Feasibility of Air Capture

by

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Submitted to the Engineering Systems Division
in partial fulfillment of the requirements for the degree of

Master of Science in Technology and Policy

at the
Massachusetts Institute of Technology
June 2010

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ABSTRACT

Capturing CO_2 from air, referred to as Air Capture, is being proposed as a viable climate change mitigation technology. The two major benefits of air capture, reported in literature, are that it allows us to reduce the atmospheric carbon concentration, the only technology to do so, and that it can tackle emissions from distributed sources. Technically, air capture is not a new technology; industrial applications can be traced back to the 1930s.

This thesis explores the feasibility of this technology as a climate change mitigation option. Two different pathways of air capture are assessed in this dissertation, direct air capture, which uses a chemical process to capture CO_2 and biomass coupled with carbon capture and sequestration, which utilizes the biological process of CO_2 capture by biomass.

The cost of direct air capture reported in literature is in the range of $100/tC and $500/tC ($27/tCO_2 - $136/t$CO_2$). A thermodynamic minimum work calculation performed in this thesis shows that just the energy cost of direct air capture would be in the range of $1540-$2310/tC ($420-$630/tCO_2) or greater. To this, one must add the capital costs, which will be significant. This shows that the cost of this technology is probably prohibitive. The difficulty of air capture stems from the very low concentration of CO_2 in air, about 400 ppm. A section in this work elaborates on the difficulties associated with designing such an absorption system for direct air capture.

The pathway of biomass coupled with carbon capture and sequestration looks more promising from a cost perspective. This work puts its avoided cost in the range of $150/t$CO_2$ to $300/$CO_2$. However, the land requirement of this process is a concern. Sequestering 1 Gt of CO_2 this way will require more than 200,000 square miles of land.

In summary, direct air capture has a prohibitively high mitigation cost, which is not comparable to the other climate change mitigation options. Such high costs make relying on this technology for mitigating carbon emissions a poor policy decision. The pathway of biomass coupled with carbon capture and sequestration has reasonable costs and could be used to offset certain emissions. However, the large land requirement may limit the amount of offsets available. All in all, air capture should not be considered as a leading carbon mitigation option.

Thesis Supervisor: Howard J. Herzog
Senior Research Engineer, MIT Energy Initiative

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ACKNOWLEDGEMENTS

My last few months have been so busy writing this work that I often forgot that it would get done some day. Admittedly, there were times when all I wanted to do was to finish this thesis as soon as possible. Now that I am almost at that cherished moment, I cannot help feeling sad that this wonderful journey is coming to an end. Studying at MIT has been a dream come true for me and that the dream is getting over is yet to sink in. I need to thank more than a handful of people who have made this dream a memorable experience.

The bulk of my learning at MIT has come from my research experience, which has educated me exceedingly well on the concepts of Energy, Climate Change and Carbon Capture and Sequestration. So much so, that my enthusiasm about these topics has made my friends stay away from me lately.

For my research work and this thesis, I had the absolute privilege and honor of working with Howard Herzog, who is arguably one of the most knowledgeable persons in this field in the world. I got to experience this first hand at the GHGT9 conference in Washington, DC barely a couple of months after I had started working with him. Conference attendees used to widen their eyes the moment I told them that I was working with Howard. I have been in awe ever since.

Working directly with him has been the best mentoring I could have ever hoped for. Not only has he instilled in me better researching and report writing skills, but also has he made me a more responsible researcher. Blame it on the nature of the topic I was working with, but I have come to appreciate the issues with misreporting in technology and policy. I am sure there have been many moments where I have not lived up to the high standards set by Howard in his work but I hope that he had a positive experience overall.

I thank the Carbon Sequestration Initiative for their support in my research. I also thank Prof. Jerry Meldon, from Tufts, for some of the enriching discussions we had on this topic, Chemical Engineering, IITs and India.

There has to be a special mention of all the people in my lab who made my long days spent here a very enjoyable experience. These extremely talented people are Ashleigh Hildebrand, Gary Shu, Yamama Raza, Michael Hamilton, Sarah Bashadi, Ellie Ereira, Sam O’Keefe, Rob Brasington, Michel Follman and Christina Botero. I am sure they are all destined for much bigger and better things and I hope we stay in touch, both personally and professionally.

Any day in the lab was not spent without the presence of Mary Gallagher in it. It’s amazing how much care she takes of everyone in the lab and helps out. I have been really lucky to have her in the lab and have no words to thank her for all the help she has rendered me over the last two years.

I have to thank a few people in my department for their time and support. The foremost person in this regard is Sydney Miller, whose undying enthusiasm for helping students is unparalleled. Also a big thanks to Ed Ballo for the administrative help, pep talk on running and his trips

around the city. There are numerous TPPers whom I should definitely thank but the space might become a constraint should I decide to do that. However, some names deserve mention: Rahul Kar, Paul Murphy and James Merrick for their constant companionship and bearing with my personality.

Last but not the least, a round of thanks to the people who have been the solid support my life is built upon, my family. My parents have been the biggest inspiration in my life. I always believe that if I had the will power of my father and the diligence of my mother, or even if one of those qualities, I would have been unbeatable. Sadly, genes can only get you so far! I don’t get to say this very often but I am sure I have had the best upbringing in the world!

I have realized lately that my little sister is not that little anymore and have come around to see her as a friend, these last few years. And what a great friend Yama has been! I hope that I have lived up to the double billing of a big brother she can look up to, and a friend she can trust at the same time.

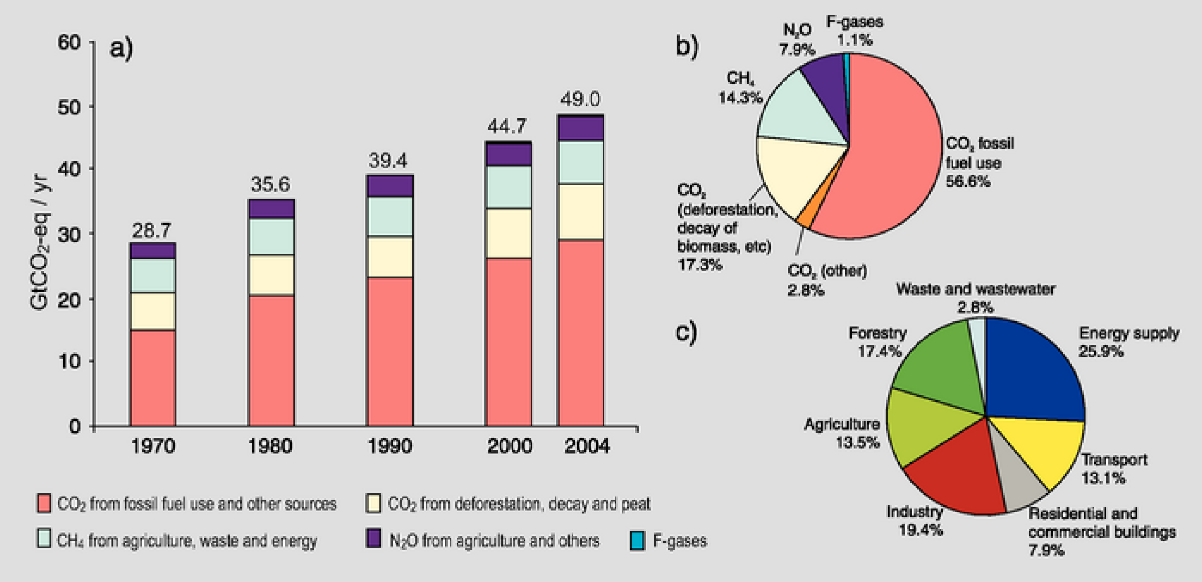
My stay at MIT has not only been the most enriching professional experience of my life, it has also made my personal life very special. I have found ‘the’ special person and so look forward to sharing my life with her. In such a short time, Bhawani has become an integral part of my life. My days are planned around her phone calls and I could not have asked for a better alarm clock! Here’s to an extremely happy and satisfying life together!

Finally, I have always been awed by the prospect of studying at one of the most respected educational institutions of the world. I have strived to be a worthy citizen of this hallowed institution and not dilute its history. Today, I hope that my research is worthy of bearing the stamp of this school and that I have added something to the awe-inspiring body of research at the Massachusetts Institute of Technology.

1. Introduction

1.1 Context

The emissions of Greenhouse Gases (GHG) have gone up by 70% between 1970 and 2004 and carbon dioxide (CO_2) is the most important anthropogenic GHG as reported by IPCC in their Fourth Assessment Report on Climate Change (IPCC, 2007). The emissions of CO_2 have grown by 80% between 1980 and 2004 (IPCC, 2007). It is also reported with very high confidence that the global atmospheric concentrations of GHGs have gone up significantly since 1750 as a result of human activities and that the net effect of all this has been that of warming (IPCC, 2007). The total emissions, measured in CO_2-eq, is shown in Figure 1-1 below.



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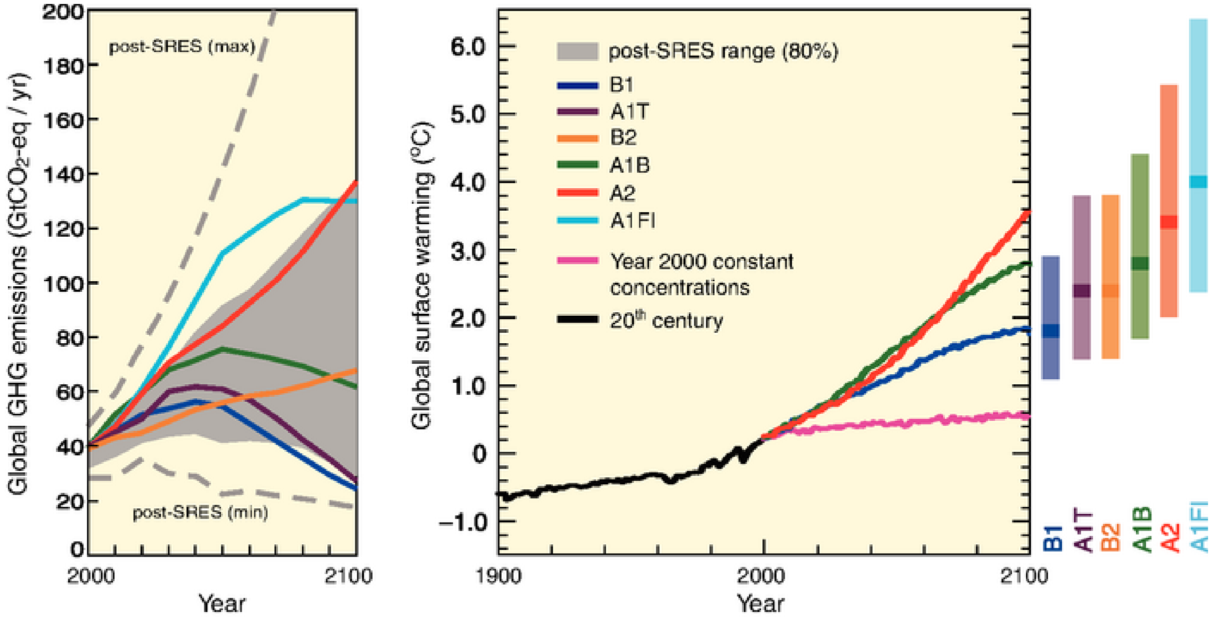
The report predicts that the global GHG emissions, measured in CO_2-eq, would rise by 25-90% between 2000 and 2030, with fossil fuels maintaining its dominance in the energy mix (IPCC, 2007).



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The report shows an unprecedented rise in global temperatures due to the buildup of GHG in the earth's atmosphere, which may lead to catastrophic events around the world (IPCC, 2007). Based on the findings in the report, pressure is being imposed on major emitter countries to reduce their emissions of GHGs. This is not an easy task given the huge dependence of the world on fuels rich in carbon, which are the major sources of carbon dioxide emissions. This dependence will not change easily or in the near future as it is believed that the extremely low cost of these carbon-rich fuels is the reason behind their abundant use. The chart below shows that 87% of the world's energy needs are met by these relatively cheap carbonaceous fuels. As the low carbon and carbon-free fuels will take some time in getting competitive on price with these carbon-rich fuels, this change can be assumed to be a slow, long process.

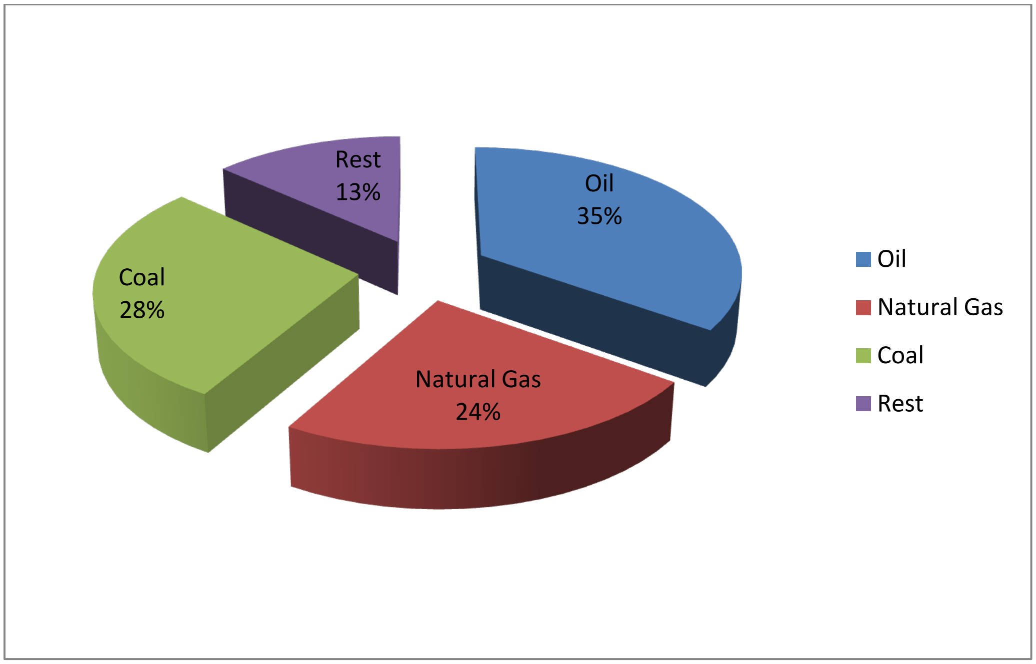

Figure 1-3: Share of the different sources of energy in the total primary energy consumed (EIA,2009)

The slow, long change towards a low carbon energy portfolio is not clearly determined. There is not a well defined path towards that low carbon emissions goal and there are strong fears that we might overshoot the emission target. In that case, there could be a need of a technology that sucks carbon out of the atmosphere and brings us back to the emission goal. There are also certain papers that conclude that there is a need for some solutions that can reduce the stock of CO_2 already present in the atmosphere. This stock of CO_2 would take a very long time to get dissipated if we depended only on the natural processes (Keith, 2009). Therefore, looking at processes that reduce the concentration of CO_2, faster than the natural rate of removal through natural sinks such as the oceans and the trees, could be important. Removing CO_2 from the atmosphere (termed "Air Capture") is definitely an interesting concept and its exact role in climate change mitigation deserves investigation.

Another suggested role for air capture is its ability to offset emissions from distributed sources, which are more than half of the total current emissions. Essentially, for certain applications, fossil fuels could continue to be used as an energy source as long as air capture could offset their emissions. For example:

"Collection of CO_2 from the air opens up new options and possibilities. It makes it possible to retain a transportation sector that is based on an extremely convenient energy source of hydrocarbons. It opens up for sequestration a multitude of dispersed carbon dioxide emitters which otherwise would require a potentially costly rebuilding of the infrastructure that relies on a carbon free energy form, e.g. electricity or hydrogen." (Lackner et al., 1999)

Air capture technology has gained the attention of the top most policy makers in the country. John Holdren, President's Science Advisor, and Steve Chu, Secretary of Energy, each mentioned that air capture is an option that may be needed for stabilizing global CO_2 concentrations during their visits to MIT in the spring of 2009.

There are three important ways of doing it currently:

- Direct Air Capture: This methodology uses chemical processes to capture CO_2 from air
- Biomass coupled with Carbon Capture and Sequestration: This process uses biomass energy to drive a power plant and capture the CO_2 emitted using conventional CCS. The CO_2 is captured by trees that produce biomass in a sustainable manner.
- Enhancing Natural Sinks: This process is executed by enhancing the natural sinks artificially to capture more CO_2 from air. The natural sinks could be the oceans, soil or even specially grown trees which capture CO_2 at an enhanced “rate”. This topic is beyond the scope of this thesis but more information can be found in the IPCC Special Report on Land Use, Land Use Change and Forestry, 2000.

1.2 Motivation

The concentration of CO_2 in air is about 390 parts per million (ppm), which is about 300 times more dilute than the concentration of CO_2 in a flue gas stream, about 12% by volume. In general, separation costs for a specific compound depend on how dilute this compound is in the starting mixture, as illustrated by the Sherwood plot (see Figure 1-4).

