

**A Project Report on**

**DYNAMIC MODELLING, SIMULATION AND  
COMPARISON OF LARGE SCALE CO<sub>2</sub> CAPTURE IN  
COAL FIRED POWER PLANT USING VARIOUS  
AMINE SOLVENTS**

**In partial fulfilment of the requirements for the degree in  
Bachelor of Technology in Chemical Engineering**

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**Department of Chemical Engineering  
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2014**



**CERTIFICATE**

This is to certify that the thesis entitled “**Dynamic Modelling, Simulation and Comparison of Large Scale Carbon Dioxide Capture in Coal Fired Power Plant using Various Amine Solvents**” submitted by Mr. Swaraj Panda, Roll no. 110CH0082, in partial fulfilment of the requirements for the award of degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the report has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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## ABSTRACT

The concentration of Carbon Dioxide ( $\text{CO}_2$ ) is rapidly increasing in the atmosphere with the economic and industrial development which hugely affects the living environment and the global climate.  $\text{CO}_2$  capturing is an excellent option to reduce its concentration from the environment which is a major concern among scientists and nations. Chemical absorption in post combustion capture of carbon dioxide ( $\text{CO}_2$ ) technology is the most feasible and economical technology to capture  $\text{CO}_2$ . In the present work, the efficacy of  $\text{CO}_2$  capturing were studied for three different amine solvents-monoethanolamine (MEA), a mixed solvent composed of methyldiethanolamine (MDEA) and piperazine (PZ), called activated MDEA (a-MDEA) and aqueous ammonia ( $\text{NH}_3$ ) solution. In the first part of this study, an Aspen Plus simulation model was developed and in the second part, the simulation model was used to carry out sensitivity analyses. The different key parameters for different solvents were also determined and analysed in the present study. For MEA, the key parameters were the effects of type of packing, solvent temperature and absorber height on the reboiler duty. Activated-MDEA has two key process parameters which are variation of PZ concentration in the mixed solvent and the solvent to feed ratio with the  $\text{CO}_2$  recovery and energy consumption in the reboiler of the stripper. Finally, a complete state-of-art study was done for aqueous  $\text{NH}_3$  solution on several key parameters like  $\text{NH}_3$  concentration,  $\text{CO}_2$  loading, absorber height, temperature of absorber and stripper, flow rate of lean and rich solvent, boilup ratio, condenser temperature, regeneration energy and the reboiler duty. In the final part of the study, an overall comparison is done between the three solvents by taking cost economics into consideration and thus recommending the best solvent for  $\text{CO}_2$  capturing in Post Combustion Capture using chemical absorption. Energy consumption is the major challenge for this process. Paralleling more columns or capturing a part of the overall flue gas can reduce the energy consumption.

**Keywords:** Amine Solvents;  $\text{CO}_2$  Capture; Chemical absorption; Methyldiethanolamine; Monoethanolamine; Piperazine

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## NOMENCLATURE

<b>Symbols</b>	<b>Subscripts</b>
<i>a</i> effective interfacial area ( $m^2m^{-3}$ )	<i>Amb</i> ambient
<i>A</i> cross-sectional area ( $m^2$ )	<i>Col</i> column
<i>c</i> molar concentration ( $molm^{-3}$ )	<i>Cond</i> conduction
<i>d</i> diameter (m)	<i>FG</i> flue gas
<i>E</i> enhancement factor (-)	<i>HX</i> heat exchanger
<i>G</i> gaseous mole flow ( $mol s^{-1}$ )	<i>i</i> species ( $1 \leq i \leq N$ )
<i>h</i> specific molar enthalpy ( $J mol^{-1}$ )	<i>in</i> inlet
<i>H</i> Henry constant ( $molm^{-3} atm^{-1}$ )	<i>Iso</i> insulation
<i>k</i> mass transfer coefficient ( $m s^{-1}$ )	<i>j</i> balance element
<i>L/G</i> liquid to gas ratio ( $m^3m^{-3}$ )	<i>Lean</i> lean solvent
<i>L</i> liquid mole flow ( $mol s^{-1}$ )	<i>r</i> reaction number ( $1 \leq i \leq R$ )
<i>M</i> molecular weight ( $kg mol^{-1}$ )	<i>Rich</i> rich solvent
<i>N</i> molar flow ( $mol s^{-1}$ )	<i>Reac</i> reaction
<i>Q</i> heat flow ( $J s^{-1}$ )	<i>Vap</i> evaporation
<i>R</i> universal gas constant ( $J mol^{-1}K^{-1}$ )	<b>Superscripts</b>
<i>s</i> wall thickness ( $m$ )	<i>B</i> bulk
<i>S</i> surface area ( $m^2$ )	<i>g</i> gas phase
<i>t</i> time (s)	<i>gl</i> gas to liquid
<i>T</i> absolute temperature (K)	<i>I</i> interface
<i>V<sub>m</sub></i> molar volume ( $m^3 mol^{-1}$ )	<i>L</i> liquid phase
<i>z</i> absorber column axis coordinate (m)	<i>lg</i> liquid to gas
<b>Greek symbols</b>	<i>ls</i> liquid to solid
$\alpha$ heat transfer coefficient ( $J s^{-1}m^{-2} K^{-1}$ )	<i>meas</i> measured
$\gamma$ activity coefficient	<i>s</i> solid column
$\epsilon$ void fraction of structured packing	<i>sa</i> solid to environment
$\eta$ separation efficiency	
$\theta$ temperature ( $^{\circ}C$ )	
$\Delta\theta$ temperature difference (K)	
$\lambda$ thermal conductivity ( $J s^{-1}m^{-1} K^{-1}$ )	
$\rho$ mass density ( $kgm^{-3}$ )	
$\xi$ relative column height	
$\chi$ mole fraction	
$\psi$ fractional volume holdup	
$\phi$ fugacity coefficient	

Carbon dioxide is a characteristic gas that permits daylight to enter the earth and then it additionally keeps a portion of this light from transmitting back into space, consequently warming the planet. More the carbon dioxide more will be the capture of sun's heat and thus more will be the global warming. This warming of the world's atmosphere is the impact of excessive CO<sub>2</sub> emissions. Human innovations such as transportation vehicles and rapid industrial development especially the power and steel plants use the fossil fuels extensively and discharge additional Carbon dioxide into the air. Since we've added (and keep on doing) this carbon dioxide to the environment, our Earth is getting more and more hot, which causes the temperature of the planet to gradually climb, a wonder called global warming. Carbon dioxide isn't the main contributing gas for this. Others incorporators are water vapor, methane, nitrous oxide, hydrofluorocarbon, perfluorocarbon and sulphur hexafluoride. Researchers appraise that worldwide Greenhouse gas outflow, because of human activities, expanded 70 % between 1970 and 2004. Carbon dioxide outflows alone developed 80 % in the same period. Numerous specialists accept that the methodology of carbon capture and sequestration can help us to get this number down to a safe level.

The Intergovernmental Panel on Climate Change expect the warming of the atmosphere framework, the expansion of worldwide normal temperature to the watched increment of the anthropogenic greenhouse gas (GHG) fixations in the climate. Carbon dioxide (CO<sub>2</sub>) is viewed as the most essential GHG, because of the reliance of world economies on fossil powers, since their burning action are the most imperative wellsprings of this gas. CO<sub>2</sub> capturing activities are expanding in the most recent decades primarily because of the increment of anthropogenic emanations. The methods including CO<sub>2</sub> capture and sequestration is picking up consideration on mainstream researchers as an elective for decreasing CO<sub>2</sub> emanation, lessening its focus in encompassing air. On the other hand, a few mechanical, economic and ecological issues and in addition security issues stay to be fathomed, for example, the accompanying needs: building of CO<sub>2</sub> capture effectiveness, decrease of procedure expenses, and check of natural practicality of CO<sub>2</sub> stockpiling. Carbon capturing includes trapping the carbon dioxide at its emanation source, transporting it to a stockpiling area (generally profound underground) and separating it. These methods we could conceivably get overabundance CO<sub>2</sub> right from the fossil fuel power plants, making greener vitality. Carbon capturing has really been used for quite some time. The oil and gas commercial enterprises have utilized carbon capturing for a long time as an approach to improve oil and gas recuperation. Just as of late have we have begun pondering catching carbon for natural reasons.

Presently, most of the research activities concentrates on carbon capturing at fossil fuel-controlled vitality plants, the wellspring of the greater part of man-made CO<sub>2</sub> emanations. Large portions of these power generation plants depend on coal to make vitality, and the blazing of coal transmits CO<sub>2</sub> into the climate. A few researchers imagine a future where all new power plants utilize carbon capture. There are three fundamental steps to carbon capturing and sequestration (CCS) - trapping and detaching the CO<sub>2</sub> from different gasses, transporting this caught CO<sub>2</sub> to a stockpiling area, and putting away that CO<sub>2</sub> far from the environment (underground or profound in the ocean). Carbon capture and sequestration is the

procedure of catching waste CO<sub>2</sub> from huge point sources, for example, power generation plants based on fossil fuels, transporting it to a stockpiling site and keeping it safely for further use. Besides they have been implemented into various innovative methods like artificial photosynthesis, creation of green steel and a lot of more. CO<sub>2</sub> capturing engineering is fundamentally done in 3 methodologies- pre-combustion capture, post-combustion capture, oxy-fuel combustion capture.

## 1.1 Carbon Dioxide Capturing Approaches

### 1.1.1 Post Combustion Capture

CO<sub>2</sub> is evacuated after burning of the fossil fuel. This is the plan that is connected to fossil-fuel blazing power plants. Here, carbon dioxide is caught from vent gasses at power generation stations or other huge point sources. The engineering is well comprehended and is right now utilized within other modern requisitions, despite the fact that not at the same scale as may be needed in a business scale power generation stations.

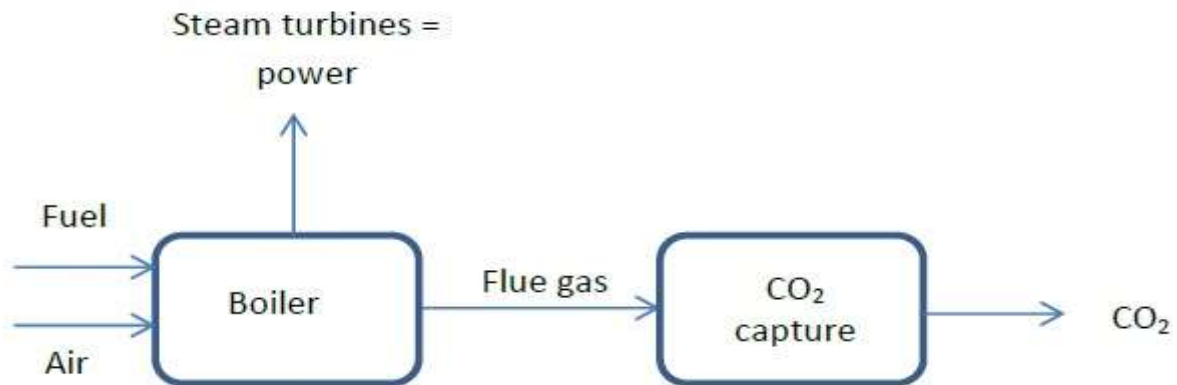


Figure 1 Post Combustion Capture

The greatest profit for utilizing this methodology is that it permits us to retrofit more seasoned power generation plants, by including a "channel" that helps trap the CO<sub>2</sub> as it goes up a fireplace or smokestack. This channel is really a solvent that assimilates carbon dioxide. The solvent can later be warmed, which will discharge water vapor and abandon a concentrated stream of CO<sub>2</sub>. Post-ignition carbon capturing can keep 80 to 90 percent of a power plant's carbon emanations from entering the environment. Anyway the post-ignition methodology obliges a ton of vitality to pack the gas, enough for transport.

### 1.1.2 Pre Combustion Capture

The engineering for pre-combustion capturing method is broadly connected in compost, substance, vaporous fuel (H<sub>2</sub>, CH<sub>4</sub>), and power generation. In these cases, the fossil fuel is part of the gas oxidized, in a gasifier. The ensuing syngas (CO and H<sub>2</sub>) is moved into CO<sub>2</sub> and H<sub>2</sub>. The ensuing CO<sub>2</sub> might be caught from a moderately unadulterated fumes stream. The H<sub>2</sub> can now be utilized as fuel; the carbon dioxide is uprooted before ignition happens.

The CO<sub>2</sub> is evacuated after ignition of fossil energizes, yet before the vent gas is stretched to environmental weight. This plan is connected to new fossil fuel smouldering force plants, or to existing plants where re-driving is an option. Pre-ignition carbon capturing is as of now being used for regular gas, and gives a much higher convergence of CO<sub>2</sub> than post-burning. The pre-combustion methodology is lower in expense, yet it's not a retrofit for more established fossil fuel fired power plant generators. Similarly as with post-ignition, pre-ignition carbon capture can keep 80 to 90 % of a power plant's CO<sub>2</sub> outflows from entering the air.

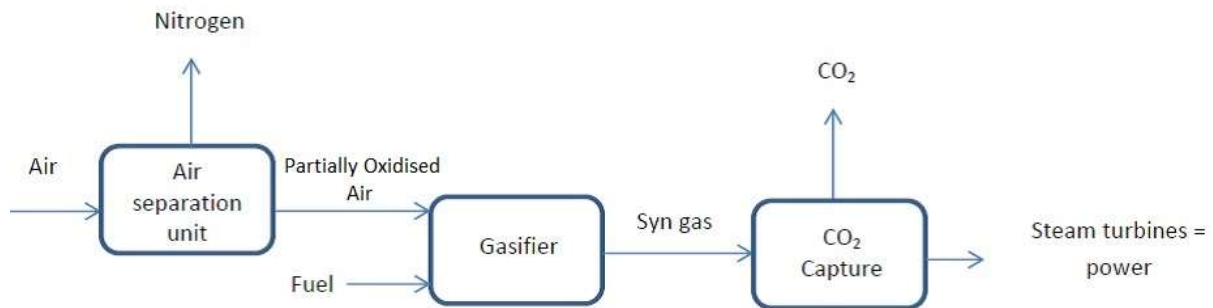


Figure 2 Pre Combustion Capture

### 1.1.3 Oxy-Fuel Combustion

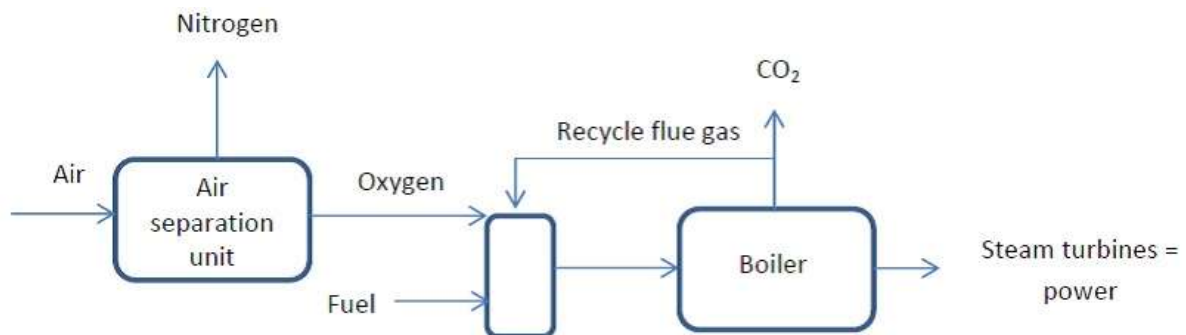


Figure 3 Oxy-Fuel Combustion

The fuel is blazed in oxygen rather than air. To cut down the ensuing fire temperatures to regular levels throughout the process of ignition, cooled pipe gas is re-flowed and infused into the burning chamber. The vent gas comprises of primarily carbon dioxide and water vapour, which becomes heavy on cooling. The outcome is a very nearly unadulterated carbon dioxide stream that might be transported to the sequestration site and put away. Courses of action in power generation plant focused around oxy-fuel ignition are frequently alluded to as "zero emanation" cycles in light of the fact that CO<sub>2</sub> put away is not a separation evacuated from the pipe gas stream yet from the vent gas stream itself. The system is encouraging; however the beginning air detachment step requires a considerable measure of vitality. The steam and carbon dioxide are differentiated by cooling and layering the gas stream. The

oxygen needed for this procedure increments cost; however analysts are creating new procedures with expectations of cutting this expense down. Oxy-fuel burning can keep 90 % of a power plant's discharges from entering the air.

