Techno-Economic Analysis of Capturing Carbon Dioxide from the Air

Positioning the Technology in the Energy Infrastructure of the Future

by

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ABSTRACT

As the global community raises concerns regarding the ever-increasing urgency of climate change, efforts to explore innovative strategies in the fight against this anthropogenic threat is growing. Along with other greenhouse gas mitigation technologies, Direct Air Capture (DAC) or the technology of removing carbon dioxide directly from the air has received considerable attention. As an emerging technology, the cost of DAC has been the prime focus not only in scientific society but also between entrepreneurs and policymakers. While skeptics are concerned about the high cost and impact of DAC implementation at scales comparable to the magnitude of climate change, industrial practitioners have demonstrated a pragmatic path to cost reduction. Based on the latest advancements in the field, this dissertation investigates the economic feasibility of DAC and its role in future energy systems. With a focus on the economics of carbon capture, this work compares DAC with other carbon capture technologies from a systemic perspective. Moreover, DAC's major expenses are investigated to highlight critical improvements necessary for commercialization. In this dissertation, DAC is treated as a backstop mitigation technology that can address carbon dioxide emissions regardless of the source of emission. DAC determines the price of carbon dioxide removal when other mitigation technologies fall short in meeting their goals. The results indicate that DAC, even at its current price, is a reliable backup and is competitive with more mature technologies such as post-combustion capture. To reduce the cost, the most crucial component of a DAC design, i.e., the sorbent material, must be the centerpiece of innovation. In conclusion, DAC demonstrates the potential for not only negative emissions (carbon dioxide removal with the purpose of addressing past emissions), but

also for addressing today's emissions. The results emphasize that by choosing an effective scale-up strategy, DAC can become sufficiently cheap to play a crucial role in decarbonizing the energy system in the near future. Compared to other large-scale decarbonization strategies, DAC can achieve this goal with the least impact on our existing energy infrastructure.

هَذَا مِن فَضلِ رَبِّی

تقدیم به:

پدر و مادر عزیزم،

که با مهر شان عشق ورزیدن، با صبر شان پشت کار، با همت شان بلند نظری،

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CHAPTER 1

INTRODUCTION

The Intergovernmental Panel for Climate Change (IPCC) defines Carbon Dioxide Removal (CDR) as: "Anthropogenic activities removing CO_2 from the atmosphere and durably storing it in geological, terrestrial, or ocean reservoirs, or in products (Masson-Delmotte et al. 2018)." CDR – or negative emissions – is inevitable if the goal is to limit the global temperature increase to 1.5 °C above the preindustrial era (Masson-Delmotte et al. 2018). Some studies suggest that CDR is crucial even to meet the Paris Agreement's 2 °C temperature rise objective by the end of the century (Edenhofer et al. 2014; Gasser et al. 2015; Rogelj et al. 2015; van Vuuren et al. 2013). This means reaching a net-zero carbon emission is no longer sufficient and we need to address the past emissions by obtaining a net-carbon negative energy system. Apart from the urgency of CDR to prevent a climate catastrophe, it appears to be the only solution that can return the atmospheric carbon dioxide concentration to the preindustrial level and reverse some of the already conspicuous changes in the global climate patterns. Returning to the preindustrial atmospheric CO_2 level would take thousands of years if we rely on natural sinks of carbon dioxide (Archer et al. 2009; Archer 2005).

Negative Emissions Technologies

While the world is far from reaching the net negative carbon emission, technologies for pulling carbon dioxide out of the environment are already available (National Academies of Sciences 2019; Haszeldine et al. 2018; Caldecott, Lomax, and Workman 2015). Negative Emissions Technologies (NETs) are technologically feasible, even though their scalability and cost remain ambiguous (Smith et al. 2016; Anderson and Peters 2016). If commercialized, an essential advantage of NETs is decoupling emissions from their source. In other words, NETs do not differentiate between emissions from large point source emitters (e.g., a power plant or a cement plant) and emissions from mobile sources (e.g., a car, a ship or an airplane). Therefore, aside from reducing the level of atmospheric CO_2 when a net-zero emission is achieved, NETs can be utilized today on our path for achieving the net-zero emission goal. It is also necessary to start early implementation and scale-up of NETs for the time we need them to address our past emissions (this time is around mid-century based on the 2018 IPCC reports).

Most NETs capture carbon dioxide directly from the air through biological, chemical, or physical processes. Only a handful of technologies currently qualify as NETs (National Academies of Sciences 2019; Haszeldine et al. 2018):

- Coastal blue carbon; ocean fertilization and alkalization: Coastal blue carbon or blue carbon refers to the utilization of tidal marshland and salt-water wetlands to increase the stored carbon in the form of plants and sediments (National Academies of Sciences 2019). Increasing the blue carbon storage capacity is mainly performed in a coastal ecosystem, while oceans' fertilization (Buesseler and Boyd 2003) and alkalization (Rau et al. 2013) refer to open ocean approaches. Iron fertilization includes increasing phytoplankton biomass in nutrient-rich surfaces of the Southern ocean aiming to increase the CO_2 uptake rate (Martin 1990). Similarly, the CO_2 uptake rate could be increased in ocean alkalization by increasing the pH of ocean waters through different chemical processes (Phil Renforth and Henderson 2017).
- Terrestrial carbon removal with sequestration by land management and afforestation: This includes management and practices that increase and maintain the amount of

terrestrial carbon stored in the biosphere (National Academies of Sciences 2019; Griscom et al. 2017). In this category, the emphasis is on the biomass inventory that lasts for several decades (e.g., woody biomass, coarse woody debris, and soil organic matter).

- Bioenergy with Carbon Capture and Sequestration (BECCS): This includes energy production from biomass-based fuel and combining it with electricity or heat generation and carbon capture and sequestration. BECCS was first introduced in 2001 as a means for climate mitigation and then further investigated as a NET (D. W. Keith 2001; Obersteiner et al. 2001; Creutzig et al. 2015). BEECS is the most frequently used NET in climate prediction models (Integrated Assessment Models) and is mentioned as the most mature NET (Edenhofer et al. 2014; Rogelj et al. 2015; van Vuuren et al. 2013; Azar et al. 2010).
- Combined Mineral Capture and Storage (CMCS): CMCS or enhanced weathering includes chemical fixation of the atmospheric carbon dioxide by reactions with minerals (i.e., magnesium and calcium-rich minerals) (Seifritz 1990; Klaus S. Lackner et al. 1995). Mineralization reactions are relatively slow (National Academies of Sciences 2019; Klaus S. Lackner et al. 1995). Mineralization can happen *ex situ* where minerals are ground and transported to react with CO_2, or *in situ* where the capture process happens through the pores in a natural rock formation (National Academies of Sciences 2019). The third form of carbon mineralization, *surficial*, can happen when CO_2 is reacted with suitable industrial waste with high surface area (National Academies of Sciences 2019; Stolaroff, Lowry, and Keith

2005). CMCS may also be utilized as safe storage by mineralization of a highly concentrated CO_2 stream produced by another form of capture.

- Direct Air Capture (DAC) with carbon sequestration (DACCS): DAC is the process of capturing CO_2 directly from the air through a chemical or physical bond with a sorbent material. DAC as a climate mitigation strategy was first introduced by Lackner and colleagues (KS Lackner, Grimes, and Ziock 1999). To date, several privately and publicly funded projects have developed large-scale DAC units (Sanz-Pérez et al. 2016; Fasihi, Efimova, and Breyer 2019).

To limit the temperature rise to 1.5 °C without a significant overshoot, the IPCC predicts the need for negative emissions on an order of 100-1000 Giga ton of CO_2 ($GtCO_2$) by the end of the century (Masson-Delmotte et al. 2018). This amount is roughly equal to 2-20 years of global carbon emission given the current emission rate. The 100-1000 Gt of CDR, especially in the second half of the century, can be presumed as the final opportunity to meet the climate goals, considering the absence of robust strategies needed to satisfy sustainable emission reduction on a global scale. The development of NETs occurs to be a solution to prevent a climate catastrophe and to maintain the current rate of economic growth; however, in part, it relies on cost reduction and technological advances in these technologies (National Academies of Sciences 2019; Fuss et al. 2014; Smith et al. 2016). This makes it crucial to address the uncertainties and challenges in the cost, scalability, and environmental side-effects of the currently available NETs. This dissertation aims to elaborate on some of these uncertainties, address them and identify future areas of research necessary for a better understanding of the large-scale CDR feasibility.

Oceans are the largest carbon reservoir with a capacity of about 38000 Gt of Carbon (GtC) (Phil Renforth and Henderson 2017) and, on the surface, are tightly coupled with the atmosphere (Sabine and Tanhua 2010). Oceans are a natural sink of CO_2; however, it takes them hundreds of thousands of years to reduce the atmospheric CO_2 concentration to the preindustrial level (Lord et al. 2016). Multiple experiments have been conducted to increase the uptake rate of CO_2 in the Southern ocean (Coale et al. 2004; Boyd et al. 2000; Smetacek 2001), but a noticeable result requires large-scale manipulation in the marine environment and ocean chemistry (Feely et al. 2004; Andersson, Mackenzie, and Lerman 2005). This raises concerns about unwanted and uncertain adverse environmental impacts in the complex ocean ecosystem (P. Renforth, Jenkins, and Kruger 2013; Strong et al. 2009; Chisholm, Falkowski, and Cullen 2001). Similarly, large-scale biological capture and sequestration, both in the form of afforestation and BECCS, is associated with a significant land-use change and competition with food production (Smith et al. 2016; Williamson 2016). BEECS is the dominant technology discussed in the NET literature; however, its viability for large-scale implementation remains highly uncertain (Smith et al. 2016; Williamson 2016; Bonsch et al. 2016; Heck et al. 2018; Vaughan and Gough 2016). As an example, to capture 1000 $GtCO_2$, the total terrestrial biomass must increase by about 50%.[1] This not only requires a substantial amount of land, but is associated with unknown environmental

[1] The capacity of the terrestrial biomass is estimated between 450 and 650 Gt of carbon (Prentice et al. 2001). Adding 1000 $GtCO_2$ (equivalent to 270 Gt of C) requires a 40%-60% increase in the capacity of the terrestrial biomass storage. Assuming a constant ratio of stored carbon to land, an average of 50% more land is required for the suggested negative emissions target by the IPCC.

impacts due to water consumption and land-use change (Smith et al. 2016; Bonsch et al. 2016).

Combined Mineral Capture and Storage (CMCS) and Direct Air Capture (DAC) remove carbon dioxide from the air by a physical or chemical sorption process. The significantly dilute CO_2 concentration in the air dictates some cost and technological constraints to the system and mandates some unique sorbent characteristics (Shi et al. n.d.). Silicate material in CMCS chemically binds CO_2 in the form of carbonate (usually calcite or magnesite) (National Academies of Sciences 2019; Klaus S. Lackner et al. 1995). A relatively slow rate of reaction for CO_2 mineralization imposes another challenge on CMCS (Klaus S. Lackner et al. 1995); however, this technology has the advantage of combining the capture and storage steps. The *in situ* capacity of CMCS is limited, and with the assumption that regeneration of the minerals via the calcination process is energy-intensive and expensive, increasing in CMCS capacity by providing fresh minerals through mining and crushing is associated with a high cost (National Academies of Sciences 2019).

Unlike CMCS, the capture and storage processes are not tied together in DAC. Therefore, DAC offers more flexibility for CO_2 storage or utilization after the capture process. Since the global concentration of carbon dioxide is more or less constant (Elliott et al. 2001), DAC can be exploited as a means of *in situ* CO_2 production where it is needed. This eliminates the cost of CO_2 transportation (K.S. Lackner 2009; D. W. Keith, Ha-Duong, and Stolaroff 2006).

Direct Air Capture (DAC)

This dissertation focuses on DAC technology. Even though in its infancy, DAC has been identified as one of the most promising NETs in terms of scalability and minimizing unknown risks associated with technology (D. Keith 2009). Unlike BECCS, DAC is a net consumer of energy and in large-scales, it is not constrained by planetary limits (Heck et al. 2018). DAC has a significantly smaller footprint and water consumption compared to BECCS (Smith et al. 2016). Carbon dioxide is a more or less inert gas in the atmosphere, while in the ocean, it is involved in the carbonate ions equilibrium (Lord et al. 2016; Feely et al. 2004). Therefore, it is easier to assess the potential risks and impacts of DAC. Additionally, compared to oceans, the mass of unwanted molecules that must be processed to capture 1 ton of CO_2 is 10 times smaller in the air and this decreases the energy intensity of DAC. DAC has a much simpler life-cycle input/output analysis to measure the absolute amount of carbon removed from the environment and does not face the carbon accounting challenges of the bioenergy and biofuel Life-Cycle Analysis (LCA) (Gough and Upham 2011; Cherubini and Strømman 2011; McKone et al. 2011; Wiloso et al. 2016). As mentioned, DAC eliminates the need for CO_2 transportation while BECCS, similar to post-combustion capture, requires a pipeline infrastructure for transporting CO_2 from power plants to storage cites (N. Johnson, Parker, and Ogden 2014). Finally, DAC has a higher potential for cost reduction through learning compared to CMCS (National Academies of Sciences 2019).

Even though on a cost reduction path, DAC is still expensive for large-scale implementation as a climate mitigation technology. The National Academies of Sciences (2019) (NAS) states that “limitations in basic science and engineering knowledge to [*sic*] do not appear to limit the deployment of manufactured direct air capture processes today. Rather, the absence of a natural economic driver, such as a cost on carbon, limits the rapid testing and deployment of direct air capture."

A natural economic driver is achievable if DAC cost approaches the price of merchandise carbon dioxide sold in different industries. This work investigates cost reduction pathways for DAC and applications for the technology to be implemented at commercialization scales. DAC has attracted attention from the public sector, as well as different private companies and research groups around the world (Sanz-Pérez et al. 2016; Bourzac 2017; E. Bajamundi et al. 2019; Cressey 2015). Climeworks, a Swiss company focusing on DAC commercialization, has built its first pilot plant in Hinwil, Switzerland (Gertner 2019). Carbon Engineering in Canada (Krauss 2019) and Silicon Kingdom Holding Ltd in a joint project with Arizona State University in the United States (*Bloomberg.Com* 2019; *Reuters* 2019), are among the companies currently pursuing commercialization of DAC. Each one of these companies has developed their unique DAC system varying in the type of sorbent, the choice of the passive or active contactor (i.e., using blowers versus the exploiting the kinetic energy of wind for contacting air and sorbent) and the choice of unit scale (i.e., small modular designs versus large-scale plants). Additionally, DAC sorbent design is a rapidly growing field of research and every year, tens of new sorbent materials are introduced by researchers all around the world (Sanz-Pérez et al. 2016; Shi et al. n.d.; Goeppert et al. 2012). This environment of active research and development has put the DAC technology under the spotlight with questions about the large-scale feasibility of technology.

DAC Integration in Energy Systems

The role of DAC, in a future energy system, has been a major source of disagreement in the policymaker and scientific community. This is largely due to comparing DAC with other classical chemical separation processing without considering the principal difference of DAC and more innovative separation approaches (K.S. Lackner 2009). When compared with the traditional separation processes with similar concentrations of the target material, DAC cost estimation will be strikingly high (House et al. 2011). However, Lackner (2013) argues an incremental skimming of CO_2 off the air, while using the free of charge kinetic energy in a passive system, makes DAC fundamentally different than mainstream separation processes.

DAC skeptics criticize its relatively higher initial cost compared to other carbon capture technologies such as post-combustion capture (House et al. 2011; Socolow et al. 2011; Mazzotti et al. 2013) and some studies point out challenges that an exceedingly large-scale DAC implementation may be faced (Realmonte et al. 2019). Even when considered as an option, DAC is often limited to its application as a NET which must be implemented only after the current emission rate is reduced to zero. Some refer to DAC as an option for reducing emissions from smaller mobile sources of CO_2, where large point source capture technologies cannot be implemented, or for capturing the leftover emissions after large point source capture (Klaus S. Lackner and Brennan 2009). However, DAC is not typically considered as a mitigation technology for large point source emissions which are responsible for almost half of the total global emission. Even for emission reduction from small mobile sources such as cars, airplanes, and trains, replacing fossil fuel with electricity and energy storage is often mentioned as a more reliable alternative. The state of turmoil about the future of DAC can only be resolved when a better understanding of its potential applications is achieved in different sectors of the global energy system.

DAC Application in the Electricity Sector

According to the United States Environmental Protection Agency (EPA), electricity generation is responsible for about 28% of total greenhouse gas emissions in the United States (EPA 2018). As the main large point source emissions, CO_2 from coal and natural gas power plants can be reduced or eliminated by pre-combustion, oxy-combustion and post-combustion technologies (Metz et al. 2005). DAC has not been considered as an option for carbon removal from the electricity sector. This work, on the other hand, takes a step forward and investigates the DAC potential for the decarbonization of electricity generation.

Even though DAC cost has been proven to be cheaper than initial estimations,[2] the technology is still expensive as compared to the \$50-100/tCO_2 cost of post-combustion capture (McKinsey and Company 2008; Rochelle 2009; Socolow et al. 2011). Post-combustion capture is often mentioned as an economically feasible solution for new power plants, with high efficiency and utilization levels. Many of the existing coal and natural gas power plants, however, are not designed for post-combustion capture

[2] Among DAC cost estimations the >\$1000/tCO_2 by House et al. (2011) and \$600/tCO_2 by the American Physical Society (Socolow et al. 2011) are the highest. This high cost was opposed by Lackner's (K.S. Lackner 2009) and Keith's (D. W. Keith, Ha-Duong, and Stolaroff 2006) predictions (\$220 and \$136/tCO_2, respectively). Furthermore, the cost of Climeworks' pilot plant (Gertner 2019) and Carbon engineering's calculations for a large-scale process (D. W. Keith et al. 2018) invalidated the high-end estimations of DAC cost.

and even those that can be retrofitted will experience a considerable increase in the cost of electricity production (Rao and Rubin 2002).

The cost of post-combustion capture for decarbonizing the existing fossil fuel-burning power plants has been rarely studied (Zhai, Ou, and Rubin 2015). One would expect that the cost of post-combustion capture in the existing energy infrastructure is higher than what it is typically perceived. This study investigates the cost of decarbonizing of the existing US natural gas power plant fleet. Natural gas-fired electricity generation is the main focus in this work since it has been on the rise in the United States and is slowly replacing the coal-fired electricity (EPA 2016). The majority of the natural gas electricity is produced by Natural Gas Combined Cycle (NGCC) plants and a small fraction of it comes from peaker plants (e.g., gas turbines and internal combustion engines) which provide electricity during the peak demand (EPA 2016). This dissertation considers post-combustion capture for the NGCC fleet since peaker power plants are not typically considered for carbon capture and storage. Peak load power plants can be assumed as emitters between large point source and small mobile emitters. These plants are stationary, however, many of them are scattered in a large geographical area and their emission rate is smaller than other power plants since they only operate during peak hours. Here, DAC is considered as an alternative to address CO_2 emissions from these plants. This raises the first research question of this analysis:

RQ1. How does the implementation of direct air capture and post-combustion capture technologies compare in the decarbonization cost of the existing natural gas power plant fleet in the United States?

The cost of capture by post-combustion capture and DAC may start decreasing if more power plants are retrofitted and more DAC units are built. It has been empirically observed that adoption and diffusion of a technology result in a cost reduction in the unit output of that technology (Wright 1936). This observation is known as the impact of learning-by-doing. The cumulative production of solar photovoltaic (PV) modules, for instance, has increased by 35 folds between 2007 and 2017. As a result, the cost of solar PV has reduced from about $4 to $0.35 per Watt in this period (Comello, Reichelstein, and Sahoo 2018). In this dissertation, a cost projection model based on learning-by-doing is developed to estimate the large-scale cost of post-combustion capture and DAC technologies.

Two different scale-up strategies are assumed in this work. Post-combustion capture units are inherently large and custom-made to match the specific plant and flue gas stream that they are designed for. According to the economy of scale, the cost of post-combustion capture is reduced when the unit size increases. On the contrary, the design of a DAC unit is relatively more flexible since DAC is a stand-alone unit and the input stream (air) is more or less consistent. CO_2 processing after capture will not be affected if one large-scale, custom-made DAC unit or multiple smaller modular units deliver the required CO_2. Therefore, unlike post-combustion capture, the nature of DAC offers two different scale-up pathways. However, the economy of scale or mass-production - which one facilitates the cost reduction?

In this study, scale-up and learning through mass production of small modular DAC units are compared with the learning of custom-made large post-combustion plants. The hypothesis is that DAC will experience a more effective cost reduction, and this will result in a competitive DAC price when it comes to the decarbonization of the US NGCC power plant fleet. This study considers a range of different scenarios for each technology to answer the question:

RQ2. How do mass production and economy of scale compare in cost reduction through learning-by-doing when it comes to direct air capture and post-combustion capture for decarbonization of the US natural gas power plant fleet?

In this case study, the initial lower cost of post-combustion capture is challenged by the imperfection of a real-world energy system (i.e., the existing US NGCC power plant fleet) when a high level of decarbonization is desirable. In the next step, the potential of DAC as a complementary technology for large point-source capture is analyzed. Finally, the cost of large-scale post-combustion capture and DAC are projected and compared.

A Sorbent-Based Techno-Economic Model for DAC

The challenge of capturing carbon dioxide from the atmosphere demands an unconventional family of sorbents. Even though high CO_2 affinity at low partial pressures (about 0.4 millibars) is a crucial property, an excessively large binding energy between a sorbent and CO_2 molecules is not desirable. A strong sorbent-CO_2 bond results in an energy-intensive and expensive sorbent regeneration process. The National Academies of Sciences (2019) emphasizes the need for improvement in DAC sorbent performance as an important cost reduction strategy. In a well-designed DAC system, sorbent must comprise a large portion of the total weight and its cost significantly influences the total cost of the capture (Azarabadi and Lackner 2019). DAC sorbent development is a fast-growing area of research and every year a variety of sorbent ranging from liquid hydroxide solutions to porous amine-based solid sorbents are suggested for DAC (Sanz-Pérez et al. 2016; Shi et al. n.d.).

Although DAC sorbents can be liquid or solid, the NAS report estimates a higher improvement and cost reduction potential for solid sorbents (National Academies of Sciences 2019). Most of these sorbents are composed of a highly porous material (i.e., zeolite, activated carbon, etc.) either with or without an amine functional group attached to it (Shi et al. n.d.). The current sorbent development efforts have been mainly focused on improving the capture capacity, kinetics and regeneration energy, however, the testing is mostly conducted in laboratories under controlled conditions (Azarabadi and Lackner 2019). While many of the newly synthesized materials show a promising capture capacity and kinetics, they frequently lack information about their performance and cost for large-scale deployment. Sorbent longevity in the real-world DAC condition in addition to sorbent commercial cost are largely neglected among the sorbent developer community. These two parameters are closely tied to each other and they are as important as capacity and kinetics to assess the commercialization potential of a new DAC sorbent (Azarabadi and Lackner 2019). This dissertation investigates the relative importance of each one of these sorbent characteristics (capture capacity, kinetics, longevity, and sorbent cost) in determining the cost of DAC to answer the question:

RQ3. What effect do sorbent characteristics and cost have on the cost of direct air capture?

Another way of looking at this problem is to set a CO_2 price target as an exogenous variable taken from a CO_2 market. The DAC business developer does not have control over the price target; however, it can choose a sorbent that makes the business profitable. To make such a decision, this work develops a model to determine a maximum affordable budget for each sorbent. The model determines the sorbent budget by considering the given sorbent characteristics (i.e., capacity, kinetics, and longevity) and the CO_2 price target. Such a model can answer the previous research question rephrased as:

RQ3. How can the commercialization potential of a DAC sorbent be quantified based on its characteristics and the CO_2 market?

The generalized techno-economic model developed in this work provides a net present value (NPV) equation for any sorbent regardless of its capture mechanism and system specifications. This allows calculating the maximum allowable budget for any given DAC sorbent. The maximum allowable budget is an important indicator that shows how much a DAC sorbent is worth rather than how costly its production will be. When compared with the cost of sorbent production, the maximum allowable budget demonstrates the commercialization potential of a sorbent.

Dissertation Outline

This dissertation is structured in 7 chapters and the following chapters focus on answering the research questions raised in this introduction:

- Chapter 2: This chapter discusses DAC integration into the existing energy system and elaborates on the short-term and long-term roles of DAC in facilitating carbon emission reductions as well as negative emissions. This section further investigates the complementary role of DAC in the decarbonization of the transportation sector and electricity generation. It will cover a broad overview of how the research questions posed in this dissertation can fill important knowledge gaps when DAC deployment is considered in energy systems. Finally, this chapter argues how the implementation of DAC in the current energy system is in line with the promise of negative emissions in the second half of the century.

- Chapter 3: The third chapter focuses on calculating the impact of post-combustion capture retrofit on the cost of electricity and carbon capture by extracting electricity generation data for the US NGCC power plant fleet. Two main databases, EPA's Emission & Generation Resource Integrated Database (eGRID) (EPA 2016) and EIA's form 923 (EIA 2018) are used for NGCC plants' data. Operational data and plant characteristics for each NGCC unit in the United States are extracted from the two aforementioned databases. After developing a post-combustion retrofit cost analysis model, the cost avoided CO_2 is estimated for each NGCC unit. Finally, the cost of DAC is compared to the cost of post-combustion capture at different decarbonization levels.
- Chapter 4: When a learning-by-doing is considered for DAC and post-combustion capture, the cost model recalculates new CO_2 capture costs for all power plants. The impact of learning-by-doing has been observed only empirically and a sensitivity analysis is necessary for a reliable comparison between the future costs of post-combustion capture and DAC. This chapter considers different scenarios consisting of a range of learning rate values and initial costs for each technology. Finally, the cost of the total decarbonization is minimized by finding the optimum carbon reduction portfolio consisting of post-combustion capture and DAC.
- Chapter 5: Built upon maximizing the net present value of a DAC system, this chapter develops a generalized Techno-Economic Analysis (TEA) to valuate a

sorbent based on its characteristics (cyclic capacity, cycle time, and degradation rate), CO_2 market, and system's capital and operating and maintenance (O&M) costs. The model output is the maximum allowable budget for a sorbent and its operational lifetime. In this model, lifetime is not only a function of the sorbent material but also dependent on other system costs such as capital and O&M costs. With a commercialization perspective, this model is especially helpful in identifying the most important parameters that the future DAC sorbent research should focus on.

- Chapter 6: This chapter demonstrates different applications of the sorbent TEA model and considers case studies to show the usefulness of the model. A comprehensive list of DAC sorbent and their characteristics are collected from the literature and their commercialization feasibility is assessed by the model. It also shows how the same model can be used for optimizing DAC operation by changing cycle time in a device with a known sorbent.
- Chapter 7: The final chapter concludes the answers to the research questions of this dissertation and takes another look at the big picture energy system elaborated in Chapter 2. This chapter demonstrates how the previous chapters shape components of the future energy system and the other questions that must be answered to get us closer to deep decarbonization of energy systems.

Table 1. Chapter 2 summary

Chapter 2: Role of Direct Air Capture in Decarbonizing Energy Systems	
Research Question	How does direct air capture fit in the current energy system? Aside from providing negative emissions, can DAC facilitate achieving carbon-neutrality in electricity and transportation systems? What are the added values of involving DAC in the decarbonization of these systems?
Approach	By reviewing the current carbon reduction strategies for the electricity and transportation sector, this chapter establishes a framework for deep decarbonization of these systems by utilizing DAC.
Deliverable	Chapter 2 discusses potential applications for DAC out of the negative emissions realm and connects it to our existing energy infrastructure. This shows the importance of research questions answered in the following chapters.
Intellectual Merit	Chapter 2 critically reviews the limitations of the more common carbon mitigation strategies (e.g., increasing energy efficiency, utilizing renewables, and conventional carbon capture methods) from a system perspective. It then elaborates on the complementary role of DAC in addressing these limitations. This chapter puts forward a research agenda to investigate the feasibility of DAC integration in the current energy infrastructure.

Table 2. Chapter 3 summary

Chapter 3: Cost of Decarbonizing US Natural Gas Power	
Research Question	How does the implementation of direct air capture and post-combustion capture technologies compare in the decarbonization of the existing natural gas power plant fleet in the United States?
Approach	After extracting a database for the existing US natural gas power plant fleet, this work builds a cost analysis model to estimate the cost of post-combustion retrofit for each power plant. In the next step, Chapter 3 identifies the potential of DAC by comparing its cost with the cost of post-combustion capture retrofit.
Deliverable	This work resulted in a peer-reviewed journal article: (Azarabadi and Lackner 2020)
Intellectual Merit	This chapter challenges the post-combustion capture technology as comprehensive decarbonization solution for the electricity sector. This quantitative analysis shows that in a realistic energy system, the potential of post-combustion capture technology is lower than what it is perceived. As a result, DAC can be occasionally cheaper than post-combustion capture.