Originally, the Sherwood plot was an empirical relationship between the price of a metal and the concentration of the metal in the ore from which it was extracted, plotted on a log-log scale. Since its publication in 1959, the Sherwood plot has been extended to several other substances which are extracted from mixtures. The plot is shown with the approximate concentration of Carbon Capture and Sequestration (CCS) and Air Capture marked on it.

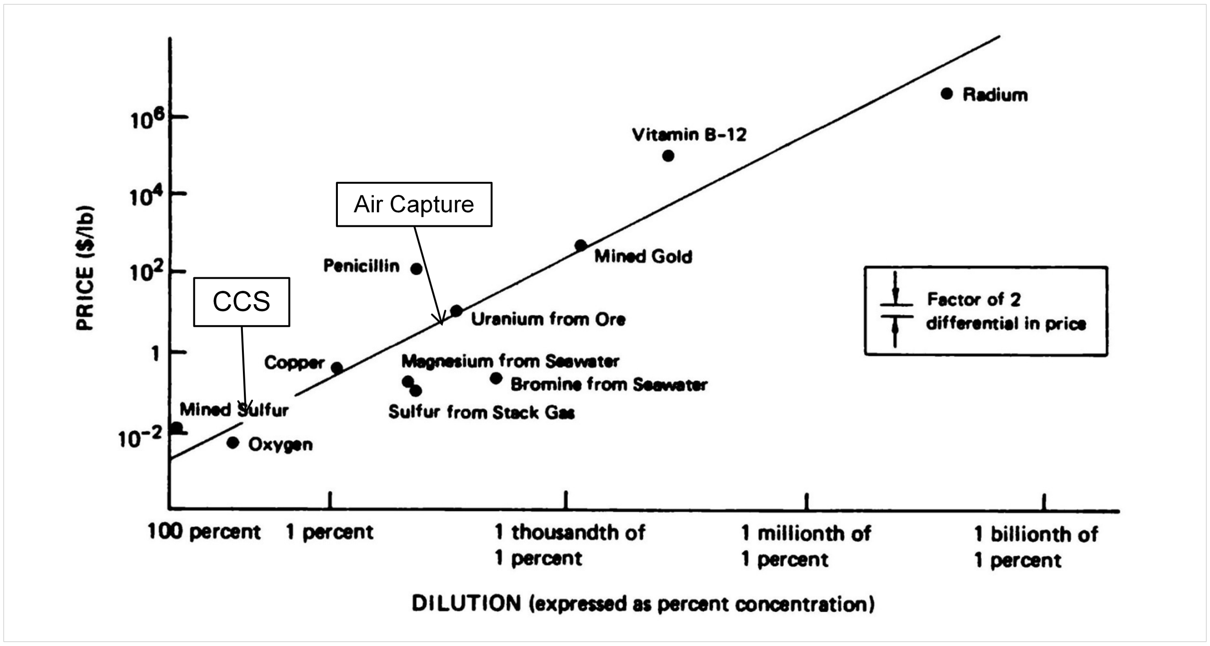

Figure 1-4: The Sherwood Plot (Sherwood, 1959)

The x-axis has the level of dilution of the mixture and the y-axis has the market price. The y-axis can be used to see a ratio of costs of two processes. As can be seen from the plot above, the ratio of costs of Air Capture and CCS is expected to be about 100. The cost of CCS is accepted to be in the range of $(200-300)/tC (\$55-82/tCO_2) (Hamilton et al., 2008). Therefore, the Sherwood plot suggests that the cost of air capture will easily run into thousands of dollars per ton of carbon.

However, proponents of direct air capture put its cost of mitigation in the range of $100/tC (\$27/tCO_2) (Lackner, 1999) to $500/tC (\$136/tCO_2) (Keith, 2006). This is in the ball park range of CCS mitigation cost at \$(200-300)/tC (\$55-82/tCO_2) (Hamilton et al., 2008). Given the background of the difference in concentration and the Sherwood plot, these numbers seem highly optimistic at best and very well could be unrealistic. Hence, this provided motivation to look more closely at the technology and costs of air capture. Since air capture is a “seductive” technology (Herzog, 2003), it is very important to understand its technical and economic feasibility.

1.3 Objectives

This thesis is an attempt to look at this technology, including its costs and feasibility, in an objective manner. In particular, this work looks to:

- *Objectively assess the technology and its costs:* This report will look to assess the mitigation cost for the first two approaches of pursuing air capture: Direct Air Capture and Biomass coupled with Carbon Capture and Sequestration.
- *Inform the role of air capture in the policy space:* Based on the technical and economic analysis, this thesis will discuss the proper role of air capture as a climate change mitigation option.

1.4 Roadmap of the thesis

Chapter 2 will discuss the history of Air Capture, which will talk about the evolution of this technology and its industrial applications over the years. Chapter 3 talks about the first pathway of direct air capture in detail. This includes the literature survey of this technology, a review of various technological options for this pathway, a critical review of cost calculations done in literature and a comparison of absorber design between air capture and flue gas capture.

The next chapter, Chapter 4, describes an alternative pathway to capture emissions from distributed sources, using biomass and conventional CCS. This method is compared to Direct Capture for costs and scaling issues. Chapter 5 provides a policy discussion on the role of Air Capture in Climate Change mitigation and Chapter 6 presents avenues for future work.

2. History of Air Capture

The technology of capturing CO_2 from air has been in use for close to 70 years now, although on a very different scale (Heinrich, 2003). The first industrial use of capturing carbon dioxide from air was reported in cryogenic oxygen plants to prevent condensed carbon dioxide in air from clogging the heat exchangers (Heinrich, 2003). Since then, there have been many other industrial uses of this technology. A brief description of the evolution of this technology in different industrial applications is written below:

2.1 Oxygen Plants

Cryogenic air separation plants started with using regenerators for the purpose of removing carbon dioxide from air in the 1940s (Castle, 2007). Regenerators comprised vessels packed with granite chips and used phase separation to achieve the separation, by the process of condensation of carbon dioxide on those chips. At first, the chips were cooled by passing the cold product gas over the chips followed by the process gas. The flow of the process gas over the cold packing resulted in condensation of water and carbon dioxide, and the process gas was cooled. This required a lot of control to ensure that the packing was cold enough for condensation at all times, lest water or carbon dioxide may get through. The outlet gas also carried some of these undesirable impurities with it (Castle, 2007).

This led to the design of a more elegant alternative in the 1960s, reversing heat exchangers (Castle, 2007). Air and cold gas waste product alternated in specific passes providing air clean up, while the product gas, required to be pure and uncontaminated was put in a separate nonreversing pass or passes. There was still a limitation on the amount of pure gases that could be produced due to the elaborate mechanism of cleaning the process air.

The increase in the demand of pure gases in the period 1970-1980 led to the development of molecular sieves that removed water and carbon dioxide at near-ambient temperatures (Castle, 2007; Flynn, 2004). Molecular sieves had higher capacity adsorbents, lower regeneration temperatures, shorter adsorption cycle times and improved design of adsorber systems. In addition, the proportion of pure product rose by the use of molecular sieves. The molecular sieve technology has been improved a lot over the years by this industry.

2.2 Space

Carbon dioxide removal from air has always been an integral part of the space program development. As human beings emit CO_2 at the rate of 1 kg/person/day, the concentration of CO_2 can go up pretty quickly in the air in a space shuttle, especially one which has more than one astronaut (Heinrich, 2003). Thus, a lot of research has gone into finding out more efficient ways to capture carbon dioxide from the air in such systems.

The initial spacecrafts, the Mercury, Gemini and Apollo used Lithium Hydroxide (LiOH) for this purpose. Lithium Hydroxide is an efficient CO_2 absorbent and reacts with gaseous carbon dioxide to form lithium carbonate and liquid water. The shuttles carry canisters of LiOH and after launch, these canisters are positioned in the Environment Control and Life Support Systems (ECLSS), which circulates the cabin air through the canisters (Perry, LeVan).

One disadvantage of the LiOH system is that it is not regenerable because of the complexity and large amount of energy needed in the process. Thus, astronauts need to pack a number of LiOH canisters that have to be replaced depending upon the number of crew members. This creates a significant challenge for longer space missions both in terms of availability of fresh canisters and storage of used ones. LiOH is also highly caustic and corrosive and thus requires special handling techniques. Due to these issues, a four bed molecular sieve system has been used in space missions since then, on Skylab, Shuttles and the Space Station (Perry, LeVan). These systems have 2 identical beds operating in parallel, which allows for a continuous operation. A zeolite molecular sieve is used for trapping CO_2 from air and a dessicant bed is used for water vapour removal. The sieve is regenerated by exposing the bed to heat and the space's vacuum and the CO_2 is vented to space.

Zeolites are crystalline materials composed of silicon and aluminium and make effective molecular sieves because of their high porosity and well defined pore sizes. The absorption efficiency of the sieves is higher at lower temperatures hence the warm cabin air is first cooled by an air-liquid heat exchanger before passing it through the beds (Heinrich, 2003). In recent years, NASA has started considering other metal hydroxides for CO_2 removal, especially those that are easily regenerable. Silver hydroxide (AgOH) seems to be satisfying the criteria of a good absorbent (Heinrich, 2003). Although AgOH is less efficient than LiOH at scrubbing CO_2, it gets easily regenerated and each canister can be reused about 60 times before being expended completely (Heinrich,2003). As astronauts spend more and more time in space, NASA continues to look at metal hydroxide absorbents for longer life regenerable systems.

2.3 Submarines

Prior to, and during, World War II, submarines were essentially surface ships which had the capability to duck under water for short periods of time (Zimble, 1963). There was sufficient energy to drive the essential systems only in the submarine for the time that it was submerged and power could not be spared to run systems for air purification. Hence, Soda Lime and Lithium Hydroxide (LiOH) were used to absorb CO_2. Soda lime is composed of a mixture of calcium hydroxide as well as sodium and potassium hydroxides, which are present as activators. It uses a chemical reaction to absorb carbon dioxide from air and by-products are water and heat. However, sodalime is sensitive to temperature and as the temperature decreases, so does its ability to absorb CO_2 (Heinrich, 2003). Lithium Hydroxide (LiOH) has a higher reaction rate with CO_2 than soda lime but there are several health and storage problems associated with it, as described in the section above (Hocking, 2005).

With the use of nuclear power in submarines, electrically powered regenerative systems were installed for the removal of carbon dioxide. At first molecular sieves were used. A standard two bed system ensured a continuous operation, with one bed in the sorption and the other in the desorption mode. Most recently, the submarines have turned to amines, for amine systems are more efficient, quieter and smaller than molecular sieve plants (Hocking, 2005). MEA (Monoethanolamine) is the most commonly used amine for its high solubility in water and its relatively low volatility (Hocking, 2005; Burcher, Rydill, 1995; Henderson, Taylor, 1988; Hook, 1997). The leakage of this amine solution to air has to be kept in check due to the toxic nature of MEA (Heinrich, 2003).

Under distress situation, however, when the submarine is disabled (DISSUB) and unable to surface for longer times, there is likely to be flooding and loss of power to run the MEA or the molecular sieve system. The guidance system of the submarines under such distress conditions recommends using LiOH canisters to capture carbon dioxide (Warkander, Lillo, 1998). Canisters are supposed to be opened and spread across the floor of the submarine for this purpose. Soda lime can also be used for this reason.

2.4 Relevance to Air Capture

The technology of capturing carbon dioxide from air has been used industrially for decades now. However, this process was always a small part of an overall process where the cost of achieving this was never a priority; in fact it was absolutely necessary to get this step done at any cost. The only objective was to get “clean air” for the process and no thought was given to the waste CO_2 captured by the process, which was mostly vented to the atmosphere. Air Capture is not only about getting “rid” of CO_2 in air but also about isolating and storing the captured CO_2. This puts an even bigger constraint on the regeneration of pure CO_2 and, in turn, on the overall cost of the process. Air capture will have to demonstrate the ability to do both, “clean” the air as well as sequester the CO_2 cheaply.

3. Direct Air Capture

3.1 Review of Proposed Schemes

The technology for direct air capture consists of two main building blocks:

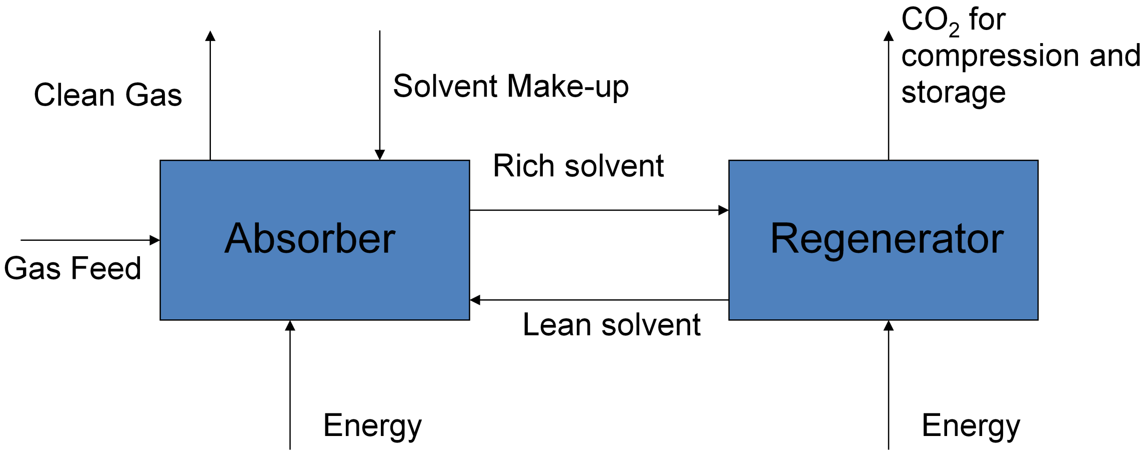

Figure 3-1: Schematic of the Direct Air Capture Equipment

The absorber is where the contacting between the sorbent and CO_2 in air takes place. The gas feed in the schematic is ambient air and clean gas is the air with a lower CO_2 concentration. The rich solvent, loaded with CO_2 from the capture, is then sent to the regenerator. The solvent is regenerated by stripping it of all CO_2, which is then sent for compression and storage and the lean solvent is sent back to the absorber for contacting with fresh air. Some solvent is lost in this regeneration process and is made up by the solvent make-up stream.