A substitute system under progress is Chemical Looping Combustion (CLC)- which involves Chemical looping that uses a metal oxide as a strong oxygen bearer. Metal oxide particles respond with a robust, fluid or vaporous fuel in a fluidized bunk combustor, transforming strong metal particles and a mixture of carbon dioxide and water vapour. The water vapour is consolidated, leaving immaculate carbon dioxide, which can then be sequestered. The strong metal particles are coursed to an alternate fluidized bed where they respond with air, transforming high temperature and recovering metal oxide particles that are re-flowed to the fluidized bed combustor.

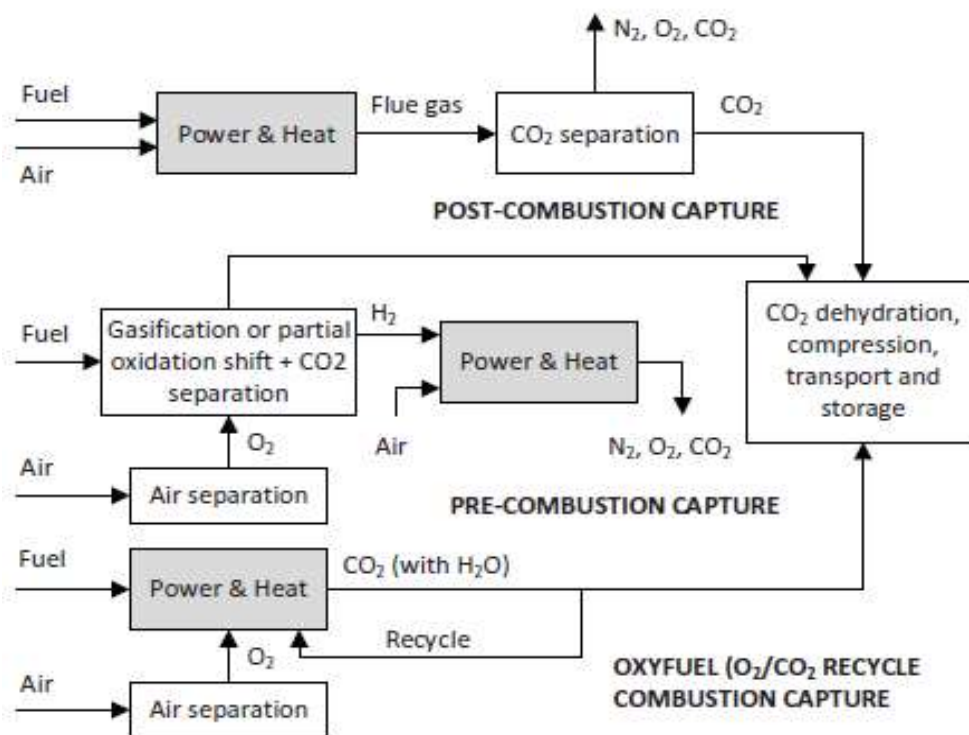


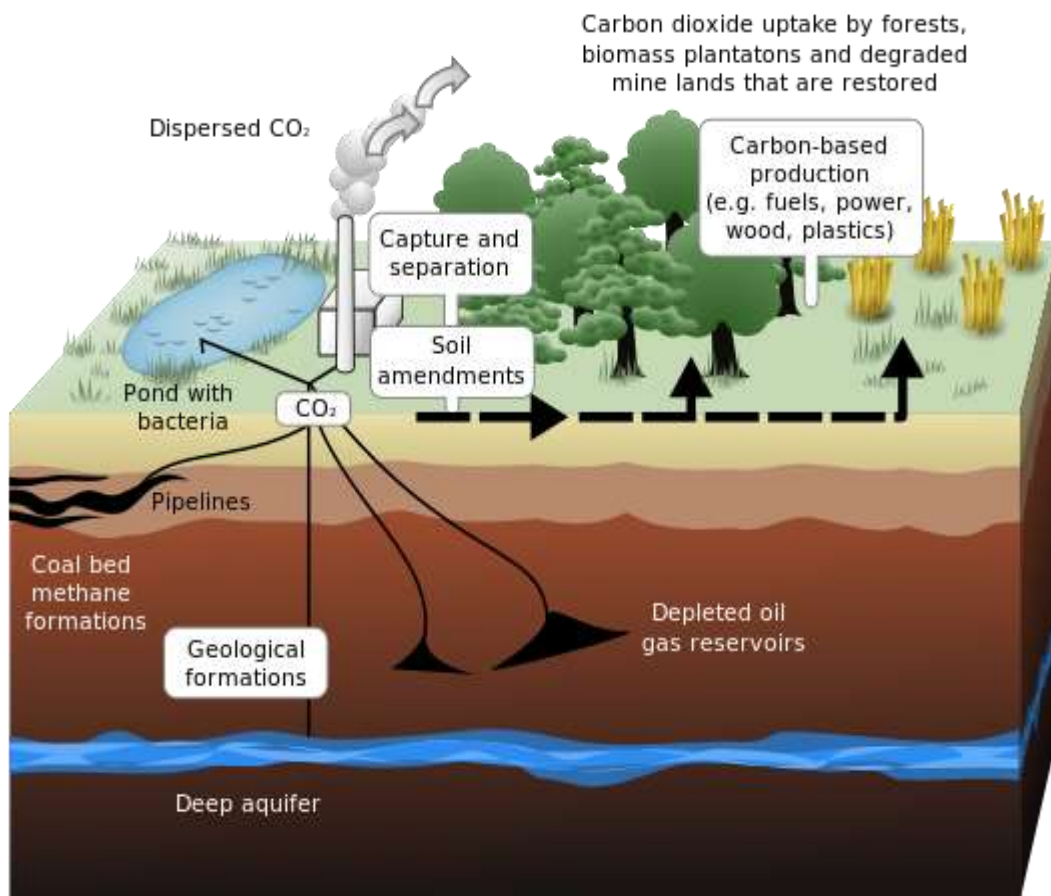
Figure 4 Technology concepts for CO<sub>2</sub> capture (adapted from Gibbins and Chalmers, 2008)

## 1.2 Transporting Carbon Dioxide

After carbon dioxide (CO<sub>2</sub>) is caught, the following step is transporting it to a stockpiling site. The current technique for transporting CO<sub>2</sub> is through a pipeline. Pipelines have been used for quite some time, and extensive volumes of gasses, oil and water move through pipelines consistently. A CO<sub>2</sub> pipeline typically starts at the location of capture and makes a trip straightforwardly to the stockpiling site, despite the fact that in a few cases, it may go to the extent that it can in the channel, then move to a tanker or boat to complete off its voyage. Everything relies upon where the source, pipeline and capacity site are found. Both people in general and private segment can claim pipelines.

Pipelines can transport CO<sub>2</sub> in three states: vaporous, solid and fluid. It is not practical to transport CO<sub>2</sub> as a solid because of its properties of freezing and blocking the pipelines and thus it is called ordinarily as dry ice. Pipelines ordinarily transport carbon dioxide in its vaporous state. A compressor "pushes" the gas through the pipeline. Once in a while a pipeline will have discontinuous compressors to keep the gas moving. The CO<sub>2</sub> must be clean (free of hydrogen sulphide) and dry. Else, it can corrode a normal pipeline, which is made of carbon manganese steel. Starting yet, there are no benchmarks set up for "pipeline quality" for carbon dioxide, yet specialists say that pipelines fabricated from stainless steel might have a brought down danger of consumption. This, notwithstanding, may not be temperate, since we might need to manufacture fresh out of the box new pipelines only for CO<sub>2</sub>.

Pipeline expenses vary relying upon the course of the pipeline (through vigorously congested territories, mountains, seaward). It's additionally conceivable to transport carbon dioxide as a fluid, utilizing boats or tanker trucks. Fluid CO<sub>2</sub> obliges low weight and a steady low temperature, so freight tanks need to be both pressurized and refrigerated.



**Figure 5 Schematic view of terrestrial and geological sequestration of carbon dioxide emissions from a coal-fired plant.**  
(source IPGC)

### **1.3 Sequestration**

Different structures have been incorporated for perpetual sequestration or storage of CO<sub>2</sub>. These structures incorporate vaporous stockpiling in different profound topographical establishments (counting saline arrangements and debilitated gas fields), and robust stockpiling by response of CO<sub>2</sub> with metal oxides to generate stable carbonates. Topographical capacity includes infusing carbon dioxide, for the most part in supercritical structure, straightforwardly into underground geographical establishments. Oil fields, gas fields, saline creations, unmineable coal creases, and saline-filled basalt arrangements have been proposed as capacity destinations. In mineral stockpiling CO<sub>2</sub> is exothermically responded with accessible metal oxides, which thusly generates stable carbonates. This procedure happens characteristically over numerous years and is answerable for an extraordinary measure of surface limestone. The IPCC assesses that a power generation plant outfitted with CCS utilizing mineral stockpiling will require 60–180% more vitality than a plant without CCS.

Reusing CO<sub>2</sub> may offer a reaction to the worldwide test of altogether decreasing greenhouse gas outflows from significant stationary (mechanical) emitters in the close to medium term, yet is normally viewed as an alternate innovative classification from CCS called CCU-Carbon Capture and Utilization

Haider et al<sup>[5]</sup> worked on the dynamic interdependence of the fossil fuel power plant with the CO<sub>2</sub> partition plant. Inside this work a dynamic process reproduction model of the assimilation unit of a CO<sub>2</sub> partition plant was produced. For depicting the compound assimilation of CO<sub>2</sub> into a monoethanolamine solution resulting into a rate based methodology was utilized. All models were produced inside the Aspen Custom Modeller® turf. Thermo-physical properties and additionally transport properties were taken from the ENRTL electrolyte non-random-two-liquid model given by the Aspen Properties® database. In this report, two simulation cases are exhibited. In the first simulation, inlet temperature of the vent gas and the lean solvent into the absorber section was changed. The outcomes were approved by utilizing trial information from the CO2SEPPL test apparatus found at the Dürnröhr force station. In a second part of the simulation, the vent gas stream to the separation plant was increased. Because of the inaccessibility of trial information an acceptance of the effects from the second simulation could not be accomplished.

Lawal et al<sup>[7]</sup> has worked broadly at Post-ignition capture by synthetic assimilation utilizing MEA solvent which is the main business technology for expansive scale for CO<sub>2</sub> capture for coal (fossil fuel) fired power generation plants. This paper displays an investigation of the dynamic responses of a post-ignition CO<sub>2</sub> capturing plant by simulation and sensitivity analysis. Such a plant consists of mainly the absorber (where CO<sub>2</sub> is first consumed) and the regenerator (where the synthetic solvent is recovered). Model advancement and approval are depicted trailed by dynamic investigation of the absorber and regenerator segments joined together with reuse. The gPROMS (Process Systems Enterprise Ltd.) propelled procedure displaying environment has been utilized to actualize the proposed work. The study gives experiences into the operation of the absorber–regenerator combo with conceivable disturbances arising from coordinated operation with a power plant. It is indicated that the performance of the absorber is more delicate to the molar L/G proportion than the real stream rates of the fluid dissolvable and flue gas. Furthermore, the criticalness of suitable water adjustment in the absorber section is indicated. A step change of the reboiler obligation shows a moderate reaction. A case including the synthesis of two fundamental CO<sub>2</sub> capturing advances (the incomplete oxyfuel mode in the heater and the post-burning solvent scrubbing) is concentrated on. The vent gas creation was changed to copy that saw with the combination. There was an introductory sharp decline in Co2 assimilation level which may not be observed in steady-state simulation.

Schneider et al<sup>[11]</sup> analysed distinctive model methodologies and found that customary balance stage models and proficiency methodologies are insufficient in the connection of dynamic reproduction of industrial reactive process of absorption. Therefore a new thorough elemental two-stage model focused around the two-film hypothesis was produced, which serves as a source of perspective description and considers the impact of synthetic responses and extra main thrusts in electrolyte frameworks on mass exchange, thermodynamic non-idealities and the effect of organized packings and fluid transport on the procedure hydrodynamics. For the model-built control and dynamic simulation, some model diminishments are obliged to point of confinement to reduce the computation time for the



numerical result. As per affectability study results, improvements for some physical parameters and linearization of the film fixation profiles have been fulfilled prompting a lessening of the aggregate number of mathematical statements significantly. The model has been connected to a modern sharp gas refinement process with numerous parallel and continuous reversible successive responses inside a multicomponent arrangement of liquid electrolytes and approved by pilot plant investigations.

A number of separation techniques are available such as membrane separation, cryogenics, physical adsorption, chilled ammonia process but they are not yet commercialised. Chemical absorption is widely used as absorption is highly effective at various CO<sub>2</sub> concentrations and relatively inexpensive.. A major drawback of absorption process is very high energy requirement.

There are various carbon dioxide capturing technologies, but out of these, PCC has some distinct advantages over others such as End-of-pipe technology-It can be easily fitted into existing power stations with minimal modifications. It has the ability for dynamic energy control of the system and it can be incorporated into steel plants, lime and cement manufacturing industries with ease.

Amines are excellent options for CO<sub>2</sub> capture especially alkanolamines which contains both amino (-NH<sub>2</sub>, -NHR, -NR<sub>2</sub>) and hydroxyl (-OH) functional groups. Primary amines (e.g MEA- monoethanolamine) are the most reactive and the tertiary amines (e.g. MDEA) are least reactive. The reason behind using amines is that they form stable carbamates and bicarbonates with CO<sub>2</sub>. These carbamates and bicarbonates can be then heated to separate CO<sub>2</sub> which can be sent for storage and then for use and the amine left can be recycled.



MEA is a phenomenal choice for PCC utilizing chemical absorptions. Experimentations were done to approve that. A solution of MEA was added to a prefilled container of vaporous carbon dioxide. It then made a vacuum when the amine captured the CO<sub>2</sub> and crushed the jug from within. The methodology is an exothermic one as the jug gets warm alongside. The carboxylated MEA consequently absorbed was separated from the pulverized flask and spilled into a cone shaped cup and acid was included. In this case, acid was utilized to discharge the amine and hence the CO<sub>2</sub> gas. CO<sub>2</sub> was released as air pockets which could likewise swell an inflatable.<sup>[8]</sup>



Figure 6 Experiment to show MEA captures CO<sub>2</sub>



Figure 7 CO<sub>2</sub> absorbed is easily separated by heating

### 3.1 Model Development

The work basically consisted of 2 parts. The first part focuses on developing an Aspen property package for the solvent. Data for chemical reactions and thermodynamic property parameter was obtained after doing extensive literature study. A simulation model for CO<sub>2</sub> capture process is then created after developing the property package. The second part of the work involved the estimation of operating parameters, CO<sub>2</sub> loading, condenser temperature, size of absorber etc.