Table 3. Chapter 4 summary

Chapter 4: The Impact of Learning-by-Doing on the Cost of Decarbonization	
Research Question	How do mass production and economy of scale compare in cost reduction through learning-by-doing when it comes to direct air capture and post-combustion capture for decarbonization of the US natural gas power plant fleet?
Approach	Focusing on the decarbonization of US natural gas power, this work compares two different scale-up approaches for DAC and post-combustion capture technologies. A cost projection model is developed to implement DAC through the mass production of relatively small and modular units. The cost of post-combustion capture, on the other hand, is projected when large custom-made units are built.
Deliverable	This work resulted in a peer-reviewed journal article: (Azarabadi and Lackner 2020)
Intellectual Merit	This chapter demonstrated how the inherent features of DAC and the flexibility in design offer an advantage in cost reduction through learning. Generally, choosing mass production over the economy of scale offers a faster price reduction path for technologies. However, only DAC can exploit this leverage. Chapter 4 quantifies this leverage and points at the most effective cost reduction strategy for DAC.

Table 4. Chapters 5 and 6 summaries

Chapters 5 and 6: A Sorbent-Focused Techno-Economic Analysis of Direct Air Capture and its Applications	
Research Question	What effect do sorbent characteristics and cost have on the cost of direct air capture? In other words, how can the commercialization potential of a DAC sorbent be quantified based on its characteristics and the CO_2 market?
Approach	Chapters 5 establishes a Net Present Value (NPV) equation based on sorbent characteristics, CO_2 market, and ongoing costs of a DAC system. Based on the NPV equation, this work develops an analytic relationship for the Maximum Allowable Budget (MAB) of DAC sorbents. Moreover, Chapter 6 discusses different applications of the model, especially measuring MAB for the existing sorbents in the literature and sorbent performance analysis in a DAC system.
Deliverable	This work resulted in a peer-reviewed journal article: (Azarabadi and Lackner 2019)
Intellectual Merit	By developing an NPV model, this analysis provides a dollar value for a DAC sorbent and determines how much a sorbent is worth. This value can be compared to the cost of production for a sorbent and determine its commercialization potential. This model demonstrates the most important sorbent characteristics and set standards for a promising DAC sorbent. In Chapter 6 the model is used to study the DAC sorbents suggested in the literature and weaknesses of each sorbent category are identified. In another application, the model is utilized to optimize the cycle time of a DAC device to achieve the minimum carbon capture cost.

CHAPTER 2

ROLE OF DIRECT AIR CAPTURE IN DECARBONIZING ENERGY SYSTEMS

To limit the global temperature rise to below 1.5 °C, a net-zero carbon economy must be achieved by midcentury (Masson-Delmotte et al. 2018). Establishing a sustainable energy infrastructure demands a radical shift in our engineering mindset and lifestyle. The urgency of climate change mandates a portfolio of short and long-term mitigation measures since the decarbonization of the global energy system does not have a single simple solution. In this chapter, the goal is to contemplate the status quo for the United States' transportation and electricity generation systems and examine the proposed sustainable solutions for their decarbonization. In the United States, transportation and electricity generation are collectively responsible for about 60% of total greenhouse gas emissions (EPA 2018), so this discussion is mainly focused on these two sectors. Toward the end of this chapter, the impact of Direct Air Capture (DAC) on the current system is elaborated in detail and the added value derived from DAC as a short and long-term solution is investigated.

Electricity Generation and DAC

Electricity generation is responsible for 28% of the US total greenhouse gas emissions (EPA 2018). About two-thirds of the emissions come from coal-fired power plants while burning natural gas in gas turbines and steam generators are responsible for the rest (EPA 2016). Different strategies have been offered for reducing the electricity-related emissions including:

- Improving efficiency: Efficiency improvement in electricity generation, as well as end-user consumption, can rapidly reduce greenhouse gas emissions from the electricity grid (Edenhofer et al. 2014). Moreover, the more efficient practice of dispatch shifting, in a way that the majority of generation (baseload) comes from lower-emitting units, can further reduce the carbon dioxide emissions.

- Switching fuels: Increasing the share of renewable electricity and extending the life of existing nuclear plants can reduce the emissions from electricity generation (Masson-Delmotte et al. 2018; Edenhofer et al. 2014). Converting coal-fired boilers to natural gas, or co-firing natural gas units can also reduce the amount of CO_2 emissions. Biofuels burning boilers also offer a reduction in greenhouse gas emissions.
- Implementing Carbon Capture and Storage (CCS): Capturing carbon dioxide from power plant stacks, before entering the atmosphere, and storing it in deep underground storage reservoirs has been suggested as a solution for decarbonizing fossil fuel power plants (Metz et al. 2005). CCS combined with biofuels combustion for electricity generation can potentially result in negative carbon emissions.

Most of the aforementioned strategies can reduce the amount of greenhouse gas emissions from electricity generation; however, they cannot fulfill deep or full decarbonization of the electricity sector. The Intermittency issue for solar and wind electricity is a technological obstacle for a 100% renewable-powered electricity grid. Although solutions such as grid extension as well as short-term and long-term storage from several hours to several months can increase the penetration of renewable electricity into the grid, they are still not commercially available (Schaber, Steinke, and Hamacher 2012; Blakers, Lu, and Stocks 2017; Esteban, Zhang, and Utama 2012; Steinke, Wolfrum, and Hoffmann 2013; Pleßmann et al. 2014). A high renewable electricity integration would also require the management of annual storage cycles to address seasonal mismatches between supply and demand. Even year-to-year variability in regional insolation can be significant (Che et al. 2005; Deser and Blackmon 1993).

CCS is considered a solution as long as the technological challenges for a fully renewable electricity grid exist. When it comes to CCS for large-scale electricity generation, post, pre, and oxyfuel-combustion technologies are usually considered as the only feasible options for CO_2 mitigation (Metz et al. 2005). Post-combustion capture, mainly in the form of amine scrubbing units, is a relatively mature technology that has gained a lot of attention in the decarbonization of the existing energy infrastructure. Amine scrubbing can theoretically capture emissions from the tailpipe of any fossil fuel-fired power plant without making a significant change on the electricity generation block of the plant. However, this technology consumes heat and electricity produced within the plant and thus lowers its output, unless larger or auxiliary boilers are installed. When widely implemented, this technology along with newly built plants with pre-combustion capture (namely Integrated Gasification Combined Cycle or IGCC plants) are expected to extensively reduce electricity-related CO_2 emissions (Metz et al. 2005).

Retrofitting an existing power plant with CCS is challenging from a technical and economic standpoint. Depending on the plant’s capacity, efficiency, age, and utilization level, the cost of the retrofit can vary significantly; however, retrofitting an existing power plant is typically more expensive than building a new plant with CCS and it dramatically increases the cost of electricity generation (Rao and Rubin 2002). Therefore, CCS is not generally assumed to be a practical option for many of the existing power plants, especially the older, less efficient ones that operate with a low utilization level (Zhai, Ou, and Rubin 2015).

A new power plant designed with CCS appears to be a more attractive option for CO_2 reduction; however, this does not guarantee cheap CCS. Generally, the cost of a post-combustion capture system increases the total capital cost of a power plant by 2-3 folds (Fout et al. 2018; T. L. Johnson and Keith 2004; Gerbelová et al. 2013), and depending on the power plant location, the cost of CO_2 transportation could significantly increase CCS expenses. Moreover, the cost of CCS is a function of a power plant's utilization level and this parameter fluctuates depending on the change in electricity demand, especially for non-baseload power plants. Peak load plants, for instance, might operate only a few hours per day. In 2016, roughly 45% of total fossil fuel-fired generating units in the United States were characterized as peaking power plants (EPA 2016). Implementing CCS units for these plants will not be economical even if they are new.

The capacity factor is a parameter that exhibits the utilization level of a power generating unit and is defined as:

$$CF = \frac{Annual\ Electricity\ Generation\ (MWh)}{Nameplate\ Capacity\ (MW) \times 8766(h)}$$

A Capacity factor of 1.0 in a year means a unit operated fulltime, full capacity in that year. As shown in Table 5, the United States Environmental Protection Agency (EPA) identifies baseload, intermediate, and peak load power plants based on their capacity factor (EPA 2016).

Table 5. Power plant categories based on utilization level

Power Plant Category	Capacity Fact Range
Baseload	CF > 0.8
Intermediate load	CF > 0.2 & CF < 0.8
Peak load	CF < 0.2

An easy way to observe the share of each category from the total electricity generation is to plot the cumulative annual generation against the capacity factor of each generating unit. Figure 1 shows this curve for the US coal power plant fleet operation for several years between 2009 and 2018 (data from EPA 2016). While roughly 20% of the generation in the early years (2009 and 2010) comes from the baseload plants, the share of these plants reduces to less than 10% in 2014 through 2018. In other words, the upward trend of the curves demonstrates that the utilization level of the US coal-fired power plants has been on the decline. This is mainly due to an increase in natural gas production and an increase in the number of natural gas-fired generating units. The share of natural gas in the utility-scale electricity generation has increased from 23% in 2009 to over 35% in 2018 (EPA 2016). The lower utilization level increases the cost of CCS even more (Zhai, Ou, and Rubin 2015), while an early retirement of these coal plants due to environmental consideration forces an economic loss upon society.

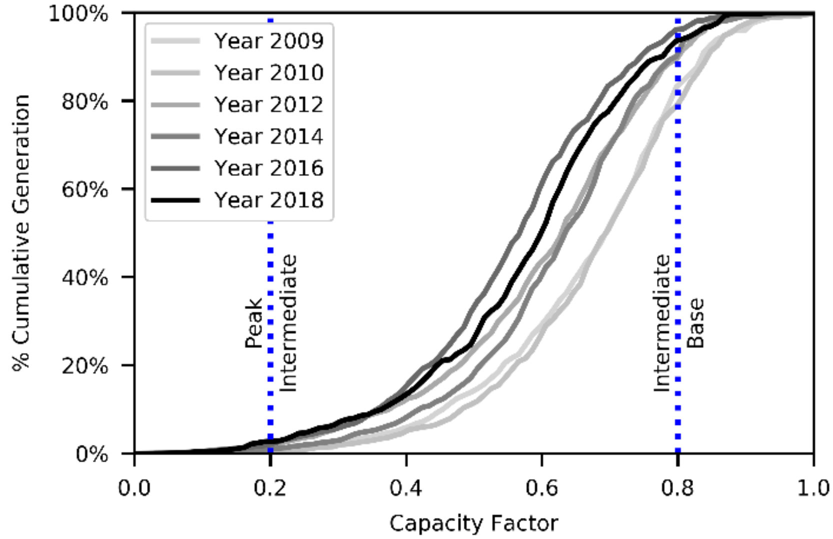

Figure 1. Cumulative annual generation of US coal-fired power plant fleet against capacity factor.

A similar pattern of decline in the utilization level is expected to be observed for all fossil-fuel plants (coal and natural gas) as the share of renewables increases in the grid. In the United States, the annual utility-level electricity generation from solar and wind, as intermittent renewable sources, has respectively increased by 70 and 3.5 folds since 2009 (EPA 2016). To facilitate the integration of solar and wind electricity into the grid, the dispatchable power plant fleet (mainly natural gas plants) must decrease their output level during peak hours of intermittent electricity generation (when the sun is shining and the wind is blowing). This lower utilization level makes it more expensive to capture CO_2 from these plants. Additionally, a high level of fluctuation in the natural gas plants' output, and as a result, a highly volatile flue gas stream, imposes an additional challenge on the operation of a CCS system such as post-combustion capture. The absorption and stripping columns in a post-combustion capture process cannot easily handle high fluctuations in the input gas stream (Y.-J. Lin et al. 2012).

DAC, as a standalone CCS unit, is not attached to a power plant and this could be essential to cost reduction for decarbonization of the electricity grid. A DAC device can be optimized to operate when electricity is cheap or in some locations when the excessive solar electricity is curtailed. Consequently, the cost of carbon capture by DAC will be independent of a specific power plant and utilization level. Even when all the conditions for post-combustion capture are provided and its cost is lower than DAC, the optimum CO_2 removal efficiency for this technology is typically between 70%-95% (Rochelle 2009). DAC, on the other hand, can remove the residual CO_2 emissions and go beyond that to address the background and lifecycle emissions of electricity generation by power plants (van der Giesen et al. 2017).

Considering the inherent limitations of post-combustion capture, this dissertation investigates the true potential of this technology for decarbonization of the electricity grid and compares its cost with that of DAC. As a case study, this work focuses on electricity generation from the existing US natural gas power plant fleet. Natural gas-fired power plants generate about 35% of the total US electricity (EPA 2016). Based on 2016 data, this case study estimates the cost of post-combustion capture for those generating units that are suitable for CCS retrofit and compares the cost with that of DAC. Put differently, the cost of post-combustion capture is treated as a tangible reference to evaluate the role of DAC in the decarbonization of the US electricity grid.

The result of this work illustrates that although separating CO_2 from the air (400 ppm concentration) is thermodynamically more challenging than separating it from a power plant flue gas (between 5-15% concentration), DAC can occasionally be more affordable than post-combustion capture. DAC can avoid idle capital in plants that are not highly utilized or prevent large capital expenditure on plants that are difficult to retrofit because of their age or site-specific challenges. DAC can also avoid transporting CO_2 over large distances. The goal is to quantify these differences.

Transportation and DAC

The US transportation sector is responsible for roughly 29% of total greenhouse gas emissions (EPA 2018). Over half of the emission comes from gasoline and diesel burned by passenger cars and light trucks and the remaining is from the rail, air and marine transportation (EPA 2018). Various solutions have been proposed for reducing transportation-related emissions. These solutions are including but not limited to:

- Using alternative fuels: This includes the wide-spread implementation of hybrid and electric vehicles as well as switching to low-carbon fuels such as Compressed Natural Gas (CNG) for buses or biofuels for passenger cars (Edenhofer et al. 2014).
- Optimizing operating practices: This solution generally includes reducing engine idling (Canada 2011; Shancita et al. 2014). This can be done by optimizing operation habits for light and heavy-duty vehicles (Shancita et al. 2014; Stodolsky, Gaines, and Vyas 2000), voyage planning for ships (Sherbaz and Duan 2012; McCollum, Gould, and Greene 2010), and reducing the average taxi time for airplanes (McCollum, Gould, and Greene 2010; Deonandan and Balakrishnan 2010; Edem, Ikechukwu, and Ikpe 2016).
- Improving fuel efficiency: Improving the efficiency of jet and internal combustion engines by redesigning, implementation of hybrid engines, and other methods can reduce the emissions from the transportation sector (McCollum, Gould, and Greene 2010; Morrell 2009; Daggett, Hendricks, and Walther 2006). Weight reduction by

implementing novel materials and improvements in the aerodynamic design of vehicles are also effective solutions for reducing greenhouse gas emissions (McCollum, Gould, and Greene 2010; Lee et al. 2001).

- Optimizing travel demand: Improving travel efficiency by investment in public transportation and more innovative urban planning can reduce the number of miles that people travel by personal vehicles and as a result reduces the emissions from transportation (Marshall 2008; Hankey and Marshall 2010; Glaeser and Kahn 2010).

While these solutions are necessary to reduce carbon emissions, they are not sufficient for a zero-carbon transportation system. Even electric vehicles, which do not emit carbon dioxide while operating, can be an emitter depending on the carbon intensity of the electricity grid in the location they are used. Although an electric vehicle is more efficient than an internal combustion vehicle, it basically converts mobile emissions to a point source emission from the electricity grid.

When long-term sustainable solutions for decarbonization of the transportation sector are considered, two main solutions are available. One is the use of electric vehicles fueled with renewable electricity and the other is hydrogen-burning vehicles fueled with renewable hydrogen (i.e., hydrogen produced by water electrolysis with renewable electricity).

These options are constrained not only by technological limitations but also by financial ones. Renewable electricity for charging electric vehicles is not yet available in large scales. Similarly, current hydrogen production is not fully sustainable since about three-quarters of hydrogen comes from natural gas (IEA 2019). Onboard hydrogen production by methanol reforming has been suggested for onboard carbon capture

(Damm and Fedorov 2008); however, the process is far from commercialization and requires a considerable change in the existing transportation infrastructure. Energy storage in the form of electricity or liquid hydrogen is yet to be demonstrated for commercial aviation and marine transportation. Additionally, significant uncertainty is associated with the cost of energy storage and transportation infrastructure when these technologies are employed at scale. The small volumetric energy density of hydrogen (even when stored in the liquid form) imposes a significant constraint on hydrogen storage and use in the form of fuel (Sinigaglia et al. 2017).

DAC can offer several advantages when considered as a means for emission reduction from the transportation sector. As a technology in its infancy, DAC has a relatively high initial cost; however, it is already implemented in commercial scales and its cost is decreasing (Gertner 2019; D. W. Keith et al. 2018; Fasihi, Efimova, and Breyer 2019; Climeworks 2020). CO_2 emissions from transportation in all forms can be captured by DAC with no significant change in the current transportation infrastructure. DAC application in the transportation system may prolong the use of fossil fuel, although this is not considered a sustainable alternative in the long run (Jamieson 1996; A. C. Lin 2013). However, DAC offers a relatively straightforward path towards emission reduction until more sustainable alternatives become widely available.

A generalized, easy to understand, yet conclusive mathematical model is necessary to assess the feasibility of DAC for different applications and comparing it with the alternatives that are still under development. The second part of this dissertation (Chapters 5 and 6) is dedicated to the development of this model and its applications. One of the unique features of this model is that it can receive the price of carbon reduction as an input constraint that has to be met by the DAC system to be economically feasible. This constraint can be adopted from the total cost of the alternative mitigation technologies (i.e., electric or hydrogen vehicles), so the model provides the minimum requirements of an economically feasible DAC system.

The economic model is focused on the most essential component of a DAC device, the sorbent. The sorbent dictates the efficiency and regeneration energy of the process and comprises a considerable portion of the cost in a DAC device. Improvements in sorbent characteristics (e.g., CO_2 capacity, kinetics, and stability) can immensely affect the cost of DAC. In this analysis, the Net Present Value (NPV) for a DAC device is calculated based on various costs (including sorbent cost) and the cash flow generated from selling the captured CO_2. Based on different scenarios for the price of CO_2 (cash flow), the model generates a dollar value as the maximum allowable cost (budget) for a sorbent.

Different CO_2 (or CO_2-eq) prices based on alternative mitigation technologies could be used in the model to investigate the commercialization potential of the currently available DAC sorbents for different applications. The results demonstrate that most DAC sorbents lack the required stability to achieve a reasonable budget. An unstable sorbent which significantly degrades in less than 1000 loading-unloading cycles, must be reasonably cheap (below $1 per kg) in order to be economically sensible, while manufacturing most of the currently available sorbents costs tens if not hundreds of dollars per kg.

Negative Emissions and DAC

According to the International Energy Agency (IEA), 33 $GtCO_2$ was globally emitted to the atmosphere in 2019 (IEA 2020). The increase in the rate of CO_2 emission is far from stabilizing the concentration of atmospheric CO_2 and meeting the ambitious goals set in the Paris Agreement. Thus, pulling carbon dioxide back out of the atmosphere seems inevitable. As discussed in the previous chapter, DAC is a promising negative emissions technology because it is a straightforward technological fix for the climate change problem (Sarewitz and Nelson 2008).

CO_2 captured by DAC can be stored or sequestered safely. When coupled with the vast amount of solar electricity at peak production periods, CO_2 from DAC provides a unique opportunity for synthetic fuel production (Klaus S. Lackner et al. 2012). Liquid hydrocarbons are by far the cheapest form of energy storage, mainly because of their high energy density, ease of transportation, and ease of use. This strategy facilitates the integration of intermittent solar electricity into the electricity grid and transportation system (Lewis and Nocera 2006).

In a futuristic energy system where pipelines are the essential means of energy transportation across the United States, carbon-neutral liquid hydrocarbon from renewable electricity and DAC carbon dioxide is produced in the southwest (where solar electricity is cheap and abundant) and is transported to the power plants all around the country. Power plants can burn this carbon-neutral fuel without increasing the net total carbon emissions. Those generating units with economically viable post-combustion systems in place can capture and store the CO_2 emissions from burning the synthetic fuel and go carbon negative. Liquid hydrocarbons can be produced and cheaply stored in storage tanks during the summer (when solar electricity is abundant) for consumption in the winter.

Moreover, carbon-neutral synthetic fuel can eliminate the complications of life-cycle carbon accounting for electric vehicles. The net CO_2 emission from electric vehicles depends on the CO_2 content of the electricity grid and determining greenhouse gas emissions from electricity is associated with uncertainties and methodological challenges (Soimakallio, Kiviluoma, and Saikku 2011). Without a significant cost from building new infrastructure, the distribution system in place for fossil fuel gasoline can be utilized for synthetic fuel. Internal combustion engines will remain untouched, while the carbon-neutral liquid hydrocarbon will replace fossil-based diesel and gasoline.

Conclusion

This dissertation considers the economic feasibility of DAC in and of itself and investigates the most important parameters of a DAC system in a cost analysis. The first part of the analysis investigates the integration of DAC into the current US electricity generation system. The integration of DAC not only provides a short-term cost reduction for decarbonization in major CO_2 emitting sectors but also paves the way towards the necessary negative emissions in the second half of the century. To provide a detailed example, this dissertation explores the case study of decarbonizing US natural gas-fired power plants and compares the cost of DAC with the more conventional alternative, post-combustion capture. Future cost reduction due to the learning-by-doing phenomenon is projected for both DAC and post-combustion capture and the technological characteristics that lead to a faster cost reduction are identified. In the second part, this dissertation looks exclusively at DAC in its general form without considering a specific

DAC design. The price of CO_2 and the discount rate are two exogenous variables in this model that provide the opportunity to compare DAC with other mitigation technologies.

CHAPTER 3

COST OF DECARBONIZING US NATURAL GAS POWER

Introduction and Objectives

In the United States utility level electricity emissions, although on a gradual declining path, contributed about a third of total greenhouse gas emissions (EPA 2018). The replacement of coal with cheap unconventional natural gas is the primary reason for the recent reduction in the US CO_2 emission (EIA 2020), increasing the importance of natural gas power as a source of greenhouse gas emissions. In spite of the current reduction in emissions, the United States, along with other industrialized countries, is not on a path to deliver the promises made in Paris (Victor et al. 2017).

The main effort in the decarbonization of dispatchable electricity generation has been focused on Carbon Capture and Storage (CCS) in the form of post-combustion capture with liquid sorbents. Due to its similarity to other pollution control technologies, post-combustion capture technology is more mature than other forms of CCS. Even though it lends itself to retrofitting existing plants, post-combustion capture is usually considered for new power plants. The cost of retrofitting existing power plants is generally higher than the cost of incorporating CCS into a new plant (Rao and Rubin

2002). Nevertheless, under the aggressive scenarios for decarbonization considered today (Masson-Delmotte et al. 2018), retrofitting existing plants will be important.

Rubin and colleagues investigated the decarbonization potential of the US coal-fired power plant fleet through retrofit with commercially available amine scrubbing post-combustion systems (Zhai, Ou, and Rubin 2015). Assuming a 30% CO_2 removal goal, which is in line with the Environmental Protection Agency's (US EPA) Clean Power Plant proposal established in 2014 (EPA 2014), for each coal-fired generating unit in the 2010 US electricity grid, they concluded that 98 out of 627 units, or 24% equivalent of the US coal-fired fleet capacity, is suitable for retrofit. Their study considers a plant retrofittable if its Levelized Cost of Electricity (LCOE) after retrofit is lower than or equal to the LCOE of a benchmark new NGCC plant. Plants with higher capacity and utilization levels that are substantially amortized and can continue to operate for more than 20 years were identified as the most promising choices for CCS retrofit. An important outcome of this study was that the majority of the existing coal-fired power plants are ill-suited for post-combustion capture retrofit. This is not only due to their low efficiency or old age but also due to the low utilization level of many of these plants.

Despite the lower carbon-intensity of natural gas-fired electricity, a conversion from coal to natural gas for electricity generation falls far short of stabilizing the CO_2 concentration in air. Natural gas power plants in the United States are not generally considered for post-combustion capture; however, the majority of the natural gas generation capacity (and emissions) comes from Natural Gas Combined Cycle (NGCC) plants which could be equipped with post-combustion capture for emission reduction (Fout et al. 2018; E. S. Rubin and Zhai 2012). About 80% of natural gas electricity generation is from NGCC plants, and the remainder comes from a large number of gas and steam turbines with small capacities that are not typically considered for carbon capture (EPA 2016). Gas turbines are extensively used to generate electricity during peak hours but sit idle most of the time.

This chapter investigates the true potential of post-combustion capture technology for decarbonization of the US natural gas-fired electricity from an economic perspective and assesses the opportunity for an unconventional CCS technology, Direct Air Capture (DAC), to address the residual emissions. DAC removes CO_2 directly from the air and can, therefore, address emissions from any source.

By collecting unit-level information for the existing natural gas-fired electricity generating units, the cost of a retrofit with post-combustion capture was calculated for each unit and was compared to the cost of DAC. The cost of DAC was occasionally found to be cheaper than post-combustion capture, despite the thermodynamically greater difficulty of separating CO_2 from the air rather than flue gas (Klaus S. Lackner 2013).

Materials and Methods

The Emissions & Generation Resource Integrated Database (eGRID) (EPA 2016) was the primary source of data for this analysis. The cost of post-combustion capture retrofit was estimated for the existing NGCC units. Then the cost of the retrofit was compared with different DAC cost scenarios from commercial-scale plants and the literature.

Power Plant Databases

Typically, an NGCC unit has one or more Combustion Turbines (CT) and one Steam Turbine (ST). A power plant complex may have one or multiple NGCC units, and each NGCC unit has multiple CTs and STs. eGRID 2016 includes granular data for each CT and ST attached to the US electricity grid. The initial database was further processed to obtain a complete data record for each NGCC unit. Each record includes a unit's characteristics (nameplate capacity, age, and location) as well as its 2016 operational information (electricity generation, heat input, and CO_2 emissions). More on data mining and statistical information on NGCC units can be found in Appendix A.

The NGCC database includes 670 units. Each unit's characteristics such as age, nameplate capacity (NAMEPCAP), and net efficiency in addition to the unit's utilization level or capacity factor (CF) are the most important parameters in determining the cost of retrofit. The capacity factor is a measure of the utilization level of a power generating unit calculated as:

$$CF = \frac{GENNTAN\ (MWh)}{NAMEPCAP\ (MW) \times 8766\ (h)}$$

GENNTAN is the amount of electricity generated by a unit in one year. According to the United States EPA, units with CF < 0.2 are considered to be peakers and those with CF > 0.8 are considered baseload (EPA 2016). Figure 12 in Appendix B, plots the cumulative distribution for generation and the number of units based on their capacity factor for US NGCC and non-NGCC units.

Missing data in the original database (eGRID 2016) invalidate some of the NGCC records. 513 out of 670 data records were identified as valid and used for the calculations. See Appendix A for more details about the assumptions and methods for handling the missing data, and Appendix C for a validation analysis of the missing datapoints by a machine learning algorithm. Results from the validation analysis show that excluding the invalid datapoints does not cause a significant error in the final analysis.

Only units larger than 25 MW and younger than 25 years old were considered for retrofit in this analysis (retrofittable units). This translates to 462 out of the 513 NGCC units, which provide 95% of the total NGCC generation capacity and 96% of the NGCC electricity generation.

Retrofit Cost Calculation

The Integrated Environmental Control Model (IECM, version 11.2), developed by Carnegie Mellon University (2018) is a power plant cost analysis tool for different types of fossil fuel power plants with various environmental control units. Considering the amine scrubbing technology for post-combustion, this study adopts IECM and its cost information to build a cost model for NGCC units and their retrofits. The cost model allows to estimate the cost of avoided CO_2.

To develop the cost model, it is assumed the maximum input heat rate (or the gross power generation capacity) of a unit remains constant after retrofit; however, each NGCC unit incurs an energy penalty due to the integration and operation of the post-combustion capture system. This energy penalty typically results in an efficiency decrease between 5 and 7.5 percentage points for a new NGCC unit built with a capture system (E. S. Rubin and Zhai 2012; Fout et al. 2018; T. L. Johnson and Keith 2004; EPRI 2009; Carnegie Mellon University 2018); however, retrofitting an existing unit may result in a higher energy penalty (Rao and Rubin 2002; Gerbelová et al. 2013). For retrofits, a 10%-point loss in net efficiency is assumed. As an example, retrofitting an NGCC unit with a net efficiency of 50% results in a unit with a net efficiency of 40%. All efficiency values in this analysis are based on higher heat values or HHV.

The internal heat and electricity consumption for the amine scrubber system is responsible for the efficiency loss. The energy penalty reduces the maximum available capacity (nameplate capacity) for electricity generation in each unit. A similar level of annual electricity generation is assumed for each unit after retrofit (to prevent generation loss in the grid). Given the lower available capacity, the capacity factor of the units increases after the retrofit.

Table 6 summarizes the important assumptions and parameters used in the model. The unit retirement age and maximum economic book life (amortization duration) were both set to 30 years. The economic book life of the post-combustion capture equipment installed for each unit was assumed to be equal to the remaining lifetime of that unit. A retrofit cost factor ranging between 1 and 1.25 has been suggested to capture the additional cost and site-specific difficulties of retrofit for existing power generating units (Middleton and Bielicki 2009). The model assumes a constant retrofit cost factor of 1.15 for the NGCC fleet. Assumptions and parameters not listed in Table 6 are set to IECM default (Carnegie Mellon University 2018).

