

**Geological Sequestration Training and Research Program in  
Capture and Transport: Development of the Most Economical  
Separation Method for CO<sub>2</sub> Capture**

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# Abstract

The project provided hands-on training and networking opportunities to undergraduate students in the area of carbon dioxide (CO<sub>2</sub>) capture and transport, through fundamental research study focused on advanced separation methods that can be applied to the capture of CO<sub>2</sub> resulting from the combustion of fossil-fuels for power generation. The project team’s approach to achieve its objectives was to leverage existing Carbon Capture and Storage (CCS) course materials and teaching methods to create and implement an annual CCS short course for the Tuskegee University community; conduct a survey of CO<sub>2</sub> separation and capture methods; utilize data to verify and develop computer models for CO<sub>2</sub> capture and build CCS networks and hands-on training experiences. The objectives accomplished as a result of this project were: (1) A comprehensive survey of CO<sub>2</sub> capture methods was conducted and mathematical models were developed to compare the potential economics of the different methods based on the total cost per year per unit of CO<sub>2</sub> avoidance; and (2) Training was provided to introduce the latest CO<sub>2</sub> capture technologies and deployment issues to the university community.

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# Executive Summary

The concern over global warming has resulted in serious efforts to capture the CO<sub>2</sub> in flue gas from fossil-fueled power plants. The traditional technology used to remove CO<sub>2</sub> is the absorption process that uses monoethanolamine (MEA) as solvent. The main disadvantage of this technology is that it is an energy intensive process, with about 15 – 30% of the power generated in a power plant being used to capture CO<sub>2</sub> from flue gas. Due to this high cost of CO<sub>2</sub> capture in the amine-based process, there has been a tremendous increase in the number of investigations in the area of CO<sub>2</sub> capture during the last fifteen years.

Researchers are trying to modify the existing technology or to develop new technologies that could reduce the cost of CO<sub>2</sub> capture. As a part of this project, the economics of these new processes were evaluated and compared with a goal to identify the significant variables for the most promising processes. An effective and affordable carbon capture process is an essential part of a successful carbon capture and storage (CCS) industry. The other important part of such an industry is workforce. Future scientists and engineers are needed to design new processes and work in these processes. This project focused on both carbon capture affordability and workforce availability issues.

The objectives of this project were: (1) to evaluate the existing and proposed methods of capturing CO<sub>2</sub> from flue gas through the development of economic models, and (2) to train students and staff in carbon capture and storage technologies. The technologies studied in this project were absorption (i.e., solvent-based) processes membrane separation, and adsorption (i.e., sorbent-based) processes.

In the first year of the project, proposed absorption solvents for CO<sub>2</sub> capture were identified and the parameters needed for evaluation of each solvent in a typical adsorption process were collected. Mathematical models for estimating the size of equipment in terms of the process variables were developed and were compared to a base case model of a simple MEA absorption process. The equipment needed for a solvent-based process included absorption column, stripper column, interchanger, cooler, pump, condenser and reboiler. For each piece of equipment a correlation was developed. These correlations were used to estimate the cost of CO<sub>2</sub> captured (in \$/tonne) as a function of process variables: liquid-to-gas ratio in absorber, liquid-to-gas ratio in stripper, CO<sub>2</sub> recovery in absorber, concentration of CO<sub>2</sub> in the flue gas, heat exchanger cooling water temperature, materials of construction, make-up solvent requirements and solvent price

In the second year of this project, membrane separation technologies used for CO<sub>2</sub> capture were evaluated. Proposed and emerging membrane separation processes for CO<sub>2</sub> capture were identified and the parameters needed for evaluation of membrane processes were collected. Mathematical models for estimating the size of equipment in terms of the process variables were developed. The equipment needed for the model included membrane modules, heat exchangers and compressors. These correlations were used to estimate the total cost of CO<sub>2</sub> capture as a function of CO<sub>2</sub> permeability, N<sub>2</sub> permeability, CO<sub>2</sub>:N<sub>2</sub> separation factor,

transmembrane pressure, permeance, cooling water price, membrane price and membrane staging.

During the third and fourth year of the project, sorbent/adsorption technologies used for CO<sub>2</sub> capture were evaluated. Economic analyses of adsorption units were investigated.

Mathematical models for estimating equipment costs, total initial investment, and operating costs were prepared. An Excel spread sheet was developed and was used to estimate cost of CO<sub>2</sub> avoided as a function of different process variables for a typical adsorption system: gas velocity, CO<sub>2</sub> capture efficiency, operating pressures, feed gas CO<sub>2</sub> concentration, adsorbent price, utility prices, labor costs, equipment efficiency, interest rates, inflation, and operating costs.

The accomplishments in the training component of the project included three annual short courses where fifty students and several faculty members were in attendance. The “First Annual Tuskegee Forum on Carbon Capture and Storage (CCS) Technologies“ was held on March 8, 2010, at the Kellogg’s Conference Center on the Campus of Tuskegee University. The “Second Annual Tuskegee Forum on Carbon Capture and Storage (CCS) Technologies“ was held on April 26, 2011, at the Kellogg’s Conference Center on the Campus of Tuskegee University. The third CCS Short Course was conducted on March 11, 2013, at the Kellogg’s Center on the campus of Tuskegee University. The effort to develop spreadsheet models for the absorption, membrane, and adsorption gas separation technologies coupled with seminars and outreach opportunities served as an effective training method.

# Objective

The objectives of this project were: (1) to evaluate the existing and proposed methods of capturing CO<sub>2</sub> from flue gas through the development of economic models, and (2) to train students and staff in carbon capture and storage technologies. The technologies studied in this project were absorption (i.e., solvent-based) processes membrane separation, and adsorption (i.e., sorbent-based) processes.

# Background

The world total CO<sub>2</sub> emissions for 2006 collected by the Carbon Dioxide Information Analysis Center (CDIAC) of the Department of Energy were  $28.4 \times 10^9$  metric tons. Of this, China and U.S. accounted for  $6.10 \times 10^9$  and  $5.75 \times 10^9$  metric tons, respectively. The rapid economic growth in China and India has resulted in a much faster rate of increase in the CO<sub>2</sub> emission. The concern over the problem of global warming has resulted in major efforts to reduce this trend. Carbon Dioxide Capture and Storage (CCS) is gaining widespread interest as a possible method for reducing Carbon Dioxide concentration in the atmosphere. Whereas the CO<sub>2</sub> resulting from the combustion of fossil fuels for power generation processes represent a significant contribution to world CO<sub>2</sub> emissions, methods to capture post-combustion CO<sub>2</sub> from flue gas is the focus of this study.

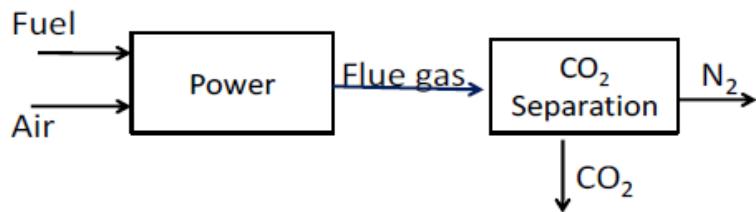
A wide range of technologies for separation and capture of CO<sub>2</sub> from gas streams currently exist, with an enormous amount of research having been conducted during the last fifteen years. They are based on different physical and chemical processes such as absorption, adsorption, membranes, and cryogenics. Most of these technologies are in the research stage. The existing commercially available technologies use a solvent (usually an amine) and absorption unit to remove CO<sub>2</sub> from the flue gas in a power plant. This process requires a large amount of energy to regenerate the solvent (in a stripping column). Other issues that increase the cost of CCS include degradation of solvents and equipment corrosion. In order to address these shortcomings, researchers have been working on different ways to modify this process and also to come up with new methods of CO<sub>2</sub> capture. The result of these investigations is that there is a tremendous amount of information on methods of CO<sub>2</sub> capture in literature. There have been studies that compared a few of these methods. These studies however, are very time consuming and requires extensive calculations and computer programming. This study sought to develop a simple assessment tool and to use this tool to assess the different CO<sub>2</sub> capture methods which are reported in the literature.

# Introduction

A comprehensive survey on post-combustion CO<sub>2</sub> capture technologies was conducted. The processes proposed for removing CO<sub>2</sub> fall into two categories: (1) modified versions of MEA absorption system; and (2) separation technologies that are used in other sectors of chemical industry. The most advanced of these CO<sub>2</sub> capture methods are described here.

For post-combustion capture methods, carbon dioxide is removed from flue gas after the fuel has been burnt with air (Figure 1). The total pressure of the flue gas is nominally one atmosphere pressure and the CO<sub>2</sub> concentration is typically 10-15%. The process of transforming this low pressure, low concentration CO<sub>2</sub> into a relatively pure CO<sub>2</sub> stream is referred to as post-combustion CO<sub>2</sub> capture. This capture step is typically followed by a compression step, where, for ease of transport (usually by pipeline) and storage, the CO<sub>2</sub> is compressed to 100 atmospheres or more.

**Figure1. Post-combustion CO<sub>2</sub> capture process**



## Characteristics of Flue Gas

Flue gas from fossil-fired power plants has characteristics as shown in Table 1. These characteristics are primary variables to be considered for process development. The primary variables are low pressure, presence of oxygen, presence of pollutants (NO<sub>x</sub>, SO<sub>x</sub>, and particulate matter), high temperature and huge gas flow rates.

**Table 1. Characteristics of fossil-fuel-combustion flue gas for power generation**

Pressure	Atmospheric pressure
CO <sub>2</sub> concentration	10-15 (% Dry Volume Basis)
O <sub>2</sub> concentration	3.3-5.5 (% Dry Volume Basis)
Pollutants	Particulates, SO <sub>2</sub> (coal, oil), NO <sub>x</sub>
Flow rate	Very high (Nm <sup>3</sup> /hr) 3,400,000 coal combustion 1000MW 3,000,000 oil combustion 1000MW 2,500,000 LNG combustion 1000MW

## Properties of Carbon Dioxide

Most removal methods take advantage of one or more of the following properties of carbon dioxide:

1. CO<sub>2</sub> is a weak acid and can be easily absorbed by alkaline solvents
2. CO<sub>2</sub> can be adsorbed onto microporous structures of solid adsorbents
3. CO<sub>2</sub> can be separated by membranes
4. CO<sub>2</sub> can be taken by many simple plants and be fixed to form of biomass
5. CO<sub>2</sub> can be separated by reducing temperature and/or increasing pressure (i.e., freezing)

A tremendous amount of progress has been made in the development of carbon capture technologies. Most of these technologies have already been employed in other industries. These technologies can be employed in the existing power generation plants to capture CO<sub>2</sub>. The main problem with these technologies is their cost.

## Technologies for CO<sub>2</sub> Capture

The first CO<sub>2</sub> capture system that was developed is an amine-based absorption system. This process, that is over sixty years old, uses monoethanolamine (MEA) and was originally developed to remove acidic gas impurities (such as H<sub>2</sub>S and CO<sub>2</sub>) from natural gas. In the 1970's several plants were constructed to produce CO<sub>2</sub> for industrial use. It was not until late 1990's that the technology was adopted for CO<sub>2</sub> sequestration. The main problem with this technology is that it is too expensive. It is an energy intensive process. About 15-30% of the power generated in a power plant should be used to capture CO<sub>2</sub> from flue gas.

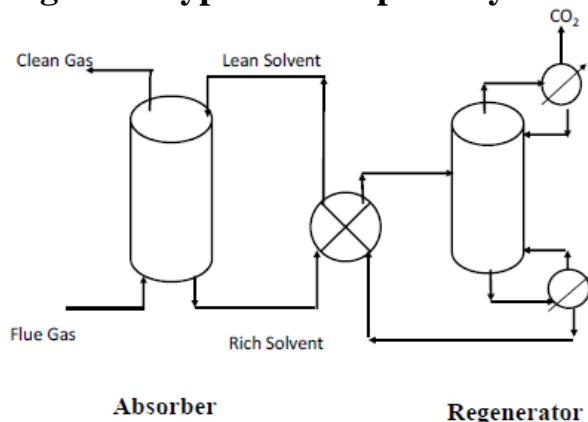
Due to this high cost of CO<sub>2</sub> capture in amine-based process, there has been a tremendous increase in the number of investigations in the area of CO<sub>2</sub> capture during the last fifteen years. Researchers are trying to modify the existing technology or develop new technologies that could reduce the cost of CO<sub>2</sub> capture. Technologies that have been proposed for CO<sub>2</sub> capture can be divided into the following categories: Absorption, Adsorption, Membrane Separation, Cryogenics, Chemical Looping, Ionic Liquids and Microbial/Algae. The first three (i.e., Absorption, Membrane, and Adsorption) separations processes have received the most attention and therefore are the focus of this study. A generalized overview description of these three primary methods is provided here:

### **Absorption Methods:**

Chemical absorption, e.g. with amine-type absorbents is well suited for CO<sub>2</sub> recovery from flue gas. A schematic diagram of a typical (solvent-based) absorption process is shown in Figure 2. The chemical reaction between CO<sub>2</sub> and amines greatly enhances the driving force for the separation, even at low partial pressures of CO<sub>2</sub>. Prior to CO<sub>2</sub> recovery, the flue gas typically needs to be cooled and treated for reduction of particulates and other impurities such as SO<sub>x</sub> and NO<sub>x</sub> to tolerable levels. A feed blower provides the necessary pressure for the pretreated flue gas to overcome the pressure drop in the absorber. Flue gas is passed into the absorption column, which typically operates within the temperature range of 40 to 45°C at the

top, and 50 to 60 °C at the bottom. The flue gas and lean amine solution contact each other counter currently in the absorber. The amine selectively absorbs CO<sub>2</sub> from the flue gas by chemically reacting with it. The chemical reaction between CO<sub>2</sub> and a solvent greatly enhances the driving force for the separation. In the second part of the process, heat is used in a regenerator to separate CO<sub>2</sub> from the solvent.

**Figure 2. Typical Absorption System**



The following solvents were identified from the literature as being the most prominent solvents for CO<sub>2</sub> capture:

- 5 M Monoethanolamine (MEA)
- 3.6 M Potassium Carbonate
- 4 M n-Methyldiethanolamine (MDEA) – 0.6 M Piperazine (PZ)
- 3.6 M Potassium Carbonate – 0.6 M Piperazine (PZ)
- 6.8 M Ammonia (12 wt%)

The traditional solvent used in this process is monoethanolamine (MEA). The process was originally used to produce CO<sub>2</sub> for the enhanced oil recovery (EOR) in the oil industry. The first plant to capture CO<sub>2</sub> was built in 1996. Since then, there has been a tremendous increase in the number of investigation in the area of CO<sub>2</sub> capture. The reason for such a great interest in developing new technologies for CO<sub>2</sub> capture is that the MEA absorption process has several shortcomings:

1. The regeneration of MEA is an energy intensive process where 15-30% of the power generated in a power plant should be used to regenerate MEA.
2. MEA is a corrosive compound. The rate of corrosion in the equipment used in the MEA absorption process is high.
3. During the absorption and desorption process, some degradation of MEA occurs. This requires removal of the degraded solvent, and addition of make-up MEA.
4. The capital cost of the MEA absorption process is high.

Scientists and engineers have been trying to modify the MEA absorption process so that the cost of CO<sub>2</sub> capture is reduced. These activities have resulted in the following proposed modifications, each which has claimed to have solved one or more of the disadvantages of the

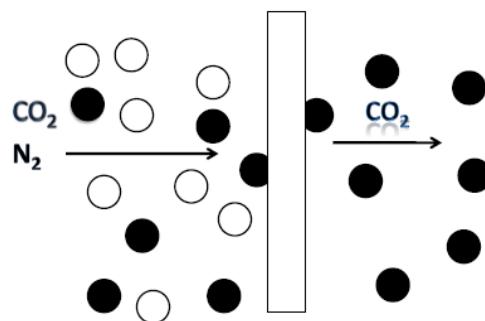
MEA absorption process:

- a. Addition of new heat recovery equipment to reduce energy cost,
- b. Change in the concentration of MEA or using inhibitors to reduce corrosion rate,
- c. Replacement of MEA with a different solvent,
- d. Replacement of MEA with a mixture of two or more solvents,
- e. Use of corrosion resistance materials of construction for equipment,
- f. Change in the operating conditions (temperature and pressure) of the process

### **Membrane Separation Methods:**

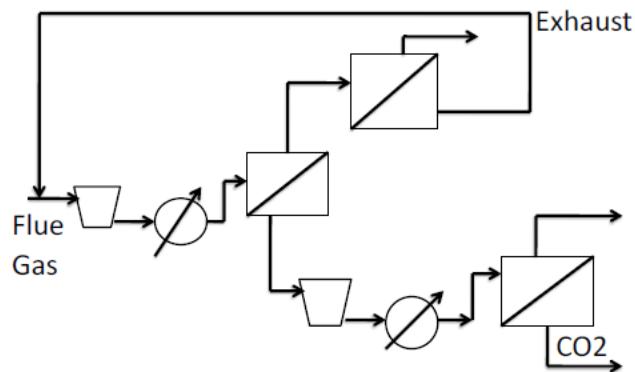
Membrane separation processes are based on the rate at which molecules of a substance (such as  $\text{CO}_2$ ) transfer through a semi-permeable membrane (Figure 3). A membrane is therefore a physical barrier between two fluids that allows one of the components of a mixture to pass. Permeation of chemicals through membranes has been studied extensively during the last thirty years. This growing interest is mainly due to its application in the separation of mixtures.

**Figure 3. Membrane Separation**



In an industrial setting, more than one stage of separation is usually needed. A typical process for a multi-stage membrane separation is given in Figure 4.

**Figure 4. Representative Membrane System Configuration**



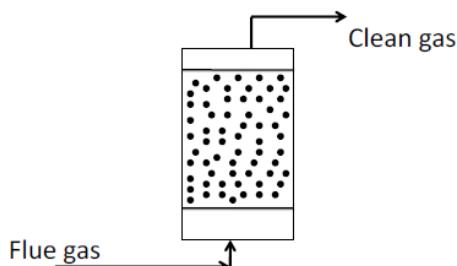
Membrane separation of gases has emerged into an important unit operations technique offering specific advantages over more conventional separation procedures (e.g. cryogenic distillation and adsorption). The potential application of a polymer as a separation membrane

depends upon the possible throughput and the purity of product. This means that both the permeability coefficient for the gas that is transported more rapidly and the selectivity should be as large as possible. However, it was found that simple structural modifications, which lead to increases in polymer permeability usually, cause losses in permselectivity and vice versa. This so-called trade-off relationship is well described in the literature. It is thus possible to find polymers that exhibit high selectivity and low permeability and vice versa, in addition to those that combine low selectivity with low permeability. New membrane materials and technologies have been proposed for simultaneous separation and capture carbon dioxide from flue gas.

### **Adsorption Methods:**

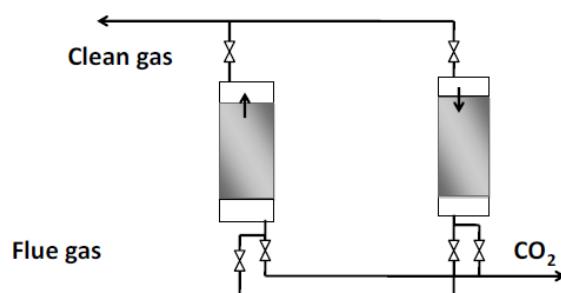
Adsorption is a process in which one or more components of a fluid are transferred to the surface of a solid. This is a separation process that is commonly used to clean fluids by removing pollutants from the fluid. The most common device for adsorption is a packed bed. The particles (adsorbent) are randomly packed in a column. The fluid passes through the bed where one or more of its components are adsorbed on the surface of particles and the rest of the fluids leave the bed (Figure 5).

**Figure 5. Adsorption process**



After the bed has been saturated with  $\text{CO}_2$ , the separation ceases and the bed is regenerated. In the regeneration step,  $\text{CO}_2$  is removed from the bed. In general there are two methods of regeneration of adsorbents: temperature swing and pressure swing. In temperature swing adsorption, regeneration is achieved by sending a high temperature purge gas through the saturated bed. In pressure swing adsorption, regeneration is achieved by reduction in pressure as shown in Figure 6.

**Figure 6. Pressure Swing Adsorption Process**



Selection of a proper adsorbent is critical for the success of this separation process. Ideally, the adsorbent should have the following characteristics: (1) high selectivity for CO<sub>2</sub>, (2) high adsorption capacity for CO<sub>2</sub>, and (3) low cost. Several adsorbents such as dolomite and hydrotalcite have been proposed for trapping CO<sub>2</sub>. These adsorbents, however, have low adsorption capacities for carbon dioxide (less than 9.8 mmol/g). The process can be improved considerably if adsorbent with much higher capacity for CO<sub>2</sub> is used. Recently, it has been reported that a few of lithium salts exhibit very high capacities for adsorbing CO<sub>2</sub>. Specifically, lithium zirconate has been shown to have CO<sub>2</sub> adsorption capacity much higher than the other adsorbents. The only problem with this material is that the rate of CO<sub>2</sub> adsorption is very low. One of the other lithium salts, namely lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>), have even higher CO<sub>2</sub> adsorption capacity. The preliminary experimental results indicate that the rate of CO<sub>2</sub> adsorption of this compound may be more than three times faster than Li<sub>2</sub>ZrO<sub>3</sub>.