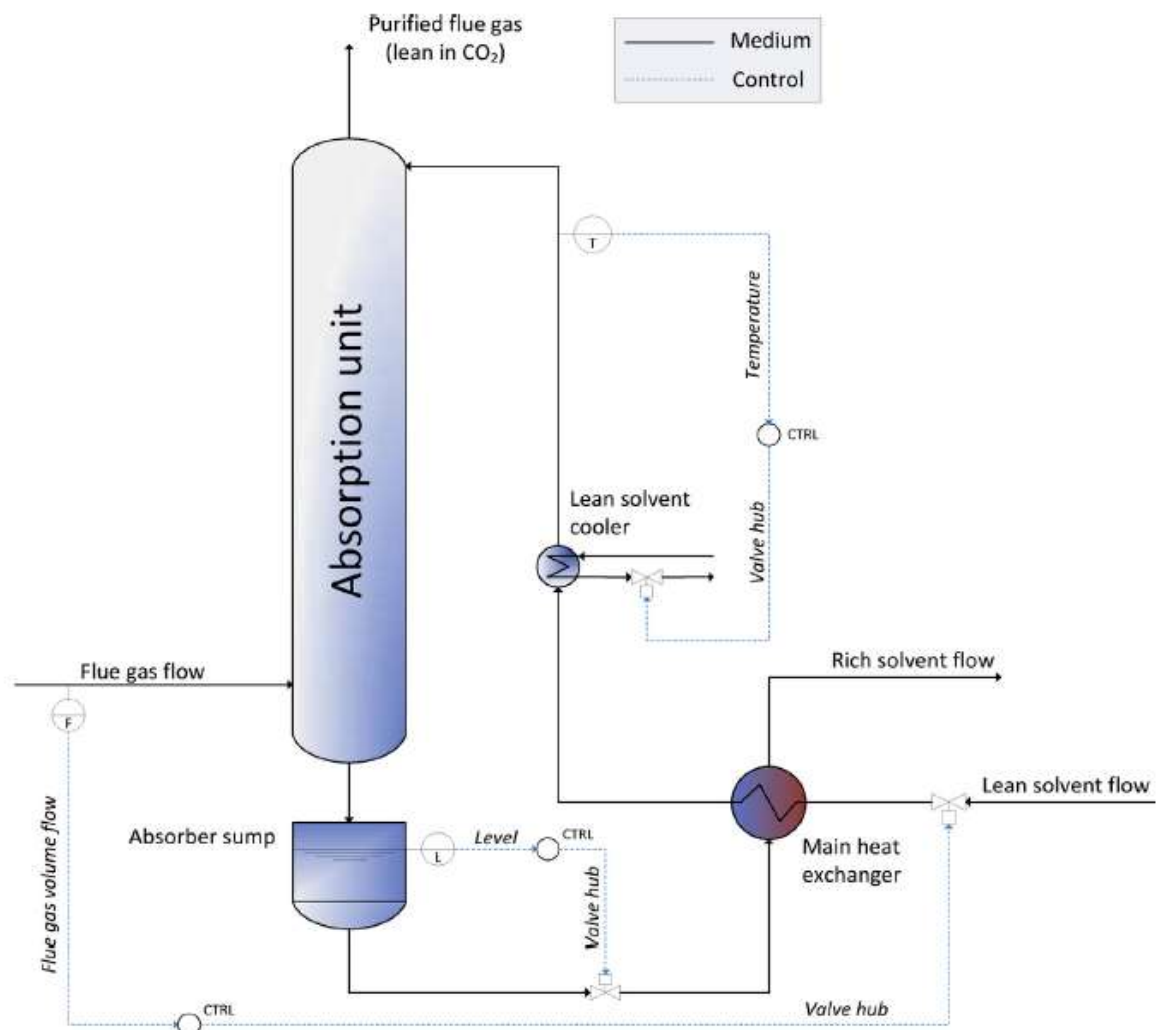


Figure 8 Transient Response Simulation Model for the Absorption of CO<sub>2</sub> into Amine Solvents. [5]

Firstly a simple model is developed for absorption with only an absorber (Haider et al)<sup>[5]</sup>. Then to study the process better, a transient response model for CO<sub>2</sub> absorption was prepared. The model was developed using Aspen Custom Modeller based on certain assumptions.

#### 3.1.1 Assumptions:

**Absorber column:** Use of rate based approach. The absorber column has structured packings to expand the net effective area of interfacial mass transfer between the vapour and liquid the phase.

**Sump:** Perfectly stirred tank model; No reaction within; Heat loss to environment is neglected.

**Heat Exchanger for cooling of the Lean Solvent:** The heat transfer equipments were modelled as plate type heat exchanger; no chemical reaction taking place inside and no loss to outside environment

**Valves and Control Circuits:** Proportional control; Based on the original value of control device, valve hubs were varied by PID control until set point was reached.

### 3.2 Absorber Column Model

Various column approaches are found in literature for modelling the chemical absorption of gases into liquids. From Schneider *et al* and Lawalet *al*, an overview of the basic model is developed. The modelling of the column is based on several assumptions as: Flow regime is plug flow in the gas and liquid phase. There is no accumulation of mass within the film region. Pressure drop correlation is linear. Phase equilibrium exists at gas/liquid interface. There is no solvent degradation. Heat losses are assumed to occur along the column axis  $z$  only. Mass balance and energy balance is done for this two film model (Figure 5).

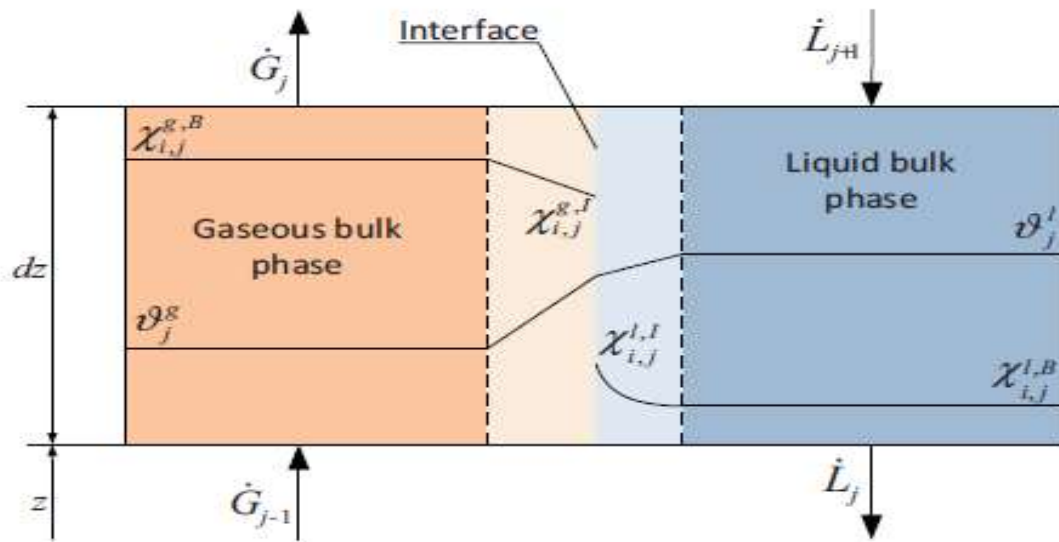


Figure 9 Chemical absorption of gases into liquids through Two-film Mass Transfer Model (Haider *et al*) [5]

#### 3.2.1 Balance for bulk Region

##### 1. Mass Balance

$$A_{Col} \varepsilon \varphi_j^g \frac{\partial \rho_j^{g,B}}{\partial t} = -\frac{\partial}{\partial z} (\dot{G}_j \mathcal{M}_j^{g,B}) - \sum_{i=1}^N (\dot{N}_{i,j}^{gl} - \dot{N}_{i,j}^{lg}) \frac{M_i}{dz}$$

$$A_{Col} \varepsilon \varphi_j^l \frac{\partial \rho_j^{l,B}}{\partial t} = \frac{\partial}{\partial z} (\dot{L}_j \mathcal{M}_j^{l,B}) + \sum_{i=1}^N (\dot{N}_{i,j}^{gl} - \dot{N}_{i,j}^{lg}) \frac{M_i}{dz}$$

## 2. Species Balance

$$\frac{A_{Col} \varepsilon \varphi_j^g}{V_{m_j}^{g,B}} \frac{\partial \chi_{i,j}^{g,B}}{\partial t} = -\frac{\partial}{\partial z} (\dot{G}_j \chi_{i,j}^{g,B}) - \frac{1}{dz} (\dot{N}_{i,j}^{gl} - \dot{N}_{i,j}^{lg})$$

$$\frac{A_{Col} \varepsilon \varphi_j^l}{V_{m_j}^{l,B}} \frac{\partial \chi_{i,j}^{l,B}}{\partial t} = \frac{\partial}{\partial z} (\dot{L}_j \chi_{i,j}^{l,B}) + \frac{1}{dz} (\dot{N}_{i,j}^{gl} - \dot{N}_{i,j}^{lg}) + \sum_{r=1}^R \dot{R}_{i,j,r}$$

## 3. Energy Balance

The energy balance needs to be solved for the vapour phase and liquid phase along with for the solid components present in the absorber. Environmental Heat Loss is not neglected and taken into consideration. This is the case for energy balance unlike the component and overall mass balance equations.

$$\frac{A_{Col} \varepsilon \varphi_j^g c_{v_j}^{g,B}}{V_{m_j}^{g,B}} \cdot \frac{\partial \vartheta_j^{g,B}}{\partial t} = -\frac{\partial}{\partial z} (\dot{G}_j h_j^{g,B}) - \frac{1}{dz} \sum_{i=1}^N (\dot{N}_{i,j}^{gl} \cdot (h_{i,j}^g + h_{evap,i,j}) - \dot{N}_{i,j}^{lg} \cdot (h_{i,j}^l - h_{evap,i,j})) + \frac{\dot{Q}_{cond,j}^{lg}}{dz}$$

$$\frac{A_{Col} \varepsilon \varphi_j^l c_{v_j}^{l,B}}{V_{m_j}^{l,B}} \cdot \frac{\partial \vartheta_j^{l,B}}{\partial t} = \frac{\partial}{\partial z} (\dot{L}_j h_j^{l,B}) + \frac{1}{dz} \sum_{i=1}^N (\dot{N}_{i,j}^{gl} \cdot (h_{i,j}^g + h_{evap,i,j}) - \dot{N}_{i,j}^{lg} \cdot (h_{i,j}^l - h_{evap,i,j})) - \frac{1}{dz} (\dot{Q}_{cond,j}^{lg} - \sum_{r=1}^R \dot{Q}_{reac,j,r} + \dot{Q}_j^{ls})$$

$$\frac{S_{Col} c_{p_j}^s}{V_{m_j}^s} \cdot \frac{\partial \vartheta_j^s}{\partial t} = 4s_{Col} (d_{Col} + s_{Col}) \cdot \frac{\partial}{\partial z} (\lambda_j^s \cdot \frac{\partial \vartheta_j^s}{\partial z}) + \frac{1}{dz} \dot{Q}_j^{ls} - \frac{\pi d_{iso}}{\frac{1}{\alpha_{sa}} + \frac{d_{iso}}{2\lambda_{iso}} \ln \frac{d_{iso}}{d_{Col} + 2s_{Col}}} (\vartheta_j^s - \vartheta_{amb})$$

The liquid phase holdup and gaseous phase holdup are related to each other as:

$$\varphi_j^g = 1 - \varphi_j^l$$

### 3.3 Development of the overall process flow diagram

After getting an idea of what happens inside the absorber column the next task involved the development of the overall CO<sub>2</sub> absorption process. Various models are available in literature. A typical process flow sheet for CO<sub>2</sub> capture process is shown in Figure 6

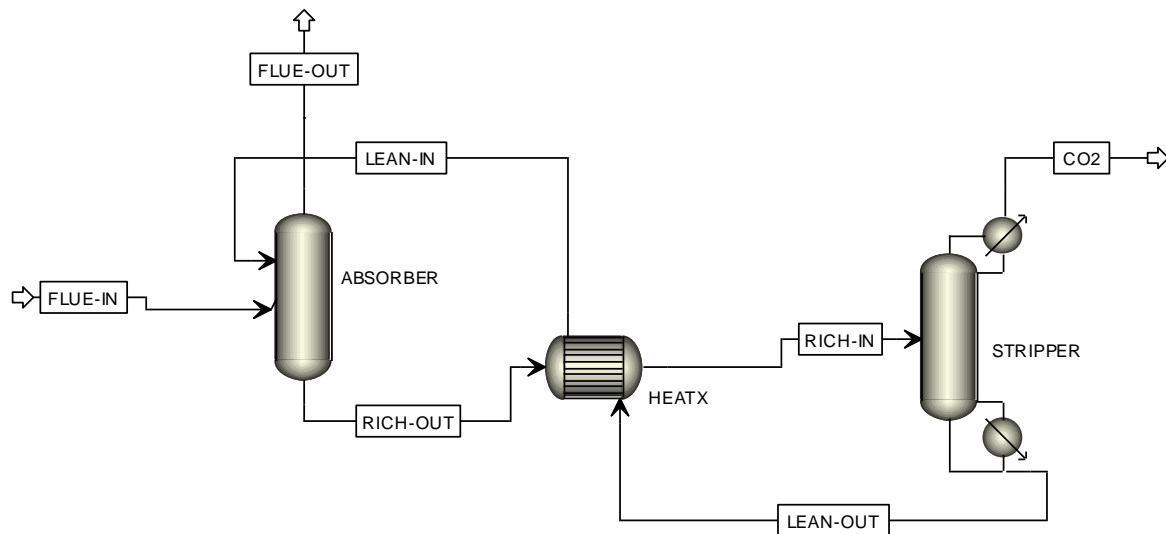


Figure 10 Simplified flow sheet of the CO<sub>2</sub> capture system.

### 3.4 Process Description

The overall process basically consists of an absorber and stripper connected to each other by means of a heat exchanger. The flue gas enters the absorber from the bottom after being cooled and desulphurized and the lean solvent (amine) flows into the absorber from the top. The amine absorbs CO<sub>2</sub> from the flue gas (which moves upward in the absorber), gets heavy after being rich in CO<sub>2</sub> and comes down out of the absorber and passes through the heat exchanger to the stripping column where CO<sub>2</sub> is stripped from the carboxylated amine, the lean amine is regenerated to the absorber and CO<sub>2</sub> is sent to storage sites or for utilisation. All sections work at encompassing weight as the low weight in the stripper can bring down the regenerator temperature in this way diminishing the prerequisite of top notch hotness source.