The Cost of avoided CO_2 (COC) is estimated by comparing the Levelized Cost of Electricity between the reference ($LCOE_{ref}$) and the retrofitted units ($LCOE_{retrofit}$) (Metz et al. 2005):

$$COC\ (\$/ton\ CO_2) = \frac{LCOE_{retrofit} - LCOE_{ref}\ (\$/MWh)}{ROE_{ref} - ROE_{retrofit}\ (ton\ CO_2/MWh)} \qquad (1)$$

ROE is the rate of CO_2 emission per MWh of electricity. The difference between $LCOE_{ref}$ and $LCOE_{retrofit}$ derives from the capital and O&M costs of the post-combustion system as well as the additional cooling capacity required for CO_2 capture. More details about the cost model are available in Appendix D.

Table 6. Assumptions in the retrofit cost model (for more details see Appendix D)

	Parameter	Assumption
NGCC Unit	Gas turbine model	GE 7FB
	Other air pollution control	None
	Cooling technology*	Wet tower
Fuel	Natural gas price	$4/MMBtu ($3.8/GJ)
	Natural gas Higher Heating Value (HHV)	22,442 Btu/lb natural gas (52.2 MJ/kg)
	CO_2 to natural gas mass ratio after combustion	2.764 kg CO_2/kg natural gas
Carbon Capture System	System type*	Amine Scrubbing – Econamine FG+
	Capture efficiency*	90%
	Transportation & Storage (T&S)	Not included
	Retrofit energy penalty	10%-point efficiency loss in power block
	Additional cooling capacity after retrofit	Yes
Financial	Year Cost Reported	2017
	Dollar type	Constant
	Discount Rate *	7.09%
	NGCC unit age reference year	2016
	NGCC unit economic book life (and retirement age)	30 yrs
	Post-combustion capture system economic book life	30 yrs – age of NGCC unit
	Additional retrofit cost factor	1.15 times of amine scrubbing equipment capital cost

*IECM default values

Results and Analysis

The retrofit cost analysis model was employed to calculate the cost of post-combustion retrofits for the US NGCC fleet. Retrofit feasibility is determined by comparing the cost of post-combustion capture with that of DAC.

Electricity and CO_2 Capture Cost Before and After Retrofit

The total US NGCC fleet capacity in the database is about 275 GW. It generated 28% of the total US electricity in 2016. For the units considered for retrofit, the weighted average LCOE is $55/MWh. For units with a capacity factor of 0.75 or higher, the average is $44/MWh which is slightly higher than the benchmark NGCC cost without CCS used in the analysis by Zhai, Ou, and Rubin (2015).

After the retrofit, an average increase of $30/MWh was observed in the LCOE ($18/MWh LCOE increase for units with a capacity factor of 0.75 or higher). The cost of avoided CO_2 (COC) varies from $46 per metric ton of carbon dioxide (ton) for the cheapest unit to over $20000/ton for the most expensive one with a weighted average of $85/ton ($53/ton average COC for units with a capacity factor of 0.75 or higher). The cost of CO_2 calculated by this model is in the typical range of power plant post-combustion capture cost in other sources ($50-$100 per ton CO_2) (McKinsey and Company 2008; Rochelle 2009; Socolow et al. 2011). These results compare well with similar studies (Carapellucci, Giordano, and Vaccarelli 2015; Gerbelová et al. 2013) for the cost of NGCC retrofit (see Appendix E).

What Does Retrofit Feasibility Mean?

Rubin and colleagues compared the LCOE of the retrofitted units with that of a benchmark NGCC unit to determine the retrofit feasibility of coal-fired power plants

(Zhai, Ou, and Rubin 2015). This analysis compares the cost of carbon capture by post-combustion with that of DAC to determine the cheaper mitigation technology for each unit. DAC is currently under commercial development by several companies around the world (Bourzac 2017; Cressey 2015). Climeworks has already achieved a capture cost of $500-$600/ton (Gertner 2019) and Carbon Engineering estimated $94-$232 per ton of CO_2 for their commercial plant (D. W. Keith et al. 2018). To account for uncertainty, this study assumes a high-end DAC cost of $550/ton based on Climeworks' report and a low-end cost of $100/ton based on Carbon Engineering's future plant. This range is consistent with the majority of the DAC cost estimations in the literature (Sanz-Pérez et al. 2016; Fasihi, Efimova, and Breyer 2019), and the cost estimations by Sinha et al. (2017) as well as Kulkarni and Sholl (2012). High-end cost estimations such as the $1000/ton by House et al. (2011) are already contradicted by the Climeworks' commercial DAC price (Gertner 2019).

Based on the cost of post-combustion capture, NGCC units are categorized into three groups based on the cost of CO_2: below $100/ton, below $550/ton, and above $550/ton.

The Retrofit Potential of the Existing NGCC Fleet

Figure 2 illustrates the results of retrofit cost analysis and comparison with the cost of DAC. Figure 2a shows the cumulative distribution of COC for those NGCC units that are considered for retrofit. The cost of post-combustion capture for about 55% of the NGCC units in this analysis is below $100/ton and 95% of the units have a COC lower than $550/ton. Note that the percentage values are based on the number of NGCC units considered for retrofit and not all the units. As mentioned in the Materials and Methods section, the model assumed a constant natural gas price at \$4/MMBtu which is in line with recent studies (Fout et al. 2018; Nezam, Peereboom, and Miller 2019). The sensitivity of these results to the price of natural gas is investigated in Appendix F.

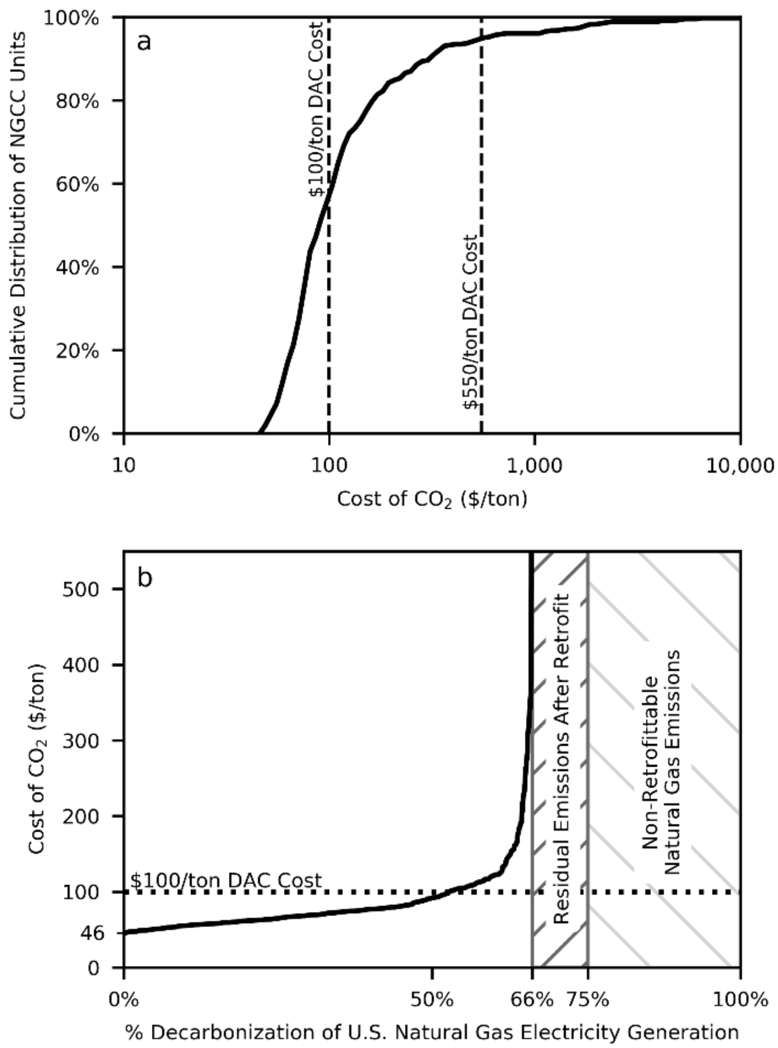

Figure 2. Initial results of natural gas power decarbonization (a) cumulative distribution of the number of retrofittable NGCC units against the cost of avoided CO_2. Dotted vertical lines show the two DAC cost scenarios. (b) cost of avoided CO_2 plotted against the percentage of decarbonization of natural gas-based electricity generation. Starting from the cheapest NGCC unit, the decarbonization cost goes up, as the remaining NGCC units become harder to retrofit. Retrofitting all retrofittable units result in a 66% decarbonization. The remaining emissions are in part the residual emissions after post-combustion capture of the retrofitted units (hatched area) and the emission from non-retrofittable natural gas units (cross-hatched). The DAC cost scenarios are shown by the y-axis limit and the dotted horizontal line.

The horizontal axis in Figure 2b represents the total CO_2 emissions from natural gas electricity generation in the US. The black curve shows the increase in the cost of carbon capture as more NGCC units are retrofitted. The cost of CO_2 for the most suitable unit for retrofit is $46/ton. Units are sorted based on their cost of retrofit, and retrofitting each consecutive unit increases the level of decarbonization of the fleet as well as the cost of CO_2. The cross-hatched area, representing units that cannot be retrofitted, contributes 25% of the total CO_2 emissions from natural gas. These include all non-NGCC types of units, among them NGCC units smaller than 25 MW or older than 25 years. The hatched area represents the residual emissions of the retrofitted units.

About 55% of the emissions can be captured at a price below $100/ton; however, the cost of CO_2 increases to over $20000/ton as one approaches 66% decarbonization. DAC, at $550/ton, is cheaper than post-combustion capture for the last few NGCC units. The remaining 34% of emissions can only be captured by DAC, even at $550 per ton. If DAC costs drop to $100/ton, it could effectively address 45% of the total natural gas emissions. This exceeds 250 million tons of CO_2 annually.

As mentioned before, the cost of CO_2 transportation is not included in this analysis. The concentration of CO_2 in the air is roughly constant everywhere; therefore, DAC can be implemented at the site of storage or utilization which eliminates the cost of CO_2 transportation (Elliott et al. 2001). The cost of transportation for post-combustion capture depends on a unit’s location and its distance from a CO_2 storage or utilization site. Calculating the unit-specific cost of transportation is out of the scope of this work; however, considering the location of the US NGCC units provides useful insights. Figure 3 illustrates that most of the NGCC generation capacity in the continental United States is concentrated along the West Coast and the East Coast. Southern states also host a large number of NGCC units. The cost of transportation per ton of CO_2 is lower when a large generation capacity is concentrated in an area. For the isolated generating units in the middle of the country, however, the cost of transportation is likely higher. As a result, some units with a relatively low cost of CO_2 may not be retrofittable due to the high cost of CO_2 transport (e.g., units labeled with a star).

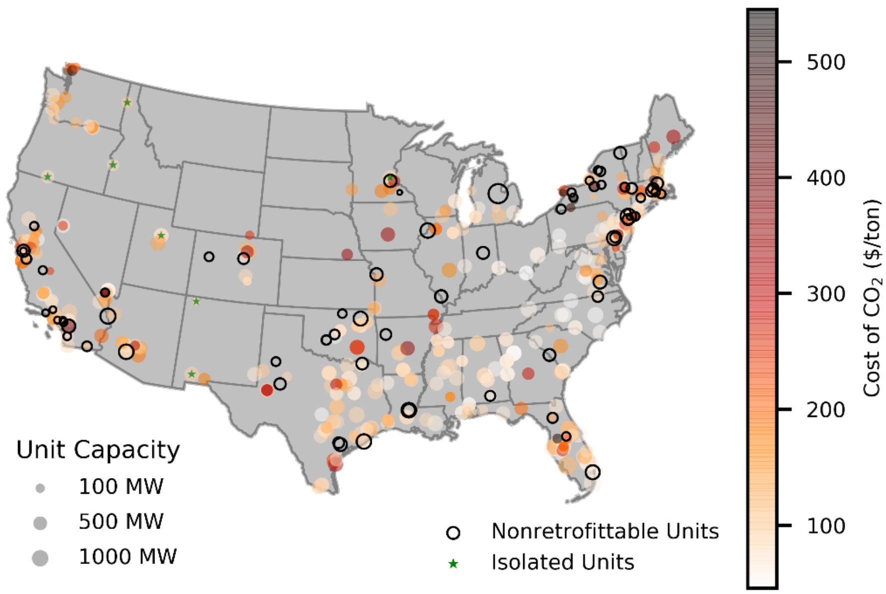

Figure 3. Distribution of the existing NGCC fleet in the continental United States. The size of bubbles represents the relative size of the units' capacity.

Identifying feasibility characteristics

The box plots shown in Figure 4 are useful for identifying the impact of the key characteristics considered in the retrofit cost calculation on the cost of CO_2. Units with a cost of CO_2 below $100/ton are likely *retrofittable* and those more expensive than $550/ton are likely *non-retrofittable*. Retrofittable units demonstrate a higher median in nameplate capacity, net efficiency, and capacity factor and a lower median in age. The interquartile range (IQR) values for retrofittable and non-retrofittable units are very well separated except for unit age. The age IQR for the retrofittable units is between 10 and 14, while non-retrofittable units have an IQR between 15 and 23. The age range overlap between the clusters is more evident when units below $550/ton are compared with those above $550/ton. In other words, the cost of retrofit is weakly correlated with units' age except for those older than 20 years. Comparing the retrofittable and non-retrofittable units by their capacity factor, on the other hand, distinctly separates the two clusters. No generating unit with a capacity factor lower than 0.2 is categorized as retrofittable.

Based on the results in Figure 4, retrofittable NGCC units are larger than 400 MW and younger than 14 years and have a net efficiency higher than 45% and a capacity factor higher than 0.5.

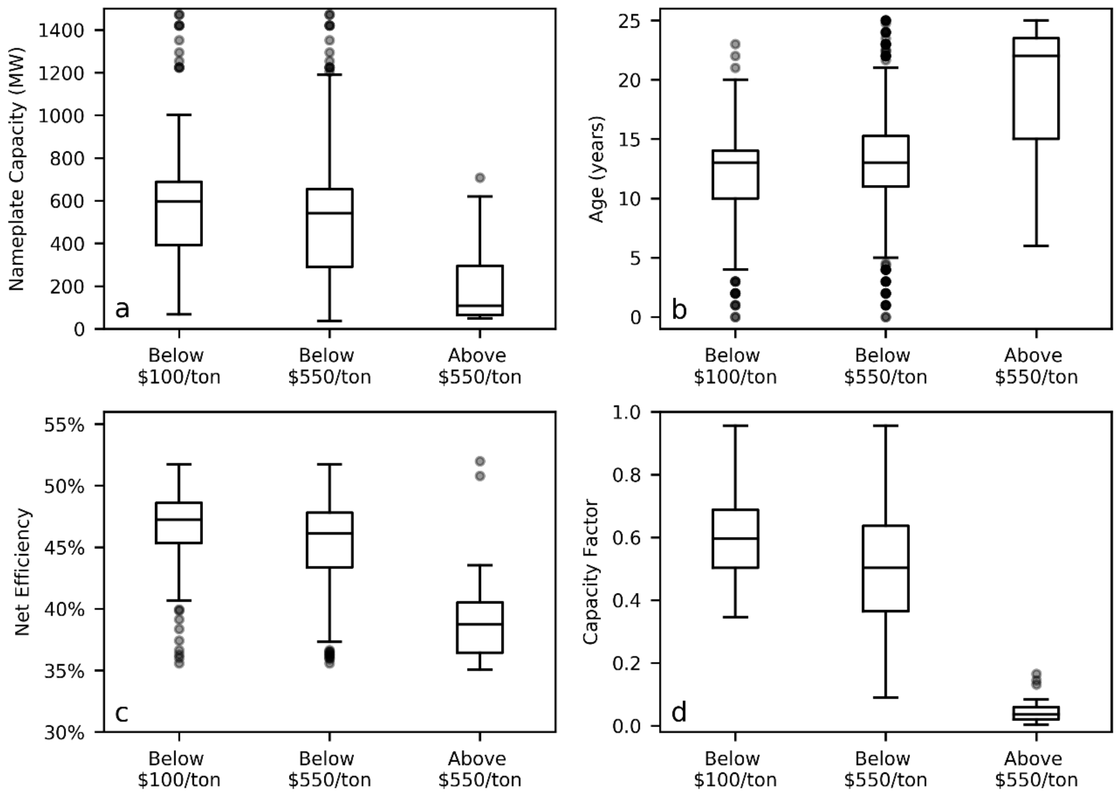

Figure 4. Box plots to identify key contributors to the cost of retrofit. The figure shows the distribution of each key parameter for the post-combustion capture cost categories (i.e., below $100/ton or retrofittable, below $550/ton, and above $550/ton or non-retrofittable). (a) Unit nameplate capacity distribution for each cost category. (b) Unit age distribution for each cost category. (c) Units' net efficiency for each cost category. (d) Unit capacity factor for each cost category.

Impact of Retrofit Decarbonization on the Grid

Both post-combustion capture and DAC consume electricity and heat. The post-combustion retrofit energy penalty reduces the generation capacity of an NGCC unit by 20-30%, so a large-scale implementation of this technology significantly lowers the amount of available capacity in the grid. To compensate for this loss, some consider employing auxiliary gas-fired generation capacities for electricity and thermal energy consumption of post-combustion capture. This increases the LCOE and cost of avoided CO_2 (Zhai, Ou, and Rubin 2015; Davison 2007). Alternatively, a flexible post-combustion capture design may make it possible to turn off the capture system during peak electricity demand hours. The shutdown of the capture system can be done either entirely (Chalmers, Leach, et al. 2009; Cohen, Rochelle, and Webber 2010) or only partially (Chalmers and Gibbins 2007; Chalmers, Lucquiaud, et al. 2009). However, such solutions come with technical challenges (Y.-J. Lin et al. 2012) and high cost of excess sorbent storage (Haines and Davison 2009).

DAC generally offers more flexibility in terms of its source of electricity. Shifting DAC's operation to off-peak hours is not as challenging as post-combustion capture since DAC is not attached to a generating unit. Because of its flexibility in geographical location, DAC units could be located at sites that have a large supply of renewable energy. Unlike post-combustion capture, a disruption in the operation of DAC does not emit more CO_2, even though Fasihi and colleagues argue the capital cost intensity of DAC mandates a high utilization level of the device for a lower cost of CO_2 (Fasihi, Efimova, and Breyer 2019). Post-combustion capture is limited to only a portion (<90%) of the emissions from flue gas and cannot address any background emissions; however, easy scale-up of DAC makes it possible to capture the lifecycle carbon emissions of a power plant (van der Giesen et al. 2017).

Post-combustion capture and DAC increase the total amount of fuel consumption (and as a result additional CO_2 emission) when they obtain their electricity from fossil-based sources. The horizontal axis in Figure 2b does not take this additional CO_2 into account and percentage values are relative to total initial natural gas-related CO_2 emissions. In the case of post-combustion capture, most of the additional emission is captured by the unit itself, but the overall capture rate is less than 90% (typically about 88%). The additional CO_2 emissions increase the cost of CO_2 transportation for post-combustion capture, while DAC does not incur this extra cost.

Final Remarks

Direct air capture is identified as one of the most promising negative emissions technologies in terms of scalability and minimizing environmental risks (D. Keith 2009). DAC is not typically compared with post-combustion capture; however, this case study exhibits how DAC can go beyond negative emissions and can complement post-combustion capture. In a scenario where complete decarbonization of the existing US natural gas power plant fleet is desired, this analysis exploits some unique features of DAC and identifies DAC as a backup if the mainstream technology (post-combustion capture) fails, either technologically or economically. Additionally, DAC’s competitive price exhibits its potential in the decarbonization of industrial sectors such as iron and steel, cement, refineries, and pulp and paper (Leeson et al. 2017).

The capacity factor is the most important attribute affecting the cost of post-combustion capture. Beyond routine maintenance or sudden failures of a generating unit, exogenous economic factors such as electricity demand and the dispatch cost of competitive power plants determine the capacity factor of a unit. When compared to post-combustion retrofit, DAC with the cost of $550 per ton CO_2 will be competitive to capture about one-third of the total CO_2 emission from natural gas-fired power plants. At a cost of $100 per ton, DAC can potentially capture up to 45% of the total emission more economically than retrofit.

The Post-combustion cost calculation in this analysis is based on retrofitting each NGCC unit separately. However, Rubin and colleagues observed that lumping multiple units in a plant and capturing their emissions by a large post-combustion unit can also lower costs (Zhai, Ou, and Rubin 2015). For the sake of simplicity, this impact has not been included in the analysis. Another simplification in the model is the assumption that the change due to CO_2 capture in the LCOE does not affect the dispatch merit order of the units or their future generation levels.

Although post-combustion capture appears to be an ideal choice for CO_2 reduction from coal and natural gas power plants, it may not be the most cost-effective method in all circumstances. The results indicate that a low capacity factor leads to a high cost of post-combustion capture, even for a new power plant. As discussed in Chapter 2, an increasing penetration of non-dispatchable renewables (wind and solar electricity) into the electricity grid will result in lower capacity factors of dispatchable generating plants including coal and natural gas-fired units. The impact of high renewable integration on the dispatchable generating units is already evident in California and Texas (Denholm and Hand 2011; ISO 2012). A DAC plant, on the other hand, operates autonomously regardless of a specific power plant's utilization level.

CHAPTER 4

THE IMPACT OF LEARNING-BY-DOING ON THE COST OF DECARBONIZATION

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Azarabadi, Habib, and Klaus S. Lackner. "Post-Combustion Capture or Direct Air Capture in Decarbonizing US Natural Gas Power?." *Environmental Science & Technology* (2020).

Introduction

In this chapter, cost reductions as a result of "learning-by-doing" were incorporated into the comparison between power plants' retrofit and Direct Air Capture (DAC). The path to scale-up and the resulting cost reductions due to learning are fundamentally different for post-combustion capture and DAC. Post-combustion capture systems are inherently custom-made to match the specific power plant and flue gas stream they are designed for, while DAC units are stand-alone and process a consistent feed of CO_2 from the air. Accounting for the different scale-up approaches, this chapter aims to project the future cost of the two technologies when implemented at scale.

The Concept of Learning-by-Doing

Historical cost trends for different technologies demonstrate a decrease in the unit cost of output as a technology is adopted and applied at increasing scales (Wright 1936; A. McDonald and Schrattenholzer 2001; Nemet 2006). It has been empirically observed that the cost of manufactured items drops by a fixed percentage (progress ratio or ε)

every time the cumulative output doubles. Values for the progress ratio are associated with uncertainty and they differ from technology to technology (A. McDonald and Schrattenholzer 2001; E. S. Rubin et al. 2015). The generally learning curve equation is defined as:

$$Y = a\,\varepsilon^{\log_2 X} = a\,X^{\log_2 \varepsilon} \tag{2}$$

In equation (2), Y is the unit cost of the output after the cumulative production of X units. Variable a is the cost of a unit at the beginning of learning, and ε is a constant fraction for each technology. The learning rate parameter (LR) is defined as:

$$LR = 1 - \varepsilon$$

To complicate matters further, cost reduction is not solely a result of learning-by-doing, but other important factors such as R&D, knowledge spillover, labor and system optimization, and public policy are involved in reducing costs of a technology (E. S. Rubin et al. 2015; E. Rubin et al. 2004). But due to lack of data, most studies employ a one-factor learning curve only considering the impact of cost reduction through learning. Nemet and Brandt (2012) consider learning and R&D in their cost projection model for DAC and argue that about 90% of the buy down effort is spent on the learning. It is also worth noting, that these other factors are not independent of cumulative production. While the progress ratio is aiming to capture cost reductions that correlate with the size of cumulative production, it would be overly simplistic to consider them solely driven by learning-by-doing or experience.

A constant reduction in cost for every doubling in cumulative output, implies a power law for the cost of the n-th unit as function of n. Figure 5 shows a power function fitted to the historical cost of solar PV modules and cumulative production. This power function incorporates learning-by-doing, but also any other impacts on the cost curve. As shown, an average cost reduction of 24% can be observed for every doubling in cumulative production of solar PV, indicating a cost reduction that scales like the -0.4 power of the cumulative number of units produced.

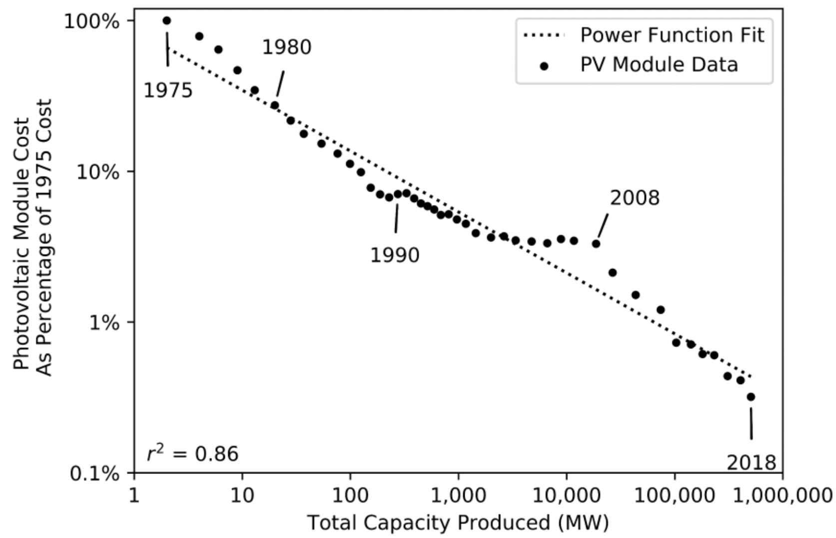

Figure 5. Cost reduction of solar PV against the cumulative capacity of PV modules produced. Data is acquired from multiple sources (Earth Policy 2015; IEA 2018, 201; Mints and Donnelly 2012; Feldman et al. 2015; *The Economist* 2012; C. Goodrich et al. 2013). Dollar values are adjusted to 2018-dollar.

The concept of learning-by-doing is widely used in academia and policy analysis to project future costs of technologies, especially in the energy and environmental domains (Nemet 2006; E. Rubin et al. 2004; E. S. Rubin et al. 2007; Jamasb 2007; Schmidt et al. 2017). When there is no historical learning curve for a multi-component system, one can use a component-based learning curve to break the system into its components and use available learning data for each component (E. S. Rubin et al. 2015). This analysis adopts a component-based learning model to project the future cost of the two carbon mitigation technologies.

Lastly, the projected future costs are used to demonstrate an example of total decarbonization of the US natural gas fleet by a combination of the two capture technologies. The results show that post-combustion capture alone is not sufficient for a deep decarbonization and there exists an optimum combination of the two technologies which minimizes the total cost of decarbonization.

Learning-by-Doing for DAC

Background

Since the need for carbon removal has only been recently recognized, it is not surprising that DAC is still an immature and underdeveloped technology. DAC technology is much younger than many other concepts still considered novel. For example, fuel cells, have been invented in the 19th century (Andújar and Segura 2009), the electric car has its roots in the 19th century (Guarnieri 2012; Sulzberger 2004), and has been produced in significant numbers already in the early 20th century (Ludvigsen 2008).

DAC is today in a much better position than solar photovoltaic was at its inception in the early 1960s. Photovoltaic modules had to come down in cost more than hundred-fold, before they became competitive with conventional energy sources (Wirth 2020; Elshurafa et al. 2018; Samadi 2018). By contrast, DAC has a shorter cost reduction journey to become competitive in carbon removal and carbon avoidance markets. Currently, Climeworks captures CO_2 from the air at the cost of $500-$600/ton (Gertner 2019). Considering the threshold for economic viability around $100/ton (National Academies of Sciences 2019; Klaus S. Lackner et al. 2012; D. W. Keith et al. 2018; Klaus S Lackner 2014), this means a cost reduction of less than tenfold is sufficient for economic viability of the technology. The much less challenging requirement for cost reductions compared to those of renewable energy sources represents a big advantage, and the goal here is to provide a quantitative assessment for a possible DAC price trajectory.

DAC Learning Model

For a technology such as DAC, both capital and operating and maintenance (O&M) costs are subject to learning. But given the highly diverse capture mechanisms of an emerging technology like DAC (Sanz-Pérez et al. 2016; Fasihi, Efimova, and Breyer 2019; Shi et al. n.d.), it is difficult to accurately distinguish these costs. To address this issue, the model assumes that at least some part of the cost (capital and O&M) follows the empirically established rule of the learning curve, while a portion of the cost remains constant regardless of technological advancements and learning. The former cost component is the *reducible cost* and the latter is the *residual* or *irreducible cost*:

$$DAC(n) = c(n) + r \tag{3}$$

Where $c(n)$ represents the reducible and r represents the residual portion of DAC cost.

The reducible cost is affected by the maturity of the technology (n or the implemented capacity). It makes sense not to break the cost up into capital and O&M cost, firstly due to data scarcity for a general DAC design, and secondly because of certain O&M costs that will be subject to learning and improvements while others are unlikely to be helped by innovation. The same holds for capital cost. The amount of raw materials used in the construction of a DAC device is likely to be reduced over time, the cost of raw materials which are already abundant in today's infrastructures are unlikely to be reduced very much because cumulative demand increased by a small fraction. Some costs in the system may be reduced with innovation and an increase in energy efficiency.

However, cost reduction and energy conservation cannot go beyond a cost floor and the thermodynamic minimum energy requirement (Yeh and Rubin 2012; Jamasb and Kohler 2007).