# Evaluation of CO<sub>2</sub> Capture Methods

## Criterion for comparison between different CO<sub>2</sub> Capture Methods

A specific objective of this project is to conduct an evaluation of different CO<sub>2</sub> capture methods based on a set of specific criteria. The goal is to have a method for comparing all these processes so that the most promising, in terms of economics, can be identified. There are many CO<sub>2</sub> capture technologies and each technology has many different possible process set ups. It is important to understand that for a given technology if the process set up is changed to reduce for example energy cost, then other factors in the process will change too. Whereas the objective of this study was to develop a *simple assessment tool* and to use this tool to assess the different CO<sub>2</sub> capture methods, the evaluation criteria was established not to lower energy cost, but to minimize the process cost per unit of CO<sub>2</sub> captured.

The cost of a process consists of two elements;

$$\text{Total Cost} = \text{Initial Costs} + \text{Operating Costs}$$

The initial cost of adding CO<sub>2</sub> capture unit to the existing power plant process is the sum of the following costs:

$$\text{Initial Costs} = \text{Equipment} + \text{Installation} + \text{Instrumentation} + \text{Piping}$$

The costs of installation, instrumentation and piping are usually given as a percentage of equipment cost. For a fluid processing plant, these percentages are 47%, 36%, 68%, respectively (Peters, 2003). Therefore, the fixed cost of CO<sub>2</sub> capture unit is given by the following equation:

$$\text{Fixed Cost} = (2.51) \times (\text{Equipment Cost})$$

The operating cost of a process is given by the following equation:

$$\text{Operating Cost} = \text{Energy cost} + \text{Raw material cost} + \text{Maintenance cost} + \text{Labor cost}$$

The energy cost is given by:

$$\text{Energy Cost} = \text{Steam cost} + \text{Electricity cost}$$

The maintenance cost depends on the material of construction for equipment. For example if stainless steel equipment is used, the maintenance cost will be lower than if carbon steel equipment are selected. Labor cost depends on the type and number of equipment in the process. Raw material cost depends on the cost and the flow rate of fresh solvent, adsorbent or other materials needed for the process.

Fixed cost is a one-time cost and operating cost is an annual cost. In order to combine them together one uses depreciation factors. The annual cost of a process is therefore given by:

$$\text{Annual cost} = (\text{Fixed cost}) (\text{depreciation factor}) + \text{operating costs}$$

The fixed cost and operating costs depends on the flow rate of flue gas entering the CO<sub>2</sub> capture process. For comparison purposes, it is advantages to use annual cost of process per unit of CO<sub>2</sub> captured. Therefore the objective function that is used in this project is:

$$\text{Objective Function} = \text{Annual cost per unit of CO}_2 \text{ captured}$$

## Development of Mathematical Models

### **Cost Model:**

Cost models were developed for the leading separation processes (i.e. adsorption, membrane separation, absorption). The different variations of the systems that have been proposed in the literature were identified, and for each process, cost models were developed.

The fixed/initial costs consist of:

- Process-specific equipment (e.g., columns, membrane modules, etc.)
- Heat exchangers
- Pumps
- Compressors
- Reboiler
- Condenser
- Cooler
- Specialized equipment
- Installation costs
- Instrumentation costs
- Piping costs

The operating costs consist of:

- Cost of steam
- Cost of electricity
- Cost of water
- Labor cost
- Maintenance cost
- Cost of raw materials (e.g., makeup solvent, sorbent, etc.)

The two set of models (fixed costs and operating costs) were combined to develop an overall cost model that could be used to estimate the cost per year per tonne of CO<sub>2</sub> captured and/or avoided for a specific variation of the process.

### **Absorption Model:**

**Absorption Column:** The rate of mass transfer from gas phase to the inter-phase between gas phase and liquid phase is given by:

$$N_A = K_G a (P_A - P_{Ai}) \quad (1.1)$$

Where  $N_A$  is rate of mass transfer per unit volume, mol/(s. m<sup>3</sup>)

$P_A$  is partial pressure of component A in gas phase, atm

$P_{Ai}$  is partial pressure of component A at inter-phase, atm

$K_G$  is mass transfer coefficient in gas phase, mol/(s. m<sup>2</sup>. atm)

$a$  is interfacial area of packing per unit volume, m<sup>2</sup>/m<sup>3</sup>

The rate of mass transfer in the liquid phase is given by the following equation:

$$N_A = K_L a (X_{Ai} - X_A) \quad (1.2)$$

Where  $X_{Ai}$  is concentration of component A in liquid phase at inter-phase, mol/m<sup>3</sup>

$X_A$  is concentration of component A in the bulk of liquid phase, mol/m<sup>3</sup>

$K_L$  is the mass transfer coefficient in liquid phase, m/s

The rate of mass transfer of component A can also be written in terms of an overall mass transfer coefficient:

$$N_A = K_{GO} a (P_A - P_A^*) \quad (1.3)$$

Where  $K_{GO}$  is overall mass transfer coefficient, mol/(s. m<sup>2</sup>. atm)

$P_A$  is partial pressure of component A in vapor in equilibrium with liquid phase, atm

But from equilibrium condition:

$$P_A = H X_A \quad (1.4)$$

Where  $H$  is Henry's Law Constant, atm.m<sup>3</sup>/mol.

At the inter-phase, the two phases are at equilibrium:

$$P_{Ai} = H X_{Ai} \quad (1.5)$$

From equation (1) and (2) one can get:

$$P_A - P_{Ai} = \frac{N_A}{a K_G} \quad (1.6)$$

$$X_{Ai} - X_A = \frac{N_A}{a K_L} \quad (1.7)$$

Substitution of equations (4) and (5) into (7) yields:

$$\frac{P_{Ai}}{H} - \frac{P_A^*}{H} = \frac{N_A}{a K_L} \quad (1.8)$$

or

$$P_{Ai} - P_A^* = \frac{H N_A}{a K_L} \quad (1.9)$$

Combining equations (6) and (9) one can get:

$$P_A - P_A^* = N_A \left( \frac{1}{a K_G} + \frac{H}{a K_L} \right) \quad (1.10)$$

Substitution of equations (3) into (10) yields:

$$\frac{1}{a K_{GO}} = \frac{1}{a K_G} + \frac{H}{a K_L} \quad (1.11)$$

The mass transfer in the liquid phase can be written as the sum of a kinetics coefficient (due to chemical reaction) and a diffusion coefficient (due to the diffusion of reactants and products).

$$\frac{1}{K_L} = \frac{1}{K_K} + \frac{1}{K_D} \quad (1.12)$$

The coefficient due to kinetics is given by

$$K_K = (K C D_A)^{0.5} \quad (1.13)$$

Where: K is the rate constant

C is concentration of solvent in liquid phase

D<sub>A</sub> is diffusion coefficient of CO<sub>2</sub> in gas phase and pressure

Oyeneka (2007) has done a study of the effect of temperature and pressure on the different components of the overall mass transfer coefficient: He has shown that at low temperatures (in the absorber), the resistance in the gas phase and the diffusion in liquid phase are negligible and equation (11) is simplified to:

$$K_{GO} = \frac{(K C D_A)^{0.5}}{H} \quad (1.14)$$

At higher pressure and temperatures (stripper) the kinetic term is not significant and most of the resistance to the mass transfer is due to diffusion of components in liquid phase.

The height of the packing in the absorber can be found by writing material balance equation:

Let N<sub>G</sub>: molar flow rate of gas

$$-N_G dy_A = K_{GO} a (P_A - P_A^*) Adz \quad (1.15)$$

$$= K_{GO} P_T a (y_A - y_A) Adz \quad (1.16)$$

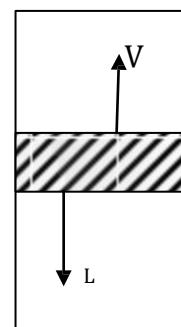
Where: y<sub>A</sub> is mol fraction of A in the gas phase

A is cross sectional area of column, m<sup>2</sup>

Z is height of packing

The height of column z can be found by integration of equation 16.

$$\frac{K_{GO} a A P_T}{N_G} \int dz = - \int_{in}^{out} \frac{dy_A}{y_A - y_A} = \int_{in}^{out} \frac{dy_A}{y_A - y_A} \quad (1.17)$$



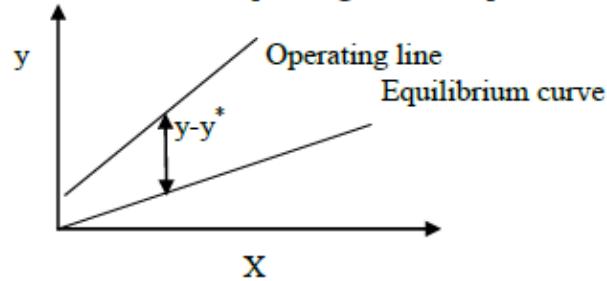
$$\frac{K_{GO} a A P_T}{N_G} Z = \int_{in}^{out} \frac{dy_A}{y_A^* - y_A} \quad (1.18)$$

Let:

$$NTU = \int_{in}^{out} \frac{dy_A}{y_A^* - y_A} \quad (1.19)$$

Where NTU is called number of transfer units.

The term  $y_A^* - y_A$  can be calculated from the operating line and equilibrium curves as shown below:



Operating line can be found from material balance:

$$y_A = \frac{L}{V} X_A + y_{A\ out} - \frac{L}{V} X_{A\ in} \quad (1.20)$$

Where: L is volumetric flow rate of liquid,  $\text{m}^3/\text{s}$

V is molar flow rate of gas, mol/s

Equilibrium curve is given by Henry's law as:

$$y_A^* = \frac{H}{P_T} X_A \quad (1.21)$$

Substitution of equations 20 and 21 into 19 and performing the integration yields (Wankat, 2007):

$$NTU = \frac{1}{1 - \frac{H}{P_T} \frac{V}{L}} \ln \left[ \left( 1 - \frac{H}{P_T} \frac{V}{L} \right) \cdot \left( \frac{y_{A\ in} - y_{A\ out}^*}{y_{A\ out} - y_{A\ out}^*} \right) + \frac{H \cdot V}{P_T \cdot L} \right] \quad (1.22)$$

But:

$$y_{A\ out}^* = \frac{H}{P_T} X_{A\ in} \quad (1.23)$$

Therefore:

$$NTU = \frac{1}{1 - \frac{H \cdot V}{P_T \cdot L}} \ln \left[ \left( 1 - \frac{H \cdot V}{P_T \cdot L} \right) \cdot \left( \frac{y_{A\ in} - \frac{H}{P_T} X_{A\ in}}{y_{out} - \frac{H}{P_T} X_{A\ in}} \right) + \frac{H \cdot V}{P_T \cdot L} \right] \quad (1.24)$$

The height of absorber is therefore given by the following expression:

$$Z = \frac{N_G \cdot H}{a A P_T (K C D_A)^{0.5}} \frac{1}{1 - \frac{H \cdot V}{P_T \cdot L}} \ln \left[ \left( 1 - \frac{H \cdot V}{P_T \cdot L} \right) \cdot \left( \frac{y_{A\ in} - \frac{H}{P_T} X_{A\ in}}{y_{out} - \frac{H}{P_T} X_{A\ in}} \right) + \frac{H \cdot V}{P_T \cdot L} \right] \quad (1.25)$$

This equation shows that the height of absorber depends on the following parameters  
Vapor velocity, U

Nature of solvent (H, K, C)

Temperature, T

Inlet and outlet compositions of  $\text{CO}_2$  in the solvent,  $y_{\text{Ain}}$ ,  $y_{\text{Aout}}$   
 Interfacial area of packing  
 Ratio of vapor to liquid flow rates

The interfacial area (a) depends on the type of packing used in absorption column and the condition in the column. Odna et al. (1968) developed the following correlation that can be used to estimate a.

$$\frac{a}{a_t} = 1 - \text{Exp} \left[ -1.45 \left( \frac{\sigma_c}{\sigma} \right)^{0.75} \cdot \left( \frac{L}{a_t \mu_L} \right)^{0.1} \cdot \left( \frac{L a_t}{\rho_L^2 g} \right)^{-0.05} \cdot \left( \frac{L^2}{\rho_L \sigma a_t} \right)^{0.2} \right] \quad (1.26)$$

Where:  $a_t$  is total surface area of packing,  $\text{m}^2/\text{m}^3$

$\sigma$  is surface tension, dynes/cm

$\sigma_c$  is critical surface tension of packing material, dynes/cm

$L$  is superficial mass velocity of liquid,  $\text{Kg}/(\text{m}^2 \cdot \text{s})$

$\mu_L$  is viscosity of liquid,  $\text{Kg}/(\text{m} \cdot \text{s})$

$g$  is gravitational acceleration,  $\text{m}^2/\text{s}$

$\rho_L$  is density of liquid,  $\text{Kg}/\text{m}^3$ .

Total surface area of packing can be found from Perry (1997).

### Stripping Model:

The height of stripping column can be found from the material balance equation:

$$-L dX_A = K_{LO} a (X_A - X_A^*) dz \quad (2.1)$$

Where:  $L$  is volumetric flow rate of liquid,  $\text{m}^3/\text{s}$

$X_A$  is concentration of A in liquid,  $\text{mol}/\text{m}^3$

$X_A^*$  is concentration of A in liquid in equilibrium with gas phase,  $\text{mol}/\text{m}^3$

$K_{LO}$  is overall mass transfer coefficient based on liquid phase,  $\text{m}/\text{s}$  and is given by:

$$\frac{1}{a K_{LO}} = \frac{1}{a K_L} + \frac{1}{a H K_G} \quad (2.2)$$

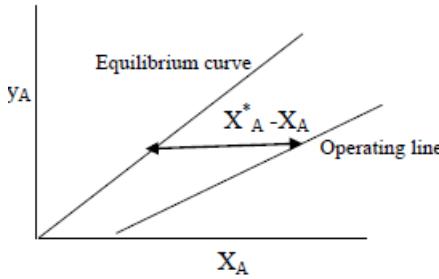
Equation 2.1 can be rearranged as follows:

$$\int_{in}^{out} \frac{dX_A}{X_A - X_A^*} = -\frac{K_{LO} a A}{L} \int dz \quad (2.3)$$

Or:

$$Z = \frac{L}{K_{LO} a A} \int_{out}^{in} \frac{dX_A}{X_A - X_A^*} \quad (2.4)$$

The term  $X_A - X_A^*$  is found from the operating line and equilibrium curve:



From Henry's law:

$$y_A P_T = H X_A^* \quad (2.5)$$

And from equation (1.20)

$$y_A = \frac{L}{V} X_A + y_{A\text{out}} - \frac{L}{V} X_{A\text{in}} \quad (1.20)$$

Substitution of equations 5 and 1.20 into equation 4 and subsequent integration yields:

$$Z = \frac{L}{K_{LO} a_A} \left[ \frac{1}{1 - \frac{P_T L}{H V}} \right] \ln \left[ \left( 1 - \frac{P_T L}{H V} \right) \left( \frac{X_{A\text{in}} - X_{A\text{out}}^*}{X_{A\text{out}} - X_{A\text{out}}^*} \right) + \frac{P_T L}{H V} \right] \quad (2.6)$$

Where

$$X_{A\text{out}}^* = \frac{P_T y_{A\text{in}}}{H} \quad (2.7)$$

Substitution of equation 7 into 6 yields:

$$Z = \frac{L}{K_{LO} a_A} \left[ \frac{1}{1 - \frac{P_T L}{H V}} \right] \ln \left[ \left( 1 - \frac{P_T L}{H V} \right) \left( \frac{X_{A\text{in}} \frac{P_T y_{A\text{in}}}{H}}{X_{A\text{out}} \frac{P_T y_{A\text{in}}}{H}} \right) + \frac{P_T L}{H V} \right] \quad (2.8)$$

The overall mass transfer coefficient  $K_{LO}$  is given by equation (2). In the stripper the mass transfer coefficient in the liquid due to kinetics ( $K_k$ ) is very small and can be neglected. Therefore the overall mass transfer coefficient can be written as:

$$\frac{1}{K_{LO}} = \frac{1}{H K_G} + \frac{1}{K_D} \quad (2.9)$$

$K_G$  (mass transfer coefficient in the gas phase) and  $K_D$  (mass transfer coefficient in the liquid phase) are found from correlations given by Onda et al. (1968).

$$\frac{K_G R T}{a_t D_G} = 5.23 \left[ \frac{G}{a \mu_G} \right]^{0.7} \cdot \left[ \frac{\mu_G}{\rho_G D_G} \right]^{\frac{1}{3}} \cdot [a_t d_p]^{-2.0} \quad (2.10)$$

$$K_D \left( \frac{\rho_L}{\mu_L g} \right)^{\frac{1}{3}} = 0.0051 \left[ \frac{L}{a \mu_L} \right]^{\frac{2}{3}} \cdot \left[ \frac{\mu_L}{\rho_L D_L} \right]^{\frac{1}{2}} \cdot [a_t d_p]^{0.4} \quad (2.11)$$

Where:  $G$  is superficial mass velocity of gas,  $\text{Kg}/(\text{m}^2 \cdot \text{s})$

$\mu_G$  is viscosity of gas,  $\text{Kg}/(\text{m} \cdot \text{s})$

$\rho_G$  is density of gas,  $\text{Kg}/\text{m}^3$

$d_p$  is nominal packing diameter, m

$D_G$  is diffusion coefficient in the gas phase,  $\text{m}^2/\text{s}$

$D_L$  is diffusion coefficient in liquid phase,  $\text{m}^2/\text{s}$

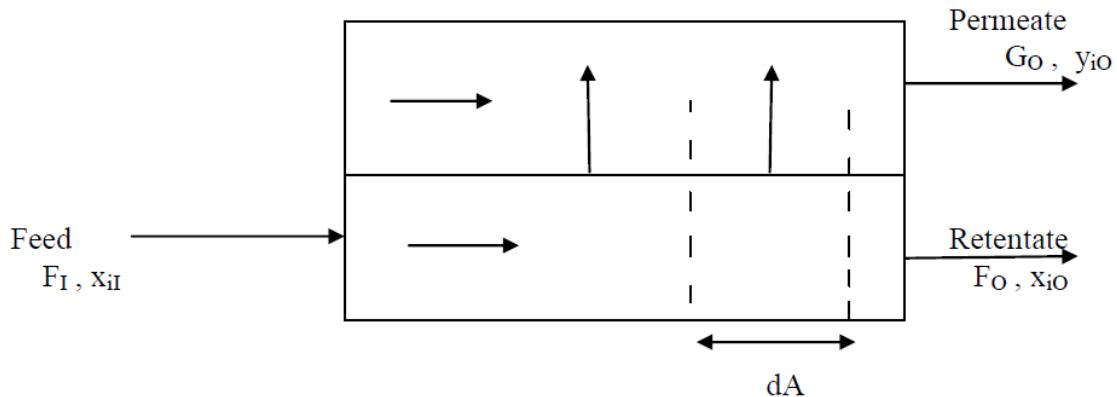
$K_D$  is mass transfer coefficient in liquid phase,  $\text{m}/\text{s}$

$K_G$  is mass transfer coefficient in gas phase,  $\text{mol}/(\text{atm} \cdot \text{m}^2 \cdot \text{s})$

### **Membrane Separation Model:**

Based on the solution-diffusion theory (Fick's law) and the mass balance equations, a set of differential and algebraic equations can be derived, describing the performance of membrane module. Several authors have presented models based on various assumptions. The equations presented below are based on model presented by Shindo et al. [1985].

Shindo et al. [1995] developed a method for calculating the permeation rate of a multi component gas mixture through single stage membrane for different flow patterns. Co-current flow for a permeation stage is shown in the Figure below.



The overall material balance over a differential area of A is:

$$dG = -dF = dA \sum_{i=1}^n \frac{P_i}{L} (p_h x_i - p_L y_i) \quad (1)$$

Where:

F – is the flowrate of mixture in the feed side.

G – is flowrate of mixture in the permeate side.

A – is membrane area.

P<sub>i</sub> – is permeability of component.

x<sub>i</sub> – is mole fraction of component *i* in the feed side.

y<sub>i</sub> – is mole fraction of component *i* in the permeate side.

p<sub>h</sub>, p<sub>L</sub> - are the pressures on the feed side and permeate side respectively.

L – is thickness of membrane.