### 3.5 Model Specifications

An Aspen Plus model for CO<sub>2</sub> capture consisting of an absorber, stripper and a heat exchanger is developed. After creating Aspen property package for different solvents after extensive literature research the next important task is the estimation of operating parameters like CO<sub>2</sub> loading, condenser temperature, size of absorber etc. It is important to employ a modelling approach wherein the reaction rates and rigorous mass transfer and heat transfer calculations are implemented to truly capture the behaviour of the system. Both the equilibrium-based (Radfrac) and rate-based model (Ratefrac) in Aspen Plus could be utilized to reproduce the CO<sub>2</sub> catch framework. Radfrac model recognizes thermodynamic equilibrium for the procedure model. This model does not need setting the pressure and the extent of the segment. On the other hand, Ratefrac model treats the separation process as a high temperature and mass exchange handle and expect the equilibrium just arrives at the gas and fluid interface. In correlation to Radfrac, Ratefrac can re-enact the CO<sub>2</sub> ingestion and

recovery process all the more exactly and can investigate the impacts of the span of the section on the procedure. The Ratefrac model needs thorough initiation, for example, the extent of the segments, pressing and properties of the retentive and liquid holdup. These data are obtained from industry but we have limited or no such information for CO<sub>2</sub> absorption using different amine solvents. Along these lines, the Radfrac model is firstly used to gauge the key working parameters and afterward Ratefrac is utilized to get impacts of working parameters on the target parameters. The RateFrac model is adopted for simulating the absorber. The flow model is counter-current. The Electrolyte-NRTL method and the Redlich–Kwong equation of state are used for the computation of the properties of the liquid phase and vapour phase respectively.

### 3.6 Simulation

For the simulation of the complete flowsheet, the flue gas properties after desulphurisation are obtained from a typical 500 MW coal-fired power plant. The CO<sub>2</sub> concentration for a coal fired power plant is typically in the range of 12-14%. It is required to provide the diameter and height of the column while doing rate based calculations. It is decided to maintain the size of the columns on the basis of approach to flooding. A design factor of 70% flooding approach is chosen since which allows some safety factor in the case where there is a sudden change in operating conditions. The flue gas flow-rate from a power plant is high (~2200 tons/hr from a 500 MW power plant)<sup>[12]</sup>. There is also a limit on the pressure drop of the column which led to a constraint on the calculation of the diameter of the column.

Flow rate = 2124 tons/hr

Pressure = 101 kPa

Temperature = 298 K

Volume Fraction:

Nitrogen = 75.73 %

Carbon dioxide = 12.43 %

Water Vapour = 11.84 %

Impurities like O<sub>2</sub>, Ar, SO<sub>2</sub> and NO<sub>x</sub> are also present in the flue gas stream. The effect of O<sub>2</sub> on the degradation of amine solvent is small and can be neglected. Ar has no effect on chemical reaction. SO<sub>2</sub> and NO<sub>x</sub> can be absorbed by the amine solvent and/but their concentration is low (0.03 % and 0.02 %), so they are also neglected. O<sub>2</sub> and Ar are considered with N<sub>2</sub> as 75.73 %.

**Table 1 Specifications for the Equipment used**

Type	Value
Column internal diameter (m)	0.5
Height of packing (m)	5.98
Nominal Packing Size (m)	0.0381
Packing specific area (absorber) (m <sup>2</sup> /m <sup>3</sup> )	139
Packing specific area (regenerator) (m <sup>2</sup> /m <sup>3</sup> )	420
Cross heat exchanger heat transfer area (m <sup>2</sup> )	7
Reboiler Volume (m <sup>3</sup> )	1
Condenser Volume (m <sup>3</sup> )	2

Table 2 CO<sub>2</sub> capture with MEA

CO2 Capture- MEA								
Stream ID		CO2	FLUE-IN	FLUE-OUT	LEAN-IN	LEAN-OUT	RICH-IN	RICH-OUT
Temperature	K	277.4	323.1	358.6	446.2	446.2	355.6	355.6
Pressure	N/sqm	301325.000	101000.000	101000.000	301325.000	301325.000	101000.000	101000.000
Vapor Frac		1.000	0.149	1.000	0.000	0.000	0.000	0.000
Mole Flow	kmol/sec	2.000	12.674	2.000	222.941	222.941	276.456	276.456
Mass Flow	kg/sec	87.999	535.390	58.045	12367.136	12367.136	14278.353	14278.353
Volume Flow	cum/sec	15.028	50.206	58.704	11.505	11.505	11.931	11.931
Enthalpy	MMkcal/hr	-678.135	-3219.187	-521.904	-54090.350	-54090.350	-70403.821	-70403.821
Mole Flow	kmol/sec							
CO2		1.999	2.036	0.843	trace	trace	2.084	2.084
MONOE-01		trace	5.901	< 0.001	92.596	92.596	109.084	109.084
WATER		0.001	4.738	1.155	85.279	85.279	118.358	118.358
N2								
MDEA		trace		trace	39.146	39.146	40.837	40.837
PIPER-01		trace		0.001	5.920	5.920	6.093	6.093
Mole Frac								
CO2		1.000	0.161	0.422	18 PPB	18 PPB	0.008	0.008
MONOE-01		2 PPM	0.466	42 PPM	0.415	0.415	0.395	0.395
WATER		395 PPM	0.374	0.578	0.383	0.383	0.428	0.428
N2								
MDEA		10 PPB		38 PPB	0.176	0.176	0.148	0.148
PIPER-01		2 PPM		655 PPM	0.027	0.027	0.022	0.022

## 4.1 Results with MEA

### 4.1.1 Effect of capture percentage

Rise in the capture rate expands the reboiler duty. A steep increment was seen when the capture rate approached 95%. This is a direct result of the higher sensible heat prerequisites for this solvent.

### 4.1.2 Effect of packing

At the point when the rich solvent loading and the desired solvent flow diminishes it prompts a lessening in the desired reboiler duty. An economic optimization is important to find the trade-offs between the expense of packing and the reboiler duty.

### 4.1.3 Effect of solvent temperature

At the point when the temperature of absorption declines it prompts an increment in the main impetus for absorption. Be that as it may, the rate of the reaction and diffusivity diminish as temperature is reduced. Simulations were run at different solvent temperatures such as 20, 30 and 40 °C. The reboiler duty for diverse runs did not change much. Thus, the temperature of the solvent does not have a huge impact on the execution of the framework and it is on the grounds that the solvent has a low specific heat and it consumes the high heats of absorption rapidly



#### 4.1.4 Effect of absorber height

The absorber height was varied by keeping the column diameter constant to see the effect on the reboiler duty. It was observed that an expansion in the absorber height builds up the reachable rich loading and thus diminishes the reboiler duty. However as the absorber height expands, the pressure drop in the absorber likewise builds up and consequently the capital expense of the absorber gets higher. Subsequently, a financial optimization needs to be performed to determine the optimum height.

Primary amines are very reactive with CO<sub>2</sub> but their heats of regeneration are also very high. Similar properties are shown by secondary amine such as Diethanolamine (DEA) and Diisopropylamine (DIPA). In contrast to primary and secondary amines, tertiary amines, though gave relatively low reactivity, have very low heats of regeneration.

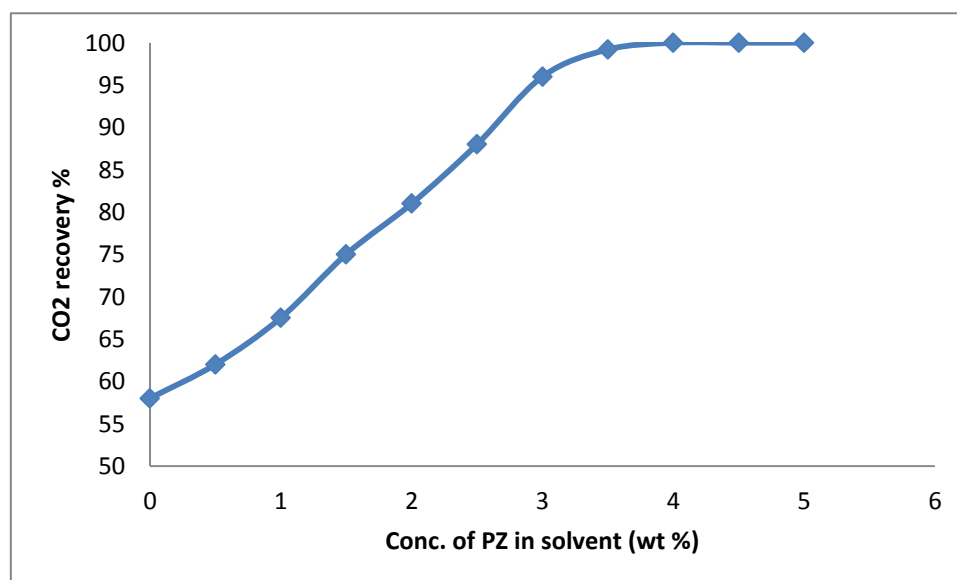
MDEA (Methyldiethanolamine) is a great alternative for such study due to its unique focal points, for example, low erosion, high loading limit, environment friendly, imperviousness to thermal and oxidative corrosion, and lower heat of regeneration over different amines. On the other hand, the primary disservice of this solvent is its moderate response rate with CO<sub>2</sub>. Ordinarily, MDEA is viewed as a perfect solvent for specifically evacuating hydrogen sulphide (H<sub>2</sub>S) from a gas stream and abandoning a lot of CO<sub>2</sub>. Therefore, an activator with a high response rate with CO<sub>2</sub> called piperazine (PZ) is added to aqueous MDEA with a run of the mill extent of 45 wt% MDEA and 5 wt% PZ. This blended solvent is called activated MDEA or a-MDEA. PZ acts as an enhancer for MDEA when responding with CO<sub>2</sub>, while a-MDEA holds MDEA's unique benefits of being artificially steady and obliging a low heat of regeneration. Hence, the blended amine dissolvable of MDEA and PZ has turned into a standout amongst the most guaranteeing solvents for CO<sub>2</sub> capture processes.<sup>[9]</sup>

## 4.2 Results with a-MDEA

**Table 3 Capture of CO<sub>2</sub> with MDEA**

CO <sub>2</sub> Capture- MDEA								
Stream ID		CO <sub>2</sub>	FLUE-IN	FLUE-OUT	LEAN-IN	LEAN-OUT	RICH-IN	RICH-OUT
Temperature	K	217.6	323.1	372.9	424.4	424.4	323.1	323.1
Pressure	N/sqm	301325.000	101000.000	101000.000	301325.000	301325.000	101000.000	101000.000
Vap or Frac		1.000	0.203	1.000	0.000	0.000	0.000	0.000
Mole Flow	kmol/sec	2.000	9.914	2.000	118.434	118.434	90.716	90.716
Mass Flow	kg/sec	88.020	535.390	37.313	6688.067	6688.067	6042.079	6042.079
Volume Flow	cum/sec	11.571	53.653	60.956	7.628	7.628	6.257	6.257
Enthalpy	MMkcal/hr	-681.887	-2946.472	-414.815	-32254.276	-32254.276	-27195.830	-27195.830
Mole Flow	kmol/sec							
CO <sub>2</sub>		2.000	2.036	0.035	trace	trace	2.037	2.037
MONOE-01								
WATER		trace	4.738	1.960	71.394	71.394	43.658	43.658
N <sub>2</sub>								
MDEA		trace	2.722	trace	40.874	40.874	38.997	38.997
PIPER-01		trace	0.418	0.006	6.166	6.166	6.025	6.025
Mole Frac								
CO <sub>2</sub>		1.000	0.205	0.017	11 PPB	11 PPB	0.022	0.022
MONOE-01								
WATER		trace	0.478	0.980	0.603	0.603	0.481	0.481
N <sub>2</sub>								
MDEA		trace	0.275	188 PPB	0.345	0.345	0.430	0.430
PIPER-01		21 PPB	0.042	0.003	0.052	0.052	0.066	0.066

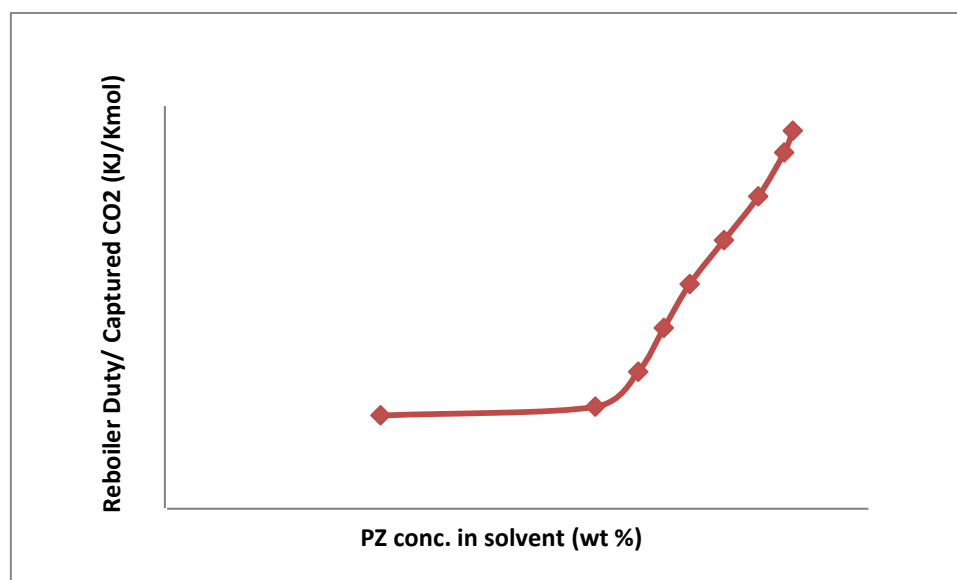
The effect of piperazine concentration on the CO<sub>2</sub> recovery in the absorber is obtained at a certain solvent to feed ratio say 2.5. Figure 11 shows that the proportion of PZ in the solution significantly affects CO<sub>2</sub> concentration in the absorber.



**Figure 11 Effect of PZ conc. in solvent in CO<sub>2</sub> recovery % in the absorber for S/F= 2.5**

It is evident from the Figure 11 that CO<sub>2</sub> recovery was dramatically increased between 0 wt% and 4 wt% but attains an almost constant value thereafter for higher piperazine concentration.

Figure 11 also represents that with every increase in 1wt % of PZ concentration in the solvent, the CO<sub>2</sub> recovery percentage gets enhanced by about 10%. It is also asserted that MDEA alone as a solvent is not effective in capturing CO<sub>2</sub> without any activator as a large amount of CO<sub>2</sub> would be left in the vented gas. Figure 12 shows the variation of reboiler duty per captured CO<sub>2</sub> with the piperazine concentration in the solvent for a fixed solvent to feed ratio of 2.5.



**Figure 12 Effect of PZ conc. in solvent on the reboiler duty per captured CO<sub>2</sub> of the stripper at S/F=2.5**

Obviously, the standardized reboiler duty increments with expanding the PZ fixations. The reason is that MDEA as an unadulterated solvent obliges a low heat of regeneration. At the point when PZ is included, the high temperature of recovery for the blended dissolvable builds essentially in light of the fact that the CO<sub>2</sub> recuperation is about 100% at 5 wt% PZ and past. Actually, at 7.5 wt% PZ, the reboiler obligation really gapped up. The effects unmistakably demonstrate that the best exchange-off between CO<sub>2</sub> recuperation and vitality utilization is around 4–5 wt% PZ. Any result quality past 4–5 wt% PZ prompts inordinate reboiler obligation with little addition in the CO<sub>2</sub> recuperation.