Using equation (3), one can rewrite the cost of DAC as:

$$DAC(n) = c_1\, n^{\log_2 \varepsilon} + r \tag{4}$$

c_1 is the initial value of the reducible cost when learning begins. The levelized cost is set such that a unit over its anticipated lifetime would break even if it could charge this amount for its CO_2 output. In other words, all costs of operation are balanced by a revenue stream equal to $DAC(n)$ times the average rate of output of a unit times its lifetime (Azarabadi and Lackner 2019).

In order to complete the model, it is necessary to specify what is meant by a unit. In principle, a unit could be a single DAC device or a small farm of DAC devices. For simplification, the model starts at an initial annual CO_2 capture capacity of 1000-ton CO_2/year ($n = 1$). Given the size of the current DAC capacity, the assumed unit capacity is comparable to the size of a small farm of CO_2 capture devices. The model could also start at a different number, e.g., the size of a single DAC unit. When a fixed progress ratio (ε) is assumed, unit capacity would not affect the doubling rate but change the value of c_1. The starting point of the model would not be at $n = 1$, but at some larger value that reflects the number of units already produced.

Learning-by-Doing for Post-Combustion Capture

Background

Conventional economies of scale lower the cost for larger post-combustion units. But obtaining more experience in the implementation of a new technology by building more units, can also reduce the cost. Based on the analysis by van den Broek et al. (2009), a component-based learning model for capital and operating and maintenance (O&M) costs as well as system performance was used to investigate the impact of learning on cost reductions in amine scrubbing retrofitting .

Compared to the learning model for DAC, the main difference here is that the learning effect is applied to the cost of CO_2 avoided (COC) through a reduction in cost components of an amine system, i.e., capital and O&M costs. Subsequently, the lower capital and O&M costs result in a lower Levelized Cost of Electricity (LCOE) after the retrofit. Therefore, based on the retrofit cost analysis model developed in the previous chapter, the cost of electricity after retrofit ($LCOE_{retrofit}$) is broken down into its components and recalculated to reflect the lower capital and O&M costs of the post-combustion capture system after learning.

Post-Combustion Capture Learning Model

Reduction in the COC through Learning-by-doing is reflected by a reduction in the cost of electricity for a retrofitted unit (smaller $LCOE_{retrofit}$) and lowering the retrofit energy penalty (smaller $ROE_{retrofit}$). This can be shown by considering equation (1) from the previous chapter:

$$COC\ (\$/ton\ CO_2)\ = \frac{LCOE_{retrofit} -\ LCOE_{ref}\ (\$/MWh)}{ROE_{ref} -\ ROE_{retrofit}\ (ton\ CO_2/MWh)} \tag{1}$$

Learning affects the capital and O&M costs of the post-combustion capture and as a result, each unit will have a lower post-retrofit LCOE compared to the pre-retrofit LCOE when learning is not considered. The following equation shows how LCOE is calculated in the model. All cost components below are affected by learning when post-combustion capture is implemented in scale (see Appendix D).

$$LCOE = \frac{NAMEPCAP \times CAP \times FCF + F_{O\&M}}{GENNTAN} + \ V_{O\&M} \qquad (5)$$

In this equation, NAMEPCAP is unit's capacity (MW), CAP is capital cost ($/MW), FCF is the fixed charge factor in (fraction/year), $F_{O\&M}$ is fixed O&M cost ($/MW/year), GENNTAN is the amount of electricity generated in one year (MWh) and $V_{O\&M}$ is variable O&M cost ($/MWh). Fuel cost is embedded in the variable O&M.

The model calculates the cost reduction for each cost component of an amine scrubber, i.e., the capital ($/MW), fixed O&M ($/MW/year), and variable O&M ($/MWh). A learning curve is also applied to the magnitude of the energy penalty of the capture system (van den Broek et al. 2009). Learning rate values for each component are extracted from the work by van den Broek et al. (2009) and summarized in Table 7. Due to the similarities between capital and fixed O&M costs, it is assumed that $F_{O\&M}$ has the same learning rate range as capital cost. When learning rates are known, the cost of each component after learning can be determined by equation (2) at any cumulative implementation level (parameter X).

The Advantage of Small Modular Mass-Produced Development of DAC

Mass-production has shown a significant cost-reduction from learning-by-doing. The computer industry, the solar industry, the wind industry, but also the automobile industry are good examples of the cost reductions that can be achieved by mass production. Staying small and scaling by numbers has advantages, as it has been observed that the cost reduction associated with doubling the output tends to be larger for technologies that produce small modular devices than for industries focused on producing custom-made large individual units (Dahlgren et al. 2013; Carelli et al. 2010; Schmidt et al. 2017). Dahlgren et al. (2013) argue that the steeper learning curve of small scale technologies compares with the empirical rule in the economy of scale for chemical plants where the cost of a unit scales with the 2/3 power of its size (Euzen, Trambouze, and Wauquier 1993; Jenkins 1997; Peters, Timmerhaus, and West 2006).

In DAC development, an important question is that whether developers should follow the traditional path of cost reduction in the power and chemical industries, i.e., the economy of scale, or should they pursue a different route for a quick cost reduction and scale-up? DAC pioneers have answered this question differently. Carbon Engineering, for instance, has designed a continuous process with the capacity of 1 Mt-CO_2/year with a projected amortization time of 25 years (D. W. Keith et al. 2018). Climeworks and Silicon Kingdom Holdings (SKH) have chosen to scale-up their processes with small modular autonomous units (Climeworks 2020). The capacity of CO_2 collector modules produced by Climeworks is about 50 t-CO_2/year which is significantly smaller than that of Carbon Engineering. This section elaborates on the advantage of the small modular scale-up approach by comparing DAC with Small Modular Reactors (SMRs) for nuclear electricity generation.

Carelli et al. (2010) argue that in an uncertain electricity market, small scale power generation provides higher adaptability, while a long-term, irreversible, and committed investment on a high out-put technology is vulnerable to market fluctuations. Similarly, the carbon dioxide removal market is susceptible to fluctuations by policy, economic growth, and public acceptance of mitigation technologies. Small Modular

DAC, even though initially more expensive than a large-scale DAC unit which exploits the economy of scale, may be preferred in maximizing investors' profit since it provides the opportunity of "wait and see" or decision making flexibility in such an uncertain market (Gollier et al. 2005; Locatelli, Bingham, and Mancini 2014). Meanwhile, a modular approach does not hinder scalability as the market matures and the investment risk premium grows higher.

A small modular technology requires a short-term investment and reduces the construction time (the impact of overnight costs) which ultimately leads to a higher net present value of the project (Dahlgren et al. 2013; Carelli et al. 2010). This is essential in an uncertain market with high discount rates. Unlike the construction of a high-output unit, small units can reduce or eliminate the need for expensive and time-consuming on-site construction (Carelli et al. 2010). The lower initial cost of a small modular unit extends DAC's niche market to a larger number of newcomers, both investors, and consumers. Moreover, a small-scale technology provides the opportunity to adapt to location-specific challenges (e.g., water and energy availability or space constraints, etc.) and implement the technology close to the final consumer (Locatelli, Bingham, and Mancini 2014).

Modularity increases consistency and makes standardization easier. Cost reduction due to learning happens with a smaller number of outputs produced (in this case capture capacity in ton CO_2 per year) and larger learning rate values has been observed for small modular technologies (Dahlgren et al. 2013; Carelli et al. 2010; Schmidt et al. 2017). It is worth noting that although standardization paves the way for faster learning, it may slow down the diversity which can lead to breakthrough innovation in a technology (Carelli et al. 2010; David and Rothwell 1996).

This analysis projects the future DAC cost considering a modular implementation of DAC units small enough to be factory-produced and shipped by standard means from the factory to the point of installation. Because of modularity, the learning curve is based on the cumulative number of units (and not the cumulative CO_2 capture capacity). Nemet and Brandt (2012) also considered a similar method to project learning for their DAC capital cost.

Materials and Methods

Unlike applying learning on an increasing number of DAC units, calculating the impact of learning on the cost of post-combustion capture retrofit is not straightforward. To achieve this, the model was designed to retrofit the cheapest Natural Gas Combined Cycle (NGCC) unit, then consider the cumulative retrofitted capacity (parameter X in equation (2)) and take the learning cost reduction into account. Then the model calculates the cost of retrofit for the next cheapest NGCC unit by the retrofit cost model from Chapter 3 and so on until retrofitting the worst retrofittable NGCC unit (the highest COC) with the lowest cost components and energy penalty.

Another challenge in applying learning formulas to generating units is the fact that different units use slightly different capture system, with different initial capital and O&M costs at the beginning of the learning curve. To address this issue, van den Broek et al. (2009) assumed that the capital and O&M cost for all units are the same if normalized for unit output or unit capacity (see Table 5 of the article by van den Broek et al.). In this analysis, instead of one datapoint, the learning model bounds each cost component by an interval. To do so, first an average and standard deviation for each cost component for all the retrofitted NGCC units are calculated. Then, the model receives a range of inputs between 1.5 standard deviation below and above the average for each cost component. This results in an upper and a lower cost of retrofit for each unit using this range of uncertainty. These bounds provide a common ground for all units to apply the learning equation (see Appendix G). Since the cost of retrofit for each unit is between the simplified upper and lower estimates, the cost of retrofit after learning falls within the upper and lower learning range as well. Included in the learning model is a reduction in the initial energy penalty with an initial value of 10%-point net efficiency loss. Appendix H elaborates on an alternative approach for incorporating learning by accounting for cost reduction in the capital and O&M costs of each unit.

The literature suggests that learning should be taken into account only after a certain amount of experience has been gained before the widespread commercial implementation of a technology (van den Broek et al. 2009; E. S. Rubin et al. 2007). Similar to Rubin et al. (2007), this work assumes a pre-learning phase equivalent to the first 3 GW cumulative capacity of retrofitted NGCC units. The pre-learning phase is an opportunity for technology practitioners to learn through trial and error in the early stage of the technology adaptation while no cost reduction is achieved.

Some have argued the necessity of a learning endpoint or a cost floor for experience curves where additional cumulative capacity does not result in further cost reduction (E. S. Rubin et al. 2007; 2015). The model in hand has taken this into account by the residual cost component for DAC. For post-combustion capture, similar to the analysis by Rubin et al. (2007), a 100 GW cumulative capacity of retrofitted NGCC units is assumed as the learning endpoint.

The range of cost components, as well as learning rates for the amine scrubbing system, are summarized in Table 7. Learning values for the amine system are collected from van den Broek et al. (2009).

Table 7. Range of cost components, learning rates, and other assumptions used for post-combustion retrofit and direct air capture cost projection

	Parameter	Value	Learning Rate
post-combustion capture	Retrofit energy penalty	10%-point efficiency loss in power block	2% - 7%
	Capital cost[*]	\$550 - \$1090 per kW-net power[†]	6% - 17%
	Fixed O&M cost[*‡]	\$5.2 - \$53 per kW-net power per year	6% - 17%
	Variable O&M cost[*]	\$2.4 – \$4.8 per MWh-electricity	10% - 30%
	Pre-learning capacity	3 GW cumulative retrofitted capacity	N/A
	Learning endpoint	100 GW cumulative retrofitted capacity	N/A
Direct Air Capture	Initial reducible cost (c_1)	\$50 - \$450/ton	10% - 20%
	Residual cost (r)	\$50-\$100/ton	0%
	DAC device capacity	1000 ton /year	N/A
	Pre-learning installed capacity	First 60 units	N/A
	Learning endpoint	Implemented with the residual cost	N/A

[*]Values range between 1.5 standard deviations below and above the mean for all of the considered NGCC units.
[†]The capital cost range in this table includes the 1.15 multiplier accounting for the additional difficulty of a retrofit.
[‡]Due to its similarities with capital cost, the model uses the same learning rate range for the Fixed O&M cost.

Learning Results

The area shaded gray in Figure 6a illustrates the probable range of post-combustion capture costs with learning. The positive slope of the curves at the beginning of post-combustion implementation (a very short section at the left-hand side of the curve) demonstrates the pre-learning phase. Learning starts after retrofitting 3 GW of NGCC capacity (equivalent to the first 6 NGCC units). After the pre-learning phase until about 50% decarbonization level, the cost of CO_2 is roughly constant and below $100/ton. Cost reductions from learning effectively balance out cost increases from retrofitting less-suitable units. After that point, the cost of CO_2 capture starts increasing rapidly, going beyond $1000/ton at 66% decarbonization. As discussed in Chapter 3, post-combustion capture cannot go beyond 66% decarbonization since the CO_2 capture efficiency is set to 90% and some NGCC units as well as all other non-NGCC units are deemed non-retrofittable.

Similarly, to integrate DAC learning into the model, an upper and a lower limit of initial reducible cost (c_1) and residual cost (r) were used (equation (4)). Based on the discussed advantages of small, modular technologies and observed learning curves for other similar scale-up strategies (for solar PV, fuel cells, and electrolysis), a 20% learning rate is chosen for the higher learning limit of DAC (Nemet 2006; Schmidt et al. 2017; E. S. Rubin et al. 2015). The lower limit DAC cost assumption ($50/ton) is in line with long-term DAC cost projections from similar studies (Fasihi, Efimova, and Breyer 2019; Nemet and Brandt 2012; Broehm, Strefler, and Bauer 2015). Table 7 above, also summarizes the assumptions in the cost reduction analysis of DAC.

Figure 6b shows how the cost of DAC decreases if it is implemented for decarbonization of US natural gas-fired electricity. Compared to amine scrubbing, DAC is a young technology; therefore, a more conservative pre-learning phase equivalent to 60 units (versus 6 units for amine scrubbing) was used in the model. Because of the smaller capture capacity of individual units, it is hard to see the pre-learning phase in the graph. As shown in the figure, capturing CO_2 directly from the air, regardless of the emission source, makes it possible for DAC to take decarbonization beyond the technological and economical limit of post-combustion capture and achieve a 100% decarbonization. The cheapest DAC scenario approaches the minimum cost (residual cost of $50/ton) immediately after the beginning of large-scale implementation, while the expensive scenario reaches a final cost of $210/ton.

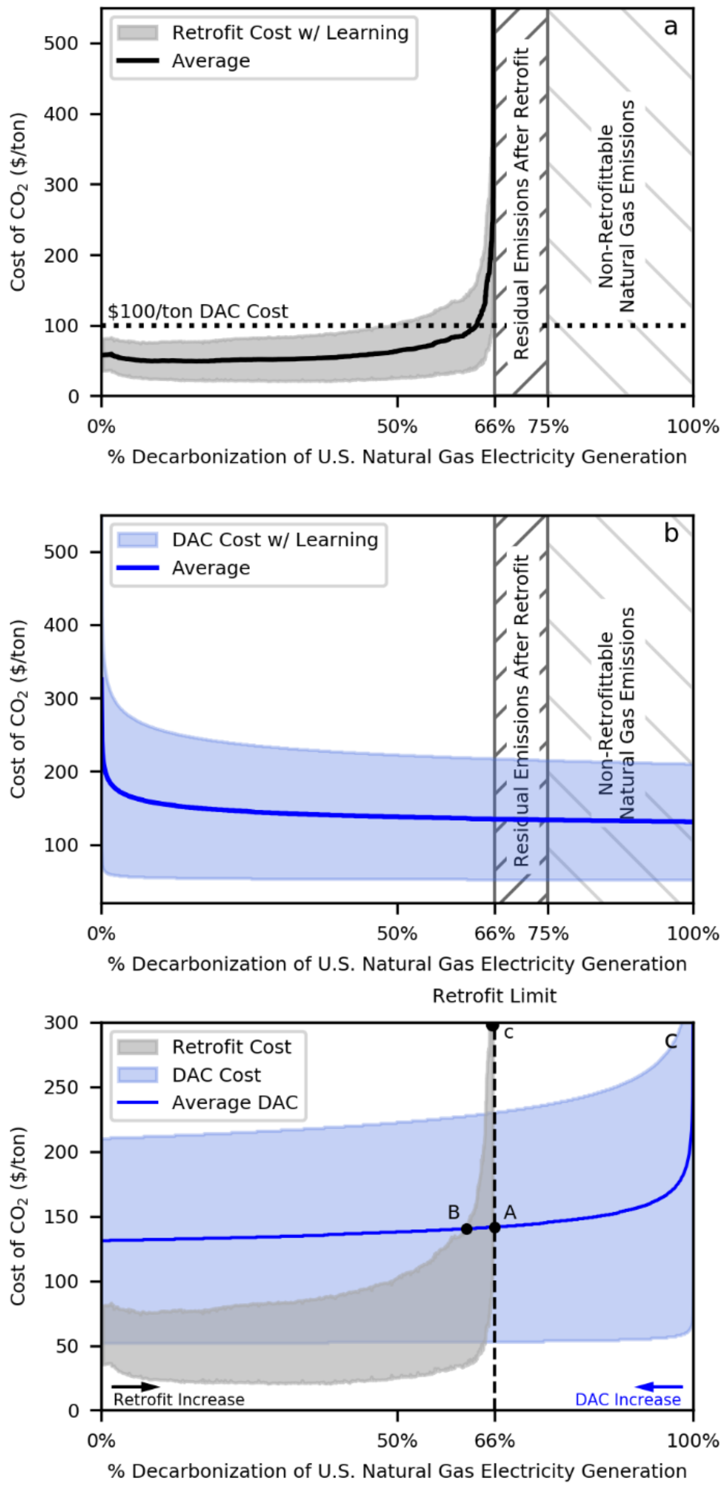

Figure 6. Cost of CO_2 against decarbonization level considering the impact of learning-by-doing for (a) post-combustion capture retrofit, (b) direct air capture, and (c) 100% decarbonization plan for the US natural gas power plant fleet by both technologies. The effect of learning-by-doing on the cost of CO_2 is accounted for both technologies.

The Optimum Mix of DAC and Post-Combustion Capture

Figure 6c combines the two cost curves in Figure 6a, b into one plot. It reverses the DAC cost curve because it is assumed that DAC is first implemented for those units that are not retrofittable. In effect, DAC's cost curve starts at the right-hand side of the plot. The overlap between the shaded areas demonstrates that in certain scenarios DAC could be competitive with post-combustion capture. The learning approaches are quite different. Even with very conservative learning rates for DAC, the modular mass production of the technology is far more effective than the expensive and long-term capital investment for custom-made post-combustion capture systems.

In this analysis, at least one-third of the total emission can only be captured by DAC. This is equivalent to about 200 million tons of CO_2 annually captured by 200000 DAC units. The cheapest DAC scenario is across the board cheaper than the most expensive retrofit scenario. If one assumes the cheapest scenarios for both technologies, DAC would account for slightly more than one-third of the emission capture.

Assuming that DAC is the sole option for decarbonization of the non-retrofittable units, an early implementation of this technology will also reduce the cost of carbon capture for the retrofittable units. As an example, consider the average DAC cost scenario shown with the blue curve in Figure 6c. The initial cost of $325/ton is the starting point and when employed for one-third of the emission, the technology becomes relatively mature at the cost of $140/ton (point A). If the cost of post-combustion retrofit follows the lower limit scenario, retrofits will be cheaper than DAC to address the 66% retrofittable emissions and DAC does not penetrate beyond 34%. On the other hand, if the upper limit reflects the cost of retrofitting, the mature DAC becomes cheaper than retrofitting the last few retrofittable NGCC units and DAC can penetrate up to point B (39% DAC share). This effectively reduces the total cost of decarbonization (saving would be equal to the gray shaded area between A, B, and C). DAC's penetration and the resulting cost reduction in decarbonization can be different depending on where the actual learning curves for DAC and post-combustion capture end up. It is worth noting that the technology implementation timeline is crucial and such a saving in decarbonization happens only if DAC becomes cheaper than its current price through early implementations. Similar to this conclusion, the National Energy Technology Laboratory emphasizes the importance of an early cost reduction for Carbon Capture, Utilization, and Storage (CCUS) technologies (Withum, Babiuch, and Krulla 2012).

Conclusion

When the impact of learning-by-doing is considered, differences in nature and scale-up approaches of the two technologies resulted in a more dramatic cost reduction for DAC. To keep the model simple and minimize assumptions, this analysis does not account for elapsed time and assumes a static system of NGCC units. In reality, however, learning happens over time. Time-dependent factors such as fluctuation in electricity demand as well as new policies and investment in R&D for each technology can significantly affect the cumulative installed capacity and consequently cost reduction by learning. Incorporating all of these different factors increases the complexity of the model yet does not guarantee an improvement in its accuracy.

The scope of this analysis is narrowly focused on CO_2 emissions from natural gas. The impact of learning for DAC would be even more dramatic if decarbonization of other sectors (e.g., transportation) are included. Learning-by-doing for different mitigation technologies used in different sectors (e.g., post-, pre-, and oxyfuel combustion in electricity generation or batteries in transportation) happens in parallel since most of these technologies address emissions from a specific sector. DAC, on the other hand, would experience cumulative learning since it is a global decarbonization solution for any kind of CO_2 emissions.

CHAPTER 5

A SORBENT-FOCUSED TECHNO-ECONOMIC ANALYSIS OF DIRECT AIR CAPTURE

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Azarabadi, Habib, and Klaus S. Lackner. "A sorbent-focused techno-economic analysis of direct air capture." *Applied Energy* 250 (2019): 959-975.

Introduction

This chapter introduces a novel approach for techno-economic analysis of Direct Air Capture (DAC) technology. This analysis is based on the available budget for constant and ongoing expenses over the lifetime of a DAC device. The budget is based on the income cash flow from the captured carbon dioxide. There are three main components to the costs of a DAC device: first, the capital cost includes the value of process equipment in addition to start-up and pre-production expenses; second, operating and maintenance cost accounts for labor, material, and energy costs during operation and maintenance of the DAC equipment; third, the model explicitly break out sorbent costs. The report by the National Academies of Sciences (2019) accentuates the importance of sorbent cost in the DAC total cost and suggests sorbent cost reduction as one of the main cost reduction strategies for DAC technologies relying on solid sorbents.

Figure 7 illustrates a schematic diagram for a generic DAC system. Ambient air with a more or less constant composition is the source of CO_2 and a liquid or solid sorbent binds the CO_2 molecules in the capture stage. Capture is based on the physical or chemical interaction between CO_2 and the active ingredient of the sorbent (Sanz-Pérez et al. 2016). In the capture stage, CO_2 binds to the sorbent and in the regeneration stage, the captured CO_2 is separated from the sorbent. The required energy for detaching CO_2 from the sorbent can be provided by heat, exposure to near-vacuum pressure, or moisture. Different combinations of temperature, pressure, and moisture swings can be used, and an optimal choice will depend on the type of sorbent. After the CO_2 has been removed from the sorbent in a regeneration chamber, the regenerated sorbent is ready for reuse while the captured CO_2 is further processed, e.g., compressed and stored.

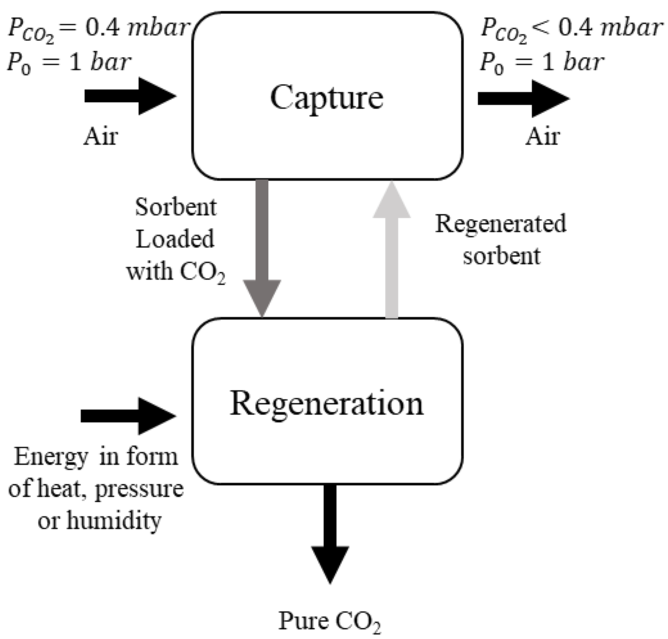

Figure 7. A schematic view of a DAC device.

Different research groups have proposed various approaches to DAC with sorbents ranging from hydroxide solutions to solid amine sorbents (Sanz-Pérez et al. 2016). All have in common a capture cost that exceeds that of post-combustion scrubbing. The main challenge for DAC is that CO_2 in the air is about 300 times more dilute than in a typical flue gas stream.

Both, Kulkarni and Sholl (2012) and Sinha et al. (2017) provide detailed simulations for two DAC processes taking advantage of solid sorbents. Both analyses evaluate the required energy and materials for different steps of the processes and estimate the cost of DAC; however, Kulkarni's study is only focused on operating costs.

Sinha et al. (2017) propose a Temperature Vacuum Swing Adsorption (TVSA) process using a monolith structure coated with two different Metal Organic Framework (MOF) sorbents. i.e., MIL-101(Cr)-PEI-800 (Darunte et al. 2016) and mmen-Mg_2(dobpdc) (T. M. McDonald et al. 2015).[3] Since these sorbents are not available in the market, the authors estimate their prices by considering the value of their raw material components. The analysis results in the minimum required energy for each sorbent and it estimates promising total costs of $75-140/t CO_2 for MIL-101(Cr)-PEI-800 and $60-190/t CO_2 for mmen-Mg_2(dobpdc). Additionally, they identify the most important parameters for a techno-economic analysis (e.g., sorbent price, loading, and unloading time) and determine the sensitivity of the costs to variations in these parameters. Sinha et al. did not include the cost of CO_2 compression in their analysis.

Kulkarni and Sholl (2012) developed a model for a Temperature Swing Adsorption (TSA) process using the silica-based sorbent of TRI-PE-MCM-41 (Belmabkhout, Serna-Guerrero, and Sayari 2010). In one approach, the process is tuned to take advantage of diurnal cooling and heating to minimize the energy input to the TSA cycle. A second approach includes the use of steam as a source of heat and as a sweep gas to facilitate desorption on the surface of the sorbent. Both processes are evaluated for

[3] In shorter forms, these sorbents are occasionally referred to as MIL-101(Cr) and Mg_2(dobpdc).

different climate conditions and sources of steam and a capture price of $100/t CO_2 was estimated. Capital expenses are not included in this analysis.

Sorbents represent a significant part of a DAC system and in a well-designed system represent a large fraction of the total mass. As a sorbent goes through numerous loading and unloading cycles, its quality and performance deteriorate. Degradation or loss occurs due to exposure to the ambient environment (sunlight, wind, particulate matters, etc.) or natural destruction under process conditions (humidity, high temperature, or pressure). Deterioration of the sorbent material can affect the performance of a DAC device; therefore, it is important for the sorbent to be maintained above a minimum quality. Because of its high volume and deterioration during the process, DAC sorbents cost can be comparable to, or even higher than the other two expense categories.

Synthesizing new DAC sorbents is a growing field of research aiming to reduce the cost of DAC. Every year, state-of-the-art sorbents with improved capture and regeneration characteristics are made in laboratories without accurate cost estimates for commercial scales (Sanz-Pérez et al. 2016). An improved sorbent with enhanced characteristics often comes at correspondingly higher costs. This raises the question of which parameters are most important in evaluating a DAC sorbent?

This chapter elaborates on a model to address this issue. The model can estimate the value of a newly developed sorbent with known characteristics and the estimated value can be compared to the production and commercialization costs of the sorbent. The next chapter discusses the applications of the model including the ability to estimate the cost of CO_2 capture with a newly developed sorbent with a known price and characteristics. And finally, the model optimizes the exposure time of a given sorbent in a DAC device to minimize the price of the captured CO_2.

Modeling

The cost of CO_2 captured by a DAC device, adjusted to present values, is the sum of three different expenses. First, there are the Operating and Maintenance (O&M) costs ($N_{O\&M}$). They include energy, material, and maintenance costs associated with loading and unloading a sorbent. Second is the sorbent material cost (N_S). The sorbent is purchased at the beginning of the operation and a scrap value of zero is assumed at the end of its lifetime. N_S can be broken up into the price of the sorbent (V_S) and the cost associated with its installation (I_S). The sorbent itself could be a composite material, with different material and synthesis cost, as for example with a porous substrate functionalized by amines. The installation cost also may include multiple components. A simple cost estimation could also include the expense of downtimes associated with the installation. In summary, $N_S = V_S + I_S$. There is no discount factor, as the entire expense occurs at the start time.

Lastly, there is the capital cost of the balance of the plant. Hardware in a DAC device is significantly more robust than the sorbent and does not physically depreciate on time scales as short as a sorbent lifetime. But the value of money spent on the purchase of the hardware goes down with the discount rate. Therefore, the third running expense is the net cost of the plant (N_{BoP}) which is the difference between the initial purchase price (V_{BoP}) and its discounted scrap value.

As the sorbent goes through loading and unloading cycles, its performance will be adversely affected by ambient and operational conditions. Thus, the degraded sorbent needs to be replaced after a certain period of time or a certain number of cycles. For simplicity, the cost calculations are based on one lifetime of the sorbent (t_{life}). The remainder of the DAC device, which is roughly in the same condition as a new device, is assumed to be returned at the same price it was purchased for after one sorbent lifetime. Calculations in Appendix I show that the results are not sensitive to the simplifying assumption that costs are calculated for a single sorbent lifetime, as long as one evaluates the system at a zero net present value. Appendix J shows that for systems with a positive net present value the optimal choice of the sorbent lifetime is shorter and becomes very short if the sorbent cost is low.

