Atmospheric Carbon Capture: A Review on Current Technologies and Analysis of Energy Consumption for Various Direct Air Capture (DAC) Systems

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ATMOSPHERIC CARBON CAPTURE: A REVIEW ON CURRENT TECHNOLOGIES AND ANALYSIS OF ENERGY CONSUMPTION FOR VARIOUS DIRECT AIR CAPTURE (DAC) SYSTEMS

by

Jennifer Barri Perskin

A Thesis Submitted to the College of Engineering Department of Mechanical Engineering in Partial Fulfillment of the Requirements for the Degree of Master of Science in Mechanical Engineering

Embry-Riddle Aeronautical University
Daytona Beach, Florida
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ATMOSPHERIC CARBON CAPTURE: A REVIEW ON CURRENT TECHNOLOGIES AND ANALYSIS OF ENERGY CONSUMPTION FOR VARIOUS DIRECT AIR CAPTURE (DAC) SYSTEMS

by

Jennifer Barri Perskin

This thesis was prepared under the direction of the candidate’s Thesis Committee Chair, Dr. Sandra Boetcher, Research Fellow and Professor of Mechanical Engineering, Daytona Beach Campus, and Thesis Committee Members Dr. Rafael Rodriguez, Associate Chair and Associate Professor of Mechanical Engineering, Daytona Beach Campus, and Claus Daniel, Ph.D., Carrier, and has been approved by the Thesis Committee. It was submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering.

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I would like to express my deepest gratitude to my advisors and committee members throughout my research and collegiate career. Dr. Boetcher, thank you for being my thesis advisor and for your invaluable patience and guidance throughout this process. Dr. Rodriguez, thank you for sparking my interest in the HVAC field, and for your vast wisdom and wealth of experience that has inspired me throughout my studies. Claus, thank you for your technical expertise, passionate participation, and input to this research. Thanks should also be given to the DAC research group led by Dr. Von Hippel for their continued support and contribution.

I am also grateful to my lab mates, classmates, and fellow graduate students for making my time at Embry-Riddle Aeronautical University like no other. Special shout-outs to Nick and Yang. Friends like you come once in a life-time and I’m excited to see you both do great things in life.

Lastly, I would like to thank my parents, Jo Ann and Jeffrey, my brother, Daniel, and my partner, Charles, for always believing in me and supporting me. And thank you to my cats, Rumi and Katsuji, for all the joy and comfort over the years.

Thank you all, this accomplishment would not have been possible without you.
Carbon dioxide (CO₂) capture is a crucial approach to reducing greenhouse gases in the atmosphere to directly combat climate change. Major components of the technology to desublimate CO₂ at cryogenic temperatures are mature and have the potential to be applied to build large Arctic/Antarctic direct-air CO₂ capture plants. Pressure swing adsorption another gas separation technique used in industry today that can be modified for atmospheric carbon capture. The discussion of energy consumption for cryogenic and combined direct air capture systems is explored in this study. The investigation of precompression of atmospheric air for a direct-air capture CO₂ system using an attached “waste- cool” precooler is examined. In this novel approach, a thermodynamic model based on psychrometric theories is evaluated to determine the required work input of the system at various inlet compression ratios and various inlet temperatures. Turbine recovery is also considered for the potential to capture “waste energy.” A pressure swing adsorption unit is evaluated as another modification to the cryogenic system to minimize energy consumption.
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Significance of the Study

All living things are made of carbon, as carbon is an essential building block of all organic matter. Carbon is continuously cycling through our entire ecosystem [Dey et al., 2022], as seen through the Carbon Cycle in Figure 1.1. The Carbon Cycle elucidates the fluctuations of carbon throughout the atmosphere, ocean, and lithosphere between carbon sources and carbon sinks. A source is described as an activity or process that emits carbon dioxide (CO$_2$) into the atmosphere. Sources can be anthropogenic, such as power plants [Nassar et al., 2017], or natural, such as volcanoes [Plank and Manning, 2019]. Carbon sinks absorb and store CO$_2$. Carbon sinks can also be anthropogenic, such as afforrestation [Humpenöder et al., 2014], or natural, such as the ocean [Quéré et al., 2016].

Figure 1.1: A visual representation of the Carbon Cycle, referenced from [NOAA, 2019]
In the Pre-Industrial Era (1750 and earlier), carbon sources and carbon sinks counteracted one another and stabilized the CO₂ concentration to approximately 280 ppm [Stein, 2022]. However, in the past two centuries, human activities have increased emissions at a rate quicker than carbon sinks can handle. Activities like agriculture, industry, waste disposal, deforestation, and fossil fuel consumption produce copious amounts of greenhouse gases (GHG) into the atmosphere [Wuebbles and Jain, 2001]. GHGs are gases in the Earth’s atmosphere with the ability to trap solar infrared radiation and re-emit back to Earth, raising the planet’s temperature through a greenhouse effect. Some greenhouse gases (GHGs) include carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), flourinated gases, and water vapor (H₂O). GHGs are crucial for life on Earth, as scientists say the planet’s average temperature would be approximately 33°C colder than without the naturally occurring greenhouse effect [NAP, 1992]. However, anthropogenic GHG emissions, not natural, are the area concern. Anthropogenic activities are estimated to have caused 1°C of global warming since the Pre-Industrial Era [IPCC, 2018].

CO₂ has gained the most traction in terms of climate change above the other GHGs for numerous reasons. Out of all the GHGs, CO₂ is the most abundant, by a significant amount. In 2020, CO₂ was the largest contributor of the total GHG emissions in the US for that year, almost 80% (Figure 1.2). In comparison to other GHGs, it is difficult to quantify the lifetime of CO₂ in the atmosphere due to the varying timescale of the CO₂ processes in the Carbon Cycle. However, the Intergovernmental Panel on Climate Change (IPCC), an intergovernmental body under the United Nations created to assess science related to climate change and provide policymakers at all levels of government with knowledge, recommendations, and potential risks associated with climate change, estimates 15-40% of CO₂ emissions until 2100 will remain in the atmosphere for more than 1000 years. [IPCC, 2014b]. CO₂ has the highest positive radiative forcing (RF) [IPCC, 2014a] of all GHGs. RF is a measure of how much a climate driver contributes to climate change. RF is the energy difference per area of a driver entering and leaving the atmosphere. A positive
RF indicates a "warming effect" such that the energy entering the atmosphere is more than the energy leaving the atmosphere. As seen in Figure 1.3, CO$_2$ has the highest positive RF, and the rate of increase in total RF of GHGs is surpassed by CO$_2$. CO$_2$ emissions from anthropogenic activities is the largest driver of climate change [Forster et al., 2007].

Figure 1.2: GHG emissions in 2020 from the US. CO$_2$ emissions are the largest contributor of total GHGs. [EPA, 2022]

Figure 1.3: Radiative forcing of GHGs over time. CO$_2$ contributes the most to the total radiative forcing of all GHGs, and has steadily increased since the 1950’s.
The conference of parties (COP) is an international global climate summit held annually by the UN to evaluate the current status of and reach an international agreement to combat climate change. COP21 in 2015, or better known as the Paris Climate Conference that produced the Paris Agreement, was the first time ever an international agreement was globally accepted to recognize and combat climate change. The Paris Agreement is intended to limit global warming to below 2°C, preferably under 1.5°C [UN, 2015]. United Nations (UN) Secretary General Antonio Guterres expressed his concern and urgency for action against climate change at the conclusion of COP27 in November 2022, “Climate chaos is a crisis of biblical proportions. The signs are everywhere. Instead of a burning bush, we face a burning planet.” [UN, 2022]

Efforts have been and are currently underway to decrease CO\textsubscript{2} emissions, a process called decarbonization. Decarbonization can happen in many sectors: transportation, energy generation and consumption, the built environment, agriculture, and land use. In the energy generation sector, switching to low-carbon energy generation methods will lower CO\textsubscript{2} emissions. Countries around the world are implementing renewable energy grids. Iceland, Norway, Costa Rica, Brazil, and Canada generate more than 60 percent of their energy through hydropower [Kroposki et al., 2017]. Solar photovoltaic (PV) energy generation increased 22% from 2020 to 2021 worldwide, with the US generating almost 150,000 GWh of energy through solar in 2021 [IEA, 2022c], [IEA, 2023]. In the transportation sector, switching to electric vehicles (EVs) over conventional internal combustion engine vehicles decreases GHG emissions [EPA, 2023]. Around the world, the EV market share has steadily increased from 2013, as seen in Figure 1.1 [Sanguesa et al., 2021]. In the built environment, new policies are enforced to lower the global warming potential of refrigerants in HVAC systems [Voigt, 2021] and increase energy efficiency in newly constructed buildings [Commission, 2022]. In agriculture and land use, promoting sustainable farming practices such as regenerative agriculture to improve soil health can improve the Carbon Cycle to draw CO\textsubscript{2} from the atmosphere [Rhodes, 2017].
Table 1.1: EV Market share as a percentage of total vehicle sales in that country per year from 2013-2020. Most countries have seen an increase in EV sales over time. Data adapted from [Sanguesa et al., 2021].

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<td>6.10</td>
<td>13.84</td>
<td>22.29</td>
<td>27.40</td>
<td>29.00</td>
<td>39.20</td>
<td>49.10</td>
<td>55.90</td>
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<tr>
<td>Iceland</td>
<td>0.94</td>
<td>2.71</td>
<td>3.98</td>
<td>6.28</td>
<td>8.70</td>
<td>19.00</td>
<td>22.60</td>
<td>45.00</td>
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<td>2.52</td>
<td>3.20</td>
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<td>11.40</td>
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<tr>
<td>The Netherlands</td>
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<td>6.70</td>
<td>2.60</td>
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<td>0.23</td>
<td>0.84</td>
<td>1.31</td>
<td>2.10</td>
<td>4.20</td>
<td>4.90</td>
<td>5.40</td>
</tr>
<tr>
<td>Canada</td>
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<td>0.28</td>
<td>0.35</td>
<td>0.58</td>
<td>0.92</td>
<td>2.16</td>
<td>3.00</td>
<td>3.30</td>
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<tr>
<td>France</td>
<td>0.83</td>
<td>0.70</td>
<td>1.19</td>
<td>1.45</td>
<td>1.98</td>
<td>2.11</td>
<td>2.80</td>
<td>11.20</td>
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<tr>
<td>Denmark</td>
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<td>2.29</td>
<td>0.63</td>
<td>0.40</td>
<td>2.00</td>
<td>4.20</td>
<td>16.40</td>
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<td>0.66</td>
<td>0.90</td>
<td>1.16</td>
<td>1.93</td>
<td>2.00</td>
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<td>0.59</td>
<td>1.07</td>
<td>1.25</td>
<td>1.40</td>
<td>1.90</td>
<td>22.60</td>
<td>45.00</td>
</tr>
<tr>
<td>Japan</td>
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<td>0.68</td>
<td>0.59</td>
<td>1.10</td>
<td>1.00</td>
<td>0.90</td>
<td>0.77</td>
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Nonetheless, we are not decarbonizing fast enough. Although renewable energy generation reached record highs, in order to meet a Net Zero Emissions target by the IEA, renewable energy generation must be near 23,000 TWh by 2030, while renewable energy was near 8,000 TWh in 2021. As seen in Figure 1.5, the rate of growth for renewable energy production is not increasing fast enough to meet emission targets. On a global scale, CO$_2$ emissions from fossil fuels and industry are not decreasing. In fact, annual CO$_2$ emissions increased over 50% from 2010 to 2021 (see Figure 1.4) [Ritchie et al., 2020]. In order to meet the goal of limiting Earth’s temperature increase to 1.5°C (the Paris Agreement threshold), global anthropogenic CO$_2$ emissions must decline from 45 percent of 2010 levels by 2030 [IPCC, 2018].
Figure 1.4: The annual CO$_2$ emissions from fossil fuel and industry over time, and global CO$_2$ concentration in the atmosphere. Emissions and overall concentration have steadily increased since the 1950’s.