In contrast to primary and secondary amines, tertiary amine like MDEA has relatively low reactivity with CO<sub>2</sub> and the desired reactivity can be obtained by using an activator such as PZ with a certain weight fraction of 5% in the solution which is difficult to maintain. The main disadvantage of this solvent is its slow reaction rate with CO<sub>2</sub>.

Contrasted with MEA and a-MDEA, aqueous ammonia has focal points of high CO<sub>2</sub> loading limit, no retentive corrosion and low energy necessity. Also it has the capability of catching CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub> in the pipe gas at the same time and transforming quality-based chemicals, for example, ammonium sulfate and ammonium nitrate.<sup>12</sup> Therefore aq. ammonia solution is acknowledged as the most guaranteeing solvent for the substantial scale CO<sub>2</sub> capture process. The impacts of NH<sub>3</sub> concentration and temperature of the lean solvent on CO<sub>2</sub> evacuation effectiveness is studied utilizing a continuous assimilation system.<sup>3</sup> The CO<sub>2</sub> evacuation productivity arrived at 90 % at high NH<sub>3</sub> concentration.

### 4.3 Results with aq. NH<sub>3</sub> solution

**Table 4 CO<sub>2</sub> Capture with aq. NH<sub>3</sub> soln.**

CO <sub>2</sub> Capture- NH <sub>3</sub>								
Stream ID		CO <sub>2</sub>	FLUE-IN	FLUE-OUT	LEAN-IN	LEAN-OUT	RICH-IN	RICH-OUT
Temperature	K	257.5	323.1	231.1	271.0	271.0	243.4	243.4
Pressure	N/sqm	301325.000	101000.000	101000.000	301325.000	301325.000	101000.000	101000.000
Vapor Frac		1.000	0.899	1.000	0.000	0.000	0.000	0.000
Mole Flow	kmol/sec	2.000	27.938	2.000	455.086	455.086	169.564	169.564
Mass Flow	kg/sec	48.244	535.390	54.987	8093.907	8093.907	3057.515	3057.515
Volume Flow	cum/sec	13.785	663.988	37.564	11.344	11.344	4.087	4.087
Enthalpy	MMkcal/hr	-238.821	-2587.440	-314.908	-49399.445	-49399.445	-18392.698	-18392.698
Mole Flow	kmol/sec							
CO <sub>2</sub>		0.526	2.036	0.776	9.026	9.026	5.081	5.081
MONOE-01								
WATER		trace	4.738	trace	101.564	101.564	33.164	33.164
N <sub>2</sub>								
MDEA								
PIPER-01								
AMMONIA		1.474	21.164	1.224	344.495	344.495	131.319	131.319
Mole Frac								
CO <sub>2</sub>		0.263	0.073	0.388	0.020	0.020	0.030	0.030
MONOE-01								
WATER		4 PPB	0.170	trace	0.223	0.223	0.196	0.196
N <sub>2</sub>								
MDEA								
PIPER-01								
AMMONIA		0.737	0.758	0.612	0.757	0.757	0.774	0.774

Simulation results for aqueous NH<sub>3</sub> solution involved the analysis of both absorption and regeneration processes. The key task after the simulation was to find out the operating parameters of both the processes. Size of absorber, NH<sub>3</sub> concentration, flow rate and CO<sub>2</sub> loading are the operating parameters of CO<sub>2</sub> absorption process. The target parameters are CO<sub>2</sub> removal efficiency, CO<sub>2</sub> loading of rich solvent (RICH-IN), temperature of the lean solvent and NH<sub>3</sub> concentration in exit gas. Operating parameters for CO<sub>2</sub> regeneration process are boilup ratio, condenser temperature and temperature of rich solvent (RICH-IN).

#### 4.3.1 Analysis of CO<sub>2</sub> absorption process

##### 4.3.1.1 Effect of Size of Absorber

The residence time of lean solvent and flue gas in the absorber increase with the increase in the size of the absorber. As a result of which the removal efficiency of CO<sub>2</sub> (Figure 13) and its loading in the rich solvent (Figure 14) increase and regeneration energy decreases. Beyond a certain value of 12 m diameter and 20 m of packed height, this increase is not significant. So the optimum diameter is 12 m and optimum height of packing is 20 m.

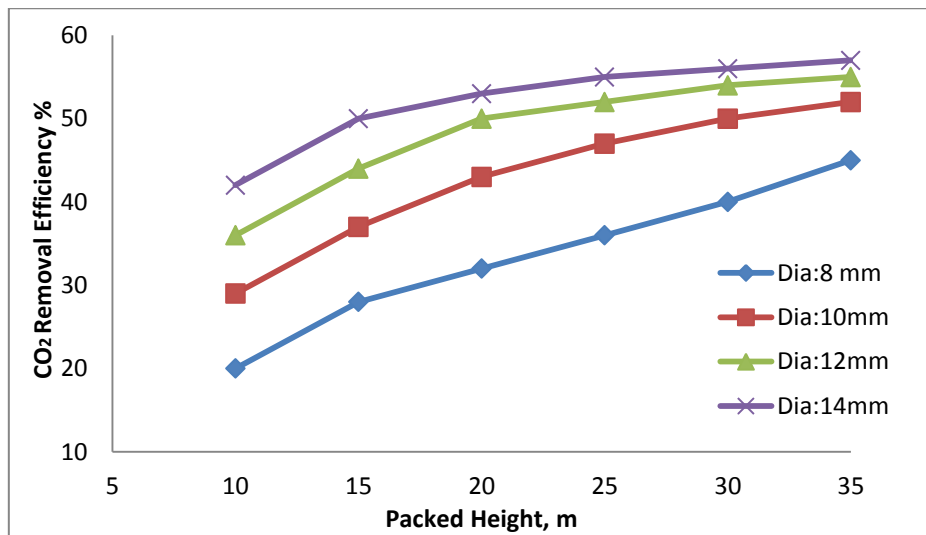


Figure 13. Effects of the size of absorber on the CO<sub>2</sub> removal efficiency

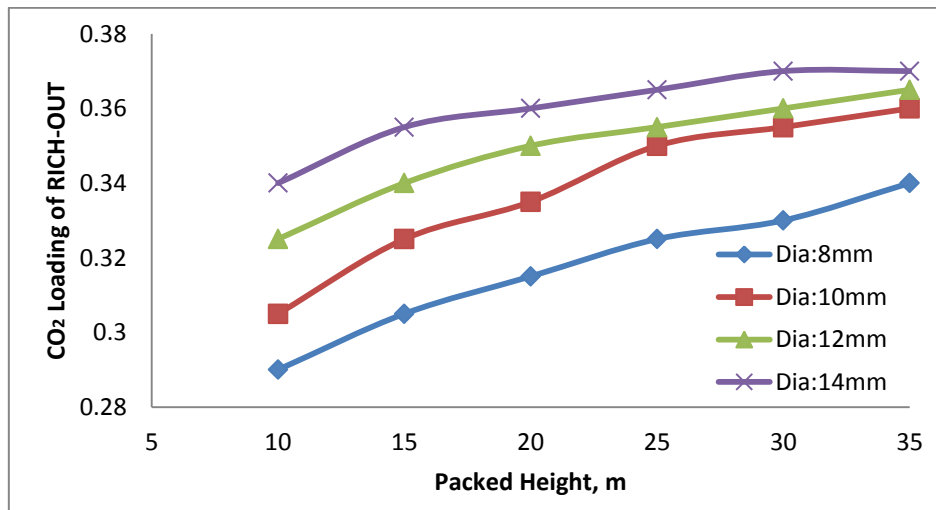


Figure 14 Effects of the size of absorber on the CO<sub>2</sub> loading of rich solvent

#### 4.3.1.2 Effect of the NH<sub>3</sub> Concentration on the lean solvent

Both the NH<sub>3</sub> concentration in exit gas and CO<sub>2</sub> removal efficiency increase rapidly with the increase of NH<sub>3</sub> concentration in the lean solvent (Figure 15). This rapid increase stabilises after the NH<sub>3</sub> concentration becomes 3 mol/L. CO<sub>2</sub> absorption increases with this relatively low increase of NH<sub>3</sub> concentration thus increasing the CO<sub>2</sub> output. However at larger NH<sub>3</sub> concentration, more NH<sub>3</sub> will be generated in the reboiler and thus absorbed in the condensate and more CO<sub>2</sub> product will be absorbed by this newly formed solution of NH<sub>3</sub>. It can be seen from the Figure 16 that CO<sub>2</sub> output reaches a peak value at the NH<sub>3</sub> concentration of 3 mol/L and then falls down which is the optimum concentration of ammonia in the lean solvent.

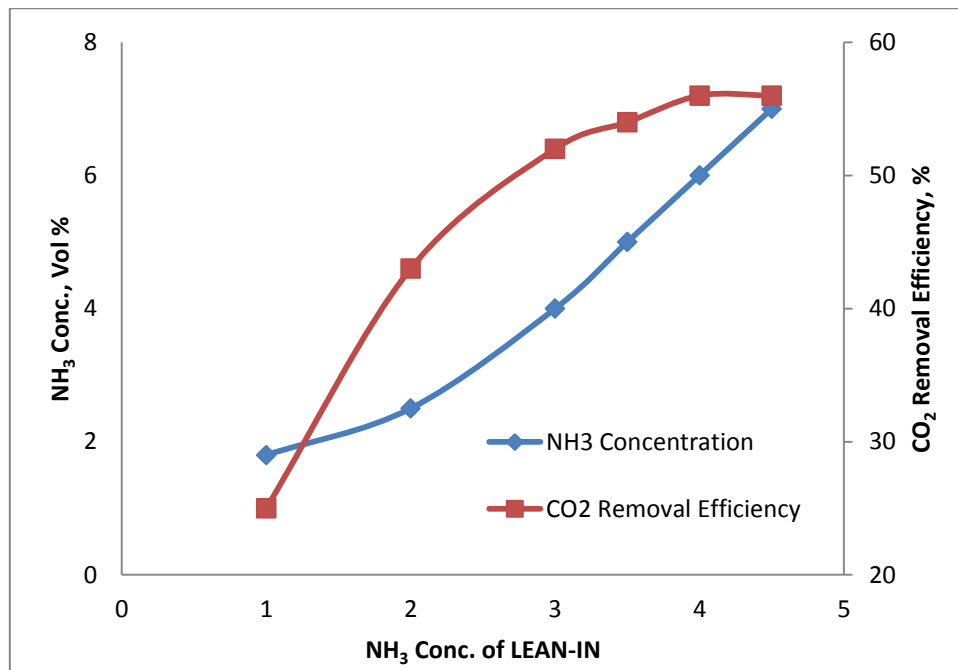


Figure 15 Effect of NH<sub>3</sub> concentration of the lean solvent on CO<sub>2</sub> absorption process

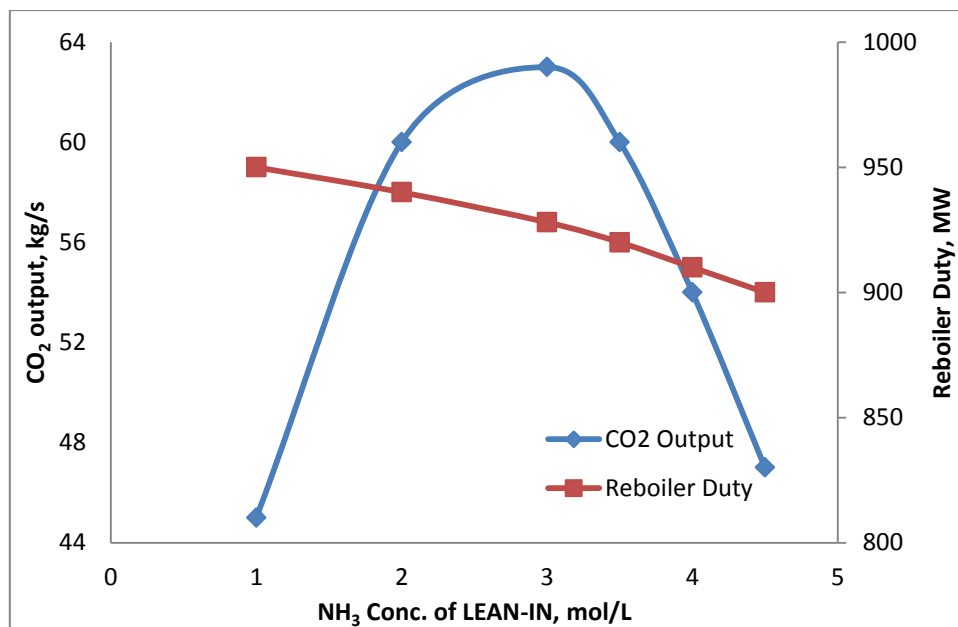


Figure 16 Effect of NH<sub>3</sub> concentration of the lean solvent on CO<sub>2</sub> regeneration process

#### 4.3.1.3 Effects of flow rate of the lean solvent

It is evident from the Figure 17 that with an increase in the flow rate of lean solvent (LEAN-IN), the NH<sub>3</sub> concentration inside the exit gas stabilises and then slightly increases however the increase in the removal efficiency of CO<sub>2</sub> is very rapid. At constant boil-up ratio, the reboiler duty increases linearly with the increase in the flow rate of LEAN-IN. As a result of which the CO<sub>2</sub> output also follows the similar trend (Figure 18). It can be concluded that the increase in flow rate improves CO<sub>2</sub> absorption but alongside it increases the heat requirement of regeneration.