The net present value of a DAC system can be written as:

$$NPV_0 = N_{rev} - (N_{O\&M} + N_{BoP} + N_S)$$

N_{rev} is the net present value of the revenue generated from selling CO_2 during the operation of the device. $N_{O\&M}$, N_{BoP}, and N_S are costs, discounted to present time for operation and maintenance, the balance of the plant, and sorbent, respectively. Here the subscript '0' is meant to signify that the calculated NPV is for a single sorbent lifetime. The value of NPV_0 is a function of t_{life}. The net present value for a system that continues through an unlimited number of cycles can be viewed as a geometric sum of NPV_0 weighted with the discount factor e^{-t_{life}/τ_M}. τ_M accounts for discounting (Appendix I):

$$NPV = \frac{NPV_0}{1 - e^{-t_{life}/\tau_M}}$$

For a business to be profitable, the net present value, regardless of its time basis, must be equal to or greater than zero. Therefore, the following condition has to be satisfied at some point during the operational lifetime of an economically viable DAC device:

$$NPV_0 = N_{rev} - (N_{O\&M} + N_{BoP} + N_S) \geq 0 \qquad (6)$$

The net present value is a function of the time the device runs. All NPV curves start negative because of the initial cost of the sorbent. As a DAC operation starts, the NPV starts to increase due to the revenue generated from the CO_2. At the same time, the O&M and BoP expenses are added to the system and as the capture capacity of the sorbent deteriorates, those costs overcome the generated revenue. At this point in time, the NPV reaches its maximum and starts to decrease. It is economically rational to stop the operation at the maximum NPV and call this point in time t_{life}.

Figure 8a illustrates the NPV curves for two DAC devices with different cost components. The dotted line shows a DAC device that starts in the downslope of the NPV curve. This device never obtains an NPV of greater equal than zero at a positive lifetime. From the start, the device will be losing money on its operation and it is not economically viable. The solid line shows a system with a maximum NPV of zero at a positive time. This DAC business reaches its breakeven point at the maximum of the NPV curve somewhere after starting its operation. Again, the business would be losing money should it operate beyond the maximum NPV.

At t_{life}, the first derivative of the NPV equation with respect to time must be zero:

$$@\ t = t_{life} \qquad \frac{dNPV_0}{dt} = n_{rev} - \left(n_{O\&M} + \dot{N}_{BoP}\right) = 0 \qquad (7)$$

n_{rev}, $n_{O\&M}$, and $\dot{N}_{BoP}$ are derivatives of the revenue, O&M, and BoP functions, respectively. As mentioned earlier, sorbent cost (N_S) is not a function of time, so it does not contribute to the derivative. Given N_{rev}, $N_{O\&M}$, and N_{BoP} costs as functions of time, t_{life} can be calculated.

It is intuitive that a DAC device must continue its operation as long as it is increasing the NPV. At any given moment, profits accrue from the revenue generated by capturing CO_2 minus the cost O&M and BoP. At some point, the decreasing revenues (due to sorbent performance degradation) will be matched by the expenses. Beyond that point, profits turn into losses that lower the NPV. When profits drop to zero the operation must stop. Equation (7) compares the rate of revenue generation n_{rev} with the rate of the added costs ($n_{O\&M}$ and $\dot{N}_{BoP}$) and defines t_{life} as the time when the revenue and expenses are equal.

It is important to note that finding t_{life} does not necessarily guarantee the economic viability of a DAC business. Figure 8b illustrates this point. The three curves show NPV of three DAC devices with the same N_{rev}, $N_{O\&M}$, and N_{BoP} costs. After finding t_{life} from equation (7), it is easy to notice that the value of N_s shifts the NPV curve up and down. The dotted line represents a high sorbent cost which results in a negative NPV value even at its maximum. The other two curves, on the other hand, satisfy the condition in equation (6) and NPV has a maximum of greater than or equal to zero. The DAC device represented by the dashed line has a better economy than the one represented by the solid line. In this work, however, the focus is on DAC devices with NPV curves similar to the solid line to find the breakeven point for the cost of the sorbent. In other words, finding the sorbent cost with the assumption of $NPV = 0$ produces a Maximum Allowable Budget (MAB) for the sorbent price in a given system and guarantees any prices lower than that result in a positive NPV after some run time of the device.

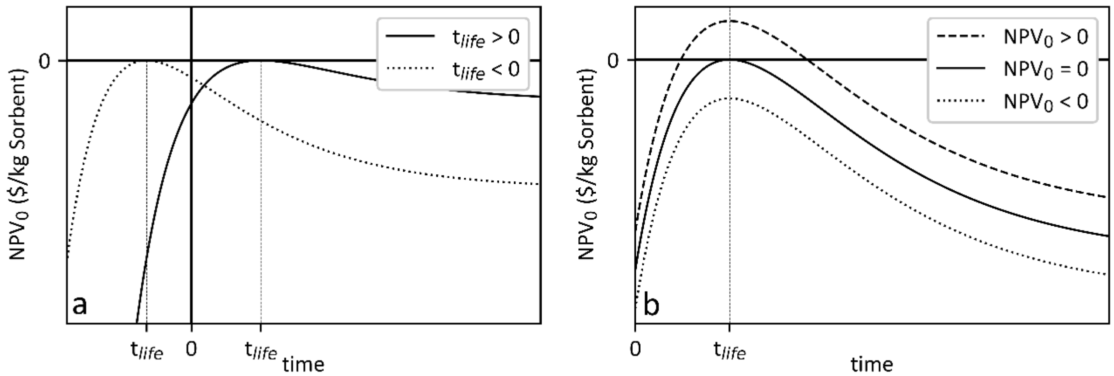

Figure 8. Possible scenarios for DAC NPV (a) compares a positive and negative lifetime, and (b) shows the impact of sorbent cost on a DAC set up with a positive lifetime.

In conclusion, for an economically viable DAC device, both conditions at equations (6) and (7) must be satisfied. The lifetime of the device can be calculated from equation (7), but a positive t_{life} does not guarantee a positive NPV. The MAB for a sorbent that results from equation (6) ensures a zero NPV for a given DAC device. The next section describes the NPV components (N_{rev}, $N_{O\&M}$, and N_{BoP}) and uses them in equations (6) and (7) to find t_{life} and sorbent MAB.

Revenue

At the beginning of the operation, a DAC sorbent captures CO_2 with its full capacity but as it goes through numerous cycles, the capture capacity of the sorbent degrades due to physical or chemical deterioration or both. Additionally, for the net present value calculations, the rate of revenue generation in time t should be discounted to produce the value in the present time. Therefore, the present value of the revenue generated per unit time (or revenue generation rate) will be:

$$n_{rev}(t) = \frac{P\ C_0}{t_{cycle}}\ e^{-t/\tau_D}\ \ e^{-t/\tau_M} \tag{8}$$

P is the market price of carbon dioxide per unit mass, C_0 is the initial capacity of sorbent (the amount of CO_2 captured per cycle), and t_{cycle} is the duration of one loading and unloading cycle. τ_D is the time constant of the sorbent capacity degradation, and τ_M is a time constant that accounts for the time value of money.

Different sorbents will degrade by different mechanisms and for most sorbents, degradation has not been fully explored. For DAC sorbents, an exponential rate of degradation for sorbent capacity loss is a particularly simple assumption that would be typical for degradation due to chemical interactions of uniform sorbent sites with ambient reactants like oxygen. In the few studies where degradation of amine-containing CO_2 sorbents is investigated over long times (Sayari and Belmabkhout 2010; Sayari, Heydari-Gorji, and Yang 2012; Heydari-Gorji and Sayari 2012), exponential and linear approximations fit equally well. Zhang et al. (2015) and Gebald et al. (2013) conducted stability experiments with ≥100 cycles for their proposed sorbents. Again, the available data may not be sufficient to draw a definitive conclusion on the best fit for sorbent degradation; but alternative fitting functions (e.g., linear degradation) do not show a noticeable improvement in the fit. The assumption of an exponential decay makes it possible to provide an analytically closed form of the model. However, the assumption can be simply changed in the model when more evidence becomes available. Degradation is further discussed in this chapter.

For simplification, the time constants can be combined in one effective time constant (τ_{eff}) as:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_D} + \frac{1}{\tau_M} = f + r$$

Where f is the degradation rate and r is the instantaneous discount rate. The present value of the total revenue generated by the sorbent can be calculated by integrating equation (8) over the lifetime of the sorbent:

$$N_{rev} = \int_0^{t_{life}} n_{rev}(t)\, dt = \frac{P\, C_0\, \tau_{eff}}{t_{cycle}} \left(1 - e^{-t_{life}/\tau_{eff}}\right) \tag{9}$$

Running Expenses

Assuming a constant O&M cost per unit time ($n_{O\&M_0}$), the present value of the rate of future expenses for O&M at time t becomes:

$$n_{O\&M} = n_{O\&M_0}\, e^{-t/\tau_M} \tag{10}$$

Similar to the revenue equation, the total O&M cost is resulted from integrating equation (10) over the lifetime of the sorbent:

$$N_{O\&M} = \int_0^{t_{life}} n_{O\&M}(t)\, dt = n_{O\&M_0}\, \tau_M \left(1 - e^{-t_{life}/\tau_M}\right) \tag{11}$$

For the balance of the plant, an initial capital cost of V_{BoP} per kg of the sorbent is assumed for the DAC device at the beginning of its operation. Assuming a constant scrap value, the net present contribution of the capital cost over t_{life}, i.e., the capital loss, can be calculated as:

$$N_{BoP} = V_{BoP} \left(1 - e^{-t_{life}/\tau_M}\right) \tag{12}$$

The rate of capital loss resulting from equation (12) is given by the derivative with respect to t_{life}:

$$\dot{N}_{BoP} = \frac{V_{BoP}}{\tau_M}\ e^{-t_{life}/\tau_M} \tag{13}$$

Lifetime and Sorbent Cost Calculation

n_{rev}, $n_{O\&M}$, and $\dot{N}_{BoP}$ (from equations (8), (10) and (13)) can be substituted into equation (7):

$$\frac{P\ C_0}{t_{cycle}}\ e^{-t_{life}/\tau_{eff}} = n_{O\&M_0}\ e^{-t_{life}/\tau_M}\ + \frac{V_{BoP}}{\tau_M}\ e^{-t_{life}/\tau_M}$$

The equation can be simplified when divided by e^{-t_{life}/τ_M}, and t_{life} can be calculated:

$$t_{life} = \ \tau_D\ ln(\frac{PC_0/t_{cycle}}{n_{O\&M_0}\ +\ V_{BoP}/\tau_M}) = \ \tau_D\ ln(1/\alpha) \tag{14}$$

Where:

$$\alpha = \frac{n_{O\&M_0}\ +\ V_{BoP}/\tau_M}{PC_0/t_{cycle}} \tag{15}$$

Variable α can be defined as the portion of income cash flow spent on the O&M and the BoP at the beginning of the operation. The multiplier $ln\ (1/\alpha)$ converts the decay time (τ_D) into the lifetime. The multiplier is a function of the sorbent revenue generation rate, as well as the O&M and BoP costs of the system. For a viable business, $\alpha < 1$. This results in a positive lifetime.

With the total revenue as well as the total O&M and capital costs (from equations (9), (11) and (12)), equation (6) can be written as:

$$\frac{P\ C_0\ \tau_{eff}}{t_{cycle}}\ \left(1 - e^{-t_{life}/\tau_{eff}}\right)\ -\ \left(n_{O\&M_0}\ \tau_M(1 - e^{-t_{life}/\tau_M}) + V_{BoP}(1 - e^{-t_{life}/\tau_M}) + N_S\right)\ = 0$$

If t_{life} is substituted from equation (14), N_S is determined as:

$$N_S = \frac{P\, C_0\, \tau_M}{t_{cycle}} \left(\frac{\tau_{eff}}{\tau_M} \left(1 - \alpha^{\frac{\tau_D}{\tau_{eff}}} \right) - \alpha \left(1 - \alpha^{\frac{\tau_D}{\tau_M}} \right) \right) \qquad (16)$$

Since the net present value is equal to zero, the value of N_S in equation (16) allocates the Maximum Allowable Budget (MAB) to a unit mass of a specific sorbent. It is important to note that MAB is not necessarily the price of the sorbent. In other words, the model determines a cap on the sorbent cost for a specific sorbent in a known DAC process and CO_2 market. Any sorbent price below the calculated MAB will make the DAC process profitable. It is important to note that in the case that the sorbent price is lower than the MAB, the lifetime has to be reoptimized (see Appendix J).

Parameter Connectivity

Out of five inputs to the model, market parameters (CO_2 price and discount rate) are exogenous variables over which a DAC practitioner has little to no control. Additionally, when a DAC design is committed to a specific sorbent, characteristics such as capacity and degradation rate are unchangeable. The only free parameter left is the cycle time. t_{cycle} is defined as the sum of loading and unloading times:

$$t_{cycle} = t_{load} + t_{unload}$$

Because of the slower CO_2 uptake rate in high loadings, it may not be economically viable to wait until the chemical equilibrium is achieved and the sorbent is fully loaded (see Chapter 6). Similarly, based on the sorbent and its unloading kinetics, t_{unload} can be chosen at any value. Therefore, cycle duration (t_{cycle}) is inherently a design parameter in a DAC system. Change in t_{cycle}, however, may influence the capacity of the sorbent and the rate of its degradation. Therefore, it is important to understand the interconnectivity between these parameters to develop a model appropriate for a specific system.

The relationship between capture capacity and loading time is different for different sorbents. Typically, the uptake rate is faster at the beginning of the loading cycle and the realized capacity has an approximately linear relationship with the loading time. In high CO_2 loadings, the loading kinetics becomes much slower, possibly to the extent that maximum capacity is achieved at infinite time. As a result, loading times are usually reported in the form of half capacity duration which is the required time for the sorbent to reach half of its full capacity. The value of the loading and unloading times become particularly important when the impact of cycle duration on the CO_2 price and the economy of DAC is investigated in Chapter 6.

Chemical and physical processes are responsible for the capacity loss of a solid DAC sorbent. Most solid sorbents proposed for DAC are amine-containing. These sorbents are generally tolerant to the presence of moisture. However, it has been shown that CO_2-induced formation of urea, even under mild capture condition, can result in a capacity loss (Sayari and Belmabkhout 2010; Sayari, Heydari-Gorji, and Yang 2012). Thermal stability and stability in the presence of oxygen is another concern for amine-based sorbents (Heydari-Gorji and Sayari 2012; Goeppert et al. 2019). Amine leaching over time (Goeppert et al. 2019) or sudden loss of weakly bound amines (Fan et al. 2014) can also decrease the capacity of DAC sorbents. Sorbent aging over extended periods of time (i.e., several years) can also reduce its capacity (Goeppert et al. 2019). For all of these mechanisms, it is reasonable to assume that the rate of loss is proportional to the amount of sorbent sites available, hence the decay rate is expected to be exponential.

Two degradation categories are considered in this study. One form of degradation proceeds with clock time, as was discussed by Goeppert et al. (2019), and a constant exponential rate of degradation per unit time is assumed. Degradation in this category occurs due to exposure of a sorbent to ambient conditions such as sunlight, high/low temperature, humidity, and particulate matter. As a result, the degradation rate is independent of t_{cycle}. Sorbents in this category have a constant lifetime regardless of cycle duration and the number of cycles they go through. A clock-based degradation rate is denoted by f_t in this model. As mentioned before, the sorbent degradation is implemented in the model by the parameter τ_D and it relates to f_t as:

$$\tau_D = \frac{1}{f_t}$$

In the second group of sorbent degradation processes, every time a sorbent goes through a loading and unloading cycle, its performance is slightly affected. This happens due to operational conditions such as changes in temperature, pressure, and water vapor concentration. Degradation occurs with each cycle and a constant exponential degradation rate is assumed per cycle. As a result, sorbents in this group live for a known number of cycles and their clock-based lifetime is directly affected by t_{cycle}. A cycle-based degradation rate is indicated by a dimensionless number, f_{cycle}. For such sorbents, the cycle-based lifetime (the number of cycles) is constant. To compare the two degradation mechanisms, an equivalent time-based degradation rate can be approximated for this group:

$$f_t{}' = f_{cycle}/t_{cycle}$$

f_t' is the equivalent of f_t in the first degradation category. In reality, the degradation of a DAC sorbent may be a combination of these two categories and in that case, an effective time constant of degradation can be used in the model:

$$\tau_D = \frac{1}{f_t + f_t'}$$

The connection between capacity, degradation rate, and cycle duration becomes important when t_{cycle} is varied, for example in the optimization of the performance of a given sorbent. In order to find the optimum $\mathrm{t_{cycle}}$ in different conditions, these relationships are further elaborated in Chapter 6. Table 8 summarizes the model.

Table 8. Sorbent TEA model summary

Model inputs	
Material Based	C_0: initial CO_2 capture capacity of sorbent [mass CO_2/mass sorbent] t_{cycle}: duration of one loading/unloading cycle [time] f_t or f_{cycle}: exponential rate of degradation (in the form of τ_D)
Market Based	P: unit mass price of CO_2 [$/mass CO_2] r: discount rate [1/time] (in the form of τ_M)
System Based	${n_{O\&M}}_0$: O&M cost per unit time per unit mass of sorbent [$/time/mass sorbent] V_{BoP}: capital cost per unit mass of sorbent [$/ mass sorbent]
Model outputs	
MAB: maximum allowable budget spent on sorbent [$/mass sorbent] t_{life}: lifetime of sorbent [time]	
Assumptions	
NPV_0 calculation is based on one lifetime of the sorbent material, but the results would not be different if one assumes infinite numbers of sorbent lifetimes.	

Dimensionless Analysis

A comprehensive understanding of a model with five input variables in addition to several outputs is not an easy task. In the real world, each one of the input variables summarized in Table 8, can change over a wide range.

Dimensionless numbers introduce many advantages in models similar to this. As pointed out by Ruzicka (2008), dimensionless numbers simplify a model and reduce the number of variables necessary for describing a system. Furthermore, they make it less complicated to compare different sorbents with completely different characteristics. And finally, when defined carefully, dimensionless parameters have a clear meaning which contributes to a better understanding of a complex system.

Different combinations of the variables at hand produce several dimensionless quantities; however, a dimensionless number related to money (μ) and a dimensionless number measuring time (ϑ) provide useful information about a DAC system:

$$\mu = \frac{P\ C\ \tau_M}{t_{cycle}\ N_S}$$

$$\vartheta = \frac{\tau_D}{\tau_M}$$

The dimensionless numbers include all inputs and outputs of the model and categorize them in terms of monetary and time-related variables. If one takes a closer look, μ represents the ratio of the revenue stream per cycle (PC) to the sorbent budget per cycle ($\frac{t_{cycle}\ N_S}{\tau_M}$). The variable ϑ, on the other hand, represents the ratio of the sorbent's gross lifetime to the money's lifetime. A third dimensionless variable is α which measures the rate of expenditures, summing operation, maintenance, and depreciation of the balance of the plant, relative to the rate of revenue (equation (15)).

As shown in Appendix K, equation (16) can be rewritten in terms of dimensionless quantities only:

$$\mu = \left(\frac{\vartheta}{1+\vartheta} \left(1 - \alpha^{1+\vartheta}\right) - \alpha \left(1 - \alpha^{\vartheta}\right) \right)^{-1} \tag{17}$$

Equation (17) shows the relationship between the three dimensionless parameters characterizing the DAC system. Figure 9 shows μ plotted against ϑ for different α values. The log-log graph showing the ratio of allocated revenue to the sorbent in different ranges of ϑ. When ϑ goes to infinity, the sorbent degrades very slowly and has a long lifetime. In this case, μ goes to $\frac{1}{1-\alpha}$ which is the ratio of revenue to the sorbent budget at the beginning of the operation. This result is intuitive since a robust sorbent does not have a capacity decay. The α ratio applies to every moment of operation and not just the beginning when the capacity is highest. If ϑ goes to zero, μ goes to infinity. This means for a sorbent with a very short lifetime and fragile structure, the sorbent budget (denominator of μ) has to be extremely small to make DAC economically viable.

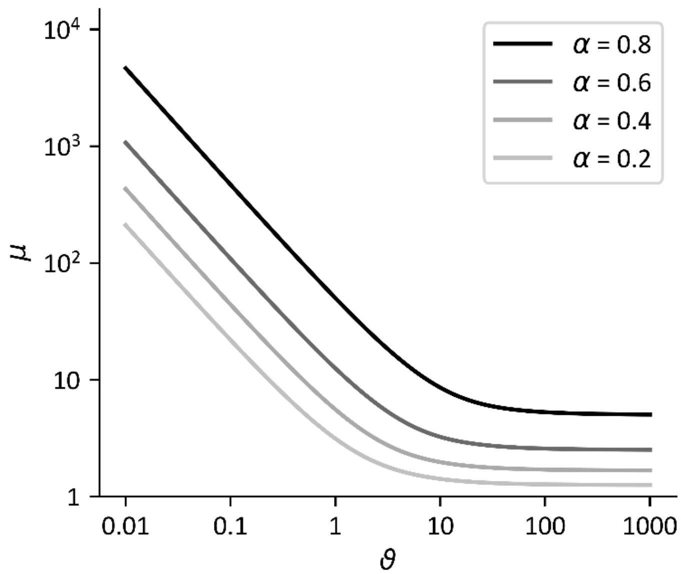

Figure 9. Dimensionless numbers in the sorbent cost analysis model. The figure shows the relationship between dimensionless numbers μ and ϑ for different α values.

Scope of the Model

With small adjustments, the model can be used for different applications. When developing the model, no DAC specific assumptions were made, therefore, it can be generalized to other gas separation processes with solid sorbents including post-combustion scrubbing or natural gas sweetening.

Post-combustion capture with solid sorbents is a growing field of research. Replacing aqueous amine solutions with solid sorbents offers several advantages. Choi and colleagues argue that solid sorbents decrease the required energy for regeneration (Choi, Drese, and Jones 2009). Additionally, a capture system with a solid sorbent has far less sorbent loss due to evaporation, and corrosion in the system is decreased (Choi, Drese, and Jones 2009).

Because of the more intense operational conditions, flue gas scrubbing systems are more complicated than DAC systems. Despite these differences, the principal of the two capture processes is the same and critical parameters in flue gas scrubbing can be translated to fit the model developed in this work.

Samanta et al. (2012) have summarized the important parameters for techno-economic analysis of a scrubbing process with solid sorbents and these parameters are sufficiently similar to the parameters discussed in the DAC cost model. The equilibrium capacity of a sorbent, under different pressure, temperature, and CO_2 concentration, is fairly similar to the capacity used in the DAC cost analysis model. Furthermore, kinetics data of loading and unloading, or collectively cycle duration, are equivalent to t_{cycle} in the DAC model. Particle/bed characteristics is another important parameter that affects both the capacity and kinetics of the loading process. Fluidized-bed contactors, for instance, contributes to faster kinetics as well as a better gas-solid contact. This positive impact is reflected in a higher capacity and a shorter cycle time. Higher pressure drops, however, may result in higher O&M costs. Furthermore, fluidized-bed contactors accelerate the degradation process of the sorbent and this can be incorporated in the degradation rate (f_t or f_{cycle}). Similarly, flue gas contamination with moisture and other combustion products (such as SO_2) can affect the degradation rate of a CO_2 sorbent. Other process and equipment parameters such as regeneration temperature in temperature swing adsorption (or vacuum pressure in pressure swing adsorption) and removal efficiency can also be reflected in the capital and operating costs of the system to fit into the model developed here. Table 9 summarizes the important parameters and their corresponding input of the model.

Table 9. List of relevant DAC and post-combustion capture parameters

Post-combustion parameter	Model input
Sorbent equilibrium data	$C_0,\ t_{cycle}$
Kinetics data	t_{cycle}
Particle/bed characteristics	$C_0,\ t_{cycle}, f_t$
Regeneration method	$N_{O\&M}, N_{BoP}, t_{cycle}, f_t$
Regeneration energy	$N_{O\&M}, N_{BoP}$
Flue gas contamination	f_t, N_{BoP}

CHAPTER 6

SORBENT COST MODEL APPLICATIONS

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Azarabadi, Habib, and Klaus S. Lackner. "A sorbent-focused techno-economic analysis of direct air capture." *Applied Energy* 250 (2019): 959-975.

Introduction

The previous chapter presented a detailed techno-economic analysis model for the Direct Air Capture (DAC) technology based on the sorbent. By calculating the maximum allowable budget (MAB) for a newly developed sorbent, the model can provide an approximate but pragmatic target for the commercial-scale cost of the sorbent in a CO_2 market with a particular CO_2 price. Conversely, with a known sorbent cost, one can estimate the minimum required price of CO_2 to make a DAC business profitable. Both applications provide information on how a change in sorbent characteristics, or in the DAC system affects the cost. This chapter advances the DAC techno-economic analysis by discussing several applications of the model and by critically investigating the commercialization of the state-of-the-art DAC sorbents.

Analysis of Two Examples

As an emerging technology, DAC cost is still very uncertain. All model inputs (summarized in Table 8) can have a wide range of values that depend on sorbent choice and process design. This section presents an analysis based on the work by Sinha et al. (2017) where they investigate DAC cost for two sorbents MIL-101(Cr)-PEI-800 and mmen-Mg_2(dobpdc). The model elaborated in Chapter 5 can accept the detailed cost data in addition to the sorbent characteristics (capacity, cycle time, and degradation time) from the work by Sinha et al. and find the MAB for their sorbents. Table 10 summarizes the different cost components of the Temperature Vacuum Swing Adsorption (TVSA) DAC system calculated by Sinha and colleagues. O&M cost includes steam, blower, and vacuum pump expenses. As mentioned earlier, Sinha et al. did not include compression cost in their model; however, Kulkarni and Sholl (2012) reported that compression up until the production of a sequestration-ready CO_2 stream (14 MPa) accounts for 25% of the total O&M cost. The cost of the monolith, the blowers, and the vacuum pump make up the total capital cost. Sinha et al. assumed a lifetime of 1 to 3 years for the sorbents; therefore, sorbent expenses are reoccurring in their model. Since the novel sorbents are not commercially available for bulk purchase, the authors have estimated their cost based on the cost of the ingredients. Sinha et al. (2017) report their costs per ton of CO_2 captured. In contrast, this work references all costs to a kilogram of the sorbent. Table 11 summarizes the parameters for the sorbents introduced by Sinha and coworkers.[4]

Table 10. DAC system cost components from Sinha et al. (2017)

Parameter	Unit	MIL-101(Cr)	Mg_2(dobpdc)
Capital Cost	per ton CO_2	$29	$24
O&M Cost	per ton CO_2	$41	$26
Sorbent Cost	per ton CO_2	$5-70	$10-140

[4] In shorter forms, these sorbents are occasionally referred to as MIL-101(Cr) and Mg_2(dobpdc)

Table 11. Recalculated data from Sinha et al. (2017) to use in this work

Parameter	Unit	MIL-101(Cr)	Mg_2(dobpdc)
Capacity	mmol CO_2/g sorbent	1	2.9
Cycle Time	min	40	75
V_{BoP}	per kg of sorbent	\$155.48	\$194.03
$n_{O\&M_0}$	per kg of sorbent per min	\$4.63 × 10^{-5}	\$4.42 × 10^{-5}
Sorbent Cost	per kg of sorbent	\$7-30	\$25-100
α	P = \$50/t, r = 5%	1.11	0.74
	P = \$75/t, r = 5%	0.74	0.49

Using equation (15) with two different sets of CO_2 price and discount rate, the parameter α was calculated based on the capacity, cycle time, V_{BoP}, and $n_{O\&M_0}$ values in Table 11. The discount rate is assumed to be 5% per year after inflation adjustment. This number agrees with a long-term return on capital (Piketty and Zucman 2014).[5] With a CO_2 price of \$50 per ton, MIL-101(Cr)-PEI-800 has $\alpha > 1$. Given the high capital and O&M cost in this system, even the initial cash flow is lower than the expenses for O&M and the cost of the balance of the plant. This results in a negative lifetime and the DAC device will not be economically feasible. If the CO_2 price increases to \$75 per ton (or the discount rate decreases), the α value will be below 1 and the DAC process will be feasible.

If the unit price of a given sorbent were known, the model would be able to calculate the cost of the captured CO_2. This application of the model is further discussed in detail in this chapter and in Appendix L. In this example, assuming a sorbent price of \$30 per kilogram for MIL-101(Cr)-PEI-800, the cost of CO_2 capture by this sorbent will be roughly \$95/t of CO_2. This clarifies that a \$30/kg sorbent is not able to produce carbon

[5] Implicit in this assumption is that the investment at hand is low in risk. For early DAC installations, the required return is likely to be higher.

dioxide at \$50/t. The lifetime of the investment, t_{life}, is assumed to be 3 years in this example.

Sinha and coworkers did not consider natural degradation of the sorbents in their model and a sudden-death scenario with lifetimes of 1-3 year for the sorbents is assumed in their model. A negligible degradation rate in sorbent capacity, however, results in an infinite lifetime of the system in this study. Therefore, using equation (14), degradation rates (or τ_D values) were adjusted to result in a lifetime of 1-3 years. Consecutively, MAB was calculated by equation (16). Table 12 compares the results with the range of the estimated bulk costs by Sinha et al. (2017) for the sorbents. Following Hart and Sommerfeld (1997) they estimated sorbent cost as between 2 and 8 times the raw material costs of the ingredients of the chemical synthesis.