Material balance for component *i* is given by

$$-d(x_i F) = d(y_i G) = dA \frac{P_i}{L} (p_h x_i - p_L y_i) \quad (2)$$

The conditions for the mole fractions are:

$$\sum x_i = 1 \quad (3)$$

$$\sum y_i = 1 \quad (4)$$

From equation (2)

$$- [x_i dF + F dx_i] = dA \frac{P_i}{L} (p_h x_i - p_L y_i) \quad (5)$$

Or

$$- F dx_i = x_i dF + dA \frac{P_i}{L} (p_h x_i - p_L y_i) \quad (6)$$

Substitution of equation (1) into (6) yields

$$- F dx_i = x_i \left[ - dA \sum \frac{P_i}{L} (p_h x_i - p_L y_i) \right] + dA \frac{P_i}{L} (p_h x_i - p_L y_i) \quad (7)$$

Or

$$dx_i = - \frac{dA}{F} \left[ \frac{P_i}{L} (p_h x_i - p_L y_i) - x_i \sum \frac{P_i}{L} (p_h x_i - p_L y_i) \right] \quad (8)$$

Or

$$\frac{dx_i}{dA} = - \frac{P_i}{FL} (p_h x_i - p_L y_i) + \frac{x_i}{FL} \sum P_i (p_h x_i - p_L y_i) \quad (9)$$

And from equation (1):

$$\frac{dA}{dF} = \frac{-1}{\sum \frac{P_i}{L} (p_h x_i - p_L y_i)} \quad (10)$$

Multiplying equation (9) and (10)

$$\frac{dx_i}{dF} = \frac{\frac{P_i}{FL} (p_h x_i - p_L y_i) - \frac{x_i}{FL} \sum P_i (p_h x_i - p_L y_i)}{\sum \frac{P_i}{L} (p_h x_i - p_L y_i)} \quad (11)$$

$$\frac{dx_i}{dF} = \frac{P_i (p_h x_i - p_L y_i) - x_i \sum P_i (p_h x_i - p_L y_i)}{F \sum P_i (p_h x_i - p_L y_i)} \quad (12)$$

The relationship between  $x_i$  and  $y_i$  at any point in the membrane unit can be found by the integration of equation (2) from inlet conditions to any arbitrary point.

$$-\int d(x_i F) = \int d(y_i G) \quad (13)$$

$$-[x_i F - x_{iI} F_I] = (y_i G) \quad (14)$$

Or:

$$y_i = \frac{x_{iI} F_I - x_i F}{G} \quad (15)$$

Where  $x_{iI}$  is mole fraction of component I in the feed, and  $F_I$  is the flow rate of feed.

But,

$$G = F_I - F \quad (16)$$

Therefore;

$$y_i = \frac{\frac{P_i}{L}(p_h x_i - p_L y_i)}{\sum \frac{P_i}{L}(p_h x_i - p_L y_i)} \quad (17)$$

Equation (17) is valid for all the points except at inlet ( $F_I - F = 0$ ). At the inlet where  $A=0$ , the mole fraction  $y_i$  is obtained by a limiting process of the L'Hopital's rule as  $F \rightarrow F_I$

$$y_i = \frac{\frac{P_i}{L}(p_h x_i - p_L y_i)}{\sum \frac{P_i}{L}(p_h x_i - p_L y_i)} \quad F = F_I \quad (18)$$

The ratio of any two members of equation (18) is given by;

$$\frac{y_i}{y_j} = \frac{P_i(p_h x_i - p_L y_i)}{P_j(p_h x_j - p_L y_j)} \quad F = F_I \quad (19)$$

For a binary mixture (CO<sub>2</sub> and N<sub>2</sub>) equations (10) and (12), (17) and (19) are simplified to:

$$\frac{dA}{dF} = \frac{-L}{P_1(p_h x_1 - p_L y_1) + P_2(p_h x_2 - p_L y_2)} \quad (20)$$

$$\frac{dx_1}{dF} = \frac{P_1(p_h x_1 - p_L y_1) - x_1 [P_1(p_h x_1 - p_L y_1) + P_2(p_h x_2 - p_L y_1)]}{F [P_1(p_h x_1 - p_L y_1) + P_2(p_h x_2 - p_L y_2)]} \quad (21)$$

$$y_1 = \frac{x_I F_I - x_1 F}{F_I - F} \quad F \neq F_I \quad (22)$$

$$\frac{y_1}{y_2} = \frac{P_1(p_h x_1 - p_L y_1)}{P_2(p_h x_2 - p_L y_2)} \quad F = F_I \quad (23)$$

Equations (20) and (21) can be integrated and used with equations (21) and (22) to calculate the compositions of the two streams leaving the membrane unit x<sub>10</sub> and y<sub>10</sub> and the area of the membrane needed (A). The initial conditions for the equations are:

At A = 0 → F = F<sub>I</sub>, x<sub>1</sub> = x<sub>1I</sub> and

$$\frac{y_1}{y_2} = \frac{P_1(p_h x_{1I} - p_L y_1)}{P_2(p_h x_{2I} - p_L y_2)} \quad (24)$$

Or

$$\frac{y_1}{1 - y_1} = \frac{P_1(p_h x_{1I} - p_L y_1)}{P_2[p_h(1 - x_{2I}) - p_L(1 - y_1)]} \quad (25)$$

Equation (25) is used to find the initial value of y<sub>1</sub>.

The upper bound of integration is specified based on the requirements for the outlet conditions (F = F<sub>o</sub>).

Solving Permeation Equations: The first step in solving the design equations for the membrane is to calculate the composition of permeate at inlet (A = 0).

Let

$$\frac{P_1}{P_2} = q \quad (26)$$

$$\frac{p_L}{p_H} = p_r \quad (27)$$

Equation (25) can be written as

$$\frac{y_1}{1-y_1} = \frac{q[x_{1I} - p_r y_1]}{1-x_{1I} - p_r(1-y_1)} \quad (28)$$

or

$$(p_r - qp_r)y_1^2 + (1 - x_{1I} - p_r + qp_r + qx_{1I})y_1 - qx_{1I} = 0 \quad (29)$$

Let

$$a = p_r - qp_r \quad (30)$$

$$b = 1 - x_{1I} - p_r - qp_r + qx_{1I} \quad (31)$$

$$c = -qx_{1I} \quad (32)$$

Equation (29) is therefore written as

$$ay_1^2 + by_1 + c = 0 \quad (33)$$

The mole fraction of component 1 in the permeate at inlet is given by:

$$(y_1)_{inlet} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (34)$$

The second step in the calculations is to solve the two differential equations 20 and 21. Substitution of equations 26 and 27 into 20 and 21 yields:

$$\frac{dA}{dF} = \frac{-L}{p_H p_L [q(x_1 - p_r y_1) + (x_2 - p_r y_2)]} \quad (35)$$

$$\frac{dx_1}{dF} = \frac{q(x_1 - p_r y_1) - x_1 [q(x_1 - p_r y_1) + x_2 - p_r y_2]}{F[q(x_1 - p_r y_1) + x_2 - p_r y_2]} \quad (36)$$

Let:

$$q(x_1 - p_r y_1) = V \quad (37)$$

$$(x_2 - p_r y_2) = W \quad (38)$$

Equations 35 and 36 are simplified as follows :

$$\frac{dx_1}{dF} = \frac{V - x_1 [V + W]}{F[V + W]} \quad (39)$$

$$\frac{dA}{dF} = \frac{-L}{p_H P_2 [V + W]} \quad (40)$$

These differential equations can be converted to regular equations as follows:

$$\frac{A^{(n+1)} - A^{(n)}}{\Delta F} = -\frac{L}{p_H P_2 [V^{(n)} + W^{(n)}]} \quad (41)$$

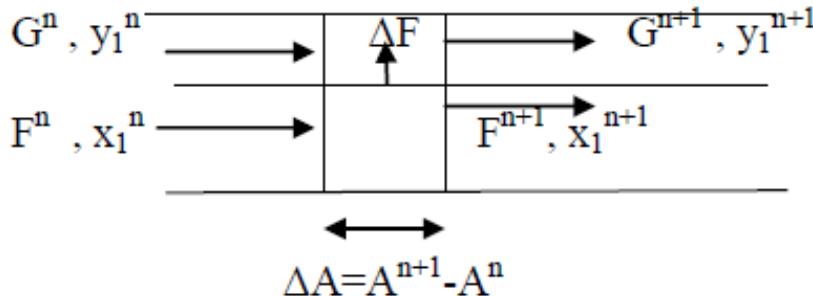
$$\frac{x_1^{(n+1)} - x_1^{(n)}}{\Delta F} = \frac{V^{(n)} - x_1^{(n)} [V^{(n)} + W^{(n)}]}{F^{(n)} [V^{(n)} + W^{(n)}]} \quad (42)$$

Or:

$$A^{(n+1)} = A^{(n)} - \frac{L(\Delta F)}{p_H P_2 [V^{(n)} + W^{(n)}]} \quad (43)$$

$$x_1^{(n+1)} = x_1^{(n)} + \frac{\Delta F [V^{(n)} + x_1^{(n)} (V^{(n)} + W^{(n)})]}{F^{(n)} [V^{(n)} + W^{(n)}]} \quad (44)$$

Equations 43 and 44 can be solved using an iterative method.  $\Delta F$  is the change in flow rate of feed (the high pressure side of membrane) over a small area of the membrane as shown in the Figure below.



### **Adsorption Model:**

A mathematical model was developed to predict the sorbent-based separation of CO<sub>2</sub> / N<sub>2</sub>. The model is based on the following assumptions:

1. Thermal effects are negligible
2. Total pressure remains constant
3. The absorption behaviors are described by the Langmuir Isotherm
4. The absorption rule is approximated by the linear driving force (LDF) expansion
5. Fluid flow is governed by plug flow model with no axial dispersion

Component material balance in the gas phase is given by the following equation:

$$\epsilon \frac{\partial C_i}{\partial t} + \frac{\partial (CV)}{\partial Z} + (1 - \epsilon) \rho_s \frac{\partial q_i}{\partial t} = 0 \quad (1)$$

Where:

C<sub>i</sub> : Concentration of Component in gas phase, mol / cm<sup>3</sup>

t : Time, s

V : Superficial velocity, cm/s

Z : Axial Distance, cm

€ : porosity of bed

ρ<sub>s</sub> : density of solid, mol/cm<sup>3</sup>

q<sub>i</sub> : Concentration of Component i in solid phase, mol/kg

Overall Material Balance (for Constant pressure) is given by:

Where:

$$C \frac{\partial V}{\partial Z} + (1 - \epsilon) \rho_s \sum \frac{\partial q_i}{\partial t} = 0 \quad (2)$$

$$C = \sum C_i \quad (3)$$

For adsorption of a spherical particle subject to a step change in the surface concentration, the LDF describes the absorption rate using the following equation [Glueckauf and Coates]:

$$\frac{\partial q_i}{\partial t} = K_i (q_i^* - q_i) \quad (4)$$

Where:

q<sub>i</sub><sup>\*</sup> : Equilibrium solid phase concentration of *i*<sup>th</sup> component (mol/kg)

K<sub>i</sub> : Lumped mass transfer coefficient for the *i*<sup>th</sup> component (1/s)

The mass transfer coefficient, K<sub>i</sub> ; was calculated from the following equation:

$$K_i = 15 D / R^2 \quad (5)$$

Where:

D : Effective pore diffusivity, cm<sup>2</sup> / s

R: Radius of particles, cm

Absorption equilibrium is represented by Langmuir equation:

$$Q_i^* = m_i b_i C_i / [1 + \sum b_i C_i] \quad (6)$$

Where:

$m_i$  : Langmuir constant for  $i^{\text{th}}$  component , mol/kg

$b_i$  : Langmuir constant for the  $i^{\text{th}}$  component,  $\text{cm}^3/\text{mol}$

Equations (1) through (6) were all solved to estimate Breakthrough Curves.

The partial differential equations were solved numerically by the reduction to set up ordinary differential equations using the “Method of Lines”. A mathematical algorithm to solve these coupled equations was developed and implemented into a computer program using MATLAB (V.7.1) Software.

Model Implementation: The mathematical model was implemented for absorption of  $\text{CO}_2 / \text{N}_2$  mixture. For a binary mixture equations (1) through (6) can be written as:

$$\partial C_1 / \partial t = -(1/\epsilon) \partial(C_1 V) / \partial Z - (1-\epsilon) / \epsilon \rho_s \partial q_1 / \partial t \quad (7)$$

$$\partial C_2 / \partial t = -(1/\epsilon) \partial(C_2 V) / \partial Z - (1-\epsilon) / \epsilon \rho_s \partial q_2 / \partial t \quad (8)$$

$$\partial q_1 / \partial t = K_1 (q_2^* - q_1) \quad (9)$$

$$\partial q_2 / \partial t = K_2 (q_2^* - q_2) \quad (10)$$

$$(C_1 + C_2) \partial V / \partial Z + \rho_s (1 - \epsilon) [\partial q_1 / \partial t + \partial q_2 / \partial t] = 0$$

$$(11)$$

$$q_1^* = m_1 b_1 C_1 / [1 + m_1 b_1 C_1 + m_2 b_2 C_2] \quad (12)$$

$$q_2^* = m_2 b_2 C_2 / [1 + m_1 b_1 C_1 + m_2 b_2 C_2] \quad (13)$$

Substitution of equations (9) and (10) into equations (7), (8) and (11) yields the following equations:

$$\partial C_1 / \partial t = - (1/\epsilon) [V \partial C_1 / \partial Z + C_1 \partial V / \partial Z] - [(1 - \epsilon) / \epsilon] \rho_s K_1 (q_1^* - q_1) \quad (14)$$

$$\partial C_2 / \partial t = - (1/\epsilon) [V \partial C_2 / \partial Z + C_2 \partial V / \partial Z] - [(1 - \epsilon) / \epsilon] \rho_s K_2 (q_2^* - q_2) \quad (15)$$

$$\partial q_1 / \partial t = K_1 (q_1^* - q_1) \quad (16)$$

$$\partial q_2 / \partial t = K_2 (q_2^* - q_2) \quad (17)$$

$$(C_1 + C_2) \partial V / \partial Z + \rho_s (1 - \epsilon) [K_1 (q_1^* - q_1) + K_2 (q_2^* - q_2)] \quad (18)$$

$$q_1^* = m_1 b_1 C_1 / [1 + m_1 b_1 C_1 + m_2 b_2 C_2] \quad (19)$$

$$q_2^* = m_2 b_2 C_2 / [1 + m_1 b_1 C_1 + m_2 b_2 C_2] \quad (20)$$

Equations (14) through (20) are six equations with five unknowns ( $c_1, c_2, q_1, q_2, V$ ). The following algorithm is used to solve the equations:

1. The Variation of velocity with respect to distance (Z) is approximated as:

$$\partial V / \partial Z = [V_{n+1} - V_n] / \Delta Z \quad (21)$$

$$V_{n+1} = V_n - \Delta Z \rho_s [(1 - \epsilon) / (C_1 + C_2)] [K_1 (q_1^* - q_1) + K_2 (q_2^* - q_2)] \quad (22)$$

$$\partial V / \partial Z = -\rho_s [(1 - \epsilon) / (C_1 + C_2)] [K_1 (q_1^* - q_1) + K_2 (q_2^* - q_2)] \quad (23)$$

These equations are substituted into equations (14) and (15).

2. The method of lines is used to replace  $\partial C_1 / \partial Z$  and  $\partial C_2 / \partial Z$  with finite differences. Equations (14) and (15) are therefore converted into ordinary differential equations
3. Equations (19) and (20) are substituted into equations (14) through (17). ( $q_1^*$  and  $q_2^*$  are eliminated)
4. These four ordinary differential equations are solved by MATLAB.

Calculation of Mass Transfer Coefficient: The Diffusion Coefficient in a binary mixture is estimated from Fuller, Schettler and Giddings equation [Brodkey et al.]

$$D_{i,j} = 10^{-7} T^{1.75} [(1/M_i) + (1/M_j)]^{1/2} / [P_{atm} [(\sum V')_i^{1/3} + (\sum V')_j^{1/3}]^2] \quad (24)$$

Where:

$P_{atm}$  : Pressure, atm

$D_{i,j}$  :  $m^2 / s$

$T$  :  $^{\circ}K$

$\sum V'$  : is found by summing the atomic diffusion volume given in Table

For  $N_2$

$$\sum V' = 17.9 \quad (25)$$

For  $CO_2$

$$\sum V' = 26.9 \quad (26)$$

The molecular diffusion for mixtures is approximated with the following relation:

$$D_{m,I} = (1 - y_i) / \sum y_i / D_{i,j} \quad (27)$$

Where  $y_i$  is mole fraction of the  $i^{\text{th}}$  Compound.

Knudsen diffusion coefficient is calculated from the following expression [ Brodkey et al.]

$$D_{k,i} = 4850 d_p \sqrt{T / M_i} \quad (28)$$

Where  $d_p$  is mean macro pore diameter

$D_{k,I}$  : Knudsen diffusion coefficient,  $\text{cm}^2 / \text{s}$

The effective diffusion Coefficient is estimated from Besanquest equation [Yang]

$$D_i^e = 1 / [\tau (1 / D_{m,i} + 1 / D_{k,i})] \quad (29)$$

Where  $\tau$  is Tortuosity factor and is given by [Suzuki, et al.]

$$\tau = \epsilon_p + 1.5 (1 - \epsilon_p) \quad (30)$$

and  $\epsilon_p$  is pellet void fraction.

The film mass transfer coefficient ( $K_f$ ), is calculated from the correlation proposed by Walco and Funazkri [ Shen et al.]

$$Sh = 2.0 + 1.1 R_e^{0.6} S_c^{1/3} \quad (31)$$

Where  $Sh$  is Sherwood number and is given by

$$Sh = 2 R_p K_f / D_m$$

$S_c$  is Schmidt number

$$S_c = \mu / P_g * D_m \quad (32)$$

and  $R_e$  is Reynolds Number

$$R_e = 2 \rho_g V R_p / \mu \quad (33)$$

$\mu$  is viscosity

$\rho_g$  is density of gas

The overall mass transfer coefficient,  $K_i$ , is calculated from the following relation:

$$1 / K_i = R_p / 3 K_{f,i} + R_p^2 / [15 \epsilon_p D_i^e] \quad (34)$$

# Modeling Results and Discussion

## Absorption Studies

An Excel spread sheet was developed to calculate the cost per unit tonne of CO<sub>2</sub> for absorption processes. This is a general spread sheet that can be used for any absorption process. The program estimates the equipment cost for two separate materials of constructions: carbon steel and stainless steel and calculates the following costs:

- Cost of absorber
- Cost of stripper
- Cost of pumps
- Cost of heat exchangers
- Cost of compressors
- Cost of utilities (steam, electricity and water)
- Cost of Labor
- Cost of Maintenance
- Fixed capital investment
- Operating costs
- Total cost per year
- Total cost per tonne of CO<sub>2</sub> captured for carbon steel and a stainless steel plant.

The input data required to use the model are as follows.

Solvent Properties:

- Weight fraction of solvent
- Molecular weight of solvent
- Density of solvent
- Heat of absorption of solvent
- Average slope of equilibrium curve at the absorber's temperature
- Average slope of equilibrium curve at the stripper's temperature
- Overall mass transfer coefficient (which includes physical mass transfer and mass transfer due to chemical (it is calculated from experimental data on the rate of mass transfer)).

Flue Gas:

- Temperature of flue gas
- Mole fraction of CO<sub>2</sub> in the flue gas

Absorber Conditions:

- Temperature of solvent entering absorber
- Pressure in absorber
- Recovery of CO<sub>2</sub>(fraction of CO<sub>2</sub> recovered in absorber)

Stripper Conditions:

- Pressure in stripper
- Recovery of CO<sub>2</sub> (fraction of CO<sub>2</sub> recovered in stripper)

- Temperature of steam in the reboiler

Packing Characteristics:

- Packing diameter
- Total packing area (area per unit volume of packing)

Cost Data:

- Price of pure solvent
- Price of electricity
- Price of steam
- Price of cooling water
- Hourly labor cost
- Cost of packing per unit volume

Overall Plant Data:

- Useful life of plant
- Make up solvent as a fraction of flow rate of solvent to absorber
- Repair factor for carbon steel as a percentage of fixed capital
- Repair factor for stainless steel as a percentage of fixed capital
- Chemical Engineering (CE) cost index

The user can change many of the process variables for the absorption plant in order to optimize the process and get the cheapest cost per tonne of CO<sub>2</sub> captured. The process variables have direct effect on the cost per tonne of CO<sub>2</sub> captured. The effect of each of certain process variables on the total cost is discussed in this section.

### **Liquid to Gas Ratio in Absorber**

As the liquid to gas ratio in the absorber is increased, the height of absorber decreases (a cheaper column). However, because the circulation rate of solvent increases, the cost of stripper and the flow rate of steam in the reboiler of stripper will increase. The cost of steam has a very large effect on the total cost. Consequently, the cost per tonne of CO<sub>2</sub> captured will increase as the liquid to gas ratio increases. This is shown in Figure 1.