The most common solvent used in literature was sodium hydroxide (NaOH) and these papers are discussed below. The reaction scheme for this solvent can be represented as:

Absorber: $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

Causticizer: $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$

Calciner: $CaCO_3 \rightarrow CaO + CO_2$

Slaker: $CaO + H_2O \rightarrow Ca(OH)_2$

The technical analysis done by Baciochhi et al. (2006) uses a 2M NaOH to absorb CO_2 from air. Air, with an inlet concentration of 500 parts per million (ppm) is allowed to go over the absorber, thereby reducing the concentration of CO_2 in outlet air to 250 ppm. The absorption column is 2.8 m in height, 12 m in diameter and has the liquid to gas flow rate ratio as 1.44. It is designed for a pressure drop of 100 Pa/m. This paper uses two different reaction pathways for precipitation and dewatering of the $CaCO_3$ cake coming out from the precipitator. The first one, labeled Process Option A, consists of a train of 4 units, a precipitator, a clarification unit, a thickener and a filter press. Process option B consists of a pellet reactor for efficient dewatering of the $CaCO_3$. The schematic for Process Option A is:

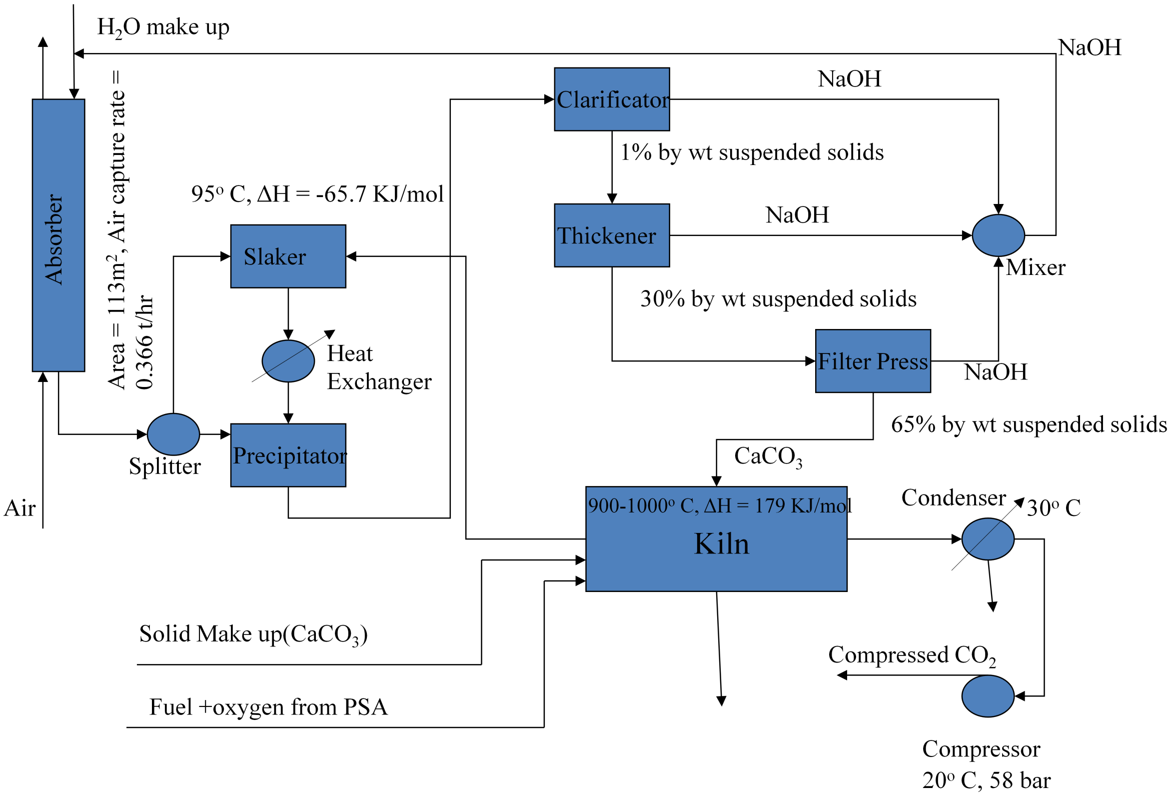

Figure 3-2: Schematic for Process Option A for Baciocchi et al. (2006)

Similarly, the schematic for Process Option B is:

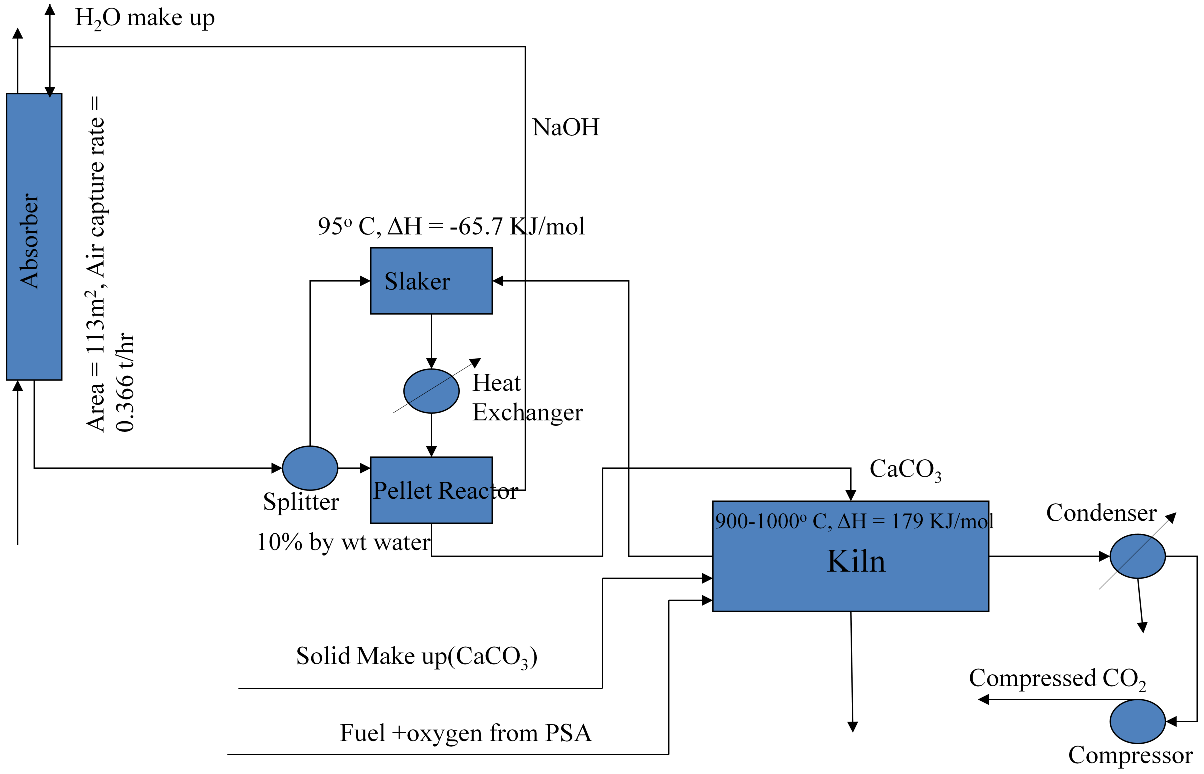

Figure 3-3: Schematic for Process Option B for Baciocchi et al. (2006)

The total fuel energy reported in the paper are 17 and 12 GJ/tCO_2 captured, respectively for the two process options, assuming the efficiency for electricity generation to be 35% and efficiency of direct utilization of thermal energy to be 75%. Calcination has the largest energy consumption in either of the processes. Using coal and natural gas for providing energy for this process is ruled out as the energy provided by combustion of coal and natural gas are 9 and 20 GJ per tonne of CO_2 released to the atmosphere, respectively. These numbers mean that if coal is used as a source of energy for air capture, the process will end up releasing more CO_2 to the atmosphere than capturing from it; for the amount of CO_2 released compared to the amount captured for the processes A and B are 189% and 133% respectively. The corresponding numbers for natural gas are 85% and 60% respectively, but the paper assumes that natural gas is 100% methane by volume. The fact that natural gas is about 70-90% methane by volume increases these numbers. Hence, the paper concludes that for driving a process like air capture, the energy has to come from sources which are carbon free.

Another paper which did a comprehensive analysis on Direct Air Capture is by Keith et al. (2006). This work uses a 3-6M NaOH solvent and an absorber 110m in diameter and 120m in height. The absorber captures 50% of CO_2 in the input stream without the use of any packing material. The CO_2 released from the kiln is captured using an amine solvent and has to be stripped of the absorbed gas at a later stage. The paper concludes by estimating that this process will break even at \$500/tC (\$136/tCO_2) captured, one-third of which is capital and maintenance cost and two-thirds is the cost of electricity required in the process. The total energy required in the process is 679 kJ/mol of CO_2, which is about 15 GJ per tonne of CO_2 captured. This number is in close agreement with the value calculated by Baciocchi et al. (2006). The equipment used by Keith et al. (2006) was another variant of the basic structure shown earlier in the chapter.

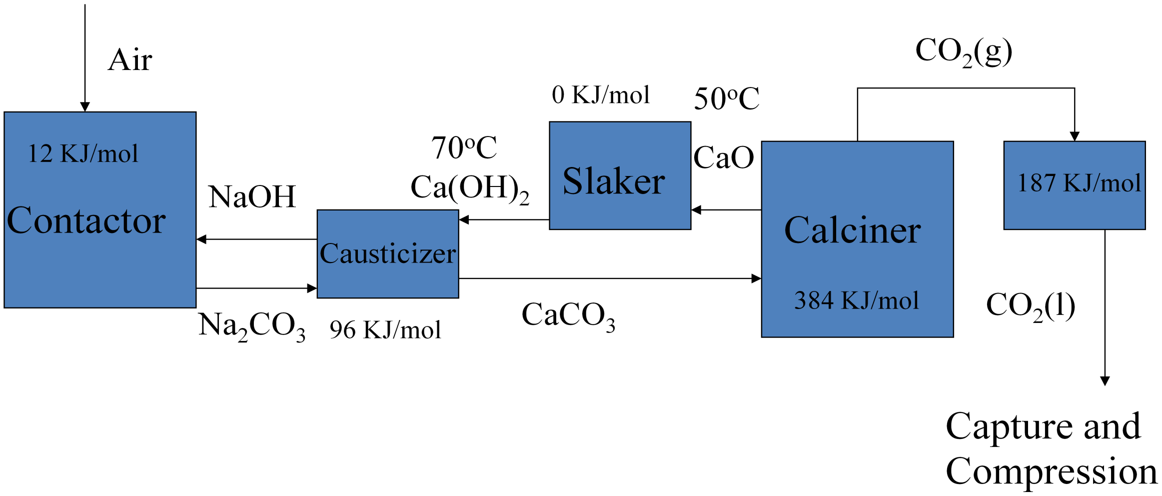

Figure 3-4: Schematic for the process used in Keith et al. (2006)

This paper has a few issues in the calculation of thermodynamic minimum energy, which need to be looked into. A quote from the paper to this effect is stated below:

> “Thus it is sensible to compare air capture with CO_2 removed from a fossil plant at a partial pressure of 10^{-2} (1%) with removal from the air at a partial pressure of 3×10^{-4}. On these grounds the intrinsic total energy penalty of air capture for delivering CO_2 at 1 atm is 1.8 rather than the 3.4 derived previously by considering the marginal energy costs of capture. Put simply, thermodynamic arguments suggest that capturing CO_2 from air requires (at minimum) only about twice as much energy as capturing 90% of the CO_2 from power plant exhaust.”

The paper has calculated the thermodynamic minimum energy requirement for air capture to be only about twice that of flue gas capture. A standard calculation of thermodynamic minimum energy of separation, shown in the Appendix B, proves this calculation to be incorrect. The ratio of minimum energy comes out to be 2.65 for the conditions used in this paper and this calculation is unequivocal. The problem is that this work uses a short cut formula for this minimum energy calculation. Quoting from the paper:

> "The minimum energy needed to extract CO_2 from a mixture of gases in which the CO_2 has an partial pressure P_0 and to deliver it as a pure CO_2 stream at final pressure P is set by the enthalpy of mixing,$k\,T \ln (P/P_0)$, where k is the Boltzmann constant (8.3 J mol^{-1} K^{-1}) and T is the working temperature."

It can be seen that the formula used in this paper for this calculation is a shortcut method of doing this calculation and not a rigorous one. The formula used is:

$$\boldsymbol{kT} \ln \left(\boldsymbol{P}/\boldsymbol{Po}\right) \qquad (1)$$

Where: T: Temperature (300K)

P: Final pressure of pure CO_2

P_O: CO_2 partial pressure

k: Boltzmann constant (8.3 J/mol.K)

The use of this shortcut formula leads to some ambiguity about whether to use the inlet or outlet partial pressures. Keith looks at air, starting with CO_2 partial pressure of 0.0004 atm, which is reduced to 0.0003 atm in the process. The flue gas is reduced to a partial pressure of 0.01 atm from 0.1 atm.

Using the inlet concentration of CO_2 in flue gas of 10% by volume, the minimum work will be 5.7 kJ/mol of CO_2, The corresponding number for air capture at an inlet CO_2 concentration of 400 ppm is 19.5 kJ/mol of CO_2. This gives the ratio of minimum work for air capture to flue gas capture is 19.5/5.7 = 3.4

The outlet concentration of CO_2 considered in this analysis is 1% by volume for flue gas capture and 300 ppm for air capture. The corresponding minimum work numbers for the two cases are 11.5 kJ/mol of CO_2 and 20.2 kJ/mol of CO_2 respectively. Thus, the ratio of minimum work at the outlet conditions is 1.8.

We assume Keith went with the 1.8 number because it better supports his case. However, as we have shown above, this number is incorrect. As shown in Appendix B, minimum work calculation is unambiguous and the correct ratio is 2.65 and not 1.8.

Zeman (2007) used a packed tower to capture CO_2 present in air at a concentration of 355 ppm using a NaOH solvent. The total net energy penalty calculated in this paper is 328 kJ/mol of CO_2 captured (see below for more details). The paper also concludes that the energy for a process like air capture has to come from renewable sources.

The setup used is shown below.

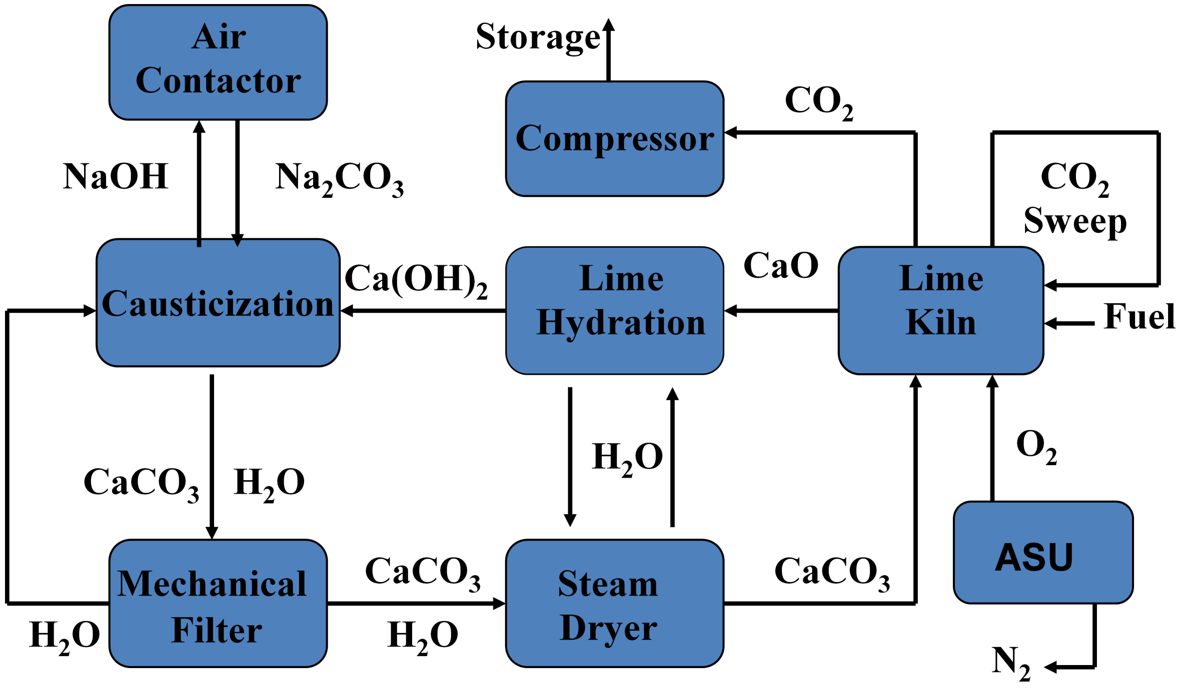

Figure 3-5: Schematic of the process used by Zeman (2007)

Zeman (2007) has included a table in the paper to provide the case for air capture being a potentially feasible process. In this table, it is shown that the thermodynamic efficiency, defined as thermodynamic work divided by the actual work, for air capture is in a similar range as the numbers from CCS using industrial solvents. As the other two processes are established industrially, the paper argues that air capture can also be as feasible as them. Quoting him from the paper:

> "The feasibility of air capture can be quantified using the concept of thermodynamic efficiency. This refers to the ratio of the thermodynamic minimum energy requirement to the actual amount of energy used in the process. We will compare air capture to

> established capture technologies, not as a direct comparison, rather how well each achieves its objective.”

Below is the table on thermodynamic efficiency from the paper:

Table 3-1: Thermodynamic Efficiency table from Zeman (2007)

Energy (kJ/mol)	Air Capture	MEA		KS-1	
		NG	Coal	NG	Coal
Thermodynamics	19.5	8.4	5.3	8.4	5.3
Actual	328	181	181	141	141
Efficiency	6.0%	4.6%	2.9%	5.9%	3.8%

Upon a more detailed analysis, there are two major problems with this table which make Zeman’s conclusion about air capture feasibility highly questionable. The first one is the value for actual energy required for air capture in Table 3-1. This value of 328 kJ/mol of CO_2 is less than half the value reported by Baciocchi et al. (2006) and Keith et al. (2006) above. Understanding Zeman’s basis was hard, since in a table he adds together electrical and heat energy, something that is incorrect to do. Further, he makes the questionable assumption that the heat of hydration of 105 kJ/mol of CO_2, generated in the drying of the $CaCO_3$ cake, can be recovered and reused. As a result, we consider this number highly optimistic.

More importantly, the thermodynamic efficiencies reported for flue gas capture using KS-1 and MEA are wrong. The problem is similar to one reported in the previous paragraph, not making a distinction between work energy and heat energy. The number used in the table is the essentially the heat requirement of the flue gas capture process. Since the thermodynamic analysis needs to be done on a second law basis (i.e., work), the number that should be used here is the work equivalent of that heat load. Specifically, in this case one extracts this heat (as steam) from a turbine in a typical plant, so the lost work is simply equal to the reduction in electricity generation of the turbine. If this is done, the thermodynamic efficiency comes out to be around 20% for coal plants (a little less for gas plants), which is equal to the efficiencies calculated in Herzog et al. (2009).

The reason for pointing out the above two examples of minimum work calculations is because air capture proponents tout them as reasons why direct air capture should be competitive. However, when done correctly, they just confirm the analysis highlighted by the Sherwood plot (Figure 1-4).

