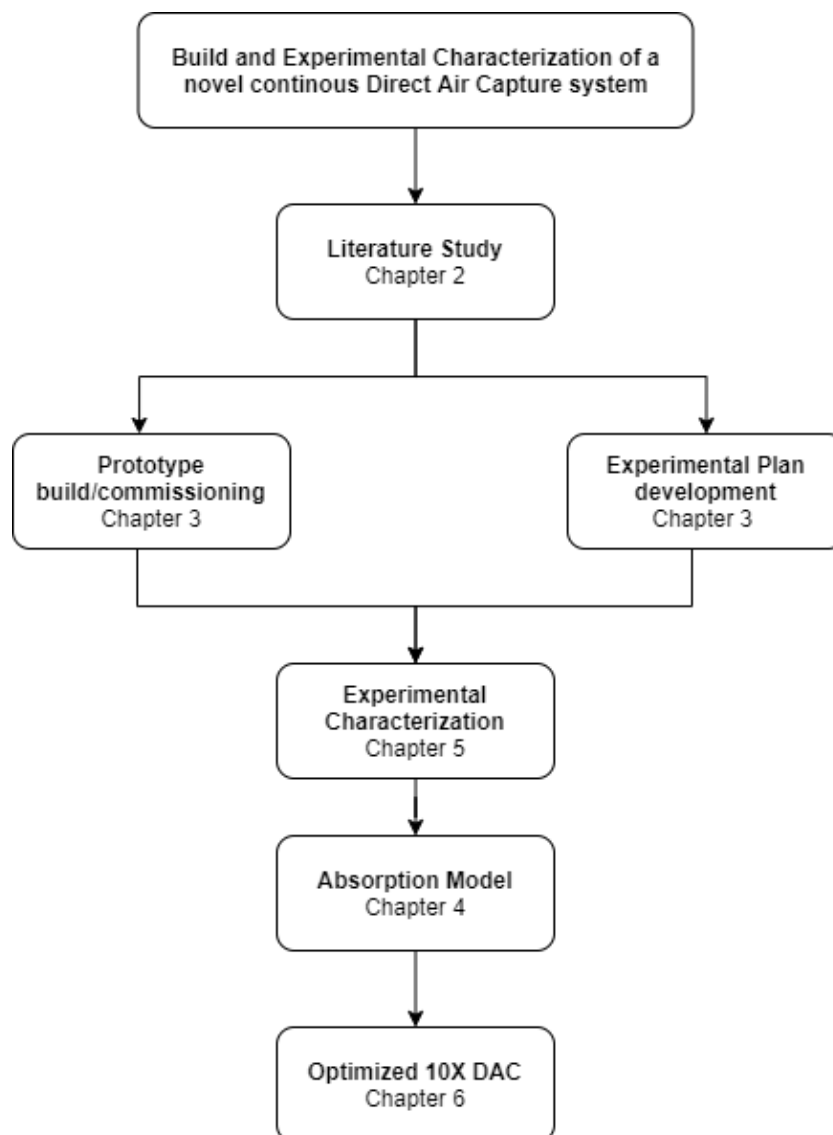


Figure 1.5: Thesis' Overview

2

Literature Review

In this chapter an overview of the background knowledge available for the development of this thesis is presented. It begins with a general explanation of what Direct Air Capture is, and how it is achieved through chemical absorption using amine based sorbents. Then, the characterization process of DAC systems is presented, what parameters are of relevance, how are they affected, and design decisions that might affect the overall performance. Finally, a journey through ZEF's DAC system is presented; from its beginnings to where the DAC system stands at the beginning of this project. Some data regarding current state of industry DAC systems is also given in the characterization section.

2.1. Direct Air Capture

Direct Air Capture (DAC) can be broadly defined as the direct extraction of CO_2 from ambient air. [5] This novel technology has many advantages, out of which some of the most relevant are the following [25]:

- Addresses emissions from distributed sources (transport sector, agriculture, etc) as well as point sources.
- Location independent process as the CO_2 source is almost globally uniform.
- Process does not deal with the contaminants that are present in flue gas streams of point sources.
- Any type of energy, potentially renewable as well, can be used to power the process.

However, DAC has the challenge of dealing with very low concentrations of CO_2 ($\approx 400\text{ppm}$). Because of this, large heats of reaction with CO_2 are required if high capture capacities are desired; this of course comes with the cost of large energy requirements for the regeneration process. The low concentration of CO_2 in DAC processes makes chemical sorption to be preferred over other capture routes due to its much more favorable equilibrium relationship [16]. The focus of this thesis is in amines based chemical absorption systems, so this technology will be further discussed.

2.1.1. Amines based CO_2 capture

Carbon dioxide capture through chemical absorption is based on the exothermic reaction of a sorbent with CO_2 , which is then reversed in a regeneration process at high temperatures[48]. A typical chemical absorption system consists of two main parts: the absorber column and the stripper column. Ambient air enters the absorber column and contacts counter-currently the CO_2 lean sorbent; moment at which the CO_2 capture takes place. Then, the rich sorbent is taken to the stripper column where thermal regeneration is carried, and the now lean sorbent is send back to the absorber column to repeat the process.

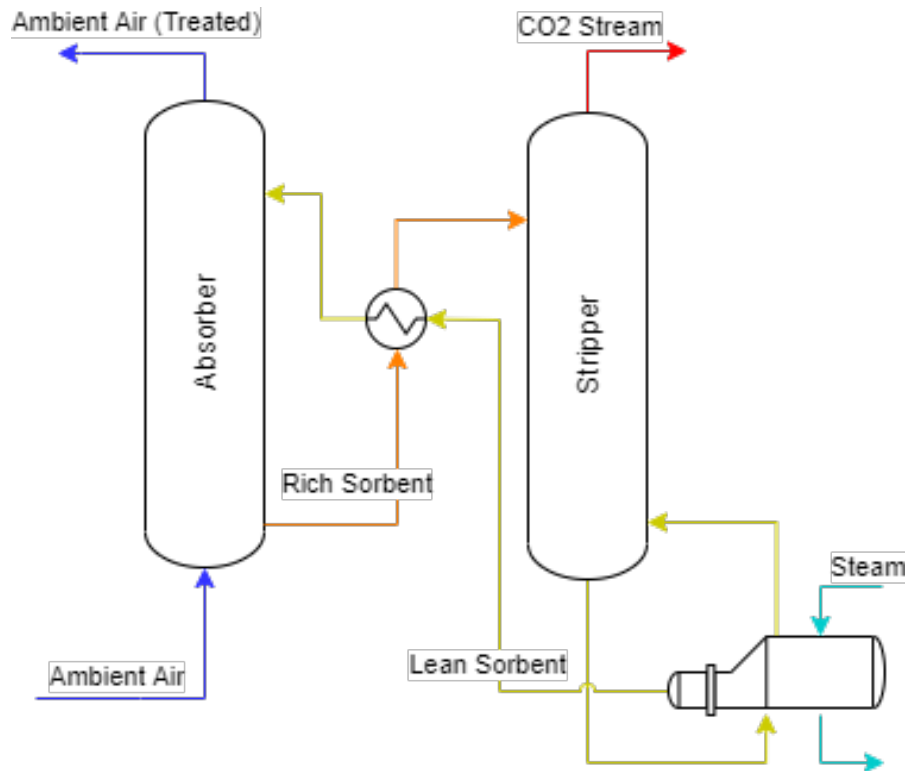


Figure 2.1: Chemical Absorption Process

Absorber Column

The absorber column is where chemical absorption takes place. In this column, an aqueous amine solution is flown downwards and brought into contact with ambient air in a counter-current manner. Amines are organic compounds derived from ammonia in which one or more of the hydrogen atoms are replaced by an organic substituent. Depending on how many hydrogen atoms are replaced, these compounds are classified as either: primary (one H_2 atom replaced), secondary (two H_2 atoms replaced) or tertiary (all H_2 atoms replaced)[48].

The absorption process can be divided into four steps: diffusion of CO_2 from the bulk of the gas to the gas-liquid interface, dissolution of CO_2 into the liquid film, diffusion of CO_2 in the thin film region and the chemical reaction of CO_2 with the amine's active group, and the diffusion of the reaction's products into the bulk of the liquid[73]. From the described process, it can be seen that the absorption of CO_2 through aqueous amine solution combines both physical and chemical processes.

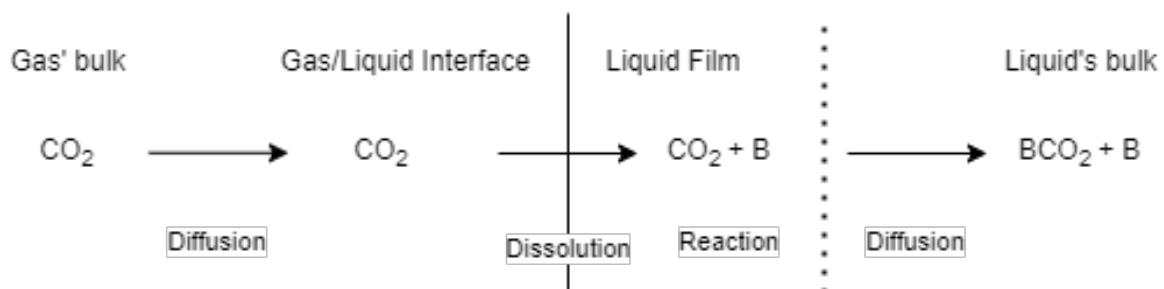


Figure 2.2: Chemical Absorption Steps

The physics of absorption can be described through the two-film theory, which assumes a phase equilibrium in the two fluids at the interface; meaning that the resistance to mass transfer is encountered in the two films regions and that there is no additional inter-facial resistance[52][47].

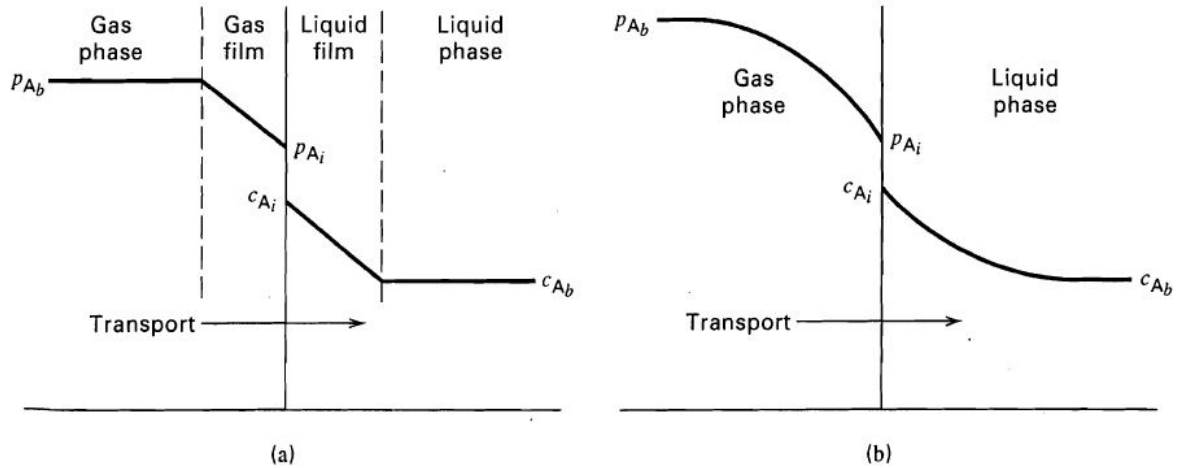


Figure 2.3: Concentration gradient for two-film theory (a) film theory (b) more realistic gradients

The diffusion of CO₂ from the bulk of the gas phase to the Gas film - Liquid film interface is described through Fick's first law of diffusion: [73]

$$J_{CO_2} = -D_{CO_2} \cdot \frac{dC_{CO_2}}{dz} \quad (2.1)$$

where **J** is molar flux (mol m⁻² s⁻¹), **D** is the diffusion coefficient (m² s⁻¹), and **c** is the concentration (mol m⁻³).

The dissolution of CO₂ from the Gas-film to the Liquid-film can be described using Henry's Law; which is applicable in our case due to the phase equilibrium assumed:

$$C_{CO_2} = H_{CO_2} \cdot p_{CO_2} \quad (2.2)$$

where **p** is the gas partial pressure under equilibrium conditions (Pa), **H** is Henry's constant (mol m⁻³ Pa⁻¹), and **C** is concentration (mol m⁻³).

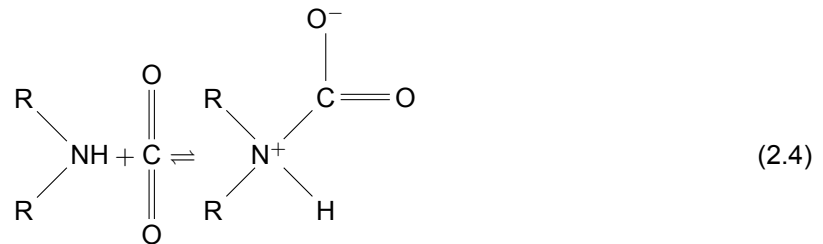
Furthermore, the diffusion of CO₂ and the products formed can also be described by Fick's law. However, it is important to mention that the determination of the diffusion coefficient in the aqueous amine solution is complex due to its reactivity, and it is usually determined through the modified Stokes-Einstein equation[53]:

$$D_{CO_2-Amine} \cdot \mu_{Amine}^{0.8} = D_{CO_2-H_2O} \cdot \mu_{H_2O}^{0.8} \quad (2.3)$$

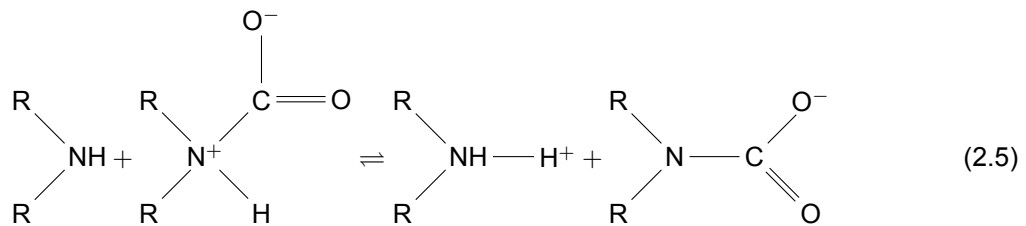
where **D_{CO₂-Amine}** is the diffusion coefficient of CO₂ in the amine (m² s⁻¹), **μ_{Amine}** is the amine's dynamic viscosity (Pa·s), **D_{CO₂-H₂O}** is the diffusion coefficient of CO₂ in water (m² s⁻¹), and **μ_{H₂O}** is water's dynamic viscosity (Pa·s).

Equation 2.3 can also be applied to find the diffusion coefficient of the products formed.

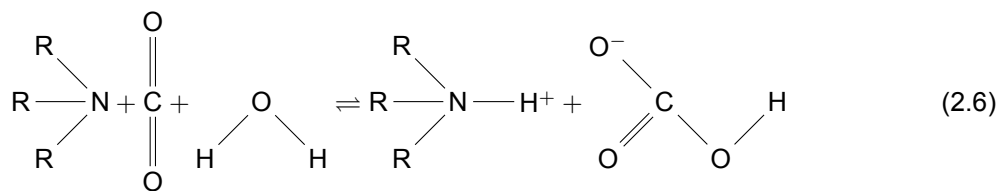
The chemistry of absorption is all about the reactions occurring between primary, secondary and tertiary amines and the dissolved/diffused CO₂. Primary and Secondary amines react with CO₂ to form carbamates through a series of steps[13][15]. First, a zwitterion is formed as follows:



Then the formed zwitterion further reacts with another amine molecule by transferring a proton and thus forming the carbamate:



At high pressure, the carbamate could be further hydrolysed to form a free amine and a bicarbonate[15]; however, in DAC processes such pressures are not used. From the above reactions, it can be seen that the maximum theoretical CO₂ loading is 0.5 mole per mole of amine. For tertiary amines, it is a single reaction in which bicarbonates are formed:



Clearly, the theoretical CO₂ loading maximum is one mole of CO₂ per mole of tertiary amine. However, tertiary amines have lower reactivity than primary and secondary amines. [15]

Stripper Column

In the stripper column, desorption, or regeneration, takes place. This is an endothermic process, so heat must be supplied in order to reverse the carbamate, or bicarbonate in case of tertiary amines, reaction. The two-film theory can also be used to explain the mass transfer process in regeneration: carbamates are converted back into CO₂. Then, H₂O and CO₂ molecules diffuse from the bulk of the liquid into the gas-liquid interface. Finally, once sufficient energy is supplied, H₂O moves into vapor phase along with the CO₂ molecules.

The rich sorbent enters the stripper column at the top stage, it flows downwards over a series of trays or packing material, where it comes in contact with the desorbed solute which is flowing upwards. The energy required to desorb the solute is supplied by a reboiler at the bottom of the column. A temperature gradient is established in the column due to the contact between gas and liquid streams; being the coldest part the top stage of the column. Each stage is considered to be at equilibrium, which allows to quantify the composition of both streams theoretically and determine the required amount of equilibrium stages through, for example, the Kremser-equation[16]. At the top of the column, a vapor product, known as the top product, is obtained which is circulated towards a condenser. Some of the condensed top product is cycled back to the column. The amount of liquid that is fed back to the column over the amount of liquid that is taken from the column is known as the reflux ratio (equation 2.7). Total desorption is never achieved, which means that some solute leaves the column along with the lean sorbent, which is called the bottom product. Some of this bottom product is evaporated and fed back to the column. The amount of vapor that is fed back over the amount of lean sorbent taken from the column is known as the boilup ratio (equation 2.8).

$$R = \frac{L}{D} \quad (2.7)$$

where **R** is the reflux ratio, **L** is the mass flow rate of liquid fed back to the column (m³ s⁻¹), and **D** is the distillate mass flow rate (m³ s⁻¹).

$$V_B = \frac{V}{B} \quad (2.8)$$

where **V_B** is the boil-up ratio, **V** is the mass flow rate of the vapor fed back to the column (m³ s⁻¹), and **B** is the mass flow rate of the bottom product (m³ s⁻¹).

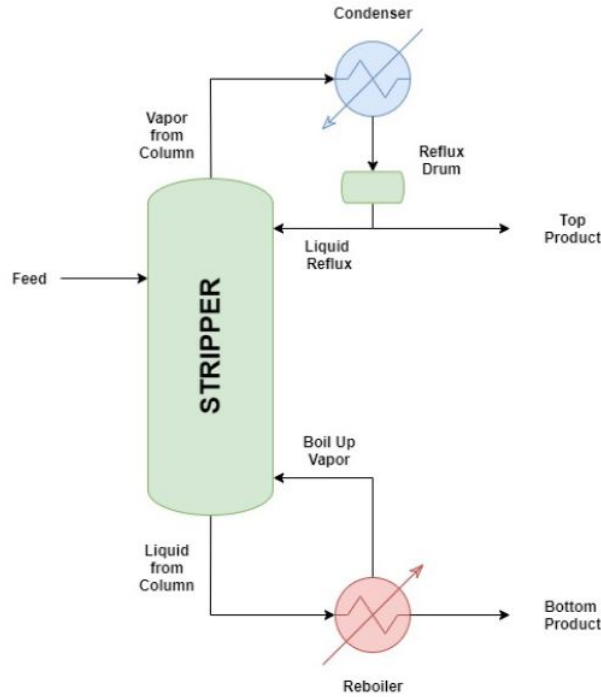


Figure 2.4: Stripper Schematics [68]

Stripping is mainly conducted in trayed towers and packed columns, while other technologies like spray towers, bubble columns, and centrifugal contactors are less used[52]. In packed columns, a large gas-liquid interface is achieved by introducing various packings into the column. Trayed columns make use of plates to create the contact interface, the liquid flows in the plates horizontally until it reaches a weir and flows downward through a downcomer from plate to plate. The gas flows upwards through perforations in the plates[16].

In the stripper column is where the vast majority of energy demand of the process is encountered. This energy demand can be divided as follows: Sensible heat, heat of absorption (or desorption), heat of vaporisation, and heat losses.

- Sensible heat: defined as the amount of thermal energy required to raise the temperature of the incoming feed to the desorption temperature[6]. This energy demand can be significantly reduced by using a heat exchanger to transfer heat between the hot lean sorbent leaving the bottom of the column and the colder rich sorbent entering the column[52].

$$Q_s = \dot{m}C_p(T_{desorption} - T_{feed}) \quad (2.9)$$

where Q_s is the sensible heat (W), \dot{m} is the mass flow rate of the stream ($\text{m}^3 \text{s}^{-1}$), C_p is the specific heat capacity of the stream ($\text{J kg}^{-1} \text{K}^{-1}$), and T is the temperature of desorption and of the incoming feed stream respectively (K).

- Heat of Absorption (desorption): the amount of thermal energy required to reverse the carbamate and bicarbonate formation reactions. The heat of desorption is a function of CO_2 loading, temperature and the type of product formed. Furthermore, primary carbamates are the hardest to regenerate, followed by secondary carbamates and bicarbonates due to a decrease in enthalpy of regeneration and bond strength[37][24][2].
- Heat of Vaporisation: the amount of thermal energy required to trigger a phase change in water from liquid to vapor. Sinha et al [57] determined experimentally that the heat of vaporisation for mixtures is higher in average than for pure water; which is explained by the extra energy required to break hydrogen bonds between water and the amine.
- Heat losses: the amount of thermal energy lost to the environment and that is a product of both the dimensions of the column and the material used for insulation.

2.2. Characterization of DAC Systems

The characterization of Direct Air Capture systems can be defined in four main categories: performance, efficiency, lifetime and cost. For each category, standard indicators have been established to compare different DAC technologies. ZEF has also established other performance indicators for their process in order to evaluate where they stand regarding the evolution of their system. In the coming subsections, each category will be presented alongside its different key performance indicators. Because of the scope of this thesis, neither the lifetime nor cost categories will be covered. However, some information on the lifetime will be given as it is such an important aspect of the direct air capture process.

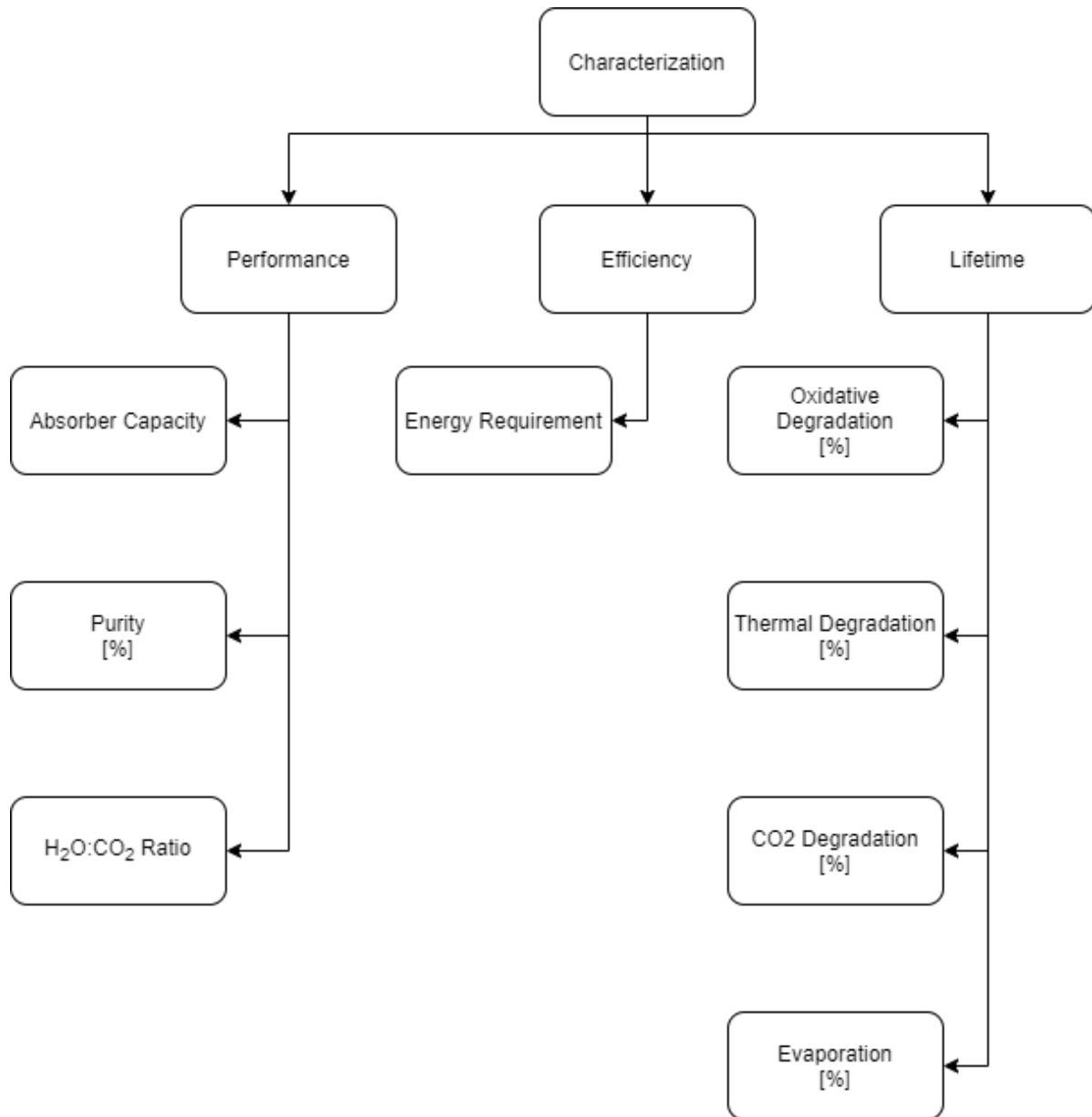


Figure 2.5: Characterization categories and indicators

2.2.1. Performance

As it can be seen in figure 2.5, the performance of a DAC system is measured in three main indicators: Absorber Capacity, Product Purity, and $\text{H}_2\text{O}:\text{CO}_2$ ratio. The first two indicators are common in industry and serve as a basis to compare different DAC processes[10]. The $\text{H}_2\text{O}:\text{CO}_2$ ratio is an indicator of interest for ZEF because of requirements from the Methanol Synthesis reactor.

Absorber Capacity

The Absorber Capacity indicator provides information on the CO₂ capture capacity of the DAC process. There are two common ways of evaluating absorber capacity: total annual capture capacity (*tonCO₂/annum*) and volumetric capture rate (*kgCO₂/m³hr*). The annual capture capacity tells how much CO₂ a DAC process is capable of removing from ambient air in a single year. However, due to the different approaches to DAC and the differences between each process, relying only in annual capture capacity can be misleading.

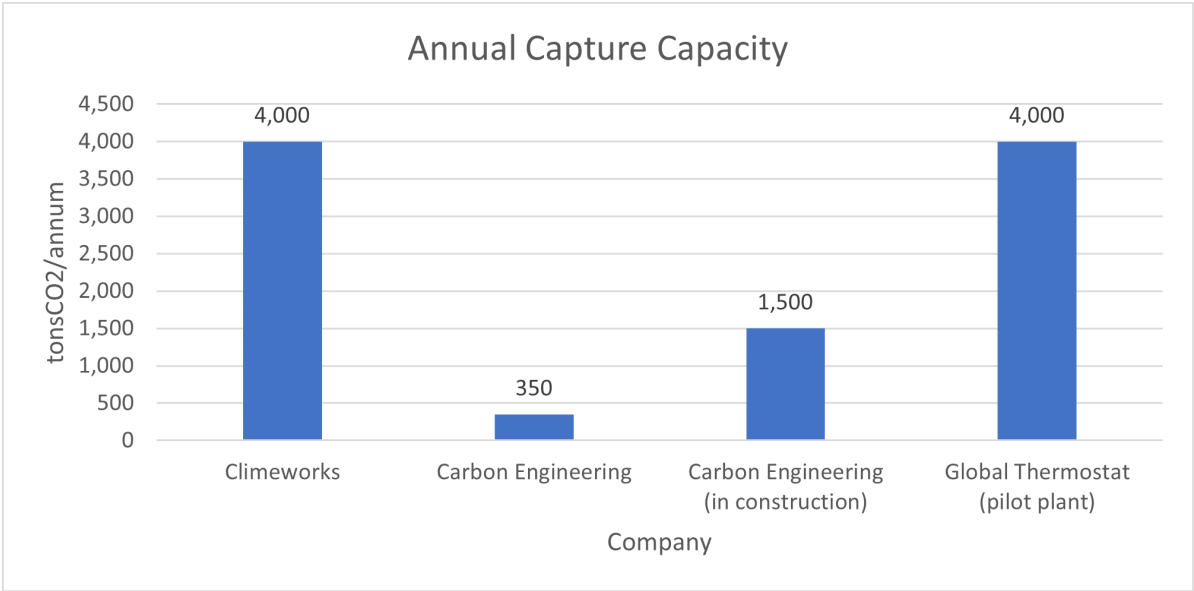


Figure 2.6: Annual capture capacity of different companies [7] [45]

Brilman [10], based only in the concentration of CO₂ in ambient air, showed that for a DAC plant to capture 1 Mton per annum of CO₂, at least 46,000 m³ per second of air must be handled (assuming complete removal of CO₂); which means the time air spends in the DAC unit should be small. Because of this, Brilman [10] proposes the volumetric CO₂ capture rate as a good performance indicator for comparisons. The lower this indicator is, the more air must be treated which makes the process more challenging and more energy intensive.

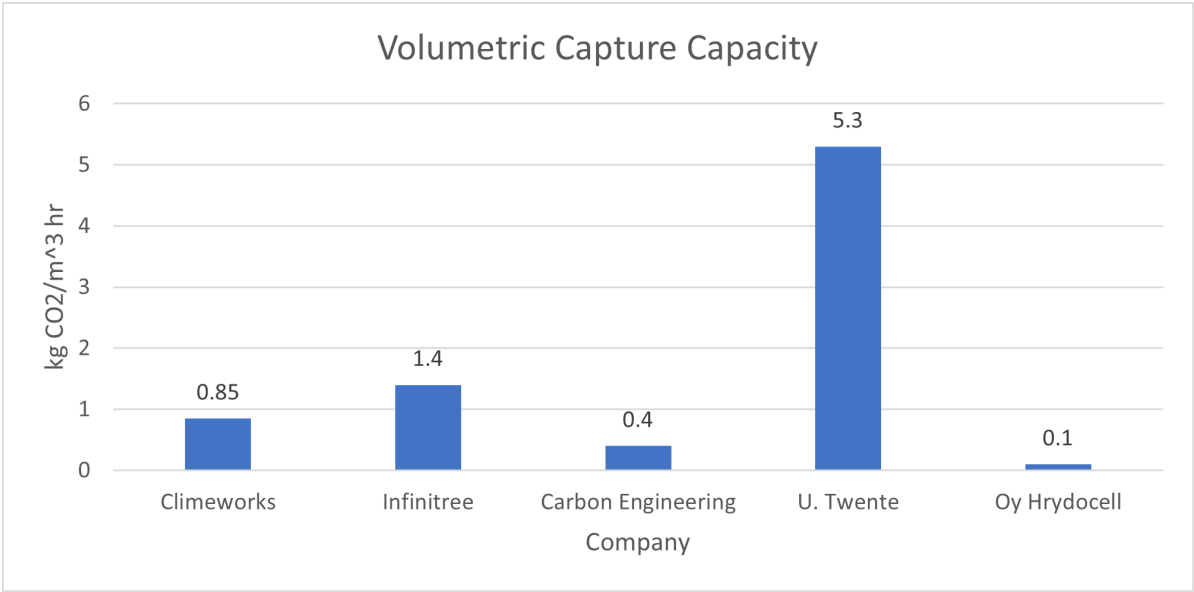


Figure 2.7: Volumetric capture capacity of different process [10]

The volumetric capture capacity also gives insights into the required installation size to reach certain CO₂ capture requirements. For example, based on figures 2.6 and 2.7, if Carbon Engineering wanted to reach the same annual capture capacity with their process as Climeworks, their installation would require at least 1142 m³, while Climeworks' process requires 538 m³.

H₂O:CO₂ Ratio

The H₂O:CO₂ Ratio performance indicator is a very important parameter in case the DAC process is used in carbon capture and utilisation technologies. If that's the case, the water and CO₂ product streams become raw materials for other processes, and their production ratio is of great interest.

In ZEF's process, the water product stream is taken to the electrolysis cell to produce hydrogen, while the CO₂ stream is pressurized and send directly to the methanol synthesis reactor. In the methanol reactor, both H₂ and CO₂ react to form methanol and water. As it can be seen in equation 2.10, the required molar ratios of the reaction are 3 H₂ molecules and 1 CO₂ molecule [46]; so, the product ratio of the DAC process must match this ratio.



2.2.2. Efficiency

The efficiency of a DAC system is measured in one main parameters: the energy requirement of the process. The energy requirement of the process not only measures the efficiency of the process, but also provides insights into the operational costs of the process.

Energy Requirement

The Energy Requirement indicator provides information on the required energy input into the system for the process to capture certain amount of CO₂, and is usually measured in two units: *GJ/tCO₂* and/or *kJ/molCO₂*. The more energy required to absorb CO₂, the less efficient the process is.

The energy requirement of DAC process can be divided as follows: Air-Sorbent contacting energy (absorber column), sensible heat (stripper column), heat of desorption (stripper column), heat of evaporation (stripper column), and other energy requirements for components such as pumps, sensors, valves, etc. Out of all these energy costs, the sorbent regeneration (sensible heat, heat of desorption, heat of evaporation) is the most energy demanding process [17][77][34].

- Air-Sorbent Contacting Energy

This is the energy required in the absorber column to bring the air and the sorbent into contact and thus allow for the capture of CO₂. In ZEF's process this can be divided into two major components: energy required for the distribution of the sorbent (pumping system), and the energy required for the circulation of ambient air (fans' energy requirement).

The power requirements of both the pumping system and the fans can be obtained by first determining the pressure drop in the system, and by knowing the volumetric flow rate of the sorbent for the pumping system, and of the air for the fans.

$$P = \dot{V} \cdot \Delta P \quad (2.11)$$

where **P** is the power (W), **\dot{V}** is the volumetric flow rate (m³ s⁻¹), and **ΔP** is the pressure drop (Pa).

- Sorbent Regeneration Energy

This is the energy required to release the captured CO₂ from the saturated sorbent so it can be used again in the absorber column. As explained in section 2.1 (Stripper column), the regeneration energy can be further divided into the following: sensible energy (equation 2.12), energy of desorption (equation 2.13) and energy of evaporation (equation 2.14).

$$Q_{\text{sensible}} = \dot{m} \cdot C_p \cdot (T_{\text{desorption}} - T_{\text{feed}}) \quad (2.12)$$

where **Q_{sensible}** is the sensible heat requirement (W), **\dot{m}** is the mass flow rate of the rich sorbent (kg s⁻¹), **C_p** is the specific heat capacity of the stream (J kg⁻¹ K⁻¹), and **T** is the temperature of desorption and of the incoming feed stream respectively (K).

$$Q_{\text{desorption}} = \dot{m} \cdot \Delta H_{\text{CO}_2} \quad (2.13)$$

where $Q_{\text{desorption}}$ is the heat of desorption requirement (W), \dot{m} is the mass flow rate of CO_2 that's released (mol s^{-1}), and ΔH_{CO_2} is the heat of reaction of CO_2 with the amines (J mol^{-1}).

$$E_{\text{evaporation}} = \dot{m} \cdot \Delta H_{\text{H}_2\text{O}} \quad (2.14)$$

where $Q_{\text{evaporation}}$ is the heat of evaporation requirement (W), \dot{m} is the mass flow rate of H_2O that is evaporated (mol s^{-1}), and $\Delta H_{\text{H}_2\text{O}}$ is the latent heat of water (J mol^{-1}).