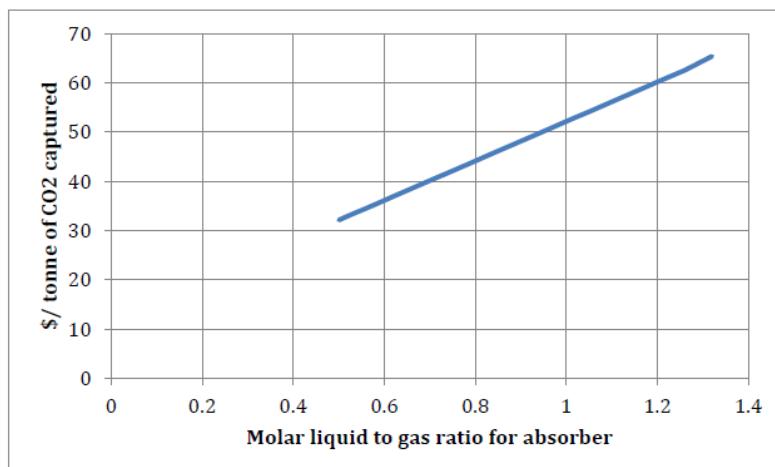


Figure 1. The effect of molar liquid to gas ratio in absorber on the cost of CO<sub>2</sub> capture.

### **Liquid to Gas Ratio in Stripper**

As the liquid to gas ratio in the stripper is increased, the flow rate of gas in the stripper decrease which will reduce the flow rate of steam in the reboiler. The result is a larger stripper column, a smaller condenser and reboiler and lower costs for cooling water and steam. The overall effect is to reduce the total cost per tonne of CO<sub>2</sub> captured. This is shown in Figure 2.

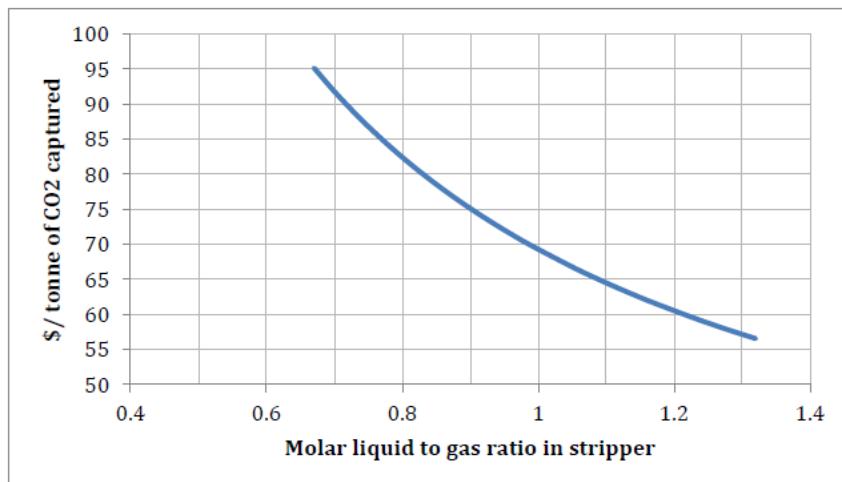


Figure 2. The effect of molar liquid to gas ratio in stripper on the cost of CO<sub>2</sub> captured.

### **Percent Recovery of CO<sub>2</sub> in Absorber**

Percent recovery of CO<sub>2</sub> in absorber is defined as the percentage of CO<sub>2</sub> in flue gas that is captured by the solvent in the absorber. As the recovery increase, a larger (and more expensive) absorption column is needed. There will also be a modest increase in the flow rate of steam in the reboiler (more CO<sub>2</sub> enters the stripping column). However, the total amount of CO<sub>2</sub> captured will increase. This means that the total cost per year will increase and the flow rate of CO<sub>2</sub> captured per year will increase too. The overall result is a decrease in the cost per tonne of CO<sub>2</sub>. The effect of recovery on the cost is given in Figure 3.

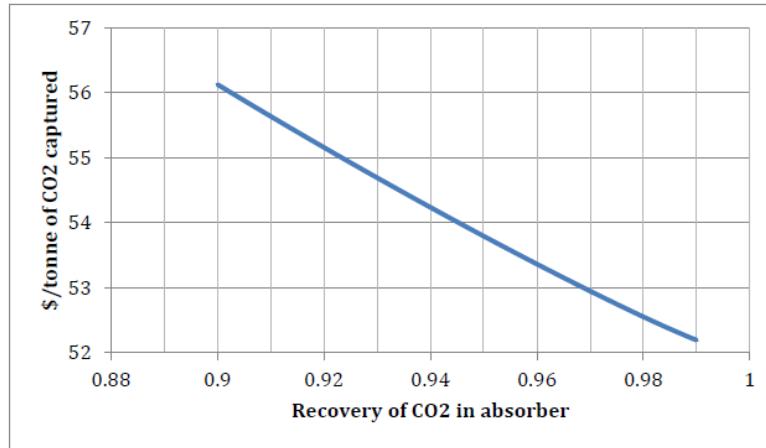


Figure 3. The effect of recovery of CO<sub>2</sub> in absorber on the cost per tonne of CO<sub>2</sub> captured.

#### **Mole fraction of CO<sub>2</sub> in Flue Gas**

As the mole fraction of CO<sub>2</sub> in the flue gas is decreased, less CO<sub>2</sub> is captured per year. The effect of reduction in the amount of CO<sub>2</sub> on the cost per year is minimal. There will be a slight reduction in the flow rate of steam in the reboiler. The overall result is an increase in the cost per tonne of CO<sub>2</sub> captured. This is shown in Figure 4.

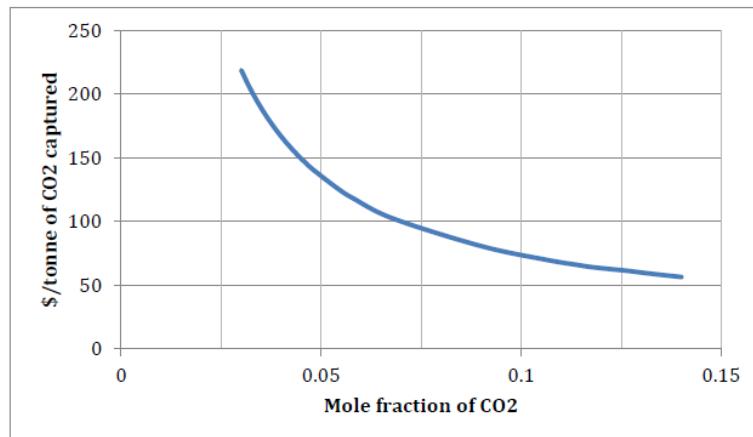


Figure 4. The effect of mole fraction of CO<sub>2</sub> in flue gas on the cost of CO<sub>2</sub> captured

#### **Temperature of Cooling Water Exiting Heat Exchangers**

As the temperature of cooling water leaving heat exchangers increases, driving force for heat transfer (log mean temperature difference) decreases and consequently the size of heat exchangers increases (a higher fixed cost). However, flow rate of cooling water needed in the heat exchangers decreases (a lower operating cost). The drop in the operating cost is more substantial than the increase in the fixed cost. The overall result is a decrease in the cost per tonne of CO<sub>2</sub>. This is shown in Figure 5.

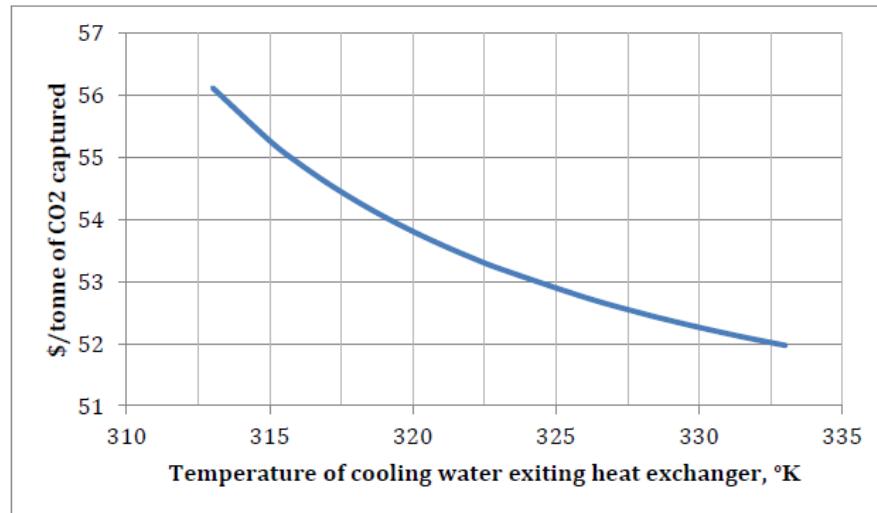


Figure 5. The effect of temperature of cooling water exiting heat exchanger on the cost of CO<sub>2</sub> captured.

### **Material of Construction**

The model predicts the cost per tonne of CO<sub>2</sub> for two different materials of construction for equipment: carbon steel and stainless steel. The stainless steel plant has a higher fixed capital but a lower repair cost. If the solvent is corrosive, a plant made of carbon steel has a fairly high repair cost. Figure 6 shows the effect of repair cost on the cost per tonne of CO<sub>2</sub> captured. For inert solvents with no significant corrosion rate, the cost of capturing CO<sub>2</sub> for the stainless steel plant is a few cents cheaper than the carbon steel plant. However, as the solvent becomes more corrosive (higher repair cost), the cost of CO<sub>2</sub> captured in a carbon steel plant can be several dollars higher than for a stainless steel plant.

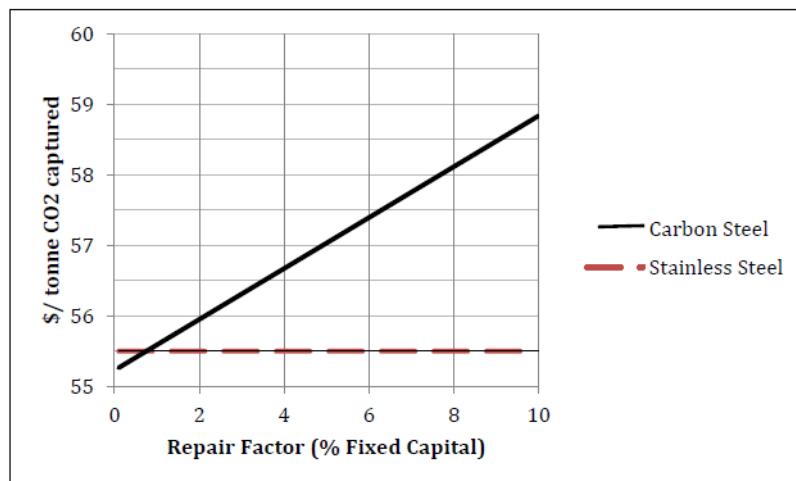


Figure 6. The effect of material of construction on the cost of CO<sub>2</sub> captured.

### **Make-up Solvent**

The amount of make-up solvent needed for an absorption process depends on the rate of circulation and degradation of the solvent. For an optimum circulation rate (that minimizes the total cost per tonne of CO<sub>2</sub> captured), the make-up solvent required depends on the properties of the solvent and the conditions in the absorber and stripper and can be represented as a percentage of circulation rate lost due to degradation. The effect of degradation rate on the cost per tonne of CO<sub>2</sub> captured is shown in Figure 7.

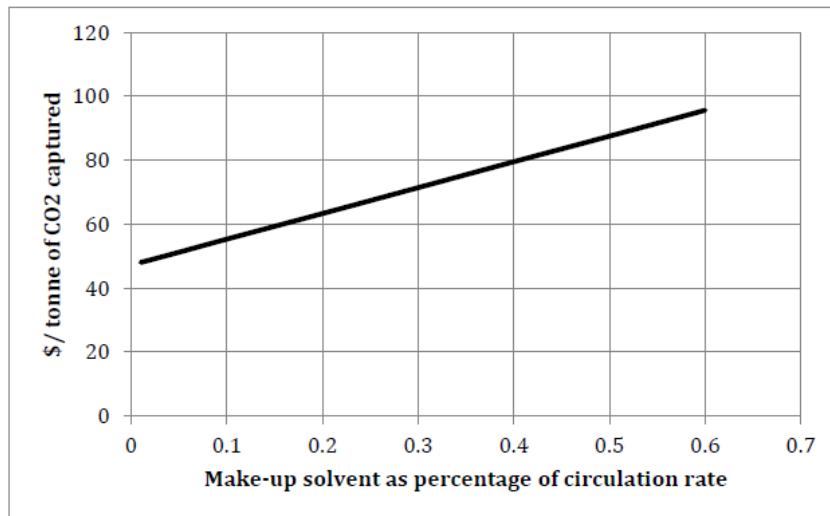


Figure 7. The effect of solvent circulation rate on the cost of CO<sub>2</sub> captured.

### **Price of Solvent**

The price of solvent has a direct effect on the operating cost of absorption process. Figure 8 shows that the cost per tonne of CO<sub>2</sub> captured increases linearly with the price of solvent.

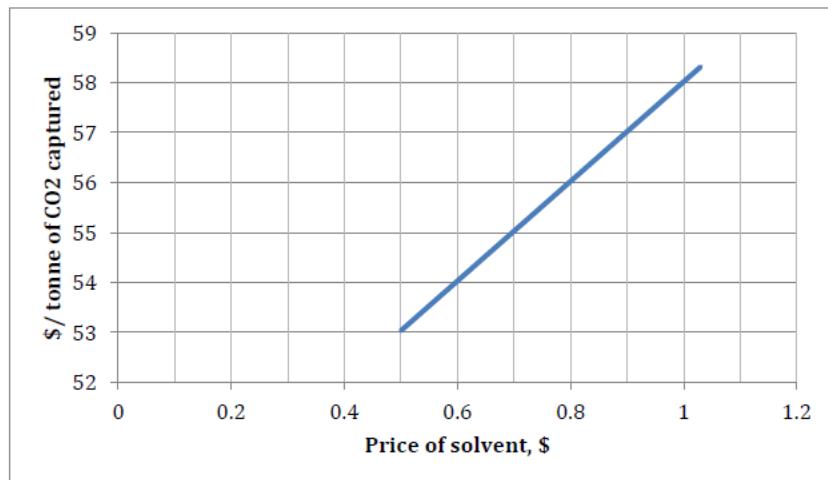


Figure 8. The effect of solvent price on the cost of CO<sub>2</sub> captured.

## Membrane Studies

Two Excel spread sheets were developed to calculate the cost per unit tonne of CO<sub>2</sub> for single stage and double stage membrane units. These are general spread sheets that can be used for any membrane process. These programs do the following calculations (based on the equations developed in the model):

- Composition and flow rate of gas leaving each stage of the membrane unit
- Area and cost of the membrane units
- Cost of heat exchangers
- Cost of compressors
- Cost of utilities (steam, electricity and water)
- Cost of Labor
- Cost of Maintenance
- Fixed capital investment
- Operating costs
- Total cost per year
- Total cost per tonne of CO<sub>2</sub> captured.

The input data needed for the spread sheet are as follows:

Flow rate of air, Kmol/s, Fin
Mole fraction of CO <sub>2</sub> in air, X1in
Permeability of CO <sub>2</sub> , Barrer, PERCO2
Permeability of N <sub>2</sub> , Barrer, PERN2
Temperature of air
Pressure on feed side of membrane, bar, PH
Pressure on permeate side of membrane, bar, PL
Thickness of membrane, m
Fraction of feed remaining , FRAC
Pressure of CO <sub>2</sub> out, bar, Pout
Price of Cooling water, \$/m <sup>3</sup>
Price of electricity, \$/KWh, Kelec
No of Hours per year, HOURS
Temperature of water into cooler
Temperature of water out of cooler
Repair factor, per cent fixed capital
Recovery period, Recoveryperiod
Membrane cost, \$/m <sup>2</sup> , Memcost
Lang factor for fixed Capital
Labor Requirements, No of skilled labor
Wages, \$/h
CE Cost Index

A Visual Basic program was developed within each spread sheet that solved the differential equations to calculate the composition and flow rates of the two streams leaving each stage of membrane, and the area of membranes. These spread sheets were

used to estimate the cost per tonne of CO<sub>2</sub> captured as a function of different parameters of the process.

The parameters and process variables have direct effect on the cost per tonne of CO<sub>2</sub> captured. The most important parameters for the membrane processes are as follows:

- Permeability and selectivity of membranes
- Pressure difference across the membranes
- Fraction of the feed remaining as raffinate
- Ratio of pressures on the two sides of membranes
- Number of stages of membranes
- Prices of cooling water and electricity
- Price of membranes
- Temperature of cooling water exiting heat exchangers

The effect of each one of these parameters on the cost of CO<sub>2</sub> removal is evaluated.

### **The effect of Permeability and selectivity of membranes**

A data base developed for the permeability and separation factors was used to estimate the cost per tonne of CO<sub>2</sub> removed for different membranes. The results are shown in Figures 9-12. As the permeability of membranes for CO<sub>2</sub> (and consequently for N<sub>2</sub>) increases, the cost per tonne of CO<sub>2</sub> decreases. There is no clear relationship between the separation factor and the cost (Figure 11). There are several membranes that have been developed for CO<sub>2</sub> separation from nitrogen that have very low permeability for CO<sub>2</sub> and for N<sub>2</sub>. The results of calculations for these types of membranes are given in Figures 12 and 13. As it can be seen from these figures, the cost of CO<sub>2</sub> removal is extremely high for this class of membranes.

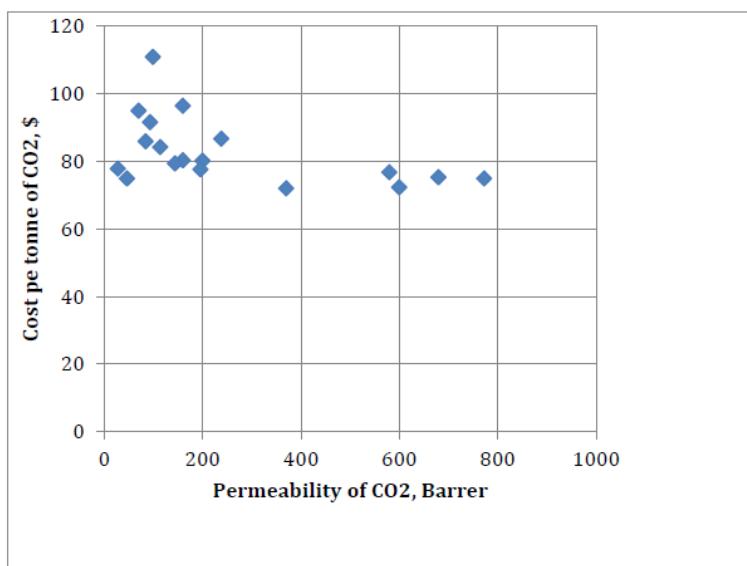


Figure 9. The effect of permeability of CO<sub>2</sub> on the cost per tonne of CO<sub>2</sub> captured for a single stage membrane system.

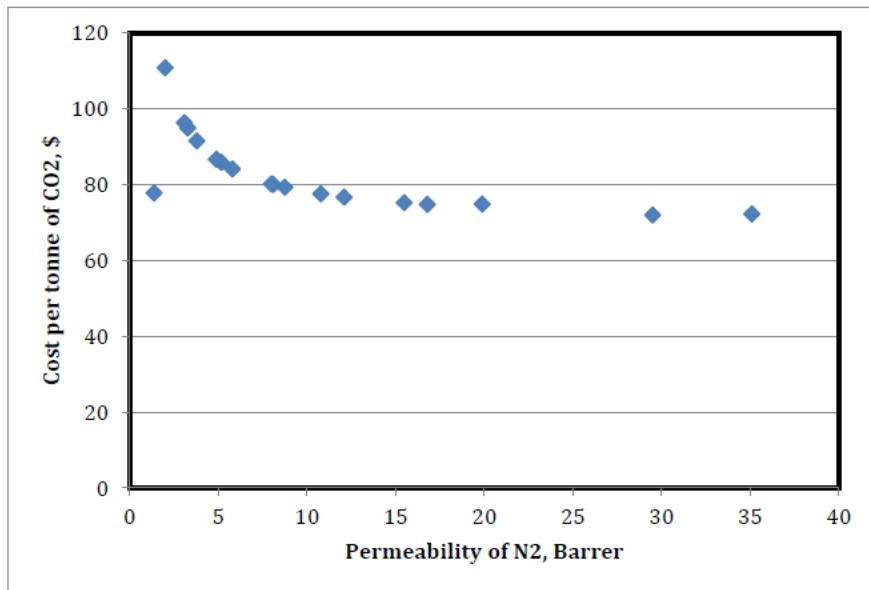


Figure 10. The effect of permeability of N<sub>2</sub> on the cost per tonne of CO<sub>2</sub> captured for a single stage membrane system.

