James Coker, candidate for the degree of Master of Applied Science in Process Systems Engineering, has presented a thesis titled, *Mass Transfer and Emission Studies on a Catalyst-Aided CO2 Absorption and Desorption in a Post Combustion CO2 Capture Plant*, in an oral examination held on August 15, 2018. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

The mass transfer study of a catalyst aided absorption and desorption with the intent of minimizing the energy requirement for the solvent regeneration as well as improving the absorption efficiency of the solvent was carried out. This included the selection and screening for suitable amine solvents for the absorption and desorption process using a bench scale pilot plant. The solvent screening process was evaluated in terms of absorption efficiency, cyclic capacity of amine, height requirement of the column and the overall mass transfer coefficient of both the absorber and desorber. Solvents used were 5M monoethanolamine (MEA), 5M MEA-2M methyl diethanolamine (MDEA) and 2M 2-Butylaminoethanol (BEA)-2M 2- amino 2 methyl 1 propanol (AMP).

For process improvement, the selection and screening of a number of solid base catalyst to improve the absorption of CO₂ was also carried out. The improvement of CO₂ absorption with the selected solid base catalyst, K/MgO, for the absorption process and a solid acid catalyst, HZSM-5 for the desorption process was evaluated using the bench scale pilot plant. The result reveals the tremendous improvement with the addition of the catalyst in terms the overall mass transfer coefficient which translates into a shorter absorption and desorption column. A 46% increase in cyclic capacity, 95% and 45% increase in the overall volumetric mass transfer coefficient for the absorption (K_GAV) and desorption columns (K_LAV) respectively was obtained for the application of both catalyst.

A parametric study including effect of desorption bed temperature, absorber catalyst weight, solvent inlet temperature to the absorber, solvent flowrate, solvent blend ratio and hybrid desorption catalyst (HZSM-5 and γ-Al₂O₃) effect were studied. Results
also showed the effect of gas flowrate, solvent flowrate and the \%K on MgO as the most controlling parameters in the capture process.

An emissions study on volatile organic matter from amine degradation showed the emission of ethanol, acetone, acetaldehyde and ammonia as components of the emissions from the absorber. An economic analysis on the operating cost of CO\textsubscript{2} capture showed the introduction of the absorber catalyst as more economical with energy penalty of 232 Watts per kg of CO\textsubscript{2} produced.
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DEDICATION

I would like to dedicate this work to my parents, Mr. and Mrs. Coker and to my younger siblings Kenneth Coker and Archibald Coker
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NOMENCLATURE

wt.% - weight percentage

HTc- calcined hydrotalcite

SLPM- Standard liters per minute

mLpm- milliliters per minute

$K_{Ga}$- Overall Volumetric mass transfer coefficients, $\frac{kmol}{m^3.kPa}$

$K_{La}$- Overall Volumetric mass transfer coefficients, $\frac{1}{hr}$

$P_1$- pressure in autoclave reactor before $N_2O$ injection, kPa

$P_2$- pressure in autoclave reactor after $N_2O$ injection, kPa

$V_g$ - volume of the gas in autoclave reactor $m^3$

$R$ is the universal gas constant, kJ/kmol.K

$Z_{N2O}$ is compressibility factors of $N_2O$.

AAD- Absolute average deviation, %

BEA - 2-Butylaminoethanol

AMP – 2- amino 2 methyl 1 propanol

MEA- Mono ethanolamine

MDEA- Methyl diethanolamine

$F^\text{in}_{CO_2}$ - the flowrate of CO$_2$ in the feed gas, mol/s.
$F_{CO_2}^{out}$ the flowrate of CO$_2$ in the exit gas, mol/s.

$y_{A,G}$ mole fraction of component A in gas bulk, mol/mol

$y_{A,i}$ mole fraction at gas interphase, mol/mol

$k_G$ the gas phase mass transfer coefficient, $\frac{kmol}{m^3 K Pa}$

$N_A$ - The mass flux of component A across the gas-liquid interface, $\frac{kmol}{m^2 s}$

$H$ -the Henry’s law constant, $\frac{kPa m^3}{kmol}$

$E$ - enhancement factor

$y_{A,*}$is the mole fraction of component A in the gas phase in equilibrium with the concentration of A in the bulk liquid, mol/mol

$dZ$ -an element of the absorption column with height

$Y_{AG}$- the mole ratio of component A in the bulk gas,

$G_1$ the molar inert flow rate (total gas without component A)

$S$-the cross-sectional area of the column.