Brilman et al [10], through a bit different division of the different energy requirements of a DAC process, quantified the energy demand of an hypothetical DAC system:

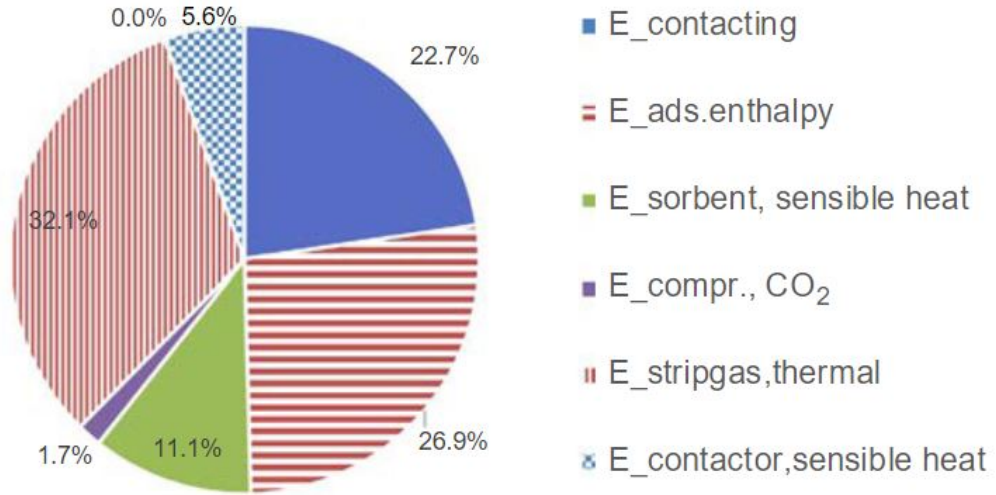


Figure 2.8: Cost distribution for energy costs for a hypothetical amine sorbent process [10]

As can be seen in figure 2.8, the energy cost for the sorbent regeneration is by far the largest in the process with an approximate energy demand of 70% of the total energy requirement.

2.2.3. Lifetime

Although the lifetime characteristics of the sorbent will not be covered in this thesis, it is worth keeping in mind how the performance of the sorbent is affected by degradation. As it can be seen in figure 2.5, the lifetime of the sorbent is mainly affected by three things: oxidative degradation, thermal degradation and evaporation losses [70][17][28]. Sorbent degradation affects the performance of the DAC process; so, it is important to maintain a minimum quality [5].

The first two types of degradation mechanisms act via irreversible chemical reactions of O_2 (oxidative) and CO_2 (thermal) with the amine active sites at high temperatures, effectively reducing the sorbent capture capacity. Evaporation losses occur also at high temperatures and are related to the vapor pressure of the sorbent; this type of losses not only have a cost penalty as more sorbent needs to be added, but also have a negative environmental impact [59].

Oxidative Degradation

Oxidative degradation of amines may be explained through two radical mechanisms: electron transfer or hydrogen abstraction [30]; and it is measured by the amount of degradation products emitted/formed, or the amount of amine lost. In an experimental study with MEA, Leonard et al [28] investigated the effects of O_2 concentrations and the effects of temperature in oxidative degradation:

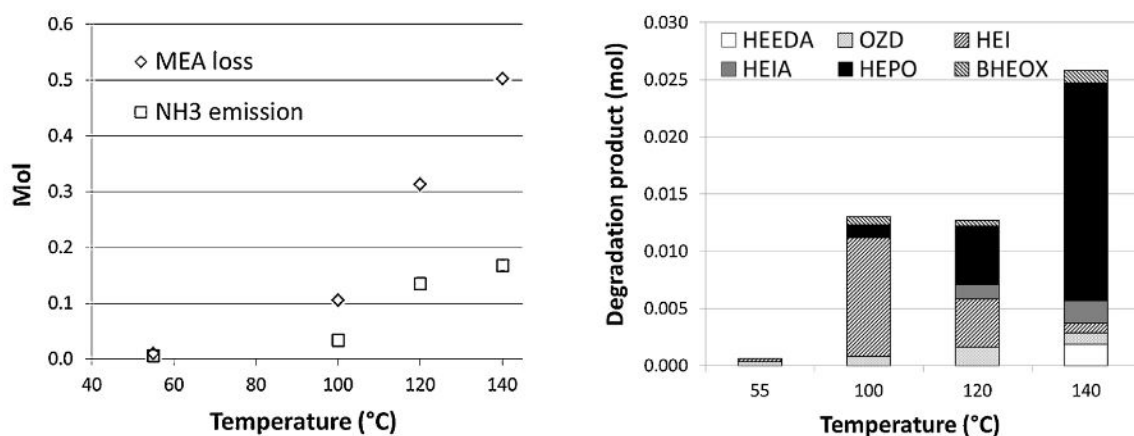


Figure 2.9: Oxidative degradation: Temperature effect in: MEA losses (left), the formation of degradation products in liquid (right) [28]

Since O_2 concentrations are somewhat constant in ambient air, the most interesting effect in oxidative degradation is the one of temperature (figure 2.9). As can be seen, oxidative degradation are triggered at higher temperatures, hinting that it occurs the most at the stripping section of the DAC process.

Thermal Degradation

Thermal degradation mainly occurs in the presence of CO_2 and at temperatures above $100^\circ C$ [70]. However, thermal degradation has also been seen at temperatures higher than $200^\circ C$ without the presence of CO_2 , where molecule cleavage takes place [28]. Because the regeneration of amine-based sorbents occurs at temperatures way below $200^\circ C$, only the thermal degradation in presence of CO_2 is of interest.

Evaporation Losses

Evaporation losses occur when molecules at the surface of a liquid break the liquid phase inter-molecular forces and escape into the gas phase, and is measured by the percentage loss of the solvent. As stated by Gowda [22], there are several factors that influence evaporation rates: vapor pressure, temperature, surface area, flow rate, inter-molecular forces.

2.3. Factors affecting characterization

There are many factors that affect the different characterization categories and parameters explained in section 2.2. In this section, these factors will be explained per DAC system component: sorbent, absorber column, stripper column, and also external parameters. It is important to acknowledge that not every single affecting factor will be covered, but those that are of interest to ZEF and/or those that are to be measured/monitored during the characterization process.

2.3.1. Sorbent

The sorbent selection is a crucial design step in the DAC system since this component affects every single category of the characterization parameters. As discussed, ZEF uses liquid aqueous amine based sorbents, which have many parameters that characterize their performance, focus will be given to the following: cyclic capacity, regeneration energy, and viscosity

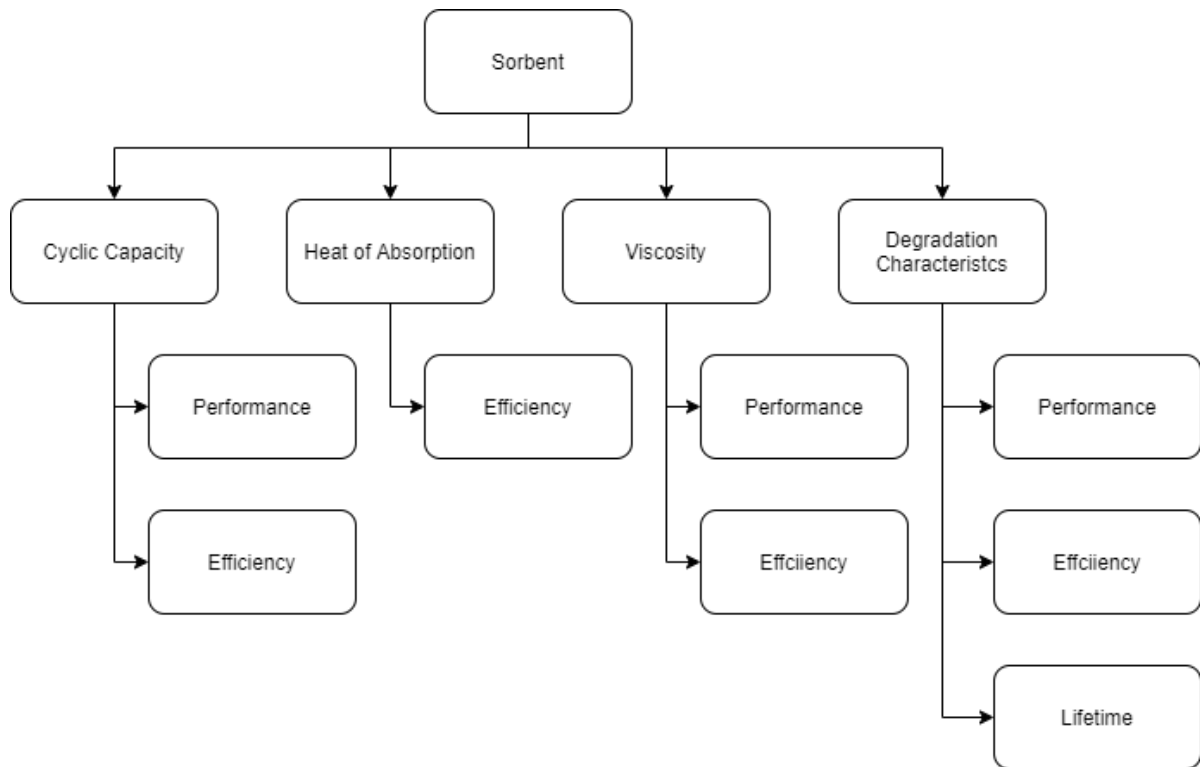


Figure 2.10: Sorbent's characteristics and their influence in DAC system characterization

Cyclic Capacity

The cyclic capacity of a sorbent is defined as the difference between its rich and lean loading [9]. The rich loading is the maximum amount of CO₂ that a given sorbent is capable of capturing in equilibrium. Theoretically, TEPA having five amine sites (two primary and three secondary)[4] has a maximum CO₂ rich loading of 2.5 molCO₂/molTEPA. However, in practice this loading is not reached for several reasons: CO₂ solubility, amine concentration, diffusion and kinetics limitations.

The lean loading of a sorbent is defined as the CO₂ concentration in the sorbent after the regeneration process. Ideally, all the captured CO₂ would be released during regeneration. In practice this is not the case and is also explained by the same phenomena as rich loading.

The importance of cyclic capacity in the performance characteristics is simple: the higher the cyclic capacity, the more CO₂ can be removed per cycle and thus the higher the Absorber Capacity. A higher cyclic capacity has the potential of reducing the Energy Requirement of the process. At higher cyclic capacities, a required total output can be reached with less cycles and thus less energy is spent.

Heat of Absorption

As explained before, the regeneration energy can be divided in different components. In a aqueous amine solution characterization procedure, Goetheer et al [15] proposed a sorbent focused division of the total regeneration energy (equation 2.15). About 50-60% of the total energy of regeneration comes from the heat of CO₂ absorption [15][43], so lowering this component of the regeneration energy will bring big savings in terms of total energy consumption.

$$E_{\text{regeneration}} = E_{\text{heat of absorption}} + E_{\text{sensible heat}} + E_{\text{heat of vaporization}} \quad (2.15)$$

The heat of absorption is usually high for primary and secondary amines, while for tertiary amines it tends to be lower. One would be tempted to say that simply the amine with the lowest heat of absorption should be selected. However, as explained before, due to the very low CO₂ concentration in ambient air, sorbents with high heat of absorption are required; so a balance must be met. In their solvent characterization study, Goetheer et al [15] measured the heat of absorption of different amines at room temperature and pressure and CO₂ loading for different aqueous amine solution. They identified group C as promising sorbents for CO₂ absorption; however, this study was performed for post combustion

purposes. In a similar study, Barzagli et al [8] showed that a high yield production of amine carbamate is decisive for an efficient CO₂ capture; thus primary and secondary amine are better in DAC processes.

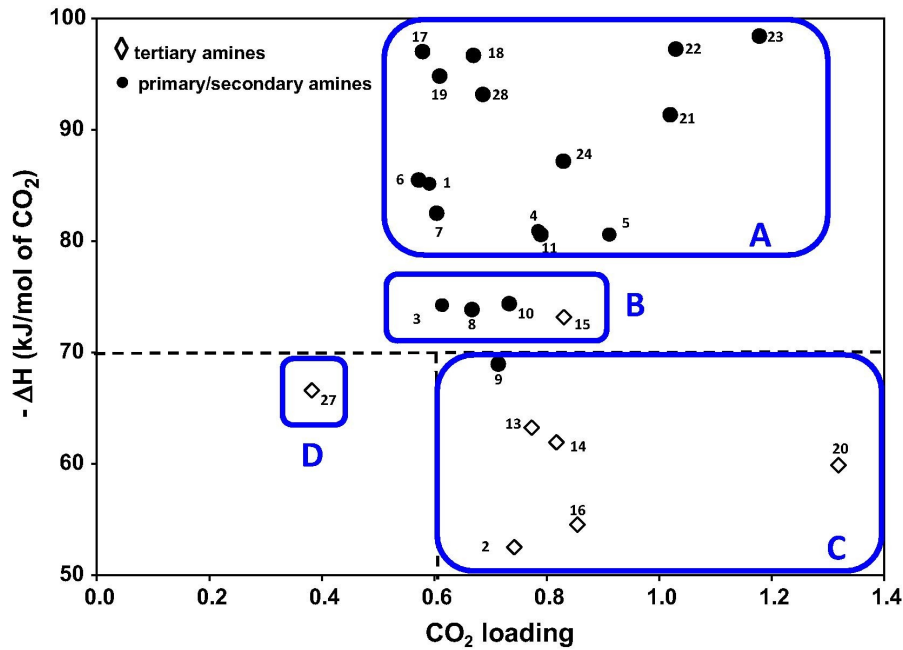


Figure 2.11: Heat of absorption (kJ/mole of CO₂) of aqueous amine solution at 313.15 K and atmospheric pressure [15]

The importance of the heat of absorption in the efficiency characteristics has a dual effect: on one side, a low heat absorption is desired if the total regeneration energy is to be lowered (thus decreasing the total energy requirement). On the other hand, high heats of absorption are desired to increase the capture efficiency of the process. Thus, an optimal must be selected.

Viscosity

The viscosity of the sorbent plays a major role in both the performance and efficiency of the DAC process. To begin with, viscosity has a major limiting effect on the diffusion of CO₂ into the thin film region as explained by the modified Stokes-Einstein equation (equation 2.3). The higher the viscosity, the lower the diffusion coefficient and thus the less CO₂ will be diffused into the thin film for chemical absorption with the amines' active sites. While characterizing a novel solvent, Apaiyakul et al [3] compared the viscosity and CO₂ diffusion coefficient of their solvent to that of common solvents, where the more viscous solvents showed lower diffusion coefficients. Furthermore, Miller et al [35] studied the effects of adding PEG to TEPA. In the study, it was found that PEG supported the promotion of diffusion of adsorbed CO₂ through decreasing the TEPA viscosity.

The viscosity also plays a role in the energy requirements of the process. Besides influencing diffusion as explained before, it also plays a major role in the energy demand for the solvent distribution (pumping energy). Due to the highly laminar nature of the flow distribution in the system, effect of viscosity can be analytically determined by the pressure drop caused through Darcy-Weisbach equation (equation 2.16), which shows that at higher viscosity a higher pressure drop must be overcome by the pumping system; translating to higher energy requirements (equation 2.11).

$$\frac{\Delta p}{L} = \frac{128}{\pi} \cdot \frac{\mu Q}{D_c^4} \quad (2.16)$$

where Δp is the pressure drop (Pa), L is the length of the pipe (m), μ is the dynamic viscosity of the fluid (Pa·s), Q is the volumetric flow rate of the fluid (m³ s⁻¹), and D_c is the hydraulic diameter of the pipe (m).

Clearly, the role of viscosity in both the performance and effectiveness of the process is of importance: less viscous solvents are beneficial in terms of performance (diffusion related mechanisms) and in terms of energy demand (pumping energy, effectiveness in removal).

2.3.2. Absorber Column

The absorber column plays a major role in determining the performance and efficiency of the DAC process. The choice of design of the absorber column, how the sorbent and air are distributed, the total volume of the column and the effective contact area between sorbent and air, all affect the characteristics of the process.

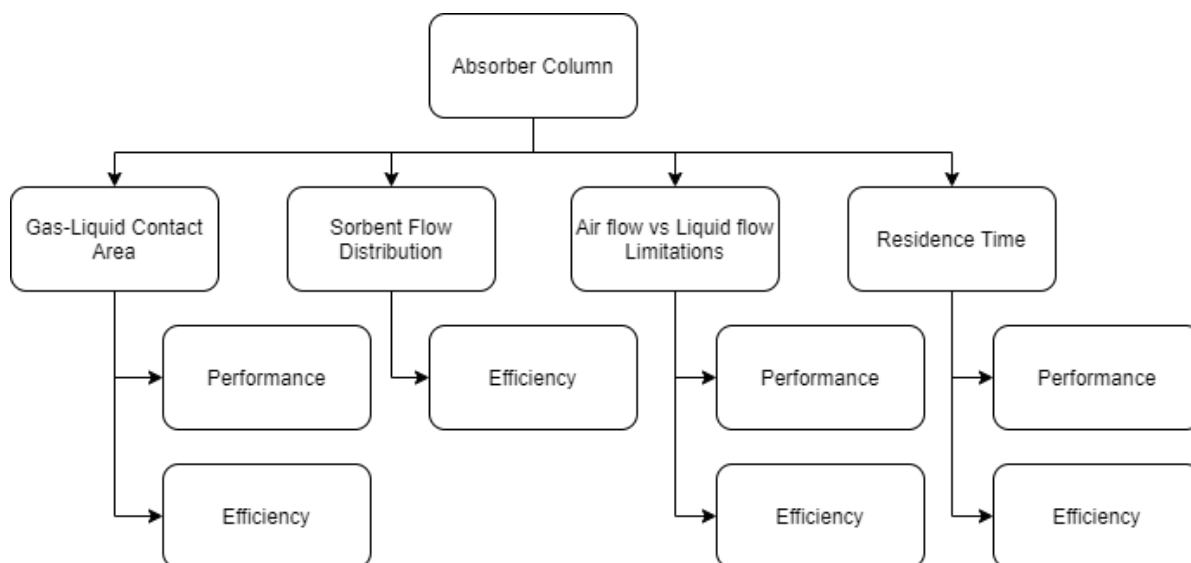


Figure 2.12: Absorber Columns's characteristics and their influence in DAC system characterization

Gas-Liquid Contact Area

As explained in section 2.1.1 through the two-film theory, chemical absorption occurs mainly in the thin film region of the sorbent. Because of this, maximizing the contact area between the air and the sorbent is vital. Furthermore, the effect of the contact area can also be understood through the different models used in literature for absorption kinetics. In packed columns, the type of columns where mostly all models are based on, the contact area is referred to as the interfacial area, and many correlations between the surface area of the packing and this interfacial area have been proposed. General agreement is found in that the packing's interfacial area greatly impacts the liquid-side mass transfer coefficients; the volumetric mass transfer coefficient increases with increase of surface area [60] [67][27][19].

The contact area affects the performance of the DAC process by affecting the chemical absorption process: the higher the effective contact area between the gas and liquid in the absorber column, the more CO₂ can be captured.

Sorbent Flow Distribution

Closely related to the Gas-Liquid Contact Area is the Sorbent's flow distribution. To begin with, the flow distribution must maximize the contact area between air and sorbent. The majority of DAC processes in industry use chemical adsorption through supported amines, so the flow distribution is not of concern in this type of DAC processes. Carbon Engineering uses packed columns for the sorbent distribution. The issue with packed columns is first the challenge to actually determine the contact area as discussed previously, but they also come with a high pressure drop (air side) which adds to the energy demand of the process[60][10]. ZEF uses an innovative approach to the sorbent distribution that overcomes pressure drop issues.

The sorbent distribution mechanism also needs to both effectively and homogeneously distribute the sorbent across the sorbent so that the volume of the column is effectively used. Furthermore, because ZEF operates in a continuous process, the distribution mechanism should also be designed in such a way that the pressure drop across the process, and thus the energy requirements, are minimized. Again, Darcy-Weisbach equation can be used to understand the effect of: long lengths of pipes, small hydraulic diameters, etc.

Clearly, the design of the Sorbent Flow Distribution affects the performance by affecting the capture capacity of the column (homogenous distribution, contact area). Also, it can affect the efficiency of the process by both affecting the removal efficiency as well as the energy demand.

Air flow vs Liquid flow limitations

The air's mass flow rate and sorbent's mass flow rate both have an effect in the performance and efficiency of the DAC process. Studies by Fu et al [20] and Xu et al [74] have analyzed the effects of mass flow rate of both sorbent and air on the overall mass transfer coefficient of the absorption process. As it can be seen in figure 2.13, increasing the sorbent flow rate has a positive effect in the overall mass transfer coefficient; this is due to more free amine-active sites being available per time, and also by a reduction in the film thickness.

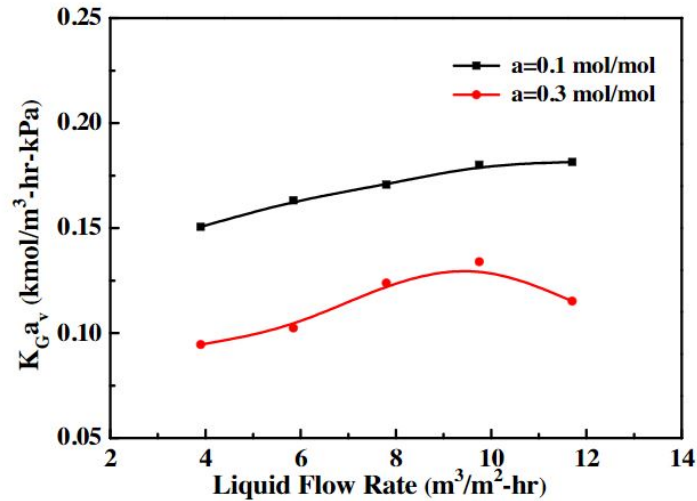


Figure 2.13: Effect of liquid flow rate on overall mass flow rate [74]

On the other hand, according to the same studies, increasing the air flow rate does not have a significant impact in the overall mass transfer; as can be seen in figure 2.14. According to Fu et al, this is due to the mass transfer process being mainly controlled by the resistance in the liquid phase.

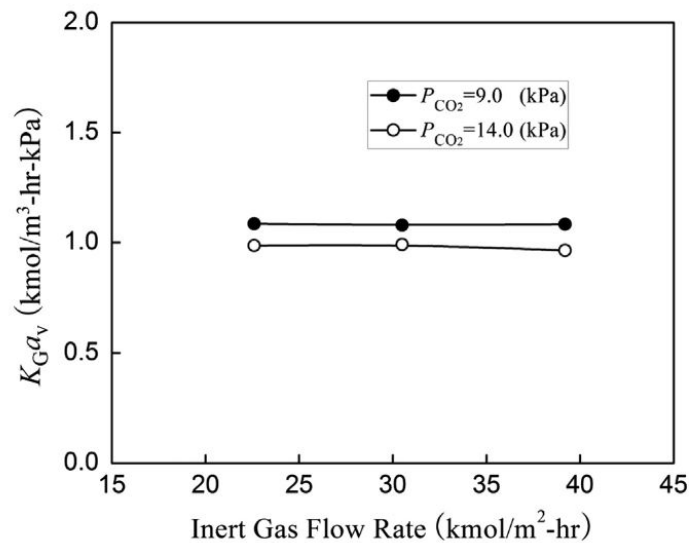


Figure 2.14: Effect of gas flow rate on overall mass flow rate [20]

It is important to mention that both studies, and majority of studies in same topic, were performed in packed columns. So any other flow distribution design, like ZEF's, could potentially give different results. Understanding if the absorber column is air side or fluid side limited allows to better optimize the working parameters, and thus has an effect in the overall performance and efficiency of the process.

2.3.3. Stripper Column

The Stripper Column design and operational parameters have great influence in all the characterization categories. The choice between trayed or packed columns, the residence time, the regeneration working conditions, whether reflux is used or not, and the use of heat exchangers all exert different effects on the characteristics of the DAC process.

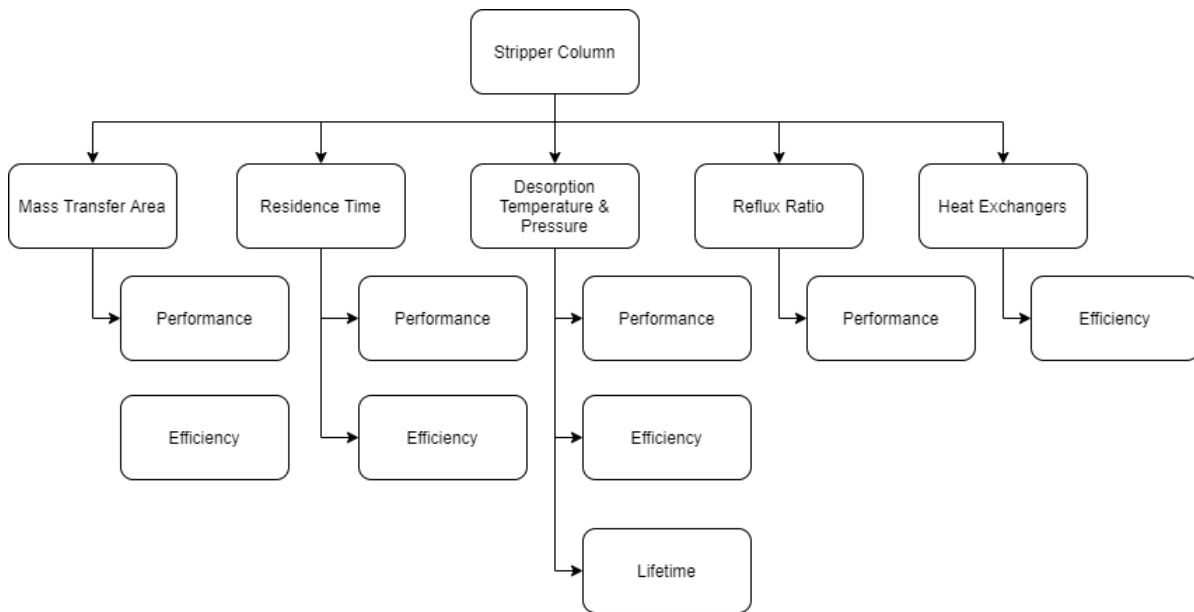


Figure 2.15: Stripper Columns's characteristics and their influence in DAC system characterization

Mass Transfer Area

Similarly as with the Absorber Column, maximizing the mass transfer area (contact area between gas and liquid in the stripper) is fundamental to improve the regeneration process in the stripper. As mentioned before, several models to predict both gas-side and liquid-side mass transfer coefficients showing the influence of mass transfer area are found in literature.

As with the Absorber Column, maximizing the mass transfer area of the Stripper column affects the performance in terms of how much CO_2 is released, as well as affects the efficiency by affecting the cycle's capacity.

Residence Time

Dubhashi [69] and van de Poll [68] proved that the regeneration process is mass transfer limited when compared to reaction kinetics. Because of this, the residence time in the stripper column plays such a crucial role. In simple terms, enough time should be allowed to the sorbent to reach its vapor liquid equilibrium loadings for the regeneration conditions. If the residence time is too low, then the maximum cyclic capacity possible of the process is not obtained.

Desorption Temperature & Pressure

The Desorption Temperature and Pressure effect is better explained through Vapor-liquid equilibrium (VLE), VLE describes the state of coexistence of a gas and a liquid phase for a particular species. For a mixture, this means that the liquid phase of one of the components at certain temperature and pressure is in equilibrium with its vapor phase at the same temperature and pressure. This allows to determine the composition of both gas and liquid phases for a given pressure and temperature.

Given the fact that ZEF works at ambient pressure, work has been performed in the temperature dependence of VLE for sorbents used in the process. As mentioned before, in a stripper column a temperature gradient is created, which means that at different stages different equilibrium compositions can be reached. The design of a stripper column must be such that the VLE at each stage is exploited to its maximum potential.

Downing [14] developed experimental VLE curves for the ternary mixture of TEPA-Water- CO_2 for certain temperatures, as well as for the binary mixture of TEPA-Water (vapor curves). Then, Downing developed a model used to extrapolate and obtain data for higher temperature and pressure ranges. Through this model, and the experimental data, several isotherms were plotted. These curves can be used to determine the theoretical cyclic capacity of the process, and thus showcase the importance of desorption temperature:

- Absorption is carried at ambient temperature 20°C (293.15°K), and the partial pressure of CO_2 is that of ambient air (0.04 kPa).
- Using ambient temperature and partial pressure of CO_2 , the rich loading is determined from the VLE curves.
- The desorption temperature is selected to be, for example, 120°C (393°K), and the system pressure is atmospheric pressure (100 kPa). Based on vapor curves, this corresponds to a water partial pressure of 75-80 kPa.
- The remaining pressure, 25-20 kPa, represents the partial pressure of CO_2 .
- Using the desorption temperature and the partial pressure of CO_2 , the lean loading is determined from the VLE curves.

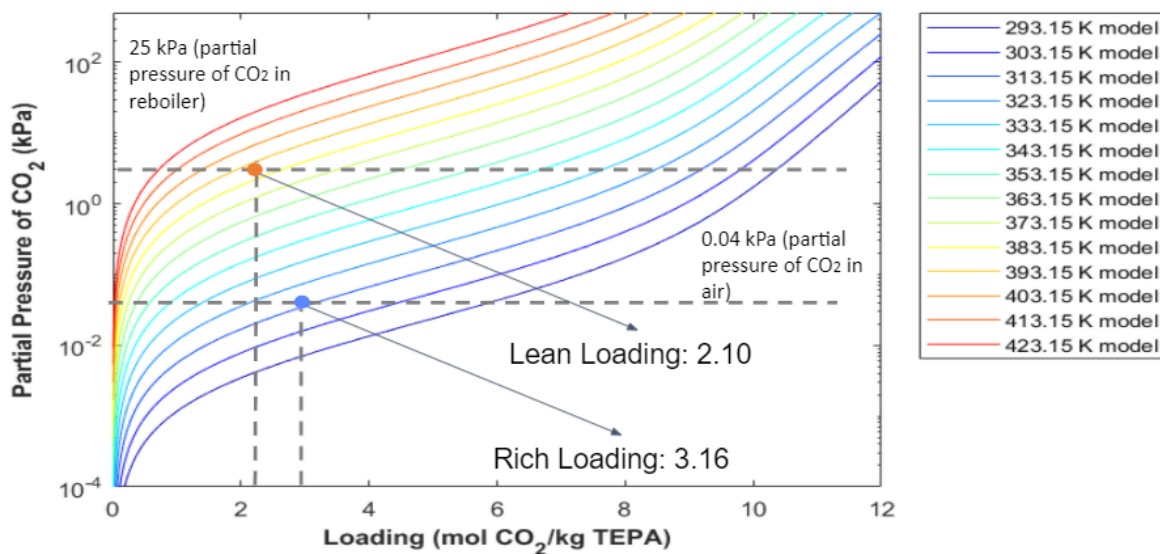


Figure 2.16: VLE for sorbent ternary mixture at 1 bar and different temperatures [14]

As can be seen in figure 2.16, the selection of higher desorption temperatures would give a lower lean loading, and thus a higher cyclic capacity.

Furthermore, and as was explained in the lifetime section, temperature has a major role in degradation effects. At higher temperatures not only is degradation triggered, but also the degradation rate increases. So, although as high a regeneration temperature is desired for performance purposes, a limit must be set in order to have good lifetime characteristics.

Reflux Ratio

The Reflux Ratio plays an effect in both performance and efficiency of the process. Burak et al [16] proposed a minimum reflux ratio as follows:

$$R_{\min} = \frac{\frac{x_D}{x_F} - \alpha_{AB} \frac{1-x_D}{1-x_F}}{\alpha_{AB} - 1} \quad (2.17)$$

where R_{\min} is the minimum reflux ratio, x_D is the liquid mole fraction of the distillate, x_F is the liquid mole fraction of the feed, α_{AB} is the relative volatility; which adapts to the desired top product purity. In an extreme case, if the top product is wanted as pure product, equation 2.17 simplifies to:

$$R_{\min} = \frac{1}{(\alpha_{AB} - 1) x_F} \quad (2.18)$$

Although reflux ratio has a positive effect on product purity, it has a negative effect in energy requirements. Any recirculated water into the stripper represents an extra amount of water that needs to be evaporated; thus increasing the energy demand of the process. It is clear then that an optimal point must be met in order to make the best use of the positive and negative effects of the reflux ratio in the characteristics of the DAC process.

Heat Exchangers

The implementation of heat exchangers in the stripping cycle has a great effect in the overall energy demand of the process. To begin with, the heat exchanger used in the reboiler section of the stripper column has a great effect in the effectiveness of how much heat is transferred from the heating fluid to the rich sorbent. The more effective the heat exchanger is, the more effectively the energy input into the reboiler is used. Furthermore, a rich-lean sorbent heat exchanger can be used to pre-heat the coming cold rich sorbent with the waste heat of the lean sorbent leaving the stripper column.

The efficiency of a heat exchanger is defined by the amount of heat exchanged between the fluids and the available heat to be transferred [23]:

$$\varepsilon \equiv \frac{q}{q_{\max}} \quad (2.19)$$

where q is the recovered heat (W), q_{\max} is the maximum available heat (W), which can be determined as follows:

$$q_{\max} = C_{\min} (T_{h,i} - T_{c,i}) \quad (2.20)$$

where C_{\min} is the smaller Heat Capacity rate between the hot and cold fluid ($W K^{-1}$), and $T_{h,i}$, $T_{c,i}$ are the inlet temperature of the hot and cold fluid respectively ($^{\circ}K$). Furthermore, q in equation 2.19 can be defined as:

$$q = UA\Delta T_{lm} \quad (2.21)$$

where U is the overall heat transfer coefficient ($W m^{-2} K^{-1}$), A is the effective heat transfer area (m^2), and T_{lm} is the mean log temperature difference ($^{\circ}K$), found through:

$$\Delta T_{lm} = \frac{\Delta T_2 - \Delta T_1}{\ln(\Delta T_2/\Delta T_1)} = \frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1/\Delta T_2)} \quad (2.22)$$

In the case of plate heat exchangers, ΔT_1 and ΔT_2 are determined as follows:

$$\begin{aligned} \Delta T_1 &\equiv T_{h,1} - T_{c,1} = T_{h,i} - T_{c,o} \\ \Delta T_2 &\equiv T_{h,2} - T_{c,2} = T_{h,o} - T_{c,i} \end{aligned} \quad (2.23)$$

The more effective the rich-lean heat exchanger is, the more energy savings can be obtained in terms of sensible energy (energy required to bring the rich sorbent to the desorption temperature). It is clear then that the use of heat exchangers, and how effective they are, can improve the efficiency of the DAC process in terms of energy requirements.

2.3.4. External Parameters

External parameters are related to environmental conditions in which the system is operating. Amongst the many weather characteristics, the following are of interest in the characterization process: Humidity, Temperature and CO₂ Concentration.

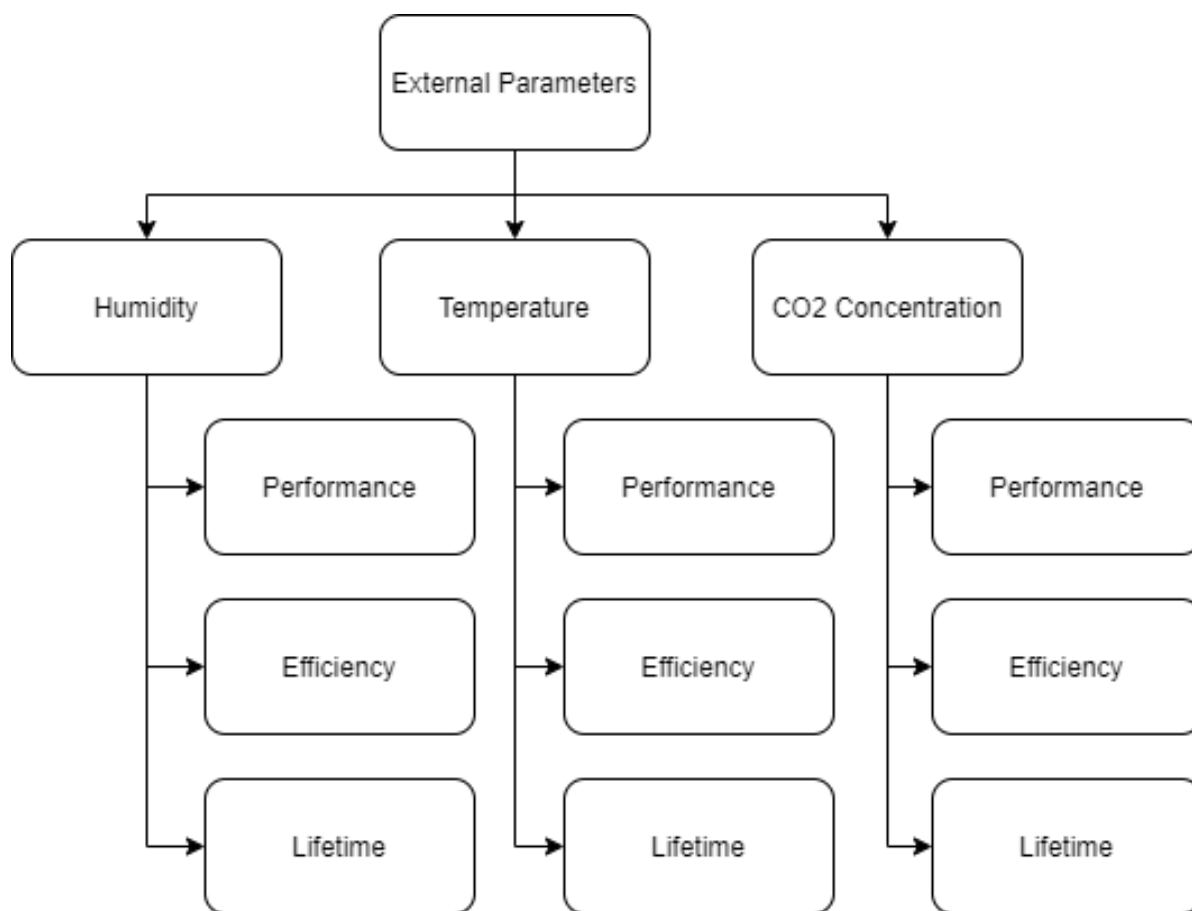


Figure 2.17: External Parameters' characteristics and their influence in DAC system characterization

Humidity

The absolute humidity is a measure of the amount of H₂O in the air. Humidity is a very important factor that can cause significant differences in the performance, efficiency, and lifetime of the DAC process. In the performance aspect, there is great agreement on how the presence of moisture improves the performance of DAC processes by increasing its loading capacity [26]. In an study performed by Yu et al [78], the H₂O-CO₂-TEPA interactions were studied to determine how the presence of water affected the amine's capture capacity. It was determined that the presence of water facilitated the accessibility of secondary amines sites to CO₂ by a reduction of viscosity, and also the presence of water promoted the formation of hydronium carbamate and carbamic acid; which pumps up the amine efficiency to 1 mol CO₂ per mol TEPA.