Lackner et al. (1999), in one of his earlier papers, used calcium hydroxide as the solvent to capture CO_2 from air in a natural draft absorber, 300m in height and 115m in diameter at the top. The system described here is very different from any other found in literature. Water is pumped to the top of the absorber, which cools the air. This cooling of air at the top causes a downdraft of air inside the tower, which could reach a speed in excess of 15 m/s generating a flow of nearly 15 km^3 of air per day through the tower. This could be used to drive wind turbines or flow over CO_2 absorbers. Such a tower could generate 3-4 MW of electricity even after pumping the water to the top. The amount of CO_2 carried by the air in such a setup is 9500 tons per day, which is equal to the output of a 360 MW power plant, or the CO_2 output of a vehicle fleet of a city of 700,000 people. Such a tower would amount to $9 million, still extremely cheap compared to the cost of a power plant, $300-$400 million.

Lackner et al. (1999) also makes a different argument to pitch for direct air capture. The argument is that wind carries with it a flow of kinetic energy, of which a part is converted to electric energy. At a wind speed of 10 m/s, this kinetic energy equals an energy flux of 600 W/m^2. The equivalent CO_2 flux through the same area equals an energy flux of 100,000 W/m^2. Thus CO_2 is a far more concentrated source of energy than the kinetic energy harnessed by the windmill. Based on this logic, the paper says that since the windmills appear economically viable, direct capture of CO_2 should also be economical.

This paper puts the cost of this process between $\$10/tCO_2$ to $\$15/tCO_2$, half of which is expected to be in capital investment. Using the higher cost number of $\$15/tCO_2$, the total cost of eliminating 22 billion tons of CO_2 emissions each year would represent a yearly cost of $330 billion globally.

A recent paper by Lackner (2009) describes a system that no longer uses a hydroxide solvent. The solvent in his latest work is a resin and the physical structure also underwent a complete overhaul. The detailed system for direct air capture using an ion exchange resin composed of a polystyrene backbone with quarternary amine ligands attached to the polymer. The resin acts like a strong base, analogous to NH_4^+, where each hydrogen has been replaced by an organic carbon chain attached to the polymer matrix. The solvent has a very low binding energy but the uptake rate is reported to be greater than 1M NaOH solution. The sorbent can exist in 3 states, a bi carbonate state, a carbonate state and a hydroxide state. However, the reaction uses the change of state between the carbonate and bicarbonate to absorb CO_2 and the sorbent is never allowed to go back to the hydroxide state. Water vapor at 45^oC is used to regenerate the resin, which makes the process best suited to desert climate. Extremely cold temperatures and a tropical climate, with a high relative humidity, both limit the operation of the device.

The paper is not very clear on the mass transfer dynamics. It switches between claims that the reaction is air side limited to saying that it is sorbent side limited. In addition to that, the regeneration method used in this system is very place dependent and will not work under all environmental conditions. As said in the paper, this system is best designed for a desert climate and some other conditions will limit the operation of the device.

The total energy consumption is estimated at 50 kJ/mol of CO_2, which is equal to a second law efficiency of approximately 50%. This value is about 1/10 of those calculated by Keith et al. (2006), Baciocchi et al. (2006) or Zeman (2007). The concept of second law efficiency, or thermodynamic efficiency, has been dealt in great detail in the Appendix B.

The cost of the physical system designed to capture a ton per day of CO_2 is estimated at $200,000 for the first equipments, which could drop to $20,000 in due course of time. Thus, the first prototypes are assumed to break even at $200/t$CO_2$ and the nth plant cost could drop to as low a value as $16/t$CO_2$ at a 5 ¢/kWh electricity price.

The table on thermodynamic efficiency in Zeman (2007) shows a value of 6% for efficiency. The values calculated in papers by Baciocchi et al. (2006) and Keith et al. (2006) show that thermodynamic efficiency for direct air capture is in the 2-3% range. Hence, the thermodynamic efficiency reported in Lackner (2009) does not seem credible. The same can be said of his cost numbers.

Pielke (2009) used the cost range of \$100/tC (\$27/tCO_2) - \$500/tC (\$136/tCO_2) given in literature, to calculate the cost of air capture for the different IPCC CO_2 concentration stabilization scenarios. The paper calculates the cost as a percentage of the global GDP up to 2100 for CO_2 stabilization at 450 and 550 ppm. This calculation is performed for different global GDP growth rates. The costs of air capture for CO_2 stabilization come out to be in the range between 0.3% to 3 % of global GDP. These numbers seem to be in the same range as those shown in Stern (2007) and IPCC (2007). Using these numbers, this paper argues for a bigger role for air capture in the climate change debate.

The issue with this paper is that it takes the mitigation costs reported in Keith et al. (2006) and Lackner (2006) at face value. These numbers are used to conduct the sensitivity analysis for the overall cost of air capture mitigation. As it can be shown in the argument above and a later chapter, these costs are not very reliable. Hence, the entire analysis of this paper needs to be reevaluated.

Air capture has caught the fancy of people outside the scientific journals too and there are a few prominent articles in mass media on this technology. Jones (2009) was a news feature in Nature concluding that “increasingly it looks like air capture will be needed”. The benefit of air capture, the paper argues, is that all the CO_2 need not be pulled out, allowing the capture percentage to be flexible. The paper quotes Keith et al. (2006) that thermodynamics makes the task only twice as hard as flue gas capture (an erroneous calculation as showed above). This report emphasizes that further research on air capture should be pursued.

The other prominent article on air capture in mass media came in The Economist (2009). It quotes Dr. Lackner on the cost of the process, which is at \$200/tCO_2 currently and can go down to \$30/tCO_2 in the long run.

The literature also states that an important attribute for air capture is that the process is technically location independent, that it can be sited anywhere. It can be set up at, or close to, a CO_2 sink, which will obviate the need to build any additional pipelines to pump the liquid CO_2 to the storage locations. However, it does not mention that costs also go up as a result of setting up the process at greenfield sites, which may not be near industrial infrastructure. Thus, the advantage that air capture is location independent may come at a higher cost of building such systems far away from industrial infrastructure.

3.2 Estimating Cost based on Minimum Work

The minimum work can be used to estimate the cost of air capture. The minimum work depends on the capture percentage; however the change is not very significant for the range of capture percentages of interest. Using a representative number for the minimum energy required for air capture as 20 kJ/mol CO_2 (462 kWh/tC), the cost of air capture can be estimated.

Here, we assume that the cost of electricity is 10 ¢/kWh to find out the minimum cost of the process. The cost of electricity might not seem high at 10 ¢/kWh, when the current levelized cost for coal is around 7 ¢/kWh, but it is actually the cost of carbon free electricity. Air capture, to be feasible, requires a carbon free electricity source for capturing carbon. The use of any fossil fuel generated electricity will only end up releasing more CO_2 to the atmosphere than capture (Baciocchi *et.al.*, 2006). Both coal with CCS and nuclear are in the range of 10¢/kWh.

Given this cost of carbon free electricity, the minimum energy cost is **$46.2/tC**. This assumes the process is ideal with 100% thermodynamic and thermal efficiencies. This is also just the energy cost, without factoring even a single dollar for the capital cost. However, we know operating at the thermodynamic minimum requires infinite capital costs, so we must assume some efficiency. It is shown in Table 3-1, that the thermodynamic efficiency for air capture is 6%. As said earlier, thermodynamic efficiency calculated in the other papers are in the 2-3% range. Using this range, the energy cost can then be estimated as **$1540-$2310/tC ($420-$630/tCO_2)**. Adding in the capital cost will increase this estimate significantly. This calculation shows that many of the total cost numbers reported in the literature ($100-500/tC ($27-136/tCO_2) are not very believable.

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3.3 Comparison between Air Capture and Flue Gas Capture

By looking at the basis of absorption processes, one can start understanding why direct air capture is so much more expensive than flue gas capture. Many air capture papers in literature do not appreciate the difference in the absorber/stripper design between flue gas capture and air capture. In this section, we will explore the differences.

3.3.1 Amount of material handled

Some sort of absorber will be used to capture CO_2 from an incoming air stream, causing a drop in the CO_2 concentration in the exit stream. This rate of capture of CO_2 can be written in an equation form as follows:

$$\Delta \boldsymbol{CO_2} = \boldsymbol{C_{CO2}} \times \boldsymbol{f} \times \boldsymbol{A} \times \boldsymbol{v} \qquad (2)$$

Where ΔCO_2= Rate of CO_2 captured, mol/s

C_{CO2} = Inlet concentration of CO_2, mol/m^3

f = fraction of inlet CO_2 captured

A = Cross sectional area of the column, m^2

v = linear velocity of vapor in the column, m/s

Rewriting this equation in terms of the Area of the column, we get:

$$\boldsymbol{A} = \frac{\Delta \boldsymbol{CO_2}}{\boldsymbol{C_{CO2}} \times \boldsymbol{f} \times \boldsymbol{v}} \qquad (3)$$

As a rule of thumb in absorber design, linear velocity of gas in a column varies between 2-3 m/s for the optimum performance of the column. Hence, the term v is the equation above could be taken as a constant. For a fixed capture rate, we get the following relationship:

$$\boldsymbol{A = \frac{C_1}{C_{CO2} \times f}} \tag{4}$$

Where $\boldsymbol{C_1}$ = Constant term

This equation shows that the cross sectional area of a column is inversely proportional to the inlet CO_2 concentration and the fraction of CO_2 captured. Thus, as the inlet concentration of CO_2, or the fraction captured, goes down, the cross sectional area required goes up.

The inlet concentration of CO_2 is 300 times smaller in air capture compared to flue gas capture. Using the formula above, the cross sectional area of the absorber required for air capture would be 300 times the value for flue gas capture (as would the amount of gas processed).

It is often stated that since the supply of air is essentially limitless, the capture percentage for air capture could be freely varied and need not about 90% as in flue gas capture. The formula above makes it clear that the lower the capture percentage, higher is the required cross sectional area of the column. Thus, if the capture percentage is lowered from 90% to 25%, for the same rate of capture of CO_2, the cross sectional area required (as well as the amount of air processed) for air capture goes up by a factor of 3.6 (the amount of air processed would be over 1000 times that of flue gas capture for an equivalent amount of CO_2!). Such high cross-sectional areas of the absorber for air capture will result in significantly larger capital costs compared to flue gas capture. The increased gas flow will almost surely result in significantly higher energy requirements for the blowers and fans[1].

3.3.2 Absorption Driving Force

The absorption process is shown by the schematic below:

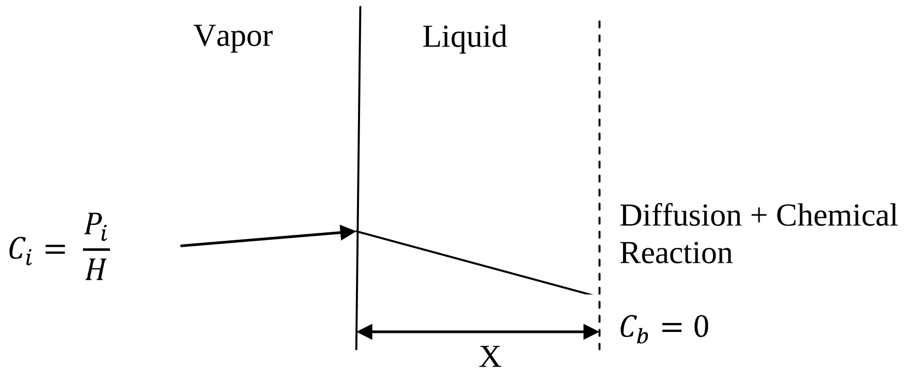

Figure 3-6: Schematic of a gas to liquid absorption process

CO_2 from the vapor phase will diffuse to the vapor-liquid interface. At the interface, the process of dissolution of CO_2 in the liquid is governed by Henry's Law. Henry's Law states that the equilibrium amount of a solute dissolved in a liquid is directly proportional to the partial pressure of that solute in the vapor. The Henry's constant, H, depends on the solute, solvent and the temperature. From the interface, the CO_2 diffuses into the liquid and reacts with the solvent. In the bulk liquid, all the CO_2 is reacted, so its concentration is zero. The length of the boundary

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[1] Because the column height depends on how much CO_2 needs to be removed per unit of cross sectional area and the absorber kinetics (see next section), one cannot make quantitative statements about energy requirements for the fans and blowers based on volume of air alone.

layer (X) depends of the reaction kinetics; the faster the reaction, the smaller the boundary layer. Experience has shown that these absorption processes are generally controlled by mass transfer in the liquid phase. Assuming this is the case, the gradients will be as shown in Figure 3-6. For this case, the molar flux is given by:

$$\boldsymbol{J = D\frac{dC}{dX}} \tag{5}$$

Where, D = Diffusivity of CO_2 in water (assuming aqueous based solvent)

dC = Concentration driving force $(C_i - C_b)$

X = Length of the boundary layer for CO_2 diffusion

The equation above defines the relationship between molar flux diffusivity, concentration driving force and length of path of diffusion. Diffusivity in the equation is defined for a particular gas in a liquid. For both the solvents of concern in the case of air capture or flue gas capture, diffusivity is calculated for the dissolution of CO_2 in water.

3.3.2.1 Comparison between flue gas capture and air capture using amines as sorbent for both

The first difference to note is that the concentration driving force is much less in the air capture case because of the much smaller partial pressures in the vapor phase. This results in smaller fluxes, which translate to larger reactor volumes to capture an equivalent amount of CO_2.

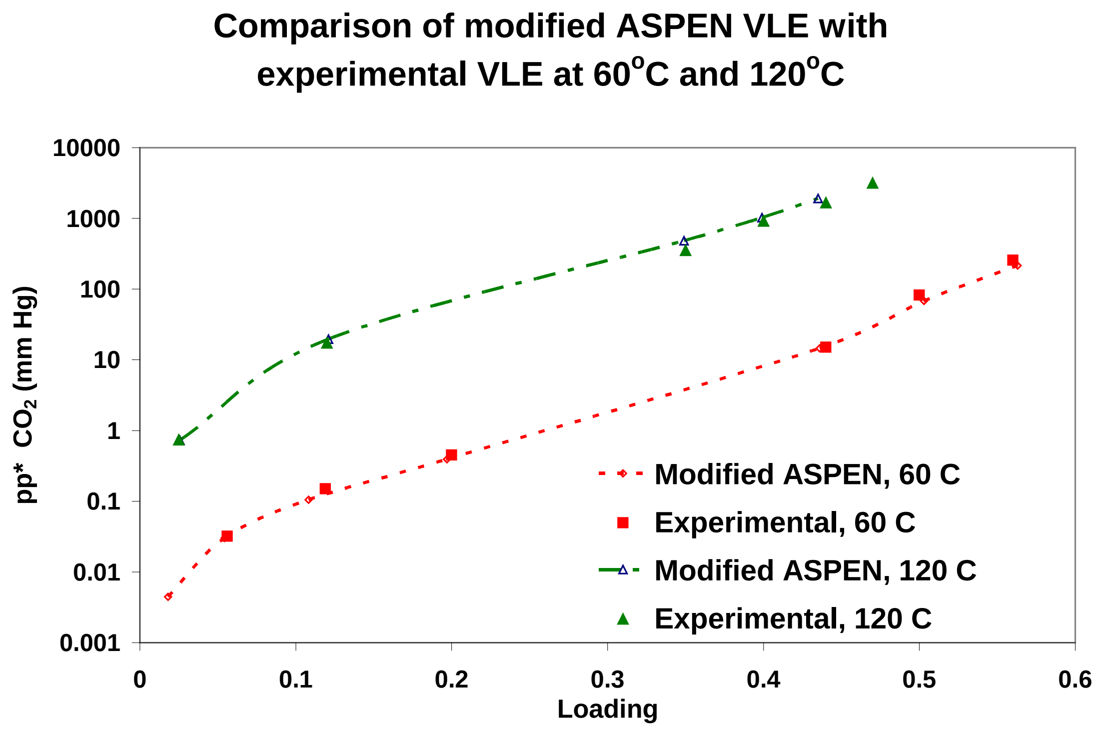

Figure 3-7: Comparison of modified ASPEN VLE with experimental VLE at 60°C and 120°C **(Kothandaraman 2010)**

The low CO_2 concentrations also raise an issue with solvent loadings and the reboiler duty of the stripper. From Figure 3-7, the partial pressure of CO_2 in air can be used to calculate the loadings in the column. The CO_2 concentration in the input stream is 400 ppm; the partial pressure of CO_2 at this concentration is about 0.3 mm Hg. At this low partial pressure of CO_2, the rich loading in the column is about 0.15[2]. This is about 1/3 of the rich loading of 0.5 calculated in Kothandaraman (2010) for flue gas capture. The lean loading for flue gas capture in that work is

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[2] This is using the 60°C curve which is indicative of the absorber. Note that we cannot operate at equilibrium, but need to lower the loading to account for a concentration driving force.

calculated as 0.15, leaving a difference of 0.35 between the rich and the lean loading. Now, rich loading for air capture is around 0.15 so the lean loading will have to be lower than that. If the air capture lean loading is 0.1, seven times the amount of solvent flow will be needed compared to flue gas capture.