Figure 1.5: Renewable energy generation by technology from 2010 to 2021 and evaluated for 2030 sustainability goals. Data adapted from [IEA, 2022b]
To make the situation more egregious, there are some sectors where decarbonization is difficult. A 2014 study discussed the feasibility of decarbonizing industries where decreasing CO$_2$ emissions will be a challenge [Davis et al., 2018]. These industries include transportation (aviation, shipping, long-distance road), material production (iron, steel, cement), and load-following electricity. In 2021, these "hard-to-eliminate' CO$_2$ emissions accounted for almost 30 percent of the share of global GHG emissions [Ritchie et al., 2020]. In the a special IPCC report, it is stated "The deployment of carbon dioxide removal (CDR) to counterbalance hard-to-abate residual emissions is unavoidable if net zero CO$_2$ or GHG emissions are to be achieved.” [IPCC, 2022]

Decarbonization will not solely solve climate change. A multi-prong approach utilizing different practices such as carbon removal technologies, decarbonization, and carbon emissions reductions must be used in conjunction to slow down and eventually reverse global warming. Carbon removal technologies, also known as carbon dioxide removal (CDR) or negative emission technologies (NET), cover a wide variety of approaches to decrease CO$_2$ emissions from the atmosphere. Some of these approaches include carbon capture with utilization and storage (CCUS), afforestation, or bioenergy with carbon capture and sequestration [Press, 2019].

CCUS is the process that captures CO$_2$ emissions from sources such as coal-fired power plants or ambient air environments, and reuses or stores it so it will not enter the atmosphere. CCUS encompasses 4 technologies: pre-combustion, oxy-combustion, post-combustion, and direct air capture. Figure 1.6 and Table 1.2 reflect the mechanisms and operating conditions for each technology [Lai et al., 2021].
Figure 1.6: Four subcategories of DAC systems, pre-combustion, oxy-combustion, post-combustion, and direct air capture.

Table 1.2: The operating pressure, temperature, and CO\textsubscript{2} concentration for different CCUS technology.

<table>
<thead>
<tr>
<th>CCUS Technology</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
<th>CO\textsubscript{2} Concentration (%)</th>
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<tr>
<td>Pre-combustion</td>
<td>14-70</td>
<td>200-450</td>
<td>15-60</td>
</tr>
<tr>
<td>Oxy-combustion</td>
<td>1</td>
<td>-55</td>
<td>17-70</td>
</tr>
<tr>
<td>Post-combustion</td>
<td>1</td>
<td>40-60</td>
<td>3-20</td>
</tr>
<tr>
<td>Direct Air Capture</td>
<td>1</td>
<td>25</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Pre-combustion carbon capture removes CO\textsubscript{2} from the fossil fuel before combustion occurs. This method uses a controlled gasification process to produce synthesis gas (or syngas) to be used for power generation. This approach is advantageous because the CO\textsubscript{2} concentration is relatively high, between 15\% – 60\% [Sanz-Perez et al., 2016]. Due to the high concentrations of CO\textsubscript{2} in the gas stream, pre-combustion carbon capture can be more efficient than other CCUS, however there are high capital costs are associated with gasification process meaning other technologies are more cost-effective [DoE, 2022]. R&D is directed towards improving the gasification stage, advanced turbine systems for increased efficiency, and sorbent material to lower costs.

Oxy-combustion carbon capture is the process of combustion using an oxygen-rich inlet gas stream, yielding exhaust gas comprised of mainly of CO\textsubscript{2} and H\textsubscript{2}O. The concentration
of CO₂ in the exhaust gas stream is very high, up to 70%, and the CO₂ can be captured by condensing the water in the exhaust stream. Oxy-combustion requires large amounts of oxygen in the system compared to the other CCUS technology, increasing overall costs. Oxy-combustion is advantageous because of the limited NOx emissions due to the removal of nitrogen in a preliminary step, high CO₂ concentrations in the exhaust stream, and the applicability to existing power plants [DoE, 2022].

Post-combustion carbon capture separates CO₂ from flue gas streams. The concentration of CO₂ in exhaust gas is between 3% – 20%. Due to low concentration of CO₂ and low operating pressure of the exhaust stream, this method requires larger volumes of air to be processed, overall increasing energy requirements and costs. As most anthropogenic CO₂ emissions come from stationary sources with combustion systems, such as coal or gas power plants, post-combustion capture is advantageous because it can be retrofitted to existing power plants to capture carbon at the source [Metz et al., 2005]. Amine scrubbing is a well-established and currently deployed post-combustion CC technology, utilizing amine-based solutions to absorb CO₂ from exhaust gas [Rochelle, 2009].

Direct Air Capture (DAC) carbon capture is the process of removing CO₂ from ambient air conditions. Compared to the other CCUS technology, a major disadvantage of DAC is the low CO₂ concentration in ambient air conditions, approximately 0.04%. However, DAC is advantageous because it does not require to be placed in a specific location (i.e., point source carbon capture). Pre-combustion, oxy-combustion, and post-combustion CO₂ capture requires system placement near a powerplant or CO₂ source. Costs associated with transporting the captured carbon to storage facilities can be avoided.

While some of the NETs are commissioned today, the scale at which these technologies are deployed will not make a crucial impact to mitigate climate change [Sovacool et al., 2022]. In contrast to other CDRs, DAC has the potential to be scaled up to remove large amounts of CO₂ [Press, 2019]. Additionally, other NETs face significant barriers for upscaling, such
as land use, economic and social viability.

**Statement of the Problem**

There are 18 pilot DAC plants operating around the world capturing 0.01MtCO$_2$ per year, however DAC must be scaled up to 60 MtCO$_2$ per year by 2030 to meet target goals [IEA, 2022a]. DAC technology is still in its infancy and requires more research and development into evaluating the performance of large scale plants in order to meet targets for mitigating climate change [Sovacool et al., 2022]. Recommended research includes system modeling for large scale carbon capture to determine energy consumption [Press, 2019].

**Purpose Statement**

The purpose of this thesis is to model the energy consumption of novel DAC systems for large-scale use. These systems utilize a combination of DAC techniques to minimize energy consumption. The systems to be evaluated are shown in Figure 1.7. This thesis will answer the following questions

1. What are the mechanisms for direct air systems?
2. What is the energy consumption analysis for DAC?
3. How can DAC processes combine to increase the efficiency of carbon capture?
Figure 1.7: Proposed DAC systems evaluated in the present study to determine energy consumption.
Figure 1.7: Proposed DAC systems evaluated in the present study to determine energy consumption (cont.)

Scope of Study

The scope of this research is atmospheric cryogenic CO₂ capture. Modifications are made to the cryogenic system to improve energy performance of the system. In Chapter 2, background is given on DAC, cryogenic systems, PSA systems, and sorbent material atmospheric carbon capture. Chapter 3 is the energy analysis of the systems in Figure 1.7. Chapter 4 discusses the results from the system model calculations from Chapter 3. Chapter 5 will conclude the research and summarize the major findings.

Limitations

Assumptions are made to simplify the system model. A major assumption is assuming the fluid stream behaves as an ideal gas. A gas behaves as an ideal gas when the compressibility factor $Z$ is equal to 1. This occurs when the state pressure is small relative to the critical pressure and/or the state temperature is large relative to the critical temperature.

The mass flow rate of air entering and leaving the system is constant. Fluid properties
are considered constant at each state. Precompression of low temperature atmospheric air is assumed to be isothermal. The turbine is assumed to be adiabatic and isentropic. The heat exchanger is also assumed adiabatic. For PSA, there is no heat transfer between the gas molecules and the sorbent material. The rate of adsorption and desorption is in equilibrium. No axial mass or thermal dispersion is considered in this study.

**Variables**

- $c_v$: specific heat at constant volume
- $d_p$: diameter of sorbent particle
- $H$: total enthalpy
- $H_{air}$: total enthalpy of air
- $H_{CO_2}$: total enthalpy of CO$_2$
- $h_{CO_2,desub}$: specific enthalpy of desublimated saturated CO$_2$
- $h_{ig}$: specific latent heat of sublimation
- $h_x$: specific enthalpy at state x
- $K$: equilibrium constant $k_a/k_d$
- $k_a$: adsorption rate constant
- $k_d$: desorption rate constant
- $m_{air}$: mass of air
- $m_{air,x}$: mass flow rate of air at state x
- $m_{CO_2}$: mass of CO$_2$
- $m_{CO_2,desub}$: mass flow rate of desublimated CO$_2$
- $m_{CO_2,x}$: mass flow rate of CO$_2$ at state x
- $n$: compression ratio
- $P*_x$: compression pressure
- $P_{ads}$: adsorption pressure
- $P_i$: partial pressure of the adsorbate component i
\( P_{\text{total}} \) adsorption pressure plus pressure drop across the chamber

\( P_{\text{vap},x} \) vapor pressure at \( T_x \)

\( P_x \) pressure at state \( x \)

\( q_i \) amount of adsorbed component \( i \) per unit mass of adsorbent

\( q_{\text{max},i} \) maximum amount of adsorbate component \( i \) the adsorbent can hold

\( \dot{Q}_r \) heat transfer rate required to desublimate \( \omega \)

\( R \) universal gas constant

\( s_x \) specific entropy at state \( x \)

\( T_{\text{ads}} \) adsorption temperature

\( T_C \) temperature of the cold environment

\( T_{\text{desub}} \) desublimation temperature

\( T_H \) temperature of the hot environment

\( T_x \) temperature at state \( x \)

\( u \) specific internal energy

\( u_s \) superficial fluid velocity \( x \)

\( v_{\text{ads}} \) specific volume at adsorption step

\( W_c \) work of the compressor

\( W_{\text{in}} \) total net work to run DAC system

\( W_{\text{PSA}} \) work of the compressor

\( W_r \) work of the cryocooler

\( W_t \) energy recovery from the turbine

\( y_i \) mole fraction of component \( i \)

\( Z \) compressibility factor

**Greek Letters**

\( \beta \) coefficient of performance (COP) for a reverse-Brayton cryocooler
\[ \beta_{\text{Carnot}} \] carnort COP
\[ \gamma \] specific heat ratio \( c_p/c_v \)
\[ \varepsilon \] void fraction of the PSA chamber
\[ \varepsilon_{\text{HX}} \] heat exchanger effectiveness
\[ \zeta_{\text{ads}} \] rate of adsorption
\[ \zeta_{\text{des}} \] rate of desorption
\[ \eta \] second law efficiency
\[ \theta \] fraction of the sorbent surface covered in sorbate
\[ \theta_v \] fraction of the sorbent surface vacant and available for adsorption
\[ \phi \] sphericity of the sorbent particles
\[ \omega \] mass fraction of desublimated \( \text{CO}_2 \)

**Definition of Terms**

- **adsorption**: adhesion of molecules to a surface
- **cryogenic distillation**: gas separation technique via the difference of component boiling points in a gas mixture
- **adsorbate**: molecules of species that adhere to surface
- **adsorbent**: surface in which molecules adhere to
- **fouling**: accumulation of solid in the heat exchanger due to low temperatures

**List of Acronyms**

- **CC**: carbon capture
- **CO\textsubscript{2}**: carbon dioxide
- **DAC**: direct air capture
- **GHG**: greenhouse gas
$\text{H}_2\text{O}$ water/water vapor
HVAC heating, ventilation, and air-conditioning
HFC hydrofluorocarbons
IPCC intergovernmental panel of climate change
IEA international energy agency
CH$_4$ methane
N$_2$O nitrous oxide
NC no compression
PPM parts per million
PFC perfluorocarbons
PC precompression
PSA pressure swing adsorption
RF radiative forcing
TR turbine recovery
Chapter II

Literature Review

Anthropogenic atmospheric CO₂ plays the largest role among greenhouse gasses in modifying Earth’s climate [Strassmann et al., 2008], and several research groups are working on CO₂ removal from energy production and industrial-process flue gas as well as directly from the air. The major capture processes include adsorption, absorption, membrane separation, and cryogenic capture [Aaron and Tsouris, 2005], [Choi et al., 2011].