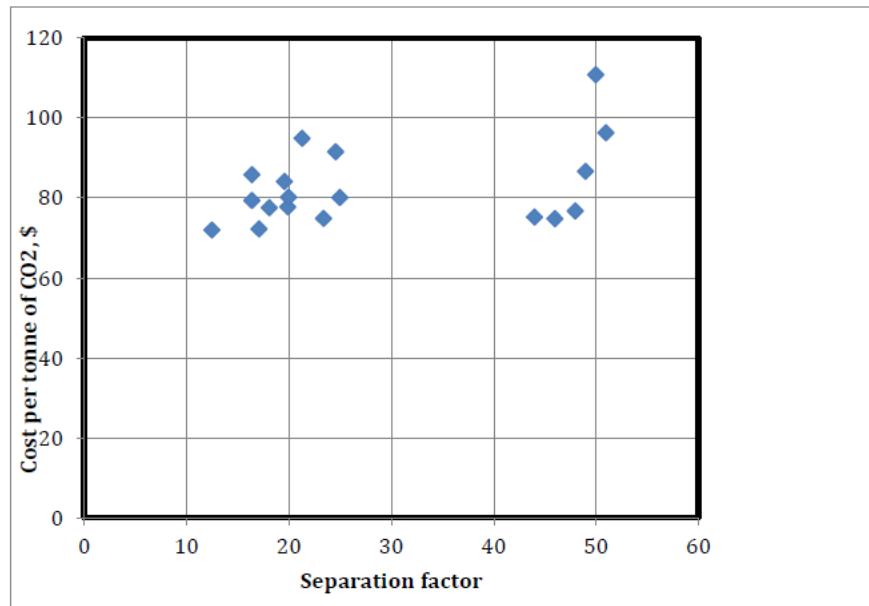


Figure 11. The effect of permeability of N<sub>2</sub> on the cost per tonne of CO<sub>2</sub> captured for a single stage membrane system.

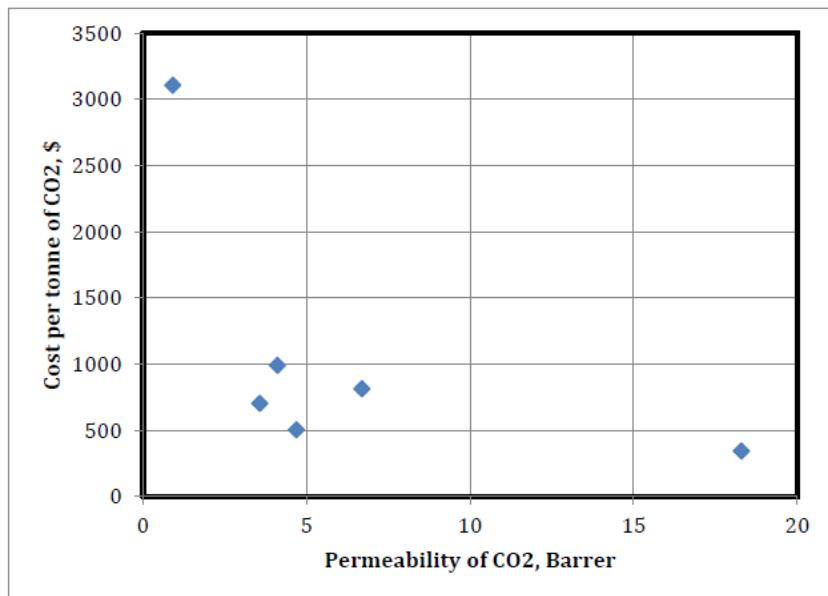


Figure 12. The effect of permeability of CO<sub>2</sub> on the cost per tonne of CO<sub>2</sub> captured for membranes with low permeabilities in a single stage membrane system.

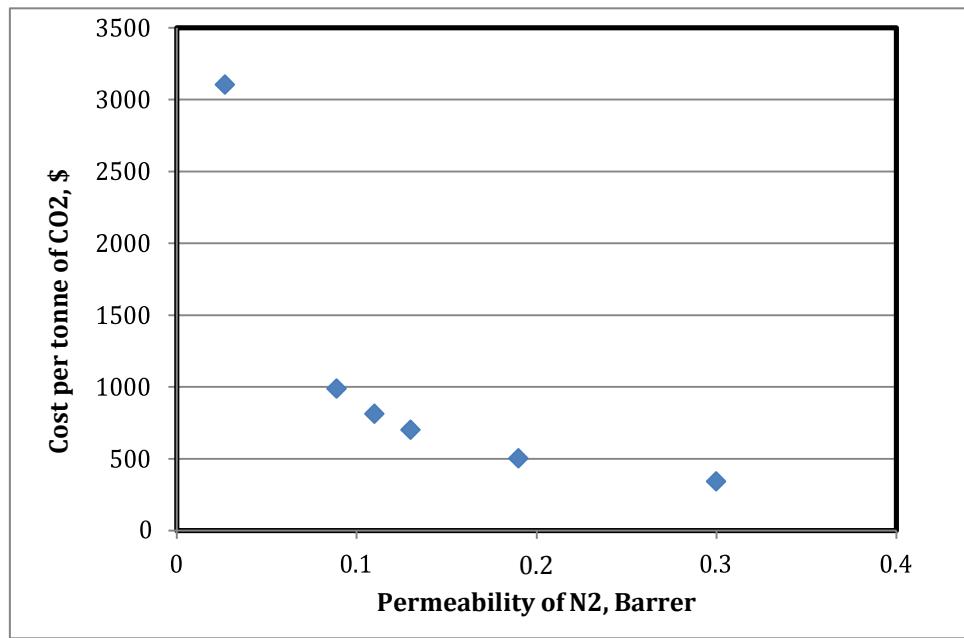


Figure 13. The effect of permeability of N<sub>2</sub> on the cost per tonne of CO<sub>2</sub> captured for membranes with low permeabilities in a single stage membrane system.

### **The Effect of pressure difference and pressure ratio across the membrane**

The effect of pressure difference and pressure ratio across the membrane on the cost of CO<sub>2</sub> removal is given in Figures 14 and 15 for a single stage and two stage membrane arrangements respectively. For a given pressure ratio, as the pressure difference across the membrane increase, the cost per tonne of CO<sub>2</sub> captured is decreased. This is true for both the single stage and two stage arrangements. As the pressure ratio is increased from 10 to 20 (for the same pressure difference), the cost increases. This shows that the membranes should be operated at lower pressure ratios.

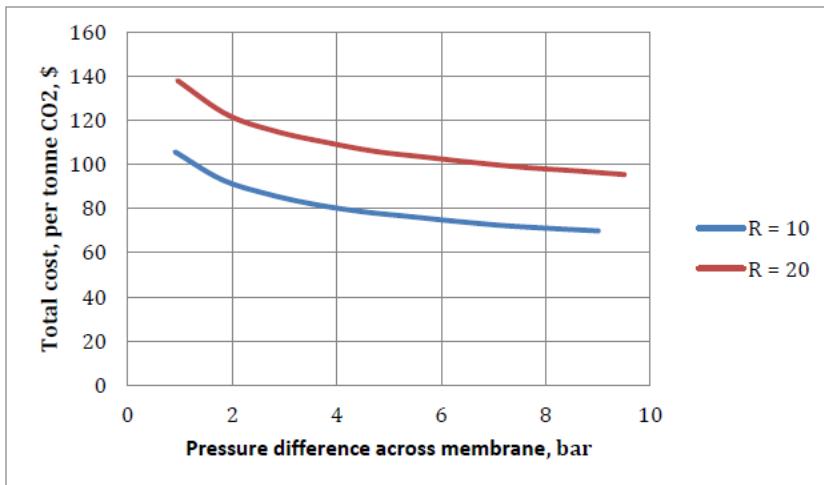


Figure 14. The effect of pressure difference across the membrane on the cost per tonne of CO<sub>2</sub> captured for a **single state membrane** system. R is the ratio of pressures on the two sides of membrane.

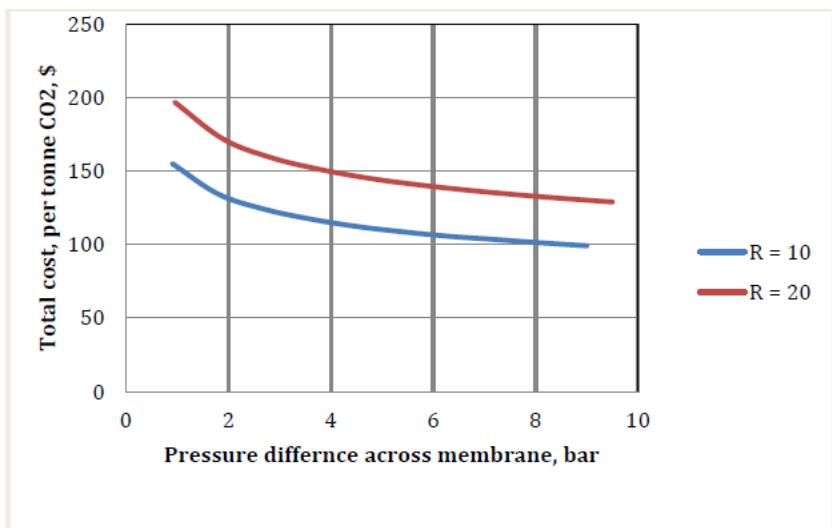


Figure 15. The effect of pressure difference across the membrane on the total Cost per tonne of CO<sub>2</sub> captured for a **two-stage membrane** system. R is the ratio of pressures on two sides of membrane.

### **The effect of fraction of feed remaining as raffinate**

The fraction of the feed that does not pass through the membrane raffinate) has a direct effect on the cost per tonne of CO<sub>2</sub> captured. As the fraction of feed remaining increases, the cost increases as well. This is shown in Figure 16.

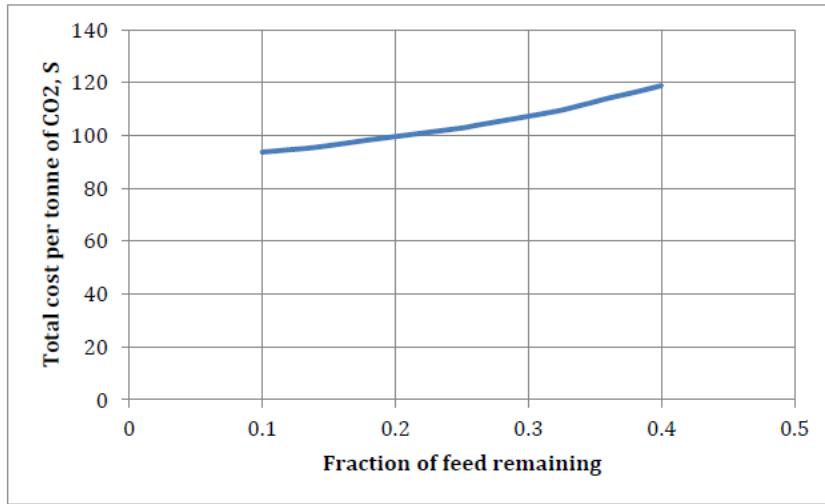


Figure 16. The effect of fraction of feed remaining as raffinate on the total cost per tonne of CO<sub>2</sub> captured for a two-stage membrane system.

### **The effect of price of cooling water**

The effect of the price of cooling water on the cost per tonne of CO<sub>2</sub> captured is given in Figures 17 and 18. As the price of water increase the cost per tonne of CO<sub>2</sub> will increase slightly.

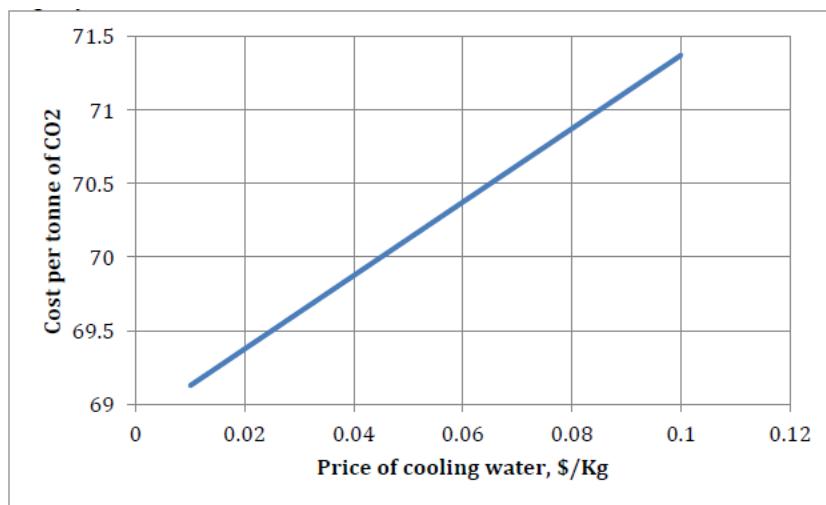


Figure 17. The effect of price of cooling water on the cost per tonne of CO<sub>2</sub> captured for a single stage membrane system

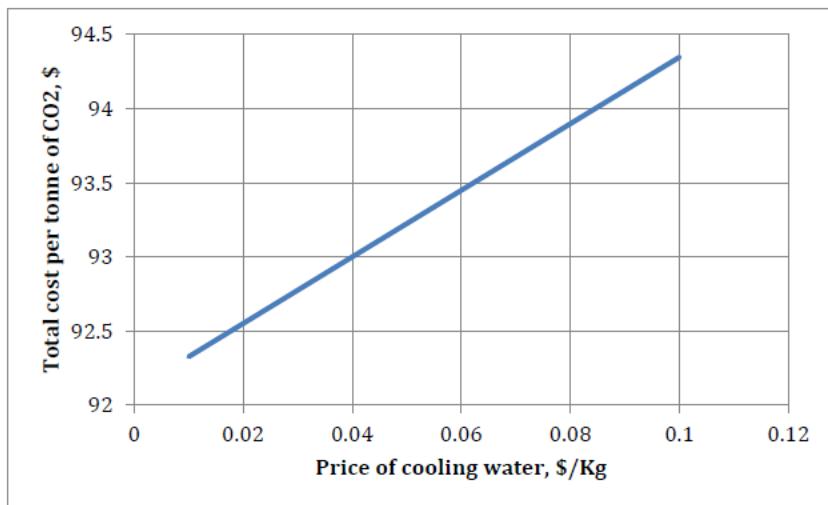


Figure 18. The effect of price of cooling water on the total cost per tonne of CO<sub>2</sub> captured for a two-stage membrane system.

### **The effect of price of membrane**

As predicted, the price of the membrane (\$/m<sup>2</sup>) has a direct effect on the cost per tonne of CO<sub>2</sub> removed. However as the price per meter square increases from \$15.00 to \$30.00, the cost per tonne of CO<sub>2</sub> increases slightly (Figure 19).

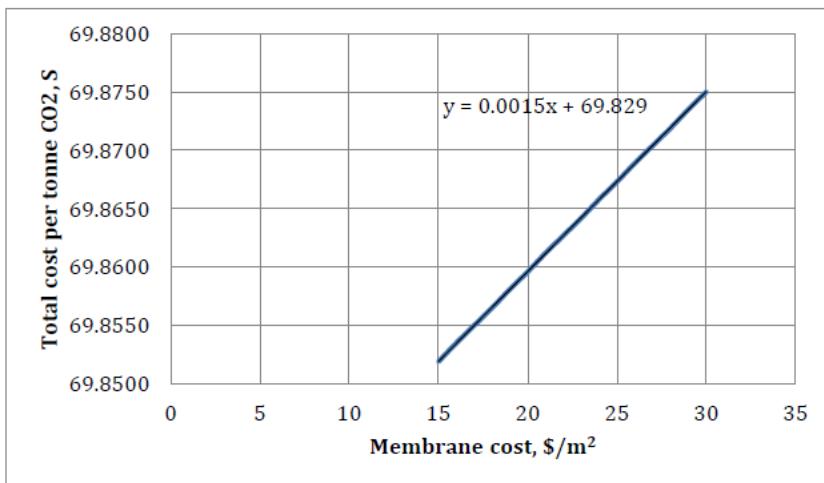


Figure 19. The effect of cost of membrane on the total cost per tonne of CO<sub>2</sub> captured for a single stage membrane system.

### **The effect of price of electricity**

The effect of price of electricity on the cost per tonne of CO<sub>2</sub> removed is shown in Figures 20 and 21. As the price of electricity increases, the cost increases considerably. This is mainly due to the amount of electricity needed for the compressors in the process.

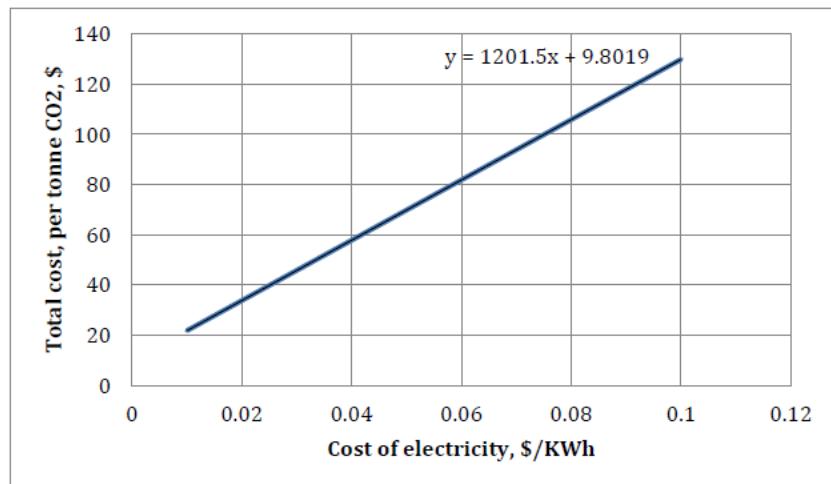


Figure 20. The effect of cost of electricity on the total cost per tonne of CO<sub>2</sub> captured for a single stage membrane system.

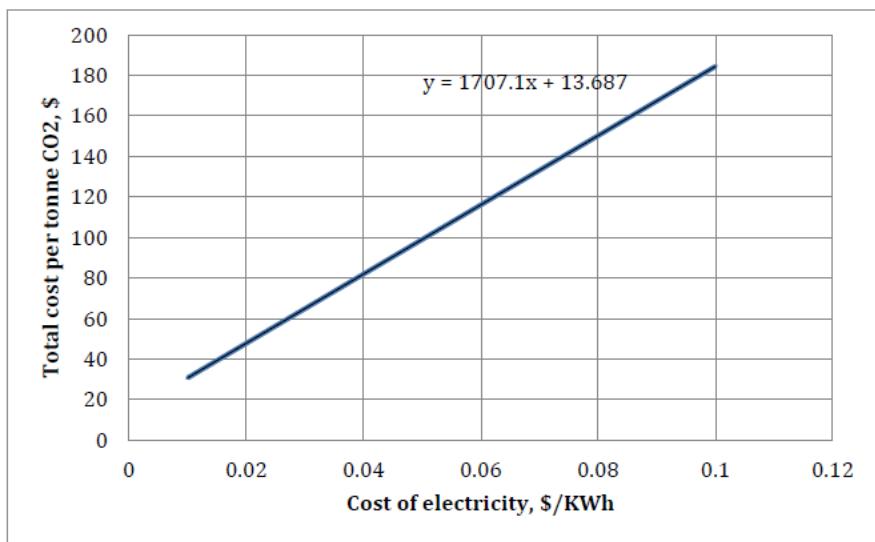


Figure 21. The effect of price of electricity on the total cost per tonne of CO<sub>2</sub> captured for a two-stage membrane system.

### **The effect of temperature of cooling water out of heat exchangers**

The effect of temperature of cooling water exiting heat exchangers on the cost of process is given in Figure 22. As the temperature increases, the cost per tonne of CO<sub>2</sub> removed decreases.

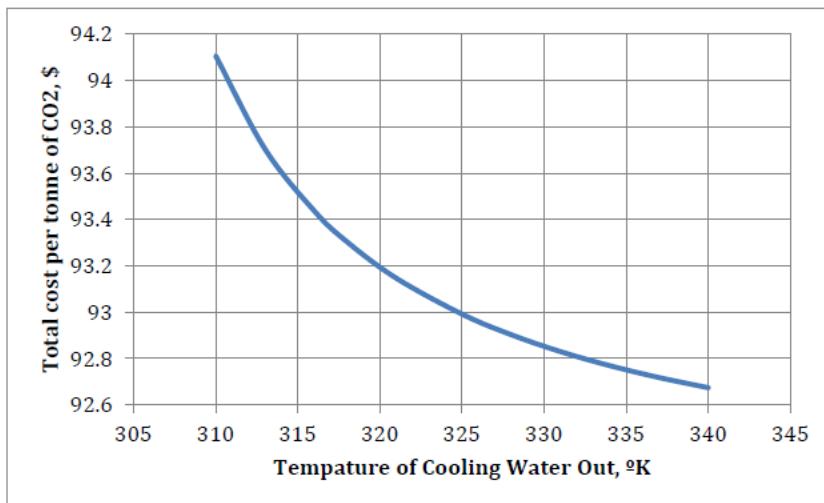


Figure 22. The effect of temperature of cooling water out of heat exchangers on total cost per tonne of CO<sub>2</sub> for a two-stage membrane system.