This increase in CO₂ capture does come at a cost, as more water is present in the ambient air, and thus more is captured, the energy demand of the process increases as the presence of water increases the energy requirements for heating up the rich stream, and also increases the latent energy demand (more water needs to be evaporated).

Temperature

The ambient temperature at which the DAC process takes place has a big influence in the performance, efficiency and lifetime characteristics. Temperature's effect in the performance characteristics needs to be tackled from a kinetics perspective. As explained before, CO₂ absorption is an exothermic reaction and from a thermodynamic perspective it is positively influence by lower temperatures. However, lower

temperatures come with the penalty of reduced diffusion rates due to the trend of viscosity increase at lower temperatures.

In a review paper, Kong et al [26] gave a great summary on current literature information in the effects of temperature in the kinetics of CO₂ capture. The kinetic-temperature (KT) factor was introduced to measure the dependence of CO₂ capture on temperature. A large KT factor means faster kinetics with increasing temperature, KT factors close to 0 mean low sensitivity to temperature changes, and negative values decreasing kinetics with increasing temperatures. Amines with higher molecular weight tend to exhibit large KT factors, while amines with lower molecular weights show less significant dependence with temperature [26]. It is important to mention that almost all studies are under flue gas capture conditions, with limited data given for DAC processes.

The efficiency of the DAC process can also be affected by the ambient temperature in terms of overall energy demand. At lower ambient temperatures, the temperature gradient between stripper column and ambient air increases thus increasing the heat losses in this part of the process.

CO₂ Concentration

Carbon Dioxide is the spotlight factor of the entire DAC process, as it represents the main driving force. As shown through VLE curves in previous section, at higher CO₂ partial pressures more CO₂ is captured per mol sorbent. This is something that is also seen in the difference in carbon capture capacities (kg/m³ hr) between point-source capture processes and DAC capture processes: 63 and 0.4 respectively [10].

Given that the CO₂ concentration levels in ambient air are relatively constant around the planet and through time, no great effects are expected by CO₂ concentration in DAC processes.

2.4. Direct Air Capture at ZEF

ZEF began with an chemical adsorption process carried in batches, but soon realized that this was not the most efficient nor cost effective route to follow. This realization made ZEF change to a chemical absorption route coupled to a continuous process.

ZEF started working in chemical absorption processes using channel flow absorption columns. Through the works of Sinha [58] and Colaco [11], the first steps into chemical absorption were taken; the major take of their work was the understanding that CO₂ capture is a diffusion limited process, and thus all optimization needed to be made in the liquid side of the process.

Through the work of Serrano [54] and Ova [44] a strong understanding on how direct air capture actually works was established. To begin with, the diffusion limited characteristic of the process was experimentally proven, and also it was determined that the diffusion coefficient of CO₂ is two orders of magnitude less than that of water.

Again, through the work of Sinha [56] the first absorption column of ZEF was fully characterized. Through this work, it was proven how the viscosity of the sorbent increased significantly with an increase of CO₂ loading; something limiting to the process and that proved that channel flow was not the best approach.

Through the work of Dowling [14], the Vapor Liquid Equilibrium of CO₂ with the sorbent was for the first time experimentally determined and modelled. Her work allow to understand better the driving force of the absorption process, and at the same time proved how challenging it was to model.

de Matteis [15] tried to tackle the challenges faced by channel flow in terms of viscosity through the implementation of different mixing strategies. However, through his work it was proven that only non-passive mixing techniques would counter act the effects of viscosity increase. This was deemed not acceptable as the main goal was to keep the process as simple as possible. Parallely, the work of Mulder [38] focused on finding a suitable diluent for the selected amine sorbent trying to also reduce the viscosity increase with increasing CO₂ loading.

Sanz [50] and Nagulagama [39] carried the full system (absorption and regeneration) of ZEF's newly proposed DAC process with their so called MiniDAC system. Furthermore, Dubhashi [69] carried the dynamic characterization of ZEF's stripper column and later modelled said system.

2.4.1. Major takeaways from ZEF's trajectory

As shown, ZEF has done great work in the world of DAC, through its numerous teams vast knowledge has been acquired, and design decisions have been made which has brought ZEF to its current DAC

prototype: the miniDAC (figure 2.18). To summarize, the major decisions/conclusions are:

- ZEF works in a continuous chemical absorption process. Both the absorber column and stripper column work at ambient pressure due to simplicity.
- Channel flows are not efficient for the process, thus an alternative liquid distribution system is used in ZEF's process.
- ZEF uses TEPA-PEG sorbent solutions with varying ratios.
- Characterization of small (in terms of production) systems has been carried.
- Performance parameters, such as Space Time Yield, can be achieved by varying independent parameters. Thus systems can be designed with target values of the performance parameters.

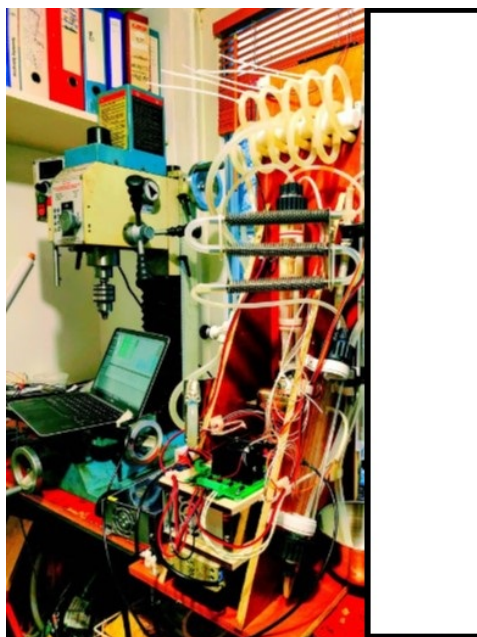


Figure 2.18: ZEF's DAC prototype today

The miniDAC is the predecessor of the 10X DAC system. It is thanks to the findings of the miniDAC characterization that ZEF has been able to design the 10X, which will be explained in detail in its own chapter.

2.5. Major Conclusions

From the research previously done at ZEF, and the information found in literature, the following major conclusions can be drawn:

- The characterization of a DAC system is divided in four main categories: performance, efficiency, lifetime and cost.
- The absorption process is diffusion limited, so sorbent distribution should be such that the thin film region is "refreshed" in the absorber column.
- Sorbent viscosity plays a major role in the absorption process given the mass transfer limitations of such processes.
- The cyclic capacity is dependent on the sorbent type, absorption/desorption kinetics and the regeneration conditions (temperature, pressure).
- Oxidative and Thermal degradation play a major role in both the performance and lifetime of the process.
- The vast majority of the energy demand comes from the regeneration process.
- Ambient conditions play a major role in the performance, efficiency and lifetime of the process.

2.6. Research Objectives and Questions

This thesis' primary goals are the build and the complete characterization of ZEF's 10X DAC system. To tackle this, the task at hand has been divided in two main categories, each with a set of research questions:

1. Experimental Characterization.

- 1.1 What are the characteristics of ZEF's 10X DAC system and how does it compare to the expected performance/model predictions?

- 1.2 What is the effect of environmental conditions in the performance of ZEF's 10X DAC system?

2. Design Optimization

- 2.1 How would an optimized DAC system design look like?

The DAC Process Design will be tackled in chapter 3, where details of ZEF's DAC system alongside with reasoning behind design decisions will be given. The modelling work performed during the thesis worked will be presented and explained in chapter 4. The Experimental Characterization represents the bulk of this thesis and will be tackled in the Results & Discussion section of this thesis. Finally, the Design Optimization will be tackled in its own chapter where suggestions for improving ZEF's models and the 10X DAC system design will be given based on the findings of the characterization process.

Experimental set-up

In this chapter, the design of the built and characterized 10X Direct Air Capture prototype is presented. The experimental plan for the characterization of the system is also introduced and explained. Finally, the measurements performed during experiments are explained alongside with the required equipment and calculations.

3.1. 10X DAC Prototype

The work of this thesis focused on the build and commissioning of the 10X DAC prototype designed by ZEF. However, in order to better understand the functioning, and the effort involved in the goal of this thesis, a brief explanation of the prototype's design is presented. For details of the build process, please refer to appendix C.

The 10X DAC system is the first full scale prototype that ZEF develops for its process. It consists of a full Direct Air Capture system with an absorption and a regeneration section. The sorbent used is tetraethylenepentamine (TEPA) diluted with Polyethylene glycol (PEG) in a certain ratio. The 10X DAC expected performance and design criteria is presented in table 3.1. For ease of understanding, the design will be presented in three main sections: sorbent, absorber section, and regeneration section.

Table 3.1: Design Criteria

Parameter	Value	Unit
CO ₂ Output	0.00217	[molCO ₂ /s]
H ₂ O:CO ₂ Ratio	3:1	[-]
Energy Demand	<400	[kJ/molCO ₂]
Absorber Header	Injection Molding	[-]

3.1.1. 10X DAC Sorbent

The 10X DAC system design is based in the use of TEPA diluted with PEG in a TEPA:PEG weight ratio of 1:2.5 as a sorbent. The reason for this selection is the availability of experimental data and models on the sorbent's performance from previous worked done by ZEF.

Primarily, ZEF has been able to characterize the performance of this sorbent in terms of its capture capacity versus the driving force of the process.

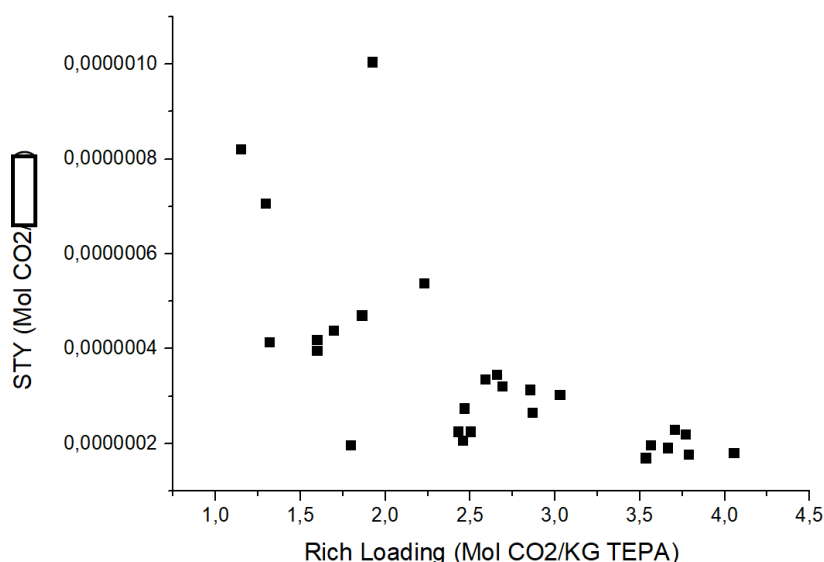


Figure 3.1: TEPA:PEG 1:2.5 performance [40]

(Note: specific units have been removed from y-axis due to Intellectual Property concerns)

3.1.2. Absorber Column

Absorber Sizing

Note: The sizing of the absorber column can be found in Appendix F,

Sorbent Distribution System

The next design aspect of the absorber column was the header, which works as the sorbent distribution system. Besides being required to distribute the sorbent homogeneously in the entire column, the challenge of the absorber header was that the design was required to be mass manufacturable through injection molding. Because of this, the absorber header designed consists of a plates stack-up.

Through the stack-up, three different sections through which the sorbent has to flow were designed: Inlet section, Cross-channel section, and Contraction section.



Figure 3.2: Absorber Header Sections

For each section of the header, the pressure drop to be experienced by the fluid was designed. The first step was to determine whether the flow would be laminar or not through Reynold's number. The higher Re expected to be experienced is 17.5, meaning that the **flow is highly laminar**. Due to the

nature of the flow, it was possible to apply the Darcy-Weisbach equation to each section and design for the desired pressure drop.

$$\frac{\Delta p}{L} = f_D \cdot \frac{\rho}{2} \cdot \frac{v^2}{D_H} \quad (3.1)$$

where:

Δp	= pressure drop	[Pa]
L	= length of the section	[m]
f_D	= Darcy friction factor	[-]
ρ	= fluid's density	[kg/m ³]
v	= mean flow velocity	[m/s]
D_H	= hydraulic diameter	[m]

For laminar flow regimes such as the ones experienced in the absorber column, the Darcy friction factor can be analytically solved for.

$$f_D = \frac{64}{Re} \quad (3.2)$$

The designed pressure drops for each section are summarized in table 3.2.

Table 3.2: Pressure drop design

Section	Design	unit
Inlet	14.1	[mbar]
Cross-channel	2.5	[mbar]
Contraction	30.4	[mbar]

Since the contraction section is the last section before the sorbent enters the absorber column's mass transfer area, by designing it with a pressure drop twice as high as the previous one, it is expected that the header is fully filled before the the sorbent exits the contraction section; thus being distributed in the entire column.

Air Distribution in the column

The air distribution system in the column is composed of two inlets at the bottom of the column, and two air outlets at the top; which allow to have a counter-current flow of air with respect to the sorbent. The column is fully enclosed by a polypropylene enclosure, guaranteeing that air only enters and exits through the designated ports.



Figure 3.3: Absorber Column

3.1.3. Regeneration Section

The regeneration section consists of a **packed stripper column**. The selected packing by ZEF consists of a 3D printed PA-12 geometry with a void fraction of 50%. The thermosyphon is heated using oil as a heating fluid, which is supplied through an external oil bath. The column fluid level is controlled through a u-tube open to ambient pressure, and has been placed such that the column has a hold up volume of 1.8 L.

The stripper outlet is connected to a total condenser, where the gas products are condensed before entering the connected flash tank. In the flash tank, CO₂ exits as a gas product, while H₂O is collected as a liquid.

As part of the regeneration section, a Rich-Lean Heat Exchanger has been installed to make use of the available heat in the lean sorbent leaving the column to pre-heat the rich sorbent that will enter the stripper column. This heat exchanger is an Alfa-Laval plate heat exchanger with a heat transfer area of 0.5 m².

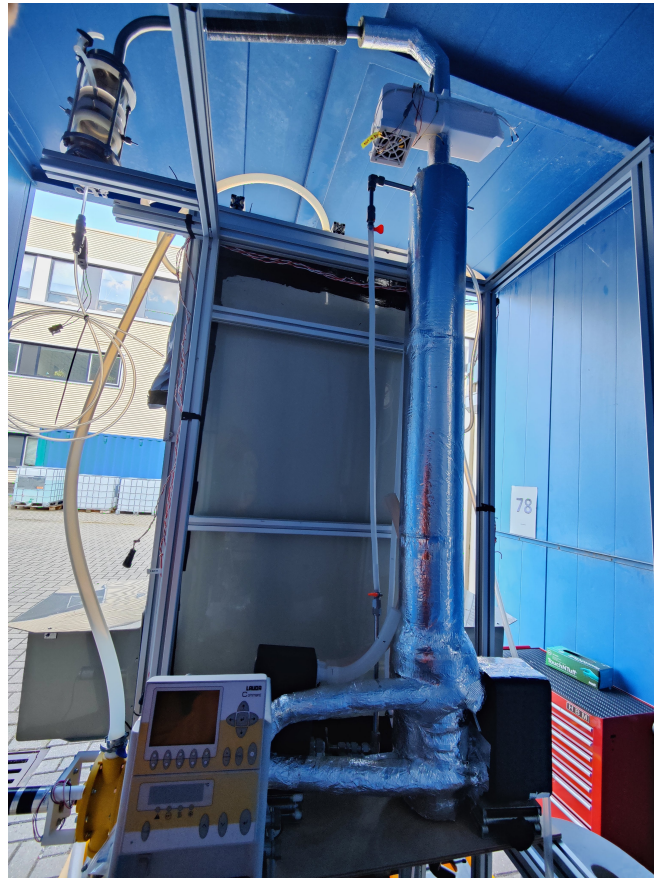


Figure 3.4: Regeneration Section

3.1.4. Other Mechanical Components

Besides the aforementioned major components, the 10X DAC design also includes:

- Two air fans with a combined capacity of up to 2800 m³/hr.
- Air filters at the inlets of the absorber column.
- A recycle pump with a capacity of up to 220 ml/rev for the absorber column circulation.
- A polypropylene enclosure to isolate the absorber column from the outside.
- A 38L sump for the sorbent.
- A stripper pump for the sorbent circulating in the stripper column.
- Insulation material to reduce heat losses in the regeneration section.

3.1.5. Process Flow and Measurement points

Figure 3.5 shows the P&ID of the DAC prototype, and the measurement points of the prototype are explained in table 3.3

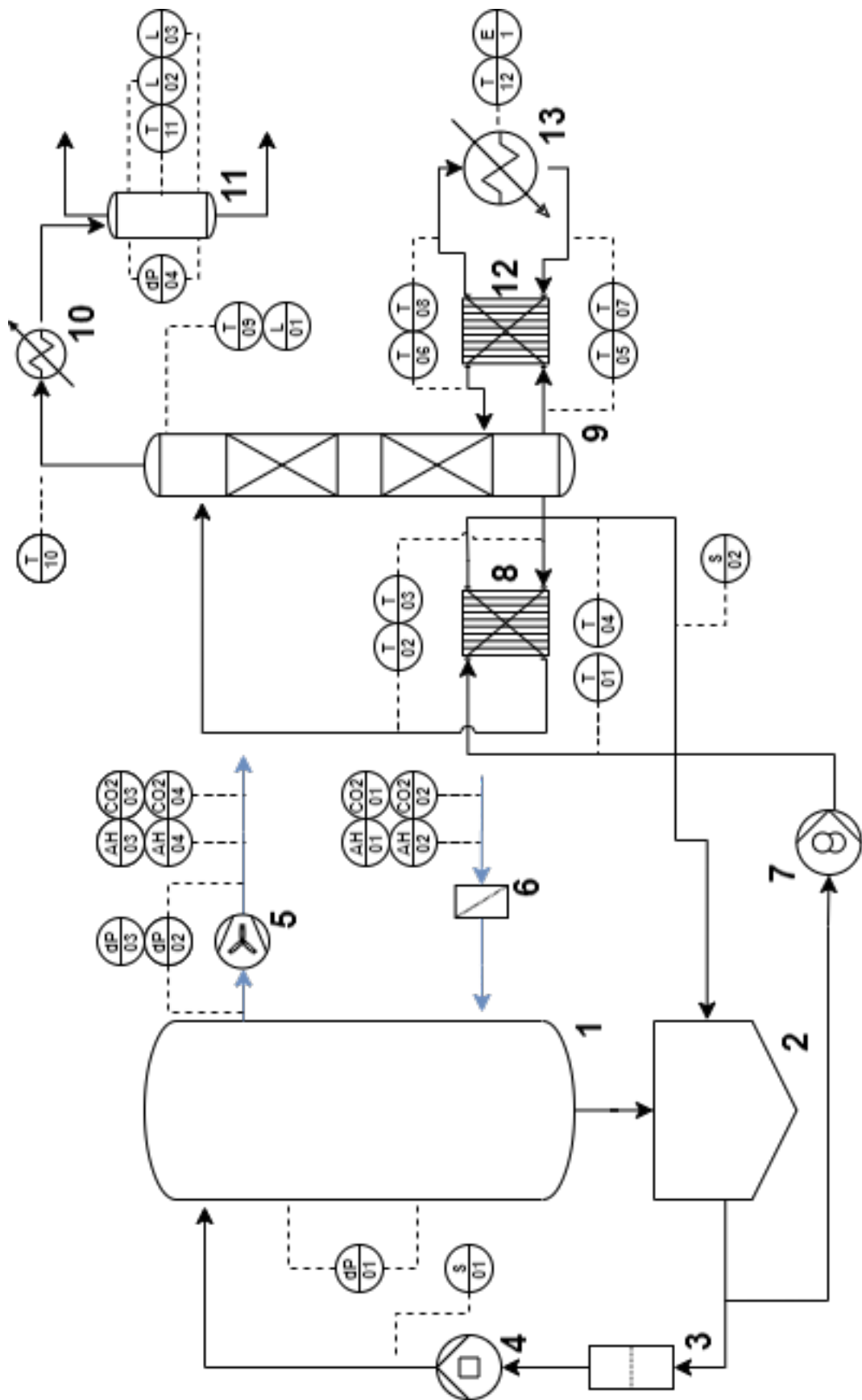


Figure 3.5: P&ID diagram of 10X DAC prototype

Table 3.3: 10X DAC Measurement points

Symbol	Measurement Parameter	Unit
AH01	Absolute Humidity Inlet Left	[gr/m ³]
AH02	Absolute Humidity Inlet Right	[gr/m ³]
AH03	Absolute Humidity Outlet Left	[gr/m ³]
AH04	Absolute Humidity Outlet Right	[gr/m ³]
CO201	CO2 Concentration Inlet Left	[ppm]
CO202	CO2 Concentration Inlet Right	[ppm]
CO203	CO2 Concentration Outlet Left	[ppm]
CO204	CO2 Concentration Outlet Left	[ppm]
dP01	Pressure Drop Absorber Column	[Pa]
dP02	Pressure Drop across Fan Left	[Pa]
dP03	Pressure Drop across Fan Right	[Pa]
dP04	Pressure Drop Flash Tank	[Pa]
E01	Energy Consumption Oil Bath	[W]
L01	Level Sensor Stripper Column Top	[-]
L02	Level Sensor Flash Tank Top	[-]
L03	Level Sensor Flash Tank Bottom	[-]
S01	Sample Collection - Rich Sorbent	[-]
S02	Sample Collection - Lean Sorbent	[-]
T01	Temperature Cold Sorbent In	[°C]
T02	Temperature Cold Sorbent Out	[°C]
T03	Temperature Hot Sorbent In	[°C]
T04	Temperature Hot Sorbent Out	[°C]
T05	Temperature Thermosyphon Bottom	[°C]
T06	Temperature Thermosyphon Top	[°C]
T07	Temperature Oil In	[°C]
T08	Temperature Oil Out	[°C]
T09	Temperature Stripper Top	[°C]
T10	Temperature Ratio Sensor	[°C]
T11	Temperature Flash Tank	[°C]
T12	Temperature Set Oil Bath	[°C]

All of the required sensors for the measurement points are managed through a common PCB, and the data from each sensor is plotted live in a Graphical User Interface (GUI) as well as saved for later data analysis.

The process flow is described as follows:

- The Recycle Pump (4) draws sorbent from the Sump (2) into the Absorber Column (1), where it is homogeneously distributed across the entire absorber area.
- Air is drawn by the Air Fans (5) into the Absorber Column (1), where it flows in a counter-current manner, and the CO₂ & H₂O capture takes place. The now rich sorbent is sent back to the Sump (2).
- The Stripper Pump (7) draws sorbent from the Sump (2) into the regeneration section, where it first enters the Rich-Lean Hex (8) to be pre-heated before entering the Stripper Column (9).
- The pre-heated sorbent enters the Stripper Column (9), where it is further heated by the Thermosyphon until it reaches the regeneration temperature set by the Oil-bath (13).

- Once the regeneration temperature is reached in the Stripper Column (9), both H₂O and CO₂ are desorbed. The vapor exits the column through the top and goes to through the Total Condenser (10), where the product is condensed before entering the Flash Tank (11). In the Flash Tank (11), CO₂ and H₂O are separated; the CO₂ exits as a gas product through the top, while the water exits as liquid through the bottom.
- The lean sorbent leaving the Stripper Column (9) goes through the Rich-Lean Hex (8) and its available heat is used to pre-heat the cold rich sorbent. Then, the lean sorbent is sent back to the Sump (2).

3.2. Experimental Plan

The 10X DAC prototype characterization can be divided into three parts: Absorber Characterization, Stripper Characterization, and Full System Characterization. For each part, experiments with different objectives were performed; which are enumerated individually.

3.2.1. Absorber Characterization

The main goal of the absorber characterization was to determine the absorber's carbon capture capacity. To do so, experiments were only the absorber column was running (i.e. no regeneration of the sorbent) were performed.

1. **Space Time Yield vs Driving Force:** in order to quantify the effect of the driving force in the carbon capture process, experiments were performed in which sorbent samples were taken in specific time intervals. Ambient conditions were logged, and samples were analysed using FTIR to determine the change in CO₂ loading over time.
2. **Space Time Yield vs Viscosity:** in order to quantify the effect of viscosity in the carbon capture process, experiments were performed in which the sorbent's residence time, and the number of mass transfer elements per meter absorber were logged and used to determine the sorbent's viscosity from experimental fits done previously at ZEF (see appendix D). Ambient conditions were logged, and samples were analysed using FTIR to determine the sorbent composition over time.

Assumptions:

- Air is considered to be distributed equally and in the entire mass transfer area of the absorber.
- The recycle pump, being a positive displacement pump, delivers a sorbent mass flow rate proportional to the selected RPM.
- No leaks in system, thus no sorbent loses and air only enters and exits through the designed inlets and outlets respectively.
- Sorbent composition in the system is uniform. Time between sample taking is above 5 times the residence time in the absorber sump.
- Sample collection process is valid.

3.2.2. Stripper Characterization

The main goal of the stripper characterization was to determine the stripper's capability to regenerate the rich sorbent. To do so, experiments were the absorber column's setting were fixed (i.e. sorbent and air mass flow rates), and the stripper column was ran were performed.

1. **Lean loading vs Residence Time:** in order to quantify the effect of residence time in the lean loading achieved by the regeneration process, experiments were performed in which the residence time in the stripper column was varied and samples were collected in specific time intervals. The samples were analysed using FTIR to determine the CO₂ concentration after the regeneration process.

Assumptions:

- The set-up is assumed to be leak tight, which was tested before experiments.
- Feed flow rate is assumed to be constant, and the magnitude set by the RPM of the feed pump.
- Sample collection process is valid.

3.2.3. Full System Characterization

The main goal of the full system characterization was to determine the overall CO₂ & H₂O production of the prototype, the performance of the Rich-Lean Hex, and the total energy demand of the process. To do so, experiments where the absorber column's setting were fixed (i.e. sorbent and air mass flow rate), and the stripper column was ran were performed.

1. **CO₂ Output:** in order to quantify the CO₂ production capacity of the system, experiments were performed in which sorbent samples were taken in specific time intervals, and were the CO₂ production was physically measured after the flash tank. The sorbent samples were analysed using FTIR to determine the CO₂ cyclic capacity of the process.
2. **H₂O output:** in order to quantify the H₂O production capacity of the system, experiments were performed in which sorbent samples were taken in specific time intervals, and were the H₂O production was physically measured after the flash tank. The sorbent samples were analysed using FTIR to determine the H₂O cyclic capacity of the process.
3. **H₂O:CO₂ Ratio:** in order to quantify the product ratio of the system, experiments were performed in in which sorbent samples were taken in in specific time intervals, and were the CO₂ & H₂O production was physically measured after the flash tank. The sorbent samples were analysed using FTIR to determine the H₂O & CO₂ cyclic capacity of the process, and thus determine the product ratio.
4. **Rich-Lean Hex:** in order to determine the heat exchanger's performance characteristics, experiments in which the heat transfer coefficient and efficiency could be determined were performed. During the experiments, the inlet and outlet temperatures of the hot and cold streams were logged, as well as the respective mass flow rates.
5. **Energy Demand Process:** in order to quantify the energy demand of the process, experiments were performed in which the entire system was ran. During the experiments, the oil-bath power input was measured in order to determine the total energy demand of the process. Measurements were taken to determine the different components of the energy demand: sensible heat, heat of desorption, actuators and losses.

Assumptions:

- Neither TEPA nor PEG are volatile, meaning the stripper product is a binary mixture consisting only of CO₂ and H₂O.
- Both the recycle and stripper pump provide a constant mass flow rate which is controlled through RPM.
- Entire set-up is assumed to be leak tight, and thus gases exit only through the flash tank outlet, and no air enters the system besides through the absorber inlets.
- Sample collection process is valid.

3.2.4. Experimental Plan Summary

The entire experimental plan can be found in table 3.4.

Table 3.4: Experimental Plan

Stage	Components	Measurements	Outputs
Absorber Characterization	Absorber Column	Ambient Conditions Sorbent Composition Residence Time Mass Transfer Element Number of Mass Transfer Elements Fans PWM CO ₂ Concentration	STY vs Driving Force STY vs Viscosity
Stripper Characterization	Full System	Feed Mass Flow Rate Sorbent Composition	Lean Loading vs Residence Time
Full System Characterization	Full System	CO ₂ Output H ₂ O Output Oil-bath Input Inlet & Outlet Temperature Cold Stream Inlet & Outlet Temperature Hot Stream Feed Mass Flow Rate	CO ₂ Produced H ₂ O Produced H ₂ O:CO ₂ Ratio Energy Demand Process Rich-Learn Hex performance

3.3. Measurements

For the experimental characterization of the prototype, several performance indicators must be measured/quantified (table 3.4). To do so, different techniques were used and calculations were performed, which will be presented in the following subsections.

3.3.1. Space Time Yield (STY)

The Space Time Yield (STY) is a parameter that indicates how much CO₂ the process is capable of capturing per unit volume and per unit time (i.e. the capture capacity of the system). To determine this parameter, two different methods were used: sorbent composition measurements, and CO₂ concentration in the air stream measurements.

Sorbent Composition Measurements

The STY can be determined through the sorbent composition as follows:

$$STY = \frac{\Delta C \cdot W_{TEPA}}{V_{Absorber} \cdot dt} \quad (3.3)$$

where:

STY	= Space Time Yield	[molCO ₂ /m ³ ·s]
ΔC	= change in CO ₂ loading between samples	[molCO ₂ /kgTEPA]
W _{TEPA}	= weight of TEPA in system	[kg]
V _{Absorber}	= volume of absorber column	[m ³]
dt	= time between samples	[s]

The absorber volume and the TEPA weight were known fixed parameters, so what had to be determined was the change in CO₂ loading. To do so, first a sampling methodology was established:

1. Sample collection point was established after the recycle pump in order to ensure well-mixing.
2. The time between samples was never lower than 5x the residence time in the sump.
3. 1 to 2 ml of sample was always collected, labelled and stored for later analysis.
4. Samples were always analysed at the end of each experiment.
5. Duplos were always performed in the analysis stage to ensure sample was well mixed and the concentrations were homogenous.

The sample analysis was performed using an Agilent Cary 630 FTIR machine, which gave an infrared spectrum of the sorbent sample. This spectrum was then taken to the TQ Analyst software,

where a pre-defined calibration allowed to quantify the weight percentage of all the components in the sample. For details on the FT-IR machine and the calibration, please refer to Appendix A.

Sample No	Component	FTIR 1			FTIR 2		
		Concentration (wt%)	Uncertainty	Measurement Fit	Concentration (wt%)	Uncertainty	Measurement Fit
C-5-2-L	TEPA	21	4.582	98.1	20.86	4.564	98.1
	PEG200	58.02	3.290		58.11	3.302	
	Water	16.64	3.670		16.56	3.687	
	CO2	0.24	0.951		0.22	0.944	

Figure 3.6: Example results from sample analysis

With the weight percentages, the concentration of CO₂ in the sample was determined as follows:

$$C = \frac{CO_2 w.t.\% * 1000}{MW_{CO_2} * TEPA w.t.\%} \quad (3.4)$$

where:

C	= CO ₂ concentration in sample	[molCO ₂ /kgTEPA]
CO ₂ w.t.%	= weight percentage of CO ₂	[%]
TEPA w.t.%	= weight percentage of TEPA	[%]
MW _{CO₂}	= Molecular weight of CO ₂	[g/mol]

By knowing the CO₂ concentration of each sample, and the time taken between samples, the STY was determined as indicated in equation 3.3.

CO₂ concentration in air stream measurements

The STY can be determined through the CO₂ concentration in the air stream as follows:

$$STY = \frac{\Delta CO_2 \cdot \dot{v}_{air} \cdot 1000 \cdot \rho_{air}}{3600 \cdot V_{Absorber} \cdot MW_{air}} \quad (3.5)$$

where:

STY	= Space Time Yield	[molCO ₂ /m ³ .s]
ΔCO ₂	= Change in CO ₂ concentration in air	[molCO ₂ /molAir]
\dot{v}_{air}	= Volumetric flow rate of air	[m ³ /hr]
ρ_{air}	= Density of Air	[kg/m ³]
V _{Absorber}	= volume of absorber column	[m ³]
MW _{air}	= Molecular weight of air	[g/mol]

The experimental setup is equipped with CO₂ concentration sensors in the air inlets and outlets. These sensors measure CO₂ in parts per million, and have a bias of +/- 30ppm. The readings of the sensors are converted into the required units, and used in equation 3.5.

The volumetric flow rate of air was determined by the measured pressure drop across the fans, and the fan calibration provided by the manufacturer. By having the volumetric flow rate of air and the CO₂ concentration change, the STY was determined as indicated in equation 3.5.

3.3.2. Driving Force

The driving force of the CO₂ capture process is given by the difference between the CO₂ vapour liquid equilibrium loading and the current CO₂ loading in the sorbent.

$$dC = C_{VLE} - C_{Rich} \quad (3.6)$$

where:

dC	= driving force	[molCO ₂ /kgSorbent]
C_{VLE}	= VLE Loading	[molCO ₂ /kgSorbent]
C_{Rich}	= current CO ₂ loading	[molCO ₂ /kgSorbent]

The current CO₂ loading is determined through FTIR as explained in subsection 3.3.1.

The VLE loading is a function of the sorbent type, sorbent temperature, the partial pressure of CO₂, and the current CO₂ loading in the sorbent (see appendix D). In the DAC process, the partial pressure of CO₂ is assumed constant and with a value of 0.4 mbar.

$$C_{VLE} = f(Sorbent, T, p_{CO_2}, C_{Rich}) \quad (3.7)$$

Previous work done at ZEF [14] developed experimental fits and data for VLE loadings of TEPA:PEG 1:2.5 at different CO₂ partial pressures and temperatures. This data was then fitted to several adsorption models and to the Clausius-Clapeyron equation to develop a model capable of determining the VLE loading at different conditions. Said model was used in this thesis to determine the VLE loading for the experimental conditions.

3.3.3. Viscosity

Viscosity plays a major role in the CO₂ capture process as it influences the diffusion mechanism significantly. Previous work done at ZEF developed experimental fit models in which the viscosity could be determined from certain measurable process parameters. The required parameters are the number of mass transfer elements per meter, the residence time of the mass transfer elements and the volumetric flow rate of the sorbent in the absorber column.

$$\mu = f(n_d, \tau, \dot{m}_{absorber}) \quad (3.8)$$

All the required inputs to the models can be experimentally measured, and then the model is used to compute the sorbent's viscosity in that given moment (see appendix D).

3.3.4. Lean Loading

The lean loading of the sorbent gives a measure of how close the sorbent is regenerated to VLE conditions in the stripper. To do so, samples are collected and the sorbent composition is analysed as explained in subsection 3.3.1. The sample collection methodology is the same except for the following amendments:

- The sample collection point of the lean sorbent was established at the hot stream outlet of the Rich-Lean Hex.