Kothandaraman (2010) published a graph for reboiler duty plotted against the rich and lean loading, which is relevant in the discussion above. Figure 3-8 shows that the reboiler duty of the absorber scales non-linearly with lean loading in a column (Kothandaraman, 2010).

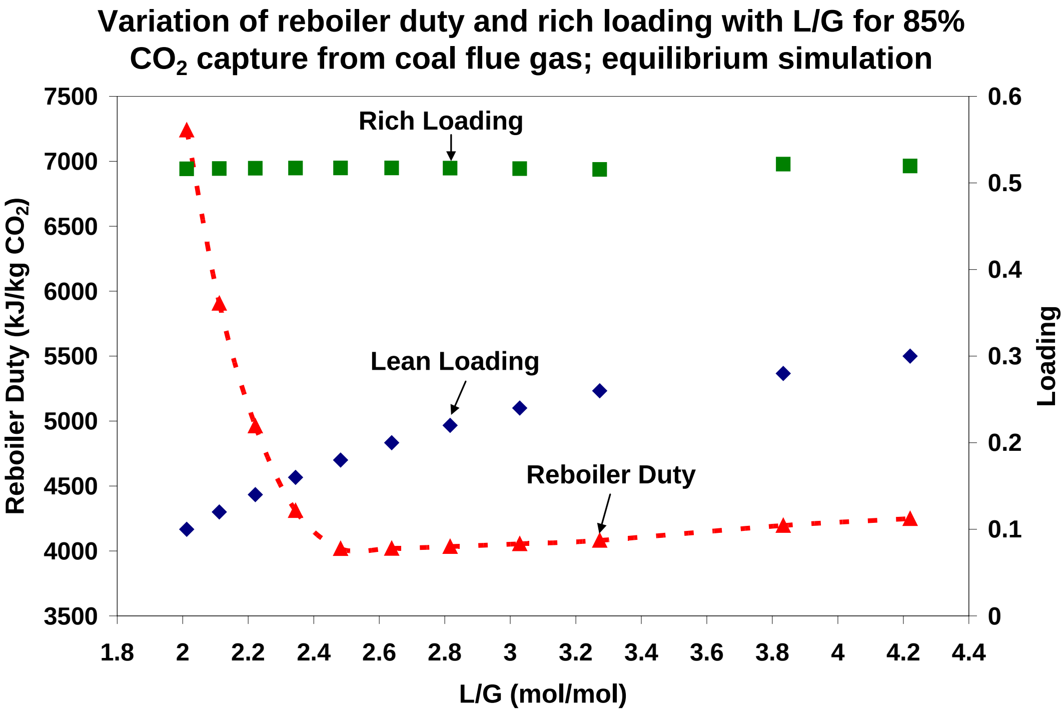

Figure 3-8: Variation of reboiler duty and rich loading with L/G for 85% CO_2 capture from coal flue gas; equilibrium simulation (Kothandaraman, 2010).

Figure 3-8 shows that at the values of lean loading discussed in the preceding paragraphs, the reboiler duty goes up exponentially. Thus, the low lean loading for air capture shall come at a much higher cost of reboiler duty. For the sake of calculation, let’s assume that the lean loading is 0.05 and the difference between the loadings is 0.1. The reboiler duty for a lean loading of 0.05, from Figure 3-8, is off the graph, probably around 7500 kJ/kg CO_2. This is more than twice times the reboiler duty for flue gas capture in Kothandaraman (2010). To reduce the reboiler duty, let’s assume again that the lean loading is 0.1. Here, the reboiler duty is 7000 kJ/kg CO_2, about 50% higher than flue gas, but as mentioned above, requiring seven times the solvent flow. From this discussion, it can be seen that this process will always be stuck with both the disadvantages of a high solvent requirement and a very high reboiler duty.

In summary, if one used amines for air capture it would result in large absorber volumes, large solvent flows and large reboiler duties. While our analysis is qualitative, one sees it is very much in line with results implied from the Sherwood plot.

3.3.2.2 Comparison between air capture, using hydroxide as the sorbent, and flue gas capture using amines

Because amines are impractical for air capture, literature studies commonly use hydroxides as the air capture solvent. In this section, the amine based flue gas capture is compared with NaOH based capture from air. The absorption reaction from air using hydroxide is much faster than amines. This shrinks the diffusion boundary layer in the liquid, X in Figure 3-6, resulting in higher fluses. Hence, the volume of an air capture absorber using a hydroxide sorbent is more comparable to the volume required for an amine based flue gas absorber.

However, the chemical reaction between CO_2 and the hydroxide binds the gas to the solvent in an irreversible fashion, meaning the solvent cannot be regenerated by a simple temperature swing.. This makes the task of solvent regeneration more complex and expensive energy intensive, resulting in much greater costs. This illustrates an inconvenient truth in designing many chemical engineering processes – everything is a trade-off. Using a stronger base as a solvent helps overcome the small concentration driving forces present in air capture, but require a much more complex and expensive regeneration process.

4. Air Capture via Biomass with Carbon Capture and Sequestration

4.1 Introduction

Earlier chapters have shown that the chemical capture of CO_2 from air is a very costly process. Thermodynamics does not allow the process of chemical capture to be run at costs which are at par with the other technologies for climate change mitigation. However, there is an alternate way in which atmospheric stock of carbon can be reduced, through the use of biomass energy. Photosynthesis, the original inspiration behind air capture, provides that system for capturing CO_2 from air. This chapter shall look to assess the costs of this system and see if this pathway of air capture could become feasible going forward.

CO_2 could also be captured in power plants fuelled with biomass, or fossil-fuel plants with biomass co-firing. Recently it has been recognized that biomass energy used with CO_2 capture and storage (BECS) can yield net removal of CO_2 from the atmosphere. The CO_2 put into storage comes from biomass which has absorbed CO_2 from the atmosphere as it grew, provided the biomass is not harvested at an unsustainable rate. The overall effect is referred to as ‘negative net emissions’.

Biomass fuels produce similar or slightly greater quantities of CO_2 per unit of fuel energy as bituminous coals; thus, the CO_2 concentration of flue gases from these fuels will be broadly similar. This implies that the cost of capturing CO_2 at large power plants using biomass may be broadly similar to the cost of capturing CO_2 in large fossil fuel power plants in cases where plant size, efficiency, load factor and other key parameters are similar. At present, biomass plants are small in scale (less than 100 MW_e) (IPCC Special Report on CCS, 2005). This means that the resulting costs of production with and without CCS are relatively high compared to fossil alternatives. Full CCS costs for biomass could amount to 110 US$/tCO$_2$ avoided (IPCC Special Report on CCS, 2005).

Applying CCS to biomass-fuelled or co-fired conversion facilities would lead to lower or negative CO_2 emissions, which could reduce the costs for this option, depending on the market value of CO_2 emission reductions. A limited number of studies have looked at the costs of such systems combining capture, transport and storage. The capturing of 0.19 MtCO$_2$/yr in a 24 MW_e biomass IGCC plant is estimated to be about 80 US$/tCO$_2$ net captured (300 US$/tC), which corresponds to an increase in electricity production costs of about 0.08 US$/kWh (IPCC Special Report on CCS, 2005). Keith et al. (2006) also made a calculation for Biomass with Capture and Sequestration pathway. The cost of air capture through this route is reported as $160/tC (~$44/tCO$_2$) for the price of electricity at 3.5 ¢/kWh and about half of that for an electricity price of 5-7 ¢/kWh. It should be kept in mind that these studies are relatively old and the costs have escalated since then. Hence, one should use caution when directly comparing the costs generated in this report with those reported above.

The prospects for biomass energy production with CO_2 capture and storage might be improved in the future if economies of scale in energy production and/or CO_2 capture and storage can be realized (IPCC Special Report on CCS, 2005). So if bio-energy systems prove to be viable at scales suitable for CO_2 capture and storage, then the negative emissions potential of biomass might become globally important. However, it is currently unclear to what extent it will be feasible to exploit this potential, both because of the uncertainties about the scale of bio-energy conversion and the extent to which dedicated biomass energy crops will play a role in the energy economy of the future.

This chapter looks at one such system in greater detail.

4.2 Background

The system basically consists of a few simple building blocks: a fixed tract of land, a power plant driven by biomass energy and a conventional CCS setup. The process consists of harvesting the piece of land sustainably to produce a steady stream of biomass, which feeds into the power plant that produces electric power. The emissions resulting from the plant operations are then captured and sequestered using the conventional Carbon Capture and Sequestration (CCS) equipment. The energy required to drive the plant's capture equipment is derived from the electrical energy output of the plant and any excess electricity is sold for credit. The schematic of the model is shown below.

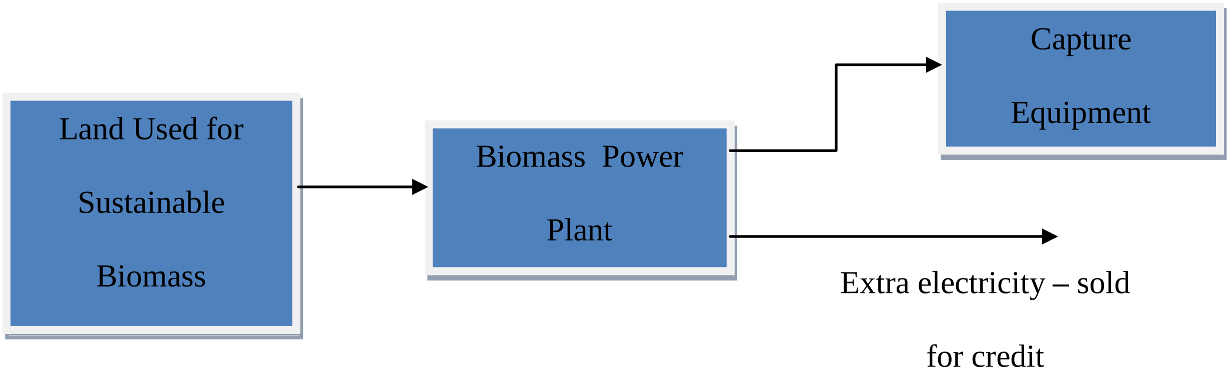

Figure 4-1: The schematic showing the Biomass coupled with CCS process description

The stock of carbon captured from the atmosphere is burnt in the power plant and the emissions captured and sequestered by the CCS equipment. The fact that the emissions are captured and sequestered makes this process a carbon negative process, or a CO_2 sink, which

is the case with the Direct Air Capture. Melillo et al. (2009) worked on the fugitive emissions associated with land use changes, both direct and indirect, in the production of biofuels from bioenergy. Direct fugitive emissions are those that are linked to the production, such as emissions due to the use of fertilizer, equipments etc. on the land. These are the emissions that are considered in the work here. Indirect emissions are linked to changing land practices, for example change of a wetland to a crop land. Such land use changes could result in significant carbon emissions. However, indirect emissions are excluded from the scope of this work.

As written above, the biomass for the plant's output is grown from a fixed tract of land. This would require proper upkeep of the land to keep it fertile, ideally for infinite time, through the use of fertilizers and nutrients. The manufacture and use of fertilizers and additional nutrients would lead to some CO_2 emissions, as will the transportation of biomass to the plant and other maintenance operations too. These emissions are called as life cycle emissions or fugitive emissions. This concept shall be dealt in detail later in this chapter.

In order to provide a clear comparison with Direct Air Capture, the avoided cost of the process, in $/tCO_2$ will need to be ascertained. Along with its cost, land required for this process could become a major constraint. Trees capture carbon biologically, where the rate of capture is very slow as compared to any chemical process. Hence, the land required for this process could be an issue, which needs to be further explored for feasibility.

In summary, this chapter has the following two objectives:

1. *Calculate avoided cost of the process*
2. *Calculate land area required for the operation of a standard sized power plant, say a 500 MW one. This will be extrapolated to estimate the land requirement of this process*

A model was built to satisfy both the objectives. The calculations were performed for a standard 500 MW plant and the detailed calculations are documented in the appendix. The inputs of the model as well as the formula used for avoided cost are discussed, some in this chapter and the rest in the appendix.

4.3 Model Inputs

The inputs required for this type of a model can be divided into two important components:

- Land
- Power Plant, including the CCS equipment

4.3.1 Land

The inputs for the land depend on the biomass used in the model, as the growth rate of biomass, and in turn the land area required depends on the type of biomass used. There is a wide variety of biomass considered in studies in literature and their growth numbers vary by a huge margin. For the purposes of this study, switchgrass was chosen as the biomass. Switchgrass turned out to be an ideal source of biomass on several counts: it is a perennial grass species which can tolerate diverse growing conditions and requires very low maintenance (McDonald et al., 2006; McLaughlin et al., 1999). This is the reason why it is widely distributed within North America (McLaughlin et al., 1999). Hence, this could be seen as a standard biomass for this kind of analysis.

Using switchgrass as the biomass, the inputs required in the land area calculation would be the growth rate and the moisture and carbon content of switchgrass. We have chosen the growth rate of switchgrass of 12 tons per hectare per year on a dry basis (IPCC, 2000; Hall and House, 2003) and the carbon content of switchgrass of 48% by weight on a dry basis (Robinson et al., 2003; Jenkins et al., 1998). The moisture content of switchgrass is taken as 70% (Keith et al., 2003; Jenkins et al., 1998)

4.3.2 Power Plant

The plant considered is an IGCC biomass fired power plant. The inputs for such a plant will include the plant's overall thermal efficiency, for both the reference[3] and the capture plants. The

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[3] The term, reference plant, indicates an IGCC biomass power plant without the capture equipment installed.

capture and reference plant efficiencies are 22% and 31% respectively (Bergholz,2009). On the project finance side, the Total Plant Cost (TPC) for capture and reference plants are \$9407/kWe and \$5308/kWe respectively (Bergholz, 2009).

The Operation and Maintenance (O&M) costs of capture and reference plants are \$17/MWh and \$8/MWh respectively, from Hamilton et al. (2008). These O&M costs in Hamilton et al. (2008) are calculated for a supercritical pulverized coal (SCPC) power plant. The O&M costs for a biomass power plant are expected to be higher than those for a coal plant (Bergholz, 2009). Still, we use them in our analysis as a preliminary evaluation of this model and any future work in this regard would include updating the O&M costs for a biomass power plant. This update would further increase the avoided cost of this process. However, we do a sensitivity analysis later in the chapter to see the variability of the avoided cost numbers with O&M costs. The annual carrying charge is taken as 15.1% (Hamilton et al., 2008) and capacity factor used is 85.1% (Hamilton et al., 2008).

To calculate the amount of biomass required to drive a standard 500 MW power plant, the heating value of switchgrass will be needed. The heating value is the amount of energy contained in a unit mass of the biomass, which is used as 19.3 MJ/Kg (Robinson et al., 2003; Jenkins et al., 1998). The capture rate is assumed to be 90%, that is, we capture 90% of the CO_2 emissions that result from the biomass power plant operation.

4.4 Calculations and formulae used

4.4.1 Avoided Cost

Choosing the formula for avoided cost was not a straightforward decision with this biomass plant model. The standard avoided cost formula used when calculating this cost for coal plants with CCS is:

$$Avoided\ Cost\ \left(\frac{\$}{tCO2}\right) = \frac{COE\ for\ a\ capture\ plant - COE\ for\ a\ reference\ plant}{CO2\ emitted\ for\ a\ reference\ plant - CO2\ emitted\ for\ a\ capture\ plant} \tag{6}$$

However, since we are dealing with negative emissions, this equation does not apply. The formula used to calculate the avoided cost for the negative emissions is:

$$Avoided\ Cost\left(\frac{\$}{tCO2}\right) = \frac{Cost\ of\ Electricity\ for\ a\ capture\ plant - Cost\ of\ carbon\ free\ electricity}{(CO2\ captured\ by\ the\ plant - CO2\ emitted\ in\ the\ life\ cycle\ of\ a\ capture\ plant)} \tag{7}$$

1. ***Cost of electricity for a capture plant:*** This is the cost of electricity produced at a biomass plant with carbon capture and sequestration. The value is obtained using the calculation methodology used by Hamilton et al. (2008), as shown in the appendix.

2. ***Credits for electricity:*** Any extra electricity output of the plant is sold for credit, in turn reducing the avoided cost of the plant. This is carbon free electricity, the price of which is not exactly clear and can only be known in the future when carbon is priced. However, a parametric calculation was performed for a reasonable set of cost of carbon free electricity. The cost is taken in the range of 8¢/kWh to 12¢/kWh.

3. ***CO_2 captured by the plant:*** The amount of CO_2 captured in the process, assuming the capture rate equal to 90%.