DAC has been used for other purposes besides climate change mitigation such as spacecraft life support [Sherif and Knox, 2005] or on submarines. DAC was first introduced to the scientific community as a CO₂ mitigation strategy in 1999 by Lackner [Lackner et al., 1999]. Lackner evaluated the thermodynamic feasibility of collecting CO₂ using Ca(OH)₂ (calcium hydroxide) in a liquid solvent system. Lackner argued that although the CO₂ concentration in ambient air conditions is low, it is not too low for DAC to be unachievable.

The first step of DAC is to intake large quantities of air to be put in contact with an agent or environment that will remove the CO₂ from the gas stream. The CO₂ is sequestered and concentrated from the air. The agent is then recycled through a state-altering process that regenerates the material for continued use. If the air it to be in contact with an environment for carbon capture, the environment is held to a state where CO₂ removal occurs. The final step of DAC is the transportation of CO₂ to a long-term storage site [Sovacool et al., 2022]. The scope of this research does not include the transportation step in DAC. The following sections will review materials used to capture carbon, and will provide an in-depth overview on cryogenic distillation and pressure swing adsorption for DAC.

Sorbent Material for DAC

This section will discuss sorbent material used for DAC systems. Commonly used
CO$_2$ adsorbents can be classified into the following groups: aqueous (liquid) solvents, solid sorbents, membranes, and resins as seen in Figure 2.1.

![Sorbent Type Diagram]

**Figure 2.1:** Overview on sorbent materials used in carbon capture.

In liquid DAC systems, gas molecules concentrate in the solvent medium through a mechanism called absorption. In contrast for solid DAC systems, the gas molecules concentrate to the surface of the sorbent through a process called adsorption. Figure 2.2 visually represents the difference between absorption and adsorption for carbon capture.
Aqueous solvents use a strong basic hydroxide solution to capture CO$_2$. The CO$_2$ molecules react with ions in the solution to produce a carbonate precipitate. The solvent has a high CO$_2$ capacity and uptake, however the precipitate by-product requires high temperatures to later release the CO$_2$. Liquid amines are also commonly used for post-combustion capture, also known as amine scrubbing. Liquid amines have high CO$_2$ adsorption capacity, but they are corrosive to system equipment and can have harmful effects on the local environment [Leonzio et al., 2022].

Solid sorbents encompass a wide variety of materials. Firstly, they can be characterized through the bond strength to the CO$_2$ molecule, also called the heat of adsorption [McQueen et al., 2021]. Physical adsorption through weak intramolecular forces, or physisorption, occurs when the heat of adsorption is less than 15 kcal/mol = 63 kJ/mol. Chemical adsorption through strong covalent bonds, or chemisorption, occurs when the heat of adsorption is greater than 15 kcal/mol = 63 kJ/mol. Solid sorbents are comprised of various precursors and can be modified for desired characterizes. Sorbents can be carbon-
based, non-carbon based, or amine-functionalized. Solid sorbents are porous materials and are also organized based on the pore size [Abd et al., 2020]. The International Union of Pure and Applied Chemistry classifies pore size as

1. Micropores: \( \leq 2 \) nm
2. Mesopores: 2-50 nm
3. Macropores: \( \geq 50 \) nm

Resins are another category of sorbent material that have recently been researched and developed for direct air carbon capture [Wang et al., 2020]. Ion exchange resins utilize the moisture swing adsorption mechanism, or a humidity swing, to capture and release CO\(_2\). Resins can be modification with amine functional groups to affect surface properties and capture performance. Resins have a lower energy adsorption and desorption requirement compared to liquid or solid sorbents; however, it is not as technologically mature.

**Desired Sorbent Characteristics.**

There are many properties of sorbents that must be evaluated to determine applicability for DAC. The sorbent material should meet certain criteria for both economical and operational requirements. When examining sorbent criteria, ideal sorbents should have high CO\(_2\) adsorption rate and capacity, high selectivity, easy regeneration with cyclic performance, cost-effective operation, high availability, and stability (chemically, thermally, structurally). The adsorption capacity or loading is the amount of adsorbate taken up by the adsorbent per unit mass (or volume) of the adsorbent [Abd et al., 2020]. Selectivity of a sorbent is the ratio of CO\(_2\) capacity to another gas capacity [Abd et al., 2020]. Sorbents for carbon capture should have a high adsorption capacity and high selectivity for CO\(_2\).

Specific surface area is another key criteria for selecting a sorbent material. The specific surface area is the surface area (SA) per unit mass. A material that is more porous has an
increased specific surface area. Figure 2.3 demonstrates that a more porous material has a higher specific SA. In Figure 2.3, there is a uniform cube with length of each side of 10 m. The SA of the cube is equal to the area of a side a cube multiplied by 6 sides (600 m²). The specific SA is equal to the total SA divided by the mass of the cube, so the specific SA is 6 m²/g. In the bottom of Figure 2.3, the same cube is now divided in half in each direction to expose a new surface. The lengths of the side of each cube are 5 m and now there are 8 cubes. The specific SA of this new configuration is 12 m²/g. A material having a greater pore structure and distribution will also have a larger specific SA. Modifications to increase a sorbent material specific SA will increase its performance for carbon capture.

Figure 2.3: Specific SA is a crucial characteristic of sorbent material for CO₂ capture. In the figure, it is shown that a more porous material will have a higher specific SA.

Well Performing Sorbents for DAC.

As mentioned previously, physical adsorption interactions between CO₂ molecules and the sorbent surface are governed through weak intramolecular forces. These forces are
highly dependent on the surface area of the sorbent material [Oschatz and Antonietti, 2018]. Thus, materials with larger surface areas are desirable for DAC. Solid sorbent materials that are currently employed or being researched for DAC carbon capture are activated carbon (AC), metal organic frameworks (MOFs), zeolites, silica gels, and carbon nanotubes [Ozkan and and, 2022], [Liu et al., 2021]. Carbon-based materials have good structural stability and resistance to moisture, but surface inertness make them ineffective in low CO₂ concentration [Hao et al., 2011]. Zeolite-based materials have high selectivity for CO₂ in dilute gas streams but are prone the water degradation. Silica-based materials require surface modification to be used for carbon capture [Lai et al., 2021]. Metal organic frameworks (MOFs) also have a high affinity for CO₂ in dilute concentrations, but are sensitive to water as well. [Gargiulo et al., 2020], [Hu et al., 2018].

[Kumar et al., 2015] evaluated how water vapor affects the performance of 5 sorbent materials for DAC: one chemisorbent TEPA-SBA15 (mesoporous silica) and four physisorbents Zeolite 13X (zeolite), HKUST-1 (MOFs), Mg-MOF-74/Mg-dobdc (MOFs), SIFSIX-3-Ni (hybrid material). Temperature-programmed desorption (TPD) experiments were ran on the sorbents. TPD is used to indicate the water vapor affinity and required regeneration energy of the sorbent material. The results from the TPD experiments show that chemisorbent TEPA-SBA-15 performed better than the physisorbents in terms of water affinity. Zeolite 13X performed the worst of the physisorbents. Stability tests were also performed on the sorbents at 40°C and 75% humidity to represent their shelf life over 1, 7, and 14 days. Zeolite 13X performed the best of the physisorbents in the stability tests. Although zeolites exhibit a high affinity for H₂O [Shi et al., 2022], this is not an issue in ultra low temperature environments where humidity levels are negligible. This is discussed further in Chapter 3.
[Madden et al., 2017] extended the experiments of [Kumar et al., 2015] to 10 other physisorbents: 4 hybrid ultramicroporous materials (HUMs) SIFSIX-3-Cu, SIFSIX-2-Cu-i, DICRO-3-Ni-i and MOOFOUR-1-Ni, 5 prototype MOFs ZIF-8, DMOF-1, UiO-66, UiO-66-NH2 and MIL-101, and 1 ultra microporous metal-organic material (MOM) Ni-4-PyC. These sorbents were tested similarly as in the previous study to determine simulated DAC performance and the affect of water vapor on performance. SIFSIX-3-Cu performed the best in DAC environments, however it also performed the worst in stability tests. The study found that physisorbents have a lower regeneration energy than chemisorbents, which may offset the poor performance in some categories.
[Bao et al., 2022] evaluated the performance of Zeolite 13X for CO₂ enrichment to achieve an increased target concentration at the exit stream. An enrichment factor, defined as the ratio of exit CO₂ concentration to inlet CO₂ concentration peaked at 9, indicating an increase from 400ppm to 3600ppm. The enrichment factor is also called concentration factor in literature [Wilcox et al., 2017]. Additionally, cyclic tests determined good cyclic stability of Zeolite 13X after 20 cycles. Overall, Zeolite 13X is a promising sorbent for DAC.

Cryogenic Arctic/Antartic DAC

Cryogenic DAC capitalizes on CO₂ possessing the highest phase-transition temperature of the atmospheric gases (see Table 2.1), except for water vapor (which is easy to eliminate via desiccant wheel or cooling, either due to low ambient temperatures or by conventional refrigeration).