The results from the FTIR analysis are used to calculate the CO₂ concentration in the sorbent as indicated in equation 3.4. For a fair comparison of lean loading in different residence times, the samples that had the same number of cycles (passes through the stripper column) were the ones compared.

The regeneration temperature, which was kept fixed during the experiments, is used to determine the VLE loading in the stripper column bottom, and this loading is determined to be the lowest possible obtainable by the regeneration process.

3.3.5. Residence Time

The residence time in the stripper is a crucial process parameter as it indicates how long the sorbent is allowed to spend in the regeneration step of the DAC unit. For the experiments, the residence time is a function of the hold-up volume in the stripper, and the mass flow rate of the feed stream.

The hold-up volume of the stripper is a fixed parameter determined by the design. The volumetric flow rate into the stripper is determined by the stripper pump, and can be quantified through an experimental calibration performed to the pump that relates the flow rate to the RPM of the device (see appendix B).

Table 3.5: Residence times during experiments

Experiment	\dot{v} [ml/s]	Residence time [min]
1	3.81	8.3
2	4.4	7.2
3	5.0	6.3

3.3.6. CO2 Produced

The CO2 produced during experiments is one of the major performance indicators of the system. To determine this parameter, two different methods were used: sorbent composition measurements, and physical CO2 output measurements.

Sorbent composition measurements

The CO2 output of the process can be determined through the sorbent composition as follows:

$$CO2_{output} = CC \cdot (\dot{v}_{feed} \cdot \rho_{sorbent}) \cdot (TEPA_{w.t.\%}/100) \quad (3.9)$$

where:

$CO2_{output}$	= CO2 produced	[molCO2/s]
CC	= Cyclic Capacity	[molCO2/kgTEPA]
\dot{v}_{feed}	= volumetric flow rate into stripper	[m ³ /s]
$\rho_{sorbent}$	= density of sorbent	[kg/m ³]
TEPA w.t.%	= weight percent TEPA in sorbent	[%]

The density of the sorbent is assumed constant and it is a known parameter. The sorbent composition is determined as explained in subsection 3.3.1, with the difference that both Rich and Lean sorbent samples are collected simultaneously and their compositions are analysed.

The cyclic capacity is determined by knowing the sorbent composition as follows:

$$CC = C_{Rich} - C_{Lean} \quad (3.10)$$

where:

CC	= Cyclic Capacity	[molCO2/kgTEPA]
C_{Rich}	= Rich sorbent CO2 loading	[molCO2/kgTEPA]
C_{Lean}	= Lean sorbent CO2 loading	[molCO2/kgTEPA]

The Rich and Lean loadings are determined from the sorbent composition as indicated in equation 3.4. Once the cyclic capacity is determined, the CO2 production through the sorbent composition is determined as indicated by equation 3.9.

Physical Measurement

The CO2 production was physically determined by measuring the gas output of the flash tank, which is assumed to consist only of CO2. To do so, a measurement device was devised with common lab equipment.

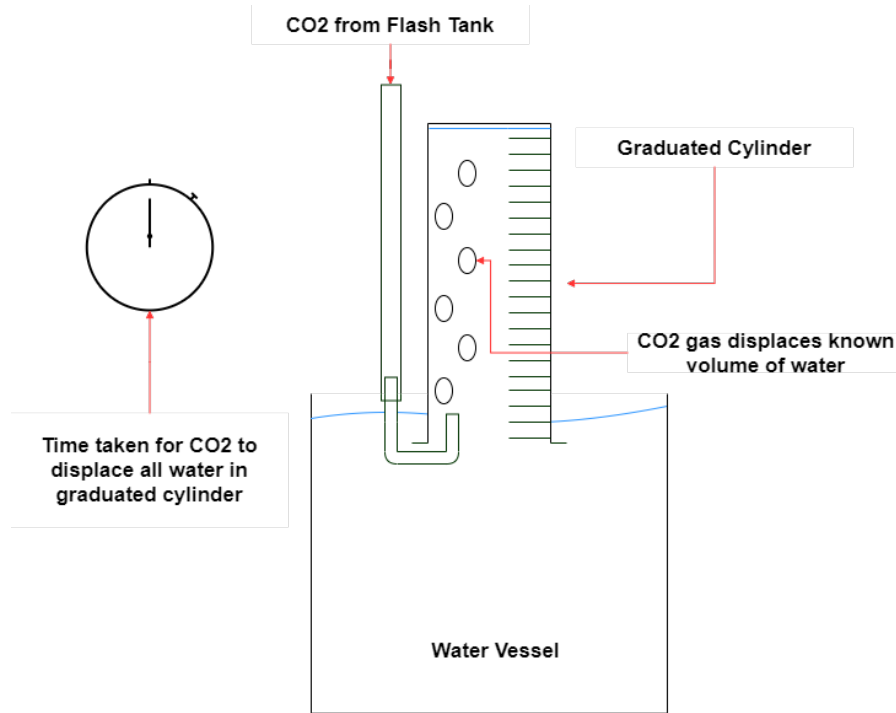


Figure 3.7: CO2 Measuring device schematic

The working principle of the device consists in quantifying the time it takes for the gas outlet stream to displace a known volume of water. Then, the CO₂ production is determined as follows:

$$CO2_{output} = \frac{V_{water}}{t} \quad (3.11)$$

where:

$CO2_{output}$	= CO ₂ production	[ml/s]
V_{water}	= Volume of water displaced	[ml]
t	= time taken to displace the volume of water	[s]

The calculated CO₂ production was then converted into molCO₂/s for comparison with the other method.

3.3.7. H₂O Produced

The H₂O production of the process is an important performance indicator for ZEF as it required for the other subsystems of the microplant. To determine this parameter, two different methods were used as with the CO₂ production: sorbent composition measurements, and physical measurements.

Sorbent composition measurements

The H₂O production quantification through sorbent composition was done similarly as the CO₂ production quantification. The only difference being that instead of using CO₂ concentrations, now H₂O concentrations are required. The sorbent composition analysis is exactly the same, and the H₂O concentration is determined as follows:

$$C_{H_2O} = \frac{H_2O_{w.t.\%} \cdot 1000}{MW_{H_2O} \cdot TEPA_{w.t.\%}} \quad (3.12)$$

where:

C_{H_2O}	= H2O Loading	[molH2O/kgTEPA]
H2O w.t.%	= H2O weight percentage in sorbent	[%]
TEPA w.t.%	= TEPA weight percentage in sorbent	[%]

Similarly to equation 3.10, the H2O cyclic capacity of the process can be determined by having the H2O rich and lean loadings from the sorbent composition. Finally, the H2O output is determined in a similar manner as in equation 3.9, but using the H2O cyclic capacity.

Physical Measurements

The H2O produced by the process is all collected in the bottom of the flash tank as a liquid. The outlet of the flash tank is controlled by a ball valve that can be manually opened and closed by the user. In order to physically measure the H2O production, all that is necessary is to know the discharge volume and the time between discharges.

$$H_2O_{output} = \frac{V_{discharge}}{t} \quad (3.13)$$

where:

H_2O_{output}	= H2O produced	[ml/s]
$V_{discharge}$	= volume of water discharged	[ml]
t	= time between discharges	[s]

The quantified H2O production was then converted into molH2O/s for comparison with the other method.

3.3.8. H2O:CO2 Ratio

The H2O:CO2 product ratio is another special requirement for ZEF's DAC process, and it is determined in a molar basis. Knowing the CO2 and H2O production of the process, it is possible to determine the ratio.

$$H_2O : CO_2 = H_2O_{output} / CO_2_{output} \quad (3.14)$$

where:

H2O:CO2	= product ratio	[-]
H_2O_{output}	= H2O production	[mol/s]
CO_2_{output}	= CO2 production	[mol/s]

3.3.9. Energy Demand Process

The total energy demand of the process is an indicator of how efficient the process is. In order to determine this parameter, the heat supplied by the oil-bath to the thermosyphon reboiler was used.

$$Q_{in} = \dot{m}_{oil} \cdot C_{p_{oil}} \cdot dT_{oil} \quad (3.15)$$

where:

Q_{in}	= heat input	[W]
\dot{m}_{oil}	= oil mass flow rate	[kg/s]
$C_{p_{oil}}$	= oil specific heat capacity	[J/kg·K]
dT_{oil}	= oil temperature difference	[K]

The Cp of the oil is known and assumed to be constant regardless of temperature. The oil bath settings allow to determine the mass flow rate of the oil, and the temperature difference is determined through temperature sensors at the inlet and outlet of the thermosyphon heat exchanger.

The heat input is considered to be the total energy demand of the process, including heat losses. The heat input can be further converted into MJ/kgCO₂ or similar units by also having the CO₂ produced by the process.

3.3.10. Rich-Lean Hex Performance

The process heat integration aims to reduce the energy required by the system, it is then fundamental to determine the performance of the Rich-Lean heat exchanger. To do so, an LMTD analysis was performed for the plate heat exchanger:

$$\Delta T_{LM} = \frac{\Delta T_2 - \Delta T_1}{\ln(\Delta T_2 - \Delta T_1)} \quad (3.16)$$

where:

$$\Delta T_1 = T_{h,i} - T_{c,o} \quad (3.17)$$

and

$$\Delta T_2 = T_{h,o} - T_{c,i} \quad (3.18)$$

where:

ΔT_{LM}	= log mean temperature difference	[K]
$T_{h,i}$	= hot stream inlet temperature	[°C]
$T_{h,o}$	= hot stream outlet temperature	[°C]
$T_{c,i}$	= cold stream inlet temperature	[°C]
$T_{c,o}$	= cold stream outlet temperature	[°C]

The required temperatures are determined through temperature sensors installed at the inlets and outlets of the heat exchanger.

The maximum possible heat transfer rate is determined as follows:

$$Q_{max} = \dot{m}_{feed} \cdot C_{p_{sorbent}} \cdot (T_{h,i} - T_{c,i}) \quad (3.19)$$

where:

Q_{max}	= maximum possible heat transfer rate	[W]
\dot{m}_{feed}	= stripper pump mass flow rate	[kg/s]
$C_{p_{sorbent}}$	= specific heat capacity of the sorbent	[J/kg·K]
$T_{h,i}$	= hot stream inlet temperature	[°C]
$T_{c,i}$	= cold stream inlet temperature	[°C]

The Cp of the sorbent is known and assumed constant. The stripper pump mass flow rate is a known process parameter, and the required temperatures are determined through the inlet and outlet temperature sensors.

The actual heat transfer rate in the heat exchanger is determined in the same way as in equation 3.19, but replacing the hot stream inlet temperature by the cold stream outlet temperature ($T_{h,i} \rightarrow T_{c,o}$)

The heat transfer coefficient of the heat exchanger is determined as follows.

$$hc = Q_{actual} / (A_{hex} \cdot \Delta T_{LM}) \quad (3.20)$$

where

hc	= heat transfer coefficient	[W/m ² ·K]
Q_{actual}	= heat transferred to the cold fluid	[W]
A_{hex}	= heat exchanger heat transfer area	[m ²]
ΔT_{LM}	= log mean temperature difference	[K]

The efficiency of the heat exchanger is determined by how much of the possible maximum heat is actually transferred to the cold fluid.

$$\eta_{hex} = (Q_{actual}/Q_{max}) \cdot 100 \quad (3.21)$$

where:

η_{hex}	= hex efficiency	[%]
Q_{max}	= heat transferred to the cold fluid	[W]
$Q_{available}$	= heat available from the hot fluid	[W]

Modelling

This chapter presents the modelling work performed during this thesis. First, the newly developed absorber model will be presented and explained. Then, the stripper model, previously developed by ZEF will be explained. Finally how both models were used to determine the system's performance will be presented.

4.1. Absorber Model

The absorber model developed during this thesis deep dives into the mass transfer of CO₂ into the sorbent. Based on experimental results and several mass transfer theories, an experiment based mass transfer model has been developed that allows to determine the system performance, and that can be applied to different sorbents.

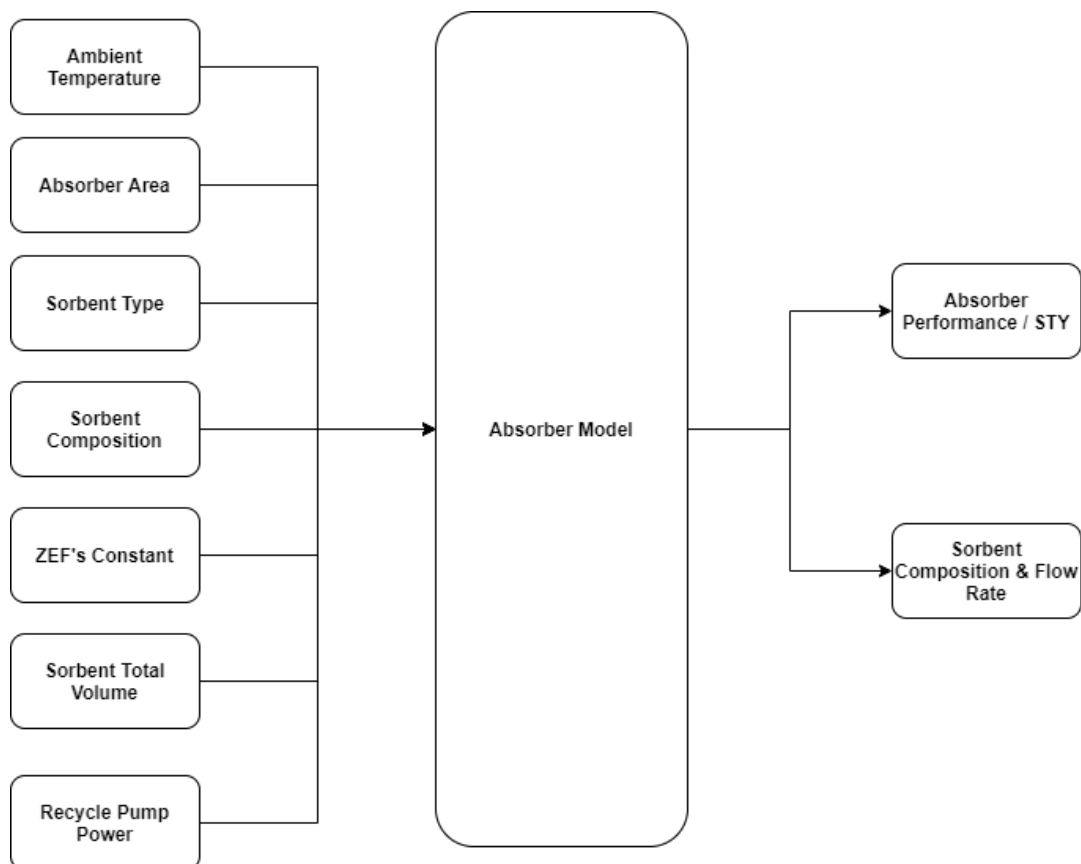


Figure 4.1: DAC Absorber Model

4.1.1. Mass Transfer Theories and Experimental fit constant

The developed absorption model **assumes a diffusion limited process** in the liquid side of the CO₂ capture process. This assumption is based not only in literature where the CO₂ absorption process is stated as diffusion limited [55][76][32] when compared to reaction kinetics, but also from the experimental results of the 10X DAC.

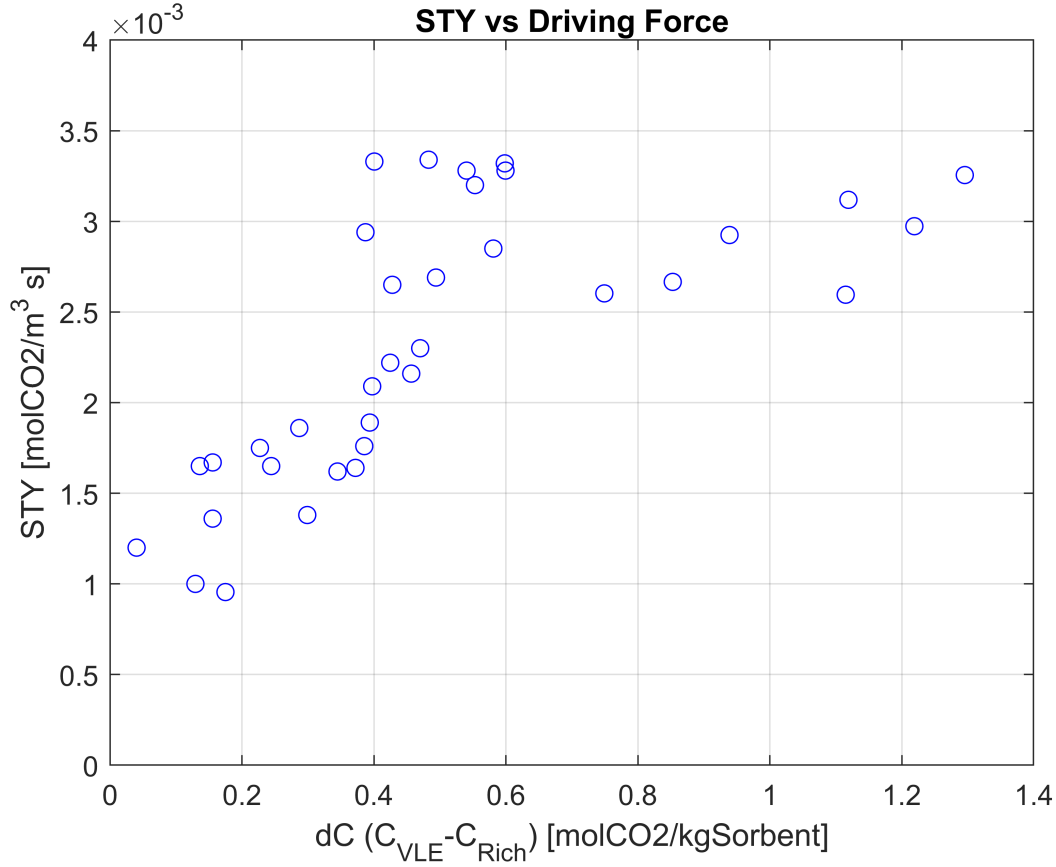


Figure 4.2: CO₂ capture capacity versus concentration gradient

As can be seen in figure 4.2, there seems to be a linear decreasing trend in the CO₂ capture capacity of the process as the driving force (i.e. concentration gradient) decreases, which is interpreted as a sign of the process being liquid side limited, and combined with literature sources stating diffusion is the limiting process, the main assumption of the model is considered valid..

The starting point of the absorber model is Fick's Law of Diffusion:

$$J = -D \frac{dC}{dx} \quad (4.1)$$

where:

J	= Molar Flux	[mol/s·m ²]
D	= Diffusion Coefficient	[m ² /s]
dC/dx	= Concentration Gradient	[mol/m ⁴]

Fick's Law states that the mass flux is a function of the Diffusion Coefficient and the Concentration gradient. To begin with, for the absorber model developed, the concentration gradient term has been changed for a driving force term:

$$\frac{dC}{dx} \rightarrow C_{VLE} - C_{Rich} \quad (4.2)$$

where:

$$\begin{aligned} C_{VLE} &= \text{CO}_2 \text{ Loading in VLE conditions} & [\text{molCO}_2/\text{kgSorbent}] \\ C_{Rich} &= \text{CO}_2 \text{ Loading in the sorbent} & [\text{molCO}_2/\text{kgSorbent}] \end{aligned}$$

This change is acceptable since the diffusion length (dx) is considered constant in all the mass transfer element.

The next term is the Diffusion Coefficient. Two equations, Stokes-Einstein and Wilke-Chang, were considered when solving for this coefficient.

Estimation of Diffusion Coefficients	
<p style="text-align: center;">Stokes-Einstein equation</p> $D = \frac{k_B T}{6\pi\mu R_0}$ <p> D – diffusion coefficient μ – solvent viscosity R_0 – solute radius k_B – Boltzmann's constant T – temperature (K) </p>	<p style="text-align: center;">Wilke-Chang equation</p> $D = \frac{7.4 \times 10^{-8} (\phi M_2)^{0.5} T}{\mu V_1^{0.6}}$ <p> D – diffusion coefficient μ – solvent viscosity ϕ – factor for solute-solvent interaction V_1 – Molar volume of solute at boiling point T – temperature (K) M_2 – Molecular weight of solvent </p>

Figure 4.3: Estimation of the Diffusion Coefficient [49]

As seen in figure 4.3, the diffusion coefficient seems to always be directly proportional to temperature, and inversely proportional to sorbent's viscosity. The differences between both equations is tackled by the experimental constant developed in the model that will be introduced later.

Furthermore, three mass transfer theories were considered in the development of the absorber model (table 4.1). Due to the nature of ZEF's DAC process, where mass transfer elements are assumed to mix as they flow through the column, the Surface Renewal Theory by Danckwerts was selected to further develop the absorber model.

Table 4.1: Mass transfer models

Theory/Model	Description	Equation
Two-film Theory	Assumes the existence of a film of thickness (δ) through which molecular diffusion takes place under steady state conditions [36]	$k_L = D/\delta$
Penetration Theory	Assumes that all liquid elements present in the gas-liquid interphase are exposed to the gas, and the mass transfer can be expressed in terms of contact time (Θ). [36]	$k_L = 2\sqrt{D/\pi\Theta}$
Surface Renewal Theory	Assumes that the liquid is composed of two regions, interfacial region & bulk region, and that the liquid elements are constantly replaced (renewed) by liquid elements in the bulk. [36]	$k_L = \sqrt{D \cdot S}$

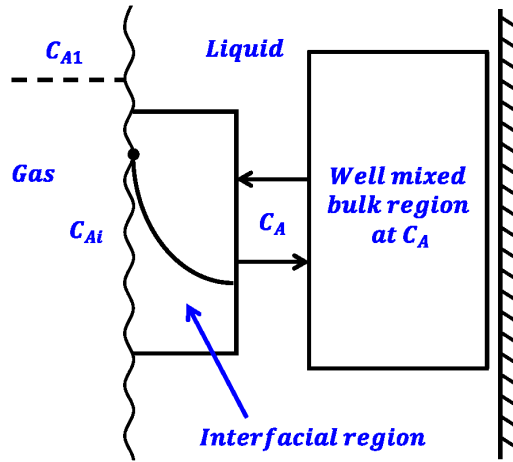


Figure 4.4: Schematics of Surface Renewal Theory [36]

In the Surface Renewal theory, the liquid is treated as one large well mixed bulk region, which interfacial region is constantly renewed. The theory assumes that at any given time, liquid elements in the interface are being replaced (renewed) by fresh elements from the bulk. The Surface Renewal Theory states that the mass transfer coefficient is a function of the Diffusion Coefficient, and the Surface Renewal Frequency (S).

$$k_L = (D_{AB}S)^{0.5} \quad (4.3)$$

where:

k_L	= Mass Transfer Coefficient	[m/s]
D	= Diffusion Coefficient	[m ² /s]
S	= Surface Renewal Frequency	[1/s]

Combining the selected mass transfer theory, alongside with Fick's Law, and replacing Mass flux by the Space Time Yield performance parameter, the Absorber model is presented:

$$STY = A * \sqrt{\frac{TS}{\mu}} * (C_{VLE} - C_{RICH}) \quad (4.4)$$

where:

STY	= Space Time Yield	[molCO ₂ /m ³ ·s]
A	= Experimental Fit Constant	[Pa·kgSorbent/K ^{0.5}]
T	= fluid Temperature	[K]
μ	= fluid Viscosity	[Pa·s]
C	= CO ₂ Loading	[molCO ₂ /kgSorbent]

The Surface Renewal Frequency needs to be addressed. Due to the nature of ZEF's absorption process, and its liquid distribution approach, the surface renewal frequency is considered to be inversely proportional to sorbent's viscosity times a constant (see appendix D); which is engulfed by the constant A in the overall equation.

$$S \propto \frac{1}{\mu} \quad (4.5)$$

Finally, putting everything together:

$$STY = A * \frac{\sqrt{T}}{\mu} * (C_{VLE} - C_{RICH}) \quad (4.6)$$

The proposed model considers not only environmental conditions, but also all sorbent properties (viscosity and VLE loading) and process specific parameters (number of mass transfer elements) that greatly influence the CO₂ capture process.

Determining A, was possible through the experimental results of the 10X DAC and the different measurements explained in section 3.3.

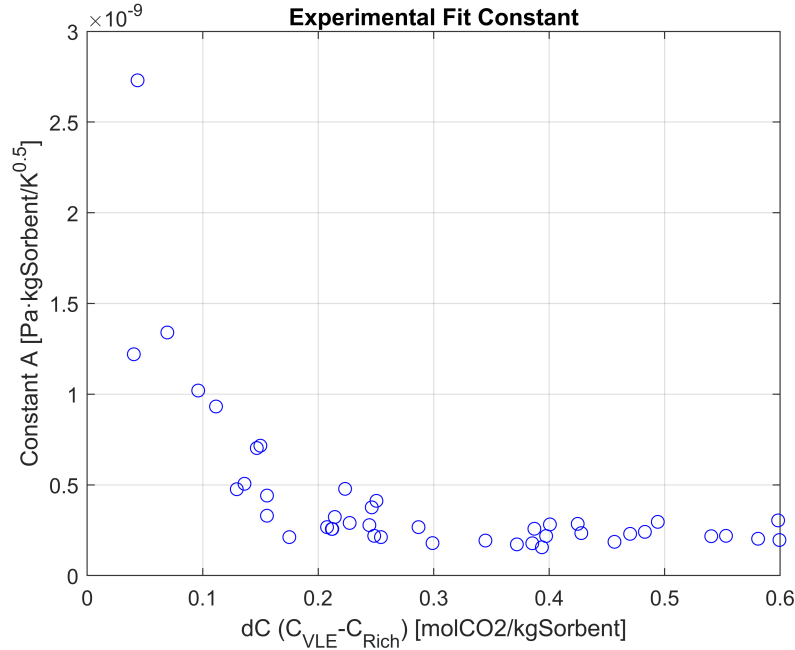


Figure 4.5: Experimental constant A

As see in figure 4.5, the proposed experimental fit constant A behaves as such until the dC value goes below 0.2 molCO₂/kgSorbent, and explodes for values below 0.15 molCO₂/kgSorbent. The reason for this is that as dC becomes smaller, the difference in loading between samples also becomes smaller, and the STY equation (see subsection 3.3.1) falls within the error of the FTIR machine; affecting the STY value and thus the constant A. For this reason, the value of A was determined as its average value between 0.2 and 0.6 molCO₂/kgSorbent.

$$A = 2.61e - 10 [Pa \cdot kgSorbent / K^{0.5}] \quad (4.7)$$

To validate the constant A, Space Time Yields for similar conditions as the experiments were calculated, and then compared to the experimental results through the Mean Absolute Error (MAE) and the coefficient of deviation between measured and predicted values.

Table 4.2: statistical comparison

	Absorber Model
MAE	4.22e-8
R ²	0.55

As can be seen in table 4.2, the accuracy of the absorber model in predicting STY values is far from ideal, but considering the MAE is one order of magnitude lower than the measured STY, it is considered acceptable to be used.

4.1.2. Model Assumptions

The assumptions used in the newly developed absorber model are the following:

- **Diffusion limited process.** Thus, the model works better in the liquid side limited region of the CO₂ capture process where CO₂ absorption has been suggested to be diffusion limited.
- **Sorbent temperature same as ambient temperature.** This is not completely true as the CO₂ capture reactions are exothermic and the sorbent temperature would be slightly higher than ambient temperature.
- **Surface renewal frequency (S) inversely proportional to sorbent's viscosity.** This assumption is based in the fact that all other parameters that could affect the surface renewal process are kept constant in the process.
- **Constant CO₂ partial pressure.** Valid for DAC processes.
- **Constant water loading in the sorbent.** Water VLE is accomplished faster than CO₂, so the water loading in the sorbent is assumed to be at VLE from the start. Not enough data was obtained to create a model for water capture.

4.1.3. Model Inputs and Outputs

The required inputs for the absorber model, as shown in figure 4.1, are as follows:

- **Ambient Temperature:** air temperature entering the system, required input to determine VLE loading values, Space Time Yield, and sorbent's viscosity.
- **Absorber Volume:** volume of air-sorbent contactor, required input to determine the amount of CO₂ captured, and subsequently the sorbent composition leaving the absorber column.
- **Sorbent Type:** amine to diluent ratio, required input to determine the VLE loading values, Space Time Yield, and sorbent's viscosity.
- **Sorbent Composition:** initial sorbent composition (CO₂ and H₂O Loading) entering the absorber column, required input to determine VLE loading values, mass fractions, sorbent's viscosity and composition after going through the absorber column.
- **Experimental fit constant:** explained in section 4.1.1, required input to determine Space Time Yield.
- **Sorbent Total Volume:** volume of sorbent in the entire system, required input to determine mass fractions, and sorbent composition after going through the absorber.
- **Recycle Pump Power:** total power supplied to the recycle pump, required input to determine number of mass transfer elements in the absorber column.

Table 4.3: Absorber Model Inputs

Symbol	Input Parameter	Unit
T_{amb}	Ambient Temperature	[°C]
L_{abs}	Absorber Length	[m]
$S_{sorbent}$	Sorbent Type	[-]
C_{CO_2}	CO ₂ Loading	[molCO ₂ /kgSorbent]
C_{H_2O}	H ₂ O Loading	[molH ₂ O/kgSorbent]
A	ZEF's Constant	[-]
V_{total}	Total sorbent volume	[L]
$P_{RecyclePump}$	Power Recycle Pump	[W]

The outputs of the absorber model, as shown in figure 4.1, are the following:

- **Space Time Yield (CO₂ Capture Performance):** based on the sorbent's viscosity, ambient temperature, number of mass transfer elements, and the driving force (VLE loading and CO₂ loading difference), the Space Time Yield of the process is determined at any moment.

- **Sorbent Composition:** based on the Space Time Yield, the absorber area and the time of the process, the final sorbent composition (CO₂ Loading and H₂O Loading) is determined.
- **Sorbent Flow rate:** based in the power supplied to the recycle pump and the sorbent viscosity, the mass flow rate of the sorbent is determined.

Table 4.4: Absorber Model Outputs

Symbol	Output Parameter	Unit
STY	Space Time Yield	[molCO ₂ /m ³ s]
C_{CO_2}	CO ₂ Loading	[molCO ₂ /kgSorbent]
C_{H_2O}	H ₂ O Loading	[molH ₂ O/kgSorbent]
$\dot{m}_{recycle}$	Recycle Stream Flow Rate	[kg/s]

4.1.4. Model Description

The absorber model workflow (for one iteration), as seen in figure 4.6, is as follows:

1. **Weight Percentages:** with the sorbent type and initial sorbent composition, the weight percentages of each component (TEPA, PEG, CO₂, H₂O) are computed.
2. **Viscosity:** with the sorbent temperature, and the weight percentage of each component, the viscosity of the sorbent is determined through a neural network fit of measured viscosities during experiments (see appendix D).
3. **VLE Loading:** with the H₂O loading and sorbent temperature, the VLE CO₂ loading is computed through the corresponding sorbent VLE curves.
4. **Recycle Pump Flow Rate:** with the sorbent' viscosity and the power supplied to the recycle pump, the total mass flow rate is computed.
5. **Mass Transfer Elements:** with the total mass flow rate, and the viscosity of the sorbent, the mass transfer is computed.
6. **Space Time Yield:** with all the required parameters, it is now possible to compute the Space Time Yield of the process.
7. **Final Sorbent Composition:** with the process' STY, absorber length and time elapsed, it is possible to determine the amount of CO₂ captured. Then, combined with the total volume, the final sorbent composition (CO₂ Loading and H₂O Loading) is computed.

The final composition can then be sent back as an input and the model computes the new Space Time Yield. This can be performed for varying temperatures as well.

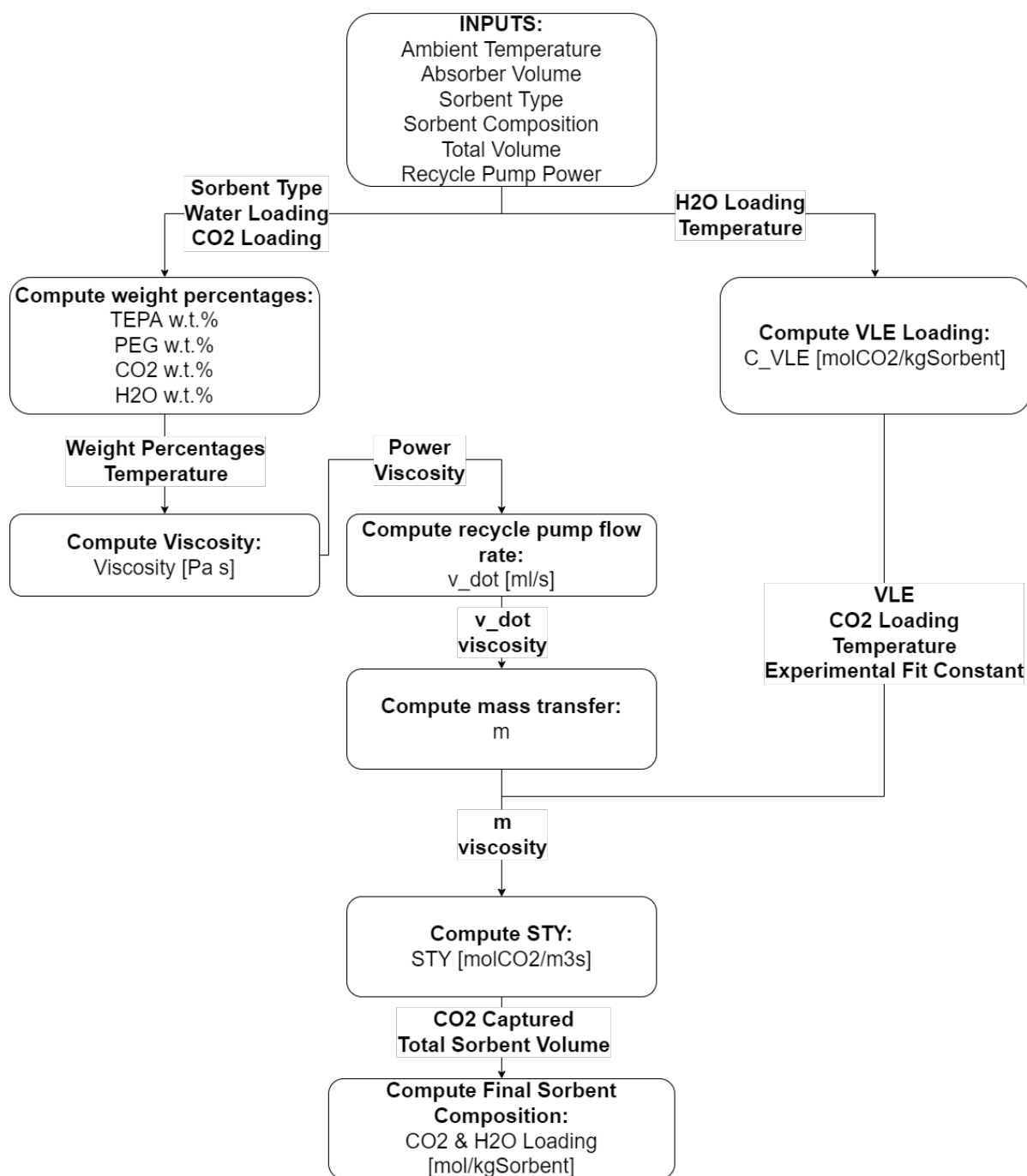


Figure 4.6: Absorber Model Description

4.2. Stripper Model

The stripper model used during this thesis is the result of the work performed by Dubhashi [69], Vidyarthi [71], and other previous efforts performed by former members of ZEF. A brief explanation will be given, but for detailed presentation of the stripper model please refer to the work of the aforementioned authors.