$L_1$ - the molar inert liquid flowrate,

$\rho_m$ the molar density of the solution, mol/m$^3$

$x_{AL}$ the bulk liquid mole fraction of component A, mol/mol

$x_{A,*}$ the bulk liquid mole fraction of component A in equilibrium with the bulk gas, mol/mol

$[A^*]$- the equilibrium solubility of CO$_2$ in the amine, mol/m$^3$
D_A - the physical diffusivity of CO_2 in amine, m^2/s

k_{mn} - the reaction rate constant between the CO_2 and amine

m - the order of reaction with respect to CO_2

n - the order of reaction with respect to the amine

B_0 - the concentration of unloaded amine, mol/m^3

a - the interfacial area between the gas and liquid film, m^2/m^3
CHAPTER 1 INTRODUCTION

The current global energy demand keeps growing each year owing to the dependence of power production and petrochemical industries as a source for their raw material (Canadian Association of Petroleum Producers, 2017). Most of their dependence has been on fossil fuels such as coal, natural gas and crude oil (Canadian Association of Petroleum Producers, 2017). Demand for energy has seen an exponential growth in developing nations, and renewable energy alone will not be able to keep pace. All sources of energy, including coal, natural gas and crude oil, are needed to meet the supply requirements for an advancing world economy (Canadian Association of Petroleum Producers, 2017). The burning of these fuels to generate energy has led to the release of dangerous and environmentally adverse gases which are referred to as greenhouse gases. These greenhouse gases result in a well-known phenomenon of global warming, the gradual heating of earth surface and its immediate environment. The greenhouse gases include CO$_2$, water vapour, choro fluorocarbons (CFC) among others. These emissions result in an increased earth surface temperature, which directly affects human activities in many ways through the rapid melting of polar ice caps, the presence of heat waves, drought, and severe weather (Houghton et al., 1990; IEA, 2005).

Greenhouse gases absorb ultraviolet radiation from the sun. The sun initially emits ultraviolet rays direct to the earth surface and its atmosphere. The sun rays reflect from the earth surface but are trapped in the atmosphere as greenhouse gases absorb these rays as infrared radiation. The absorbed energy for the greenhouse gases is transferred to the earth's atmosphere by radiation resulting in the gradual warming of the earth surface. This is referred to as global warming. These greenhouse gases are largely produced by both
industrial activities from the burning of fossil fuel as well as anthropogenic activity. However, Steinfeld et al. (2006) explained that greenhouse gases are also critical for regulation of the earth's surface since without it the atmosphere and the earth surface would be -6°C not 15°C. The greenhouse gases include carbon dioxide, methane, water vapour and nitrous oxide. Out of these, carbon dioxide has been identified as the most contributing greenhouse gas.