Table 12. Results compared with data from Sinha et al. (2017)

Assumptions	parameter	Unit	MIL-101(Cr)	Mg_2(dobpdc)
Cost estimation by Sinha et al.				
Cost as 2-8 times ingredient cost	Sorbent Price	per kg of sorbent	$7-30	$25-100
Budget estimation in this work				
P = $50/ton, r = 5%	α		1.11	0.74
1-year lifetime	τ_D	year	-	3.25
	MAB	per kg of sorbent	-	$5.5
3-year lifetime	τ_D	year	-	10.00
	MAB	per kg of sorbent	-	$16
P = $75/ton, r = 5%	α		0.74	0.49
1-year lifetime	τ_D	year	3.50	1.50
	MAB	per kg of sorbent	$5	$15
3-year lifetime	τ_D	year	10.00	4.25
	MAB	per kg of sorbent	$15	$43

Table 12 shows, for the CO_2 price of $75/ton, when MIL-101(Cr)-PEI-800 lives for only 1 year, the MAB falls out of the range of its estimated bulk cost. With the approximated price range, this sorbent cannot be affordable for a lifetime of 1 year. When it lasts for 3 years, on the other hand, its budget falls between the range for its estimated bulk cost and MIL-101(Cr)-PEI-800 can be a good choice if it costs between $7 to $15 per kilogram. Similarly, a lifetime of 1 year renders mmen-Mg_2(dobpdc) unaffordable. If it lasts for 3 years, however, with a CO_2 price of $75/ton, there is a chance for using this sorbent; it produces a profit at a price between $25 and $43 per kilogram. Neither of the sorbents is affordable with the CO_2 price of $50/ton.

Budget Estimation for Existing DAC Sorbents

Several research groups are developing new DAC sorbents. DAC sorbents are formed by a variety of support structures with active materials or functional groups embedded. A lack of data makes it hard to analyze these sorbents' costs. For many of them, kinetics data including cycle duration and its relationship with the capture capacity are not readily available. Not only are kinetics data in the literature scarce, but the available data are also mainly from gravimetric CO_2 uptake experiments. A DAC sorbent loaded in a monolith structure or any other contactor design, would have a different cycle duration compared to that under gravimetric uptake condition. Sujan et al. (2019) implemented their proposed DAC sorbent in a module containing sorbent's monolith fibers and investigated the impacts of different flow rates on the capture process. As a result of the data scarcity in this area, estimates should be viewed as illustrative only.

High-quality data on durability including change in the capacity as a sorbent goes through many cycles are rarely available. Even when available, capacity changes after only a few cycles have been documented, while measurements must show the behavior after many thousand cycles. This analysis includes a comprehensive literature review and Table 13, Table 14 and Table 15 list the currently available data on DAC sorbent characteristics. Some of the sorbent characteristics data from the literature are extracted from graphs, but the majority are from text and tables in the references. Also, some of the stability data are collected from experiments conducted under conditions different than that of DAC (e.g., higher CO_2 concentrations or temperature). Sorbents in the tables are categorized based on their basic support matrix.

The cost analysis model was used to estimate the MAB values of these sorbents based on the available data, which are sparse. A CO_2 price of $75 per ton and a discount rate of 5% are assumed in all calculations. As shown in equation (15), α is a function of O&M and BoP costs as well as the generated revenue. Data from Sinha et al. (2017) show α values from 0.49 up to over 1. To analyze the collected data, $\alpha = 2/3$ was chosen to fall in the middle of this range. Additionally, the $\alpha = 2/3$ implies that 1/3 of the total generated revenue at the beginning of the operation covers sorbent costs (which is one of the three major expenses in the model), and the other 2/3 pays for O&M and BoP.

As shown in the tables, MAB was calculated where degradation data are available. When cycle time (i.e., loading and unloading) data were not available, an educated guess was used. A loading time of 15 min and an unloading time equal to half of the loading time was assumed when data were not available. The results column with the available data shows that the MAB values are well below $1/kg for most of these sorbents. The calculated lifetimes in the form of cycles vary from several cycles to several thousand cycles but rarely exceeds 1000 cycles. Sorbents that undergo a larger number of cycles show a higher MAB. As stated above, these results are illustrative and show the need for further work.

In most cases, realistic sorbents costs are likely much higher. Many of sorbents considered here are made from functionalizing a porous substrate with amines. It, therefore, stands to reason that the cost of such sorbents exceeds the cost of such porous substrates plus the cost of liquid amines used to functionalize them. Typical costs for porous materials range from $1/kg to $5/kg and the amines used in the synthesis costs roughly the same as the widely used MEA solution (between \$1/kg to \$2/kg).[6] With a multiplier of two for synthesis, a cost of \$2/kg seems highly optimistic. Polymeric and carbon-based sorbents are also common in DAC. It is not realistic to assume their commercial price would be cheaper than the several times the value of their raw material (crude oil). A crude oil price of \$80 per barrel means an average price of \$0.5 per kg of oil. As a result, most of the calculated MAB values are far smaller than their expected cost; only the most valuable sorbent, TEPA-PO-1-2/50S (Goeppert et al. 2019), has a budget higher than \$2/kg with a lifetime of 13,500 cycles. The main reason for this unusually high MAB is the nominal high stability of this sorbent, even though, measuring degradation in the first 15 cycles is insufficient for a conclusive stability analysis.

It is important to note that the low MAB values in this analysis do not rule out the practicality of these sorbents, but they indicate more work is required to accurately characterize DAC sorbents. As mentioned earlier, most stability analyses do not exceed a few cycles, and sorbents behavior in longer exposure times has not been studied in depth. Capacity degradation may continue its initial sharp drop, or similar to what Fan et al. (2014) have observed, it may stabilize after an initial rapid decrease. Losing several percents of the capacity in the first few cycles, makes it challenging to argue without further data that the sorbent can survive many thousands of cycles.

In the next step, a significant improvement in the stability of these sorbents is analyzed (or at least a more detailed characterization that indicates significantly higher sorbent stability). MAB values are recalculated assuming three lifetimes of 10^4, 5×10^4,

[6] Typical support materials such as activated carbon, activated alumina, and aerogel silica are considered here. Prices are for March 2019 from alibaba.com

and 10^5 cycles. As shown in the tables, the improved MAB values are considerably higher than before, and the results are more consistent with the cost of commercial gas separation sorbents. Nevertheless, even with lifetimes of 10^4 cycles, some of these sorbents have budgets below $2/kg. These results show the importance of sorbent stability. Commercialization of a DAC sorbent will be economically feasible if it lasts for tens if not hundreds of thousands of cycles. Given the significance of sorbent stability, this work demonstrates the importance of this characteristic in the early stages of sorbent development.

Finally, sorbents with low capacity or long cycle durations, do not have a high MAB even if they last for thousands of cycles. PEI/SBA-15 (Kuwahara et al. 2012) with a cycle time above 400 mins, and a relatively low capacity of 0.19 mmol/g, has the lowest MAB among the sorbents, even if it lasts for hundred thousand cycles. Low capacity sorbents such as MCF-MAPS (Didas et al. 2012), Q-cellulose (Hou et al. 2019), and QCS/PVA (Song et al. 2018) are among the sorbents with the lowest MAB (lower than $5/kg) on the list. This proves even the best stability features cannot compensate for low capacity and a long cycle time.

Table 13. Economic model applied to DAC sorbents (silica support) with available data in the literature

Sorbent	Full Swing Capacity (mmol/g)	Cycle Time (min)*	Half Loading Data†	Number of Cycles in Stability Analysis	Results with α = 2/3 (Available Data) ‡		MAB Results ($/kg) (Stability Improved)			Ref.
					MAB ($/kg)	Lifetime (Cycle Number)	10k Cycles	50k Cycles	100k Cycles	
PEI/Ti-SBA-15 (4.3)	0.64	(369)	✓	4 cycles	0.01	32	1.46	5.01	6.94	(Kuwahara et al. 2012)
PEI/Ti-SBA-15 (8.0)	0.5	(255)	✓				1.19	4.51	6.76	
PEI/Zr-SBA-15 (7.0)	0.85	(288)	✓	4 cycles	0.0006	3	2.03	7.48	10.93	
PEI/SBA-15	0.19	(439.5)	✓	4 cycles	0.0002	4	0.41	1.32	1.76	
TEPA in silica (38%)	2.5	(334.5)	✓				5.81	20.47	28.98	(Brilman and Veneman 2013)
FS-PEI-50, <0.25	1.37	(105)	✓	4 cycles	0.01	26	3.40	14.99	26.02	(Goeppert et al. 2014)
FS-PEI(800)-50	2.4	(105)	✓	4 cycles	0.02	26	6.01	26.57	45.97	
MCF_APS_hi	1.08	(27.5)	✓				2.78	13.45	25.79	(Didas et al. 2012)
MCF_MAPS	0.17	(6.5)	✓				0.47	2.31	4.58	
SI-AEATPMS	0.2	255		40 cycles	0.05	451	0.97	3.69	5.53	(Wurzbacher, Gebald, and Steinfeld 2011)

*Data in parenthesis are educated guesses used to complete the required parameters for MAB calculations

†With this column checked, half of the full-swing capacity was used in calculations and loading time in the third column is loading halftime ($t_{1/2}$).

‡ A CO_2 price of $75/ton and a discount rate of 5% are assumed.

Table 13. (cont.) Economic model applied to DAC sorbents (silica support) with available data in the literature

Sorbent	Full Swing Capacity (mmol/g)	Cycle Time (min)*	Half Loading Data[†]	Number of Cycles in Stability Analysis	Results with α = 2/3 (Available Data) [‡]		MAB Results ($/kg) (Stability Improved)			Ref.
					MAB ($/kg)	Lifetime (Cycle Number)	10k Cycles	50k Cycles	100k Cycles	
PEI/silica	2.36	(465)	✓	4 cycles	0.0021	3	5.29	16.74	22.05	(Choi, Gray, and Jones 2011)
A-PEI/silica	2.26	(292.5)	✓	4 cycles	0.01	12	5.34	19.56	28.50	
T-PEI/silica	2.19	(315)	✓	4 cycles	0.05	81	5.10	18.29	26.22	
HAS-5.4	1	(244.5)	✓	4 cycles	0.08	332	2.39	9.14	13.81	(Choi et al. 2011)
HAS-8.4	1.4	(244.5)	✓				3.36	12.88	19.46	
HAS-9.9	1.72	(250.5)	✓				4.11	15.65	23.55	
PL-0.75	0.6	(22.5)	✓	3 cycles	0.54	3604	1.51	7.34	14.19	(Chaikittisilp et al. 2011)
TRI-PE-MCM-41(dry)	0.64	195		4 cycles	0.0013	4	3.08	12.40	19.57	(Wagner et al. 2013)
(Humid)	0.55	195		4 cycles	0.0025	9	2.64	10.63	16.78	
FS-LPEI (5000)	0.73	39	✓	100-200 cycles	0.39	2079	1.84	8.79	16.62	(Zhang et al. 2015)
PPI/SBA-15	0.76	70		50 cycle	0.08	203	3.77	17.35	31.46	(Pang, Lively, and Jones 2018)
TEPA-PO-1-2/50S	1.34	210		15 cycles	8.54	13516	6.48	25.59	39.85	(Goeppert et al. 2019)
PEHA-PO-1-2/50S	1.25	210		15 cycles	0.37	579	6.04	23.85	37.14	

Table 14. Economic model applied to DAC sorbents (Metal Organic Framework) with available data in the literature

Sorbent	Full Swing Capacity (mmol/g)	Cycle Time (min)*	Half Loading Data†	Number of Cycles in Stability Analysis	Results with α = 2/3 (Available Data) ‡		MAB Results ($/kg) (Stability Improved)			Ref.
					MAB ($/kg)	Lifetime (Cycle Number)	10k Cycles	50k Cycles	100k Cycles	
MIL-101(Cr)-PEI-800	1	40		1-3 years lifetime claimed			5.07	24.18	45.62	(Sinha et al. 2017)
MIL-101(Cr)-PEI-1.76	1.35	(112.5)	✓	3 cycles	0.007	18	3.95	17.33	29.81	(Darunte et al. 2016)
mmen-Mg_2(dobpdc)	2.9	75		1-3 years lifetime claimed			14.59	66.75	120.20	(Sinha et al. 2017; T. M. McDonald et al. 2015)
ED-Mg/DOBDC	1.55	(22.5)	✓	4 cycles			3.94	19.19	37.05	(Choi et al. 2012)
en-Mg_2(dobpdc)	2.83	(397.5)	✓	5 cycles	0.02	26	6.48	21.48	29.27	(W. R. Lee et al. 2014)
Cr-MIL-101-SO_3H-TAEA	1.12	(22.5)	✓	15 cycles	1.05	3604	2.92	14.11	27.24	(Li et al. 2016)
Mg_2(dobdc)$(N_2H_2)_{1.8}$	3.66	(480)	✓				8.23	25.65	33.62	(Liao et al. 2016)

*Data in parenthesis are educated guesses used to complete the required parameters for MAB calculations

†With this column checked, half of the full-swing capacity was used in calculations and loading time in the third column is loading halftime ($t_{1/2}$).

‡ A CO_2 price of $75/ton and a discount rate of 5% are assumed.

Table 15. Economic model applied to DAC sorbents (other supports & Ion Exchange Resin) with available data in the literature

Sorbent	Full Swing Capacity (mmol/g)	Cycle Time (min)*	Half Loading Data†	Number of Cycles in Stability Analysis	Results with α = 2/3 (Available Data) ‡		MAB Results ($/kg) (Stability Improved)			Ref.
					MAB ($/kg)	Lifetime (Cycle Number)	10k Cycles	50k Cycles	100k Cycles	
APDES-NFC-FD, 40% RH	0.44	(94.5)	✓	10 cycles	0.02	203	1.14	5.09	8.94	(Wurzbacher et al. 2012)
AEAPDMS-NFC-FD	1.39	111	✓	20 cycles			3.50	15.37	26.49	(Gebald et al. 2011)
AEAPDMS-NFC	1.28	195	✓	100 cycles	0.36	782	4.39	17.51	49.94	(Gebald et al. 2013)
CC p(NMe-3-MS OH^-)	0.37	65					1.83	8.48	15.46	(He, Li, et al. 2013)
CB-g-xPCMS-OH^-	0.14	45					0.69	3.27	6.12	(He, Zhong, et al. 2013)
polyHIPE	0.72	58.5		5 cycles	0.01	15	3.67	17.10	31.46	(He et al. 2014)
MC-55-5	2.25	(60)	✓	10 cycles	0.06	101	5.76	26.65	48.93	(J. Wang et al. 2015)
Q-cellulose	0.18	(14.8)	✓				0.47	2.28	4.47	(Hou et al. 2019)
QCS/PVA	0.18	(16)	✓	9 cycles			0.47	2.28	4.44	(Song et al. 2018)
HP20/PEI-50	2.25	(22.5)	✓	5 cycles	0.05	81	5.84	28.17	54.48	(Chen et al. 2013)
P-100-25°C	1.58	209	✓				3.87	15.22	23.70	(Shi et al. 2017)

*Data in parenthesis are educated guesses used to complete the required parameters for MAB calculations

†With this column checked, half of the full-swing capacity was used in calculations and loading time in the third column is loading halftime ($t_{1/2}$).

‡ A CO_2 price of $75/ton and a discount rate of 5% are assumed.

Sorbent Performance Optimization

The economic model can be used to optimize the sorbent performance of a DAC device, for example, by minimizing the cost of CO_2 capture. Rather than using the CO_2 price as an exogenous parameter in the MAB calculation, this model can receive a sorbent cost to estimate the cost of CO_2 captured in a DAC system. Assuming a net present value of zero, equation (16) provides a relationship between the price of CO_2 (P) and sorbent cost (N_S). If one substitutes α (which is a function of P), with a known N_S, equation (16) can be solved for P. The produced equation, however, does not have an analytic solution for P and requires a numerical solution. More details about solving this equation numerically can be found in Appendix L.

To optimize the CO_2 cost of a DAC device in hand, it is necessary to investigate the parameters that are under the control of the operator. As mentioned in Chapter 5, cycle duration (t_{cycle}), especially unloading time, is a design decision that is still open, even after the sorbent has been chosen. Although any value can be chosen for the exposure time of a given sorbent to the ambient air, the size of the CO_2 loading of a sorbent is affected by the exposure time. Similarly, the amount of CO_2 released will depend on the regeneration time. In a steady-state operation, the unloading and loading will be equal. Shorter loading times (shorter cycle times) decrease the amount of CO_2 captured per cycle. In contrast, short cycle times speed up the capture process and reduce the time-dependent expenses of the system such as the BoP. In longer cycle times, on the other hand, a larger amount of CO_2 is captured per cycle, but a fewer number of cycles will be obtained when a sorbent has a constant clock-based lifetime. Cycle duration may also have an impact on the O&M cost as well as the degradation process of the sorbent.

All of these different and occasionally opposing impacts make it is difficult to decide on an optimum t_{cycle} for a DAC system.

In order to find the optimum t_{cycle}, one needs to find the relationship between sorbent capacity and cycle time of a given sorbent. This relationship can be different depending on the geometry of the contactor and other design parameters. In absence of sufficient data for a well-established DAC contactor design, adsorption curves (sorbent capacity plotted against adsorption time) can provide a suitable starting point for such an analysis. These curves are often available in the literature and they are different for different sorbents. The optimization analysis continues with the two sorbents in the DAC cost analysis by Sinha et al. (2017). Additionally, this analysis includes a more generalized hypothetical sorbent in the model to show how an optimum t_{cycle} can be achieved for these three sorbents.

Although all adsorption curves have a concave shape with a horizontal asymptote where the maximum capacity is achieved, there is no single accurate relationship between capacity and cycle time of DAC sorbents. Adsorption data is available in the analysis by Sinha et al. (2017) and the hypothetical sorbent has a homographic relationship between capture capacity and cycle time:

$$C_t = \frac{C_0\, t}{t_{1/2} + t}$$

This equation shows the relationship between capacity (C) and cycle time (t) where C_0 is the maximum achievable capacity for a sorbent and $\mathrm{t}_{1/2}$ is the cycle time for loading and unloading with half of C_0. Figure 10 displays the adsorption curves of the three sorbents.

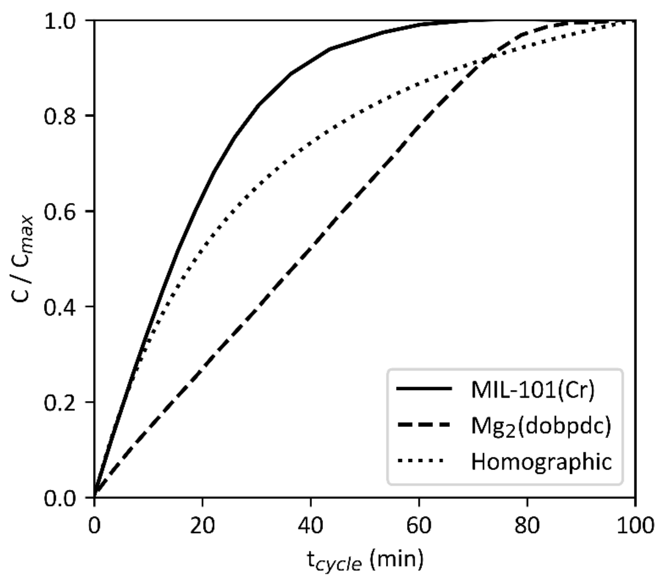

Figure 10. Normalized adsorption curves for three sorbents: MIL-101(Cr), Mg_2-(dobpdc), and the hypothetical homographic sorbent. Data for adsorption curves of MIL-101(Cr) and Mg_2(dobpdc) were collected from Sinha et al. (2017).

A range of cycle times from 1 minute to the cycle time required for a full loading and unloading swing of the sorbents was considered.[7] With this assumption and assumptions about O&M and BOP available in Table 11, the cost of the CO_2 product was calculated for different cycle times. The fraction of the nominal sorbent capacity that is utilized in the often much shorter cycle time was also estimated.

Four different scenarios were considered for CO_2 price optimization. Both the O&M cost rate and sorbent degradation rate can be assumed to be dependent or independent of t_{cycle}. In this discussion, when a rate parameter is dependent on t_{cycle}, the total change per cycle is assumed to be constant. In one case the rate (either $n_{O\&M}$ or $1/\tau_D$) is not affected by t_{cycle}; in the other one the rate times $\mathrm{t_{cycle}}$ is constant. The four scenarios are shaped around this dependency. Sorbent characteristics indicated in Table

[7] Desorption time was assumed to be proportional to the adsorption time and set to the ratio given by (Sinha et al. 2017)

11 were used for the optimization. The sorbent bulk cost estimated by Sinha et al. was used in the optimization (\$15 and \$50 per kg for MIL-101(Cr) and Mg_2(dobpdc), respectively). For the homographic sorbents, a full-cycle capacity (C_0) of 2 mmol/kg sorbent and half-cycle duration ($t_{1/2}$) of 30 mins were assumed. The O&M and capital costs were assumed to be similar to the other sorbents and its bulk price was set to \$50/kg sorbent. Reasonable and comparable degradation rates were assumed for all three sorbents. Figure 11 summarizes the results of the optimization analysis.

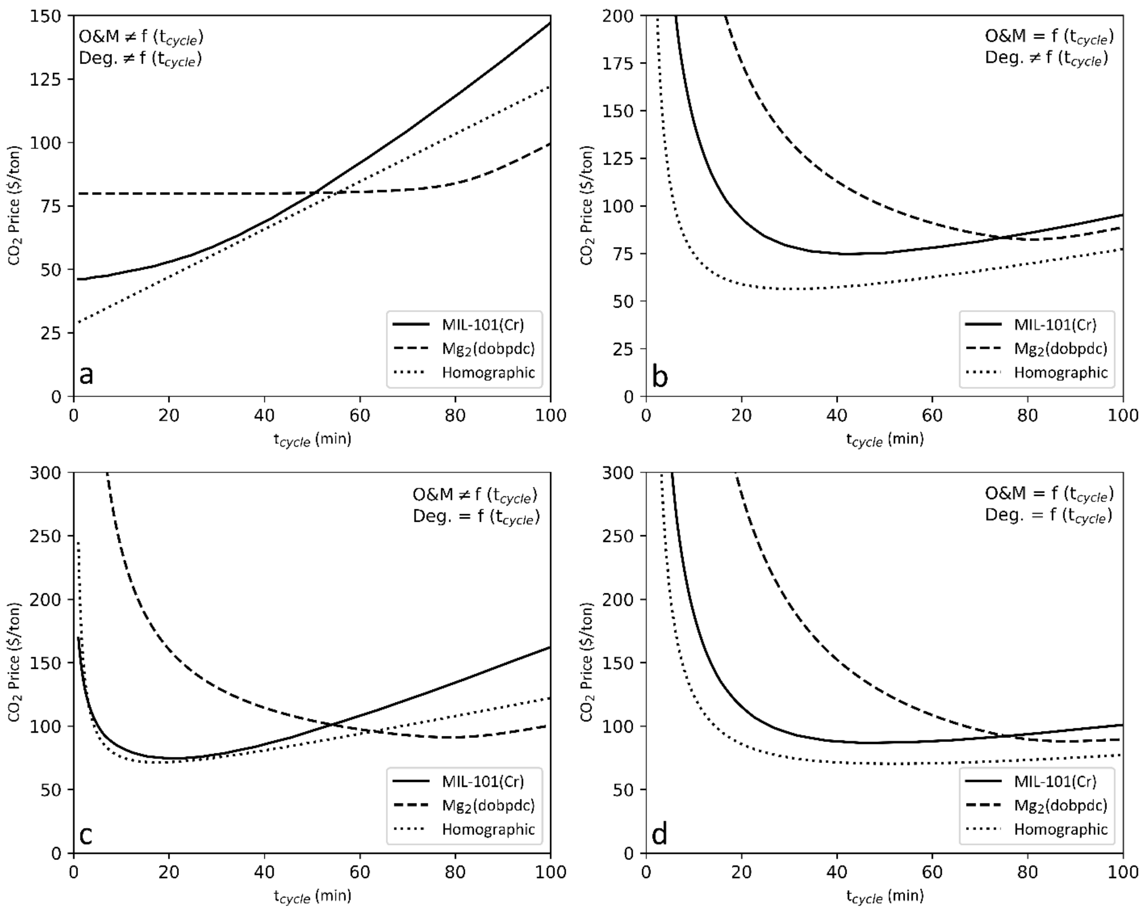

Figure 11. CO_2 price change plotted against t_{cycle} in four different scenarios (a) Both O&M cost and sorbent degradation are independent of t_{cycle}. (b) O&M cost is t_{cycle} dependent while degradation is not. (c) O&M cost is independent while degradation is t_{cycle} dependent. (d) Both the O&M cost and sorbent degradation are t_{cycle} dependent.

Figure 11a shows the scenario where both O&M and sorbent degradation values are independent of cycle duration. Shorter cycle durations are favored for all three sorbents, while Mg_2(dobpdc) shows a more or less constant CO_2 price for cycle durations up to 70 mins. MIL-101(Cr) and the homographic sorbent have similar behavior with the cheapest CO_2 in t_{cycle} values close to zero. Very short cycle durations, however, are not practically possible. Unlike scenario (a), the remaining three scenarios show infinite CO_2 prices in short cycle times. In these scenarios, either one or both of the O&M and degradation rate parameters are dependent on t_{cycle}. The CO_2 price change with t_{cycle} demonstrates a similar pattern for all three scenarios (b, c, and d). In scenario (b) where O&M cost is t_{cycle} dependent while degradation is not, each sorbent has a fixed number of hours rather than cycles. Therefore, shorter cycle durations lead to a larger number of cycles, but O&M cost which is constant per cycle gets very large as cycle times get short and it dominates the other two expenses (sorbent and BoP). In scenario (c), the degradation rate is dependent on t_{cycle} and the O&M is independent of the cycle time. In this case, sorbents live for a fixed number of cycles regardless of t_{cycle}. When the cycle are short, the operational clock lifetime is short, therefore, sorbent cost, which is a constant upfront expense, will dominate the other two and increases the total capture cost. Scenario (d), which has O&M and degradation rate dependent on t_{cycle}, observes the O&M and sorbent costs domination effect from scenarios (b) and (c). In the last three scenarios, MIL-101(Cr) and homographic produce the cheapest CO_2 in relatively shorter cycle durations, while Mg_2(dobpdc) is preferred to have a longer cycle. Table 16 summarizes the scenarios and their optimum t_{cycle}.

One can explain the similarity between the CO_2 price pattern of MIL-101(Cr) and the homographic sorbent by taking a closer look at their adsorption curves (Figure 10). Adsorption curves for these sorbents show a steeper uptake rate at the beginning, whereas Mg_2(dobpdc) starts capturing CO_2 with a slower linear rate. This higher initial capture rate makes it possible to take advantage of shorter t_{cycle} values that deliver a significant portion of the maximum capacity in a shorter time. Therefore, MIL-101(Cr) and homographic favor shorter cycle durations. The slower initial capture rate of Mg_2(dobpdc), on the other hand, makes it worth to wait longer and load the sorbent close to its maximum possible capacity. The results show that for sorbents with a faster capture rate, it is better to shorten cycle duration for a cheaper CO_2 product.

Table 16. Optimization results

Fig.	Sorbent	Optimum t_{cycle} (min)	Minimum Cost (per ton CO_2)	Assumptions
11a	MIL-101(Cr)	N/A	$46	$O\&M \neq f(t_{life})$ $Deg. \neq f(t_{life})$
	Mg_2(dobpdc)	Up to 70	$82	
	Homographic	N/A	$29	
11b	MIL-101(Cr)	39	$75	$O\&M = f(t_{life})$ $Deg. \neq f(t_{life})$
	Mg_2(dobpdc)	79	$82	
	Homographic	31	$56	
11c	MIL-101(Cr)	22	$75	$O\&M \neq f(t_{life})$ $Deg. = f(t_{life})$
	Mg_2(dobpdc)	77	$91	
	Homographic	18	$71	
11d	MIL-101(Cr)	43	$87	$O\&M = f(t_{life})$ $Deg. = f(t_{life})$
	Mg_2(dobpdc)	86	$88	
	Homographic	52	$70	

In practice, degradation mechanisms and O&M costs may not be as straightforward as in the scenarios discussed here. Maintenance costs of a DAC unit, for instance, could be a combination of the necessary procedures per so many hours or cycles of operation. This makes the real-life O&M cost somewhere between the two alternatives defined in this model. Another simplifying assumption in the optimization model is that capital cost (V_{BoP}) is assumed to be constant per kilogram of the sorbent. It has been observed that based on the economy of scale, the capital cost per unit of output decreases at larger scales. Therefore, for a larger DAC device, V_{BoP}, which is given per unit of sorbent mass, is probably lower.