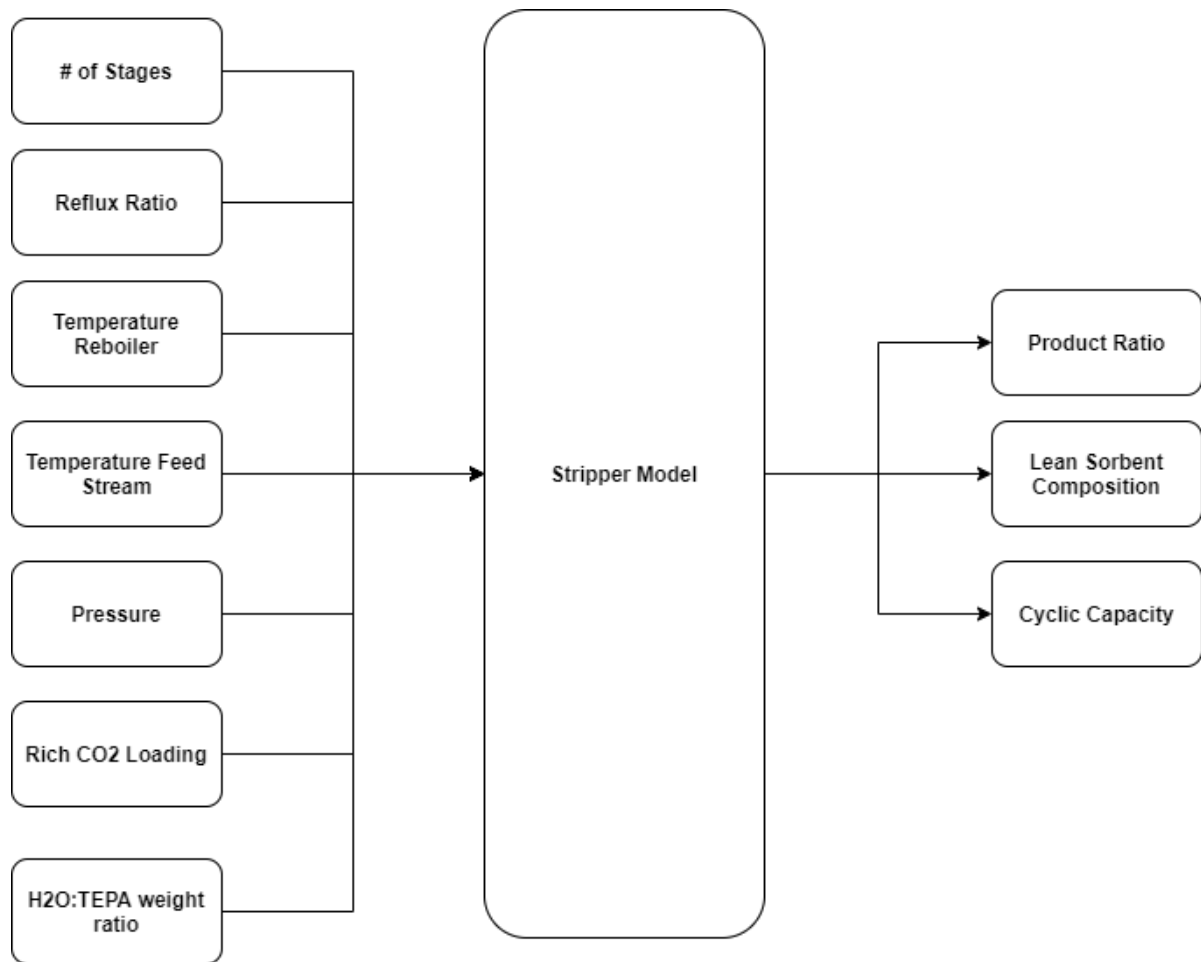


Figure 4.7: DAC Stripper Model

4.2.1. Model Assumptions

The assumption pertaining the stripper model are the following [69][71]:

- **The column is assumed to operate in equilibrium.** Vapor Liquid Equilibrium is established in each stage.
- **Sorbent mixture is assumed to be non-volatile.** Neither TEPA nor PEG evaporate, meaning that product gases are only CO₂ and H₂O.
- **No pressure drop in the stripper column.** Each stage works at the same pressure.
- **Sorbent properties are constant.** Specific heat capacity and heat of desorption of different components do not vary.

4.2.2. Model Inputs and Outputs

The model inputs, as shown in figure 4.7, are the following:

- **Number of Stages:** number of stages that compose the stripper column.
- **Reflux Ratio:** amount of water sent back to the stripper column after the top stage.
- **Temperature Reboiler:** temperature set for the reboiler at the bottom of the stripper column.
- **Temperature Feed Stream:** temperature at which the feed stream enters the stripper column.
- **Pressure:** pressure at which the regeneration process takes place.
- **Rich CO₂ Loading:** CO₂ loading of the rich sorbent entering the stripper column.
- **H₂O:TEPA Weight ratio:** amount of water in the sorbent entering in the stripper column.

Table 4.5: Stripper Model Inputs

Symbol	Input Parameter	Unit
n_{stages}	Number of Stages	[-]
r_{ratio}	Reflux Ratio	[-]
$T_{reboiler}$	Temperature Reboiler	[°C]
T_{feed}	Temperature Feed stream	[°C]
P	Column Pressure	[mbar]
L_{rich}	CO2 Rich Loading	[molCO2/kgTEPA]
$R_{H2O:TEPA}$	Weight Ratio H2O	[kgH2O/kgTEPA]

The model outputs, as shown in figure 4.7, are the following:

- **Product Ratio:** H2O:CO2 ratio in the top product obtained from the regeneration process.
- **Lean Sorbent Composition:** sorbent composition (CO2 and H2O loading) after the regeneration process.
- **Cyclic Capacity:** amount of CO2 desorbed during a single cycle in the stripper.

Table 4.6: Stripper Model Outputs

Symbol	Input Parameter	Unit
H2O:CO2	Top Product Ratio	[-]
L_{lean}	CO2 Lean Loading	[molCO2/kgTEPA]
$R_{H2O:TEPA}$	Weight Ratio H2O	[kgH2O/kgTEPA]
CC	Cyclic Capacity	[molCO2/kgTEPA]

4.2.3. Model Description

For a detailed description of how the stripper model works, please refer to the works of Dubhashi[69] and Vidyarthi [71].

4.3. Models Application

Both the Absorber and Stripper models are applied in order to determine the specific sorbent performance, and as a consequence, the overall system performance. The way both models are used is as follows:

1. The Absorber Model is ran in order to plot the STY vs Rich loading curves of the chosen sorbent and the given environmental conditions.
2. The Absorber Model is ran in order to obtain the VLE loading at the given conditions.
3. For the same sorbent, the stripper model is ran at given stripping conditions to determine the lean loading that is possible to be achieved.
4. The working envelope of the system, in terms of CO2 capture, is established. The lean loading of the stripper model represents the left most limit of the envelope, while the VLE loading represents the right most limit of the envelope.
5. The user can now select a rich loading within the working envelope. With this selection, the STY of the Absorber and the Cyclic Capacity of the process are fixed.

In a few words, the models used in this thesis allowed to create the direct air capture cycle:

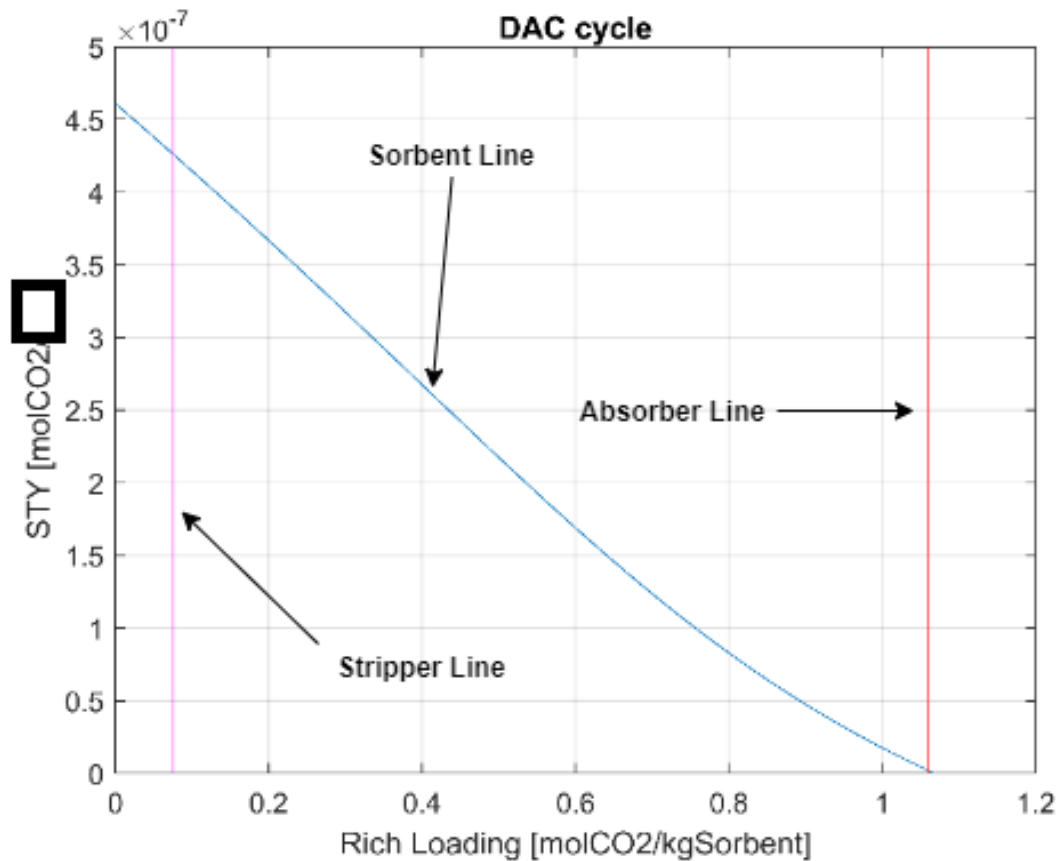


Figure 4.8: DAC Cycle

(Note: units in y-axis not fully shown due to intellectual property concerns)

The DAC cycle is presented in figure 4.8, where three lines are introduced: the sorbent line, the absorber line and the stripper line.

- **The Sorbent line** is set by the sorbent type and its characteristics, and sets the achievable performance in terms of CO₂ capture. The higher the sorbent line is, the better the carbon capture performance of the system is.
- **The Absorber line** is set by the maximum possible CO₂ loading of the process, which corresponds to the Vapor Liquid Equilibrium loading.
- **The Stripper line** is set by the regeneration process and its parameters, and represents the lowest lean loading attainable in the stripper column.

The area enclosed by the three lines is considered to be the working region of the DAC cycle. By choosing a rich loading to work with, the user defines the cyclic capacity of the system and all of the process parameters can be determined as explained in chapter ??.

Results and Discussion

In this chapter, the experimental characterization results of the 10X DAC system are presented, and the established research questions for the characteristics of the system are answered.

5.1. Experimental Characterization

Q: What are the characteristics of ZEF's 10X DAC system and how does it compare to the expected performance/model predictions?

The experimental characterization of the 10X DAC prototype, as introduced in section 3.2, had the goal of determining the absorption, desorption and full system characteristics of the built prototype during this thesis. For ease of understanding, the results of the experiments, and thus the answer to the first research question, will be given for each part of the experimental plan.

5.1.1. Absorption Characteristics

The characteristics of the absorption process in the absorber column are not only important to determine the performance of this component, but also to gain knowledge into how the whole direct air capture process actually works and be able to optimize the process later on. With this in mind, the following characteristics of the 10X DAC absorption process were looked at in detail: CO₂ vs H₂O capture in the column, Air side vs Liquid side limitations, and the carbon capture capacity.

H₂O vs CO₂ capture

In the absorber column, both H₂O and CO₂ are captured by the sorbent. Understanding which one of the two capture processes is the limiting one is of importance in order to determine in which process should optimization efforts be focused.

Figure 5.1 shows that **the CO₂ capture process is the limiting one** in the absorber column of the 10X DAC. This can be seen by the fact that the CO₂ loading takes about 14 hours to reach VLE values, while the H₂O loading within the first 2.5 hours can be seen to reach a maximum (assumed to be VLE for that given moment) and then starts to respond to absolute humidity changes in the environment.

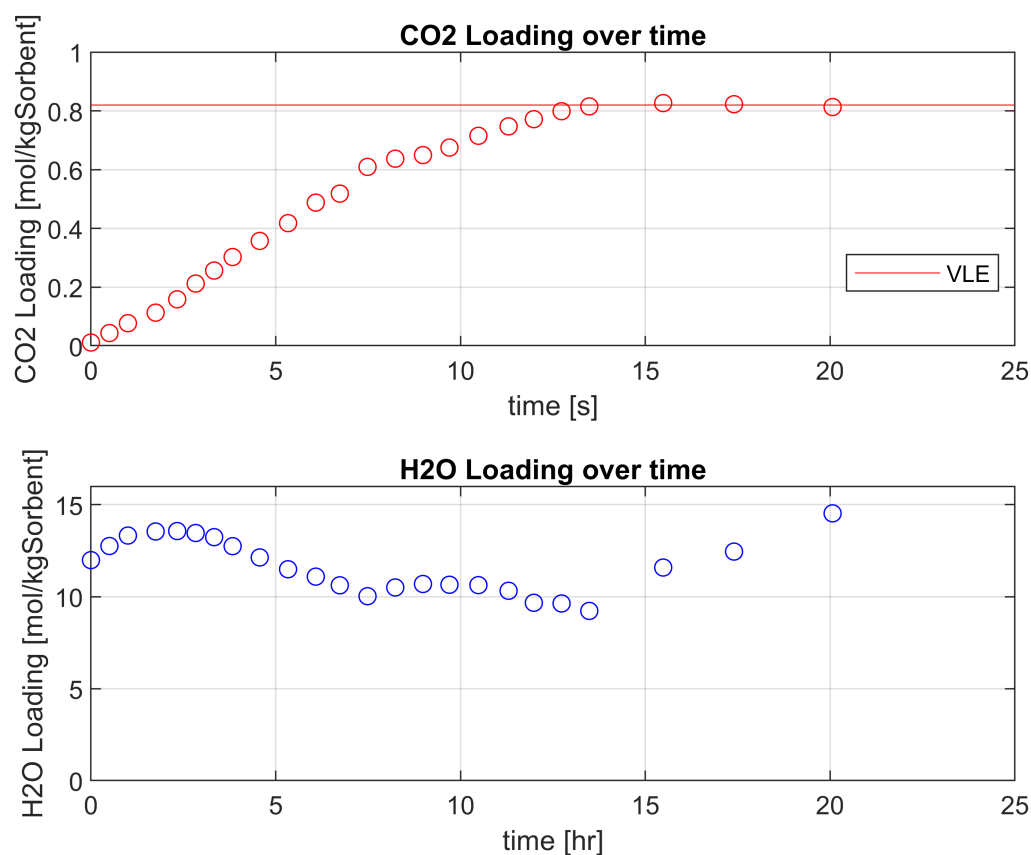


Figure 5.1: CO₂ and H₂O capture over time

Liquid side vs Air side limited behavior

Determining whether the system is liquid side or air side limited is crucial to build a better understanding of the chemical absorption process taking place in the absorber column. Knowing whether the process is liquid or air side limited allows to focus the optimization efforts in a single component instead of both.

Figure 5.2 shows the 10X DAC CO₂ capture performance as a function of the driving force of the process (i.e. concentration gradient). An air side limited process would experience no change in the magnitude of the STY as the driving force decreases. However, shown in figure 5.2, a decreasing trend in STY with a decreasing driving force can be seen. This **suggests that the chemical absorption process is liquid side limited.**

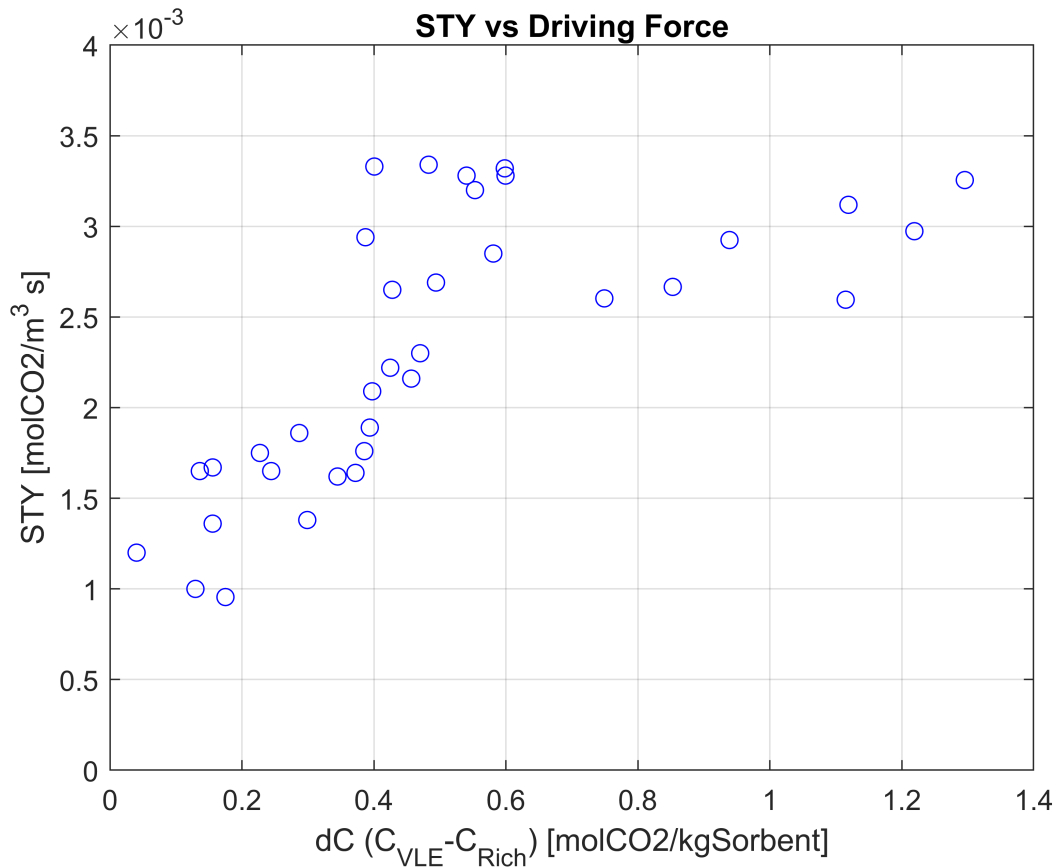


Figure 5.2: CO2 capture capacity versus concentration gradient

CO2 Capture Capacity

The CO2 capture capacity of the absorption column is one of the major performance indicators of the process, if not the biggest. Determined through the Space Time Yield of the system, this gives an indication of how much CO2 the process is capable of removing.

Figure 5.2 is used again to determine the capture capacity of the system. As it can be seen, the **highest achieved space time yield in the process was 2.7e-3 molCO2/m³.s**. This is about 50% of the expected performance as predicted through the miniDAC experiments and for which the system was designed for.

The under-performance of the 10X DAC absorption column is explained by the poor sorbent distribution and the suspected poor distribution of air. The sorbent did not get distributed in the entire absorber column area, which means that the actual mass transfer area during experiments was smaller than designed for.

Furthermore, experiments performed in the miniDAC were inside the lab, where temperature was kept constant and at about 20°C [50] [40]. During the 10X DAC characterization, temperatures as high as 32°C were experienced, which have a huge effect in the VLE loading of the sorbent as will be explained in section 5.2.

Figure 5.3 shows a carbon capture capacity comparison between ZEF's 10X DAC process and other companies, where units have been modified in order to show the capture capacity per volume of the absorber column and hour. It can be seen that ZEF's first prototype has a higher volumetric capacity (0.52kgCO2/m³.hr) than a very well established company like Carbon Engineering (0.40kgCO2/m³.hr), and it is within striking distance to Climeworks (0.85kgCO2/m³.hr).

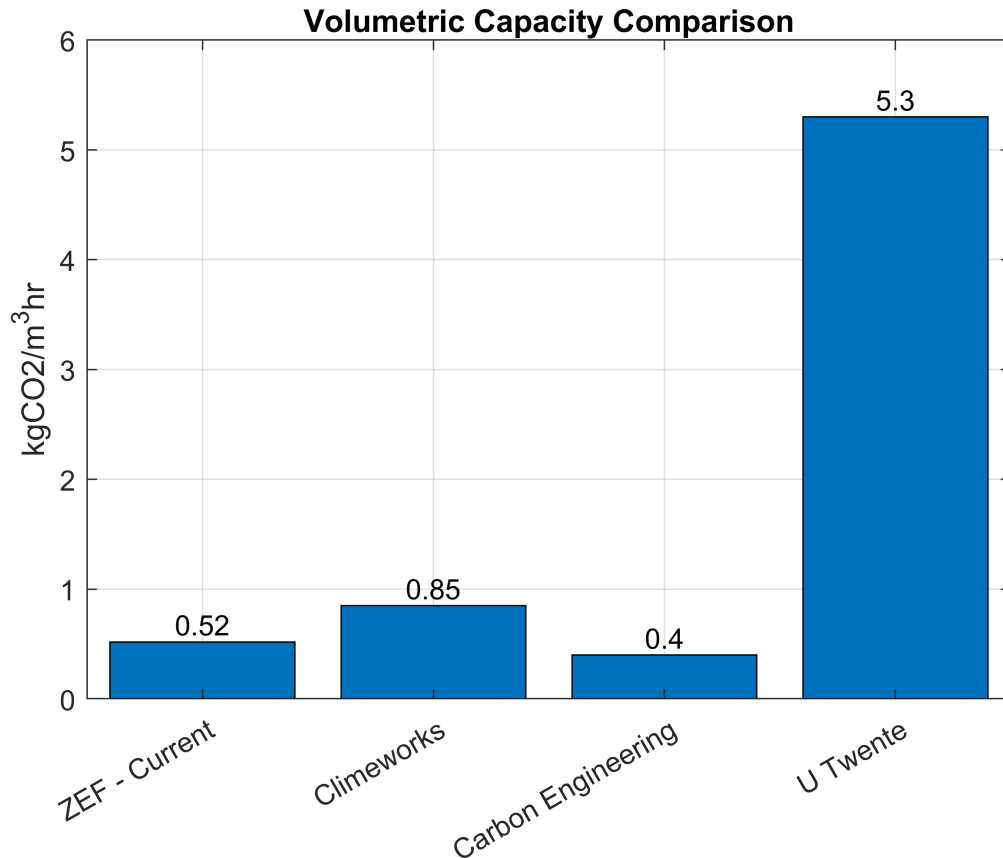


Figure 5.3: CO2 capture capacity comparison

(Note: ZEF's capture capacity is based on the volume of the air-liquid contactor section. Other companies' capture capacities are as reported by Brilman [10])

Also shown in figure 5.3 is the volumetric capacity of the University of Twente DAC prototype, which uses a novel radial flow fixed bed as an air-sorbent contactor, and furthermore uses a primary amine based sorbent. The reported results are based in an lab scale experimental set-up where adsorption experiments were performed under controlled and constant conditions [79]. The reported volumetric capacity is considerably superior to any other company in figure 5.3, however the performance of this system stills needs to be proved at larger scales and dynamic environmental conditions. Thus, it is not fair to compare University of Twente's experimental set-up performance to that of the full scale prototypes of the other companies.

5.1.2. Desorption Characteristics

The performance of the regeneration process is mainly characterized by how lean the stripper column is capable of making the sorbent before it leaves the reboiler stage. Dubhashi [69] and Van de Poll [68], as well as literature sources, have determined that the regeneration process is mass transfer limited by the diffusion of CO₂, and H₂O, through the sorbent to the top of the stripper where finally it becomes a gas product.

Being a diffusion limited process, the characterization of the stripper column consisted in determining how much time is required for the sorbent to reach VLE loadings, or close to, before leaving the column at the reboiler stage.

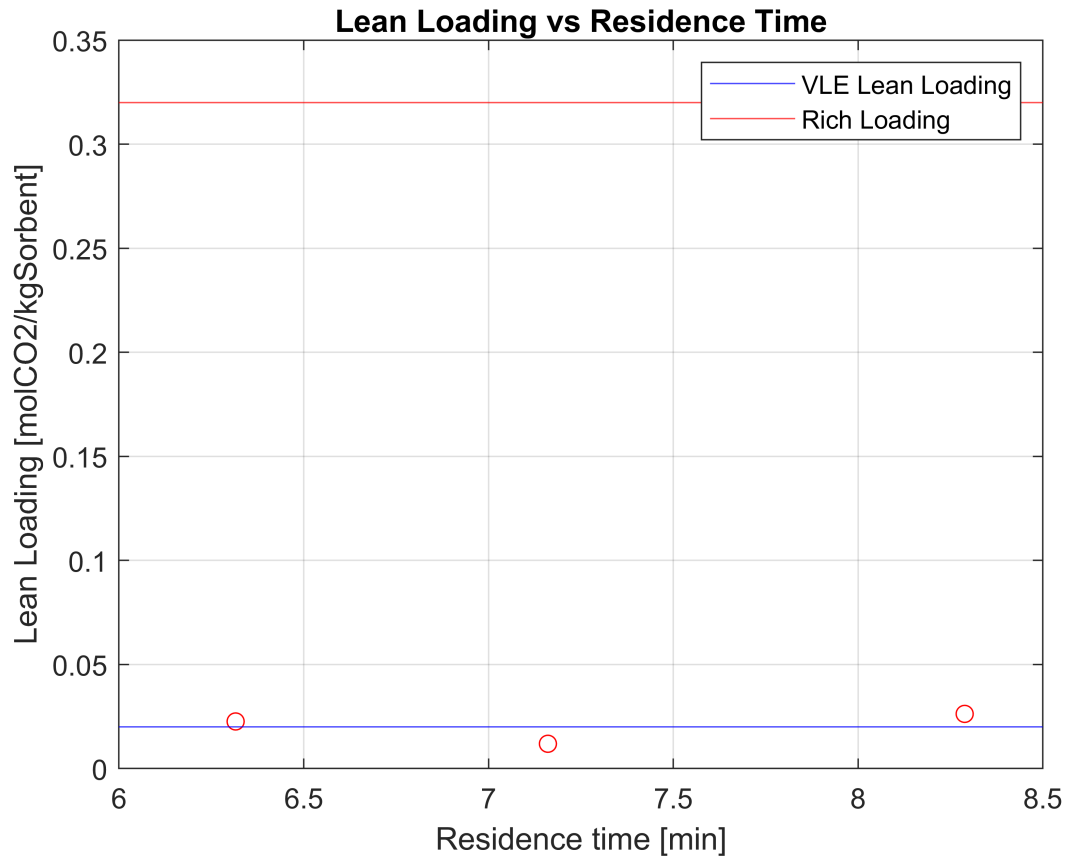


Figure 5.4: Lean loading as a function of the residence time in the stripper

As shown in figure 5.4, residence time as low as **six minutes proved to be enough time for the desorption process to reach practically VLE loadings**. Which means that the stripper column configuration used performed very well for the residence times tested during experiments.

It is important to mention that during experiments the regeneration temperature was fixed at 120°C in order to test only the effects of varying the time spent by the sorbent in the column.

5.1.3. Full System Characterization

The full system (i.e. Absorption and Desorption) characteristics allow to determine and understand the overall performance of the 10X DAC prototype. The performance of the full system was evaluated mainly through the CO₂ production achieved, and the overall energy demand of the process. Furthermore, being a special performance indicator by ZEF, the H₂O to CO₂ ratios achieved were also determined. The performance of the Rich-Lean heat exchanger was closely looked at to determine the performance of the heat integration network.

CO₂ Output

The CO₂ produced by the 10X DAC prototype is a result of the combined performance of the absorber column, and the regeneration process. Since the prototype is used as a Carbon Capture and Utilisation system, it is of importance to determine how much CO₂ becomes available to be used later on.

Table 5.1: CO₂ production

Stripper Flow Rate [ml/s]	3.81	4.41	5.00
Rich Loading [molCO ₂ /kgSorbent]	0.36	0.32	0.28
Cyclic [molCO ₂ /kgSorbent]	0.33	0.30	0.26
CO ₂ Output [molCO ₂ /s]	1.255e-3	1.28e-3	1.23e-3

As shown in table 5.1, **The 10X DAC achieved a CO₂ production of up to 1.28e-3 molCO₂/s**, which is about half of the 2.17e-3 molCO₂/s it was designed for. The reason for this is the under-performance of the absorber column, where only 50% of the designed carbon capture capacity was reached.

It is also worth mentioning that regardless of the stripper mass flow rate (i.e. the residence time) the CO₂ output remained somewhat constant ($\approx 3.5\%$ variation). This is explained by the fact that the residence times tested during experiments were enough to reach practically VLE loadings (see figure 5.4). Thus, the change in mass flow rate reflected only in the rich lean loading entering the stripper column, adjusting the cyclic capacity to reach similar productions.

H₂O:CO₂ Ratio

The methanol synthesis reaction of ZEF's micro-plant requires a H₂O to CO₂ ratio of at least 3:1 in order for the reaction to take place. For this reason, understanding the ratios achieved by the 10X DAC was of vital importance.

Table 5.2: Product Ratio

Stripper Flow Rate [ml/s]	3.81	4.41	5.00
Water Loading [molH ₂ O/kgSorbent]	8.73	11.43	10.66
H ₂ O:CO ₂ [-]	1.05	4.68	2.49

As shown in table 5.2, for a fixed regeneration temperature, **H₂O:CO₂ ratios of 3:1 are achievable**, but no trend is seen with the stripper flow rate. What was noticed is that the top product ratio is linked to water loading of the sorbent entering the stripper column; which is an effect of absolute humidity as will be discussed in section 5.2.

Rich-Lean Heat Exchanger

In an effort to reduce the sensible heat requirements in the regeneration section, and thus reduce the overall energy demand of the process, the Rich-Lean Heat Exchanger was installed in order to make use of the available heat in the lean sorbent leaving the stripper column to pre-heat the rich sorbent about to enter the column. Determining the performance of this component was crucial to understand the energy savings it provided and if its full potential was being used.

Figure 5.5 represents a snapshot of the steady state operation of the rich-lean heat exchanger. Quite noticeably is the poor performance of this component with **a heat transfer coefficient below 5 W/m²K and an efficiency below 15%**, saving only 180 W (3.2 MJ/kgCO₂).

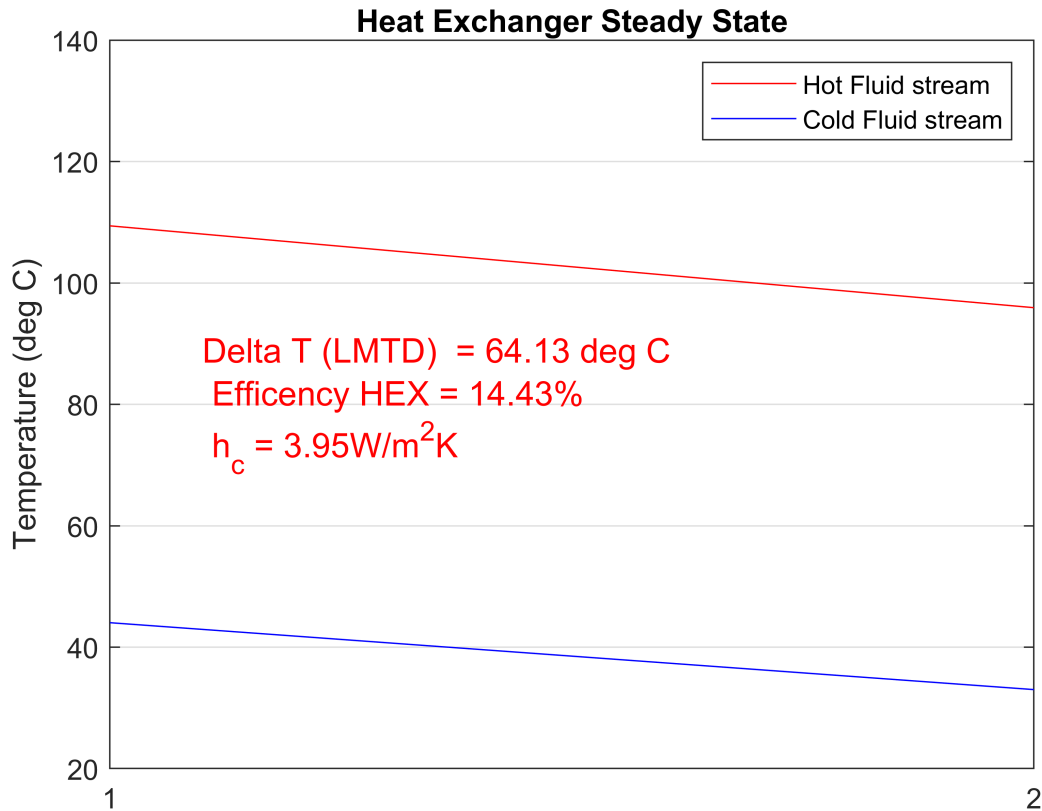


Figure 5.5: Heat Exchanger Characteristics at Steady State

The Rich-Lean heat exchanger was purchased from Alfa-Laval, so the design itself is not suspected to account for the poor performance. The reasons for the experienced results could be related to commissioning/installation of this component. It is suspected that air pockets are present between the plates, which would reduce the overall heat transfer area. Also, the poor performance could be linked to flashing in the cold sorbent stream. However, no solid conclusions could be drawn as to why the heat exchanger performance was this low.

Overall Energy Demand

How efficient the CO₂ capture process of the prototype is can be determined through the overall energy demand of the system, which can be divided in the following parts: sensible heat, heat of desorption, power demand of actuators, heat losses and reflux (additional sensible). Determining which component of the overall energy demand accounts for the biggest portion allows to identify which parts of the system should the optimization effort be focused on.

Figure 5.6 shows a break down of the overall energy demand for the three different stripper mass flow rates (i.e. residence times) tested during experiments; all carried at the same regeneration temperature. Furthermore, the expected/designed for energy demand is also presented for comparison.

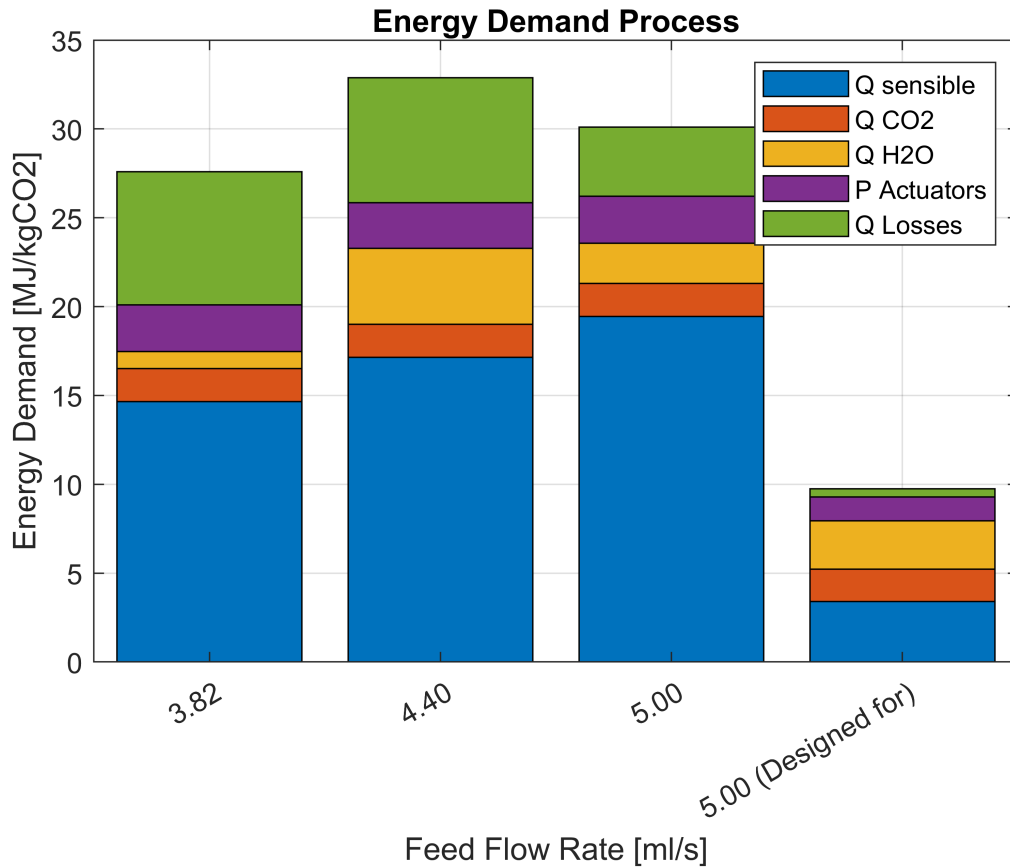


Figure 5.6: Energy Demand Process per molCO₂ produced

Quite noticeably is the big difference between expected energy demand and the determined one during experiments. Overall, **The 10X DAC has an energy demand per kg of CO₂ of up to 33 MJ**, which is 3.3 times higher than it was designed for.

Through figure 5.6 the two main culprits of the deviation between design and measured energy demand are identified: the heat losses and the sensible heat requirement. Such high heat losses are product of a poor insulation in the column. The sensible heat losses being so much higher than the designed value correspond to the poor performance experienced in the Rich-Lean Heat Exchanger.