The vast majority of human-related carbon emissions comes from the burning of fossil fuels, mostly coal, from power generation plants. CO₂ is released through the burning of solid waste, fossil fuels, trees, wood products and also as a result of certain chemical reactions from chemical production industries like cement production. The combustion of fossil fuels rich in carbon results in the release of both water vapour and the CO₂. Methane is emitted from the production and transport of coal, natural gas, and oil. Methane emissions also result from livestock and other agricultural practices and by the decay of organic waste in municipal solid waste landfills (EPA, 2018). Methane is also combustible and as well as releases CO₂. Methane is one of the most naturally occurring greenhouse gases. Nitrous oxide, a greenhouse gas with less impact, is emitted during industrial and agricultural activities as well as during combustion of fossil fuels and solid waste. Among the greenhouse gases, CO₂ is the major contributor due to its abundance (IEA, 2009). Almost 60% of CO₂ emissions are from coal-fired power generation plants and other industrial processes such as those associated with refineries and natural gas processing plants (Osei et al, 2016). Thus, the removal of CO₂ from the atmosphere is important to prevent any impact of CO₂ emission particularly for the environmental effect. As of 2010, the major economic sector responsible for the emission of CO₂ was electricity
and power production industries recording 25% of the global CO₂ emissions with China as the leading contributor. Coal is the highest contributing fuel source in the emission of CO₂ (EPA, 2018). In 2016, CO₂ accounted for 81.6% of all U.S greenhouse gas emissions from human activities. Canada’s total CO₂ emissions for 2016 was 704 megatonnes (Mt) of carbon dioxide equivalent (CESI, 2018). In 2016, the oil and gas sector, and transportation sectors were the largest GHG emitters in Canada. Together, they accounted for almost 50% of total emissions. Next to the oil and gas sector is the electricity generation sector from coal which is one of the major contributors to the release of CO₂ (Environment climate change Canada, 2018) It is the largest contributor in the U.S accounting for 28% of total greenhouse gas emissions (EPA, 2016). Recently, more than 100 countries have agreed to help solve the ever-present issue of global warming and climate change problem by reducing the CO₂ emissions by 50% in 2050 (OCED, 2008). Steps involved in achieving this goal requires the CO₂ emission to be reduced to 25% by 2020. The Government of Canada is acting on climate change domestically and internationally. Under the Copenhagen Accord, Canada subscribed to a GHG emission reduction target of 17% below 2005 levels by 2020 -- equivalent to 607 Mt based on Canada's original 2005 baseline (Environment climate change Canada, 2018). In Canada, pricing on the emissions and a potential fine have led many CO₂ emissions industries to invest in its capture and storage. The process of CO₂ capture and sequestration provides a potential approach to reducing total GHG emissions and meeting the reduction targets that have been set out.
Figure 1-1: Canada’s emissions trend (Canada national inventory report, 2016)

Figure 1-2: a) GHG emissions by gas b) GHG emissions by Sector (Canada national inventory report, 2016)
1.1 CO$_2$ capture and sequestration

CO$_2$ capture and sequestration (CCS) includes system of technologies with the target of capturing carbon dioxide released from industrial and energy-related sources and sequestering and/or storing it thereby preventing it from being released into the atmosphere. The carbon capture and storage (CCS) is a well-invested field of averting climate change which involves the reduction of the carbon dioxide content of various effluent sources either before or after the use of fuel using an appropriate capture technology. There are various storage methods of the captured CO$_2$ including sequestration or storage in gas tanks. Research into the capture and storage of CO$_2$ has received much attention for about a century majorly involving research into cost-effective methods of capture and storage. Although all developed capture technologies are capable of being implemented, the sustainability, practicality and most importantly cost effectiveness creates some constraints on what kind of and suitable technology that can be implemented. Current research involves the capture, storage and utilisation of the CO$_2$ where the focus has shifted to the use of the stored CO$_2$. CO$_2$ is also used for enhanced oil recovery. For a coal-fired power plant, 20-25% more energy is required for capturing and compressing the CO$_2$ (Hammond et al., 2014). There are several existing capture technologies. Well developed technologies are grouped under pre-combustion, post-combustion and oxyfuel combustion.
1.1.1 Oxyfuel Combustion

Oxyfuel combustion for CO$_2$ captures operates by diluting the feed stream of fuel gas with a slipstream of its flue gas continuously to produce a stream of pure CO$_2$. The fuel is also burnt in oxygen not air to eliminate the composition of nitrogen in the flue gas. The main purpose of this technology is to generate a flue gas stream with a high concentration of CO$_2$ and water vapour making it easy to separate by condensing the water vapour below 100°C at 1 atm. The recycled slipstream is also used to control the flame temperature during combustion of the fuel (Stanger et al.2015). The process of oxyfuel begins with the separation of oxygen from the air. The fuel is initially mixed with pure oxygen during combustion which produces flue gas containing the CO$_2$. A part of the flue gas is recycled continuously. Oxyfuel combustion is a potential technology for CO$_2$ capture and storage; however, the cost involved in the separation of oxygen from air, undermines the practical application of the technology.