Table 2.1: Atmospheric gases and their respective freezing temperature gases from [NOAA, 2023] https://www.noaa.gov/jetstream/atmosphere

<table>
<thead>
<tr>
<th>Gas</th>
<th>Freezing Temperature (K)</th>
<th>Concentration in Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen N₂</td>
<td>63</td>
<td>78.084%</td>
</tr>
<tr>
<td>Oxygen O₂</td>
<td>54.36</td>
<td>20.947%</td>
</tr>
<tr>
<td>Argon Ar</td>
<td>73.85</td>
<td>0.934%</td>
</tr>
<tr>
<td>Carbon dioxide CO₂</td>
<td>194.65</td>
<td>0.035%</td>
</tr>
<tr>
<td>Neon Ne</td>
<td>27.102</td>
<td>18.182 parts per million</td>
</tr>
<tr>
<td>Helium He</td>
<td>0.95</td>
<td>5.24 parts per million</td>
</tr>
<tr>
<td>Methane CH₄</td>
<td>91.15</td>
<td>1.70 parts per million</td>
</tr>
<tr>
<td>Krypton Kr</td>
<td>115.75</td>
<td>1.14 parts per million</td>
</tr>
<tr>
<td>Hydrogen H₂</td>
<td>13.95</td>
<td>0.53 parts per million</td>
</tr>
<tr>
<td>Nitrous oxide N₂O</td>
<td>182.29</td>
<td>0.31 parts per million</td>
</tr>
<tr>
<td>Carbon monoxide CO</td>
<td>68.15</td>
<td>0.10 parts per million</td>
</tr>
<tr>
<td>Xenon Xe</td>
<td>161.35</td>
<td>0.09 parts per million</td>
</tr>
<tr>
<td>Ozone O₃</td>
<td>80.95</td>
<td>0.07 parts per million</td>
</tr>
</tbody>
</table>

At first glance, this approach appears to be thermodynamically favorable because the entropy absorbed for CO₂ desublimation is the quotient of thermal power transferred from
the gas to the cryocooler divided by the temperature at which the heat lift occurs \(\dot{Q}/T\). Since \(\dot{Q}\) is fixed by the CO\(_2\) latent heat of sublimation, the magnitude of entropy lift is reduced by increasing the desublimation temperature, \(T\). Reduced cold-end entropy absorption induces corresponding reduction in cryocooler input power. Despite the apparent benefit and near-universal use of compression to that point, Yuan et al. [Yuan et al., 2014] challenged the need for compression. They found that for typical flue-gas CO\(_2\) concentrations, compression always consumes more power than the associated power reduction obtained by increasing the desublimation refrigeration temperature. Even with generous energy recovery by running the compressed gas through a turbine after CO\(_2\) extraction, compression still carries an energy penalty.

Yuan et al. [Yuan et al., 2014] found that the compression energy penalty decreases with decreasing CO\(_2\) partial pressure. However, they only examined flue gas and did not extend their study to direct-air cryogenic CO\(_2\) capture where the CO\(_2\) partial pressure is much lower than power plant effluent. Typically, for power plant flue gases, the concentration of CO\(_2\) is as high as 13-15% versus the amount of CO\(_2\) in the atmosphere, which is around 0.04% (or 400 ppm). Caustic gases, such as sulfur dioxide, are also found in flue gas and need to be handled during the CO\(_2\) desublimation process; whereas for direct-air capture (DAC) in cold climates, the need to remove other components, such as water vapor, is minimal. Furthermore, flue gas temperatures are on the order of 150°C versus below zero for DAC systems placed in arctic climates. Depending upon system design, volumetric flow rates may also be orders of magnitude less for flue gas than for DAC.

Many articles have explored flue-gas cryogenic CO\(_2\) separation using a variety of thermodynamic processes, all of which involve an initial compression step. Among reported flue-gas CO\(_2\) separation techniques where effluent is compressed, there are three main subsets: 1) Reverse-Brayton-like processes that recover some power while achieving low temperature by expanding CO\(_2\)-laden gas through a turbine [Baxter et al., 2009] [Burt et al., 2009].

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Zanganeh et al., 2009); 2) Joule-Thompson-like processes that achieve low temperature by throttling CO\textsubscript{2}-laden gas with no turbine power recovery [Li et al., 2016]; and 3) processes that do not treat CO\textsubscript{2}-laden gas as the principal working fluid and achieve low temperature by removing heat from the gas via an external cryocooler [Schach et al., 2011, Song et al., 2012, Xu et al., 2012, Swanson et al., 2012].

While several research groups mention the flue gas compression energy penalty to concentrate CO\textsubscript{2} prior to deposition, Yuan et al. [Yuan et al., 2014] were the first to formally investigate whether increased compression power to achieve decreased refrigeration power carried a net energy penalty. They found increasing flue gas pressure with no turbine energy recovery suffers energy penalties that increase with compression ratio. Surprisingly, even with generous turbine energy recovery, there remains an energy penalty for flue gas compression. In short, it always takes more power to compress than the associated power reduction obtained through desublimation refrigeration temperature for CO\textsubscript{2} concentrations in flue gas.

Cryogenic distillation is a promising approach to DAC because it 1) produces pure CO\textsubscript{2} in solid, liquid, or gas form that carries economic value and/or can be easily stored; 2) does not rely on development of new or experimental materials; and 3) is amenable to rapid scale-up to industrial production whereas the other techniques are not [Font-Palma et al., 2021].

Agee et al. [Agee et al., 2013] first described a DAC cryogenic CO\textsubscript{2} system scaled for global atmospheric CO\textsubscript{2} reduction with numerous stations sited across Antarctica. For average global atmospheric CO\textsubscript{2} partial pressure of 3.9 x 10\textsuperscript{-4} atm and average Antarctic ambient temperature of 226 K (-47.15 °C), the CO\textsubscript{2} desublimation temperature is 133 K (-140.15 °C). By placing the DAC system in Antarctica, the energy required to reduce the air temperature down to 133 K (-140.15 °C) from ambient, is significantly reduced compared to being in a location where the ambient air temperature averages around 25 °C). Another advantage of placing the DAC system in an arctic climate is that at very low temperatures,
water is largely absent from the atmospheric air. According to Fig. 2.6, which represents the maximum possible amount of moisture in the air at a particular temperature, the amount of water the air can contain exponentially decreases as the air temperature becomes colder.

A follow-on representative benchtop experiment used a liquid-nitrogen-cooled apparatus to reduce CO$_2$ content of entrapped air. CO$_2$ reduction from 443.71 ppm to 50.17 ppm (89% depletion) was demonstrated after 325 minutes by cooling to 129 K (-144.15 °C). CO$_2$ reduction from 485 ppm to 35.8 ppm (93% depletion) was achieved after 333 minutes by cooling to 125 K (-148.15 °C) [Agee and Orton, 2016]. Subsequent analysis by the present authors [von Hippel, 2018, ?] extended the research by quantifying energy requirements and scaling issues for such a system. The purpose of the current work is to examine compression of atmospheric air for cryogenic CO$_2$ capture to determine whether this unexplored low-CO$_2$ partial-pressure region of compression yields a net energy benefit.

![Figure 2.6: The absolute humidity of air at various temperatures. As temperature decreases, the humidity amount in the air tends towards zero. One can assume the humidity is negligible in ultra-low temperatures.](image-url)
Pressure Swing Adsorption DAC

DAC systems can function using a sorption-based approach for carbon capture. In the adsorption process, gas molecules of a component (the adsorbate) concentrate at the surface of a solid, (adsorbent/sorbent) due to intramolecular forces between the fluid and solid [Agarwal, 2010]. The adsorption processes are cyclic and “swing” between two steps, adsorption and desorption, and allows the adsorbent material to be regenerated for continued use. There are 2 main sorption techniques for CO\(_2\) capture: Pressure Swing Adsorption (PSA) and Temperature Swing Adsorption (TSA). PSA utilizes pressure differentials to capture CO\(_2\) and regenerate the sorbent. A compressor or pump is used to raise the pressure of the fluid to \(P_{\text{ads}}\). At high pressures, the fluid molecules have affinity to the adsorbent surface. The pressure of the fluid is decreased to \(P_{\text{des}}\) to regenerate the sorbent. Vacuum swing adsorption (VSA) is a modification of PSA technology used for carbon capture where \(P_{\text{des}}\) is less than \(P_{\text{atm}}\). TSA alternates the temperature of the sorbent to adsorb and desorb for CO\(_2\) capture and sorbent regeneration. Other less mature adsorption techniques are Moisture Swing Adsorption (MSA) and Electric Swing Adsorption (ESA). MSA uses the evaporation of water as the driving force for CO\(_2\) adsorption [Sun et al., 2021]. ESA is a variation of TSA where the heat is generated in situ passing an electric current through a conductor [Ribeiro et al., 2014]. Adsorption approaches may be combined, such as TVSA (Temperature Vacuum Swing Adsorption) or PVSA (Pressure Vacuum Swing Adsorption).

Pressure swing adsorption is an established technology used in many industrial applications. First patented by Charles W. Skarstrom in the 1960s [Skarstrom, 1958], PSA can be used for hydrogen purification, air separation, noble gas purification, CO\(_2\) capture, and other applications [Grande, 2012]. Adsorption is acclaimed for DAC due to its high efficiency in separating dilute mixtures [McQueen et al., 2021]. The Skarstrom Cycle involves a 2-bed, 4-step process demonstrated in Figure 2.8. PSA is a batch process, however by commissioning the adsorption/desorption step correctly, a continuous flow can be achieved.
The steps of the cycle are:

1. **Pressurization**: Valve is closed, air flows to increase P to $P_H$

2. **Feed**: Adsorption occurs at $P_H$

3. **Blowdown**: Valve is opened, P in chamber decreases to $P_L$

4. **Purge**: Desorption occurs at $P_L$. Air at $P_L$ flows through the chamber to flush out the adsorbate species

![Diagram showing the PSA cycle steps]

**Figure 2.7**: The PSA cycle steps.
Figure 2.8: An overview on 2-bed 4-step Skarstrom cycle. The columns are synchronized with an 180-phase shift in steps such that one column is adsorbing and the alternate column is desorbing at any given time.

[Shendalman and Mitchell, 1972] first modeled the Skastrom PSA cycle in 1972. They experimentally evaluated the separation process of He-CO$_2$ using silica gel as the sorbent material. In parallel, they derived an analytical solution for an ideal model assuming He as
an inert gas with no co-adsorption effects, equilibrium between the rate of adsorption and desorption at all times, and the adsorption model follows a linear isotherm. The pressurization and blowdown steps are assumed instantaneous. [Chan et al., 1981] extended the analysis of Shendalman and developed an equilibrium theory model for a feed mixture of 2 components, A and B, to determine cycle performance characteristics. They assumed linear isotherms, negligible dispersion axially or radially, and negligible pressure drop. The system model operates at steady state operation. The Chan model matches the Shendalman model when component B is assumed to be inert and no adsorption effects occur.

[Chue et al., 1995] compared the performance of activated carbon (AC) and Zeolite 13X on CO₂ capture from flue gas using PSA. First, they experimentally measured pure CO₂ and N₂ adsorption isotherms, and fitted the data using Langmuir Isotherms. Next, they measured the equilibrium selectivity (selectivity of CO₂ over N₂) for a binary mixture and fitted the data using the Extended Langmuir Isotherms. In both cases, Zeolite 13X was a better sorbent than AC. According to the mathematical model results, Zeolite 13X had a more favorable PSA performance over a wide range of cycle parameters than AC. Adsorption for bulk separation is better with Zeolite 13X than AC. Concurrently, Chue solved a mathematical model of a non-isothermal, adiabatic 3-bed, 7-step PSA process to compare cycle performance of the two materials to determine the better performing sorbent. In all cases, Zeolite 13X was superior.

Few models of adsorption processes for DAC systems on a holistic approach are found in literature. [Zhao et al., 2019] thermodynamically modeled a TVSA cycle to capture CO₂ from indoor environment at concentrations of 400 ppm, 700 ppm, 1000 ppm, 2000 ppm and 3000 ppm. Zhao et al approximated the work input for the vacuum as

\[
W_{pump} = \frac{1}{\eta_{pump}} RT_{des} \ln \left( \frac{P_{ads}}{P_{des}} \right) \tag{II.1}
\]
where $W_{pump}$ is the work of the pump, $\eta_{pump}$ is the efficiency of the pump, $T_{des}$ is the desorption temperature and $P_{ads}$ and $P_{des}$ are the adsorption and desorption pressures, respectively.