4. ***CO_2 produced in the life cycle of the plant:*** This concept of life cycle emissions, or fugitive emissions, was introduced earlier in the chapter. Our model assumes that the land used for growing biomass can be used indefinitely. This requires extra effort in keeping the land fertile for repeated plantation through the use of nutrients and fertilizers. There are also some emissions associated with harvesting the biomass and transporting it to the plant. All the CO_2 produced in the process is put under the label of life cycle emissions and is calculated here. The exact amount of emissions per unit of biomass energy is beyond the scope of this thesis. Instead, a parametric calculation is performed by varying fugitive emissions as a percentage of the total CO_2 produced by the power plant. These numbers are indicative ones, intended to get a sense of the range of expected values for avoided cost. Future work in this area would involve finding out the exact numbers for such fugitive emissions in tons of CO_2 per unit of biomass energy.

4.5 Land Area Calculation

Land area is calculated from the biomass requirement of the plant. The biomass required is determined by the plant’s heat rate and the heating value of switchgrass. This value is then divided by the growth rate of biomass to get the land area required. These formulae are shown in the appendix.

4.6 Results and Discussion

4.6.1 Land requirement

The land required for the case of a 500 MW biomass capture plant, with a thermal efficiency of 22%, is roughly **1016 square miles**. This land is calculated for the case of 90% capture of the plant’s CO_2 emissions. If this process has to be scaled up to the level where it could be considered as a climate change mitigation option, it has to capture and sequester about a Gigatonne (Gt) of CO_2 annually. The land required to capture and sequester 1 Gt of CO_2 through this route is **203,125 square miles**. To put this number in perspective, the land areas of a few states in US are indicated below:

Table 4-1: Land Area for different states in the US

State	Total area (in sq. miles)
California	163,707
Texas	268,601
Massachusetts	10,555

It can be seen that the land required for 1 Gt CO_2 avoided by biomass capture is more than the size of California. Committing this amount of land to the abatement of 1Gt of CO_2 each year would be a challenging task. Not only is the land requirement huge, the model has not yet considered the dynamics of maintaining the fertility of this size of land indefinitely.

4.6.2 Avoided Cost:

Using the formula discussed above for avoided cost, a range of values is obtained below. The range is because the fugitive emission in the model is parameterized for a range of probable values. At a carbon-free electricity base cost of 10 ¢/kWh, the table of avoided cost is:

Table 4-2: Avoided Cost values for a range of values for fugitive emission as a percentage of total CO_2 produced by the power plant

% of total CO2	0%	10%	20%	30%	40%	50%	60%	70%	80%	85%
Avoided Cost ($/tCO2)	177.68	199.89	228.44	266.52	319.82	399.78	533.04	799.56	1599.11	3198.22

A graph is plotted for the avoided cost. The fugitive emission on the x-axis of the graph is capped at 70% of the total CO_2 produced by the power plant. This is the area of interest for all practical purposes, as any such system will never have its life cycle emissions in excess of 70% of the total CO_2 produced by the power plant. The graph for the avoided cost shows the exponential increase in cost numbers as the fugitive emissions, as a percentage of the total plant emissions, goes beyond a limit.

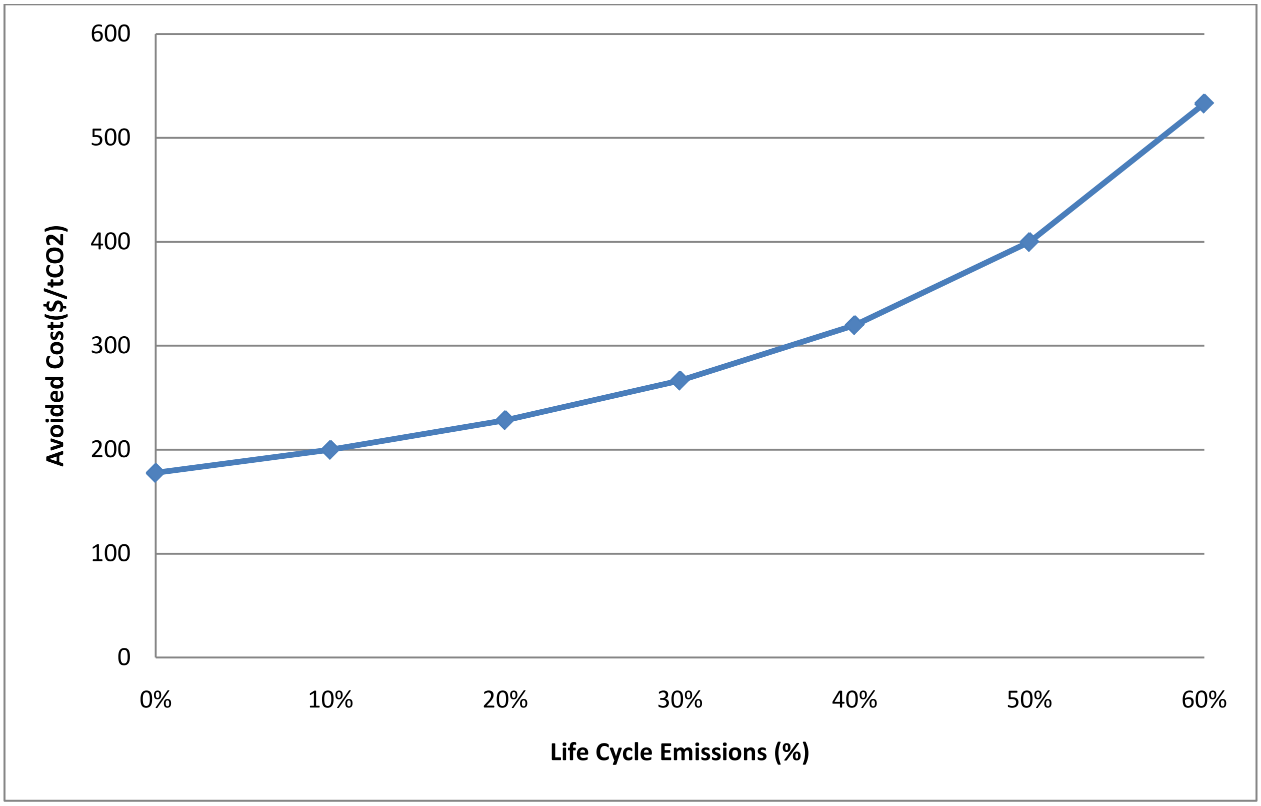

Figure 4-2: Avoided Cost curve for the biomass capture plant as a function of life cycle emissions

Overall, it does seem that the cost of this process is in the range where it can compete with the other technologies in the climate change mitigation space. However, the major issue comes in the land requirement of this model. These preliminary calculations show that the land required could be prohibitive, especially when the model assumes that the land is used indefinitely. The land management practices are beyond the scope of this work but any paper in biomass literature can provide details of how this can go wrong, especially at this scale. This report feels that this could be a major bottleneck in the feasibility of this pathway.

4.7 Sensitivity Analysis

Literature is full of data on biomass numbers and there is a significant variance in them, which could challenge the assumptions of the model presented here. The cost numbers presented above are for a fixed set of values for the biomass variables, kept as the base numbers in the calculation. However, using a fixed value for all the biomass variables would not do justice to the spread of numbers in literature. A sensitivity analysis was performed on some of the most important variables to get a range of cost numbers. This would help in stress testing the model to a wide variety of inputs. The variables on which the sensitivity analysis was performed are:

- Cost of carbon free electricity
- Growth rate of biomass
- Cost of biomass
- Total Plant Cost for a biomass plant
- O&M cost of the plant

The graphs for sensitivity analysis are shown below. Please refer to the appendix for the actual values.

4.7.1 Cost of carbon free electricity

The base cost for carbon free electricity was taken as 10 ¢/kWh. However, the number is varied between 8 ¢/kWh to 12 ¢/kWh. As the future price of carbon free electricity is not known, this analysis will help look at a range of feasible values. The graph for the avoided cost shows that higher the cost of carbon free electricity, lower will be the avoided cost of this process. However, the impact of a higher cost of carbon free electricity is not that significant, hence the model numbers can be assumed to be in the right range.

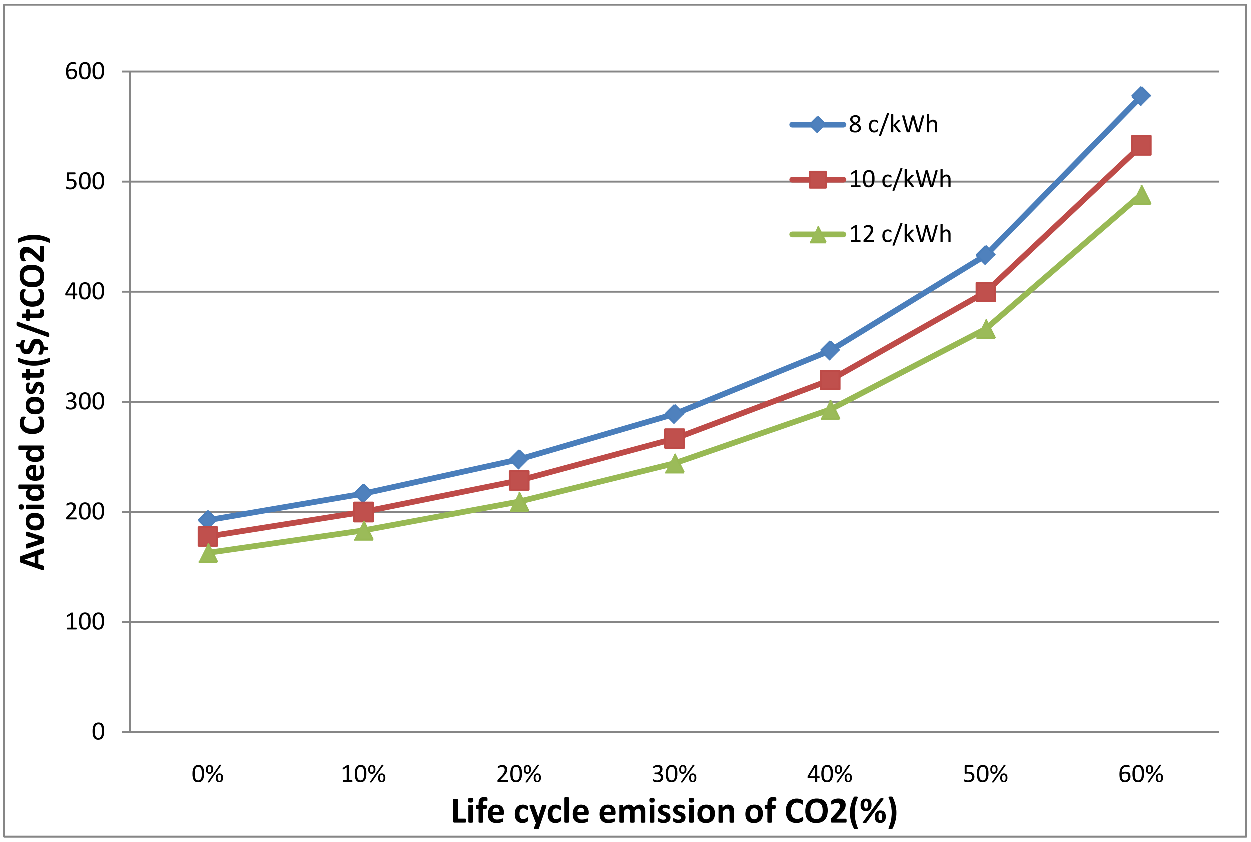

Figure 4-3: Avoided Cost numbers for a range of cost of carbon free electricity

4.7.2 Growth rate of biomass

The growth rate of biomass depends on a host of factors, from the local soil conditions to the weather patterns and other similar factors. Although switchgrass is a relatively stable biomass, when it comes to growing under various conditions, the literature still has various growth values mentioned for it. A NAS report put the growth rate as ranging from 2.3 t/ha/yr to 24 t/ha/yr. The base case number is taken as 12 t/ha/yr in the calculation above, but a sensitivity analysis is performed at the other values of biomass yields as well, as shown below. As can be seen from this graph that yield has a significant impact on the amount of land required, especially on the lower side. Hence, the model results can be affected if the actual yield is very different from the number used in the model.

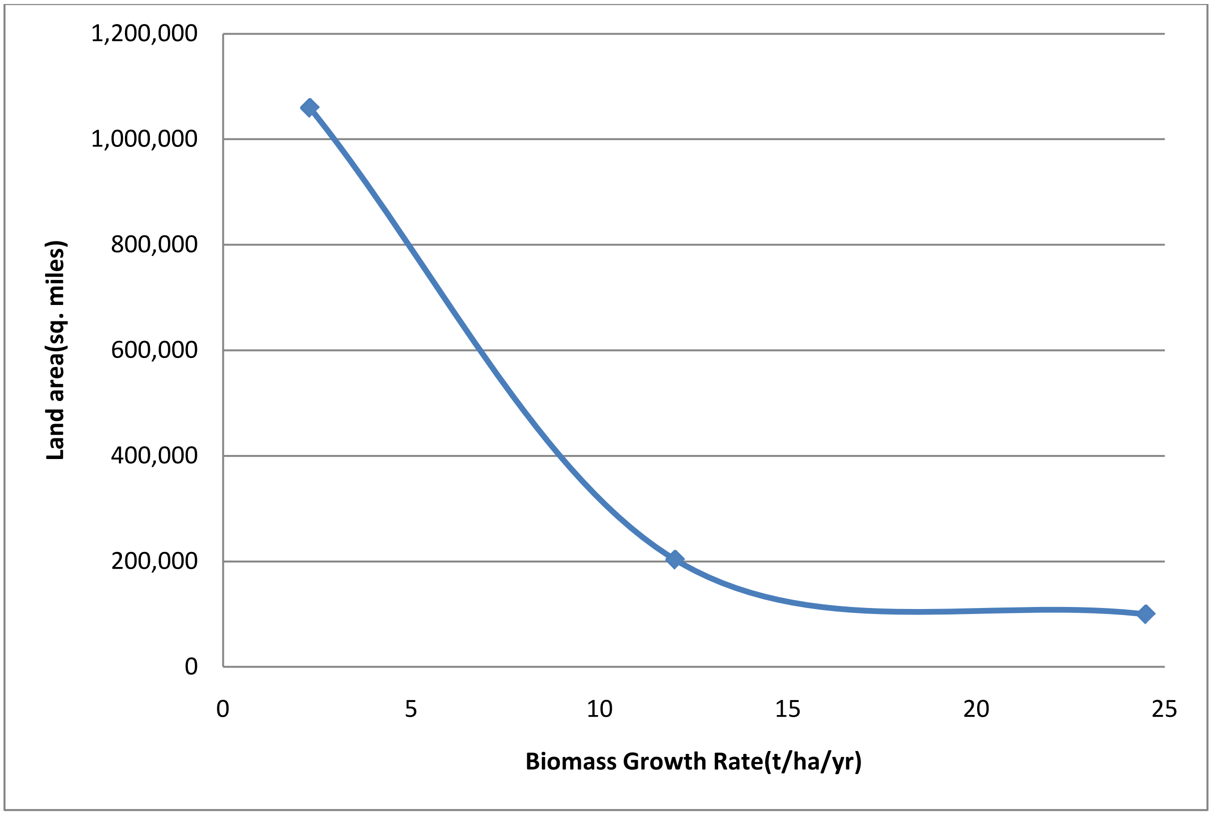

Figure 4-4: Land Area required for different biomass growth rates

4.7.3 Cost of Biomass

The delivered cost of switchgrass varies between \$3/GJ to \$8/GJ in literature. A sensitivity analysis performed for these extreme biomass cost shows a visible increase in the avoided cost for increases in the biomass cost. Hence, the model numbers would change appreciably if the delivered cost of switchgrass was different than $8/GJ by a decent margin.