1.1.2 Pre-Combustion Capture

CO$_2$ capture by pre-combustion involves capture from solid, liquid and gaseous fuels prior to combustion by first converting it into a mixture of hydrogen and carbon dioxide using the process of gasification. Here, the solid fuel is converted to gaseous synthetic fuels or reformed for gaseous fuel source. In gasification processes, a feedstock such as coal is partially oxidised in steam and oxygen or air under extreme temperature and high pressure to form synthesis gas. The syngas serves as fuel for gas turbine generator for electricity generation. The conversion to syngas and CO$_2$ allows for the easy separation
of the CO₂ by physical and chemical means which renders the fuel gas free from carbon. The CO₂ in the final gas mixture can range between 15-50% prior to separation (Department of Energy USA, 2018). The high concentration of the CO₂ favours the separation of the gas from the flue mixture. Heat is recovered from the effluent syngas to generate extra energy to offset the energy penalty for the capture process. There several currently running pilot plants of the pre-combustion plant at the national carbon capture centre, Alabama. Typically, the capture of CO₂ from the gas mixture involves mostly physical solvents like selexol or rectisol. Generally, solvents are used in absorbing the CO₂ gas before being regenerated under pressure. Pre-combustion processes, however, operate at low temperatures below 40°C. Cooling the syngas to this temperature has the potential of condensing the water from the syngas leading to hydrate formation within the pipes.

1.1.3 Post Combustion Capture

CO₂ capture by post-combustion is the most mature and advanced technology among the three (Leung et al. 2014). Contrary to pre-combustion, post-combustion is carried out on the flue gas after the fossil fuel has been burnt in excess oxygen. This allows it to integrate well in the power production where the fuel is first combusted to generate electricity, and release flue gas containing 5-15% CO₂. Due to the high risk of contamination from flue gas impurities/contaminants, post-combustion capture unit is designed to be placed after specific purification units (Zhao et al., 2016). These purification units remove contaminants like NOx, SOx and particulate matters capable reducing the efficiency of CO₂ removal. The energy penalty for the installation of the post-combustion unit as compared to pre-combustion units is lower but still high in general.
The high energy is as a result of the relatively low concentration of CO₂ resulting in a low driving force for mass transfer. Lots of technologies fall under post-combustion including adsorption, membrane separation, cryogenic separation and chemical absorption.

1.1.3.1 CO₂ capture by adsorption

Carbon dioxide can be removed from flue gas with a number of non-reactive adsorbents. These adsorbents are solids. The process differs from absorption as it is a surface phenomena unlike solvent absorption which utilizes the entire solvent for separation. The CO₂ first attaches to the surface of these sorbents. The properties of the adsorbents like pore volume and surface area allow for the selective adsorption of CO₂ unto its surface. Adsorbents including carbonaceous materials and zeolites, a crystalline material of alumina and silica. Other adsorbents include high porosity activated carbon and charcoal. The limitation of this process is its low selectivity towards CO₂; hence, it is applicable only when the required CO₂ purity is at most 90% (Radosz et al, 2008). These sorbents are physical. The chemical sorbents include CaO/CaCO₃ systems.

1.1.3.2 Membrane Technology

Membrane technology is another mature technology in the field of post-combustion capture. Membranes generally consist of thin films of the polymer membrane. The permeability and selectivity of the membranes make them an ideal separation setup for CO₂ capture. Membranes rely strongly on the relative permeabilities of different gases to cause a separation. The rate at which molecules permeate are generally due to the
relative sizes of the permeating molecules for porous membranes. For dense membranes, separation is affected by the different solubility or diffusivities of the fluid in the membrane. Membrane permeability is increased by an increase in pressure. Due to the low partial pressure of CO$_2$ in the flue gas, there is a major challenge for the membrane-based separation when compared to liquid absorbents or solid adsorbents that are thermally generated. The working principle of a membrane depends on the driving force for effecting the transfer of a gas into a liquid. There are several driving forces which include temperature, concentration and pressure differences. Most industrial membranes are prone to wetting. Membrane wetting is the condition where components of either a liquid phase (liquid water) or gas blocks the channels for a specific component separation. This reduces their effectiveness for CO$_2$ removal. Industrial membranes include PTFE and PVCL.