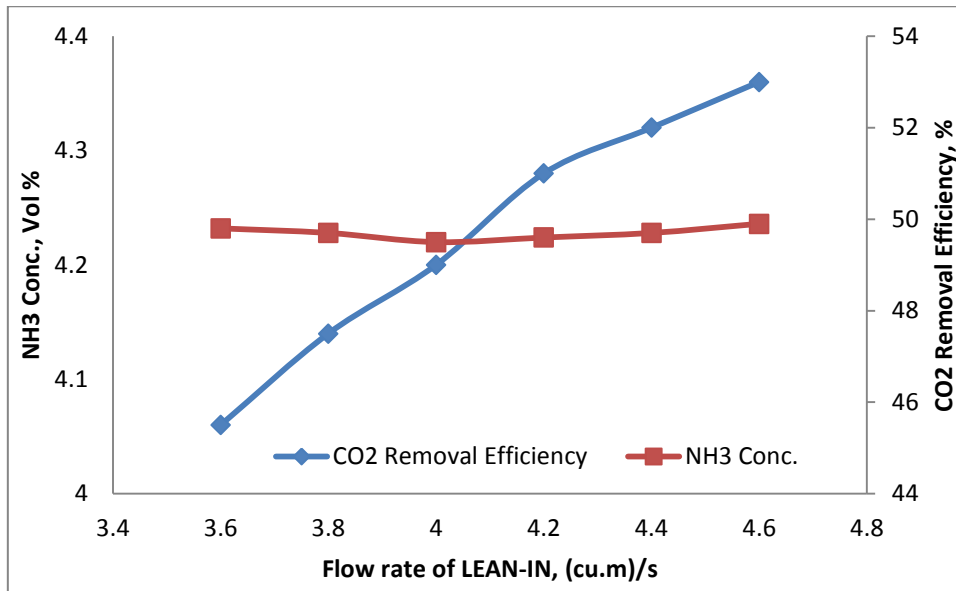


Figure 17 Effect of flow rate of LEAN-IN on CO<sub>2</sub> absorption process

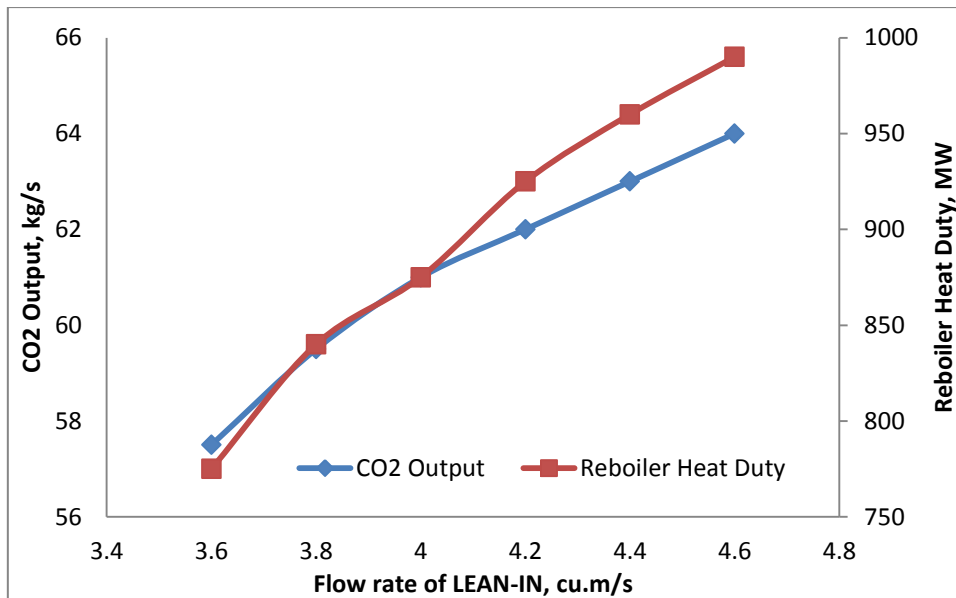


Figure 18 Effect of flow rate of LEAN-IN on CO<sub>2</sub> regeneration process

#### 4.3.1.4 Effect of CO<sub>2</sub> loading of the lean solvent (LEAN-IN)

It can be seen in Figure 19 that both the NH<sub>3</sub> Concentration of exit gas and CO<sub>2</sub> removal efficiency decrease rapidly with increasing CO<sub>2</sub> loading of LEAN-IN. This describes that for large CO<sub>2</sub> loading of LEAN-IN, NH<sub>3</sub> slip is small. Also, with the increase in the CO<sub>2</sub> loading, there is a linear increase of CO<sub>2</sub> output because the reboiler duty changes very little and the boil-up ratio and flow rate of LEAN-IN remain constant (Figure 20). The optimum CO<sub>2</sub> loading of the LEAN-IN is 0.235 for the required removal efficiency of CO<sub>2</sub>.

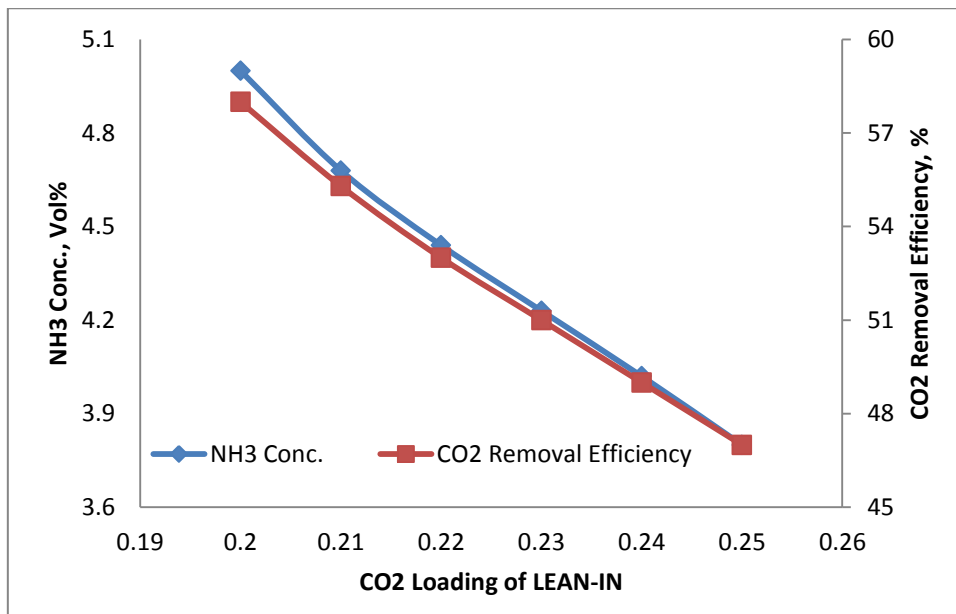


Figure 19 Effect of CO<sub>2</sub> loading of LEAN-IN on CO<sub>2</sub> absorption process

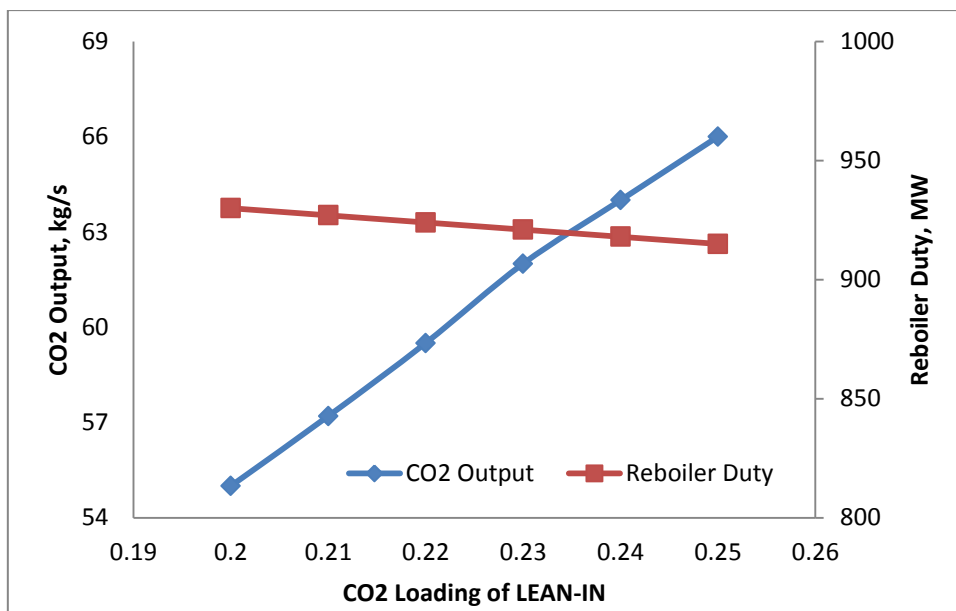


Figure 20 Effect of CO<sub>2</sub> loading of LEAN-IN on CO<sub>2</sub> regeneration process

### 4.3.2 Analysis of CO<sub>2</sub> regeneration process

#### 4.3.2.1 Effect of boil-up ratio on the CO<sub>2</sub> regeneration process

CO<sub>2</sub> and NH<sub>3</sub> outputs increase significantly with the increase in boilup ratio because of the linear increase in reboiler duty (Figure 21). However the regeneration duty follows a different trend. It first decreases a little and then increases with increase in boilup ratio (Figure 22). After a certain time the CO<sub>2</sub> output decreases after reaching a peak value because of the precipitation of newly formed aqueous NH<sub>3</sub> solution in the condenser. NH<sub>3</sub> concentration of LEAN-OUT increases initially at a fast rate because of the decomposition of various ammonium salts of carbonate, bicarbonate and carbamate at high reboiler duty. This NH<sub>3</sub> concentration decreases when the decomposition reaches peak value because of increases in the amount of NH<sub>3</sub>. CO<sub>2</sub> loading of LEAN-OUT decreases rapidly initially and then increases



slowly with the fall in  $\text{NH}_3$  concentration (Figure 23). The optimum boilup ratio is considered as 0.04.

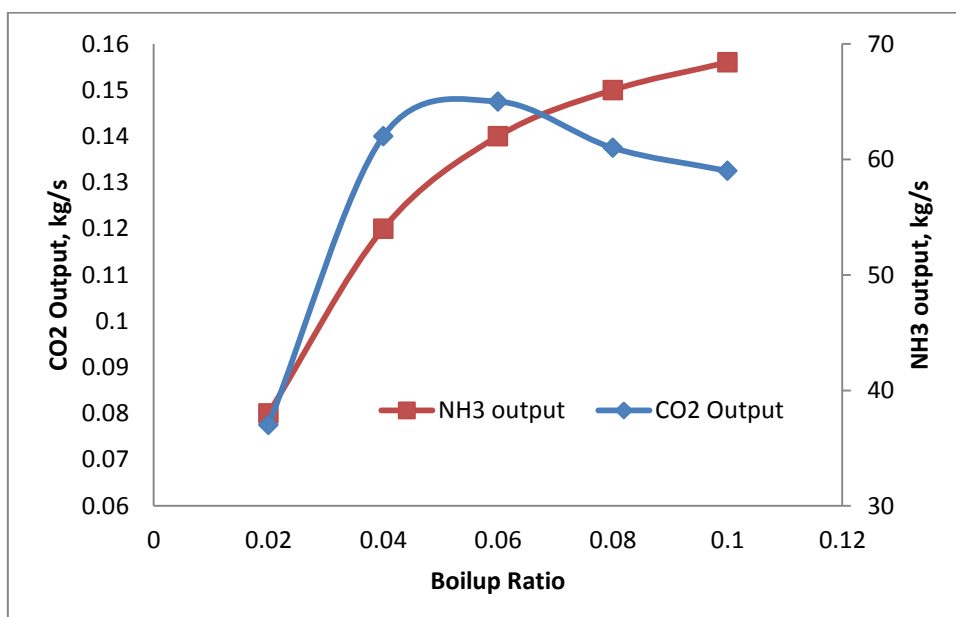


Figure 21 Effect of boilup ratio on the  $\text{CO}_2$  regeneration process for  $\text{CO}_2$  and  $\text{NH}_3$  output

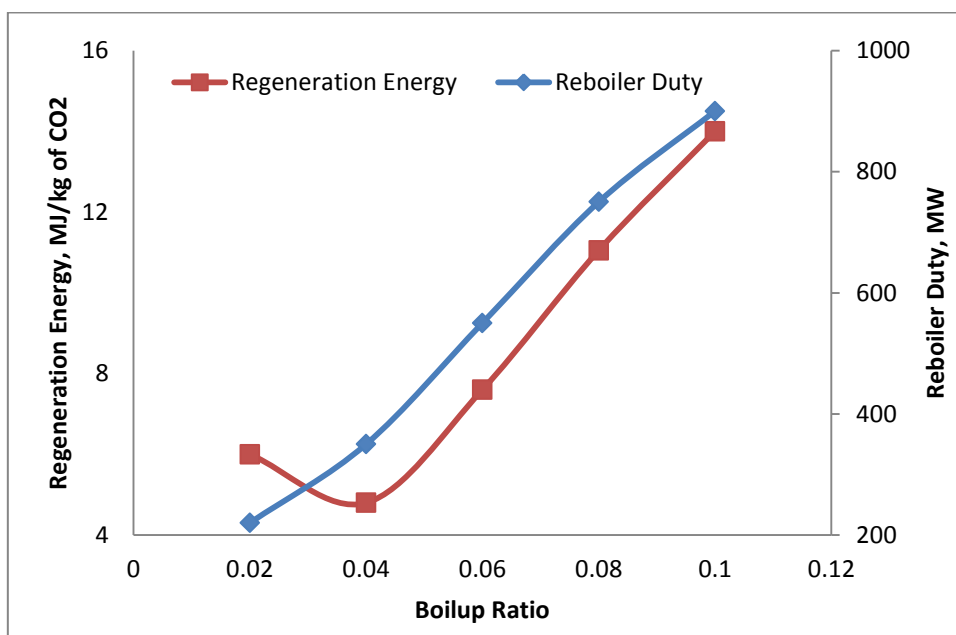


Figure 22 Effect of boilup ratio on the reboiler duty and regeneration energy of  $\text{CO}_2$  regeneration process

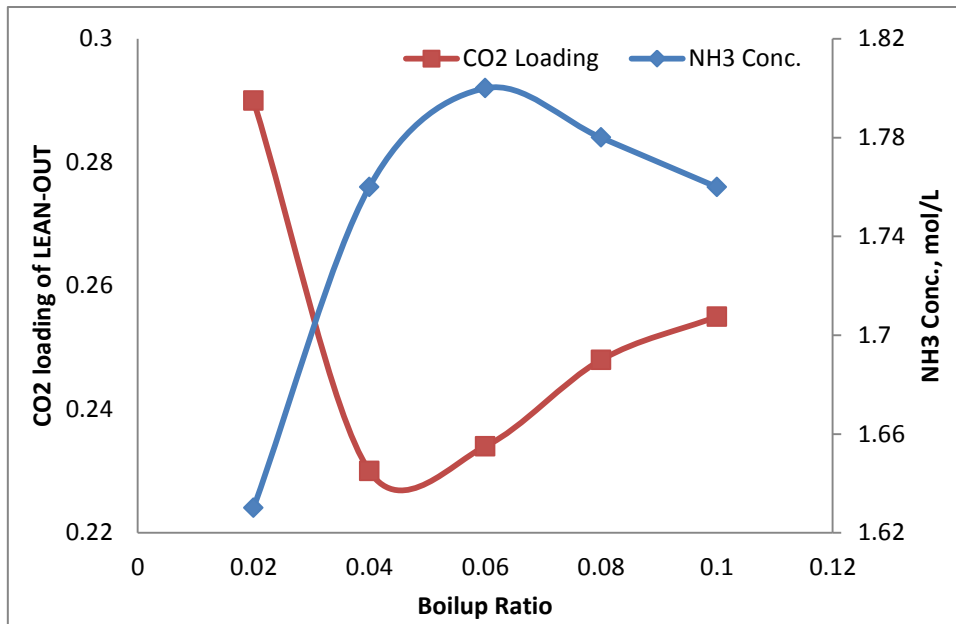


Figure 23 Effect of boilup ratio on CO<sub>2</sub> loading and NH<sub>3</sub> conc. of lean solvent of the CO<sub>2</sub> regeneration process

#### 4.3.2.2 Effect of the temperature of RICH-IN on the CO<sub>2</sub> regeneration process

With an increase in the temperature of RICH-IN, the solvent temperature in the reboiler increases with larger production of water vapour alongside. As a result more NH<sub>3</sub> is absorbed by the condensate water because of more water being condensed and thus it absorbs more amount of CO<sub>2</sub>. Both NH<sub>3</sub> and CO<sub>2</sub> outputs decrease with the increase in the RICH-IN temperature (Figure 24). The optimum CO<sub>2</sub> loading is 0.235 as determined earlier and thus the optimum NH<sub>3</sub> concentration flowing out of the stripper is 1.85 mol/L. CO<sub>2</sub> loading in LEAN-OUT and NH<sub>3</sub> concentration stabilises and doesn't change much with the increase in the RICH-IN temperature (Figure 25). The heat of regeneration increases linearly with the increase in temperature however the reboiler duty follows the opposite trend of linear decrease (Figure 26). The optimum temperature of RICH-IN is determined to be equal to 90 °C.