### **The effect of number of stages**

The effect of the number of stages on the cost can be found from Figures 14, 15 (the effect of pressure difference); Figures 17, 18 (the effect of water price); and Figures 20, 21 (the effect of electricity price). All these figures show that the cost for a two-stage membrane system is higher than for a single stage system.

## Adsorption Performance Studies

The mathematical model developed for the adsorption of CO<sub>2</sub> and N<sub>2</sub> was used to determine the effect of different process variables on performance and the results are presented here. The set of partial differential equations were solved numerically by the reduction to a set of ordinary differential equations using the “Method of Lines”. A mathematical algorithm to solve the coupled equations was developed and implemented into a computer program using MATLAB (V.7.1) Software.

The model determines the outlet adsorbate concentration at different times based on different operating conditions. The parameters used in the simulation are given in below.

### Model parameters value for simulation for Zeolite 13X

Parameter	Value
Bed porosity	0.4
Density of particles	0.00187 kg/cm <sup>3</sup>
Concentration of CO <sub>2</sub> in flue gas	4.09 x 10 <sup>-6</sup> mol/cm <sup>3</sup>
Concentration of N <sub>2</sub> in flue gas	3.68 x 10 <sup>-5</sup> mol/cm <sup>3</sup>
Mass transfer coefficient for CO <sub>2</sub>	0.0087 s <sup>-1</sup>
Mass transfer coefficient for N <sub>2</sub>	0.0182 s <sup>-1</sup>
Langmuir constant (k) for CO <sub>2</sub>	4097.3 cm <sup>3</sup> /kg
Langmuir constant (m) for CO <sub>2</sub>	0.177 mol/kg
Langmuir constant (k) for N <sub>2</sub>	23.92 cm <sup>3</sup> /kg
Langmuir constant (m) for N <sub>2</sub>	0.120 mol/kg

The model was used to determine the effect of different variables on the breakthrough curves, and the results are given below. The operating conditions for all the calculations were 1atm and 25 °C.

### The effect of inlet velocity on adsorption

The effects of inlet velocity on breakthrough curves of carbon dioxide from a mixture of CO<sub>2</sub> / N<sub>2</sub> are given in Figures 1 and 2 for bed lengths of 800 cm and 80 cm respectively. In these figures, the ratio of CO<sub>2</sub> concentration at the exit of adsorber (°C) to the concentration of CO<sub>2</sub> in the feed (C<sub>0</sub>) is plotted against time. As the velocity increases, the breakthrough curve becomes steeper and the break point time decreases. It should be noted that as the length of adsorber increases (more adsorbent), the breakthrough time increases too.

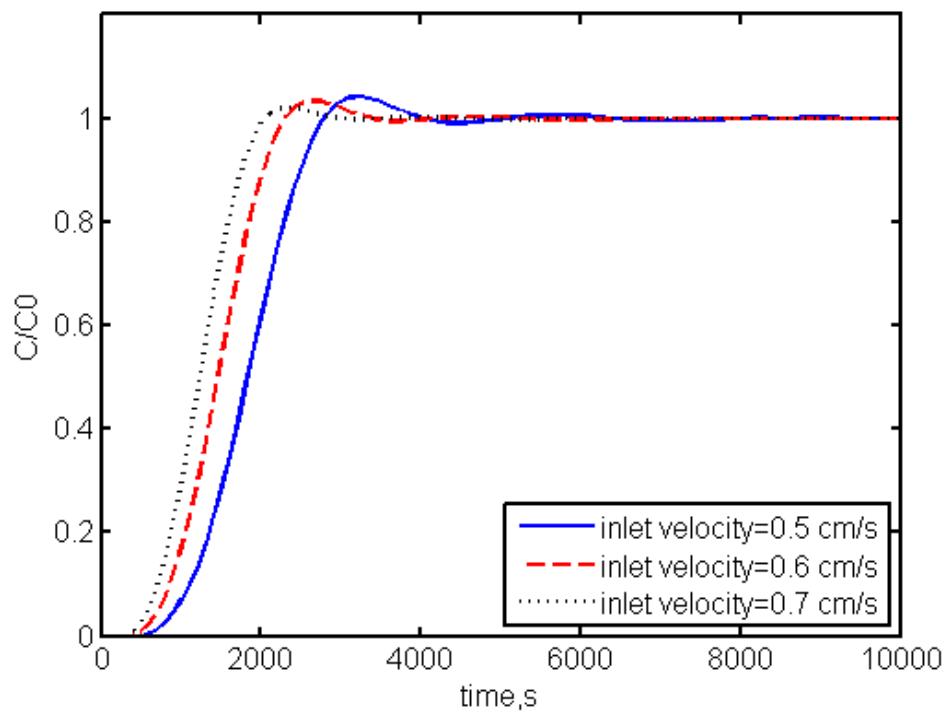


Figure 1. The effect of inlet velocity on adsorption of  $\text{CO}_2$  from a mixture of  $\text{CO}_2 / \text{N}_2$  on Zeolite 13X for a bed length of 800 cm.  $C_0$  is inlet concentration of  $\text{CO}_2$ .

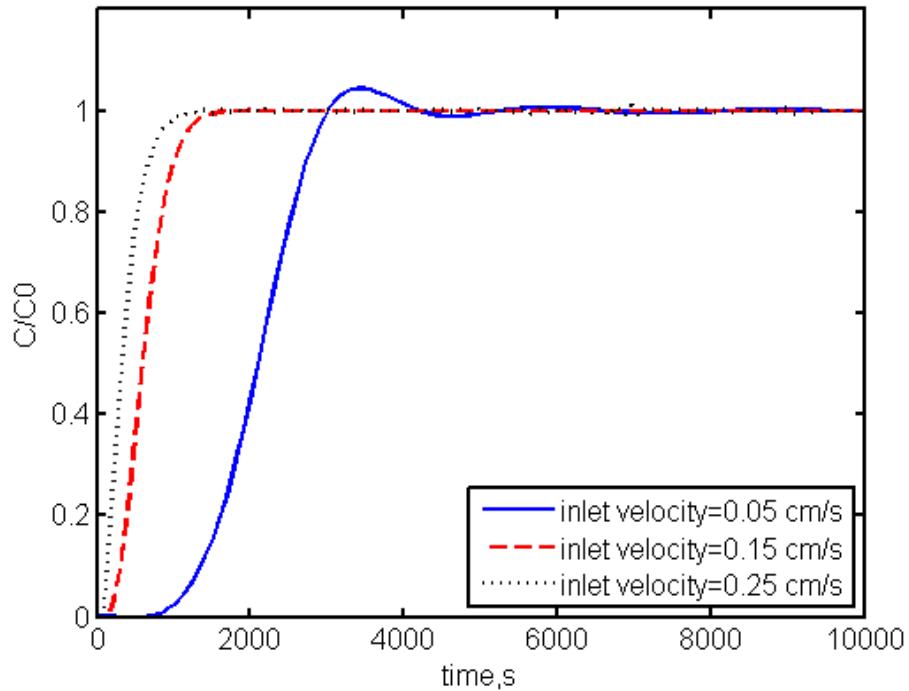


Figure 2. The effect of inlet velocity on adsorption of  $\text{CO}_2$  from a mixture of  $\text{CO}_2 / \text{N}_2$  on Zeolite 13X for a bed length of 80 cm.  $C_0$  is inlet concentration of  $\text{CO}_2$ .

### **The effect of bed height on adsorption**

The effect of bed height on the effluent adsorbate concentration is presented for inlet velocity of 0.5 cm/s in figures 3 through 7. It is observed that as the bed height increases, the breakthrough time increases. This shows that at smaller bed height the effluent adsorbate concentration ratio increases more rapidly than for a higher bed height. Smaller bed height corresponds to less amount of adsorbent. Consequently, a smaller capacity for the bed to adsorb molecules from the gaseous mixture and a faster increase in rate of adsorption is expected.

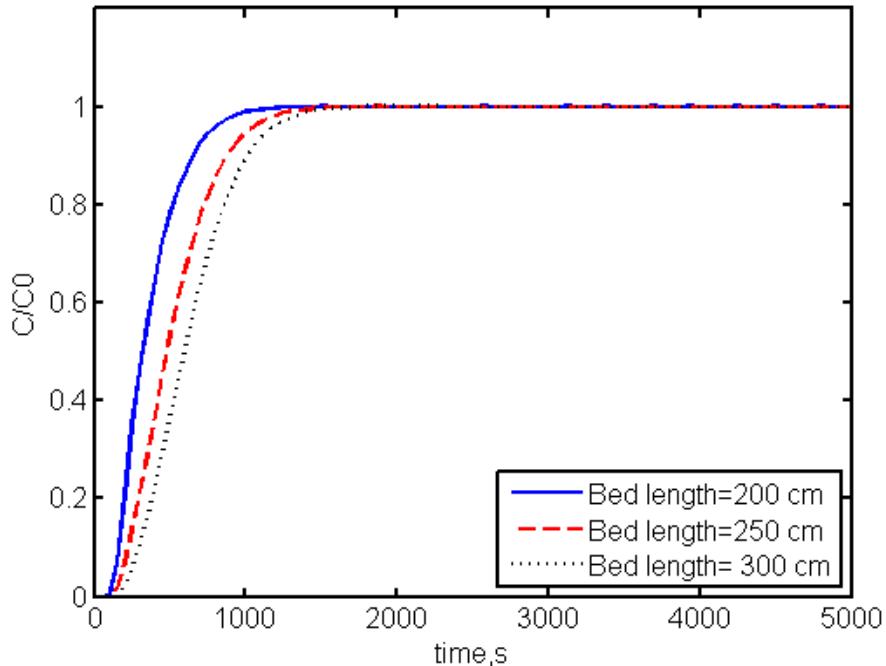


Figure 3. The effect of the length of Zeolite 13X bed on adsorption of  $\text{CO}_2$  from a mixture Of  $\text{CO}_2$  /  $\text{N}_2$  for an inlet velocity of 0.5 cm/s.  $C_0$  is inlet concentration of  $\text{CO}_2$

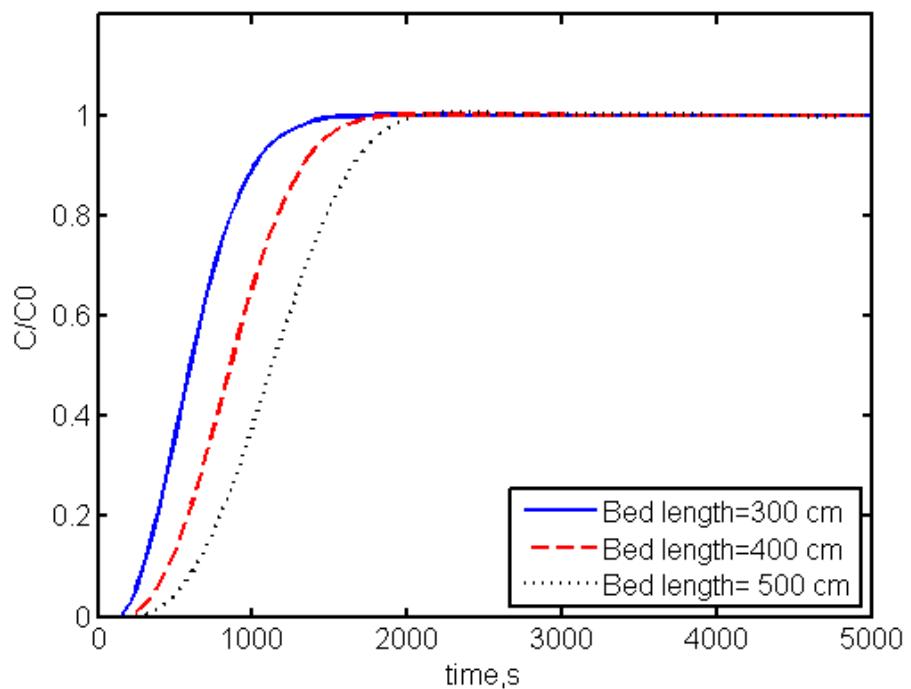


Figure 4. The effect of the length of Zeolite 13X bed on adsorption of  $\text{CO}_2$  from a mixture of  $\text{CO}_2 / \text{N}_2$  for an inlet velocity of  $0.5 \text{ cm/s}$ .  $C_0$  is inlet concentration of  $\text{CO}_2$

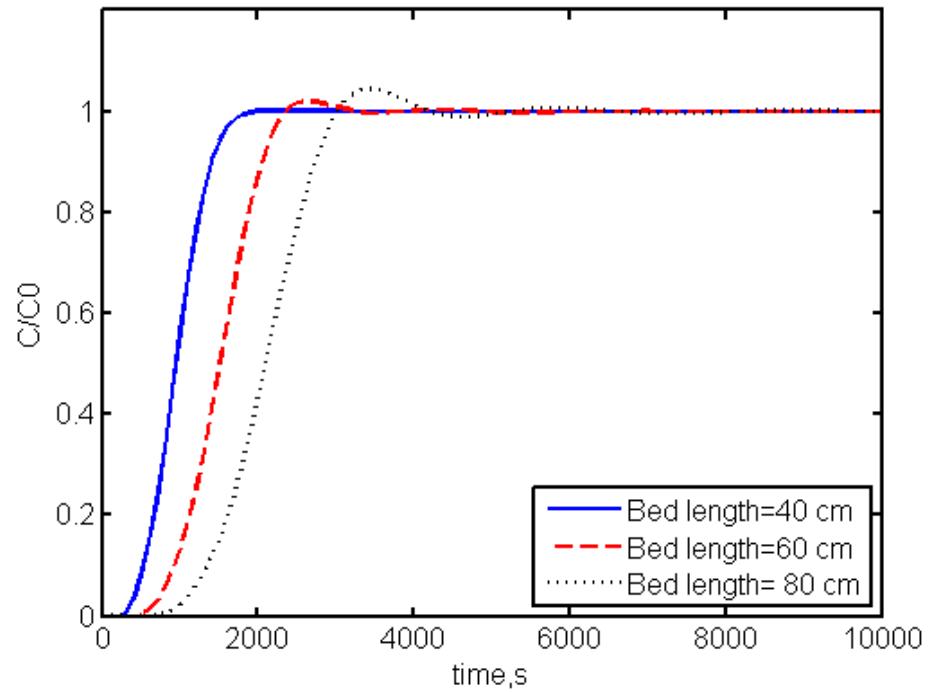


Figure 5. The effect of the length of Zeolite 13X bed on adsorption of  $\text{CO}_2$  from a mixture of  $\text{CO}_2 / \text{N}_2$  for an inlet velocity of  $0.05 \text{ cm/s}$ .  $C_0$  is inlet concentration of  $\text{CO}_2$

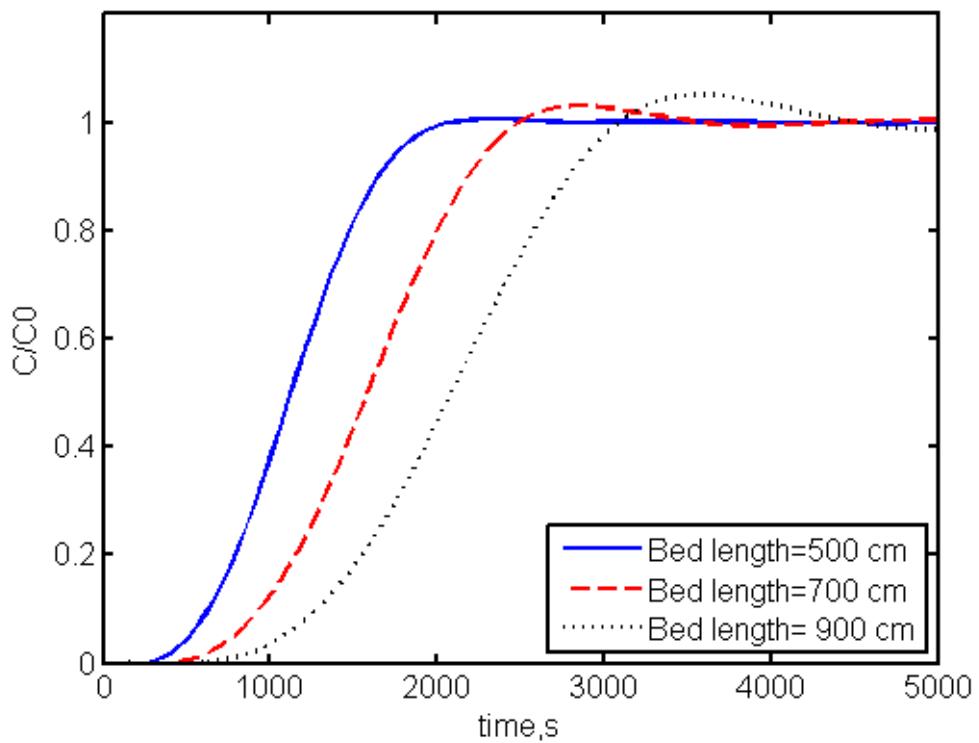


Figure 6. The effect of the length of Zeolite 13X bed on adsorption of  $\text{CO}_2$  from a mixture of  $\text{CO}_2 / \text{N}_2$  for an inlet velocity of  $0.5 \text{ cm/s}$ .  $C_0$  is inlet concentration of  $\text{CO}_2$

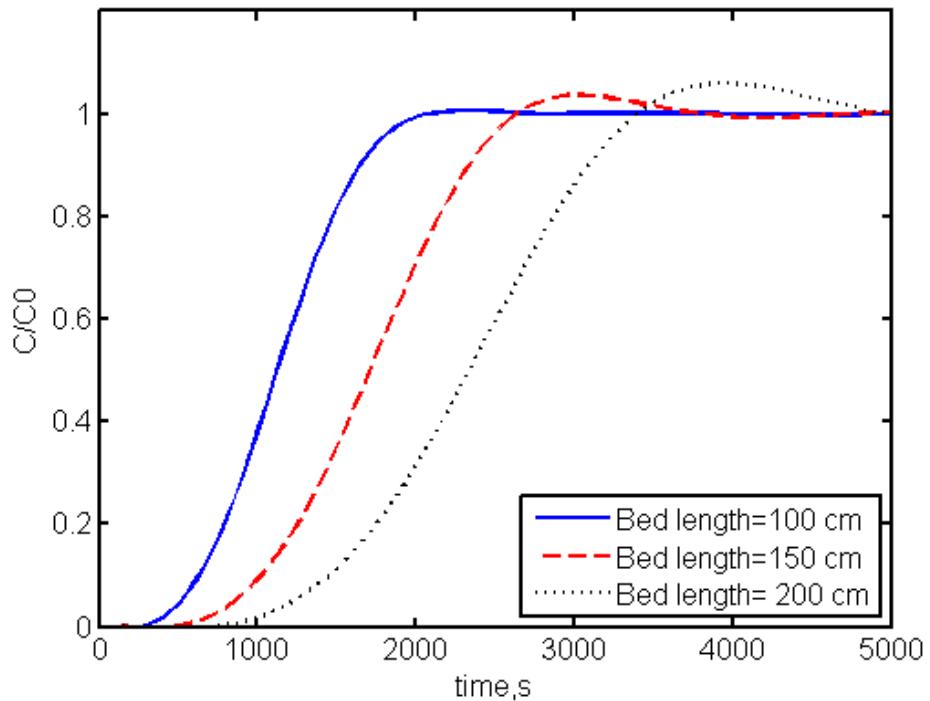


Figure 7. The effect of the length of Zeolite 13X bed on adsorption of  $\text{CO}_2$  from a mixture of  $\text{CO}_2 / \text{N}_2$  for an inlet velocity of  $0.1 \text{ cm/s}$ .  $C_0$  is inlet concentration of  $\text{CO}_2$

### **Desorption curves of CO<sub>2</sub>**

The model was also used to predict desorption of CO<sub>2</sub> from adsorbents. Desorption curves for Zeolite 13X are given in Figures 8 and 9. Figure 8 shows the effects of inlet velocity on desorption of CO<sub>2</sub> from the adsorbent. As the velocity increases from 1.05 to 1.55 cm/s, desorption curve changes slightly. In both cases, 90% of CO<sub>2</sub> is removed from the adsorbent in about 800 seconds. The effects of bed length on desorption curve are shown in Figure 9. As the bed length increase from 50 to 80 cm, the desorption curves remain almost the same, and desorption completes within 800 seconds.