[Sabatino et al., 2021] developed an analysis of a VTSA process and determined the work of the pump as

$$W_{pump} = \frac{1}{\eta_{pump}} \dot{m} c_p T \left( \frac{P_{out}}{P_{in}} \gamma - 1 \right)$$  \hspace{1cm} (II.2)

where $\dot{m}$ is the mass flow rate of the air, $c_p$ is the specific heat at constant pressure, $p_{in}$ and $p_{out}$ are the pressure of the fluid stream entering and leaving the pump, respectively. $\gamma$ is defined as $\frac{c_p}{c_p - R}$.

[Liu et al., 2022] modeled the energy consumption of a VPSA cycle as

$$EC_{ads} = \frac{1}{\eta_c y_{CO_2}} RT_{ads} \ln \left( \frac{P_{ads}}{P_{atm}} \right)$$ \hspace{1cm} (II.3)

$$EC_{des} = \frac{1}{\eta_v} RT_{ads} \ln \left( \frac{P_{atm}}{P_{des}} \right)$$ \hspace{1cm} (II.4)

where $\eta_c$ and $\eta_v$ is the efficiency of the compressor and pump, respectively, set to 0.7; $y_{CO_2}$ is the concentration of CO$_2$ in the inlet stream.

[Wurzbacher et al., 2016] developed a transient mass and heat transfer model of the desorption step of VTSA process with an amine-based sorbent APDES-NFC-FD. The model is used to evaluate the recovered gas stream during desorption and the describe the purity level of CO$_2$ at this step, a kep performance indicator for large scale DAC. The study key findings for VTSA systems are: fast diffusion in the vacuum step indicate a uniform gas
phase composition in the sorbent material, and a reference point for geometric dimensions of a desorption chamber in a VTSA system.

Various literature pieces introduce the theory of minimum separation work, or the free energy of mixing, to determine the energy consumption of carbon capture systems. [Lackner et al., 1999] noted majority of the energy consumption for a DAC system comes from regenerating the sorbent. To regenerate the sorbent, energy must be added to the system to overcome the binding energy of CO$_2$ to the sorbent. The binding energy is equal to the free energy of mixing, $G$, is given as

$$\Delta G = RT \log \frac{P}{P_0} \quad \text{(II.5)}$$

where $P$ is the regeneration pressure and $P_0$ is ambient pressure. The free energy required to separate CO$_2$ from ambient air is 20 KJ/mol. The theoretical energy is independent of separation technique. However, inefficiencies in sequestration processes can quickly accumulate and inflate the system energy consumption. Other works agreed the theoretical minimum energy consumption of carbon capture system can be explained through free energy of mixing [House et al., 2009, Wilcox, 2012, Lackner, 2013, Zhao et al., 2017, Gür, 2022]. The process is visualized in Figure 2.9.

![Figure 2.9: Schematic of the gas separation unit, modified from Wilcox, 2012.](image)

A version of Equation II.5 is shown below in Equation II.6.
$W_{\text{min}} = RT[n^{CO_2}_B \ln(y^{CO_2}_B) + n^{B-CO_2}_B \ln(y^{B-CO_2}_B)]$

$+ RT[n^{CO_2}_C \ln(y^{CO_2}_C) + n^{C-CO_2}_C \ln(y^{C-CO_2}_C)]$

$- RT[n^{A-CO_2}_A \ln(y^{A-CO_2}_A) + n^{A-CO_2}_C \ln(y^{A-CO_2}_C)]$

(II.6)

where $n^{CO_2}_B$ is the number of CO$_2$ moles in steam B, $y^{CO_2}_B$ is the mole fraction of CO$_2$ in stream B, $n^{B-CO_2}_B$ is the number of moles of all gases but CO$_2$ in Stream B, and $y^{B-CO_2}_B$ is the mole fraction of all gases but CO$_2$ in Stream B. The rest of the variables follow the same nomenclature for Stream A and C.

The actual energy consumption of a DAC system can be calculated using second law efficiency [Lively and Realff, 2016]. The second law efficiency accounts for losses in system processes, described in Equation (II.7)

$$\eta = \frac{W_{\text{min}}}{W_{\text{actual}}}$$

(II.7)

where $\eta$ is the second law efficiency, $W_{\text{min}}$ is the minimum energy, and $W_{\text{actual}}$ is the actual energy consumption of the system.

[Ruthven, 2014] argued the free energy of mixing does not sufficiently reflect the energy consumption for separating dilute concentrations CO$_2$ from air. Ruthven introduces the idea of the value function. Ruthven calculates the energy cost of DAC is 650 KJ/mol, 2 orders of magnitude greater than the minimum separation work.
Chapter III
Methodology

Energy Analysis: Precompression of Atmospheric Air

System Model Overview. A thermodynamic analysis was performed on a cryogenic refrigeration cycle to calculate the ideal compressor energy depletion in precompression (PC) and the turbine energy recovery output described in TR. The total work required to desublimate CO$_2$ is determined utilizing a novel approach adopted from psychrometrics. Psychrometrics is the thermodynamics of gas-vapor mixtures, typically applied to air-water mixtures in heating, ventilating, and air-conditioning (HVAC) analysis. For this cryogenic application, the mixture comprises air and CO$_2$. Other components will not be considered as CO$_2$ has the highest freezing temperature in atmospheric gases (see Table 2.1). The thermodynamic model, based on psychrometric principles, was adapted from [Boetcher et al., 2019] to analyze the air-CO$_2$ mixture. The system schematics are shown in Figure 3.1.

In Figure 3.1b, atmospheric air enters the compressor (State 1) and is compressed to a compression factor before entering the heat exchanger (State 1*). The compressed airstream is precooled via the heat exchanger (State 2) and enters the deposition chamber to desublimate the CO$_2$. The cold, high pressure, CO$_2$-lean airstream exits the deposition chamber (State 3), passes through the HX to precondition the incoming airstream, and then exits the system (State 4). As discussed previously, increasing the partial pressure of CO$_2$ increases the desublimation temperature. In Figure 3.1c, a similar system is used however a turbine is utilized (State 5) to recover energy from the high pressure, CO$_2$-lean airstream exiting the system.

Figure 3.1a represents the baseline system model to compare the techniques to. No precompression of atmospheric air is used. In the present study, thermodynamic modeling,
based on psychrometric principles, is applied to a theoretical DAC system to gain insight on
the energy requirement of precompression (PC) and turbine recovery (TR) systems. The
theoretical system is situated in a low-temperature Arctic/Antarctic environment, where
the ambient temperature or effective ambient temperature that takes into account night sky
radiative cooling varies between -20 °C and -90 °C and operates at a current-technology-
level feasible compression (which includes compression ratios up to 2000).
Figure 3.1: Proposed systems to evaluate the possible energy benefit of precompression of atmospheric air for a cryogenic CO$_2$ capture system.
The total enthalpy, $H$, for the studied mixture is defined as

$$H = H_{\text{air}} + H_{\text{CO}_2} = m_{\text{air}} h_{\text{air}} + m_{\text{CO}_2} h_{\text{CO}_2}$$  \hspace{1cm} (\text{III.1})$$

In this equation, $H_{\text{air}}$ and $H_{\text{CO}_2}$ are the total enthalpies of the air and CO$_2$, respectively, in the mixture, and $h_{\text{air}}$ and $h_{\text{CO}_2}$ are the corresponding specific enthalpies. The masses of air and CO$_2$ in the mixture are $m_{\text{air}}$ and $m_{\text{CO}_2}$. The following expression defines the specific enthalpy of the air-CO$_2$ mixture

$$h \equiv \frac{H}{m_{\text{air}}} = h_{\text{air}} + \frac{m_{\text{CO}_2}}{m_{\text{air}}} h_{\text{CO}_2}$$  \hspace{1cm} (\text{III.2})$$

According to conservation of mass, the mass of the air flowing through the systems in Figure 3.1 is constant and equal to $m_{\text{air}}$. The conservation of mass equation for the CO$_2$ in the deposition chamber is

$$\dot{m}_{\text{CO}_2,2} = \dot{m}_{\text{CO}_2,i} + \dot{m}_{\text{CO}_2,3}$$  \hspace{1cm} (\text{III.3})$$

Here, $\dot{m}_{\text{CO}_2,2}$ and $\dot{m}_{\text{CO}_2,3}$ are the mass flow rates of the CO$_2$ at states 2 and 3, respectively. The mass of CO$_2$ desublimated, $\dot{m}_{\text{CO}_2,i}$, which is assumed to be a saturated solid, is determined by a targeted, specified mass fraction to be desublimated (for further explanation see the Results and Discussion section) defined as

$$\omega = \frac{\dot{m}_{\text{CO}_2,i}}{\dot{m}_{\text{CO}_2,2}}$$  \hspace{1cm} (\text{III.4})$$

The mass of the CO$_2$ prior to the deposition chamber is constant; likewise, the mass of the CO$_2$ after the deposition chamber also remains constant.

\textbf{Compressor and Recovery Turbine.}
The atmospheric air, at pressure $P_1$, enters the compressor and is isothermally compressed to a pressure, $P_1^\ast$. The amount of compression is specified by the compression ratio, $n$.

$$n = \frac{P_1^\ast}{P_1} \quad \text{(III.5)}$$

The assumption of isothermal compression is a bounding idealization. Under non-isothermal compression, the fluid is heated significantly, thus partially defeating the purpose of building the DAC system in an arctic climate. It is understood that in order to obtain isothermal compression, the process is slow and an infinite amount of intercoolers are required. Isothermal compression represents the minimum additional energy-cost baseline, that is, if there is not a net benefit without considering the thermodynamics and energy cost of the intercoolers, then considering them in the analysis is a moot point. Further discussion can be seen in the Results and Discussion section. The work of the compressor, when the process is internally reversible, is defined as

$$\frac{\dot{W}_c}{m_{\text{air}}} = T_1 (s_1^\ast - s_1) + (h_1 - h_1^\ast) \quad \text{(III.6)}$$

where $T_1$ (also equal to $T_1^\ast$) is the ambient temperature, $h_1^\ast$ and $h_1$ are the specific enthalpies and $s_1^\ast$ and $s_1$ are the specific entropies of the air-CO$_2$ mixture before and after the compressor, respectively.

The TR technique includes an additional turbine recovery component that is assumed to be adiabatic and isentropic, another bounding idealization. The energy recovered from the turbine is calculated as

$$\frac{\dot{W}_t}{m_{\text{air}}} = h_4 - h_5 \quad \text{(III.7)}$$
In this equation, \( h_4 \) and \( h_5 \) are the specific enthalpies of the air-CO\(_2\) mixture before and after the turbine.