Conclusion

Direct air capture was first suggested by Lackner as a way to reduce the concentration of atmospheric CO_2 to mitigate the impacts of anthropogenic climate change (Klaus Lackner, Ziock, and Grimes 1999). Since then a significant effort has been focused on the development of novel DAC sorbents and the technology has found its place among the more traditional mitigation strategies. Given the variety of DAC methods and sorbents, a standard cost analysis model can be a useful tool firstly, to evaluate a newly developed sorbent and its potential for commercialization and secondly, to identify weaknesses and potential improvement of the technology. Such a tool can facilitate the comparison between the numerous DAC sorbents and methods suggested in the literature.

This analysis implements an operational research approach to maximize the net present value of a DAC business. The techno-economic model is not dependent on a specific DAC design and only uses widely-understood parameters. This analysis evaluates the maximum affordable budget of a sorbent in any DAC process with available data. It is important to note that in a particular CO_2 market, the model estimates how much a sorbent should cost, rather than how much its actual bulk price is or how costly it will be to produce. This approach can be applied to many different industries as long as a piece of technology is implemented for a cyclic revenue generation. Sorbent-based gas separation (e.g., post-combustion carbon capture) and photovoltaic systems are two examples that a similar approach can be implemented for a cost analysis. Several simplifying assumptions make the model easier to understand; however, more details can be easily added to the model (see Appendix M). Additions and refinements will add more realism to the model, but also take away its analytic simplicity, which helps in developing intuition about a complicated system.

The results (calculated MAB values for the currently available sorbents) show the current mainstream DAC sorbents need to undergo more thorough tests to demonstrate their viability for commercialization. Most of these sorbents are designed and tested for a controlled experimental environment rather than ambient conditions and extreme weather conditions under which a commercial DAC will have to operate. Stability of these sorbents after undergoing loading and unloading cycles is not tested very often and even when such tests are done, with some exceptions (Zhang et al. 2015), they usually do not exceed tens of cycles. This model, however, shows a reasonable budget is only achieved when a sorbent lasts for tens if not hundreds of thousands of cycles. The cost optimization analysis demonstrates that depending on the sorbent and the DAC set up, sometimes it is worth shortening cycle duration and decrease the CO_2 captured per cycle to lower the running expenses and as a result produce a cheaper CO_2.

This study also brings out the trade-off between the performance of a sorbent and its cost. In effect, one can estimate whether the additional performance is worth the additional cost. Some sorbents can be quite low in cost. Strong base anionic exchange resins can cost as little as $3/kg.[8] There will be an additional cost to shape them into an effective sorbent structure. On the other hand, high tech sorbents like MOFs are likely to be more expensive. DeSantis et al. (2017) investigate the potential for cost reduction in the large-scale production of MOFs. They conclude that with the current synthesis methods, commercialized MOFs will cost between $50-70/kg. A cost of $10 per kg cost is the lowest prediction, but this includes significant changes in the synthesis process and a reduction in the cost of raw materials. Some of the MOF sorbents considered in this study have a budget of less than $10/kg even if they last for 10000 cycles.

The results suggest that future research should pay stronger attention to degradation and cycle time of DAC sorbents. Both loading and unloading times have to be measured in real-life DAC conditions rather than in a gravimetric CO_2 uptake experiment or presence of an inert gas purge. Additionally, data scarcity in the capital and O&M costs of different DAC processes (e.g., temperature, pressure, and humidity swing processes) was found as a great obstacle to DAC feasibility studies. The importance of these parameters is also demonstrated in the 2018 NAS report (National Academies of Sciences 2019). This model along with cost analysis similar to the study by Sinha et al. (2017) helps the DAC technology advance as a potential climate mitigation strategy.

[8] March 2019 price from alibaba.com

CHAPTER 7

CONCLUSION AND FUTURE WORK

As an eminently promising climate mitigation technology, Direct Air Capture (DAC) has gained a great deal of attention among scientists, tech entrepreneurs, and policymakers. High cost as well as uncertainty in its role and potential scale, however, pose a challenge in the transition of this technology from demonstration and proof-of-concept to commercialization. DAC is solely considered as a carbon dioxide removal (or negative emissions) technology rather than a carbon dioxide mitigation tool for reducing emissions from large emitters. This is mainly due to the mainstream judgment that DAC costs significantly higher than other negative emissions or mitigation technologies. This dissertation provides a robust techno-economic analysis of this technology and assesses its role in a futuristic energy system. Through a case study and comparison with the cost of a widely studied mitigation technology, i.e., post-combustion capture, this work advanced a new way to think about the role of DAC. Furthermore, DAC sorbent, cost, and longevity were identified as crucial parameters in the commercialization of the technology.

Even though mainly considered as a technology to reverse our past emissions, DAC was unorthodoxly considered for decarbonization of large point source emitters such as power plants in this work. The main motivation of considering DAC for this application was its unique advantages over the post-combustion capture technology. DAC can be implemented as stand-alone units autonomous from a power plant or source of emission. This freedom of operation provides some advantages for DAC over the post-combustion capture technology and this dissertation quantified these advantages in terms of the cost of decarbonization of power plants.

The natural gas power plant fleet is a growing sector in electricity production in the United States. The cost analysis model developed in this work estimates the cost of post-combustion retrofit for the existing natural gas combined cycle power plants in the United States. The results suggest that the currently available DAC technology may already offer a cheaper carbon capture alternative for at least one-third of CO_2 emissions from the natural gas-related electricity generation. The high cost of retrofit is driven by the low utilization level, or capacity factor, of many of the natural gas-fired power plants. By contrast, a stand-alone DAC device offers a levelized cost of carbon capture regardless of the emission source. Although post-combustion capture is the cheaper option for highly utilized and efficient large power plants, relying on this technology for a deeper level of decarbonization will result in high costs. While the cost of decarbonization by post-combustion capture increases exponentially for some power plants, DAC provides a constant cost with a minuscule cost of CO_2 transportation. In other words, this study treats the cost of DAC as a backstop cost and a benchmark for other mitigation technologies.

Future works should focus on extending this study by estimating the cost of decarbonization from other sectors of the economy by alternative mitigation technologies and comparing their cost with that of DAC. Other large point source emitters such as steel and cement plants as well as oil refineries are suitable candidates for such comparison. Moreover, life-cycle greenhouse gas emissions of electric vehicles and their cost of net carbon reduction could be compared with DAC technology eliminating greenhouse gas emissions from other technologies. A higher percentage of non-dispatchable renewable electricity (e.g., solar and wind) in the grid results in lower utilization of the existing fossil-fuel generation capacity. Based on this analysis, lower carbon intensity of the grid due to higher penetration of intermittent renewables counterintuitively results in a higher cost of decarbonization from the remaining fossil-fuel power plants. DAC may offer a cheaper carbon capture solution at low utilization levels of a power plant. Similar case studies for locations such as Australia (where the grid is highly dependent on coal with an increasing share of solar photovoltaic in recent years) would provide interesting new insights. Table 17 summarizes the research question answered in this section and the focus of future studies in this area.

Table 17. Summary of Chapter 3 findings

Research Question	How does the implementation of direct air capture and post-combustion capture technologies compare in the decarbonization of the existing natural gas power plant fleet in the United States?
Answer	• Post-combustion capture is promising for NGCC units larger than 400 MW, younger than 14 years, more efficient than 45%, with a utilization (capacity factor) higher than 0.5. Retrofitting other generating units will result in a high cost of carbon reduction. • DAC may be a cheaper alternative in addressing emissions from non-retrofittable NGCC units as well as non-NGCC natural gas-fired generating units. DAC can also address the residual emissions from retrofitted units. • The results show that DAC is cheaper than post-combustion capture retrofit for at least one-third of natural gas-related CO_2 emissions.
Future Work	• Improving the model with high quality data from future commercial DAC units. • Extending the cost of analysis of DAC to decarbonization from other sectors of economy such as steel and cement plants, oil refineries, and transportation. • Extending the case study to other countries with a high share of intermittent renewable electricity in their grid (e.g., analyzing DAC implementation in decarbonizing the Australian electricity grid).

Dahlgren (2013) investigated the advantage of small, modular, short-lived systems over the traditional large-scale approach. The statistical observation suggests that the mass-production of small modular units results in a higher learning rate since it allows for continuous improvement and takes advantage of unexpected breakthrough technological improvement for cost reduction. In a fluctuating and uncertain market, the small scale provides the opportunity to "wait and see," which reduces investment risks and therefore encourages the early adoption of new technology. Inspired by small modular technologies such as solar photovoltaic, lithium-ion batteries, and fuel cells, this work used a similar strategy (and learning curve data) to project the future cost of DAC. Although sensitive to the chosen learning rate, these results demonstrate a promising path to cost reduction for DAC down to $100 (or less) per ton of CO_2.

This dissertation not only incorporated the impact of learning-by-doing for DAC but also estimates the future cost of post-combustion capture to project the future competition of the two technologies when implemented at large scales. The results clearly show the path dependency in scaling. Cost reduction through learning-by-doing is not expected to be highly effective for a custom-made technology such as post-combustion capture. DAC, however, can benefit from the learning advantage of small-scale technologies. This may significantly reduce the total cost of decarbonization from the electricity grid by incorporating both mitigation technologies. In some scenarios, DAC's share from the total emission capture could go considerably beyond one-third.

This work highlights new opportunities and niche markets for DAC by replacing the archaic approach of "bigger is better" with mass-production. The proposed strategy for DAC scale-up may engage a higher number of small investors and manifest a novel and more practical path towards commercialization to gain support from policymakers. A more accurate analysis of learning rate values based on more data from the forthcoming commercial DAC and post-combustion plants is a likely topic for future work. Moreover, future work should focus on a better understanding of the cost floor, or minimum achievable cost at the end of the learning phase for the DAC technology. Even though this cost is the most difficult factor to predict, from a long-term societal perspective it is the most important parameter to consider, and it is the cost that will differentiate between different DAC technologies.

Lessons learned from the development of wind turbines can provide useful insights regarding the most effective scale-up approach for DAC. This policy coupled with Feed-in Tariffs (FiTs) lowers the risk of investment in new technologies and has shown a successful trend in decreasing the cost of renewable energies all around the world. The same concept, mainly suggested for wind and solar electricity, could also be applied to DAC. Additionally, social acceptance of large-scale DAC is an area of research that has not been fully explored. Coupled with moral hazard concerns, future research should focus on the social sustainability of DAC as an emerging technology. Table 18 summarizes the research question answered in this section and the focus of future studies in this area.

Table 18. Summary of Chapter 4 findings

Research Question	How do mass production and economy of scale compare in cost reduction through learning-by-doing when it comes to direct air capture and post-combustion capture for decarbonization of the US natural gas power plant fleet?
Answer	• There is uncertainty associated with cost projection of the two technologies by learning curves. • Scale-up strategy makes a significant difference in future costs. Cost reduction through learning-by-doing would not be highly effective for a custom-made technology such as post-combustion capture. • As a stand-alone unit, cost reduction happens more effectively for DAC, while post-combustion capture cost significantly depends on the operation of the generating unit it is attached to. • DAC can lower the cost of decarbonization only if the implementation and cost reduction happens early.
Future Work	• A more accurate analysis to estimate the cost floor in the learning curve model, especially for DAC. • Taking advantage of DAC's similarities with wind turbine to optimize the scale-up strategy. • Studying the social sustainability of DAC as an emerging technology. This includes investigating the public acceptance and moral hazard of this technology.

In the short run, a hurdle that exits for cost reduction in DAC technology is the cost and caliber of the sorbent. This work was motivated by the fact that a variety of different sorbents are synthesized in laboratories every year, yet no comprehensive guideline or standard defines a “good” DAC sorbent. This study looks at this problem from a business point of view and develops a Net Present Value (NPV) analysis to put a dollar value on a sorbent based on its performance. This dollar value is called the Maximum Allowable Budget (MAB). MAB makes it possible to compare different sorbents based on their capture characteristics including the frequently overlooked parameter of sorbent degradation rate or sorbent lifetime.

This dissertation finds that the majority of the currently proposed DAC sorbents do not undergo sufficient testing for longevity assessment to come to arrive at an informed estimate. Furthermore, those that are tested are required to be significantly more robust to make them meet the commercial requirement of DAC technology. A standard DAC sorbent with a cost on the order of \$20-\$50/kg must undergo tens if not hundreds of thousands of loading and unloading cycles to provide a positive NPV. This analysis accentuates the importance of longevity testing for scientists and industrial practitioners working on DAC sorbent development.

Starting from a simple, yet useful analytical NPV model, this work built a set of standards for DAC sorbent developers and challenged the scientific practice with the goal of DAC commercialization. The model not only offers additional analysis such as cycle duration optimization for NPV maximization but also suggests a mathematical approach for the NPV analysis of similar technologies such as post-combustion capture with solid sorbents and solar photovoltaics. Future work should specifically focus on state-of-the-art

DAC designs to understand other running DAC expenses to increase the accuracy of this model. Experimental work for a better understanding of sorbent degradation mechanisms should also be incorporated into future work in this area. The NPV equation and the MAB value are dependent on the degradation mechanism (degradation per cycle or per unit time or both) and the rate of deterioration in sorbent capacity. Table 19 summarizes the research questions answered in this section and the focus of future studies in this area.

Table 19. Summary of Chapters 5 and 6 findings

Research Question	What effect do sorbent characteristics and cost have on the cost of direct air capture? In other words, how can the commercialization potential of a DAC sorbent be quantified based on its characteristics and the CO_2 market?
Answer	• An analytical model was developed to investigate the impact of each sorbent characteristic. • With a known CO2 price, the commercialization of a sorbent is mainly affected by its capacity, loading/unloading cycle time, and degradation rate. • To be competitive, a DAC sorbent has to last tens if not hundreds of thousands of cycles.
Future Work	• A more accurate understanding of other DAC expenses (capital and O&M) improves the accuracy of the sorbent budget estimation. • Investigating degradation mechanisms allows for a better optimization of sorbent performance.

The theme of this dissertation has been in advocating DAC as a backup carbon capture tool when the alternative mitigation technologies become impractical. Through the clarification of how a small, modular, mass-produced technology scales more efficiently, this study elaborates a path towards cheap commercialization as well as potential applications for the DAC technology. The hope is that researchers, investors, and policymakers continue to build on these findings and that DAC as a carbon mitigation technology (and not only as a negative emissions technology) gains even more attention.

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APPENDIX A

POWER PLANTS INFORMATION DATA MINING

Python's Pandas package was used for data mining and analysis in this study. The main sources of data for NGCC units are the unit and generator information sheets ("UNT16" and "GEN16") from the eGRID 2016 metric data spreadsheet.

First, on the generator page, NGCC units with a MWh generation record for the year 2016 were identified. NGCC units are flagged with generator prime mover types of "CA" for combined cycle steam turbine, "CT" for combined cycle combustion turbine (or gas turbine) and "CS" for combined cycle single shaft. Generator information, including the plant's name and state, DOE/EIA facility code (ORISPL), generator ID, nameplate capacity in MW, 2016 electricity generation in MWh and age were collected. Generation and capacity data for CA and CTs which belong to the same NGCC unit were identified and aggregated and a combined dataset for generation and nameplate capacity of all NGCC units including 670 records was created.

Then the emission records for these NGCC units including the plant's name and state, ORISPL, unit ID, 2016 heat input in GJ and 2016 CO_2 emissions in ton were collected to merge the generator and emission data records. Similar to the generation records, emission records belonging to each NGCC unit were combined and the aggregate heat input and CO_2 emissions dataset of all NGCC units with 655 records was created.

The generation and emission datasets were processed to match as many records as possible and merged by using ORISPL code and other information such as the comparison between the heat input and generation values. A final database including generation and emission records for the NGCC fleet was created and the efficiency (η) and capacity factor (CF) values for each NGCC units were calculated:

$$CF = \frac{2016\ Generation\ (MWh)}{Nameplate\ Capacity\ (MW) \times 8766\ (h)} \tag{18}$$

$$\eta = \frac{2016\ Generation\ (MWh)}{2016\ Heat\ Input\ (GJ) \times conversion\ factor\ (\frac{MWh}{GJ})} \tag{19}$$

Missing heat input data and obvious inconsistencies resulted in 513 valid records out of 670. Invalid records have either very high or very low net efficiencies or in a few cases, capacity factor values above 1 or below 0. For this analysis and results in the chapter, the model only uses the valid NGCC records and when results are shown in terms of total percentage, a conversion factor was used to convert the results from the valid units to all the units. Table 20 summarizes some statistical information about the generated database. Median values are calculated by the number of units. Mean values for capacity factor and net efficiency are also calculated by the number of units, while the mean for Levelized Cost of Electricity (LCOE) values is an arithmetic mean weighted by the MWh electricity generation of each unit. Minimum and maximum net efficiency values are the model assumptions; datapoints outside of the 35%-52% range are assumed to be invalid. LCOE values are only calculated for units considered for retrofit (larger than 25 MW and younger than 25 years).

Table 20. NGCC statistical information for 513 valid records

Parameter	Min	Median	Mean	Max
Nameplate Capacity (MW)	7.7	458	467	1850
Age (years)	0	14	15.3	51
Net Efficiency (HHV%)	35%	45.5%	44.5%	52%
Capacity Factor	0.002	0.47	0.46	0.96
Number of Gas Turbines in a Unit	1	2	1.9	12
Number of Steam Turbines in a Unit	1	1	1.1	4
LCOE pre-retrofit (2017$/MWh)	39.79	57.33	55.06	6,800
LCOE post-retrofit (2017$/MWh)	54.58	89.45	84.56	17000

APPENDIX B

CUMULATIVE GENERATION VERSUS CAPACITY FACTOR

In this analysis, natural gas-fired generating units are divided into two groups: NGCC and non-NGCC. NGCC units are relatively larger and are mainly utilized for intermediate-load and baseload electricity demand. Non-NGCC units, on the other hand, are mainly small gas or steam turbines widely used for peak load electricity demand. There are about 6 times more non-NGCC units than NGCC units, while NGCC units produce 5.5 times more electricity.

Figure 12 illustrates the cumulative distribution of NGCC and non-NGCC units based on their capacity factor. As shown in Figure 12a, most NGCC units operate in the intermediate-load range. Only 20% of NGCC units are categorized as peaker (capacity factor < 0.2) and they produce an insignificant percentage of NGCC electricity. On the contrary, roughly 80% of non-NGCC units are peakers and they generate about 40% of total non-NGCC electricity (Figure 12b).

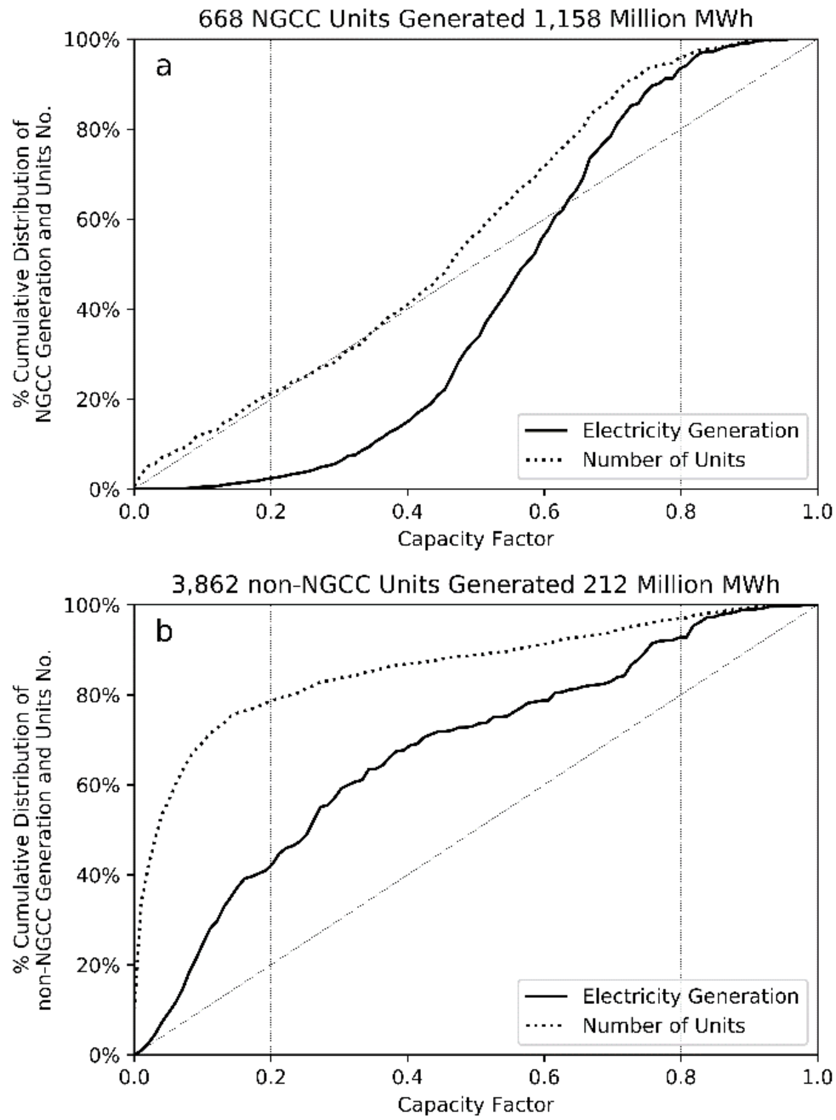

Figure 12. 2016 cumulative distribution of (a) NGCC and (b) non-NGCC natural gas units versus capacity factor. Clearly, most of non-NGCCs provide electricity only during peak demand hours while most NGCC units are categorized as intermediate-load units.

APPENDIX C

MACHINE LEARNING FOR VALIDATING POWER PLANT RECORDS

Missing heat input values result in invalid net efficiency values for some of the NGCC units. To address the issue and investigate the potential error from the invalid datapoints, one can take advantage of a simple machine learning algorithm to estimate the net efficiency of these units. Then used the estimated efficiency values and units' 2016 generation record to calculate their heat input by equation (19). Then an emission factor (ton CO_2/GJ heat input) was used to calculate CO_2 emissions for these units.

Several machine learning algorithms were used, and the K-nearest neighbor regression method resulted in the most accurate outcome (scikit-learn 2019). K-nearest neighbor method uses net efficiency value(s) of the K nearby (similar) NGCC units to estimate the net efficiency of an invalid data record. K is an optimum value which results in the highest regression accuracy. The algorithm uses nameplate capacity, capacity factor, and age as the determining attributes for net unit efficiency.

Typically, the valid datapoints are split into two categories, one for training and the other one for testing the trained algorithm. Out of a range of K values from 0 to 100, $K = 16$ was found to be the optimum value resulting in the most accurate regression for the testing set (16 nearest points used in the regression algorithm). Figure 13 shows r-squared scores of the training and testing sets for different K values.

The algorithm used $K = 16$ to estimate the net efficiency as well as heat input and CO_2 emissions of the invalid datapoints and generated an NGCC database with 668 valid records. Table 21 summarizes the same statistical information as in Table 20 (Table 20 is for the 513 originally valid records). Values in parenthesis show the percentage change compared to the values in Table 20.

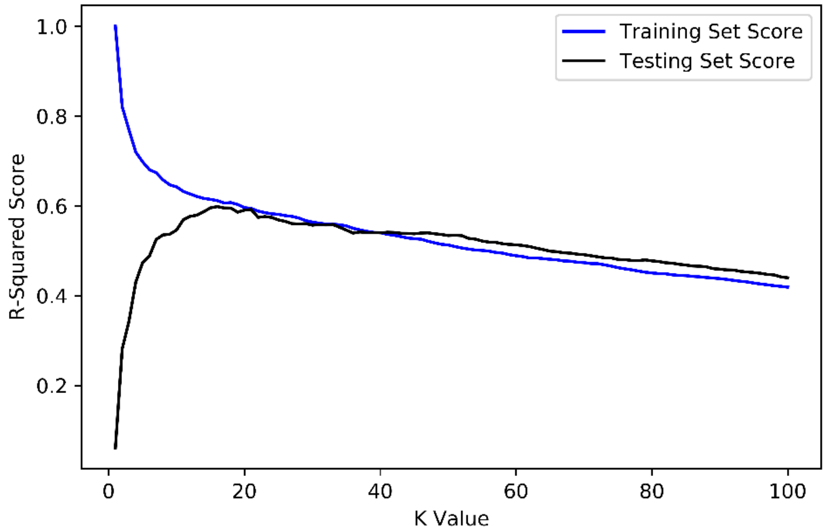

Figure 13. R-squared scores for different K values used for training the k-n algorithm and for testing the trained algorithm. The optimum K value is determined when the highest R-squared score is achieved for the testing dataset.

Table 21. NGCC statistical information for 668 valid records after using the K-nearest regression model

Parameter	Min	Median	Mean	Max
Nameplate Capacity (MW)	4.7 (-40%)	335 (-27%)	412 (-12%)	1850 (0%)
Age (years)	0 (0%)	14 (0%)	17.3 (13%)	60 (18%)
Net Efficiency (HHV%)	35% (0%)	46.2% (1.5%)	44.7% (0.5%)	52% (0%)
Capacity Factor	0.0 (0%)	0.46 (-2%)	0.43 (-6.5%)	0.96 (0%)
LCOE pre-retrofit (2017$/MWh)	39.79 (0%)	57.96 (1.1%)	55.01 (-0.09%)	567000
LCOE post-retrofit (2017$/MWh)	54.58 (0%)	90.24 (0.9%))	84.69 (0.15%)	-

As shown, the statistical description for the partially regressed data of all NGCC units and that of the originally valid datapoints are sufficiently similar. Therefore, valid datapoints are solely used in this analysis. Figure 14 illustrates the difference in the results when all datapoints are used after validation by the machine learning method. The black curve is the same as in Figure 2b. The curve includes 513 valid datapoints and with the help of the conversion factor, elaborated in section S1, extrapolates the results from the valid units to all units. The blue curve shows the same analysis including the valid and regressed datapoints. As shown, the initial point and the shape of the cost curve does not significantly differ. The main difference is the lower ratio of retrofittable emissions to non-retrofittable and residual NGCC emissions when all the datapoints are used. This difference, however, is not significant and makes the results slightly biased in favor of post-combustion capture. This is because a higher ratio of total natural gas emissions is retrofittable when valid data are used for the analysis.

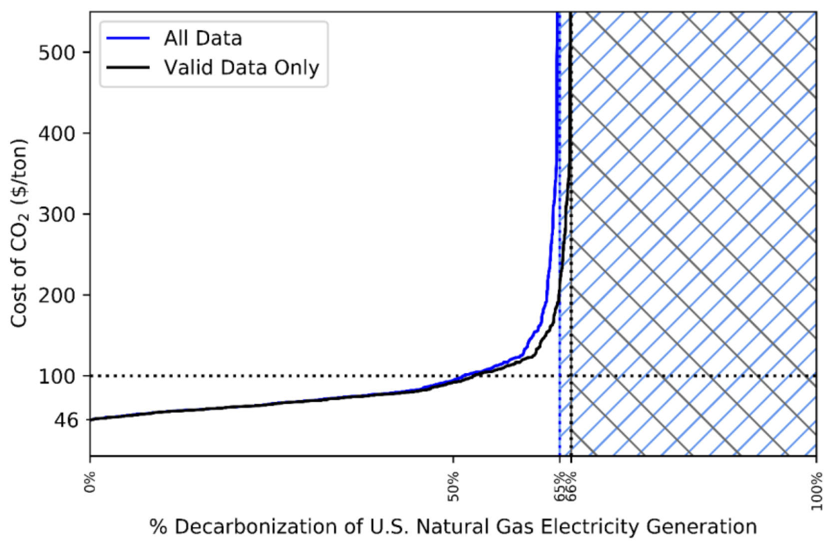

Figure 14. Comparison between cost curves plotted with the originally valid datapoints (black curve) and plotted with all data including the regressed datapoints with the machine learning algorithm (blue curve).

APPENDIX D

POST-COMBUSTION RETROFIT COST MODEL BASED ON IECM

IECM allows the user to design a power plant with various types of fuel, power block design, cooling systems, and environmental control systems and provides outstanding flexibility for changing financing and cost parameters as well as design parameters for each section of the power plant (Carnegie Mellon University 2018). The model has a systematic approach for calculating the cost, performance and mass balance around different fossil fuel power plants and emission control systems.

While IECM does not offer a cost analysis for a retrofitted NGCC unit, it provides information about the capital and operating cost of an amine-system designed for that unit. The IECM software is also useful in quantifying the retrofit-induced changes in the power block and cooling system of an NGCC unit. By extracting this information, a cost model was built around a known NGCC unit that calculates the cost of retrofit by post-combustion capture. The cost model was used to calculate the cost of retrofit for each existing US NGCC unit with valid data in the database.

IECM 11.2 only offers two models of NGCC gas turbine with fixed MW outputs, General Electric 7FB and 7FA. The more efficient 7FB model which also has a higher capacity was chosen in this analysis. The model only allows discrete values for the total capacity of an NGCC unit since the capacity of the steam turbine is fixed and only 1 to 5 gas turbines can be added to a unit. Therefore, cost information for only five different nameplate capacity values is available in the IECM (i.e., 295 MW, 590 MW, 885 MW, 1180 MW, and 1475 MW). The US NGCC units in the database, however, have a spectrum of nameplate capacities. The cost information for the five capacity values was extracted, so the model be able to interpolate the cost information of US NGCC units.

The cost model is mainly based on the total nameplate capacity and not the exact number of combustion and steam turbines.