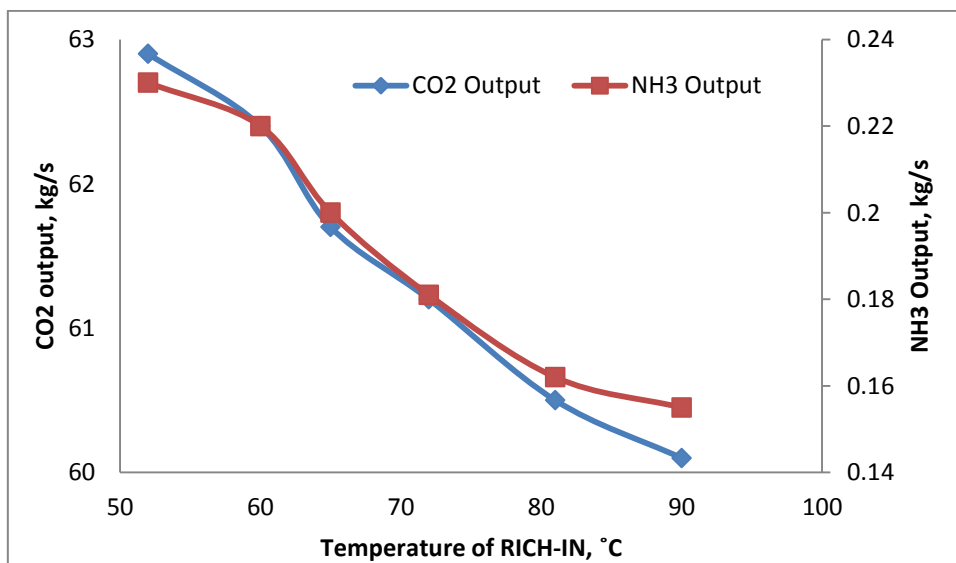


Figure 24 Effect of temperature of RICH-IN on CO<sub>2</sub> output and NH<sub>3</sub> output of the CO<sub>2</sub> regeneration process

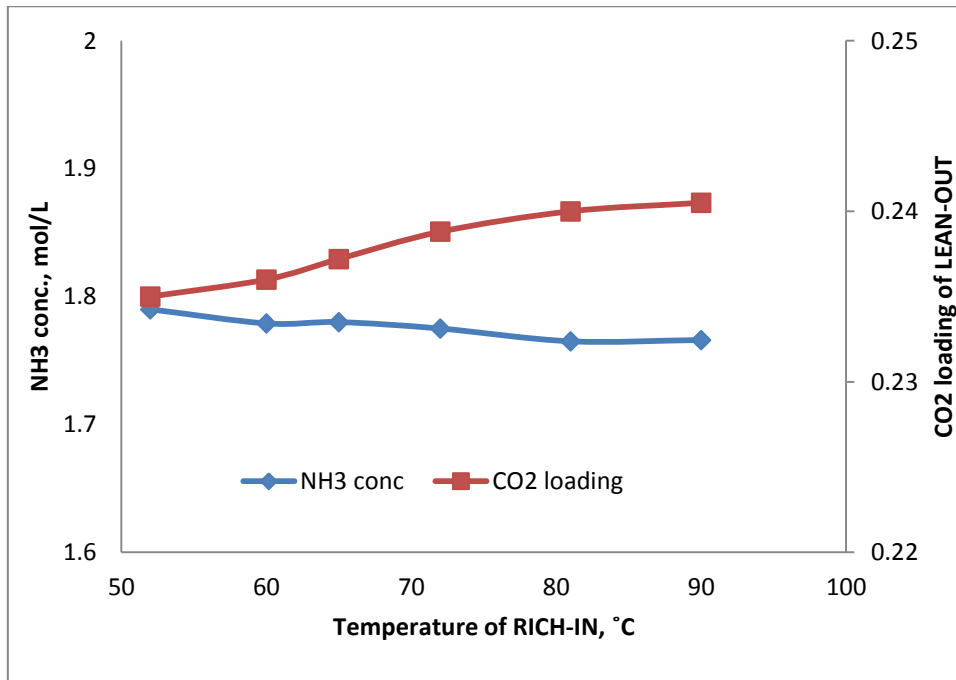


Figure 25 Effect of temperature of RICH-IN on CO<sub>2</sub> loading and NH<sub>3</sub> concentration of the regeneration process

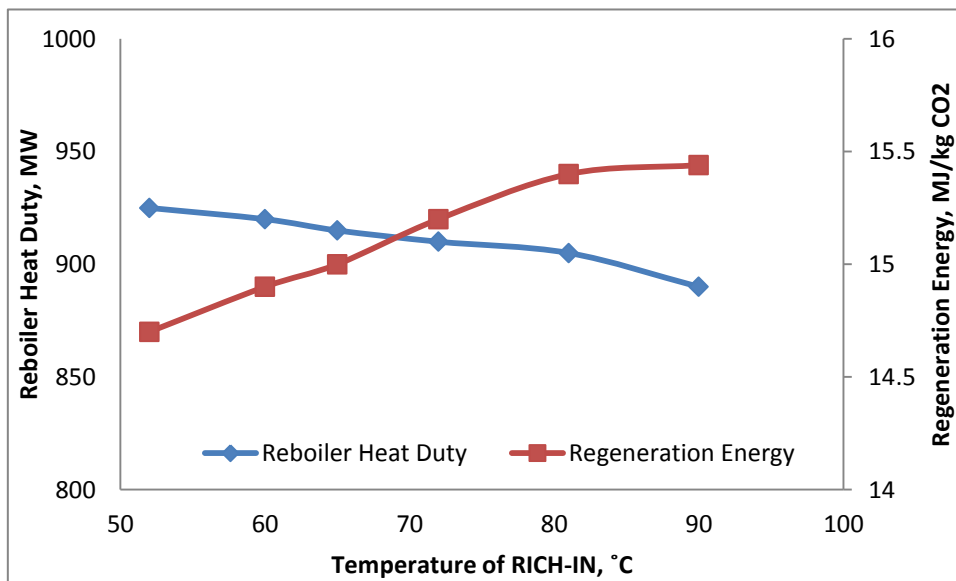


Figure 26 Effect of temperature of RICH-IN on reboiler heat duty and regeneration energy of regeneration process

#### 4.3.2.3 Effect of the condenser temperature on the CO<sub>2</sub> regeneration process

CO<sub>2</sub> output increases linearly with the increase in condenser temperature and NH<sub>3</sub> output increases slowly for lower temperatures but shows a steep rise beyond the condenser temperature of 30 °C (Figure 27). This is because of the fact that the amount of water vapour condensing inside the condenser decreases with the increase in condenser temperature thus leads to less absorption of NH<sub>3</sub> and thereby CO<sub>2</sub>. As a result, the CO<sub>2</sub> loading decreases but NH<sub>3</sub> concentration increases as shown in Figure 28. This also leads to lower reboiler heat duty. Consequently the regeneration energy also decreases (Figure 29). There is some significant precipitation problem below 30 °C so the optimum condenser temperature is taken as 30 °C.

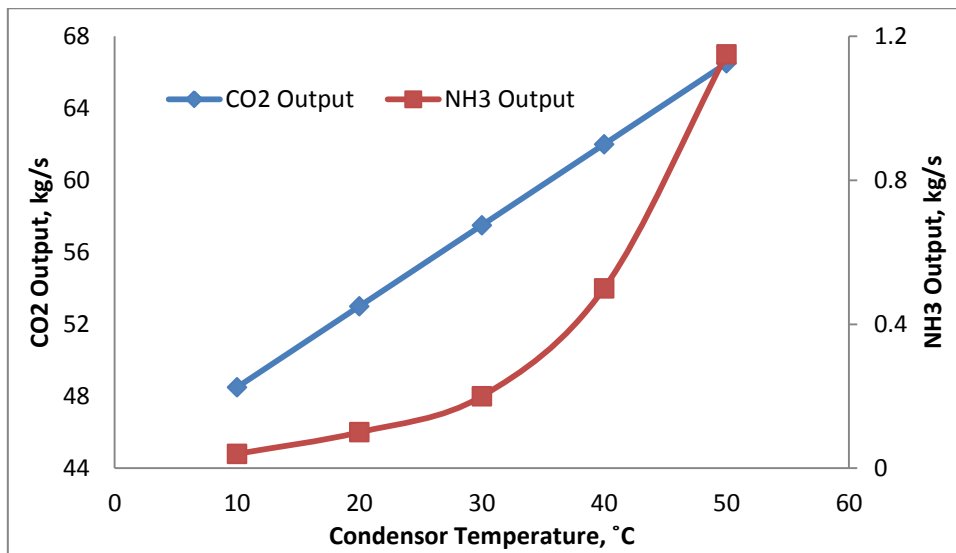


Figure 27 Effect of condenser temperature on CO<sub>2</sub> output and NH<sub>3</sub> output of the CO<sub>2</sub> regeneration process

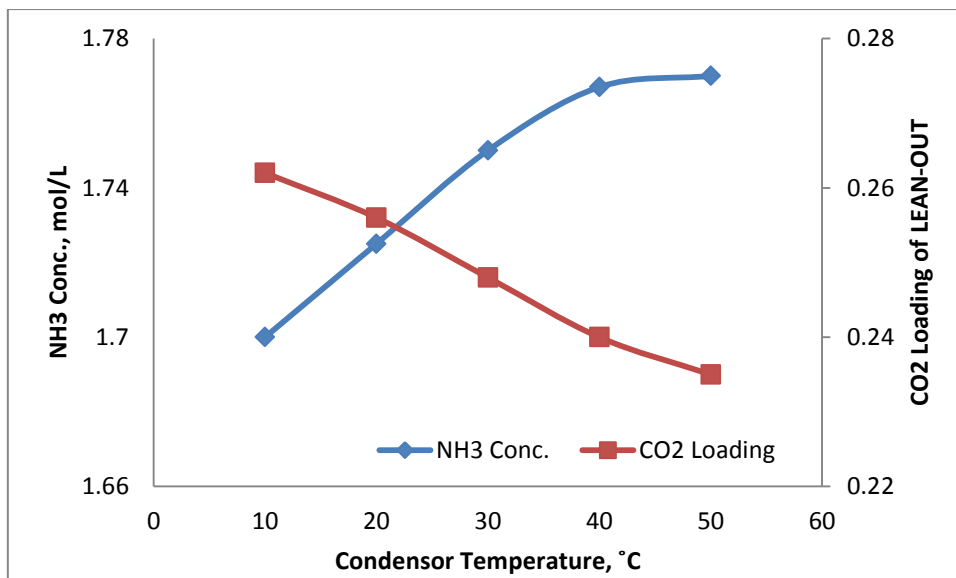


Figure 28 Effect of condenser temperature on CO<sub>2</sub> loading and NH<sub>3</sub> concentration of the CO<sub>2</sub> regeneration process

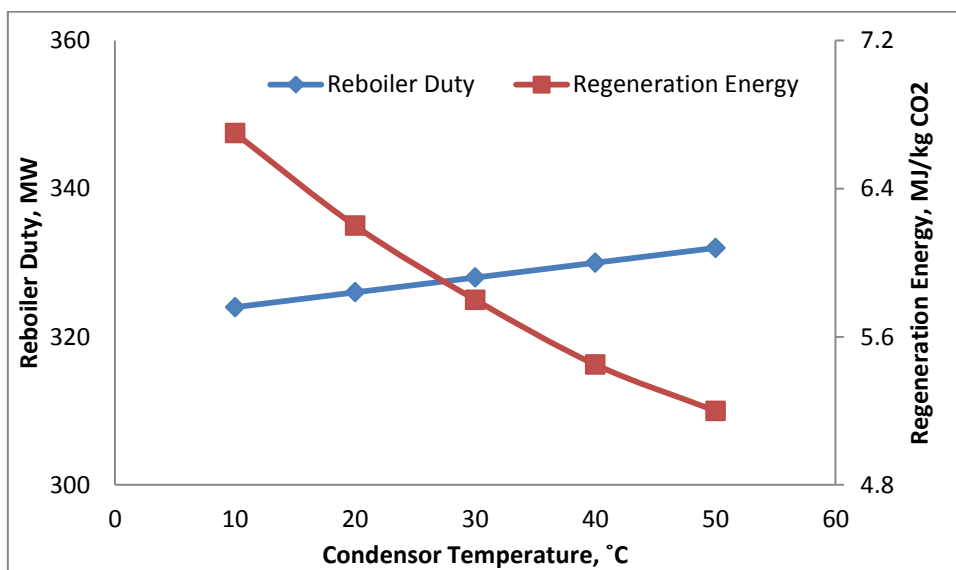


Figure 29 Effect of condenser temperature on reboiler duty and regeneration energy of the CO<sub>2</sub> regeneration process

#### 4.4 Comparison of Results for different Components

There are four important property parameters which are analysed and compared for the three different solvents- MEA, a-MDEA and NH<sub>3</sub> solution. These are CO<sub>2</sub> capture percentage, height of packing, CO<sub>2</sub> loading and Regeneration Energy (Reboiler Duty per kg of CO<sub>2</sub> Captured). The analyses are shown in Figure 30, Figure 31, Figure 32 and Figure 33.