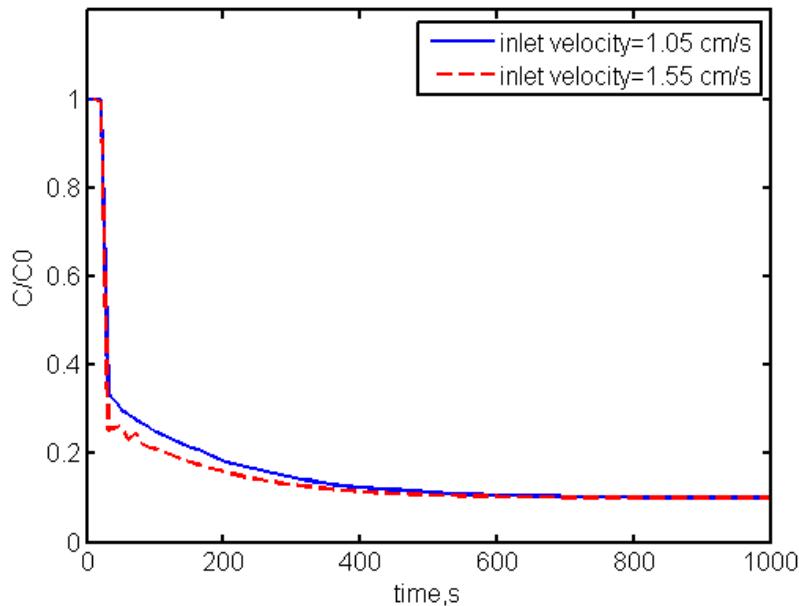


Figure 8. The effect of inlet velocity on desorption of CO<sub>2</sub> from Zeolite 13X for a bed length of 80 cm. C<sub>0</sub> is inlet concentration of CO<sub>2</sub>

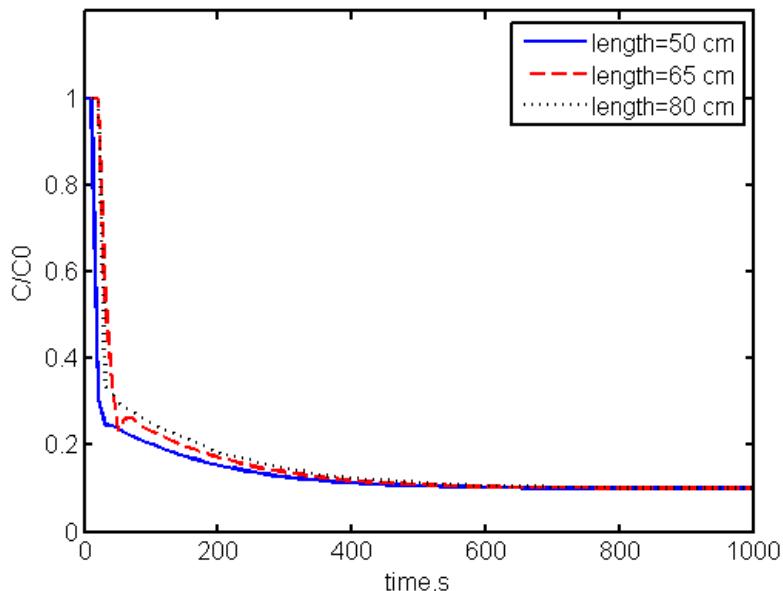


Figure 9. The effect of the length of Zeolite 13X bed on desorption of CO<sub>2</sub> for an inlet velocity of 1.05 cm/s. C<sub>0</sub> is inlet concentration of CO<sub>2</sub>

## Adsorption Cost Studies

An Excel spread sheet was developed that can be used to estimate cost of CO<sub>2</sub> avoided for an adsorption unit. The user can set the parameters for the adsorption unit, and get an estimate for the cost of capture for CO<sub>2</sub>. The model developed for the capture of CO<sub>2</sub> in an adsorption process was used to determine the effect of different process variables on the cost per tonne of CO<sub>2</sub> avoided and the results are shown in Figures 1-20.

### Velocity

The effect of flue gas velocity in the adsorber on the cost of capture is given in Figure 1. As the velocity increases, the cost per tonne of CO<sub>2</sub> avoided is creased exponentially. At velocities higher than 1.5 m/s the rate of decrease in the cost is very small and the cost remains almost constant.

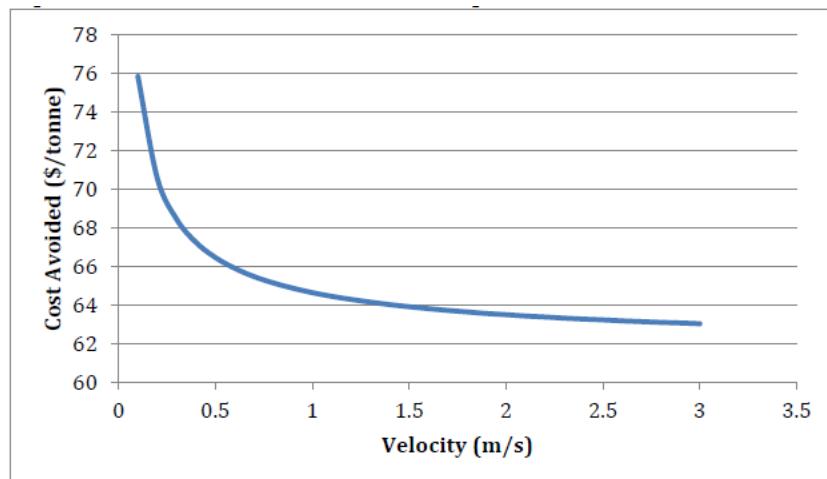


Figure 1. The effect of gas velocity in the adsorber on the cost of CO<sub>2</sub> avoided.

### Percent CO<sub>2</sub> Removal

The adsorber is designed to remove a specific percentage of the CO<sub>2</sub> from the flue gas. Figure 2 shows that as the percent CO<sub>2</sub> removal increases from 93% to 97%, the cost of capture is decreased from \$66.5 to \$62.5 per tonne of CO<sub>2</sub>.

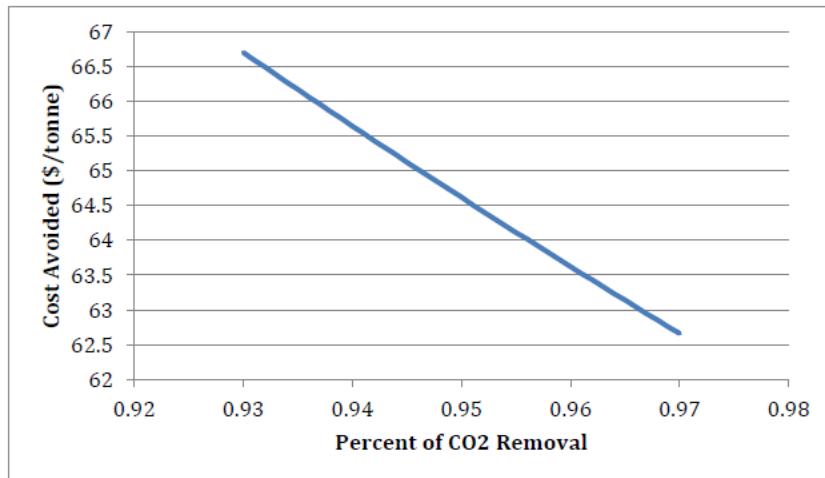


Figure 2. The effect of percent CO<sub>2</sub> recovery in adsorber on the cost of CO<sub>2</sub> avoided.

### Pressure

The effect of pressure on the cost of capture is given in Figures 3-5. The results for adsorption and desorption pressure (Figures 3 and 4) show that to reduce the cost, adsorption pressure should not be very high, and desorption pressure should not be very low. In fact the ratio of the two pressures should be as low as possible. The effect of CO<sub>2</sub> pressure on the cost is given in Figure 5. This is the pressure of CO<sub>2</sub> leaving the capture unit (to be transported through pipelines). This figure shows that the cost of CO<sub>2</sub> compression could be significant.

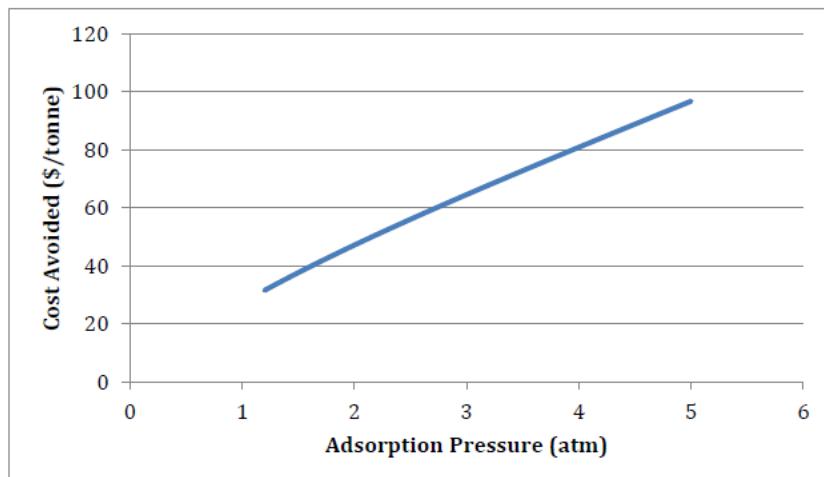


Figure 3. The effect of adsorption pressure on the cost of CO<sub>2</sub> avoided.

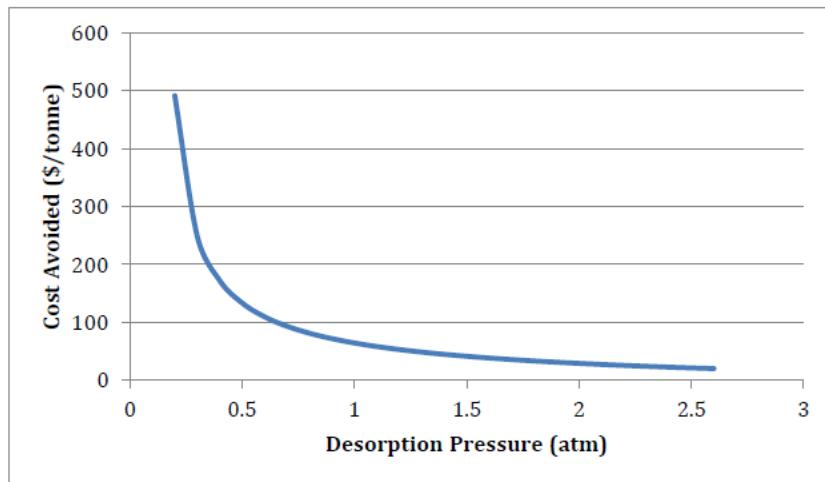


Figure 4. The effect of desorption pressure on the cost of CO<sub>2</sub> avoided.

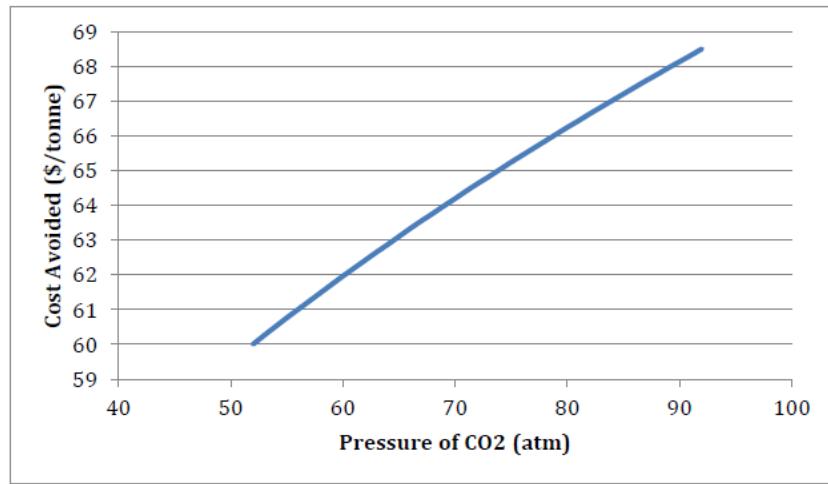


Figure 5. The effect of CO<sub>2</sub> pressure on the cost of CO<sub>2</sub> avoided.

### **Price of Adsorbent and Utilities**

The effect of the price of adsorbent and utilities are given in figures 6-8. Figures 6 and 7 show that the prices of adsorbent and cooling water do not have much effect on the cost of capture. However, price of electricity (Figure 8) has a significant effect on the total cost of CO<sub>2</sub> capture.

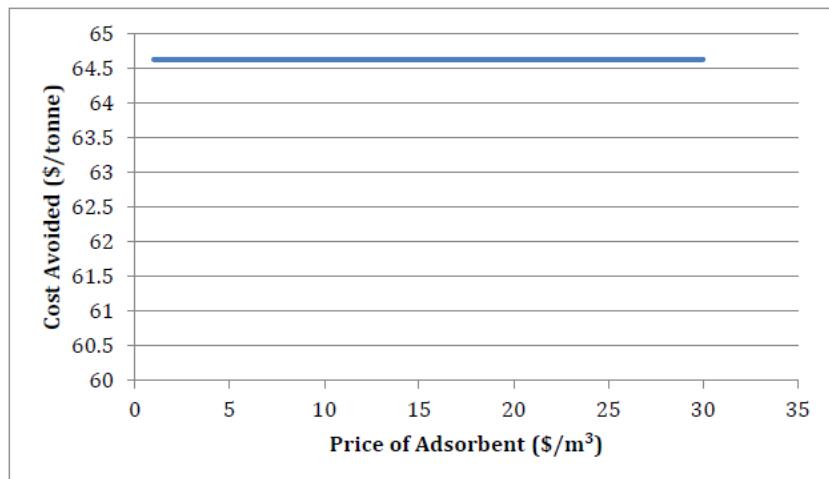


Figure 6. The effect of price of adsorbent on the cost of CO<sub>2</sub> avoided.

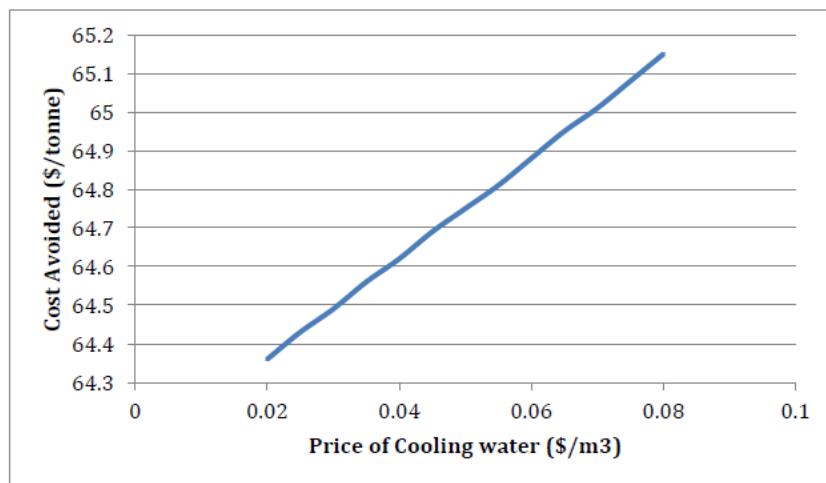


Figure 7. The effect of price of cooling water on the cost of CO<sub>2</sub> avoided.

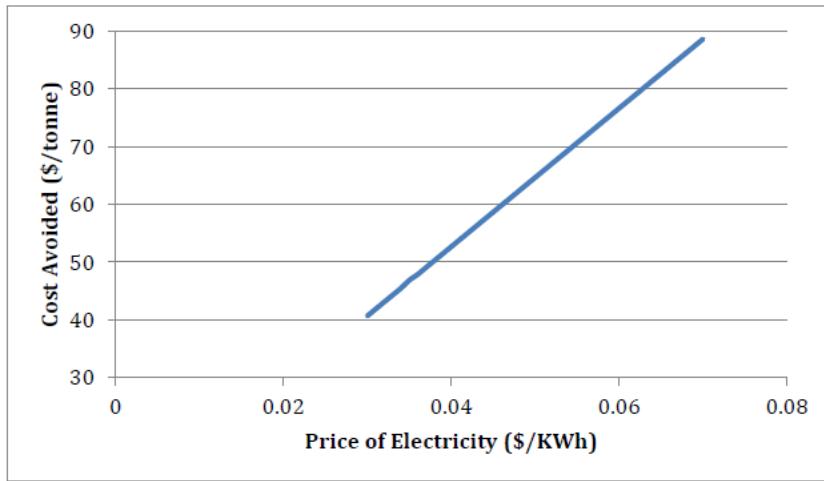


Figure 8. The effect of price of electricity on the cost of CO<sub>2</sub> avoided.

### Efficiencies

The effects of the efficiencies of compressor units (motor and compressor) are given in Figures 9 and 10. These figures show that efficiencies play an important role in managing the cost of CO<sub>2</sub> capture. A more efficient compressor unit could reduce the cost of capture significantly.

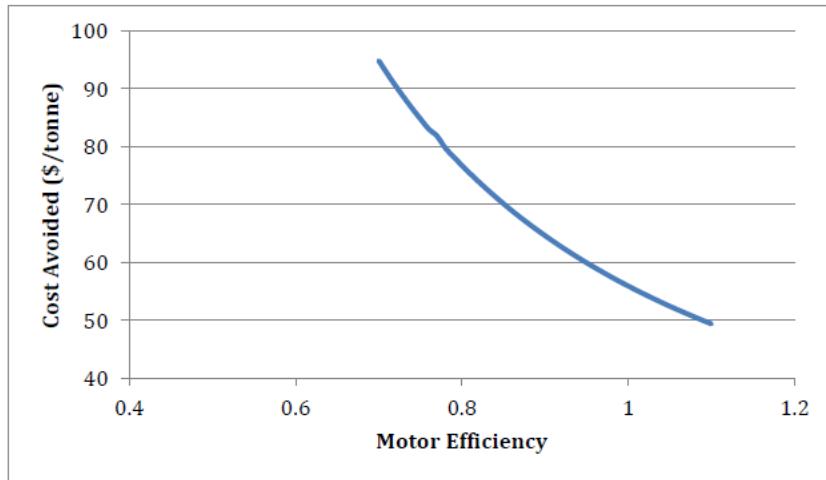


Figure 9. The effect of motor efficiency on the cost of CO<sub>2</sub> avoided.

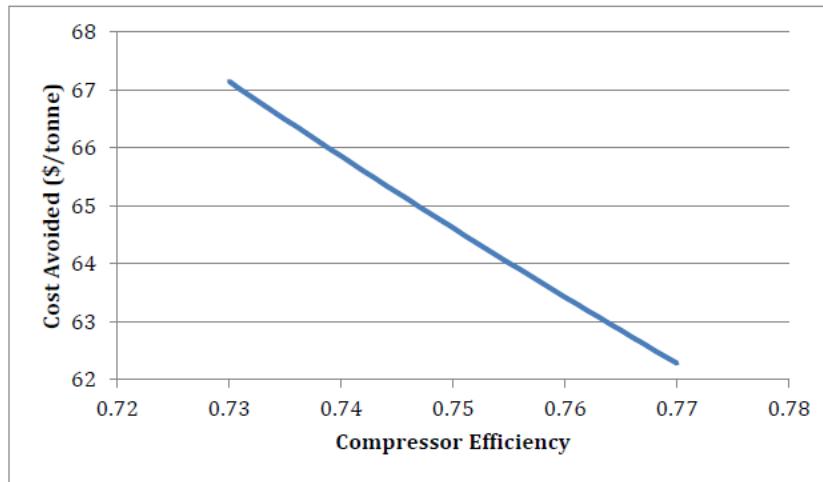


Figure 10. The effect of compressor efficiency on the cost of CO<sub>2</sub> avoided.

### Temperature

The effects of temperatures of cooling water in and out of heat exchangers and temperature of flue gas entering the unit are given in Figures 11-13. Figures 11 and 12 show that temperature of cooling water in and out of heat exchangers does not have much effect on the cost of CO<sub>2</sub> capture. Temperature of flue gas entering the adsorption unit (Figure 13) is an important factor in the cost of capture.

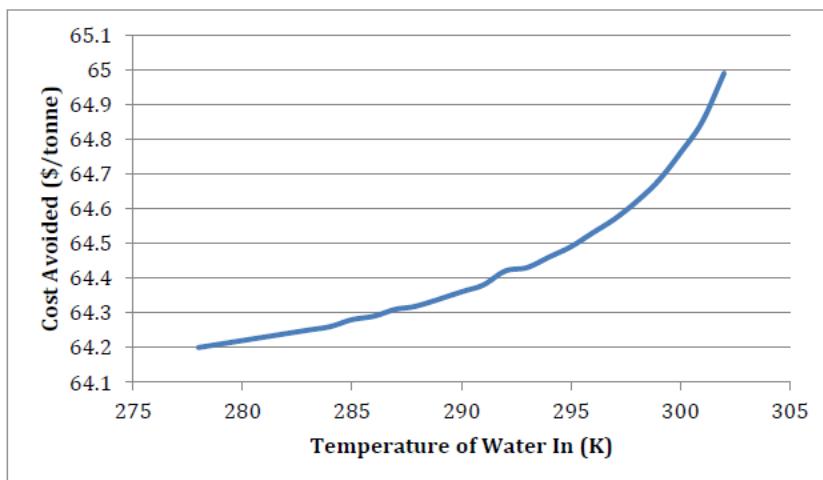


Figure 11. The effect of temperature of cooling water on the cost of CO<sub>2</sub> avoided.