1.1.3.3 Cryogenic Process

Most of the above technologies utilise one or more of either the physical or chemical properties of the CO$_2$ for separation. The cryogenic process utilises the unique solidification property of CO$_2$ as the basis of separation from other light natural gas components (Hart and Gnanendran, 2009). A high purity CO$_2$ gas has a sublimation point of -78.5°C. This is considerably higher than methane with a melting point of -182°C. In the cryogenic process, the gas is first dried to remove moisture as it can damage the compressor unit. The dried gas is cooled and slightly compressed. The compressed gas is cooled to the point just above the sublimation point of the CO$_2$. This removes any material that changes phase at a higher temperature than CO$_2$. The gas is expanded resulting in a further cooling as the temperature falls below the sublimation point of CO$_2$ thereby
producing solid CO$_2$. The solid CO$_2$ is further compressed and stored for use. The advantage of the process is in its high CO$_2$ capture ability, recovering about 99% of the CO$_2$ from the flue gas (Luis et al 2013). However, the high energy required during the successive gas compressions limits its practical application.

1.1.3.3 Absorption technology (Physical and Chemical)

Most of the above technologies are limited by cost of CO$_2$ capture. A technology that provides a better option in terms of cost and advanced capture knowledge is CO$_2$ capture by absorption. CO$_2$ capture by absorption into solvents involves the use of a liquid to remove CO$_2$ from the flue gas either by a physical or chemical interaction between the solvent and CO$_2$ gas. This technology differs from adsorption as it uses liquids for absorption instead of solids. Absorption also utilizes the entire solvent whereas adsorption is a surface phenomenon. The operating procedure of gas absorption involves two main mass transfer processes, absorption and desorption. First the flue gas rich in CO$_2$ is supplied to an absorption column where it contacts the solvent for CO$_2$ removal. The solvent becomes rich in CO$_2$ and leaves the bottom of the absorption column. The rich solvent is then supplied to a desorption column in which either a decrease in pressure or an increase in temperature will result in the release of CO$_2$. This makes the solvent lean in CO$_2$ and ready to absorb more CO$_2$. The CO$_2$ lean solvent is supplied back to the absorption column to continue the cycle. Physical absorption utilises the solubility of the CO$_2$ in the solvent.
This type of absorption is carried out in a flue gas stream with a high partial pressure of CO$_2$, since high pressure relates directly to higher solubility of a gas within a fluid (Henrys law constant). Some physical solvents include Selexol and Rectisol. Physical absorption depends on gas solubility, surface area between gas and liquid interface, and operating conditions like temperature and pressure (Sreedhar et al., 2016). The solvent is regenerated by application of pressure and a high temperature in the desorption column.

One of the prospective options to reducing the emissions of CO$_2$ from gas streams in a post-combustion capture field is absorption of CO$_2$ into chemical reactive solvents, which has recently been considered as one of the most mature and reliable CO$_2$ reduction technologies (Naami, 2013). Chemical solvents are used when the partial pressure of the CO$_2$ in the flue gas is low (<15 kPa). The principle of chemical absorption involves a chemical reaction between CO$_2$ and the solvent. This greatly reduces the resistance to mass transfer between the gas and liquid, increases the driving forces for transfer across both films, and increases the mass transfer area. Due to the low partial pressure of CO$_2$, its physical solubility in most solvents is low. Coupling this with its low partial pressure makes absorption with these chemical solvents ideal for low CO$_2$ partial pressure flue gas feeds like coal-fired power plant and natural gas. Like physical absorption, chemical solvents are easily regenerated by the application of heat in the desorption column. As a result of side reactions, chemical solvents are easily contaminated requiring solvent makeups.