In using the model, whenever a financial or technical/operational variable was not known, the default value in the IECM was used. The "Typical New Plant" option which includes an NGCC unit with a wet cooling tower was set as the default in this analysis. Due to lack of unit-specific data, the cost of land was excluded from the analysis, but the introduced error is very small (the cost of land makes difference on the order of a few cents in $/MWh value of LCOE). The natural gas composition was changed to match the average US natural gas higher heating value (HHV) extracted from the eGRID database (22,442 Btu/lb Natural Gas). Table 22 shows the natural gas composition used in the cost model.

Table 22. Natural gas composition

Natural Gas Component	Volumetric Percentage
Methane	87%
Ethane	9%
Propane	1.5%
Carbon Dioxide	1%
Nitrogen	1.5%
Total	100%

The units' retirement age and economic book life (amortization duration) were assumed to be 30 years. The book life for post-combustion units is assumed to be the remaining life of the NGCC unit and it cannot be lower than 5 years. In other words, only NGCC units younger than 25 years old are considered for retrofit. The relationship between the age and amortization level of an NGCC unit was assumed as shown in Figure 15 (Carnegie Mellon University 2018; Peters, Timmerhaus, and West 2006).

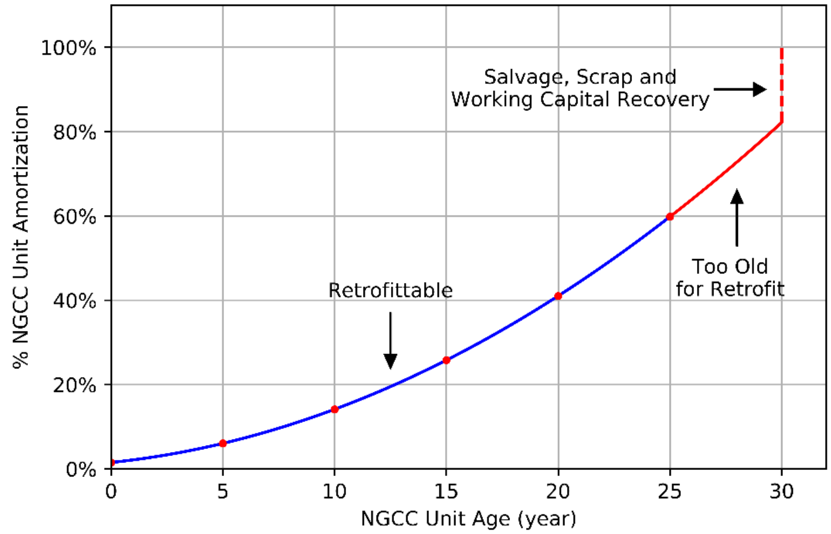

Figure 15. Relationship between age and amortization level of an NGCC unit in the cost model.

The Fixed Charge Factor (FCF), which is the fraction of the capital cost that must be recovered every year, is a function of a unit's remaining lifetime as well as the discount rate and the rate of return on different bonds and stocks and taxes. IECM's default values were used to calculate the FCF for each unit (Carnegie Mellon University 2018; E. S. Rubin 2012).

Capital and O&M costs for different unit sizes are extracted from IECM. As shown in Chapter 4, based on a zero net present value, the LCOE can be calculated for each unit:

$$LCOE = \frac{NAMEPCAP \times CAP \times FCF + F_{O\&M}}{GENNTAN} + V_{O\&M} \tag{5}$$

Where NAMEPCAP is unit's capacity (MW), CAP is capital cost (\$/MW), FCF is in (fraction/year), $F_{O\&M}$ is fixed O&M cost (\$/MW/year), GENNTAN is the amount of electricity generated in one year (MWh) and $V_{O\&M}$ is variable O&M cost (\$/MWh). Fuel cost is embedded in the variable O&M.

Retrofit-induced changes:

The IECM model and literature suggest an energy penalty equivalent to roughly 7-percentage point loss in a unit's efficiency after the retrofit. This decreases the maximum available generation capacity (MW), while the amount of CO_2 produced per MWh of electricity increases. A 10-percentage point net efficiency loss was assumed for each unit since retrofitting an existing unit is typically harder than building a new unit with post-combustion capture.

Since the amount of CO_2 produced per MWh of electricity increases, after post-combustion capture, the amount of CO_2 released to the atmosphere is more than 10% of the CO_2 emission per MWh of electricity for the reference unit before the retrofit. This net CO_2 removal efficiency is typically around 88% since the post-combustion unit captures 90% of the already increased CO_2 production, not the initial CO_2 production. As mentioned in the main body of the article, the horizontal axes in Figure 2b and Figure 6 do not take the additional CO_2 into account and the percentage values are relative to the initial CO_2 emissions of the reference units.

After the retrofit, the unit's new capital and operating costs were used in equation (5) to calculate the LCOE of the retrofitted unit. The additional capital cost after retrofit is not only due to the amine scrubber equipment but also due to the additional cooling capacity that is required. Fixed and variable O&M costs for a retrofitted unit were also estimated by comparison between a unit with and without post-combustion capture for each cost component. The capital cost of an amine scrubbing unit was multiplied by 1.15 to account for retrofit difficulties. Capital and operating costs due to transportation and storage are not included in this analysis.

When LCOE and the rate of CO_2 emission for the reference and retrofitted units are calculated, the cost of avoided CO_2 (COC) can be determined by equation (1).

APPENDIX E

POST-COMBUSTION COST MODEL SANITY CHECK

To assess the reliability of the retrofit cost analysis model, the results are compared with two similar NGCC retrofit cost analysis studies. Here, LCOE values before and after retrofit are recalculated based on the unit characteristics in these studies. As summarized in Table 23, the recalculated LCOE values and the difference between LCOE before and after retrofit are close to the published values. Based on equation (1), the difference between $LCOE_{retrofit}$ and $LCOE_{ref}$ is the key parameter in determining the cost of avoided CO_2. Therefore, the recalculated COC values are also close to the values in these studies. This validates the reliability of the retrofit cost model in this work.

Table 23. Comparison between the retrofit cost analysis model in this study and models in the literature

Nameplate Capacity (MW)	Net Eff	Capacity Factor	Fixed Charge Factor	NG Price ($/ MMBtu)	T&S Cost	$LCOE_{ref}$ ($/MWh)		$LCOE_{retrofit}$ ($/MWh)		$LCOE_{diff}$ ($/MWh)		COC ($/ton)	
						Lit	Recalc	Lit	Recalc	Lit	Recalc	Lit	Recalc
383	56.2%	0.85	0.13	6.35	10	53.9	52.1	76.6	76.3	22.7	24.2	78.8	83.7
171.3	52.7%	0.85	0.13	6.35	10	57.9	58.1	87.9	89.2	30.0	31.1	88.4	101.2
77.9	48.1%	0.85	0.13	6.35	10	63.9	67.3	102.7	108.5	38.8	41.2	105	123
970	45.6%	0.59	-	13.77	-	104	123	151	159	47.0	36	128	101.4
780	43.6%	0.68	-	13.77	-	106	126	152	162	46.0	36	119	97

The model's default Fixed Charge Factor values were used for the last two recalculations. The relatively large difference between COC values is due to different assumptions for the rate of emissions (ROEs) in different studies.

APPENDIX F

RESULTS SENSITIVITY TO NATURAL GAS PRICE

In the model, a constant natural gas price of $4/MMBtu is assumed. The estimated LCOE values are sensitive to the natural gas price, however, the cost of CO_2 capture, especially when analyzed for all NGCC units is not significantly sensitive to the natural gas price. Figure 16 illustrates the same results shown in Figure 2a with two natural gas prices, $2 and $8 per MMBtu.

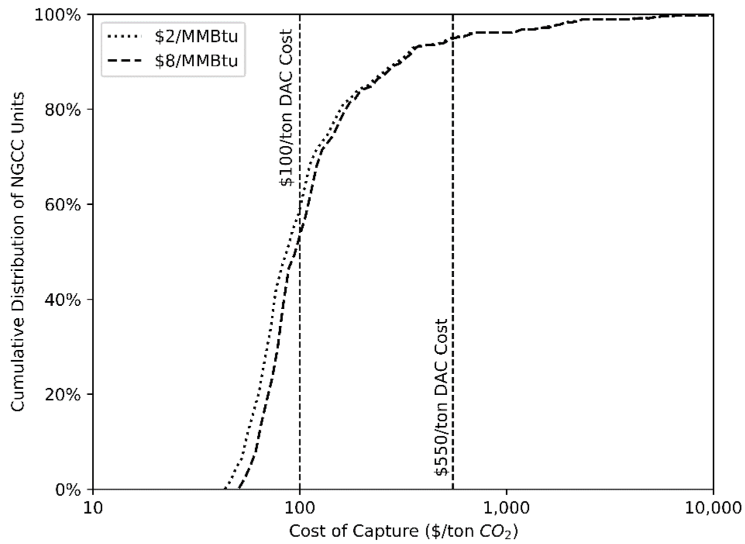

Figure 16. Cumulative distribution of the cost of CO2 capture for the NGCC units considered for retrofit. The sensitivity of the results relative to the cost of natural gas is investigated with two natural gas prices.

As shown, the percentage of units with COC below $100/ton and below $550/ton is not strongly dependent on the price of natural gas.

APPENDIX G

INCORPORATING LEARNING INTO LEVELIZED COST OF ELECTRICITY

To demonstrate the impact of learning on the cost of post-combustion capture retrofit, the LCOE and the Rate of Emissions (ROE) after retrofit should be adjusted accordingly. With known learning rates values, each cost component of LCOE (Cap, $F_{O\&M}$, and $V_{O\&M}$) are simply adjusted by equation (2) as the cumulative implementation level (parameter X) increases. The new cost components produce a post-learning LCOE value through equation (5).

As discussed in Chapter 4, the problem in this method is that the initial value of the cost components at the beginning of learning (parameter a in equation (2)) are not unique values and are different for each NGCC unit. To address this issue, one can calculate the mean and standard deviation of each cost component over all the NGCC units considered for post-combustion capture. This results in two constant values for each cost component, 1.5 standard deviations above and below the mean for that component. Table 24 summarizes these values. It also shows the final value of each component when the learning endpoint (100 GW) is achieved.

Table 24. Approximations for post-combustion cost components used in the learning calculations

Cost Component	Initial Value (3 GW Cumulative Capacity)	Final Value (100 GW Cumulative Capacity)
Cap ($/kW)	$550-$1090	$214-$792
$F_{O\&M}$ ($/kW/year)	$5.2-$52.7	$2.0-$39
$V_{O\&M}$ ($/MWh)	$2.4-$4.8	$0.45-$2.93
Energy Penalty	10%-point	7.1%-9.1%

In other words, the six initial cost values are proxies for simplifying the model and they provide an approximate cost range for each unit's post-combustion capture retrofit. To test the accuracy of the chosen proxy values, they were used to estimate a lower and an upper limit for the cost of post-combustion capture for each unit without learning. Namely, the accurate post-combustion results calculated with the cost model (Figure 2b) determined the validity of the upper and lower limit retrofit costs. Figure 17 illustrates this comparison. The black curve shows the cost of post-combustion capture for the NGCC units (no learning effect included) versus the level of decarbonization as shown in Figure 2b. The shaded area around the curve shows the lower and upper limit estimates with the cost components in Table 24. The cost components are used in equation (5) to estimate the post-retrofit LCOE and then used in equation (1) to estimate a lower and an upper approximation for the cost of CO_2.

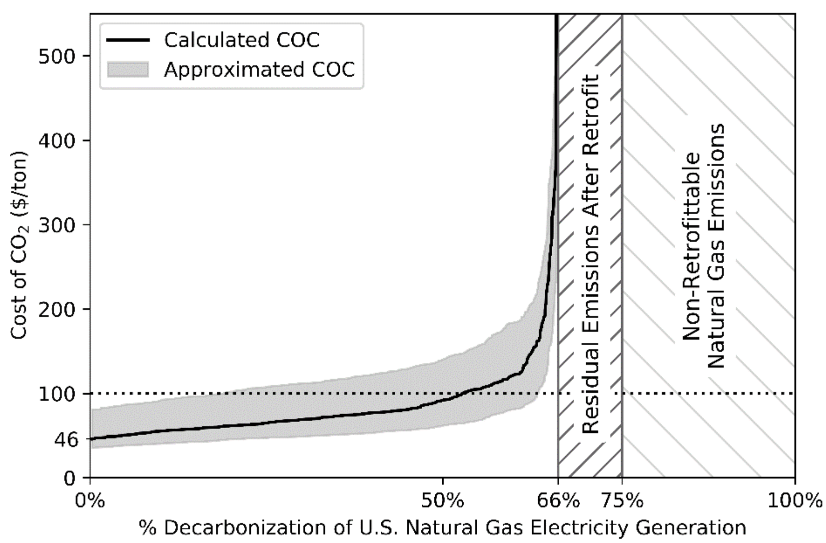

Figure 17. Comparison between the accurate calculation of COC and approximation with the proxy cost component values.

As shown in Figure 17, the upper and lower limit COCs are accurate approximations for the real cost of capture. Therefore, it is realistic to expect the cost of post-combustion captures, with the impact of learning-by-doing, will fall between the upper and lower limit costs approximations.

APPENDIX H

AN ALTERNATIVE APPROACH TO INCORPORATE LEARNING

As discussed in Appendix G, the unit-specific cost component values before learning (Cap, $F_{O\&M}$, and $V_{O\&M}$) make it difficult to project the impact of learning by equation (2). Here an alternative approach is proposed to address this issue. By dividing equation (2) by parameter a (the initial cost before learning), one can reorganize this equation:

$$Y/a = \varepsilon^{\log_2 X} = X^{\log_2 \varepsilon}$$

On the left side of this equation, there exists the ratio of a cost component after learning to its initial value with no learning. In the case of learning-by-doing, this ratio will be smaller than 1.0 and gets smaller when more experience is achieved (higher X). In this new approach, one can recalculate the Y/a ratio after retrofitting each unit when more experience is accumulated. Multiplying the Y/a ratio by the unique cost component of each unit will simply result in the cost of retrofit after learning for that unit:

$$Cost\ component\ after\ learning = (Y/a)\ \times Cost\ component\ before\ learning$$

This relationship is used for each cost component of each unit to project the retrofit cost reduction after learning. Similar to the previous method, when cost components after learning are calculated, equations (5) and (1) are used to calculate the cost of CO_2. The Y/a ratio starts at 1.0 for the first 3 GW per-learning phase and its final values for different cost components are summarized in Table 25.

Table 25. Values of Y/a learning ratio for different cost components at learning endpoint

Cost Component	Learning Rate	Final Y/a Ratio (100 GW Cumulative Capacity)
Cap & $F_{O\&M}$	6%-17%	0.38-0.72
$V_{O\&M}$	10%-30%	0.18-0.60
Energy Penalty	2%-7%	0.70-0.91

Figure 18 illustrates the probable range of post-combustion capture cost with learning. The difference between the two learning implementation methods can be noticed by comparing this figure with Figure 6a. Even though the average curves in the figures are almost identical, the method discussed in Appendix G and Figure 6a are preferred for further analysis since they provide a larger range of uncertainty.

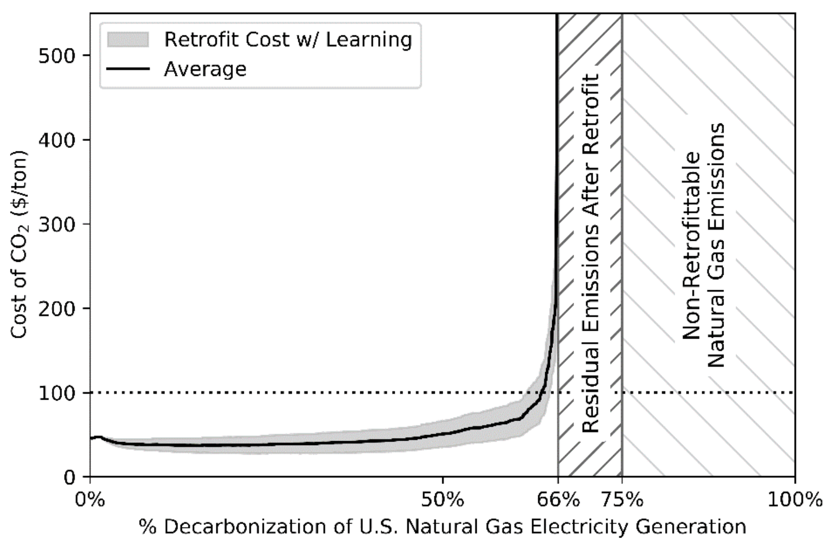

Figure 18. Cost of CO2 plotted against decarbonization level considering the impact of learning-by-doing for post-combustion capture retrofit. This figure shows an alternative method to project the cost reduction due to learning (compare with Figure 6a).

APPENDIX I

SIMULTANEOUS OPTIMIZATION OF NPV_0 AND NPV_∞

For simplification, Net Present Value (NPV) is mainly discussed in the form of NPV_0 in the model. This parameter is the net present value of a DAC device calculated for a single sorbent lifetime. NPV_∞ can be obtained by summing the discounted net present values for an infinite sequence of sorbent lifetimes. Here the goal is to show this assumption does not change the sorbent budget and lifetime calculations. The two important assumptions for calculating t_{life} and MAB are:

$$(NPV_0)_{@t_{life}} = 0$$

$$\left({}^{dNPV_0}/_{dt}\right)_{@t_{life}} = 0$$

With a DAC device that does not physically depreciate (sorbent excluded), an unlimited number of sorbent lifetimes can be achieved by an automatic replacement of the sorbent when it reaches the end of its lifetime. In such a system, t_{life} sets the replacement frequency. The net present value of such a device is denoted by NPV_∞. NPV_∞ will be the sum of all single lifetime NPV values ($NPV_0(t)$) that happen with the frequency of t^{-1}. $NPV_\infty(t)$ is then given by:

$$NPV_\infty(t) = \sum_{k=0}^{\infty} NPV_0(t)\, e^{-\left(\frac{k\,t}{\tau_M}\right)}$$

This equation is a geometric series with a fixed constant of e^{t/τ_M}. Since the constant is between -1 and 1, the sum is finite and can be calculated:

$$NPV_\infty(t) = \frac{NPV_0(t)}{(1 - e^{t/\tau_M})} \tag{20}$$

When $t = t_{life}$, we know $NPV_0(t_{life}) = NPV_0 = 0$:

$$NPV_\infty(t_{life}) = NPV_\infty = \frac{NPV_0}{(1 - e^{t_{life}/\tau_M})} = 0$$

Therefore, the condition of $(NPV_0)_{@t_{life}} = 0$, equivalently means $(NPV_\infty)_{@t_{life}} = 0$.

Additionally, for an optimum choice of t_{life}, the net present value reaches a maximum. In other words, its derivative is zero:

$$NPV_0(t) = (1 - e^{-t/\tau_M})\, NPV_\infty(t)$$

If one takes derivative on both sides with respect to time (t):

$$dNPV_0(t)/_{dt} = \left(1 - e^{-\frac{t}{\tau_M}}\right) dNPV_\infty(t)/_{dt} + \frac{NPV_\infty(t)}{\tau_M} e^{-t/\tau_M}$$

Similarly, when $t = t_{life}$, we know $dNPV_0(t_{life})/_{dt} = dNPV_0/_{dt} = 0$:

$$dNPV_0/_{dt} = dNPV_\infty/_{dt}\left(1 - e^{-\frac{t_{life}}{\tau_M}}\right) + \frac{NPV_\infty}{\tau_M} e^{-t_{life}/\tau_M} = 0$$

It is already known that $(NPV_\infty)_{@t_{life}} = 0$. As a result, the only outcome that satisfies this equality will be:

$$\left(dNPV_\infty/_{dt}\right)_{@t_{life}} = 0$$

This means the condition of $\left(dNPV_0/_{dt}\right)_{@t_{life}}$ is equivalent to $\left(dNPV_\infty/_{dt}\right)_{@t_{life}} = 0$.

APPENDIX J

AN INDEPENDENT NPV_{∞} OPTIMIZATION

The t_{life} value that maximizes NPV_0 is not always the best choice for maximizing NPV_∞. A decrease in sorbent price, for instance, can change the optimum t_{life} after implementation of the sorbent. When the sorbent price decreases, it is intuitive that replacement must happen more frequently (shorter t_{life}) because a cheaper, fresh sorbent with its higher capacity can increase the cash flow rate. On the other hand, if one only considers a single sorbent lifetime, t_{life} is not a function of sorbent price in NPV_0 maximization. Long-term optimization of a DAC device has priority over the optimization of a single sorbent lifetime and in such a scenario, NPV_∞ optimization must be reconsidered. Starting from equation (20), the impact of sorbent price (N_S) on t_{life} is investigated to optimize NPV_∞.

$$NPV_\infty(t) = \frac{NPV_0(t)}{(1 - e^{t/\tau_M})} \tag{20}$$

When $t = t_{life}$, NPV_∞ must be at its maximum, meaning the derivative of equation (20) with respect to time has to be zero:

$$dNPV_\infty/_{dt} = (1 - e^{t_{life}/\tau_M})^{-1}\ dNPV_0/_{dt} + \frac{e^{-t_{life}/\tau_M}\ (1 - e^{t_{life}/\tau_M})^{-2}}{\tau_M}\ NPV_0 = 0$$

$$dNPV_0/_{dt} + \frac{e^{-t_{life}/\tau_M}\ (1 - e^{t_{life}/\tau_M})^{-1}}{\tau_M}\ NPV_0 = 0$$

As shown in Chapter 5, $dNPV_0/_{dt}$ and NPV_0 can be substituted as functions of sorbent characteristics, CO_2 price, and the three running costs. After simplifying:

$$\frac{P\ C_0\ \tau_M\ e^{-t_{life}/\tau_D}\ (1 - e^{t_{life}/\tau_M})}{t_{cycle}} - \frac{P\ C_0\ \tau_{eff}\ (1 - e^{t_{life}/\tau_{eff}})}{t_{cycle}} - N_S = 0$$

Solving this equation for t_{life}, results in the optimum frequency of sorbent replacement (t_{life}) for a given sorbent price (N_S). Figure 19 shows this relationship.

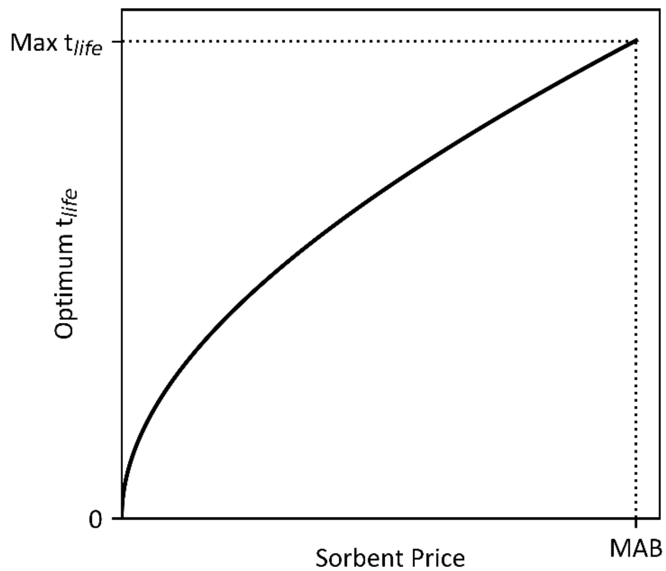

Figure 19. Relationship between optimum t_{life} and sorbent price for NPV_∞ maximization. t_{life}can also be assumed as the frequency of sorbent replacement.

When $N_S = MAB$, t_{life} has its maximum value. Therefore, t_{life} for cheaper sorbents can be expressed as a fraction of this maximum t_{life}. Additionally, N_S values can also be reported as the fraction of total capture cost (P) allocated to sorbent expenses. Maximum Sorbent Share (MSS) in CO_2 price is equivalent to the MAB in the previous figure. Figure 20 shows the relationship between these two variables.

As shown in Figure 20, these two dimensionless variables have a linear relationship and cheaper sorbents require more frequent replacement. This is to the extreme that a free sorbent has to be continuously changing ($t_{life} = 0$) to maximize NPV_∞.

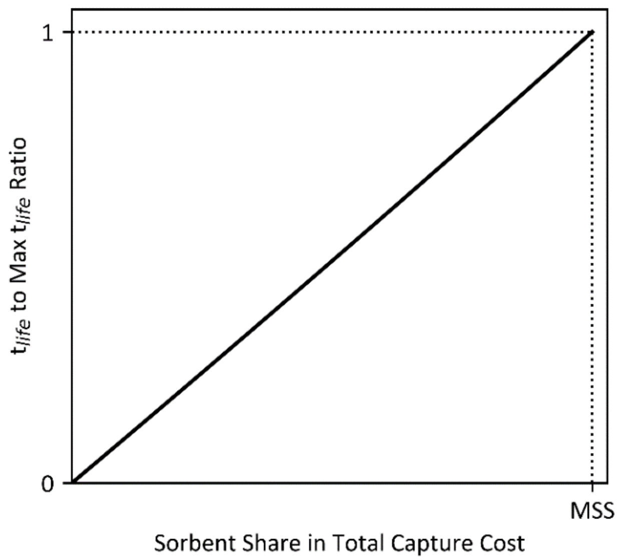

Figure 20. Relationship between the ratio of optimum t_{life} to the maximum t_{life} and sorbent share in total CO_2 price. Maximum Sorbent Share (MSS) in CO_2 price is equivalent to MAB and sorbent cannot be more expensive than t.

APPENDIX K

DIMENSIONLESS NUMBERS

Equation (16) can be rearranged to produce the dimensionless numbers $\mu = \frac{P\ C\ \tau_M}{t_{cycle}\ N_S}$ and $\vartheta = \frac{\tau_D}{\tau_M}$:

$$\mu = \frac{P\ C_0\ \tau_M}{t_{cycle}\ N_S} = \left(\frac{\tau_{eff}}{\tau_M}\left(1 - \alpha^{\frac{\tau_D}{\tau_{eff}}}\right) - \alpha\left(1 - \alpha^{\frac{\tau_D}{\tau_M}}\right)\right)^{-1}$$

And the τ ratios can be expressed in terms of ϑ:

$$1 + \vartheta = \frac{\tau_M}{\tau_M} + \frac{\tau_D}{\tau_M} = \frac{\tau_D}{\tau_{eff}}$$

$$\frac{\vartheta}{1 + \vartheta} = \frac{\frac{\tau_D}{\tau_M}}{\frac{\tau_D}{\tau_{eff}}} = \frac{\tau_{eff}}{\tau_M}$$

To produce equation (17):

$$\mu = \left(\frac{\vartheta}{1 + \vartheta}\left(1 - \alpha^{1+\vartheta}\right) - \alpha\left(1 - \alpha^{\vartheta}\right)\right)^{-1} \tag{17}$$

APPENDIX L

SOLVING THE NPV EQUATION FOR CO_2 CAPTURE COST

When sorbent price (N_S) is available, equation (16) does not have a simple algebraic expression for CO_2 price (P). Therefore, it is necessary to use an iterative numerical process.

$$N_S = \frac{P\, C_0\, \tau_M}{t_{cycle}} \left(\frac{\tau_{eff}}{\tau_M} \left(1 - \alpha^{\frac{\tau_D}{\tau_{eff}}}\right) - \alpha \left(1 - \alpha^{\frac{\tau_D}{\tau_M}}\right)\right) \qquad (16)$$

Other than the P outside the parenthesis, variable α is a function of CO_2 price (P) and this makes an analytic solution impossible. A good initial guess is necessary for a fast and reliable solution. As an initial guess, one can assume t_{life} to be equal to τ_D and according to equation (14), this results in:

$$\ln(1/\alpha) = \ln\left(\frac{P C_0 / t_{cycle}}{n_{O\&M_0} + V_{BoP}/\tau_M}\right) = 1$$

$$P_0 = \frac{e\, t_{cycle}}{C_0} \left(n_{O\&M_0} + V_{BoP}/\tau_M\right)$$

P_0 is the initial guess for finding CO_2 cost and e is Euler's number. This initial guess provides a stable and fast, solution when used in a numerical solver tool.

APPENDIX M

MODEL SIMPLIFYING ASSUMPTIONS

There are some simplifying assumptions in this initial version of the model. For instance, the DAC hardware, except for the sorbent, is assumed to be resistant to physical depreciation and has an unlimited lifetime. This assumption is not completely accurate, but hardware depreciation can be easily added to the model by introducing another time constant (τ_{dep}). The current assumption is reasonable, as long as $\tau_{dep} \gg \tau_M$. Another assumption is that the O&M cost and sorbent degradation are either constant with cycle or clock time. In reality, however, these two parameters can be a function of both. Similar to physical depreciation, the model can be easily adjusted to account for both cycle-based and time-based parameters simultaneously. Furthermore, O&M costs could change over time. For example, as the system ages, the maintenance cost could rise. Alternatively, some maintenance may simply be eliminated as the cost to fix things may not be justified after the system depreciated to a certain point. As a result, one can consider escalating the maintenance cost over time or allow maintenance costs to decrease over time. To this end, one can add yet another time constant into the model.

APPENDIX N

CO-AUTHOR PERMISSION FOR USE OF JOURNAL ARTICLE

Chapters 3, 4, 5, and 6 were written with collaboration with Dr. Klaus Lackner, who has granted his permission for use in this dissertation.