In figure 5.7 a comparison between ZEF's process energy demand and that of other companies is given. It can be seen that ZEF's process has a higher energy demand than other companies, being 6.8 times higher than the most energy efficient reported process (Carbon Engineering [10]). However, the 10X DAC is the first full scale prototype of ZEF's DAC process, while companies like Climeworks and Carbon Engineering have had full scale working prototypes since 2015[18][64]. The fact that the first ZEF prototype energy demand is within the same order of magnitude as more established companies shows the potential of the 10X DAC process.

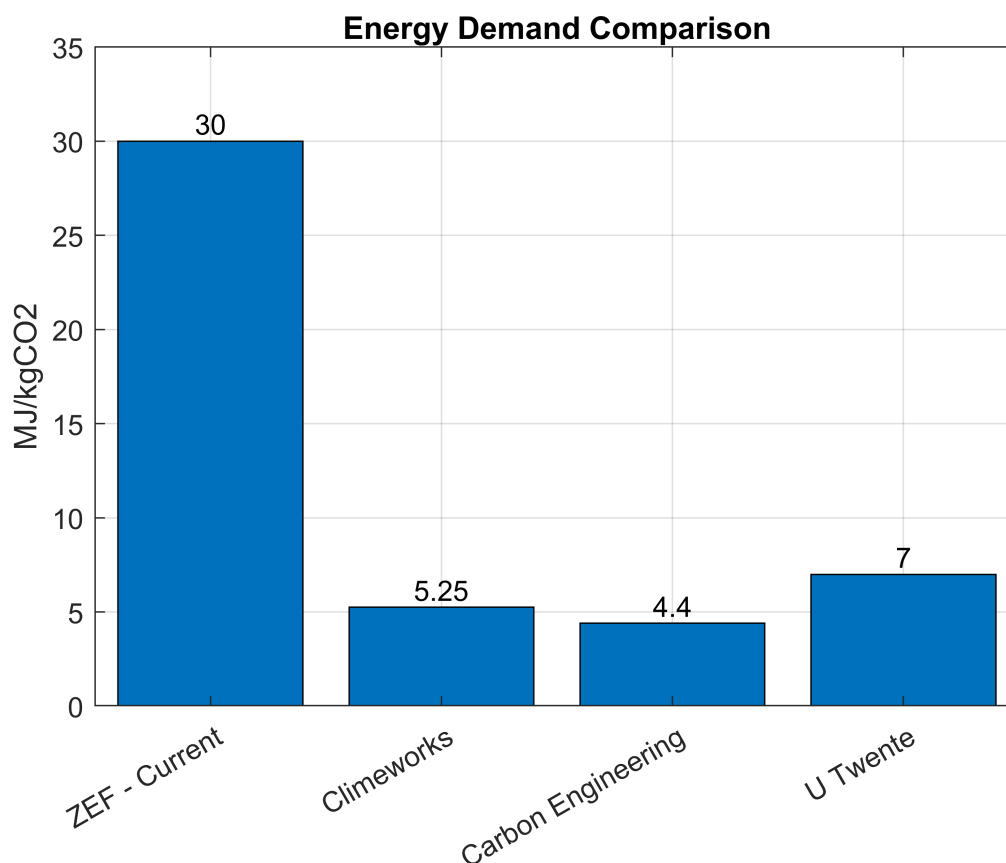


Figure 5.7: Demand comparison with other companies

(Note: Other companies' energy demands are as reported by Brilman [10])

5.1.4. Characterization Summary

- **The CO₂ capture capacity and CO₂ output of the 10X DAC are both half of what it was designed for.** Under design conditions, the 10X DAC has a STY of 2.7e-3 molCO₂/m³·s and a CO₂ output of 0.00128 molCO₂/s.
- **The 10X DAC process is liquid side limited**, which is consistent with other processes in industry.
- **Residence times as low as six minutes proved to be enough time for the lean sorbent to reach practically VLE loadings**, meaning that lower residence times could potentially be used.
- **H₂O:CO₂ ratios above 3:1 were achieved.** However, this seemed to be linked to the water loading of the sorbent entering the stripper column and not to process parameters.
- **The Rich-Lean Heat Exchanger performed poorly, with a heat transfer coefficient below 5 W/m²K and an efficiency below 15%.** Commissioning reasons are suspected to be the culprits of the experienced performance.
- **The energy demand of the process is 28-33 MJ/kgCO₂**, which is up to 3.3 times higher than the design value.

5.2. Environmental Conditions effects

Q: What is the effect of environmental conditions in the performance of ZEF's 10X DAC system?

One of the main advantages of DAC units is that they can be installed literally anywhere, which means that they can be exposed to different environmental conditions. Because of this, it is of extreme importance to understand how the DAC process is affected by the location. To do so, during this thesis focus was given to determine the effects of ambient temperature and absolute humidity on the DAC

cycle (introduced in section 4.3). More specifically, how the working envelope of the DAC process was affected by environmental conditions was determined.

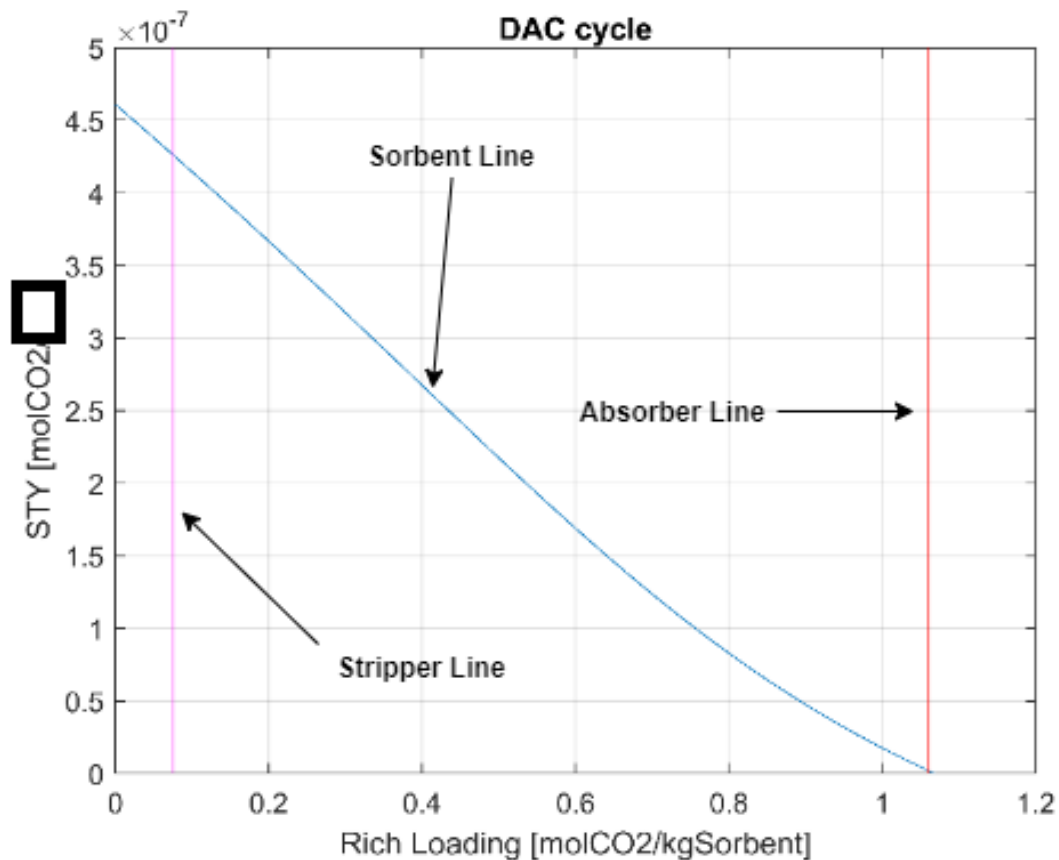


Figure 5.8: DAC Cycle Base Case

(Note: units in y-axis not fully shown due to intellectual property concerns)

Figure 5.8 represents the base case of the DAC cycle, and will allow to better understand the effects of varying temperature and varying absolute humidity. First, effects of changing temperature will be determined in how the Sorbent, Absorber and Stripper lines are affected, and what it means to the DAC process. Then, a similar study of varying absolute humidity will be done.

5.2.1. Ambient Temperature Effects

The effect of ambient temperature was studied while keeping the water loading in the sorbent constant. Three temperatures were studied, which represent the extremes of the temperatures experienced during experiments, and a middle value for ease of comparison.

Figure 5.9 shows how temperature affects the DAC cycle. To begin with, it is noticed how higher temperatures shift the sorbent line downwards; which means a decrease in the performance of the absorption column and a reduction of the working envelope. For the same rich loading, working at a higher temperature translates to a lower space time yield. Higher temperatures also shift the absorber line to the left, further decreasing the working envelope. Finally, it can be seen that ambient temperature has no effect in the stripper line as the regeneration process takes place at much higher temperatures.

Overall, it is concluded that **temperature variations affect the performance of the absorption column while effecting no direct influence in the regeneration process**. So, when designing the absorber column special care should be given to the expected temperatures to be experienced.

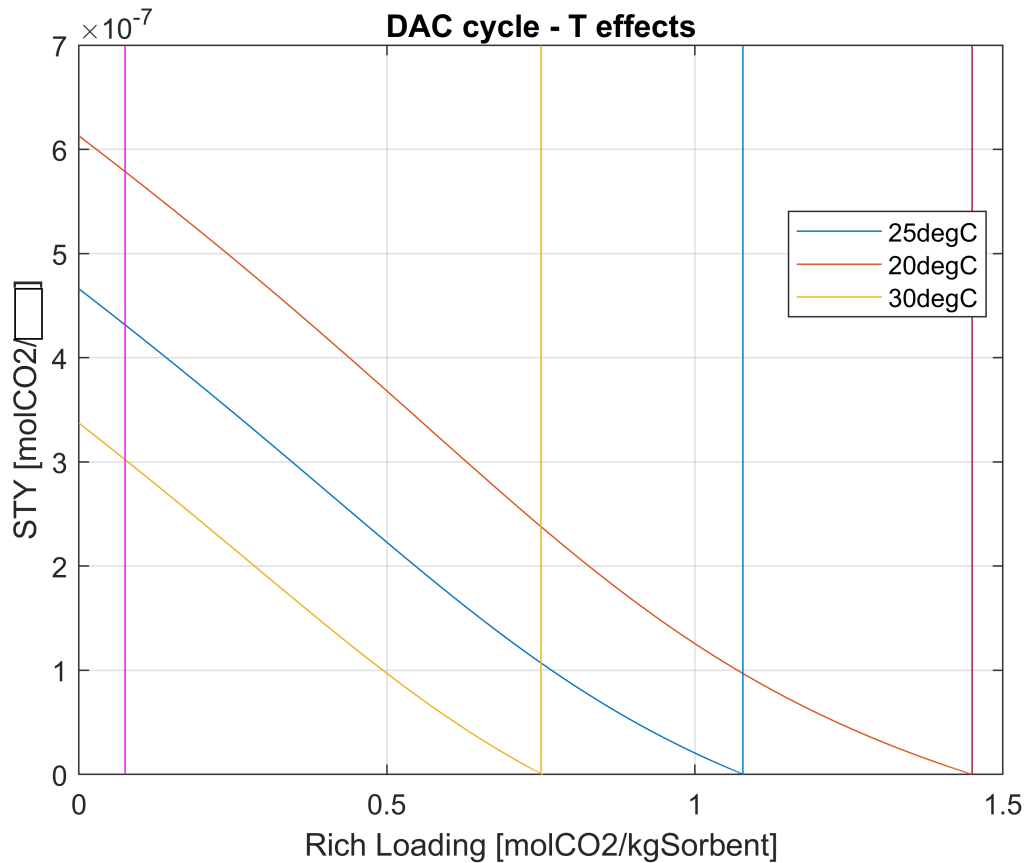


Figure 5.9: Temperature effects in DAC cycle

(**Note:** units in y-axis not fully shown due to intellectual property concerns)

Temperature effects in the absorption performance are better understood through CO₂ VLE loading changes. As seen in figure 5.10, a 5°C temperature variation can lower the CO₂ VLE loading of TEPA:PEG 1:2.5 as much as 38%; which is a significant reduction in the driving force of the process. As explained in section 4.1, the driving force (i.e. difference between VLE loading and current loading) is one of the main drivers in the performance of the absorption column, which explains why 5°C has such negative impact in the STY.

It is important to acknowledge that higher temperatures do bring a decrease in viscosity, however it seems that VLE loading is more sensitive to temperature changes than viscosity, and thus the overall effect is negative in the absorption performance.

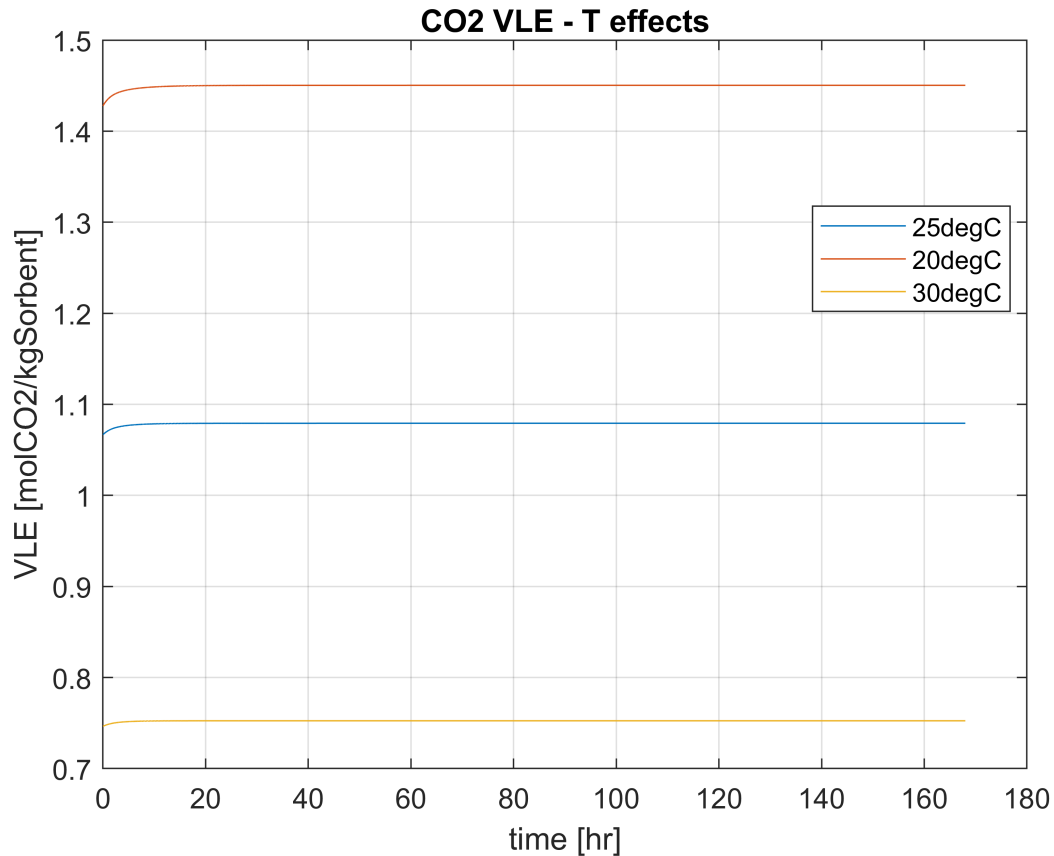


Figure 5.10: Temperature Effect in VLE

5.2.2. Absolute Humidity

The effect of absolute humidity was studied while keeping the temperature of the process constant. First, the effect of absolute humidity was studied in terms of how the water loading in the sorbent varied. Then, the effect of water loading (already linked to absolute humidity) on the DAC cycle was studied.

As seen in figure 5.11 absolute humidity increase has a positive effect in the water loading of the sorbent; the more water present in the ambient, the higher the water loading in the sorbent. This understanding helps to explain the results seen in the H₂O:CO₂ ratios (see table 5.2), if not enough water is present in the environment the required ratio can't be accomplished without some sort of control scheme.

Now that the effect of absolute humidity in the water loading of the sorbent has been established, the effect of the latter is studied in the DAC cycle. To do so, the effect of three different water loadings, which represent the two extremes observed during experiments and a middle value for ease of comparison, was determined.

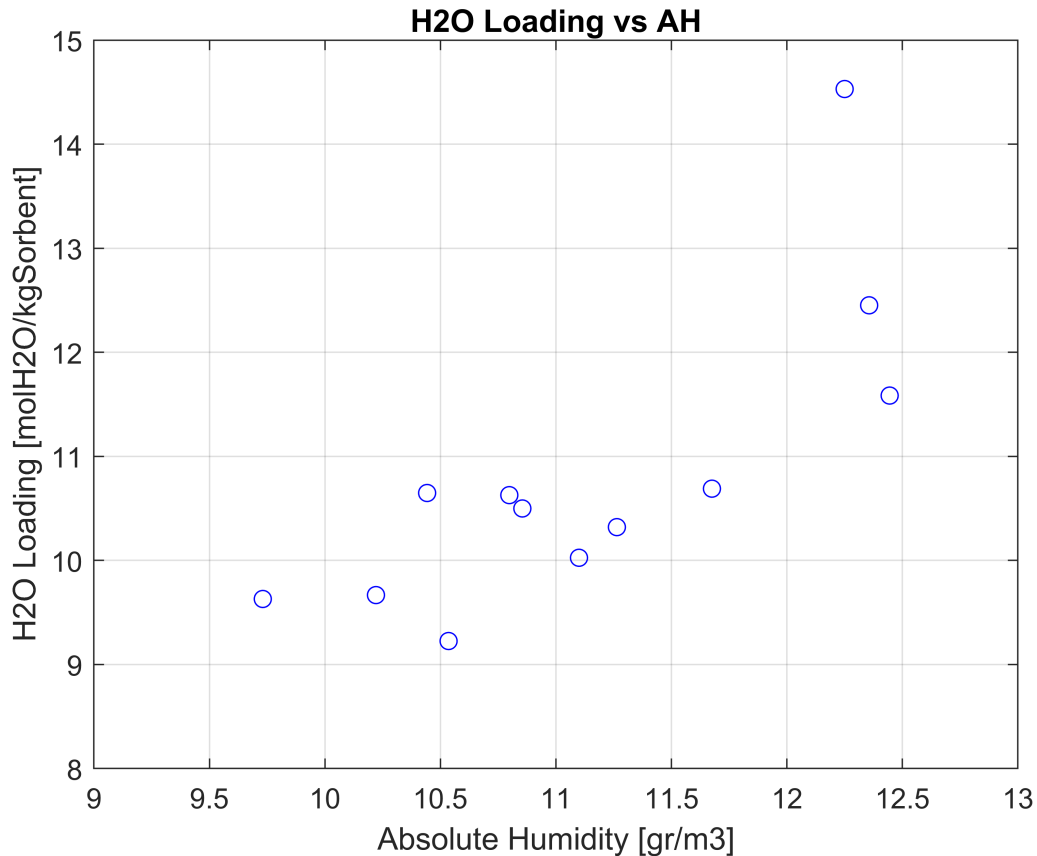


Figure 5.11: Absolute humidity effect in water loading

In figure 5.12 several things can be observed. To begin with, it can be seen that varying water loadings in the sorbent have a negligible effect in the sorbent line when compared to temperature effects; with a magnitude change in STY not greater than 4%. A similar conclusion can be drawn for the absorber line, where the change in water loading brings only about 5% difference in the VLE loading. Overall, the influence of absolute humidity in the absorption process is negligible.

On the other hand, water loading, and thus absolute humidity, plays a significant role in the performance of the regeneration process as it can be seen that the stripper line is shifted considerably. When the water loading in the sorbent drops by 2 mols per kg sorbent, the stripper line shifts right, and the working enveloped is reduced; with the achievable lean loading increasing by more than 60%. This is explained by the CO₂ VLE curves in the reboiler stage, with less water available to be desorbed, the partial pressure of CO₂ in this stage increases, and thus the CO₂ loading of the sorbent leaving the stripper column increases as well (see Appendix D figure ??)

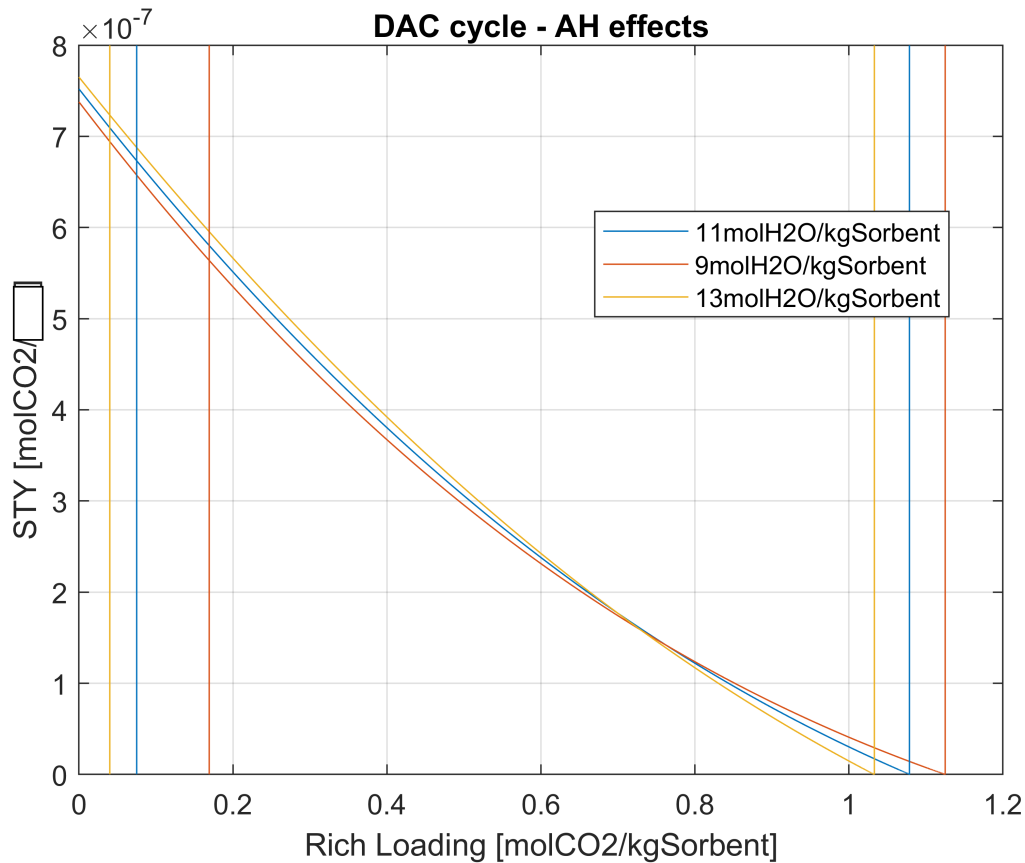


Figure 5.12: Water Loading Effect in the DAC cycle

(Note: the crossings in the STY curves may not be physical, and are explained by the limited range of the viscosity neural network; more work is to be performed in the viscosity neural network to increase the range)

(Note: units in y-axis not fully shown due to intellectual property concerns)

Overall, it is concluded that **absolute humidity variations affect the performance of the regeneration process, with negligible effects on the absorption column**. This means that when designing the regeneration process, specially the stripper column, attention should be given to the expected absolute humidity.

5.2.3. Environmental Conditions Effect Summary

- **Temperature variations play a significant role in the absorption process, while having no effect in the regeneration process.** This is mainly explained by important changes in the CO₂ VLE loading of the sorbent when temperature increases or decreases.
- **Absolute Humidity variations are negligible in the absorber column, but play a significant role in the performance of the regeneration process.** This is explained by the increase/decrease of CO₂ partial pressure in the reboiler stage of the stripper column, and thus an increase/decrease of the loading leaving the column.
- **TEPA:PEG 1:2.5 favors colder humid climates**, with a better performance in all the aspects of the DAC cycle.

5.3. Sorbent Comparison

In section 5.2, it was shown that TEPA:PEG 1:2.5's CO₂ VLE loading is very sensitive to temperature changes. Available data from previous experiments at ZEF allowed to make a comparison between the 10X DAC's sorbent and pure TEPA in terms of CO₂ VLE loadings for same environmental condi-

tions. Through this comparison, it was expected to understand which sorbent would be better for the conditions experienced during experiments.

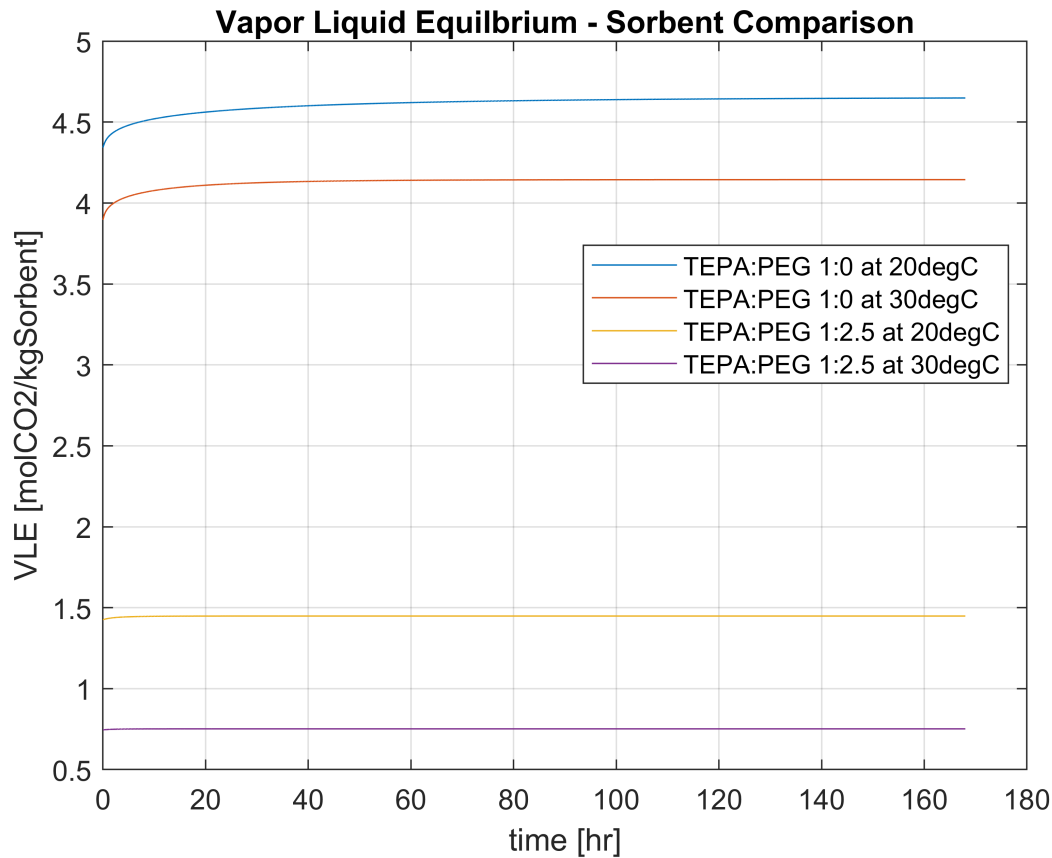


Figure 5.13: Vapor liquid equilibrium loading comparison

As shown in figure 5.13, pure TEPA's CO₂ VLE loading is much less sensitive to temperature variations when compared to TEPA:PEG 1:2.5. This suggests that **interactions between TEPA and PEG affect the CO₂ VLE loading reaction to temperature variations**, which means that the role of PEG in the sorbent is not that of a simple diluent; something that needs to be further researched.

Furthermore, the carbon capture capacity and the viscosity of both sorbents were also studied for comparison. In figure 5.14, the STY and viscosity of both sorbents for the same conditions are plotted, alongside with their corresponding stripper lines. It can be seen that although less sensitive to CO₂ VLE changes with temperature, pure TEPA STY is lower within its working envelope (to the right of the stripper line) and its viscosity is extremely high when compared to TEPA:PEG 1:2.5 at same temperature and absolute humidity.

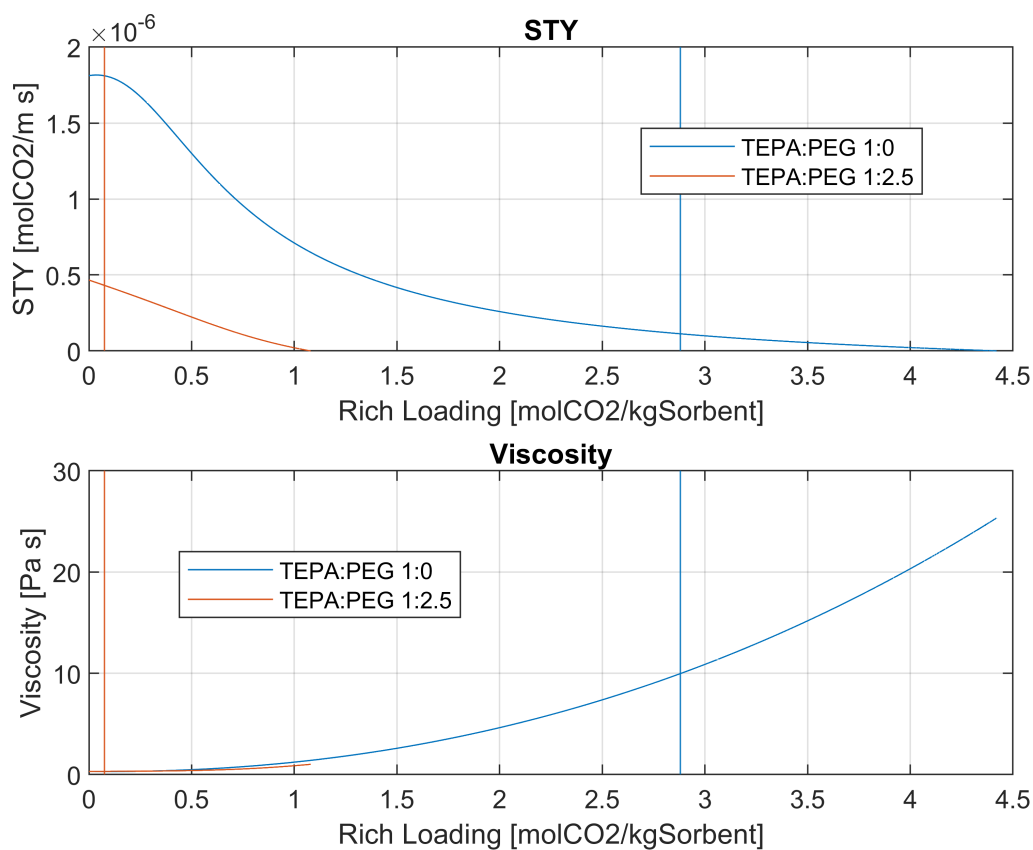


Figure 5.14: STY & Viscosity comparison

From the obtained results, it is concluded that **neither pure TEPA nor TEPA:PEG 1:2.5 are ideal sorbents for environmental conditions as the ones experienced during the 10X DAC experiments.** On one hand, TEPA:PEG 1:2.5 is too sensitive to temperature variations in its VLE loading and thus its performance is greatly affected. On the other hand, pure TEPA showcases viscosities that simply can't be handled by the sorbent distribution system, and its carbon capture performance is no better than that of TEPA:PEG 1:2.5's.

Conclusions & Recommendations

6.1. Conclusions

Reflecting back in the scope and research questions of this thesis, the main conclusions are presented in this section. To begin with, the rewards of the built and commissioning effort are presented. Then the main learnings of the characterization experiments are revisited alongside with the environmental effects main conclusions. Finally, the main takeaways of the optimization process are given.

6.1.1. Built/Commissioning of the 10X DAC

The prototype built during this thesis is a **fully functional direct air capture system capable of working in a continuous process**. The shortcomings of the first generation of the 10X are mainly in the sorbent distribution system, and the energy demand of the process, and should be addressed in future work by ZEF.

6.1.2. System Characteristics

Q: What are the characteristics of ZEF's 10X DAC system and how does it compare to the expected performance/model predictions?

The characterizations experiments performed not only allow to determine the performance and energy efficiency characteristics of the built prototype, but also gave significant insights into the DAC process in the system. Overall, the main takeaways from the experimental characterization are the following:

- **CO₂ capture is the limiting process in the absorption column.** Compared to H₂O capture, the CO₂ capture is much slower and thus optimization efforts should always focus in this part of the process.
- **The CO₂ capture process is liquid side limited.** Literature suggests that mass transfer is the limiting step when compared to CO₂ capture kinetics, so efforts to reduce diffusion limitations should always be prioritized.
- **The CO₂ capture capacity of the current 10X DAC is $2.7 \times 10^{-3} \text{ molCO}_2/\text{m}^3 \cdot \text{s}$,** which is roughly 50% lower than designed for. The experienced lower performance is product of a poor sorbent distribution system, and the high temperatures of the Dutch summer.
- **Residence times as low as six minutes proved enough time to reach VLE loadings in the regeneration process,** which means the current configuration in the stripper column's performance is satisfactory.
- **H₂O:CO₂ ratios in the product stream are highly dependent on the absolute humidity in the environment** while the regeneration temperature is constant. So a control scheme is required if the obtained product ratios are to be controlled.
- **The energy demand experienced during experiments was 1200-1400 kJ/molCO₂,** with sensible heat requirements and heat losses representing the biggest portion of the total energy demand.

- Without a sorbent change, **the energy demand of the process can be greatly optimized by addressing the sensible heat demand in the regeneration section.**
- **The volumetric capture capacity is currently higher than Carbon Engineering's** and is within striking distance of that of Climeworks.
- **The current energy demand is 5 times higher than that of well established companies** such as Climeworks and Carbon Engineering. However, the fact that ZEF's first prototype is in the same order of magnitude in energy demand compared to companies working in the field for a longer time is promising.

6.1.3. Environmental Conditions Effects

Q: What is the effect of environmental conditions in the performance of ZEF's 10X DAC system?

The characterization experiments also allowed to gain insights into the effects of environmental conditions in the DAC process. Specifically, the effects of ambient temperature and absolute humidity were determined through the presented DAC Cycle diagram. Overall, the main conclusions are the following:

- **Ambient Temperature influences the absorption process only, while Absolute Humidity affects mainly the regeneration process.** Hot and dry environmental conditions represent the worst case scenario for the DAC cycle in terms of performance and the size of the working envelope.
- **The CO₂ vapor liquid equilibrium loading of TEPA:PEG sorbent is very sensitive to Ambient Temperature**, with up to 38% reduction with a temperature increase of 5°C. The effect of this is the reduction in performance of both the sorbent and the absorption column.
- **The Absolute Humidity greatly influences the H₂O VLE loading of the sorbent**, with more water present in the environment the sorbent is capable of increasing its water loading.
- **The water loading in the sorbent entering the regeneration process highly affects the CO₂ lean loading attainable in the stripper column**, with higher water loading the more lean the sorbent can be made in terms of CO₂. This is explained by the CO₂ partial pressure reducing in the reboiler stage when more water is present.
- **Water loading (i.e. absolute humidity) dictates the top product H₂O:CO₂ ratio.** If the absolute humidity is not enough, the process can't reach the required top product ratio without a control scheme.
- **The DAC cycle is affected by both Temperature and Absolute Humidity.** Temperature shifts the sorbent line up and down, and the absorber line left and right. Absolute humidity has a negligible effect in both the sorbent and absorber lines, but shifts the stripper line left and right.

6.1.4. Optimized 10X DAC System

Q: How would an optimized DAC system design look like?

Through the optimization process, several things were noted about the overall DAC process of the 10X DAC.

- **Neither pure TEPA nor TEPA:PEG 1:2.5 are the ideal sorbents for hot and dry weather conditions.** TEPA capture performance and viscosity are not acceptable for the 10X DAC process, while TEPA:PEG 1:2.5 is too sensitive to temperature shifts in its carbon capture performance.
- **CaPex parameters and energy demand parameters act against each other when optimizing the system.** Designing for a small prototype carries a negative penalty in overall energy demand of the process, while designing for a target energy demand translates to a bigger absorption column.
- Without changing the sorbent used, **sensible heat demands bring the biggest possible savings in the overall energy demand of the process.**
- **The optimized energy demand reduces the difference compared to other companies significantly**, with a potential overall energy demand of 13 MJ/kgCO₂.

6.2. Recommendations

The first version of the 10X DAC unit gave many insights into the whole process, but also opened the team's eyes into aspects that were not fully tackled during the work of this thesis. For this reason, recommendations for future work are given. For ease of understanding, the recommendations will be given in terms of: process design, and model development.