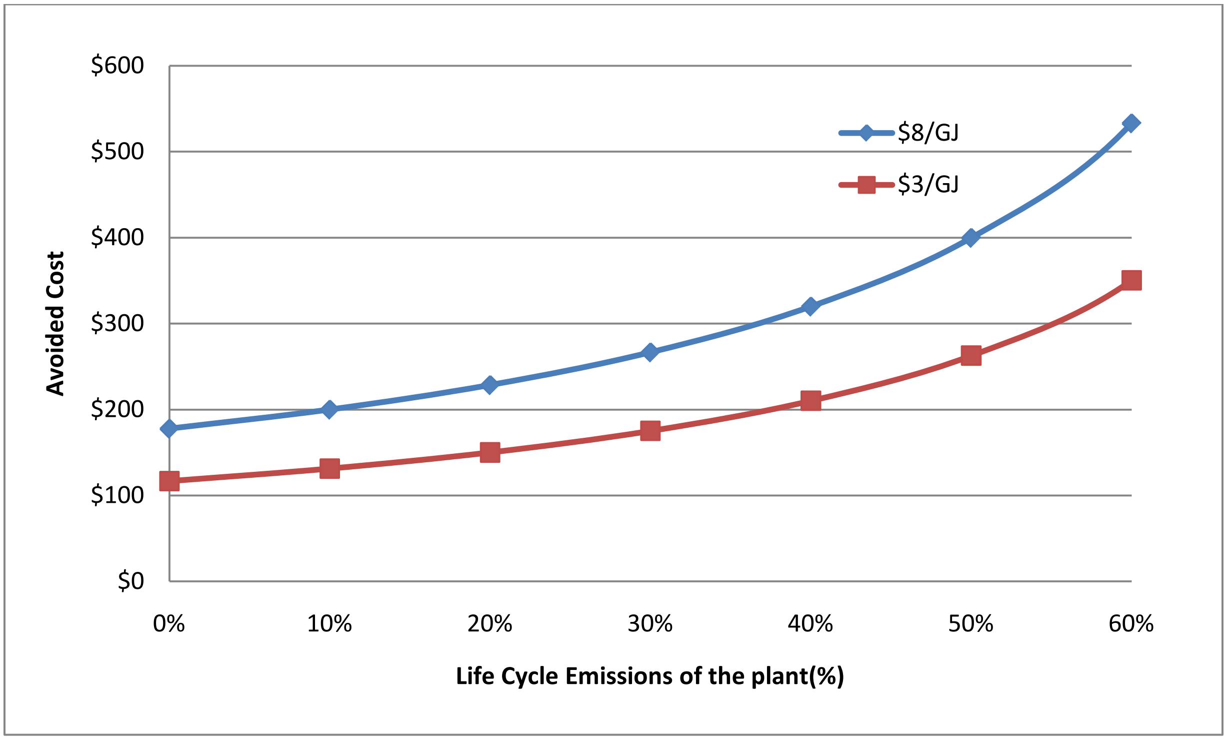

Figure 4-5: Impact of Biomass Cost on Avoided Cost

4.7.4 Total Plant Cost

Larson et al. (2009) reported a Total Plant Cost (TPC) number that is much lower than the number reported in Bergholz (2009). Although the latter number was used in the base analysis as they seemed more appropriate, the lower number was used to find the sensitivity of the model to TPC. Again, as can be seen from the graph, the avoided cost increases significantly as the total plant cost goes up. Total Plant Cost proportionally affects the Cost of Electricity, which has a direct impact on the avoided cost. Here again, a change in the Total Plant Cost number can impact the results of the model appreciably. Still, the lower values of TPC do not seem in the feasible cost range.

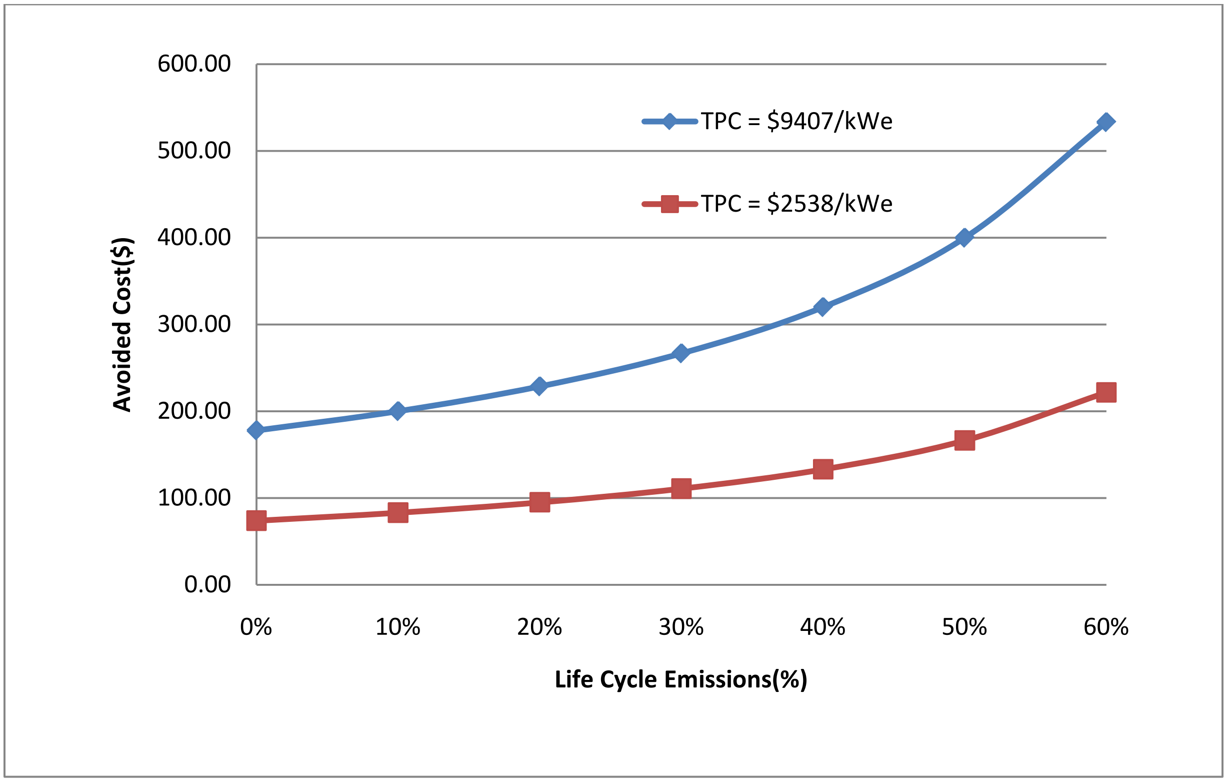

Figure 4-6: Impact of Total Plant Cost on Avoided Cost

4.7.5 O&M Costs

The impact of plant's O&M costs on the avoided cost of the process is shown below. As can be seen from the curve, even a significant increase in the O&M costs does not impact the avoided cost severely. Hence, using the O&M cost used for a coal plant will be good as a first approximation for a biomass plant.

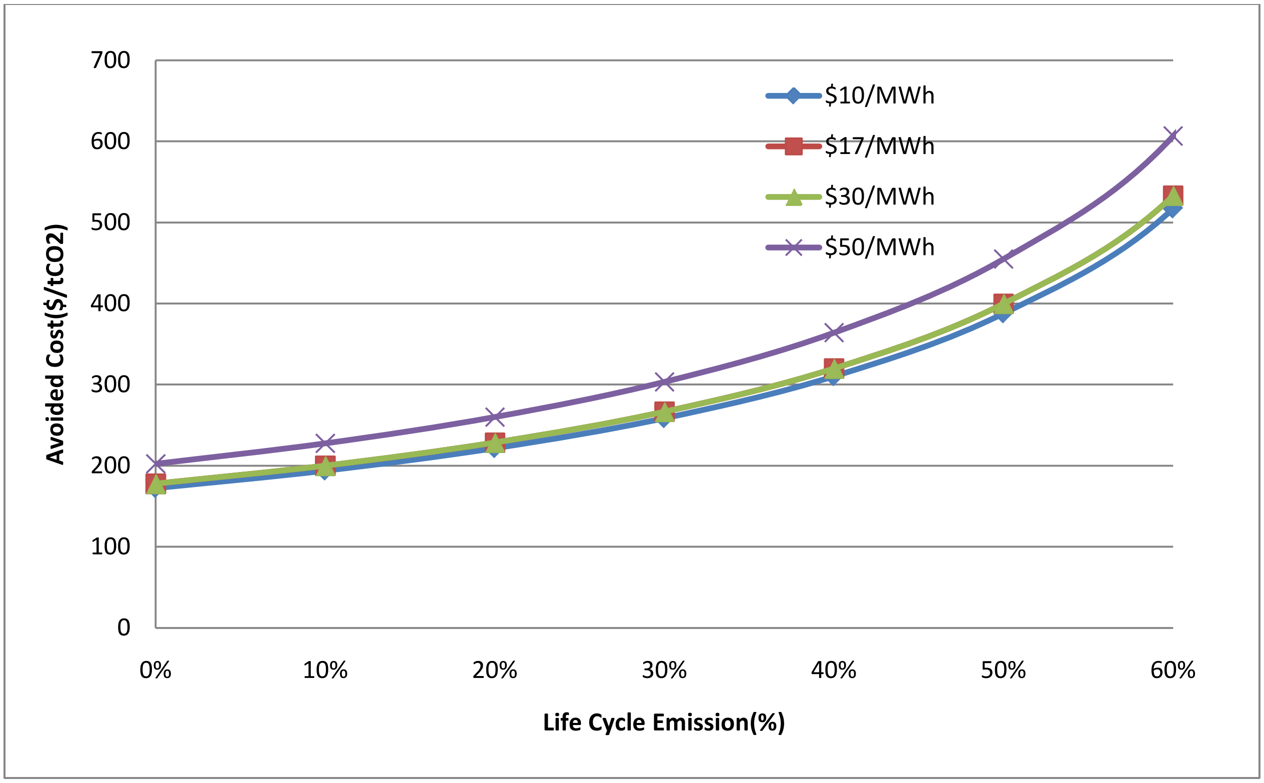

Figure 4-7: Impact of O&M Costs on Avoided Cost

5. Conclusions: Role of Air Capture in the climate change mitigation portfolio

Air Capture has been in the news lately as a prominent climate change mitigation technology. Both the scientific and the mass media have promoted this technology as one of the most important in the fight against climate change. The motivation of this work came from the desire to look at this technology in detail and assess its feasibility as a climate change mitigation option. This work never questioned the technology behind this process; industrial applications for air capture have been reported since early 1930s. These processes, as described in the chapter on history of air capture, have to separate CO_2 from the input air stream at any cost because its presence causes significant problems in their systems. Moreover, as also described in that chapter, the captured CO_2 is then vented to the atmosphere. There has to be a difference in approach in the use of air capture as a climate change mitigation technology. Not only is the captured CO_2 separated from the sorbent but is also compressed to a liquid form and sequestered. These steps of regeneration of the sorbent, by stripping off the CO_2, and sequestration of liquid CO_2 add significant complexity to the entire process. Quantifying this complexity by performing a feasibility analysis in the realm of climate change was the intended goal of this work. This would ultimately help us decide how to view the role of such a technology in the current policy debate.

This dissertation looks at two different pathways of air capture: direct air capture, using chemical sorbents and biomass energy coupled with carbon capture and sequestration.

5.1 Direct Air Capture

The analysis done for direct air capture shows it to be a prohibitively costly process. The conservative estimate for the operating cost of direct air capture came out to be **\$1540-\$2310/tC (\$420-\$630/tCO_2).** This is just the cost of energy and does not include a single dollar towards capital cost of building such plants. Such prohibitive mitigation costs prove that direct air capture cannot compete with the other viable climate change mitigation options.

Another major issue with direct air capture is the design of the absorber for it. For the same sorbent, the driving force in air capture absorbers would be 300 fold less than in flue gas absorbers for CCS. Thus, the volume of such an absorber would be hundreds of times the volume of a flue gas absorber. Moreover, both the rich and lean solvent loadings would be lower, requiring a significantly larger energy input for regeneration of the sorbent to the lower lean loadings. Using hydroxide as a sorbent can mitigate the problem of driving force as such a sorbent is very reactive. However, it is not a “reversible” reaction so its regeneration would be very expensive and complicated.

5.2 Biomass with Carbon Capture and Sequestration

Air capture via biomass with carbon capture and sequestration is another important pathway assessed in this work. The results show that this pathway has reasonable avoided costs, in the \$150-400/tCO_2 range, which is larger than those for other mitigation options but of the same order of magnitude. The biggest problem with its feasibility is the extremely high land area required for its operation. Sequestering 1 Gt of CO_2 annually via this route will require more than 200,000 square miles of land, which is 30-40% more than the land area of California. Hence, there are scale limitations to the deployment of this pathway. It has to be kept in mind is that indirect land use changes are not considered in this analysis, a highly contentious topic in literature (Melillo *et.al.*, 2009)

5.3 Role for air capture

This technology looks really “seductive” (Herzog, 2003) on paper but the feasibility study opened up a lot of issues. There are many issues associated with the implementation of this technology, primarily being its extremely high cost. It would be a stretch to believe that the climate policy of the future should be favorable towards such a costly technology, when these policies are not ready to embrace much cheaper mitigation options currently. The way air capture is being promoted, it also runs the risk of creating a moral hazard. It is reported in literature, both scientific and mass media that air capture will mitigate all the carbon emissions seamlessly, which enables us to keep using the current energy systems heavily dependent on fossil fuels. There is a definite risk of making bad policy choices today given this argument. In fact, it could be a reason why this technology has gained prominence in the policy debates at the highest level in this country.

However, I feel that such a technology can be useful as an offsetting option. It could be used to offset emissions from a particular sector, which would be very costly otherwise. Obviously, electricity generation is not one such sector. Automobile sector could be a potential area where it might be costly to mitigate emissions from every single car. However, there are other potential ways to reduce emissions from this sector, through the use of biofuels, hybrid vehicles etc.

However, one prime example of its application could be in mitigating the emissions of the aviation sector. Aviation industry is fighting hard to drastically cut its CO_2 emissions in the next few decades and this technology can help them in achieving that. Switching fuels in the aviation sector could be a costly option and air capture can be useful here.

6. Future Work

While this work has been an important first step towards understanding the feasibility issues related to air capture, there are a few important future assignments that can be performed on top of this work. First and foremost, this work left out carbon sequestration through natural sinks, or enhanced uptake by trees and oceans, from its scope. It could be instructive to analyze that important natural pathway as well.

The chapter on absorber design for air capture can be improved by performing an analysis on other absorbents being considered for direct air capture. The results of that section could be quantified further too.

The pathway of biomass with carbon capture and sequestration used a simplified model of a biomass energy fed power plant producing power, which drives a CO_2 capture equipment and sequesters its emissions. This model is very simplistic in this analysis and can be made more detailed by adding in the complexity of the biomass growth, biomass handling and plant's O&M. The fugitive emission of such a plant is also not a fixed number in this analysis and it would help to find a stricter range for that number. This analysis assumes that number in a much broader range.

7. References

"Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change" (2007) Intergovernmental Panel on Climate Change, Fourth Assessment Report.

"Scrubbing the Skies." (2009) The Economist. March 5, 2009

Baciocchi, R., Storti, G., Mazzotti, M. (2006) "Process Design and Energy Requirements for the Capture of Carbon Dioxide from air" Chem. Eng. Process. **45**, 1047-1058

Bergholz, Laura (2009) "CO_2 Capture From Biomass-Fired Power Plants" Vattenfall Internal Report

Burcher, R., Rydill, L. (1995) "Concepts in Submarine design", **Chap. 9**, Cambridge University Press

Castle, W.F. (2007) "Fifty-Years' Development of Cryogenic Liquefaction Processes", **Chap. 8**, Springer New York

Cryogenic air separation and liquefier systems by Universal Industrial Gases Inc. at: http://www.process-cooling.com/Archives/ebde76fc3c5b7010VgnVCM100000f932a8c0

Flynn, T.M. (2004) "Cryogenic engineering", **Chap.10** ,2nd edit., Informa Health Care

Hall, D.O. ,House, J.I., (1993) "Reducing Atmospheric CO2 using Biomass Energy and Photobiology" Energy Convers. Mgmt **34**, 889-896

Hamilton, M.R., Herzog, H.J., Parsons, J.E. (2008) "Cost and U.S. public policy for new coal power plants with carbon capture and sequestration." Energy Procedia

Heinrich, J.J. (2003) "Air Capture Practices" MIT LFEE 2003-001 WP.

Heinrich, J.J. (2003) "CO_2 capture from Air – Current Practices" Publication No. LFEE 2003-001-WP, Massachusetts Institute of Technology, Cambridge, MA, USA

Henderson, R.F., Taylor, K.C. (1988) "Submarine Air Quality", **Chap. 3**, National Academy Press

Herzog, H., Meldon, J., Hatton, A., (2009) "Advanced Post-Combustion CO2 Capture," prepared for the Clean Air Task Force under a grant from the Doris Duke Foundation http://www.catf.us/publications/reports/Coal_Without_Carbon.pdf

Herzog, H.J. (2003) "Assessing the Feasibility of Capturing CO2 from the Air" MIT LFEE 2003-002 WP

Hocking, D. (2005) “Air quality in airplane cabins and similar enclosed spaces”, **Pg 357-364** Springer

Hook, R.J. (1997) “An Investigation of Some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds” Ind. Eng. Chem. Res. **36**, 1779 – 1790

IPCC special report (2000) “Land Use, Land Use Change and Forestry”, Cambridge University Press

Jenkins, B.M., Baxter, L.L., Miles Jr., T.R., Miles, T.R. (1998) “Combustion Properties of Biomass” Fuel Processing Technology **54**, 17

Jones, Nicola (2009) “Sucking it up” Nature **458**, 1094-1097, April 29, 2009.