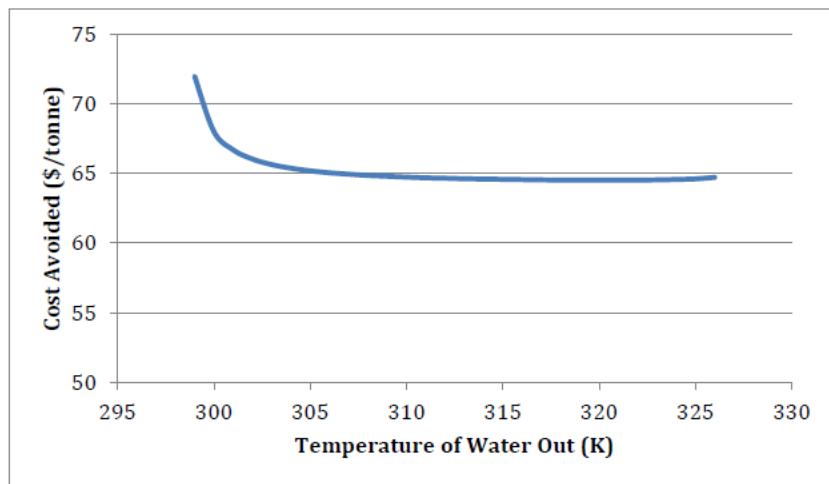


Figure 12. The effect of exit temperature of cooling water on the cost of CO<sub>2</sub> avoided.

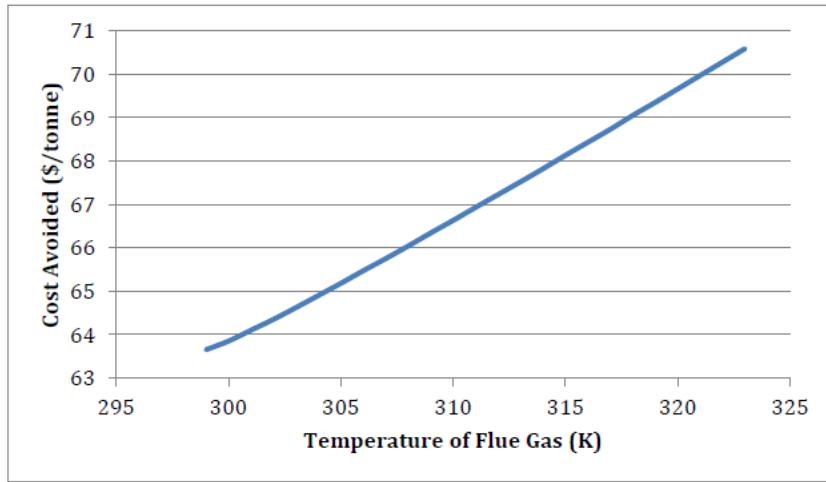


Figure 13. The effect of temperature of flue gas on the cost of CO<sub>2</sub> avoided.

### **Maintenance and Labor costs**

The effects of maintenance and labor costs are given in Figures 14 and 15. Figure 14 shows that if the maintenance cost is increased from 3% to 7% of fixed capital, cost increases by about \$1.50 per tonne of CO<sub>2</sub> avoided. The effect of labor cost (Figure 15) is less significant. If the labor cost increases from \$25/h to \$40/h, the cost of capture increases by \$0.50.

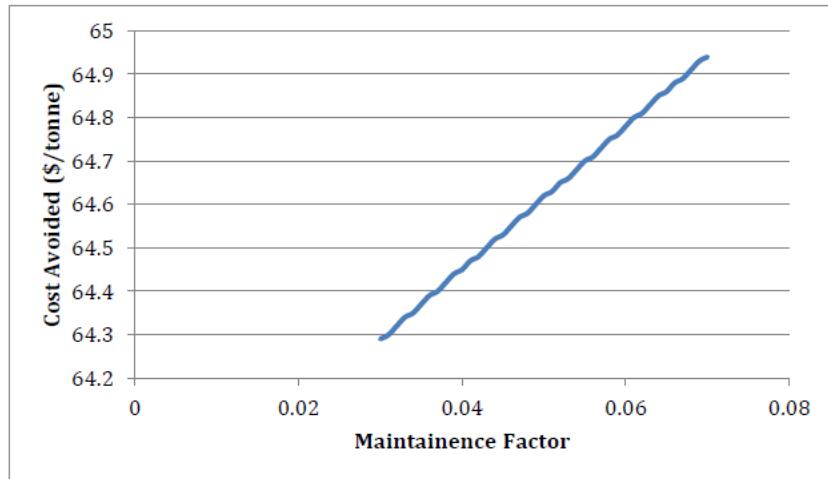


Figure 14. The effect of maintenance factor on the cost of CO<sub>2</sub> avoided.

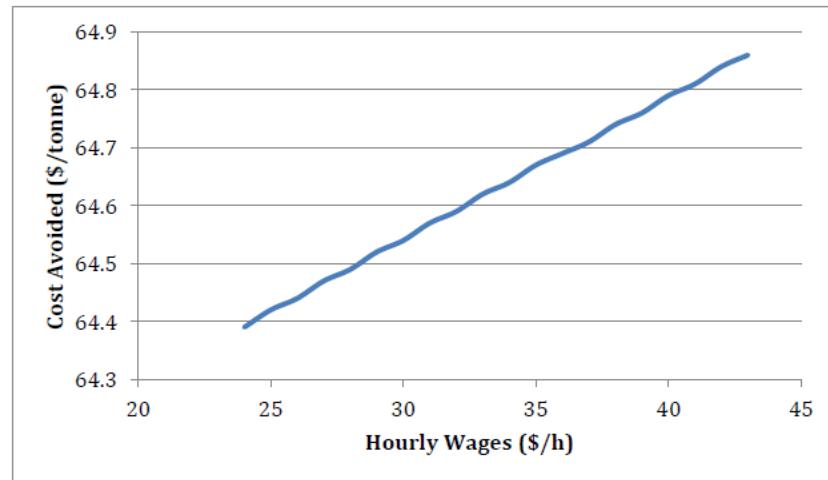


Figure 15. The effect of hourly wages on the cost of CO<sub>2</sub> avoided.

### **Interest rate and inflation**

The effects of interest rate and inflation (chemical engineering cost index) on the cost of CO<sub>2</sub> capture are given in Figures 16 and 17 respectively. These figures show that the effects are insignificant.

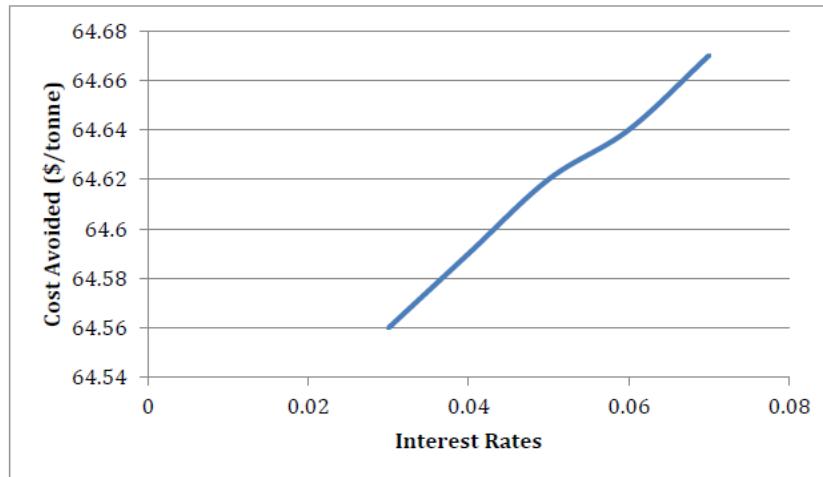


Figure 16. The effect of interest rate on the cost of CO<sub>2</sub> avoided.

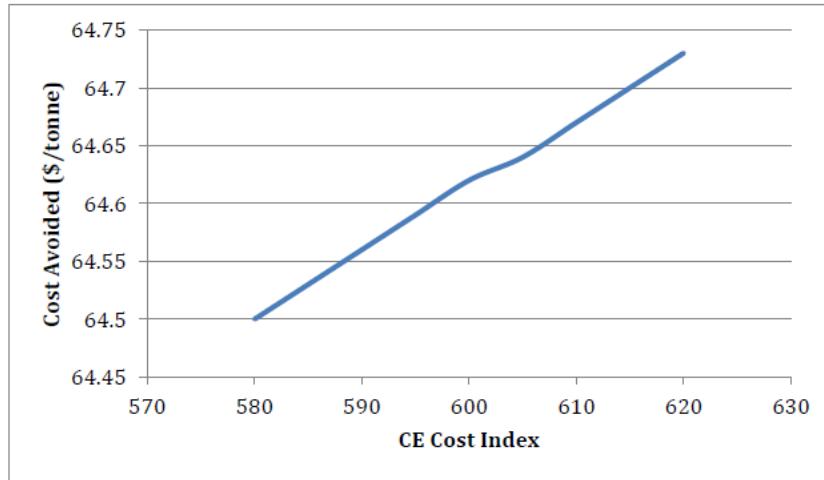


Figure 17. The effect of chemical engineering cost index on the cost of CO<sub>2</sub> avoided.

### **Other Process Variables**

The effects of Lang factor (in calculating fixed capital), hours of operation per year, and recovery period (in calculating depreciation) are given in Figures 18 through 20, respectively. Increasing Lang factor from 3.4 to 3.8 increases the cost for about \$0.40. The hours of operation has also have a small effect on the cost. If the process is operated eleven months a year (8,000 hours) instead of 10 months a year (7200 hours), the cost of capture is reduced by \$0.50 per tonne of CO<sub>2</sub>. Recovery period has no significant effect of the cost.

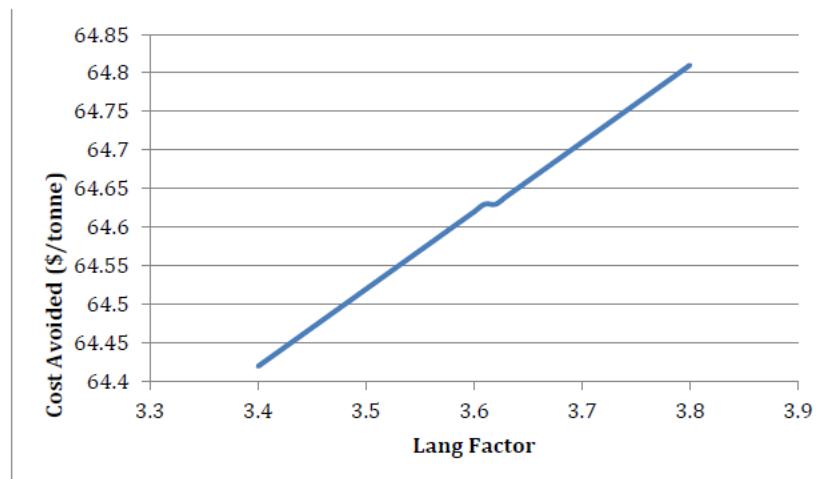


Figure 18. The effect of Lang factor on the cost of CO<sub>2</sub> avoided.

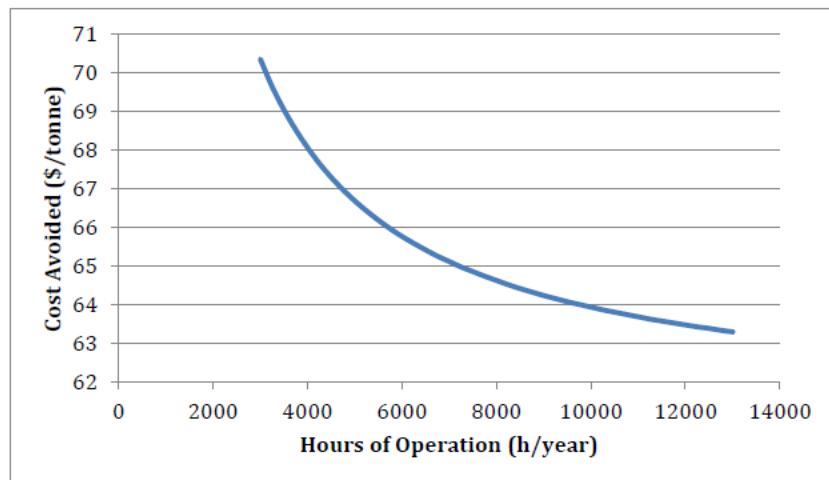


Figure 19. The effect of hours of operations per year on the cost of CO<sub>2</sub> avoided.

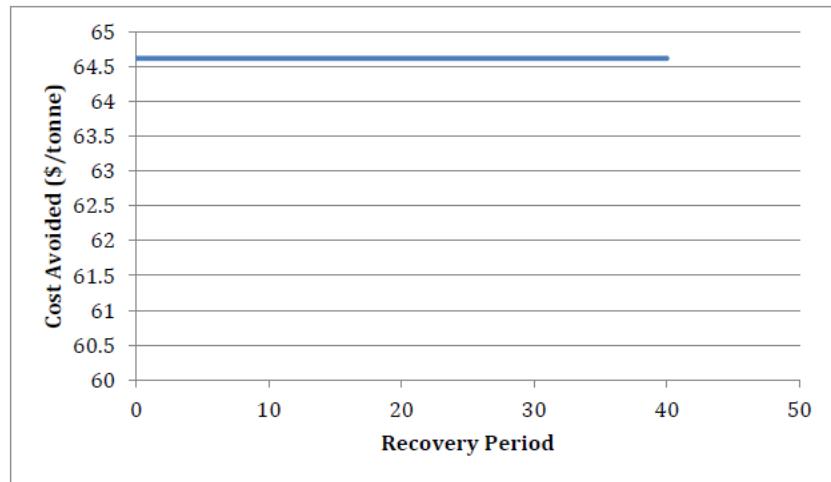


Figure 20. The effect of recovery period on the cost of CO<sub>2</sub> avoided.

# Training and Outreach

While an effective and affordable carbon capture process is an essential part of a successful carbon capture and storage (CCS) industry, the other important part of such an industry is workforce. Future scientists and engineers are needed to design new processes and work in these processes. A key objective for this project was to provide training/education in the field of study. Training and workforce preparation was accomplished student participation in the model development and evaluation activities described previously, and to a broader community through the development and implementation of short courses, networking, intern opportunities and through presentations at national meetings.

## CCS Short Course

Tuskegee University leveraged the extensive experience of its expert team to utilize and adapt existing CCS course material and teaching methods into a short course open to the university community. The short course, which included classroom lecture and interactive learning exercises, was conducted annually and covered all aspects of CCS systems. The course addressed the critical issues of capture costs, energy requirements and purity of CO<sub>2</sub> streams. National and regional experts participated as faculty for the short course.

The “First Annual Tuskegee Forum on Carbon Capture and Storage (CCS) Technologies” was held on March 8, 2010, in Kellogg’s Conference Center on the campus of Tuskegee University. Ten faculty members and over 30 students attended the workshop. There were five speakers who discussed the different aspects of CCS, as follows:

- *CCS in the Context of Energy and Climate Change Policy* – Ms. Pamela Tomski, Managing Partner, EnTech Strategies
- *Carbon Capture and CCS Research at Tuskegee University* – Dr. Nader Vahdat, Chemical Engineering Department, Tuskegee University
- *Geologic Storage & Southern Company’s Regional CCS Activities* – Dr. Jim Redwine, Geologist, Southern Company
- *CCS Projects at Shell* – Mrs. Davida D. Smith, Program Manager, Shell Lubricants
- *Key CCS Research Needs*, Mr. Logan Hansen, Geophysicist and Research Associate, EnTech Strategies

The “Second Annual Tuskegee Forum on Carbon Capture and Storage (CCS) Technologies” was held on April 26, 2011, in the Kellogg Conference Center on the campus of Tuskegee University. Several faculty members and more than forty students attended the seminar. There were three speakers who discussed the different aspects of CCS, as follows:

- Pamela Tomski, “CCS in the context of energy and climate change policy”, Presented at the Second Annual Tuskegee Forum on Carbon Capture and Storage

(CCS) Technologies, April 26, 2011, Tuskegee, AL

- Nader Vahdat, “Carbon capture and CCS Research at Tuskegee University”, Presented at the Second Annual Tuskegee Forum on Carbon Capture and Storage (CCS) Technologies, April 26, 2011, Tuskegee, AL
- David Smith, “Green Energy at Shell Company”, Presented at the Second Annual Tuskegee Forum on Carbon Capture and Storage (CCS) Technologies, April 26, 2011, Tuskegee, AL

The third CCS Short Course was conducted on March 11, 2013, at the Kellogg’s Center on the campus of Tuskegee University. Fifty students and several faculty members attended the conference. There were three presenters in the workshop:

- Ms. Pamela Tomski, Managing Partner at En Tech Strategies, and Founder and Director of Research Experience in Carbon Sequestration
- Dr. Nader Vahdat, Tuskegee University
- Dr. Craig Griffith, Petroleum Engineer with the Bureau of Ocean Energy Management

Ms. Tomski gave an overall presentation on the need for CO<sub>2</sub> capture and storage. She discussed the status of the several ongoing projects in the different states. Dr. Vahdat gave a presentation on the technologies for CO<sub>2</sub> capture. He discussed pre- combustion, oxy-combustion and post-combustion methods. Dr. Griffith gave a presentation on CO<sub>2</sub> storage and the problems associated with it. The lectures were followed by a discussion session and reception, and the presentation materials were made available to participants.

## **Tuskegee CCS Network**

The Tuskegee CCS Network was established to create a CCS professional community among students and professors. This network met on a periodic basis and provided a platform to conduct outreach on the DOE/NETL project activities as well as other CCS technologies and deployment issues. The network facilitated hands-on training opportunities and future research collaborations.

Web/print materials were developed to provide a gateway to many levels of information including project activities, updates and events; CCS background papers and issue briefs and CCS web links. Project team members facilitated network linkages to other national CCS university groups, industry and research organizations through direct contact and web site links to enhance exposure and professional opportunities for Tuskegee University students. Paperwork to establish the Energy Club of Tuskegee University was completed and details were announced at the Second Annual Forum on CCS Technologies. Based on participant levels of interest, support was given to officially establish the organization with Tuskegee University. Web site content for the Energy Club and CCS Network was also completed. Furthermore, Tuskegee student researchers working on this project attended the DOE NETL Annual Carbon Sequestration Conference in Pittsburgh where network opportunities were facilitated.

## Internships

The project team facilitated internship/exposure opportunities that provided hands-on training for students to interact with industry and research organizations active in the CCS field. Information was provided to students regarding summer internship opportunities with DOE, and discussions were held with Southern Company and Shell regarding possible internship opportunities which were available through a competitive basis; support to Tuskegee student researchers was offered to assist with application preparation and follow-up for these internships opportunities. Students were provided with information on DOE's Mickey Leland Energy Fellowship, and with information for free membership to the American Institute of Chemical Engineers and internship database. Furthermore, an internship for Tuskegee University students was created by EnTech Strategies, LLC and Southern Company under the Research Experience in Carbon Sequestration (RECS) program, in Birmingham, AL.

In addition to the internship opportunities presented, the following arrangements were made for a student visit to Washington, D.C.

- Participation in the Global CCS Institute Workshop on Global Opportunities and Strategic Directions at the Canadian Embassy;
- Appointment with U.S. Department of Energy, Office of Fossil Energy;
- Visit to Capitol Hill, Dirksen Senate Office Building, Senate Energy Committee;
- Visit to Howard University, Chemical Engineering Department, Dr. John Tharakan, Professor and Interim Chair; and
- Meeting with Tony Bray, Tuskegee alumni and President, The Booker T. Washington Foundation.

## Presentations

The following presentations/publications were completed under this project:

- Nader Vahdat, "Geological Sequestration Training and Research Program in Capture and Transport: Development of the Most Economical Separation Method for CO<sub>2</sub> Capture", Presented at the NETL/DOE Annual Meeting, February 23, 2011.
- Nader Vahdat, Marially Jean-Jacques and Kiara Moorer, "Development of a model to screen different absorption processes for possible use for CO<sub>2</sub> capture", Submitted for publication, Journal of Industrial Engineering Chemistry Research.
- Nader Vahdat, Marially Jean-Jacques and Kiara Moorer, "Development of a model to screen different absorption processes for possible use for CO<sub>2</sub> capture" presented at the Tenth annual Carbon Capture & Sequestration Conference, May 2-5, 2011, Pittsburgh, PA.
- Nader Vahdat, "Economic analysis of membrane systems for CO<sub>2</sub> capture", presented at the 2012 NETL CO<sub>2</sub> capture technology meeting Sheraton Square,

Pittsburgh, PA, July 9-12, 2012.

- Nader Vahdat, “Economic analysis of adsorption systems for CO<sub>2</sub> capture”, presented at the 2013 NETL CO<sub>2</sub> capture technology meeting Sheraton Square, Pittsburgh, PA, July 8-11, 2013.

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