6.2.1. Process Design Recommendations

Although great knowledge was developed through this thesis regarding the direct air capture process, still a lot of work is to be done to fully understand everything behind a DAC unit. The recommendations for future work on the 10X DAC process will be given for each component of it: sorbent, absorber, stripper, and other overall recommendations.

Sorbent

- **Research on different TEPA:PEG ratios:** the current ratio's VLE loading sensitivity to temperature changes represent a big challenge to the process' performance. Pure TEPA has a better response in terms of VLE loading, but its viscosity changes can't be managed by the system. There may be an optimal TEPA:PEG ratio at which the sensitivity to temperature in terms of VLE and viscosity is acceptable.
- **TEPA and PEG interaction:** it was assumed that PEG served only as a diluent for the sorbent, however the difference in VLE response to temperature between pure TEPA and TEPA:PEG indicate that the interaction between both is more complex than that. Research should be done to understand what actually happens between the two components, and how this affects the performance as a CO₂ sorbent.
- **Sorbent's lifetime characteristics:** the selection of the optimal sorbent cannot be only based on its performance and response to dynamic conditions, but also to the lifetime characteristics. Research should be done in the effects of thermal and oxidative degradation in the sorbent used under 10X working conditions (i.e. varying environmental conditions, regeneration temperatures, etc).

Absorber Column

- **Air distribution in column:** the low pressure drop of the column, coupled with the high inertia of the air stream, may lead to empty pockets being formed in the column. Air flow distribution studies should be performed to see if this is the case, and the inlets and outlets design should be revisited in order to guarantee air is distributed in the entire column.
- **Column enclosure:** the current enclosure proved to be sensitive to thermal expansion effects, and had to be constantly re-sealed. It is recommended that a new enclosure is designed which doesn't suffer from thermal effects as much as the current one.

Stripper Column

- **Packing density:** in this thesis the effect of the packing density was not studied. Research should be done on the effects of different packing densities in terms of the mass transfer performance, as well as the pressure drops experienced in the column.
- **Residence time:** the residence times tested during this thesis proved to be enough time for VLE loadings to be reached in the regeneration process, lower residence times should be tested to see below which the VLE loading is no longer achieved and mass transfer limitations become significant.
- **Stripper insulation:** the heat losses in the stripper column represent a much bigger than acceptable part of the overall energy demand, so research into how to improve the insulation should be carried to greatly reduce this energy demand component.
- **Reflux Ratio:** this thesis did not make use of the reflux condenser, thus no results in its effect were obtained. The reflux condenser has been used by ZEF as a gas wash-up stage, so it is necessary to study how this would perform in the 10X system.
- **Total Condenser design:** it was noticed during experiments that not all the product stream was condensed before entering the flash tank, and thus H₂O entered the CO₂ line. The design of the condenser should be revisited in order to give the required cooling power.

- **Higher feed temperature:** in the optimized design the feed temperature is capped at 95°C due to concerns of desorption in the rich-lean hex mainly. The possibility of going for higher feed temperature should be researched due to the potential savings in sensible heat demand.

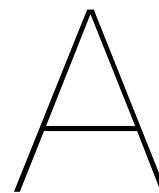
Other

- **Rich-Lean Hex:** the root cause of the poor performance of the rich-lean hex should be determined in order to be able to use the full potential of this component and increase the overall energy savings in term of sensible heat demand.
- **Electric Heater:** instead of the external oil bath for the thermosyphon heating, it would be interesting to study the possibility of implementing electric heaters. This could not only improve the efficiency, but also allows for a better regeneration temperature control.
- **CO₂ output sensors:** the 10X was originally designed to have digital sensor in the CO₂ outlet of the flash tank, however the pressure drop induced by the sensor negatively impacted the process. An in-line measuring mechanism should be devised in order to give reliable physical measurements of the CO₂ production.
- **Controlled water discharge:** the H₂O production of the 10X could be automatically measured if a solenoid valve was installed at the outlet of the flash tank. It is recommended to implement such system in order to get more reliable H₂O production measurements.
- **CO₂ product purity:** the purity of the CO₂ product is of interest both for ZEF's process and other uses of the gas a raw product, which means that the purity of this product should be determined in order to evaluate its feasibility as a raw material.
- **Unwanted emissions in product stream:** throughout this thesis it has been assumed that both TEPA and PEG are non-volatile, however this is not the case. Research should be performed into whether or not unwanted emissions, like ammonia, are present in the product stream.

6.2.2. Model Development Recommendations

The developed absorber model of this thesis should be seen as the basis for the development of a thorough absorption model in ZEF's process. With that in mind, the following recommendations are given:

- **H₂O Capture:** the developed model assumed a VLE and constant loading of H₂O in the sorbent composition. A function for the H₂O capture of the process should be implemented in which changes in the environmental conditions and sorbent properties are taken into consideration in terms of water capture.
- **Viscosity range:** the neural network fit of the developed model is limited to the experienced viscosity during experiments. The range should be expanded to include viscosity beyond these limits in order to give more reliable results of the process.
- **Sorbent temperature:** the effect of the exothermic CO₂ capture process in the sorbent temperature should be studied. The current model showed how influential a couple of degrees can be in the overall performance, so the assumption of the sorbent having the same temperature as ambient air could give misleading results.
- **Experimental constant validity:** the experimental constant used in the model is assumed to be applicable to any type of sorbent. It is necessary to determine the constant through the results of other sorbents in order to validate this assumption.
- **Sorbent degradation:** once the degradation mechanisms are better studied, a model for the degradation of the absorber should be incorporated into the overall model. This would allow to understand the performance of the process over time.
- **Connected model:** the absorber model developed in this thesis should be implemented into the models developed by ZEF (sump, stripper, flash tank) in order to understand the overall performance of the entire system under dynamic conditions.



Measurement Equipment

A.1. Fourier-Transform Infrared Spectroscopy

As mentioned in chapter 3, an Agilent Cary 630 FTIR machine (figure A.1) was used to analyse the sorbent samples collected during experiments. The working principle of such a machine is the interaction of infrared light with matter, which is absorbed at specific frequencies (or wavelengths) based on the molecular bonds present in the sample and the types of atoms present at the end of the bonds [61]. When molecules present in the sample absorb the infrared light, its bonds vibrate; these vibrations can either stretch, bend and/or wag the functional group [1].

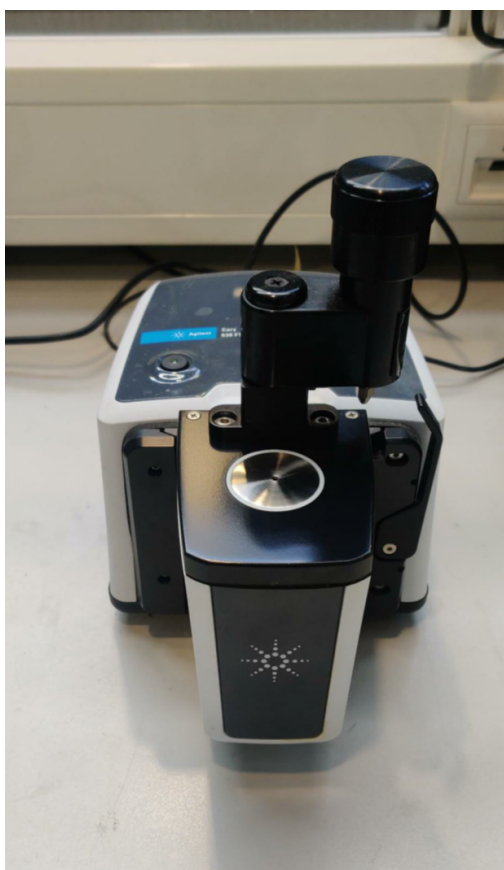


Figure A.1: Agilent Cary 630 FTIR machine

An FTIR uses an interferometer, which consists of a source, beam splitter, two mirrors, a laser and a detector. The steps of how the process works are as follow: [61]

1. Infrared energy is emitted from the source and the beam passes through an aperture which controls the amount of energy.
2. The beam now enters the interferometer where the spectral encoding takes place.
3. The beam enters the sample compartment, where specific frequencies of energy are absorbed by the sample depending on the present molecules.
4. The beam finally reaches the detector for final measurement.
5. Fourier Transform is applied to the signal and a final spectrum is obtained.

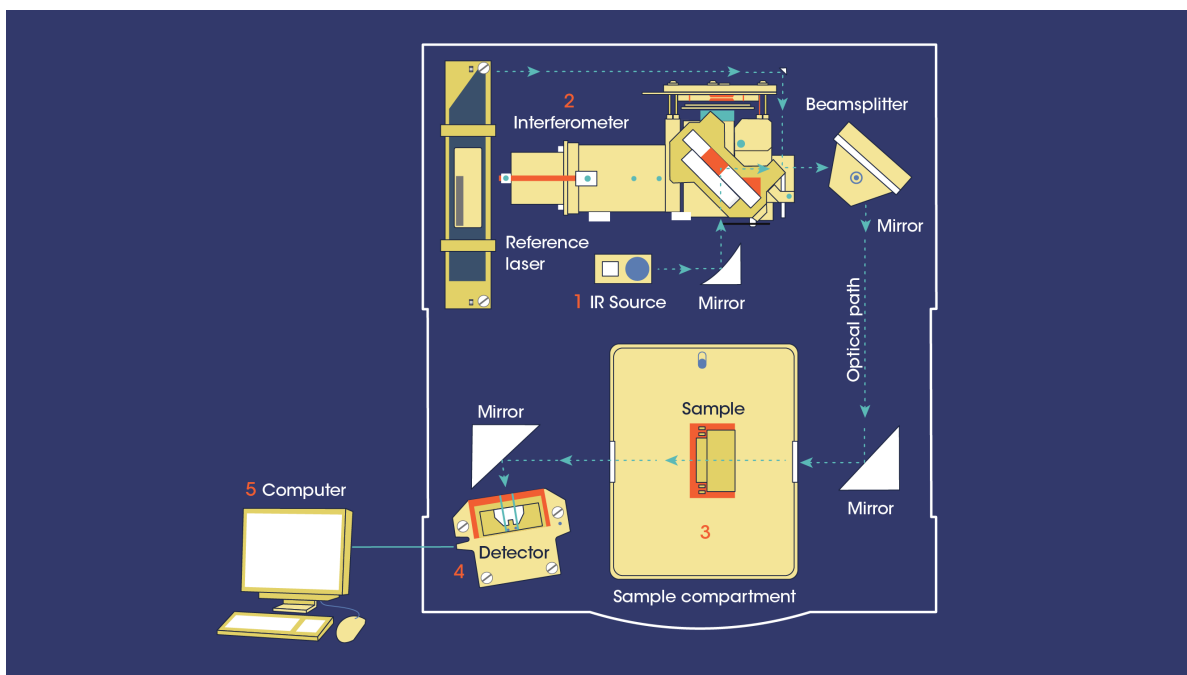


Figure A.2: Working principle of an FTIR machine [61]

Thanks to the maturity of this technique, information on the absorbance and corresponding wavelength of covalent bonds is readily available. Furthermore, information on chemical compounds such as CO₂ is also known [63].

During his thesis work, Sinha [57] developed a method to quantify the amount of each component in the obtained spectrum from the FTIR analysis. To do so, a software tool called "TQ Analyst" was used to process the information from the FTIR spectrum.

The TQ Analyst software was calibrated using reference samples with known concentrations of TEPA-PEG-H₂O-CO₂. By calibrating the software to translate the peak heights, width, location and area of the known spectra to the components present and its quantities, it was possible to know quantify unknown spectra of similar samples.

It is important to acknowledge though that the calibration only works when the sample has the chemical compounds for which it was calibrated for. Thus, if any other chemical compounds are present, the reliability of the measured quantities goes significantly down. This is something to keep in mind when degradation products begin appearing in the sorbent.

For details on how the calibration was performed, please refer to the work of Sinha [57].

A.2. CO₂ Concentration Measurements

The CO₂ concentration in the air stream entering and leaving the absorber column was measured using K30 10,000ppm sensors placed in each inlet and outlet, with a measurement accuracy of ± 30 ppm.



SE-0018

Figure A.3: K30 10,000ppm CO2 sensor

A.3. Humidity Measurements

For the measurement of absolute humidity in the ambient, a Adafruit Sensiron SHT31-D Temperature & Relative Humidity sensors were used, with a measurement accuracy of $\pm 0.3^{\circ}\text{C}$ and $\pm 2\%$ respectively. The measured values were then used to compute the absolute humidity in g/m^3 .

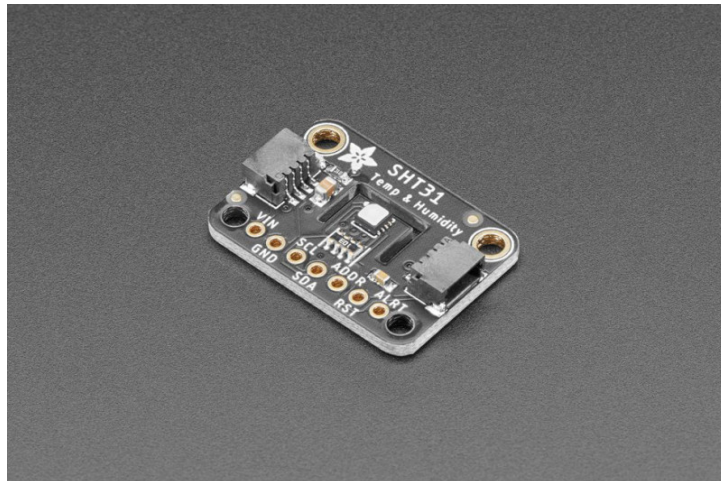


Figure A.4: Adafruit Sensiron SHT31-D sensor.

A.4. Pressure Drop Measurements

For the measurements of the pressure drop across the different components in the system (absorber column, fans, flash tank), Honeywell Differential Pressure (26PCAFA6D) sensors were used, with a measurement accuracy of $\pm 0.25\%$.

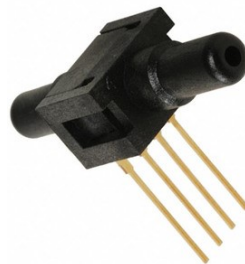


Figure A.5: Honeywell Differential Pressure Sensor (26PCAFA6D)

A.5. Temperature Measurements

For the measurement of temperature at different points of the set-up, Tegg NTC 3950 100K Thermistors Temperature sensors were used, with a measurement accuracy of $\pm 1\%$. When the NTCs were used to measure liquid temperature, this was done by installing thermowells at specific locations and then putting the NTC.

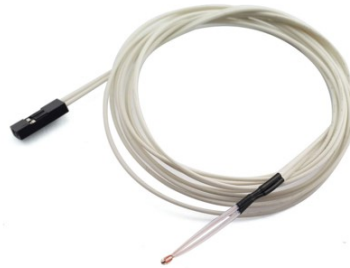
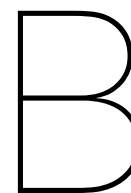


Figure A.6: Tegg NTC 3950 100K Thermistors Temperature sensor



Experimental Results

B.1. Absorption Characteristics

During the absorption characterization experiments, as many characteristics of the process were determined as the sensors and time allowed to. The main results were presented in chapter 5, but other important results were also obtained that helped in the understanding of the CO₂ capture process. In this section, complimentary results backing up the conclusions of the results sections are given, as well as other characteristics of the absorption column which are of importance.

B.1.1. CO₂ vs H₂O capture process

In section 5.1.1 it was stated that CO₂ capture is the limiting process in the absorption, and the results regarding the rich loading over time of both chemical compounds over time was presented; in which it was noticed CO₂ loading takes much longer to reach VLE values. To further backup the conclusion that CO₂ capture is the limiting process, figure B.1 shows the STY of both CO₂ and H₂O in day one of experiments; when the driving force for both compounds was its highest. Quite noticeably, the STY of H₂O can be up to two order of magnitudes higher compared to the STY of CO₂, which further backs-up the conclusion that CO₂ capture is the limiting process in the absorption column.

B.1.2. Air side vs Liquid side limitations

In section 5.1.1, results on the STY of CO₂ as a function of the driving force of the process were given, and it was noticed that the STY had a decreasing trend with decreasing driving force; which is to be expected from a liquid side limited process. Furthermore, during characterization experiments, the air mass flow rate was varied in order to see the effects in the CO₂ capture capacity. Figure B.2 shows the effect of varying the total air mass flow rate (through the PWM control of the fans) in the carbon capture capacity of the process. When the total mass flow rate of air entering the column was decreased, it can be seen that overall the STY of CO₂ reduced with the reduction of air. This is explained by the fact that as less air goes through the column, the quantity of CO₂ captured reduces; which is an air side limited behavior.

However, in figure B.2 it is also noticeably that the air was never depleted of its CO₂, which then hints towards a liquid side limited process. The contradicting results with the variation of air mass flow rate can be explained by the poor sorbent distribution explained in chapter ??, and the suspected poor air distribution in the column. When the fans are working at full throttle, there is a suspicion that empty pockets are formed in the column, and thus the >2000 m³/hr of air mainly go through the middle of the column, where sorbent does not react. This means that the air diffuses to the inter-facial region much faster than the sorbent can capture CO₂, and thus the air is non limiting. When the mass flow rate is decreased, the decrease in inertia is suspected to distribute the air more equally in the column, which is why it can be seen in figure B.2 that the CO₂ concentration out decreases, however the process is not completed air side limited in this case since the air is not depleted.

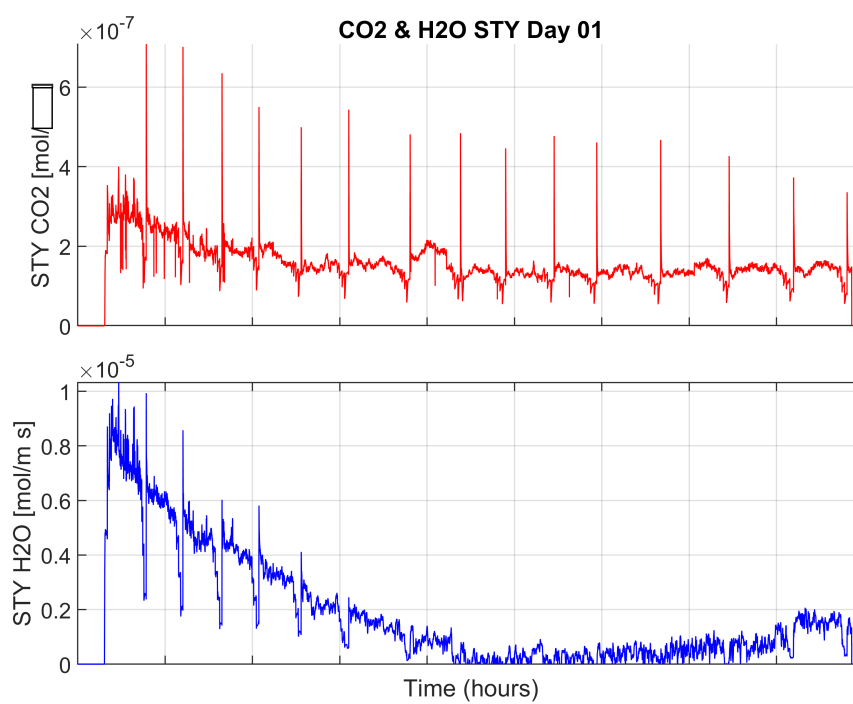


Figure B.1: Capture capacity of CO2 & H2O

(**Note:** units in y-axis not fully shown due to intellectual property concerns)

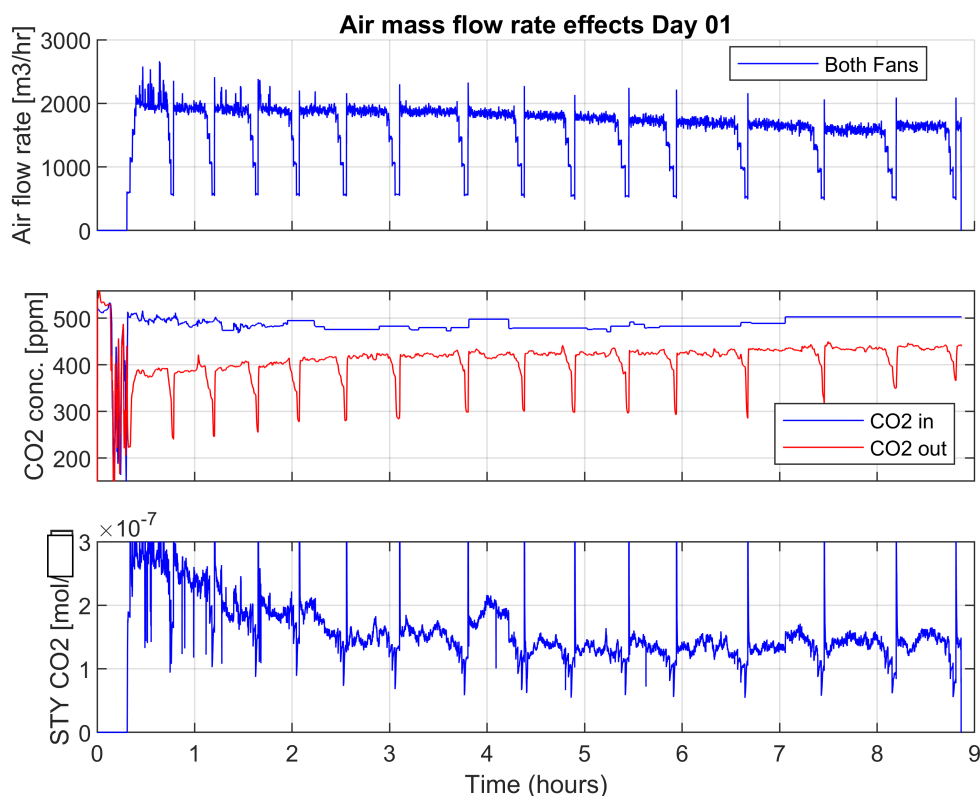


Figure B.2: Varying air flow rate effects

(Note: units in y-axis not fully shown due to intellectual property concerns)

B.1.3. Pressure drop in column

One performance indicator always given in literature regarding absorption columns is the pressure drop experienced [10], which is an indicator of the required energy that needs to be spent in order for air to be circulated in the column. Figure B.3 shows a comparison of the pressure drop in the 10X DAC absorption column compared with the pressure drops in the systems of other companies. As can be seen, the pressure drop in the absorber of the 10X DAC is within the lowest when compared to other processes. This allows ZEF to have an energy demand in the absorption column quite lower when compared to, for example, U Twente's process

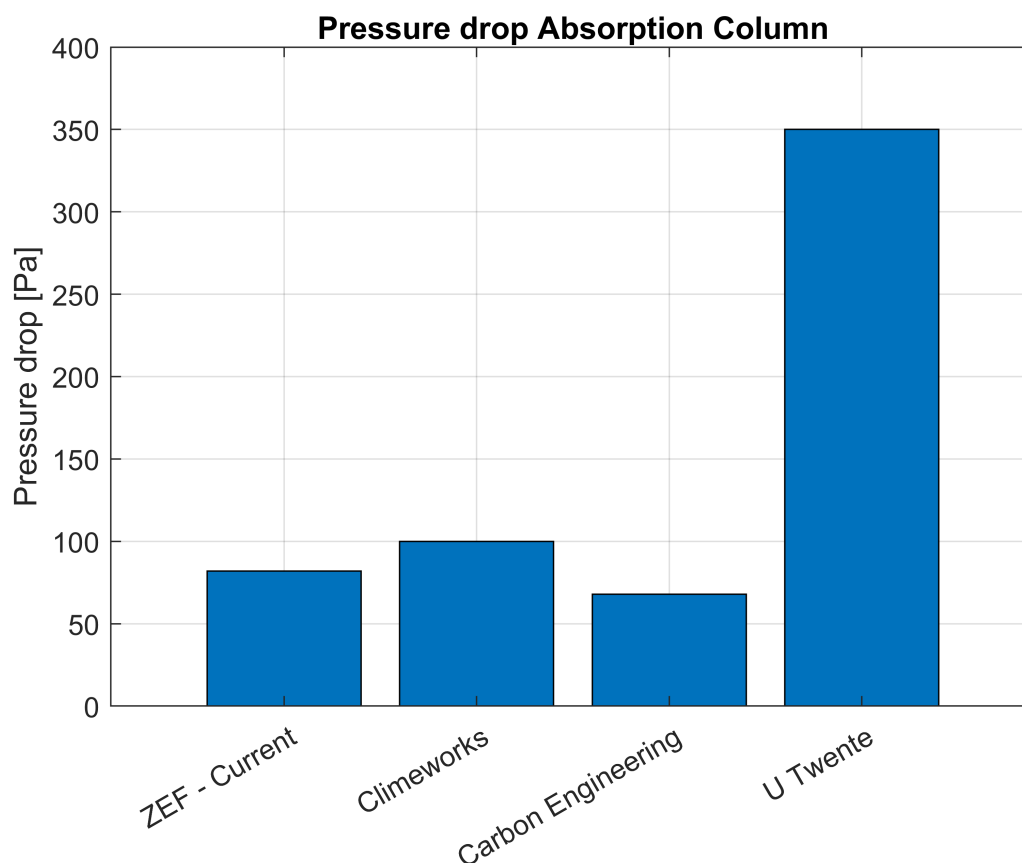


Figure B.3: Pressure drop in the absorption column comparison

B.1.4. CO₂ Capture Efficiency

Another common performance indicator when comparing CO₂ capture processes is the efficiency in the carbon capture (i.e. how much of the available CO₂ is actually removed). Hanak et al [17] stated that the removal efficiency of DAC processes is lower compared to point source capture, however it is still of interest to see how ZEF ranks against other companies. As seen in figure B.4, ZEF's process has a percent removal considerably lower than other companies. This is again explained by the poor sorbent and air distribution in the column, where the mass transfer area is not maximized.

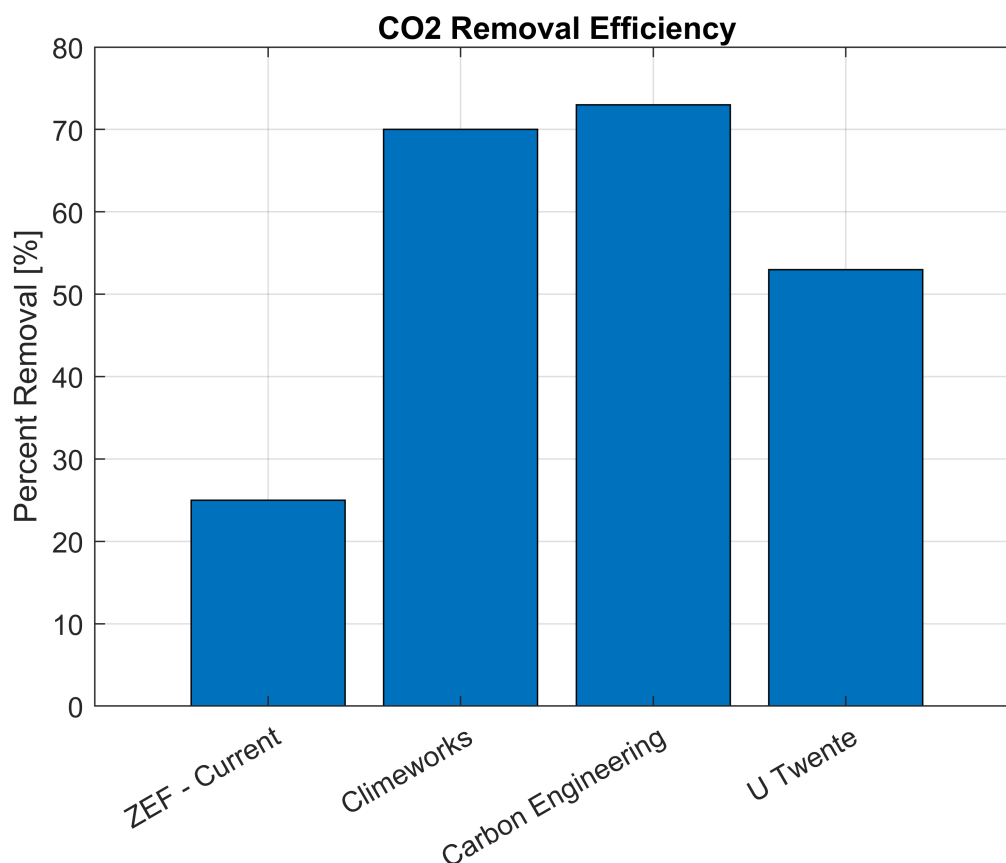


Figure B.4: CO2 Percent removal comparison

B.2. Regeneration Characteristics

The regeneration characterization focused in the required time the sorbent needs to spend in the stripper column in order to reach VLE lean loadings. However, other aspects of the stripper performance were also tracked during experiments that give insights into the regeneration process.

B.2.1. Stripper Pump Characterization

The mass flow rate going through the stripper was crucial to be determined in order to be able to know the residence time of experiments, and to calculate energy demands of the process. To do so, the stripper pump was characterized and a function to relate mass flow rate to the RPMs of the pump was made based on the results. Figure B.6 shows the results, and figure B.5 the fit results and corresponding equation.

```
Linear model Poly1:  
ans(x) = p1*x + p2  
Coefficients (with 95% confidence bounds):  
p1 =      0.5967   (0.46, 0.7335)  
p2 =      0.2307   (-0.8803, 1.342)
```

Figure B.5: fit results

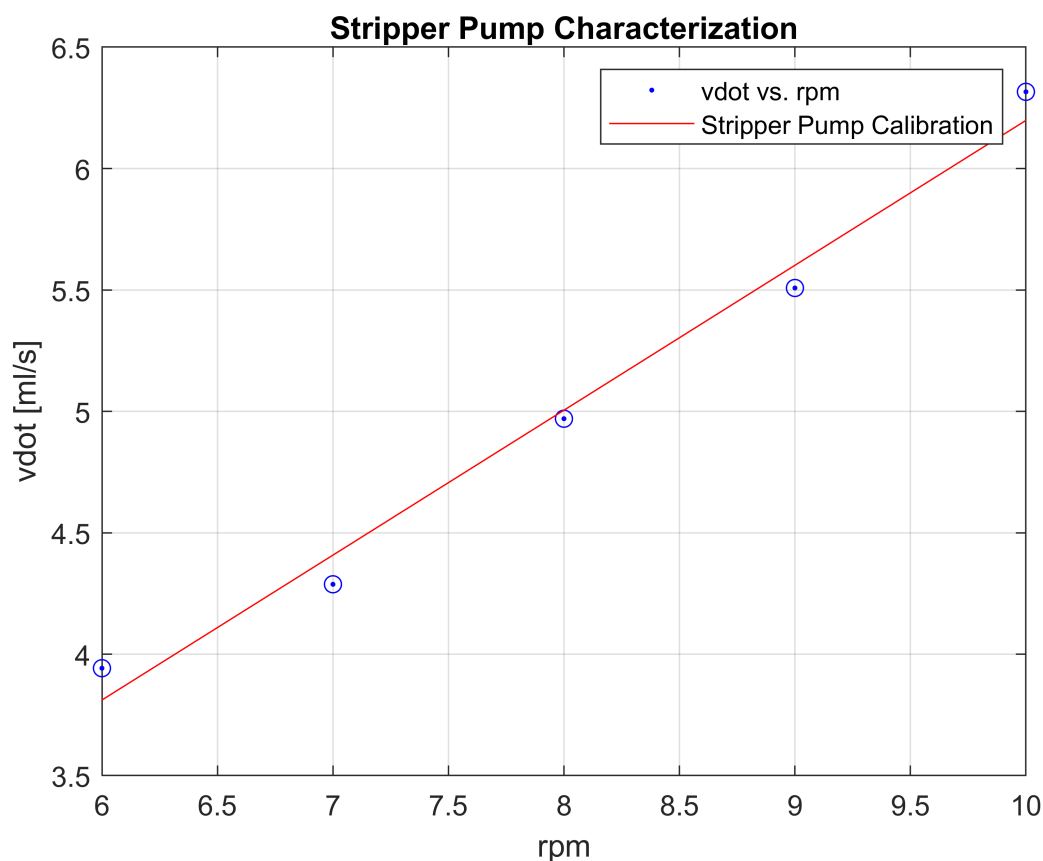


Figure B.6: stripper pump characterization

B.2.2. Start-up

How much time it takes for desorption to start occurring (i.e. the start-up time of the stripper) and how much energy this part of the process consumes was determined as well. The start-up process is considered to be accomplished when the temperature on the top stage of the stripper becomes stable. Figure B.7 shows that about 20 minutes are required for the temperature at the top stage of the stripper to reach a constant value, and that overall about 3200kJ (on average 3200W during the 20 minutes of start-up) are required in the start-up process.

B.2.3. Ratio Sensor

In the 10X DAC a temperature sensor was placed at the most high point of the regeneration section, just before the bend that takes the top products to the total condenser. The sensor placement assumes that the temperature registered is the VLE temperature of the gas that will end up in the flash tank, and so it might be used to determine the composition of the product dynamically.

As can be seen in figure B.8, the temperature of the ratio sensor responds to absolute humidity changes; which have been linked to the water loading in the sorbent in chapter 5. When the absolute humidity lowers, the temperature of the ratio sensor decreases indicating less water is present in the top product. If the temperature registered by this sensor is calibrated correctly, a dynamic reading of the product ratio could be given.

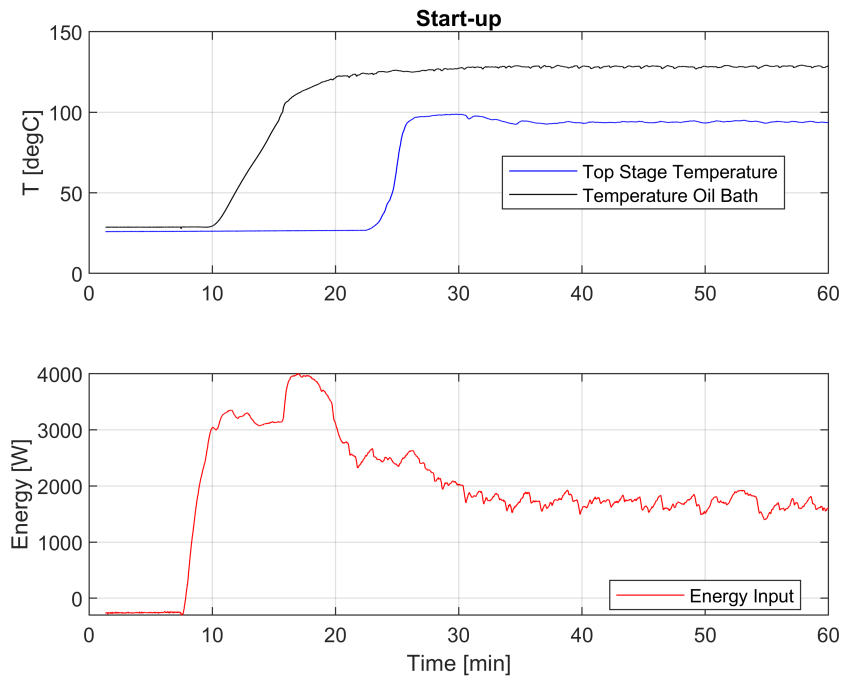


Figure B.7: Start-up time and energy demand

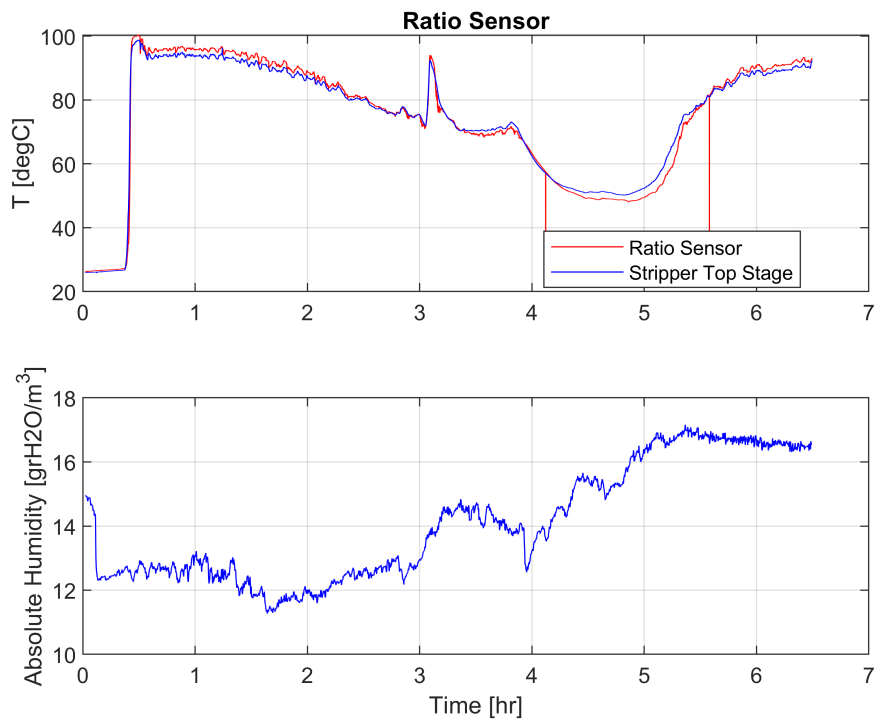


Figure B.8: Ratio Sensor readings

(**Note:** between hour 3.8 and 5 the stripper flow rate was increased to a value which the heat input was not enough for desorption to take place, so please ignore this in terms of the ratio sensor discussion.)