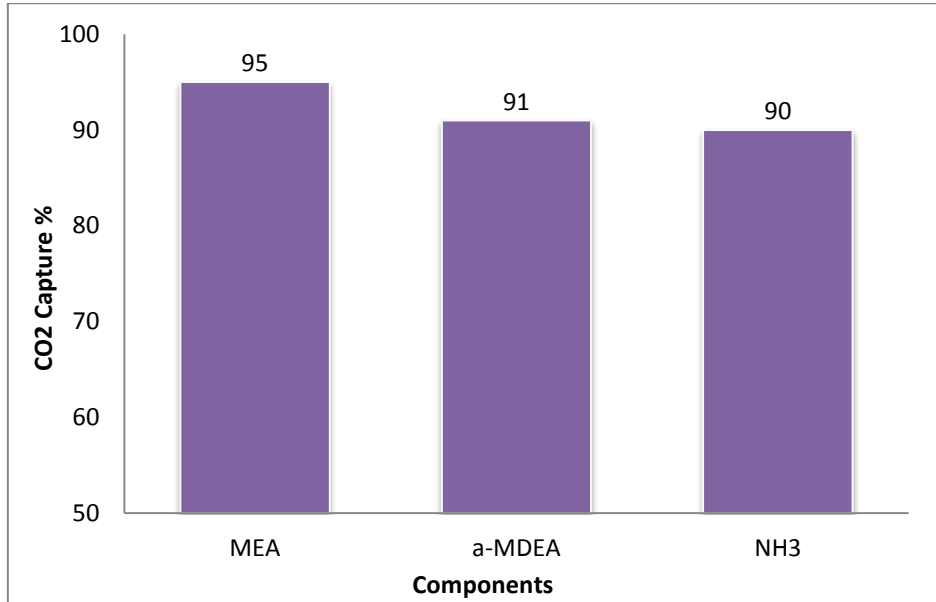


Figure 30 Comparison of Capture % of different components

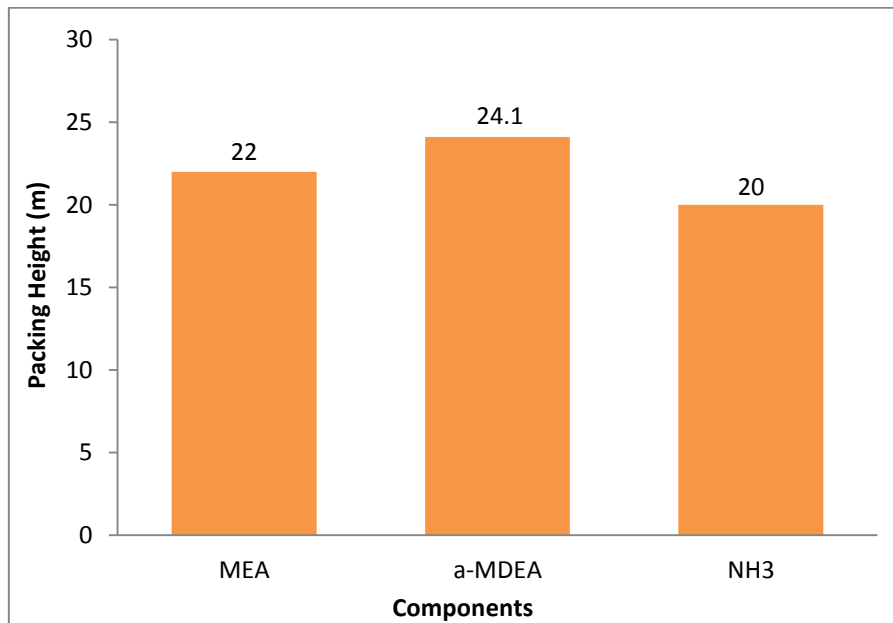
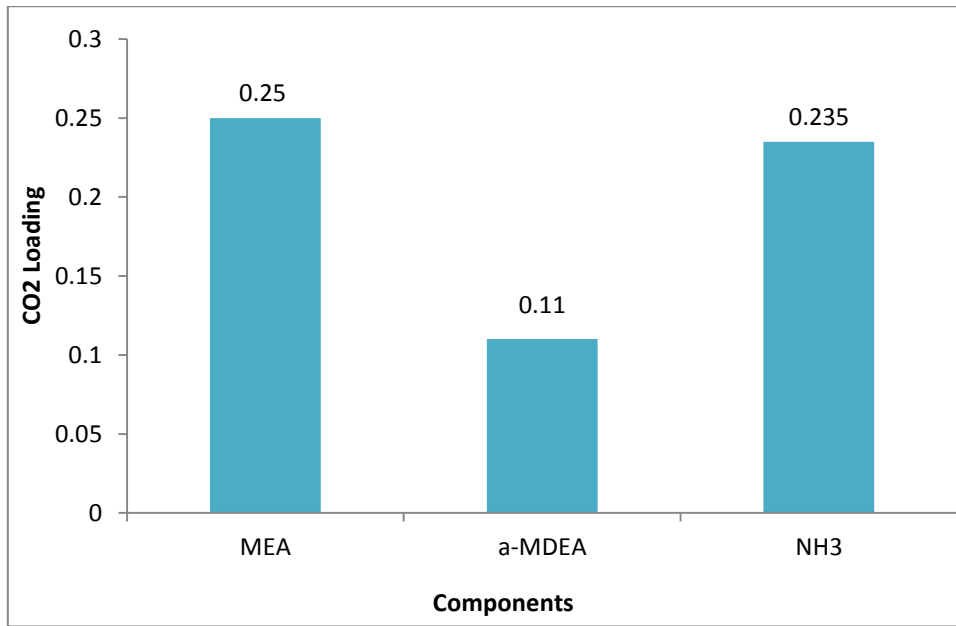
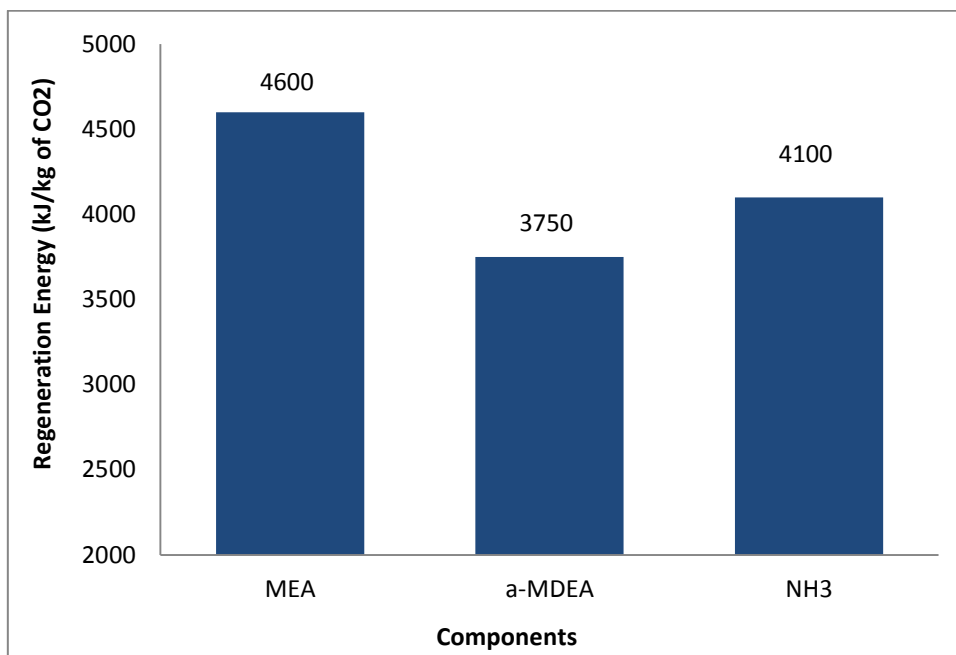


Figure 31 Comparison of Packing Height of different components



**Figure 32 Comparison of CO<sub>2</sub> Loading of different components**



**Figure 33 Comparison of Regeneration Energy of different components**

MEA has the highest capturing percentage of 95% followed by 91% for activated MDEA and 90% for NH<sub>3</sub> solution. Although MEA has very high capturing percentage but it requires very high heats of regeneration of 4600 kJ/kg of CO<sub>2</sub>. NH<sub>3</sub> also has a high value for regeneration energy of 4100 kJ/kg of CO<sub>2</sub>. If these two property parameters are taken into account then activated MDEA seems a better option with 91% capture percentage and 3750 kJ/kg of CO<sub>2</sub> as the heat of regeneration. However CO<sub>2</sub> loading in case of a-MDEA is pretty low with a value which is half of the loading of MEA and NH<sub>3</sub> solution. Moreover a-MDEA requires a large quantity of packing material evident from the packing height of 24.1 m which is 4-5 m more than the other two components. Because of these two major downsides, a-MDEA is not

proposed as the best solvents for CO<sub>2</sub> capture. So now in order to find the most economical solvent for CO<sub>2</sub> capture, the cost analysis for different solvents is implemented. For cost analysis for the solvents, there are some requisites for the cost of different parameters which include- cost of packing material, cost of regeneration heat in number of units used, cost of solvents and cost of CO<sub>2</sub> which is the profit obtained after selling it in the market based on kg of CO<sub>2</sub> captured found from the CO<sub>2</sub> capturing percentage for different solvents.

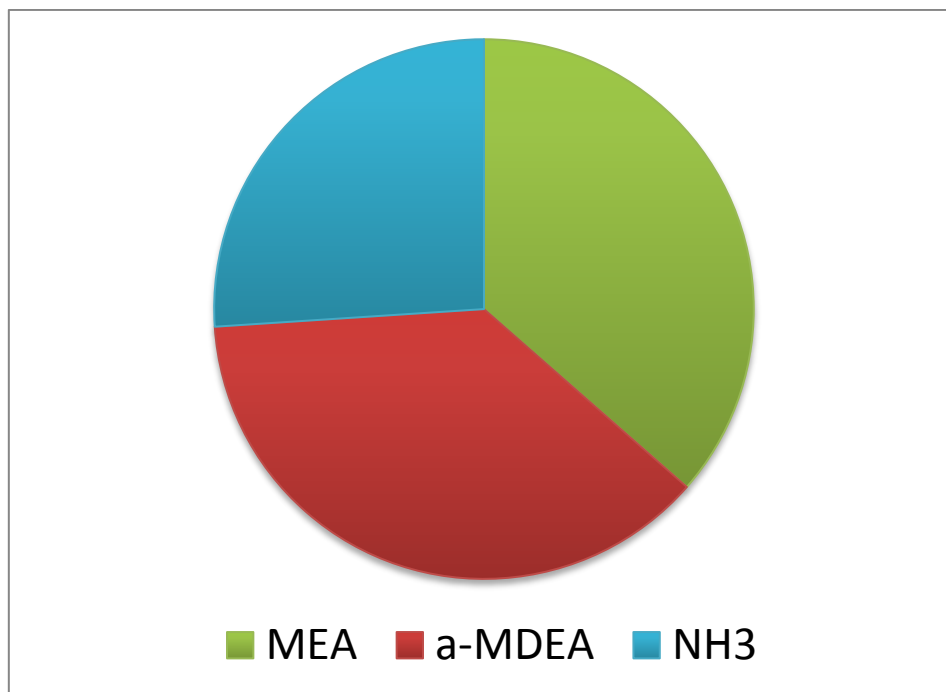


Figure 34 Comparison for the Cost Involved with different solvents

An approximate cost analysis gives the following pie chart where the ratio of cost involved in each of the method is presented. The cost involved for activated-MDEA (MDEA with piperazine activator) is the maximum and for monoethanolamine (MEA) it is almost equal to MEA solution. The cost involved for NH<sub>3</sub> solution is the least. A **percentage comparison** for the cost involved is shown in Figure 34 which is **26 %** for **NH<sub>3</sub>**, **36 %** for **MEA**, **38%** for **a-MDEA**.

Chemical absorption for capturing CO<sub>2</sub> from a flue gas has key challenges of the selection of an appropriate amine solvent and the reduction of energy consumption while maintaining the CO<sub>2</sub> emission target. In this thesis, three different amine solvents are studied namely MEA, a mixed solvent composed of MDEA and piperazine (PZ), called a-MDEA and aqueous ammonia solution. For MEA effect of capture percentage, effect of packing, effect of solvent temperature and effect of absorber height were studied with the reboiler duty. It is found that MEA process suffers several critical disadvantages, such as high heat requirement of regeneration and amine degradation by O<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, HCl. Besides most MEA based pilot plants are small scale and the amount of CO<sub>2</sub> captured per year is limited. In contrast tertiary amine like MDEA has relatively low reactivity and the desired reactivity can be obtained by using an activator such as PZ with a certain weight fraction of 5% in the solution which is difficult to maintain. The main disadvantage of this solvent is its slow reaction rate with CO<sub>2</sub>. Compared to MEA and a- MDEA, aqueous ammonia is more promising as a solvent for the large scale CO<sub>2</sub> capture process. For the CO<sub>2</sub> capture system, the suitable inner diameter and the packed height of the absorber are 12 m and 20 m, respectively. The suitable flow rate, the NH<sub>3</sub> concentration, the CO<sub>2</sub> loading, and the temperature of the lean aqueous ammonia are 4.2 m<sup>3</sup>/s, 3.0 mol/L, 0.23, and 38 °C, respectively. The suitable inner diameter and the packed height of the stripper are 10 m and 12 m, respectively. A detailed comparison is done among the three the solvents based on economic evaluation of the CO<sub>2</sub> capturing process taking into consideration four important parameters which mostly affects the economics of the process which are- CO<sub>2</sub> capturing percentage, Packing Height, CO<sub>2</sub> loading and Regeneration Energy which is the ratio of Reboiler Duty per kg of CO<sub>2</sub> captured. Based on these four parameters the solvent which had the least cost was aqueous ammonia solution and cost involved for the other two solvents was more than that of NH<sub>3</sub> solution. So NH<sub>3</sub> solution is the most economical solvent for capturing CO<sub>2</sub> from fossil fuel fired power plants in post combustion capture technology using chemical absorption.



## **RESEARCH PUBLICATIONS**

[1] Swaraj Panda, Arvind Kumar, “Dynamic Modelling, Simulation and Comparison of Large Scale Carbon Dioxide Capture in Coal Fired Power Plant using Various Amine Solvents” Under Review in Elsevier Editorial System™ for International Journal of Greenhouse Gas Control. Manuscript Number: JGGC-D-14-00193

## REFERENCES

1. Anusha Kothandaraman, Lars Nordb, Olav Bollandb, Howard J. Herzogc and Gregory J. McRae., 2009, *Comparison of solvents for post-combustion capture of CO<sub>2</sub> by chemical absorption*. Energy Procedia 1, 1373–1380.
2. Aspen Plus, 2008. *Rate-based Model of the CO<sub>2</sub> Capture Process by PZ Using Aspen Plus*. Aspen Technology, Inc.
3. Chen, H.S., Dou, B.L., Song, Y.C., Xu, Y.J., Wang, X.J., Zhang, Y., Du, X., Wang, C., Zhang, X.H., Tan, C.Q., 2012. *Studies on absorption and regeneration for CO<sub>2</sub> capture by aqueous ammonia*. International Journal of Greenhouse Gas Control 6, 171–178.
4. Dubois, L., Thomas, D., 2009. *CO<sub>2</sub> absorption into aqueous solutions of monoethanolamine, methyldiethanolamine, piperazine and their blends*. Chemical Engineering and Technology 32 (5), 710–718.
5. Haider M., Posch S., (2013). *Dynamic modelling of CO<sub>2</sub> absorption from coal-fired power plant into an aqueous monoethanolamine solution*. Chem. Eng. Research and Design. 91, 977–987.
6. J.C.M. Pires, F.G. Martins, M.C.M. Alvim-Ferraz, M. Simões, 2011. *Recent developments on carbon capture and storage: An overview* Chem. Eng. Process 89, 1446–1460.
7. Lawal, A., Wang, M., Stephenson, P., Koumpouras, G., Yeung, H., 2010. *Dynamic modeling and analysis of post-combustion CO<sub>2</sub> chemical absorption process for coal-fired power plants*. Fuel 89, 2791–2801.
8. Lawal, A., Wang, M., Stephenson, P., Yeung, H., 2009. *Dynamic modeling of CO<sub>2</sub> absorption for post combustion capture in coal-fired power plants*. Fuel 88, 2455–2462.
9. Madhasakul S., Ku H. M., Douglas P. L., (2013). *A simulation model of a CO<sub>2</sub> absorption process with methyldiethanolamine solvent and piperazine as an activator*. International Journal of Greenhouse Gas Control 15, 134–141.
10. Ruifeng Dong, Hongfang Lu, Yunsong Yu, Zaoxiao Zhang. 2012. *A feasible process for simultaneous removal of CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub> in the cement industry by NH<sub>3</sub> scrubbing*. Applied Energy 97, 185–191.
11. Schneider, R., Sander, F., Gorak, A., 2003. *Dynamic simulation of industrial reactive absorption processes*. Chem. Eng. Process. 42, 955–964.
12. Zhang M., Guo Y., (2013). *Process Simulations of large-scale CO<sub>2</sub> capture in coal-fired power plants using aqueous ammonia solution*. International Journal of Greenhouse Gas Control 16, 61-71.