**Precooling Heat Exchanger.** The heat exchanger is implemented to collect the “waste” cooled air leaving the deposition chamber to precool the ambient air entering, thus reducing the heat removal required to cool the deposition chamber to the desublimation temperature. The heat exchanger is assumed to be adiabatic so that all of the heat from the hotter fluid is transferred to the colder fluid. Assuming the capacity rates of both the hot and cold streams are equal, the effectiveness of the heat exchanger is defined as

\[
e = \frac{T_1 - T_2}{T_1 - T_3} = \frac{T_4 - T_3}{T_1 - T_3}
\]  

(III.8)

**Deposition Chamber.** The conservation of energy for the deposition chamber is

\[
\frac{\dot{Q}_r}{\dot{m}_{air}} = h_3 - h_2 + \frac{\dot{m}_{CO_2,i}}{\dot{m}_{air}} h_{CO_2,i}
\]  

(III.9)

where \( \dot{Q}_r \) is the heat transfer rate required to desublimate a mass fraction \( \omega \) of CO\(_2\). The enthalpies, \( h_2 \) and \( h_3 \), are the total specific enthalpies of the air-CO\(_2\) mixtures at their respective states. The enthalpy of the desublimated saturated solid CO\(_2\) is \( h_{CO_2,i} \).

**Cryogenic Refrigeration Cycle.**

The coefficient of performance (COP) for the reverse-Brayton cryocooler is defined as

\[
\beta = \frac{\dot{Q}_r}{\dot{W}_r}
\]  

(III.10)

where \( \dot{W}_r \) is the required work input to the cryocooler. The Carnot COP is the maximum...
theoretical COP of a system, which is defined as

$$\beta_{\text{Carnot}} = \frac{T_C}{T_H - T_C}$$  \hspace{1cm} (III.11)

Here, $T_C$ is the temperature of the cold reservoir or refrigerated space, in this case, $T_3$, which is set to the desublimation temperature, and $T_H$ is the temperature of the hot environment, which in this case is the ambient temperature, $T_1$. The second-law efficiency of the system is defined as

$$\eta = \frac{\beta}{\beta_{\text{Carnot}}}$$  \hspace{1cm} (III.12)

A conservative estimate of the maximum currently attainable second-law efficiency of cryogenic refrigeration systems is around 0.15 [Radebaugh, 2004], which is the efficiency used in the present analysis. However, higher values may be achieved with further research.

**Thermal Properties and Analysis.**

National Institute of Standards and Technology (NIST) REFPROP 10.0 [Lemmon et al., 2018] was utilized to determine thermodynamic properties of the air and the CO$_2$ at each state. Properties for air (0.7812 N$_2$, 0.2096 O$_2$, and 0.0092 Ar (on molar basis)) are calculated using an equation of state from Lemmon et al. [Lemmon et al., 2000]. Span and Wagner [Span and Wagner, 1996] developed the CO$_2$ equation of state, which includes the sublimation line.

The National Oceanic and Atmospheric Administration Muana Loa Atmospheric Baseline Observatory measured the atmospheric carbon dioxide concentration at a monthly average of 419 ppm in May 2021 [Muana, 2021]. The value of 419 ppm is directly equal to the mole fraction of CO$_2$ at the inlet of the DAC system, $x_{CO_2,1} = 0.000419$. The partial
pressure of the CO$_2$ can be calculated using the mole fraction

$$P_{CO_2,1} = x_{CO_2,1}P_1 \quad (III.13)$$

The ambient pressure was assumed to be $P_1 = 1$ atm. Additionally, the pressure for the turbine recovery case (TR) at state 5 was also assumed ambient. The compression ratio, $n$, was varied incrementally between 1 (no compression) and 2,000. Technically, the partial pressure of the air would be the partial pressure of the CO$_2$ subtracted from the total pressure. Since the resultant partial pressure of the air was extremely close to the total pressure, for ease of calculations, the partial pressure of the air was assumed to be the total pressure throughout the system (both before and after the desublimation). The DAC system target desublimated mass fraction, $\omega$, of CO$_2$ was varied between 0.1 and 0.99. The targeted desublimated CO$_2$ mass fraction was used to calculate the mass fraction of CO$_2$ remaining in the flow at state 3 ($x_{CO_2,3}$). During the DAC process, the temperature required to desublimate the remaining mass of CO$_2$ after a portion desublimates continues to decrease. Therefore, the targeted mass fraction at state 3 was used to determine the desublimation temperature, $T_3$, required to remove the total specified amount of CO$_2$.

The latent heat of sublimation, $h_{ig}$, was required to calculate the enthalpy of the desublimated solid, $h_{CO_2,i}$. Since data for the latent heat of sublimation for partial pressures of cryogenic CO$_2$ is scarce, it was estimated using the Clausius-Clapeyron equation, defined as

$$ln \frac{P_{vap,2}}{P_{vap,1}} = \frac{h_{ig}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (III.14)$$

where $R$ is the ideal gas constant, and $P_{vap,1}$ and $P_{vap,2}$ are vapor pressures at temperatures $T_1$ and $T_2$ in absolute units.
The ambient inlet temperature at state 1 was varied and set to $T_1 = -20 \, ^\circ C$, -40 °C, -65 °C, and -90 °C. As explained in von Hippel [von Hippel, 2018] and Boetcher et al. [Boetcher et al., 2019], the first three ambient temperatures are average temperatures of very cold ambient-environment sites: Snag, Yukon, Oymyakon, Russia, and Vostok Station, Antarctica, respectively, and -90 °C is reflective of taking advantage of nighttime radiative cooling at the Vostok site. The effectiveness of the heat exchanger, $\varepsilon$, was varied between 0 (no precooler heat exchanger) and 0.99. Although it is ideal to have a heat exchanger with as high of an effectiveness as possible, several values of $\varepsilon$ were tested at the low end to show the relationship between heat exchanger effectiveness and PC and TR.

It was also assumed that the mass flow rate of the air entering and leaving the system is constant and set to $\dot{m}_{air} = 1 \, \text{kg/s}$. This mass flow rate was selected to put the results on a per-unit-mass-of-air basis. The following equation is used to convert the thermal energy or work required from a per-mass-air basis to per-mass-CO$_2$ basis.

$$\frac{\dot{Q} \text{ or } \dot{W}}{\dot{m}_{CO_2,i}} = \frac{\dot{Q} \text{ or } \dot{W}}{\dot{m}_{air}} \frac{\dot{m}_{air}}{\dot{m}_{CO_2,i}}$$  \hspace{1cm} (III.15)

The total net work required per unit mass CO$_2$ to run the DAC system is

$$\frac{\dot{W}_{in}}{\dot{m}_{CO_2,i}} = \frac{|\dot{W}_r|}{\dot{m}_{CO_2,i}} + \frac{|\dot{W}_c|}{\dot{m}_{CO_2,i}} - \frac{|\dot{W}_t|}{\dot{m}_{CO_2,i}}$$  \hspace{1cm} (III.16)
Energy Analysis: Pressure Swing Adsorption

System Model Overview.

A thermodynamic analysis was performed on the PSA cycle to calculate the energy consumption to run the combined system. The work is calculated with a novel approach using adsorption isotherms and ideal gas assumptions. Figure 3.2 shows the system schematics to be evaluated.

Figure 3.2: Proposed systems to evaluate the possible energy benefit of a PSA unit in a cryogenic CO₂ capture system.
To determine the energy consumption of the PSA unit, $\dot{W}_{PSA}$, the unit can be modeled as seen in Figure 3.3. Atmospheric air is stored in a chamber using a compressor. The chamber is packed with a sorbent material. Zeolite 13X was selected as the sorbent for this system due to its high applicability in PSA systems [Bao et al., 2022]. Sorbent material characteristics and adsorbate chamber parameters are listed in Table 3.1.

![Figure 3.3: A model of the PSA system. A compressor is used to fill a chamber with air to the adsorption pressure.](image)

<table>
<thead>
<tr>
<th>Zeolite 13X Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>void fraction $\varepsilon$</td>
</tr>
<tr>
<td>particle diameter $d_p$</td>
</tr>
<tr>
<td>bulk density $\rho$</td>
</tr>
</tbody>
</table>

**Table 3.1: Characteristics of Zeolite 13X used in this study.**

**System Model Assumptions.**

The assumptions for the model are
1. Chamber with single inlet and no exit

2. Kinetic energy effects and potential energy effects are ignored

3. Tank is filled and emptied rapidly such that $Q_{CV}$ is zero

4. Isentropic relationship such that $Pv^\gamma = constant$

5. State of air entering the control volume is constant

**Ideal Gas System Model.** The gas will be modeled using the ideal gas model. The ideal gas model holds true when the compressibility factor $Z$ is equal to 1. The compressibility factor can be described as

$$Z = \frac{Pv}{RT} \quad (III.17)$$

At states where $P$ is small relative to the critical pressure and $T$ is large compared to the critical temperature, $Z \approx 1$ and the gas behaves as an ideal gas. The ideal gas law is rearranged from Equation [III.17] is described as

$$Pv = RT \quad (III.18)$$

where $P$ is the pressure of the gas, $v$ is the specific volume of the gas, $R$ is the universal gas constant, and $T$ is the temperature of the gas. Equation [III.18] can be solved to find the specific volume of the gas at state 1, $v_{1,PSA}$.

The PSA processes is assumed to be isentropic with the following relationship

$$Pv^\gamma = constant \quad (III.19)$$
where \( \gamma \) is the specific heat ratio. For air, \( \gamma = 1.4 \). The specific volume of the gas at the adsorption step, \( v_{ads} \) can be found using Equation [III.19]

**Conservation of Energy.**

Conservation of energy for a control volume is

\[
\frac{dE_{CV}}{dt} = \dot{Q} - \dot{W} + \dot{m}_i (u_i + \frac{V_i^2}{2} + g z_i) - \dot{m}_e (u_e + \frac{V_e^2}{2} + g z_e)
\]  

(III.20)

after applying all assumptions, Equation [III.20] reduces to

\[
\dot{W} = \dot{m}(du)
\]  

(III.21)

where \( du \) is the change in specific internal energy of the air from the desorption step to the adsorption step. Applying the inefficiencies in compressors, the work required of the PSA unit is

\[
\dot{W}_{PSA} = \frac{\dot{W}}{\eta_{compressor}}
\]  

(III.22)

\( \eta_{compressor} \) was set to 0.7 for this analysis. For a gas mixture following the ideal gas model, \( u \) is only a function of temperature. Thus,

\[
c_v(T) = \frac{du}{dT}
\]  

(III.23)

where \( c_v(T) \) is the specific heat at constant volume of the gas mixture at temperature \( T \). Rearranging Equation [III.23] gives
\[ du = c_v(T)dT \]  

(III.24)

The specific heat is found using REFPROP. \(dT\) is the change in temperature between the adsorption state and the atmospheric state such that

\[ dT = T_{ads} - T_1 \]  

(III.25)

**Pressure Drop in the PSA Chamber.**

The chamber is assumed to be fully packed with sorbent material Zeolite 13X, thus the compressor also needs to overcome the pressure drop across the sorbent material. The Kozeny-Carman Equation (Equation III.26) was proposed first by Kozeny in 1927 and later modified in 1925 by Carman. This equation is valid for laminar flow. The pressure drop across the sorbent is independent of the fluid density at low Re flow.

\[ \frac{\Delta P}{\Delta L} = \frac{-180 \mu (1 - \epsilon)^2 u_s}{\Phi^2 d^2 \epsilon^3} \]  

(III.26)

where \( \Delta P \) is the pressure drop across the sorbent bed, \( \Delta L \) is the height of the bed, \( \epsilon \) is the void fraction of the bed, \( d_p \) is the diameter of the sorbent particle, \( u_s \) is the superficial fluid velocity, \( \mu \) is the fluid viscosity and \( \Phi \) is the sphericity of the sorbent particles. \( \Phi \) will be assumed to be 1 for this analysis. The pressure drop found in Equation III.26 is added to the adsorption pressure \( P_{ads} \) to find the total pressure needed in the chamber to initiate the adsorption process.

\[ P_{total} = \Delta P + P_{ads} \]  

(III.27)

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Adsorption Temperature.