B.3. Full system Characteristics

The combined characteristics of the absorption and regeneration sections allow to determine the performance and efficiency of the overall process. Besides the results showed in chapter 5 other details of the overall system characteristics were also obtained. Principally, it was important to understand which part of the process had the highest energy demand.

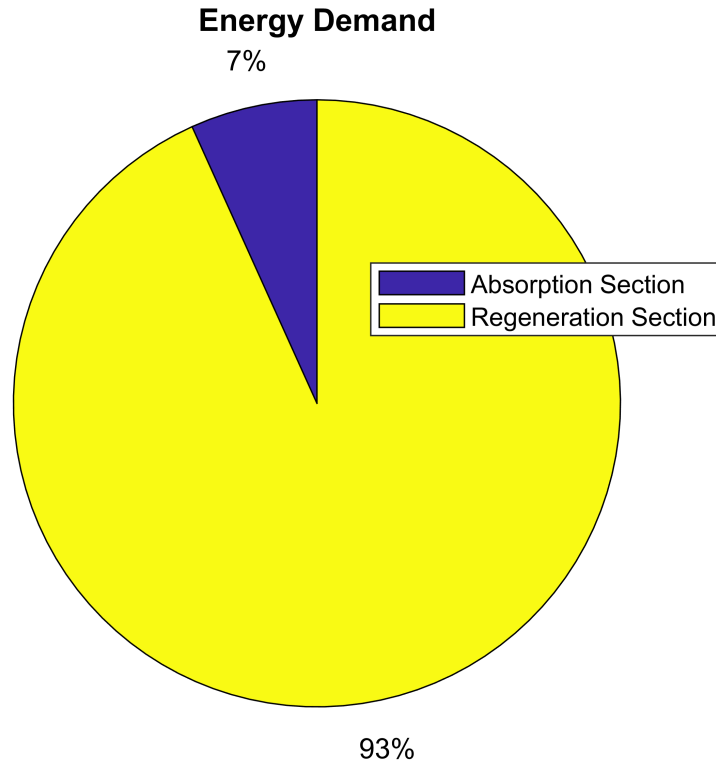
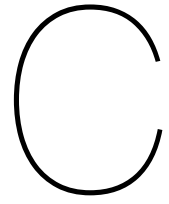


Figure B.9: Absorption vs Regeneration energy demand

As can be seen in figure B.9, the regeneration section takes practically all the energy demand of the entire process, which aligns with literature sources [10]. In ZEF's process the low energy demand of the absorption section is thanks to the low pressure drop in the column (figure B.3) which translates into low energy demand for air distribution.

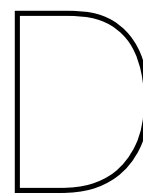
B.3.1. Air distribution in column

Note: section removed to appendix F due to intellectual property concerns



Building Process

Note: appendix moved to appendix F due to intellectual property concerns.



Modelling complimentary Info

Note: Appendix moved to appendix F due to intellectual property concerns

Literature complimentary information

Complimentary literature research findings are given in this appendix for several aspects of the DAC characteristics and the work performed by ZEF in the past.

E.1. Degradation characteristics

The degradation of the sorbent has a great impact in the lifetime, performance, and efficiency of the DAC as previously explained. Although all amines are affected by both thermal and oxidative degradation, not all of them are as sensible as others. In their study, Leupamier et al [29][30] studied the oxidative and thermal degradation effects on different amines. In the case of oxidative degradation, it was found that tertiary amines are slightly more stable than primary and secondary amines, while cyclic structures did not offer a better chemical resistance when compared to linear molecules. In the case of thermal degradation, secondary amines were found to be the least stable.

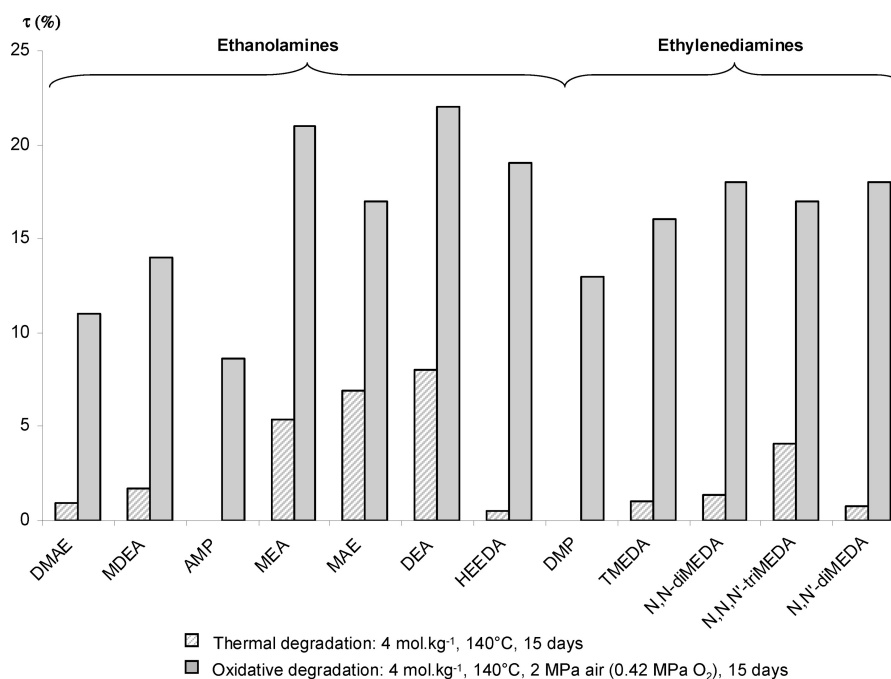


Figure E.1: Oxidative Degradation rates of the different amines with temperature and air. [30]

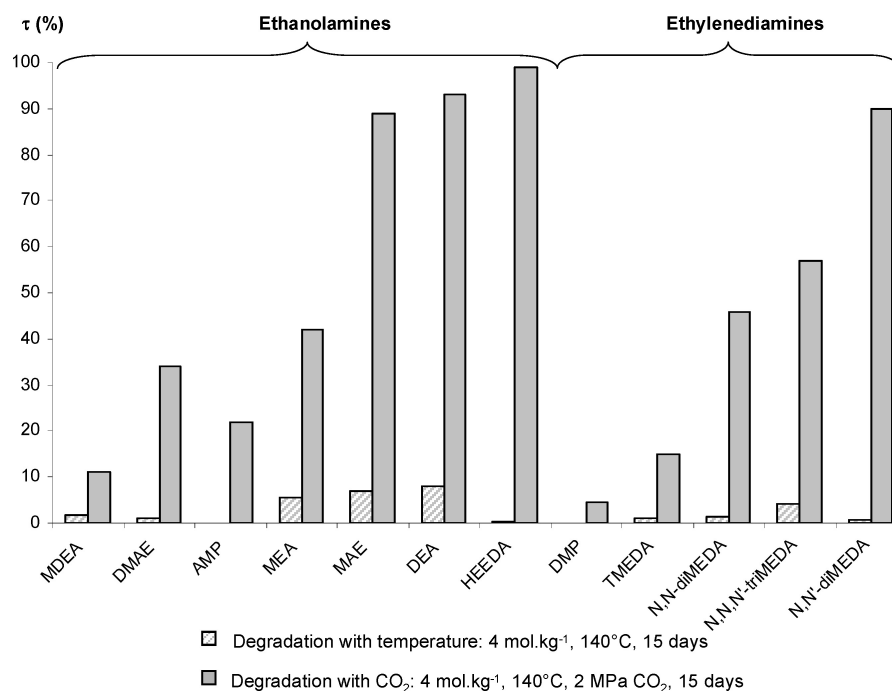


Figure E.2: Thermal Degradation rates of the different amines with temperature and air. [29]

Choosing a sorbent that is less sensible to both types of degradation not only increases the lifetime expectations of the process, but also keeps its performance and efficiency at peak values for longer time.

The presence of water has also an effect in the lifetime of the sorbent. Sayari et al [51] concluded that water presence has a positive effect in the thermal degradation (urea formation) by comparing the CO₂ uptake of different sorbents cycled in dry and humid environments (see figure E.3). In the case of oxidative degradation, there is no agreement regarding the effect of the presence of water regarding this degradation mechanism.

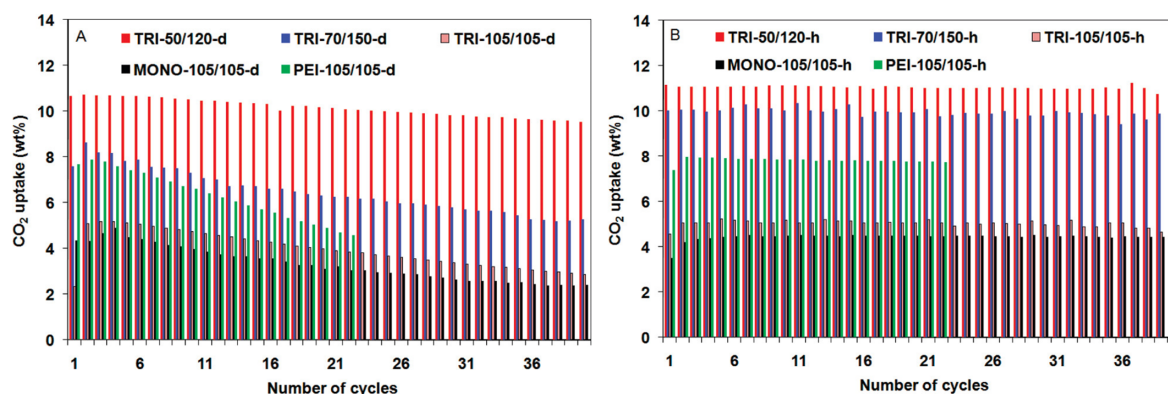


Figure E.3: CO₂ adsorption-desorption cycles over different adsorbents, (A) under dry conditions, (B) in the presence of moisture (20 °C as dew point) [51]

In terms of lifetime, the ambient temperature has a limited role in the degradation of the sorbent. As shown in section 2.3.3, degradation effects are triggered at very high temperatures (above 50°C).

Lepori et al [31] studied the effect of temperature in the vapor pressure of different organic compounds. The study found that at high temperatures the vapor pressure increases, and thus the evaporation rate. Also, it was found that for larger amine molecules ($n = 7$ vs $n = 2$ for example), the vapor pressure is lower; indicating better resistance to evaporation losses.

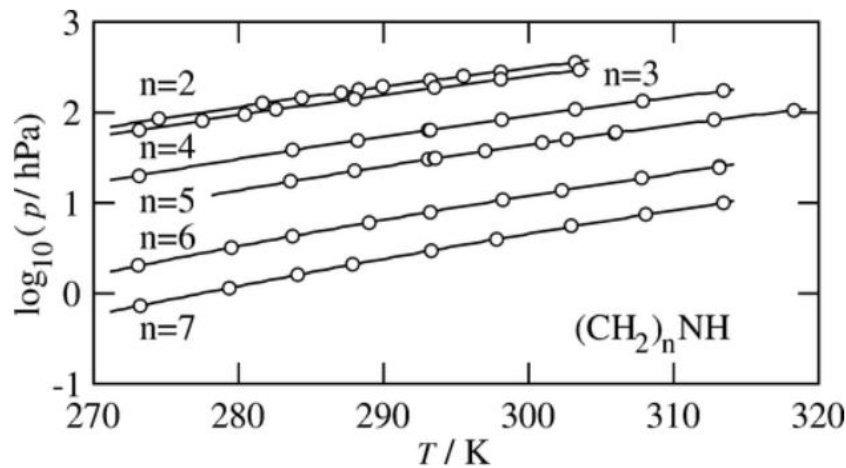


Figure E.4: Vapor Pressure vs Temperature [31]

E.2. Purity

The Purity performance indicator provides information on how pure the obtained CO_2 from DAC process is, and it is measured in percentages. During absorption, the system deals with ambient air, which contains many elements besides CO_2 . In amine-based systems, the main elements that get absorbed are: water and, of course, CO_2 . As explained before, a complete DAC system not only captures CO_2 , but also includes a regeneration process in which the captured CO_2 is released; the purity of this stream is of interest.

If the DAC process is used in carbon capture and storage technologies, then the CO_2 released in the stripper would be permanently sequestered. This requires two steps: CO_2 transport, and the permanent storage through, for example, saline aquifers. In the case of transportation, Wetenhall et al [72] studied the effect of impurities in the required pipe diameter and inlet pressure. At higher impurities percentages, bigger pipes are required, and higher inlet pressures are experienced. In the sequestration step, high purities are required to guarantee high storage efficiencies [17] [75].

In the case the DAC process is used in carbon capture and utilisation, as is the case of ZEF, the CO_2 stream would become raw material for different processes. As explained before, ZEF uses CO_2 , and hydrogen, to make methanol. So it is of great interest to have as high a purity as possible to avoid any complications in ZEF's processes. Furthermore, certain impurities, like evaporated sorbent, could negatively impact current fuel producing process, limiting the use of existing infrastructure and hence decreasing the attractiveness of DAC for carbon capture and utilisation.

E.3. DAC at ZEF

Note: moved to appendix F due to intellectual property concerns



Intellectual Property Sensitive

Note: this appendix has not been made publicly available due to intellectual property concerns.

References

- [1] (1937) *Introduction to Infrared Spectroscopy* - YouTube. URL: https://www.youtube.com/watch?v=0S_bt3JI150.
- [2] Abdurahim Abdulkadir et al. "Heat of Absorption and Specific Heat of Carbon Dioxide in Aqueous Solutions of Monoethanolamine,3-piperidinemethanol and Their Blends". In: *Energy Procedia* 63 (2014), pp. 2070–2081. ISSN: 18766102. DOI: 10.1016/j.egypro.2014.11.223. URL: <https://linkinghub.elsevier.com/retrieve/pii/S1876610214020384>.
- [3] Rattanaporn Apaiyakul et al. "Density, viscosity, physical CO₂ diffusivity, and CO₂ absorption capacity of novel blended N-methyl-4-piperidinol and piperazine solvent". In: *Energy Reports* 7 (Nov. 2021), pp. 844–853. ISSN: 23524847. DOI: 10.1016/j.egy.2021.07.056. URL: <https://linkinghub.elsevier.com/retrieve/pii/S2352484721005217>.
- [4] Ugochukwu E. Aronu et al. "Solvent selection for carbon dioxide absorption". In: *Energy Procedia* 1.1 (Feb. 2009), pp. 1051–1057. ISSN: 18766102. DOI: 10.1016/j.egypro.2009.01.139. URL: <https://linkinghub.elsevier.com/retrieve/pii/S1876610209001404>.
- [5] Habib Azarabadi and Klaus S. Lackner. "A sorbent-focused techno-economic analysis of direct air capture". In: *Applied Energy* 250 (Sept. 2019), pp. 959–975. ISSN: 03062619. DOI: 10.1016/j.apenergy.2019.04.012. URL: <https://linkinghub.elsevier.com/retrieve/pii/S0306261919306385>.
- [6] John Ray Sinnott Baldwin et al. *Chemical Engineering Design. Principles, practice and economics of plant and process design*. 2008, pp. 297–384, 986, 361. ISBN: 9780750684231.
- [7] Haley Barbour et al. *The Commercial Case for Direct Air Capture*. Tech. rep.
- [8] Francesco Barzagli et al. "Screening Study of Different Amine-Based Solutions as Sorbents for Direct CO₂ Capture from Air". In: *ACS Sustainable Chemistry & Engineering* 8.37 (Sept. 2020), pp. 14013–14021. ISSN: 2168-0485. DOI: 10.1021/acssuschemeng.0c03800. URL: <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c03800>.
- [9] Ida M. Bernhardsen and Hanna K. Knuutila. "A review of potential amine solvents for CO₂ absorption process: Absorption capacity, cyclic capacity and pK_a". In: *International Journal of Greenhouse Gas Control* 61 (June 2017), pp. 27–48. ISSN: 17505836. DOI: 10.1016/j.ijggc.2017.03.021. URL: <https://linkinghub.elsevier.com/retrieve/pii/S1750583616304911>.
- [10] Wim Brilman. "CO₂ removal from air". In: *Advances in Carbon Capture*. Elsevier, 2020, pp. 523–543. DOI: 10.1016/B978-0-12-819657-1.00023-2. URL: <https://linkinghub.elsevier.com/retrieve/pii/B9780128196571000232>.
- [11] Grevil Colaco. *Design and development of Desorption and Absorption system at Zero Emission fuels*. Tech. rep. 2019.
- [12] *COP26 THE GLASGOW CLIMATE PACT*. Tech. rep.
- [13] J. Tim Cullinane and Gary T. Rochelle. "Kinetics of Carbon Dioxide Absorption into Aqueous Potassium Carbonate and Piperazine". In: *Industrial & Engineering Chemistry Research* 45.8 (Apr. 2006), pp. 2531–2545. ISSN: 0888-5885. DOI: 10.1021/ie050230s. URL: <https://pubs.acs.org/doi/10.1021/ie050230s>.
- [14] Rebecca Anne Dowling. *An experimental and computational study of CO₂ absorption in aqueous solutions of tetraethylenepentamine*. Tech. rep. URL: [http://repository.tudelft.nl/..](http://repository.tudelft.nl/)
- [15] Nabil El Hadri et al. "Aqueous amine solution characterization for post-combustion CO₂ capture process". In: *Applied Energy* 185 (Jan. 2017), pp. 1433–1449. ISSN: 03062619. DOI: 10.1016/j.apenergy.2016.03.043. URL: <https://linkinghub.elsevier.com/retrieve/pii/S0306261916303609>.

- [16] Burak Eral, Andree de Haan, and Boelo Schuur. *Industrial Separation Processes - Fundamentals*. Second. De Gruyter.
- [17] María Erans et al. "Direct air capture: process technology, techno-economic and socio-political challenges". In: *Energy & Environmental Science* (2022). ISSN: 1754-5692. DOI: 10.1039/D1EE03523A. URL: <http://xlink.rsc.org/?DOI=D1EE03523A>.
- [18] *Fight climate change by removing CO₂ from the air*. URL: <https://climeworks.com/purpose>.
- [19] Kaiyun Fu et al. "Analysis of Mass Transfer Performance of Monoethanolamine-Based CO₂ Absorption in a Packed Column Using Artificial Neural Networks". In: *Industrial & Engineering Chemistry Research* 53.11 (Mar. 2014), pp. 4413–4423. ISSN: 0888-5885. DOI: 10.1021/ie403259g. URL: <https://pubs.acs.org/doi/10.1021/ie403259g>.
- [20] Kaiyun Fu et al. "Experimental study on mass transfer and prediction using artificial neural network for CO₂ absorption into aqueous DETA". In: *Chemical Engineering Science* 100 (Aug. 2013), pp. 195–202. ISSN: 00092509. DOI: 10.1016/j.ces.2013.04.024. URL: <https://linkinghub.elsevier.com/retrieve/pii/S0009250913002832>.
- [21] Global Monitoring Laboratory. "Carbon Cycle Greenhouse Gases". In: (). URL: <https://gml.noaa.gov/ccgg/trends/>.
- [22] Arya Kumar Gowda. *Study of amine degradation in direct air capture*. Tech. rep. URL: <http://repository.tudelft.nl/>.
- [23] Frank Incropera et al. *Fundamentals of heat and mass transfer*. Ed. by Frank Incropera. 7th. Wiley, 2011. ISBN: 0470646152, 9780470646151.
- [24] Øystein Jonassen, Inna Kim, and Hallvard F. Svendsen. "Heat of Absorption of Carbon Dioxide (CO₂) into Aqueous N-Methyldiethanolamine (MDEA) and N,N-Dimethylmonoethanolamine (DMMEA)". In: *Energy Procedia* 63 (2014), pp. 1890–1902. ISSN: 18766102. DOI: 10.1016/j.egypro.2014.11.198. URL: <https://linkinghub.elsevier.com/retrieve/pii/S187661021402013X>.
- [25] Christopher W. Jones. "CO₂ Capture from Dilute Gases as a Component of Modern Global Carbon Management". In: *Annual Review of Chemical and Biomolecular Engineering* 2.1 (July 2011), pp. 31–52. ISSN: 1947-5438. DOI: 10.1146/annurev-chembioeng-061010-114252. URL: <https://www.annualreviews.org/doi/10.1146/annurev-chembioeng-061010-114252>.
- [26] Fanhe Kong et al. "Research needs targeting direct air capture of carbon dioxide: Material & process performance characteristics under realistic environmental conditions". In: *Korean Journal of Chemical Engineering* 39.1 (Jan. 2022), pp. 1–19. ISSN: 0256-1115. DOI: 10.1007/s11814-021-0976-0. URL: <https://link.springer.com/10.1007/s11814-021-0976-0>.
- [27] I.P. Koronaki, L. Prentza, and V. Papaefthimiou. "Modeling of CO₂ capture via chemical absorption processes – An extensive literature review". In: *Renewable and Sustainable Energy Reviews* 50 (Oct. 2015), pp. 547–566. ISSN: 13640321. DOI: 10.1016/j.rser.2015.04.124. URL: <https://linkinghub.elsevier.com/retrieve/pii/S1364032115003949>.
- [28] Grégoire Léonard, Dominique Toye, and Georges Heyen. "Experimental study and kinetic model of monoethanolamine oxidative and thermal degradation for post-combustion CO₂ capture". In: *International Journal of Greenhouse Gas Control* 30 (Nov. 2014), pp. 171–178. ISSN: 17505836. DOI: 10.1016/j.ijggc.2014.09.014. URL: <https://linkinghub.elsevier.com/retrieve/pii/S1750583614002758>.
- [29] Helene Lepaumier, Dominique Picq, and Pierre-Louis Carrette. "New Amines for CO₂ Capture. I. Mechanisms of Amine Degradation in the Presence of CO₂". In: *Industrial & Engineering Chemistry Research* 48.20 (Oct. 2009), pp. 9061–9067. ISSN: 0888-5885. DOI: 10.1021/ie900472x. URL: <https://pubs.acs.org/doi/10.1021/ie900472x>.
- [30] Helene Lepaumier, Dominique Picq, and Pierre-Louis Carrette. "New Amines for CO₂ Capture. II. Oxidative Degradation Mechanisms". In: *Industrial & Engineering Chemistry Research* 48.20 (Oct. 2009), pp. 9068–9075. ISSN: 0888-5885. DOI: 10.1021/ie9004749. URL: <https://pubs.acs.org/doi/10.1021/ie9004749>.

- [31] Luciano Lepori, Enrico Matteoli, and Paolo Gianni. "Vapor Pressure and Its Temperature Dependence of 28 Organic Compounds: Cyclic Amines, Cyclic Ethers, and Cyclic and Open Chain Secondary Alcohols". In: *Journal of Chemical & Engineering Data* 62.1 (Jan. 2017), pp. 194–203. ISSN: 0021-9568. DOI: 10.1021/acs.jced.6b00576. URL: <https://pubs.acs.org/doi/10.1021/acs.jced.6b00576>.
- [32] Jinzhao Liu et al. "Kinetics and mass transfer of carbon dioxide absorption into aqueous ammonia". In: *Energy Procedia*. Vol. 4. Elsevier Ltd, 2011, pp. 525–532. DOI: 10.1016/j.egypro.2011.01.084.
- [33] Valérie Masson-Delmotte et al. *Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change Edited by*. 2021. ISBN: 9789291691586. URL: www.ipcc.ch.
- [34] Noah McQueen et al. "A review of direct air capture (DAC): scaling up commercial technologies and innovating for the future". In: *Progress in Energy* 3.3 (July 2021), p. 032001. ISSN: 2516-1083. DOI: 10.1088/2516-1083/abf1ce. URL: <https://iopscience.iop.org/article/10.1088/2516-1083/abf1ce>.
- [35] Duane D. Miller and Steven S.C. Chuang. "Control of CO₂ Adsorption and Desorption Using Polyethylene Glycol in a Tetraethylenepentamine Thin Film: An In Situ ATR and Theoretical Study". In: *The Journal of Physical Chemistry C* 120.44 (Nov. 2016), pp. 25489–25504. ISSN: 1932-7447. DOI: 10.1021/acs.jpcc.6b09506. URL: <https://pubs.acs.org/doi/10.1021/acs.jpcc.6b09506>.
- [36] Badie I. Morsi and Omar M. Basha. "Mass Transfer in Multiphase Systems". In: *Mass Transfer - Advancement in Process Modelling*. InTech, Oct. 2015. DOI: 10.5772/60516.
- [37] Pailin Muchan et al. "Effect of number of amine groups in aqueous polyamine solution on carbon dioxide (CO₂) capture activities". In: *Separation and Purification Technology* 184 (2017), pp. 128–134. ISSN: 18733794. DOI: 10.1016/j.seppur.2017.04.031. URL: <http://dx.doi.org/10.1016/j.seppur.2017.04.031>.
- [38] Gijs Mulder. *Characterization, Optimization and Design of the Sorbent System for a Continuous Direct Air Capture System*. Tech. rep. 2020. URL: <http://repository.tudelft.nl/>.
- [39] Rathish Nagulagama. *Characterization of a Direct Air Capture System and Scaling it up*. Tech. rep. 2021.
- [40] Rathish Nagulagama. *Characterization of a Direct Air Capture System and Scaling it up*. Tech. rep. 2021.
- [41] NASA. "Data.GISS_ GISS Surface Temperature Analysis (v4)_ Analysis Graphs and Plots". In: (). URL: https://data.giss.nasa.gov/gistemp/graphs_v4/.
- [42] NOAA. "Carbon Dioxide Vital Signs – Climate Change Vital Signs of the Planet". In: (). URL: <https://climate.nasa.gov/vital-signs/carbon-dioxide/>.
- [43] Jochen Oexmann and Alfons Kather. "Minimising the regeneration heat duty of post-combustion CO₂ capture by wet chemical absorption: The misguided focus on low heat of absorption solvents". In: *International Journal of Greenhouse Gas Control* 4.1 (Jan. 2010), pp. 36–43. ISSN: 17505836. DOI: 10.1016/j.ijggc.2009.09.010. URL: <https://linkinghub.elsevier.com/retrieve/pii/S175058360900098X>.
- [44] B Ova. *Direct Air Capture: An experimental approach on the desorption of CO₂ and H₂O from PEI and TEPA*. Tech. rep. URL: <http://repository.tudelft.nl/>.
- [45] Mihrimah Ozkan et al. "Current status and pillars of direct air capture technologies". In: *iScience* 25.4 (Apr. 2022), p. 103990. ISSN: 25890042. DOI: 10.1016/j.isci.2022.103990. URL: <https://linkinghub.elsevier.com/retrieve/pii/S2589004222002607>.
- [46] Vincenzo Palma et al. "State of the Art of Conventional Reactors for Methanol Production". In: *Methanol*. Elsevier, Jan. 2018, pp. 29–51. DOI: 10.1016/B978-0-444-63903-5.00002-9. URL: <https://linkinghub.elsevier.com/retrieve/pii/B9780444639035000029>.

- [47] G. Puxty and M. Maeder. "The fundamentals of post-combustion capture". In: *Absorption-Based Post-combustion Capture of Carbon Dioxide*. Elsevier, June 2016, pp. 13–33. DOI: 10.1016/B978-0-08-100514-9.00002-0. URL: <https://linkinghub.elsevier.com/retrieve/pii/B9780081005149000020>.
- [48] Stephen A Rackley. *Carbon Capture and Storage*. 2nd. Joe Hayton. ISBN: 978-0-12-812041-5.
- [49] Padmini Rangamani and Ravi Iyengar. "Modelling spatio-temporal interactions within the cell". In: *Journal of Biosciences*. Vol. 32. 1. Jan. 2007, pp. 157–167. DOI: 10.1007/s12038-007-0014-3.
- [50] M J Sanz Del Val. *Internship report Characterization and optimization of a Direct Air Capture (DAC) process*. Tech. rep. 2021.
- [51] Abdelhamid Sayari and Youssef Belmabkhout. "Stabilization of Amine-Containing CO₂ Adsorbents: Dramatic Effect of Water Vapor". In: *Journal of the American Chemical Society* 132.18 (May 2010), pp. 6312–6314. ISSN: 0002-7863. DOI: 10.1021/ja1013773. URL: <https://pubs.acs.org/doi/10.1021/ja1013773>.
- [52] J. D. Seader and Ernest Henley. *Separation Process Principles*. Second.
- [53] Teerawat Sema et al. "Absorption kinetics of CO₂ in novel formulated 2-amino-2-methyl-1-propanol and N-methyl-4-piperidinol solvent". In: *Energy Reports* 6 (Nov. 2020), pp. 143–150. ISSN: 23524847. DOI: 10.1016/j.egy.2020.08.039. URL: <https://linkinghub.elsevier.com/retrieve/pii/S2352484720312944>.
- [54] Nuria Serrano Barthe. *Nuria Serrano Barthe Absorption of CO₂ from the air using polyamines: experiments, modelling and design*. Tech. rep. URL: <http://repository.tudelft.nl/>.
- [55] Nuria Serrano Barthe. *Nuria Serrano Barthe Absorption of CO₂ from the air using polyamines: experiments, modelling and design*. Tech. rep. URL: <http://repository.tudelft.nl/>.
- [56] Mrigank Sinha. *Direct Air Capture Characterization and design of a novel absorption process*. Tech. rep. URL: <http://repository.tudelft.nl/>.
- [57] Mrigank Sinha. *Experimental study of absorption and desorption in a continuous direct air capture system to build a concept model*. Tech. rep. Delft, Netherlands: Delft University of Technology, 2019.
- [58] Mrigank Sinha. *Internship Report Experimental study of absorption and desorption in a continuous direct air capture system to build a concept model*. Tech. rep.
- [59] Hallvard F. Svendsen, Erik T. Hessen, and Thor Mejdell. "Carbon dioxide capture by absorption, challenges and possibilities". In: *Chemical Engineering Journal* 171.3 (July 2011), pp. 718–724. ISSN: 13858947. DOI: 10.1016/j.cej.2011.01.014. URL: <https://linkinghub.elsevier.com/retrieve/pii/S1385894711000416>.
- [60] L.S. Tan et al. "Factors affecting CO₂ absorption efficiency in packed column: A review". In: *Journal of Industrial and Engineering Chemistry* 18.6 (Nov. 2012), pp. 1874–1883. ISSN: 1226086X. DOI: 10.1016/j.jiec.2012.05.013. URL: <https://linkinghub.elsevier.com/retrieve/pii/S1226086X12001712>.
- [61] Simon Thain. *IR Spectroscopy and FTIR Spectroscopy: How an FTIR Spectrometer Works and FTIR Analysis | Technology Networks*. URL: <https://www.technologynetworks.com/analysis/articles/ir-spectroscopy-and-ftir-spectroscopy-how-an-ftir-spectrometer-works-and-ftir-analysis-363938#D1>.
- [62] The Editors of Encyclopedia Britannica. *Industrial Revolution*. July 2021. URL: <https://www.britannica.com/event/Industrial-Revolution>.
- [63] THE ROYAL SOCIETY OF CHEMISTRY. *Modern Chemical Techniques*. Tech. rep.
- [64] *The Story Behind Carbon Engineering | Carbon Engineering*. URL: <https://carbonengineering.com/our-story/>.
- [65] Unfccc. *ADOPTION OF THE PARIS AGREEMENT - Paris Agreement text English*. Tech. rep.
- [66] United Nations Environment Programme. *Emissions Gap Report 2020*. ISBN: 9789280738124.

- [67] P. D. Vaidya and E. Y. Kenig. "CO₂-Alkanolamine Reaction Kinetics: A Review of Recent Studies". In: *Chemical Engineering & Technology* 30.11 (Nov. 2007), pp. 1467–1474. ISSN: 09307516. DOI: 10.1002/ceat.200700268. URL: <https://onlinelibrary.wiley.com/doi/10.1002/ceat.200700268>.
- [68] Nelson Van De Poll. *Characterization and Design of a Stripper for a Continuous Direct Air Capture System*. Tech. rep. 2020. URL: <http://repository.tudelft.nl/>.
- [69] Ved Dhubashi. *Dynamic Analysis and Characterization of a Desorption column for a Continuous Air Capture process*. Tech. rep. URL: <http://repository.tudelft.nl/>.
- [70] Fernando Vega et al. "Degradation of amine-based solvents in CO₂ capture process by chemical absorption". In: *Greenhouse Gases: Science and Technology* 4.6 (Dec. 2014), pp. 707–733. ISSN: 21523878. DOI: 10.1002/ghg.1446. URL: <https://onlinelibrary.wiley.com/doi/10.1002/ghg.1446>.
- [71] Kunal Vidyarthi. *Dynamic Operation of an Integrated Direct Air Capture and CO₂ Compression System*. Tech. rep. URL: <http://repository.tudelft.nl/>.
- [72] B. Wetenhall, J.M. Race, and M.J. Downie. "The Effect of CO₂ Purity on the Development of Pipeline Networks for Carbon Capture and Storage Schemes". In: *International Journal of Greenhouse Gas Control* 30 (Nov. 2014), pp. 197–211. ISSN: 17505836. DOI: 10.1016/j.ijggc.2014.09.016. URL: <https://linkinghub.elsevier.com/retrieve/pii/S1750583614002771>.
- [73] Jennifer Wilcox. *Carbon Capture*. New York, NY: Springer New York, Jan. 2012, pp. 1–323. ISBN: 978-1-4614-2214-3. DOI: 10.1007/978-1-4614-2215-0. URL: <http://link.springer.com/10.1007/978-1-4614-2215-0>.
- [74] Bin Xu et al. "Mass transfer performance of CO₂ absorption into aqueous DEEA in packed columns". In: *International Journal of Greenhouse Gas Control* 51 (Aug. 2016), pp. 11–17. ISSN: 17505836. DOI: 10.1016/j.ijggc.2016.05.004. URL: <https://linkinghub.elsevier.com/retrieve/pii/S1750583616302195>.
- [75] Fang Yang et al. "Characteristics of CO₂ sequestration in saline aquifers". In: *Petroleum Science* 7.1 (Mar. 2010), pp. 83–92. ISSN: 1672-5107. DOI: 10.1007/s12182-010-0010-3. URL: <http://link.springer.com/10.1007/s12182-010-0010-3>.
- [76] Jiru Ying, Annie Rose Knutsen, and Dag A. Eimer. "Mass Transfer Kinetics of CO₂ in Loaded Aqueous MEA Solutions". In: *Energy Procedia*. Vol. 114. Elsevier Ltd, 2017, pp. 2088–2095. DOI: 10.1016/j.egypro.2017.03.1343.
- [77] Cheng-Hsiu Yu, Chih-Hung Huang, and Chung-Sung Tan. "A Review of CO₂ Capture by Absorption and Adsorption". In: *Aerosol and Air Quality Research* 12.5 (Oct. 2012), pp. 745–769. ISSN: 16808584. DOI: 10.4209/aaqr.2012.05.0132. URL: <https://aaqr.org/articles/aaqr-12-05-ir-0132>.
- [78] Jie Yu, Yuxin Zhai, and Steven S. C. Chuang. "Water Enhancement in CO₂ Capture by Amines: An Insight into CO₂–H₂O Interactions on Amine Films and Sorbents". In: *Industrial & Engineering Chemistry Research* 57.11 (Mar. 2018), pp. 4052–4062. ISSN: 0888-5885. DOI: 10.1021/acs.iecr.7b05114. URL: <https://pubs.acs.org/doi/10.1021/acs.iecr.7b05114>.
- [79] Qian Yu. *Direct Capture of CO₂ from Ambient Air using Solid Sorbents*. Tech. rep. DOI: <https://doi.org/10.3990/1.9789036546300>.