Keith, David (2009) “Why Capture CO_2 from the atmosphere?” Science **325**, 1654-1655, 25 September, 2009.

Keith, David W., Ha-Duong, Minh (2006) “Climate Strategy with CO_2 Capture from Air.” Climatic Change **74**, 17-45.

Lackner, K.S. (2009) “Capture of Carbon Dioxide from ambient air” The European Physical Journal Special Topics **176**, 93-106

Lackner, K.S., Grimes,P., Ziock, Hans-J. (1999) "Capturing Carbon Dioxide from Air" Sourcebook **57**(9), 6-20

Lackner,K.L., Grimes,P., Ziock,H.-J. (1999) Proceedings of the 24th Annual Conference on Coal Utilization and Fuel Systems, Clearwater, FL, USA

Larson, E.D., Jin, H., Celik, F.E., (2009) "Performance and cost analysis of future, commercially mature gasification-based electric power generation from switchgrass" Biofuels, Bioprod. Bioref. **3**,142 - 173

McDonald, S., Robinson, S., Thierfelder, K. (2006) "Impact of switching production to bioenergy crops: The switchgrass example" Energy Economics **28**,243-265

McLaughlin, S.B., Bouton, J., Bransby, D., Conger, B., Ocumpaugh, W., Parrish, D., Taliaferro, C.,Vogel, K., Wullschleger, S. (1999) "Developing switchgrass as a bioenergy crop." In: Janick J, Editor. Perspectives on new crops and new uses, Alexandria, VA: ASHS Press 1999

Melillo, J. M., Reilly, J. M., Kicklighter, D. W., Gurgel, A. C., Cronin, T. W., Paltsev, S., Felzer, B. S., Wang, X., Sokolov, A. P., Schlosser, C. A. (2009) "Indirect Emissions from Biofuels: How Important?" Science **326**, 1397-1399

Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L. (2005) "IPCC Special Report on Carbon Dioxide Capture and Storage" Cambridge University Press.

Nabuurs, G.J., Masera, O., Andrasko, K., Benitez-Ponce, P., Boer, R., Dutschke, M., Elsiddig, E., Ford-Robertson, J., Frumhoff, P., Karjalainen, T., Krankina, O., Kurz, W.A., Matsumoto, M., Oyhantcabal, W., Ravindranath, N.H., Sanz Sanchez, M.J., Zhang, X. (2000) Forestry In Climate Change Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press.

Perry, J.L., LeVan, M.D. "Air purification in closed environments: Overview of spacecraft systems" available at: http://www.natick.army.mil/soldier/JOCOTAS/ColPro_Papers/Perry-LeVan.pdf

Pielke Jr., R.A. (2009) "An idealized assessment of the economics of air capture of carbon dioxide in mitigation policy" Environ. Sci. & Pol. **12**, 216-225

Robinson, A.L., Rhodes, J.S., Keith, D.W. (2003) "Assessment of Potential Carbon Dioxide Reductions Due to Biomass – Coal Cofiring in the United States" Environ. Sci. and Technol. **37(22)**, 5081-5089

Sherwood, T. K. (1959) "Mass Transfer Between Phases", Phi Lambda Upsilon, Thirty-third annual Priestly Lectures

Stern, N., (2007) "The Economics of Climate Change: The Stern Review" Cambridge University Press.

Tierney, John (2009) "Politics in the Guise of Pure Science." The New York Times, February 23, 2009.

US Energy Information Administration (2009) "International Energy Outlook 2009", available at http://www.eia.doe.gov/oiaf/ieo/index.html

Warkandar, D.E., Lillo, R.S. (1998) "Review of Two Methods to Remove CO2 Using Seawater From Submarines During Emergency Conditions", Navy Experimental Diving Unit, Panama City, Fl available at: http://www.stormingmedia.us/35/3529/A352983.html

Zeman, F., (2007) "Energy and Material Balance of CO_2 capture from ambient air" Environ. Sci. Technol. **41**, 7558 - 7563

Zimble, J.A (1963) Trans. Ass. Industr. Med. Offs. **13**, 79 (1963)

Appendix A. Equations and Calculations for Cost and Area Estimate

Equations used

Land Calculation

$$Land\ Requirement(ha) = \frac{Biomass\ Energy\ Required\left(\frac{MJ}{year}\right)}{Heating\ Value\ of\ Biomass\left(\frac{MJ}{Kg}\right) \times Growth\ Rate\ of Biomass(\frac{Kg}{ha.\,yr})} \tag{8}$$

The land area was calculated by the following equation:

Heating Value of Biomass and Growth Rate of Biomass are both exogenously supplied. Biomass Energy Required is the only variable that needs to be calculated.

$$Biomass\ Energy\ Required\left(\frac{BTU}{year}\right) = Heat\ Rate\left(\frac{BTU}{kWh}\right) \times Plant\ Size(MW) \times Hours\ of\ Ops(\frac{hrs}{year}) \times 1000(\frac{kW}{MW}) \tag{9}$$

Using this, the land area calculation can be shown as:

Table A-1: Land Area Calculation for the biomass plant

Value	Quantity	Unit	Assumptions
Heat rate of the capture plant	15518.18	BTU/kWh	
Biomass Energy Required	5.77742E+13	BTU/year	
Biomass Energy Required	6.09518E+16	J/year	
Biomass Required	3158122871	Kg/year	
Biomass Required	3158122.87	tons/year	
Land Area Required	263176.91	Ha	
Land Area Required	1016.13	sq. miles	
Carbon Content of Biomass	1515898.98	tons/year	
CO_2 produced	5558296.25	tons/year	
Land Area Required to capture 1GT of CO_2	182812.5	Square Miles	100% capture
Land Area Required to capture 1GT of CO_2	203125	Square Miles	90% capture

The results for the sensitivity analysis mentioned in the chapter above are:

Table A-2: Land area required for different yields of biomass

	Yield(t/ha/yr)		
	2.3	12	24.5
Land Required for 1 GT CO2 avoided at 90%(sq. miles)	1,059,783	203,125	99,490

Avoided Cost

The model is built on the logic built in Hamilton et al. (2008). For the avoided cost calculation in that paper, the required inputs are CO_2 captured in the process and the different costs: plant, fuel and O&M. O&M cost was taken from that work itself but the plant and fuel costs were calculated using the following equations:

$$\text{Plant's Capital cost(\$/MWh)} = \frac{Total\ Plant\ Cost\left(\frac{\$}{kW}\right) \times Annual\ Carrying\ Charge\left(\frac{1}{year}\right)}{Capacity\ Factor\left(\frac{hrs}{year}\right) \times 1/1000\left(\frac{MW}{kW}\right)} \tag{10}$$

$$\text{Fuel Cost(\$/MWh)} = \frac{Fuel\ Cost\left(\frac{\$}{GJ}\right) \times 1055\left(\frac{J}{BTU}\right) \times Heat\ Rate\left(\frac{BTU}{kWh}\right)}{10\hat{}9\left(\frac{GJ}{J}\right) \times 1/1000\left(\frac{MWh}{kWh}\right)} \tag{11}$$

Using these equations, the avoided cost for different cost of carbon free electricity was calculated as:

Table A-3: Calculation of the Levelized Cost of Electricity (LCOE)

Overhead		Units	Value
Total Plant Cost		$/kWe	9407
CO_2 captured@90% capture		Kg/kWh	1.34
Heat Rate		Btu/kWh	15518.2
Thermal efficiency			22.00%
	Capital	$/MWh	190.77
	Fuel	$/MWh	130.97
	O&M	$/MWh	17.00
	Total	$/MWh	338.74

Table A-4: Sensitivity analysis numbers for the cost of carbon free electricity

Cost of Carbon neutral electricity (¢/kWh)	0%	10%	20%	30%	40%	50%	60%	70%	80%	85%
8	192.56	216.63	247.58	288.85	346.61	433.27	577.69	866.54	1733.07	3466.15
10	177.68	199.89	228.44	266.52	319.82	399.78	533.04	799.56	1599.11	3198.22
12	162.79	183.14	209.31	244.19	293.03	366.29	488.38	732.57	1465.15	2930.30

The following tables provide the sensitivity analysis numbers used in the chapter. The table for different Total Plant Cost is shown below. The top row is for the number used in Bergholz (2009) and the lower one for Larson et al. (2009).

Table A-5: Sensitivity analysis numbers for Total Plant Cost (TPC)

Avoided Cost($/tCO2)	0%	10%	20%	30%	40%	50%	60%	70%	80%	85%
	177.68	199.89	228.44	266.52	319.82	399.78	533.04	799.56	1599.11	3198.22
	73.92	83.16	95.04	110.88	133.05	166.31	221.75	332.63	665.26	1330.52

The table for O&M costs is:

Table A-6: Sensitivity analysis numbers for O&M costs

O&M Costs ($/MWh)	0%	10%	20%	30%	40%	50%	60%	70%	80%	85%
10	172.47	194.03	221.75	258.70	310.45	388.06	517.41	776.11	1552.23	3104.45
17	177.68	199.89	228.44	266.52	319.82	399.78	533.04	799.56	1599.11	3198.22
30	187.35	210.77	240.88	281.03	337.24	421.55	562.06	843.09	1686.19	3372.37
40	194.80	219.15	250.45	292.19	350.63	438.29	584.39	876.58	1753.17	3506.34
50	202.24	227.52	260.02	303.36	364.03	455.04	606.72	910.07	1820.15	3640.30

The avoided cost sensitivity was tested for several values of carbon free electricity. The tables below are for that cost at 8 ¢/kWh:

Table A-7: Sensitivity analysis numbers for different plant costs at 8¢/kWh cost of electricity

Value	Biomass:$3/GJ									
	0%	10%	20%	30%	40%	50%	60%	70%	80%	85%
Avoided Cost ($/tCO2)	$131.64	$148.10	$169.25	$197.46	$236.96	$296.19	$394.93	$592.39	$1,184.78	$2,369.56
	Biomass:$8/GJ									
	0%	10%	20%	30%	40%	50%	60%	70%	80%	85%
	$192.56	$216.63	$247.58	$288.85	$346.61	$433.27	$577.69	$866.54	$1,733.07	$3,466.15

Similarly, for the cost of carbon free electricity at 12 ¢/kWh:

Table A-8: Sensitivity analysis numbers for different plant costs at 12¢/kWh cost of electricity

Value	Biomass:$3/GJ									
	0%	10%	20%	30%	40%	50%	60%	70%	80%	85%
Avoided Cost ($/tCO2)	$101.87	$114.61	$130.98	$152.81	$183.37	$229.21	$305.62	$458.43	$916.85	$1,833.71
	Biomass:$8/GJ									
	0%	10%	20%	30%	40%	50%	60%	70%	80%	85%
	$162.79	$183.14	$209.31	$244.19	$293.03	$366.29	$488.38	$732.57	$1,465.15	$2,930.30

Appendix B. Thermodynamic minimum work of separation

The papers in literature on direct air capture report costs that lie in a wide range, from \$100/tC (Lackner et al., 1999; Keith et al., 2006) to \$500/tC (Keith et al., 2006). The actual cost of the system will depend a lot on the solvent used, the absorber design and the other design parameters. These parameters can vary from paper to paper, depending on the individual choice of the authors. However, there is one key parameter that will never be a function of any reaction set up; the thermodynamic minimum work of separation. Any analysis in literature cannot go below this and calculating it would help in providing a lower bound for the cost of any process.

The theoretical minimum work required to achieve a change in thermodynamic states is the net change in work potential (i.e., thermodynamic availability or exergy) of the system. The change in work potential is minimized when a flowing system undergoes a reversible isothermal, isobaric change. Therefore, the absolute minimum work required for a given separation processes is equal to the difference between the work potential of the product and feed streams, which is equal to the difference is stream exergy:

$$W_m = \bullet \mu_i \tag{12}$$

Where, μ_i is the exergy of stream i. For the isothermal, isobaric processes that we are considering, the change in work potential equals the change in the Gibbs Free Energy.

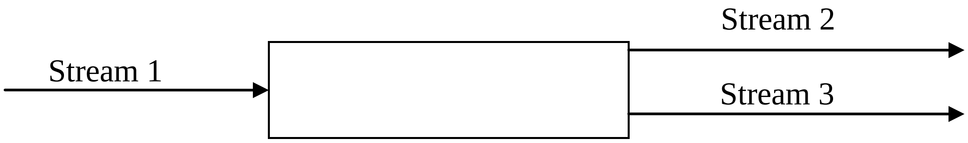

Figure B-1: Schematic of the minimum work calculation setup

In the simple case of a separation of one feed stream (stream 1) consisting of *n* substances into two product streams (streams 2 and 3) as shown above, where all streams consist of ideal mixtures, this reduces to:

$$W_m = -RT\ (N_2 \ \sum_{K=1}^{n} X_{2,K}\, lnX_{2,K} + N_3 \ \sum_{K=1}^{n} X_{3,K}\, lnX_{3,K} - N_1 \ \sum_{K=1}^{n} X_{1,K}\, lnX_{1,K}) \qquad (13)$$

Where N_j denotes the molar flow rate of stream j. Note that for non-ideal mixtures (i.e., gases and solutions), we must account for the excess properties that depend on interactions between molecules.

The calculation is done for an air capture system that captures 25% of input concentration of CO_2 and is compared with a conventional Carbon Capture and Sequestration (CCS) system, which captures 90% of its input CO_2. The capture percentages are taken as such to make a direct comparison with the numbers used in Keith et al. (2006). The input CO_2 concentration for air is taken as 400 parts per million (ppm) and the corresponding number for CCS is 10% by volume.

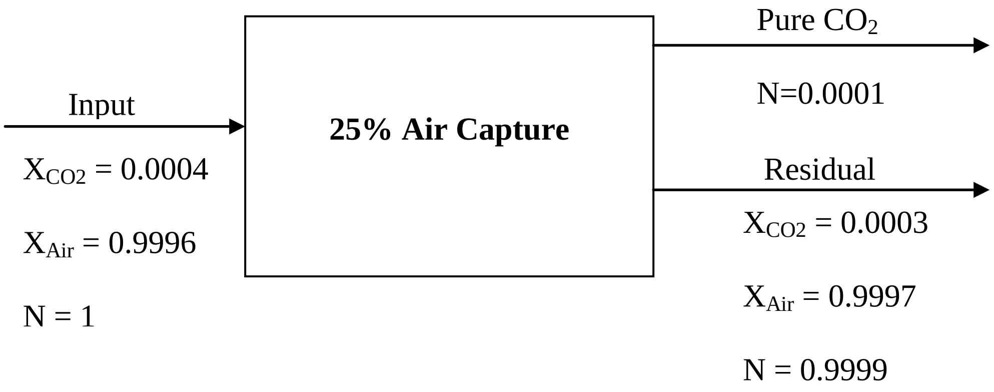

Figure B-1: Schematic of the air capture system with 25% capture

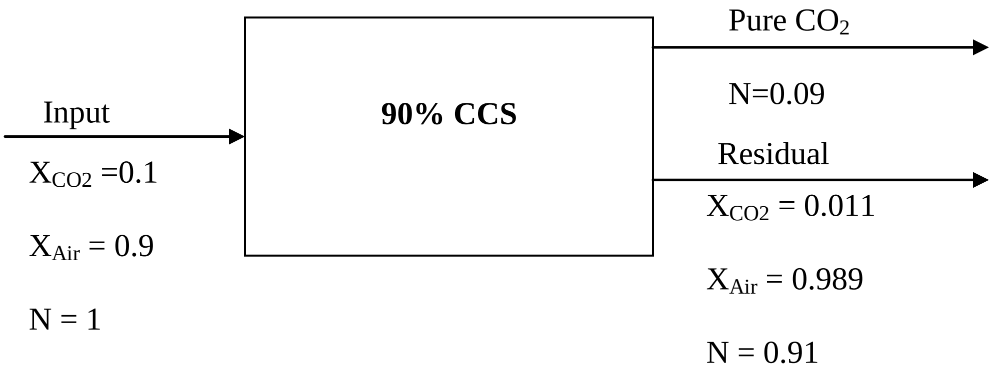

Figure B-2: Schematic of the CCS system with 90% capture

Using equation (13) for 25% capture from air, W_{min} is 19.7 kJ/mol of CO_2. The corresponding minimum work for CCS with 90% capture is 7.43 kJ/mol of CO_2.

Hence the ratio of minimum energy required for both air capture and CCS is **2.65.** This is the case for an air capture of 25% and a CCS capture of 90%. However, the air capture is not done at a fixed percentage, which is supposed to be an inherent flexibility in this process. In order to know the ratio of minimum energy required at different air capture percentage, this calculation needs to be repeated for the different capture percentages.

The following table shows the different air capture percentages and the corresponding minimum work ratios for a 90% capture in CCS:

Table B-1: Ratio of minimum work of air capture at various capture percentages to 90% capture in CCS

Air Capture percentage (%)	Ratio of Minimum Work
25	2.65
50	2.71
90	2.86