The temperature at the adsorption step, \( T_{ads} \) can be calculated rearranging Equation III.18 to

\[
T_{ads} = \frac{P_{total}v_{ads}}{R}
\]  

(III.28)

The blowdown step (see Figure 2.7) requires the pressure in the chamber to decrease. Following the ideal gas law, as pressure decreases, the temperature decreases. Thus, the temperature in the chamber will reduce to the inlet temperature \( T_1 \) and \( T_1 = T_2 \).

Adsorption Isotherms.

The Langmuir Isotherm Adsorption models describe the equilibrium adsorption process between the adsorbate species and the adsorbent at constant temperature, as seen in Figure 3.4. The Langmuir Isotherm model is useful to calculate the amount of adsorbed species per unit mass of adsorbent, \( q \). The model is often expressed in terms of \( \theta \),

\[
\theta = \frac{q}{q_m}
\]  

(III.29)

where \( \theta \) the fraction of the adsorbent surface covered in the adsorbate and \( q_m \) is the maximum amount of adsorbate that the adsorbent can hold.

Some basic assumptions are made to the model:

1. 1 adsorbent molecule per adsorbent site
2. Adsorbed molecules do not interact with one another
3. The adsorbent surface is a uniform surface
Figure 3.4: A simple adsorption model of a pure substance.

4. Monolayer adsorption

5. The rate of adsorption is equal to the rate of desorption

The rate of adsorption is expressed as

$$\zeta_{ads} = k_a P \theta_v$$  \hspace{1cm} (III.30)

where $\zeta_{ads}$ is the rate of adsorption, $k_a$ is the adsorption rate constant, $P$ is the pressure of the adsorbate, and $\theta_v$ is the fraction of vacant and available. It is also assumed that

$$\theta + \theta_v = 1$$  \hspace{1cm} (III.31)

The rate of desorption is expressed as

$$\zeta_{des} = k_d \theta$$  \hspace{1cm} (III.32)

where $k_d$ is the desorption rate constant.
Assuming equilibrium where

\[ \zeta_{ads} = \zeta_{des} \]  

(III.33)

and substituting \( K = \frac{k_a}{k_d} \), combining with equation III.31, equation III.33 becomes

\[ \theta = \frac{KP}{1 + KP} \]  

(III.34)

\( K \) is also known as the equilibrium constant.

The Langmuir Adsorption model assumes a single adsorbate species in the model. However, air is a multi-component mixture and the analysis must reflect the composition of the fluid. The Extended Langmuir Model or ELI is a modification of the Langmuir Adsorption Model to include multiple adsorbate species, as seen in Figure 3.5. Equation III.29 and III.34 are modified to Equations III.35, III.36, III.37, III.38, III.39, III.40, III.41 and III.42 to account for the mixture of gases in Earth’s atmosphere. Only nitrogen, oxygen, and argon are considered for atmospheric gases. Other gases are considered negligible in the atmosphere for this analysis.

\[ \theta_{N_2} = \frac{K_{N_2}P_{N_2}}{1 + K_{N_2}P_{N_2} + K_{O_2}P_{O_2} + K_{Ar}P_{Ar} + K_{CO_2}P_{CO_2}} \]  

(III.35)

Figure 3.5: ELI Adsorption model of a mixture with 2 adsorbate species.
\[ \theta_{N_2} = \frac{q_{N_2}}{q_{N_2,\text{max}}} \]  \hspace{1cm} (III.36)

\[ \theta_{O_2} = \frac{K_{O_2}P_{O_2}}{1 + K_{N_2}P_{N_2} + K_{O_2}P_{O_2} + K_{Ar}P_{Ar} + K_{CO_2}P_{CO_2}} \]  \hspace{1cm} (III.37)

\[ \theta_{O_2} = \frac{q_{O_2}}{q_{O_2,\text{max}}} \]  \hspace{1cm} (III.38)

\[ \theta_{Ar} = \frac{K_{Ar}P_{Ar}}{1 + K_{N_2}P_{N_2} + K_{O_2}P_{O_2} + K_{Ar}P_{Ar} + K_{CO_2}P_{CO_2}} \]  \hspace{1cm} (III.39)

\[ \theta_{Ar} = \frac{q_{Ar}}{q_{Ar,\text{max}}} \]  \hspace{1cm} (III.40)

\[ \theta_{CO_2} = \frac{K_{CO_2}P_{CO_2}}{1 + K_{N_2}P_{N_2} + K_{O_2}P_{O_2} + K_{Ar}P_{Ar} + K_{CO_2}P_{CO_2}} \]  \hspace{1cm} (III.41)

\[ \theta_{CO_2} = \frac{q_{CO_2}}{q_{CO_2,\text{max}}} \]  \hspace{1cm} (III.42)

where \( \theta_i \) is the fraction of the adsorbent surface covered with component \( i \), \( K_i \) is the equilibrium constant for component \( i \), \( P_i \) is the pressure of component \( i \), \( q_i \) is the amount of component \( i \) adsorbed per unit mass of sorbent, and \( q_{i,\text{max}} \) is the maximum amount of component \( i \) that can be adsorbed by the adsorbate.

The PSA unit is used to increase the amount of CO\(_2\) in the airstream going into the deposition chamber. To quantify the amount of component \( i \) in the airstream at State 2 in
Figure 3.2: The mole fraction of the component is calculated using Equation III.44

\[ y_i = \frac{q_i}{q_{total}} \]  

(III.43)

PPM, or parts per million, is often used to describe small amounts of a component in a mixture. The PPM of component \( i \) in the airstream at State 2 is

\[ PPM = y_i \times 1,000,000 \]  

(III.44)

Work per CO\(_2\) Captured Basis Conversion.

The work of the compressor calculated in Equation III.21 needs to be converted to a per mass unit of CO\(_2\) adsorbed.

\[ \frac{\dot{W}_{PSA}}{\dot{m}_{CO_2,PSA}} = \frac{\dot{W}_{PSA}}{\dot{m}_{air}} \frac{\dot{m}_{air}}{\dot{m}_{sorbent}} \frac{\dot{m}_{sorbent}}{\dot{m}_{CO_2,PSA}} \]  

(III.45)

The total net work required per unit mass CO\(_2\) to run the DAC system is

\[ \frac{\dot{W}_{in}}{\dot{m}_{CO_2,i}} = \frac{\dot{W}_{PSA}}{\dot{m}_{CO_2,PSA}} + \frac{|\dot{W}_{c}|}{\dot{m}_{CO_2,i}} \]  

(III.46)
Chapter III

Results

Energy Benefit of Precompression for Cryogenic DAC

In this section, results are presented for the NC case, which represents no precompression \((n = 1)\), and cases for three representative compression ratios, \(n = 400, 800, \) and 2000, with (TR) and without turbine recovery (PC). The value \(n = 400\) represents a compression ratio that may be obtained with off-the-shelf compressors, such as those used for scuba gear, firefighter breathing equipment, compressed air energy storage, blow molding manufacturing processes, and leak testing of hydraulic and pneumatic systems. A compression ratio of 800 can be obtained with specialized equipment. Finally, a compression ratio of 2000 represents a future-looking aspirational technology target. It is important to note that perfect isothermal compression is assumed, while realistically, one can achieve near-isothermal compression via the addition of intercoolers. There is an added energy cost associated with the addition of the heat exchangers, which is neglected in the present analysis. Therefore, the net work presented here for PC and TR represent best-case scenarios, and the real situation will require a multi-stage compressor with intermediate intercoolers, which is added equipment with an additional energy cost.

As mentioned earlier, pure CO\(_2\) at 1 atm desublimates at -78.5 °C. For partial pressures of CO\(_2\) below 1 atm, however, the lower the concentration of CO\(_2\), the lower the temperature required for desublimation. For the calculations, required target temperatures to desublimate specified mass fractions were needed as input to determine cryogenic cooling loads (Eqs. (III.4) and (III.9)). Figure 4.1 has been prepared to show the temperatures required to desublimate target mass fractions for various compression ratios. As can be seen in the figure, the NC case \((n = 1)\) requires significantly lower temperatures than when the air is compressed to desublimate the same mass fraction of CO\(_2\), hence further illus-
Figure 4.1: Temperature required to desublimate mass fraction $\omega$ of CO$_2$ for various compression ratios

The targeted CO$_2$ desublimated mass fraction becomes a key variable to optimize because it combines temperature with amount of resultant CO$_2$ capture.

As a baseline, Figure 4.2 shows the work required for the NC case (Figure 3.1a using a precooler with a heat exchanger effectiveness, $\varepsilon$, equal to 0.7 to desublimate various mass fractions of CO$_2$. The value 0.7 represents a well-performing heat exchanger. Achieving greater heat exchanger effectiveness often requires costly designs. As seen in Figure 4.2, as the target CO$_2$ desublimation mass fraction, $\omega$, increases, the work per unit mass of CO$_2$ decreases, that is, until $\omega$ reaches a minimum of 0.9. Attempting to desublimate larger mass fractions results in larger energy penalties due the fact that it takes increasingly lower temperatures to desublimate increasingly smaller amounts of CO$_2$. In other words,
attempting to remove the last tiny fraction of CO\textsubscript{2} out of the air is not worth the cost of cooling the air further. It is noted here that the figures for all other heat exchanger effectivenesses follow the same trend.

![Figure 4.2: Total work required for the no compression case (NC) (Figure 3.1a) to desublimate CO\textsubscript{2} at various inlet temperatures with a precooler effectiveness of $\varepsilon = 0.7$.](image)

It was found that for all cases of compression ratios and ambient inlet temperatures, precompression acting alone (PC, Figure 3.1b) is never beneficial even for idealized conditions. Therefore, for the real-life case where intercoolers will be needed (adding maintenance costs and energy expenses), precompression acting alone will require even more work than the idealized case. However, there are some cases where there may be a net-energy benefit to employing precompression with turbine recovery (TR, Figure 3.1c). Of the various inlet ambient temperatures, it was found that $T_1 = -20 ^\circ$ C had the most scenarios where the possibility of precompression with turbine recovery could potentially be beneficial.
Table 4.1 shows the comparative percentage of work per mass CO₂ required to desublimate a mass fraction $\omega$ of CO₂ between TR and NC as a function of heat exchanger effectiveness and compression ratio for an ambient inlet temperature of -20 °C. It is important to note here that when $\epsilon = 0$ there is no precooler present in the system. The grayed-out space for $\epsilon \geq 0.6$ represents cases where the precooler gets cold enough to cause the CO₂ to desublimate in the passages of the heat exchangers, thus creating fouling and other complications.

As can be seen in Table 4.1, as the compression ratio increases, there are a larger number of design-space points that could benefit by adding a precompressor with turbine recovery. However, the table only shows the percent differences between two cases for a particular $\omega$ and $\epsilon$ and not the overall comparison with regard to what system desublimates the largest mass fraction of CO₂ for the lowest energy cost. It can be seen from the table, that precompression with turbine recovery is most beneficial for systems with no precooler or precoolers with low heat exchanger effectivenesses and low target mass fractions. According to Fig. 4.2, DAC systems should operate in the range of $\omega \sim 0.9$, and it appears that precompression with turbine recovery is only beneficial if no precooler heat exchanger is present. However, as stated previously, intercoolers, which are heat exchangers, are needed for isothermal compression anyway.

Table 4.2 is used to compare the effect of the precooler with a heat exchanger effectiveness of 0.7 (a value that is considered for a well-performing heat exchanger and, for most cases, does not cause fouling—often, increasing the effectiveness of an industrial-size heat exchanger is not worth the added cost) acting alone to compression with turbine recovery if no precooler is present for $n = 400, 800, 2000$ at $T_1 = -20 \, ^\circ C, -40 \, ^\circ C, -65 \, ^\circ C, \text{and} -90 \, ^\circ C$. There is no value for $n = 2000$ at $T = -90 \, ^\circ C$ because this case went beyond the range of NIST REFPROP. As the compression ratio increases, the work input required for TR decreases; however, the cases with no compressor and turbine and only a well-performing
precooler have much less work input. It takes between 175-290% more work to run the system with a precompressor and turbine than it is to run it with the heat exchanger. It is also noted that as $T_1$ decreases, the percent differences between the cases increases, indicating that the system utilizing TR should be run at higher inlet temperatures. As Table 4.2 shows, if the choice is given between a compression/recovery system and a precooler, it always advantageous to use the precooler alone.

Although it has been determined that, even at the low concentrations of CO$_2$ found in the atmosphere, implementing precompression and turbine recovery is not feasible, from both a thermodynamics perspective and potentially a cost/maintenance standpoint, it is worthwhile to look at some trends comparing precompression with and without turbine recovery against the system with precooling only. Figure 4.3 has been prepared to show the factor increase of work required for both the PC case and TR case, compared to the baseline NC cases for various compression ratios and target CO$_2$ desublimation mass fractions for a system with a precooler with $\varepsilon = 0.7$. The factor increase of 1.0 is marked with a black dotted line. This is to note that if any of the bars are below this line, the work to run the system is less than the NC case. It is noted at some values of $\omega$, the data are not included. As previously stated, for those cases, the precooling heat exchanger causes the inlet air temperature, $T_2$, to fall below the corresponding CO$_2$ desublimation temperature, causing the CO$_2$ to prematurely solidify before entering the deposition chamber. As can be seen from the figure, precompression with or without turbine recovery always requires more energy than its corresponding no precompression case. A trend can be noted as the ambient temperature decreases, utilizing precompression and turbine recovery requires more energy to run each system.
Figure 4.3: Factor increase of work required for both the PC and TR cases, compared to the baseline NC case, all utilizing a precooler with $\varepsilon = 0.7$ and ambient temperatures of (a) -20 °C, (b) -40 °C, and (c) -65 °C. For each value of $\omega$, from left to right, the first set of bars represents $n = 400$, the second set of bars represents $n = 800$, and the third set of bars represents $n = 2000$. 
Figure 4.3: Factor increase of work required for both the PC and TR cases, compared to the baseline NC case, all utilizing a precooler with $\epsilon = 0.7$ and ambient temperatures of (a) -20 °C, (b) -40 °C, and (c) -65 °C. For each value of $\omega$, from left to right, the first set of bars represents $n = 400$, the second set of bars represents $n = 800$, and the third set of bars represents $n = 2000$. 
In this section, the results are presented for the PSA case. The energy consumption of a PSA unit is conditional to the sorbent material selected. Adsorption constants $K$ and $q_{i,\text{max}}$ are found experimentally using adsorption analyzer instrumentation. For this analysis, Zeolite 13X is selected to compare the energy to run a combined PSA-cryogenic distillation carbon capture system (PSA case) versus a cryogenic distillation system alone (NC case). Adsorption isotherms for Zeolite 13X at $T_{\text{amb}} = -50^\circ\text{C}$ used in this analysis are found in Table 4.3. The PSA unit simulated a CO$_2$ increase from ambient concentrations to 7,000 ppm. An ideal case represented in this analysis uses a simple dual-column configuration to produce a continuous flow between the adsorption and desorption steps. In the real case, a multi dual-column setup may be utilized to meet operating conditions and flow rates, adding to the equipment and overall energy cost.

Figure 4.4 shows the required energy input per mass of CO$_2$ captured to run the NC case (black) and the PSA case (purple), evaluated at $\varepsilon_{\text{HX}} = 0.7$. The heat exchanger effectiveness was selected to maximize efficiency without suffering fouling in the heat exchanger channels. As seen in the graph, it is approximately half the energy intensity to the run the PSA system compared to the NC system across all mass fractions. Increasing the inlet CO$_2$ concentration to the deposition chamber significantly reduces the energy to run the system. A thermodynamic minimum was found at $\omega = 0.9$ of 143 GJ/tonne CO$_2$ captured. This energy consumption is considerably higher than reported energy consumption of other DAC systems [Boetcher et al., 2019]. However, improvements to cryogenic distillation component efficiency and overall system optimizations may drive the energy cost down to a competitive value.

The effect of inlet CO$_2$ concentration on cryocooler work was evaluated at 400, 1,000, and 7,000 ppm. A value of 400 ppm constitutes ambient atmospheric concentrations of CO$_2$. A value of 1,000 ppm represents experimental CO$_2$ concentration increases using
Zeolite 13X. A value of 7,000 ppm reflects a theoretical concentration increase using Langmuir adsorption isotherms from the modeled PSA unit. Figure 4.5 is prepared to show the result of increasing the inlet CO$_2$ concentration on the work input to the cryocooler, $W_r$. As the inlet concentration rises, $W_r$ significantly decreases. Almost doubling the inlet concentration (from 400 ppm to 1,000 ppm) lowers the energy consumption by approximately 60%. This concludes that varying the inlet CO$_2$ concentration greatly influences the overall energy cost of the system and future endeavours should prioritize this phenomena when designing DAC systems.
To get a better understanding of the breakdown of energy consumption in the PSA case (Figure 3.2b), the work input to the PSA unit, \( W_{PSA} \) (blue), and the work input to the cryocooler, \( W_r \) (red), are compared in Figure 4.6. It is noted that \( W_r \) is a function of \( \omega \), whereas \( W_{PSA} \) does not change with \( \omega \). As seen in the graph, \( W_r \) contributes to the overwhelming majority of the energy cost for the combined system. The bulk of the energy demand originates from maintaining an ultra-low temperature environment where desublimation of dilute concentrations of \( CO_2 \) occurs.
Figure 4.6: Work of the cryocooler (red) and work of the PSA unit (blue) at $\epsilon = 0.7$. 
Table 4.1: Comparison of total work, by percentage, required to run the system with pre-compression and turbine recovery (TR, Figure 3.1c) compared to the no compression system (NC, Figure 3.1a) at $T_1 = -20 ^\circ C$ for $n = 400, 800, \text{ and } 2000$. A positive percentage means that TR takes more work than the corresponding NC case, and a negative percentage means TR takes less work than the corresponding NC case.

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Table 4.2: Percent differences in work required to run the system between TR (Figure 3.1c) and no precooler (ε = 0) and NC (Figure 3.1a) with a precooler (ε = 0.7) for various compression ratios and inlet temperatures.

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\[ T_1 = -20 \, ^\circ\text{C} \]

\[ T_1 = -40 \, ^\circ\text{C} \]

\[ T_1 = -65 \, ^\circ\text{C} \]

\[ T_1 = -90 \, ^\circ\text{C} \]

Table 4.3: Adsorption isotherm constants for Zeolite 13X at -50°C

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Chapter V

Conclusions

Global anthropogenic GHG emissions are at an all time high and are directly causing climate change. The concentration of CO$_2$ in the atmosphere has increased almost 40% over the past two centuries, leading to unimaginable negative effects on the planet. Earth’s average temperature is increasing every year and scientists have warned of catastrophic disaster if the temperature increases 2°C above pre-industrial levels. The scientific community agrees that through the reduction of GHG emissions, electrification and decarbonization of various sectors, and CO$_2$ removal activities, climate change can be alleviated.

Direct air capture of CO$_2$ is one of the many climate change mitigation strategies needed to reverse global warming. Direct air capture requires specialized systems to capture dilute CO$_2$ concentrations from atmospheric air conditions. DAC can be accomplished through different mechanisms such as cryogenic distillation, adsorption, absorption, and membrane separation. DAC has potential for large scale operation however requires more analysis to increase development rates.

The results of this study extend the analysis of Boetcher et al. [Boetcher et al., 2019] and [Perskin et al., 2022] in thermodynamically modeling a DAC system under different parameters and preconditions. A thermodynamic model was constructed using psychometric theories to model the desublimation of CO$_2$ in a DAC system. The system was modeled to include a precooling heat exchanger and a deposition chamber where the desublimation of CO$_2$ occurs. Three base systems were studied, NC (no precompression or turbine recovery), PC (precompression only), and TR (precompression and turbine recovery) at three different compression ratios, $n = 400, 800, \text{ and } 2000$. Then, a combination DAC system, PSA (pressure swing adsorption and cryogenic distillation), was modeled. A dual-column, 4-step Skarstrom Cycle PSA unit was analyzed using Extended Langmuir Models and the
ideal gas law to simulate a CO$_2$ concentration prior to the deposition chamber. The NC and PSA systems were evaluated at $T_{amb} = -50^\circ$C.

This study finds that while increasing the compression ratio of the system, there is no net energy benefit when capturing CO$_2$ given the current state-of-the-art in commercial compressor and cryocooler capabilities. The assessment of the efficiency of a precooler versus TR finds that it is more advantageous to utilize a heat exchanger precooler than pre-compression with turbine recovery in a DAC system. Combining DAC systems may yield a more efficient system. PSA combined with cryogenic capture is less energy intensive than cryogenic capture alone. In a combined DAC system with PSA and cryogenic distillation, the PSA unit has a significantly lower energy consumption than the cryocooler. Increasing the concentration of CO$_2$ entering the deposition chamber significantly decreases the required energy consumption of the cryocooler.

**Future Recommendations**

The novelty in this research lies in the preliminary modeling of a cryogenic DAC system and the combination DAC system. It is important to note that the work here represents an ongoing proof-of-concept theoretical analysis to determine energy requirements for DAC in arctic/Antarctic climates. Many assumptions are made in the present study that should be investigated further to provide a more robust energy analysis of direct air capture systems.

Exploration and development of the components in the system are crucial to performance. The dimensions of the PSA unit chamber are not taken into consideration in this study. The effect of height, depth, and length of the adsorption chamber should be modeled to optimize adsorption performance. The effectiveness of the heat exchanger is a significant component to reduce the energy consumption of the total system. Priority should be taken to design the configuration of an efficient heat exchanger that maximizes heat transfer without incurring ice accumulation (fouling) for cryogenic flow. Additionally, research
and development into the deposition chamber must occur to capture the CO₂. The process of transporting the solid CO₂ from the deposition chamber to a storage unit to allow continuous air flow throughout the system should also be considered.

The results of the case study conclude that the combination DAC system is less energy intensive than a single DAC system. One can conclude that combining other DAC mechanisms such as temperature swing adsorption, membrane separation, or chemical absorption with the established cryogenic distillation and/or pressure swing adsorption can reduce the energy consumption even further.
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