There are several chemical solvents including aqueous solutions of amines, potassium carbonate, and ammonia. Among these solvents, amines are considered to be the most advanced practical chemical solvents used for the capture of CO$_2$. Typical CO$_2$
recovery is between 80-95% with a product purity in excess of 99% (Rao and Rubin, 2002). The CO₂ rich solvent is supplied to a desorption column for regeneration. The major challenge in the capture and regeneration with amine is the high energy required for regeneration of the amine. Shi et al. (2014) identified the regeneration of amines to account for 78% of the total energy requirement of the entire process. Current research is geared towards finding suitable and optimised ways of minimizing the energy requirement for the absorption process whiles increasing the CO₂ removal efficiency. The are several amines applied in the CO₂ capture technology. A common conventional amine solvent is monoethanolamine (MEA). The amines are classified according to the number of hydrogen ions substituted or the number of alkyl groups bonded to the N-atom of the amine. These groups are: primary, secondary and tertiary amines.

Primary amines have one hydrogen ion substituted with mostly an alcohol group on the nitrogen ion. Secondary and tertiary however have two and three substituted hydrogen ions on the nitrogen ion respectively. The alkyl group attached to the amine may contain an OH⁻ ion. The OH⁻ pulls more of the shared electrons from the nitrogen onto itself resulting in a partial negative charge on the OH⁻ ion, referred to as the electron withdrawing effect. The result of this is a weakened reactivity of the solvent. For this reason, primary amines are generally the most reactive of all the solvents. Reactivity of amines with similar structure follows Primary>Secondary>tertiary. The OH⁻ however, increases the ability of the solvent to mixing with water in an aqueous solution. Primary amines include monoethanolamine (MEA), 2 methyl 2 amino 1 propanol (AMP) and methylamines. A sterically hindered amine is a primary amine that has its amino group (-NH₂) fixed to a tertiary carbon atom in the amines structure. Essentially, they do not form
carbamates. An example is AMP and KS-1 developed by Mitsubishi HI, Japan. Secondary
amines are generally less reactive than primary amine. Secondary amines however have
high solvent capacity. Tertiary amines are least reactive with the slowest kinetics. Tertiary
amines have the highest solvent capacity for CO₂. Diethanolamine (DEA),
Butylmonoethanolamine (BEA), and diphenylamine (DPA) are noted examples of
secondary amines. Tertiary amine includes triethanolamine (TEA), methyl diethanolamine
(MDEA), trimethylamine (TMA). The most studied amine is monoethanolamine (MEA),
MDEA, and piperazine (PZ). The structure of the amine plays an important role in its
activity. Cyclic amines are noted for being the most reactive all solvents. Amine-based
technologies are currently the most advanced and cost-effective means of post-combustion
CO₂ (D’Alessandro et al., 2010).

1.2 Solvent Chemistry

Amine solvents performance has been linked in resent research to its solvent
property. Research into the properties of the solvent provides key properties like side chain
length and number of alkyl group. Narku-Tetteh et al. (2017) investigated the effect of side
chain length and number of alkyl groups on the Amine CO₂ reaction performance. A lot
of research and publications have been devoted to the study of kinetics and mechanism of
the CO₂-amine reaction as well. The reaction between CO₂ and primary or secondary
amine was introduced by Caplow et al. (1968) and was later reintroduced by Danckwerts
et al. (1970). The work of these researchers revealed that the reaction mechanism for the
primary and secondary amine followed a zwitterion mechanism in a two-step process
where the CO₂ reacts first with the amine to form zwitterion which further reacts with any
base in the system to produce the carbamate in a second step. Tertiary amines are unable to react directly with CO$_2$ to form carbamate ion since there is no hydrogen ion on the amine to react with the CO$_2$. The reaction is however complete by the presence of water in a three reactants reaction to form protonated amine and bicarbonate instead of carbamate. The reaction of tertiary amines is slow; however, the ease of desorbing bicarbonates makes it a suitable option for desorption.

1.3: Absorption in Packed Columns

CO$_2$ capture in packed columns is an improved post-combustion capture technology where both the internals of the absorption and desorption columns are installed with packing material. These materials provide a high surface area for mass transfer, higher than that provided by plates. A high degree of wetting of these packing creates the high mass transfer area required for interfacial mass transfer. A high mass transfer rate results in a faster kinetics. An efficient packing either random or structured within the columns, should offer characteristics such as large surface area-to-volume ratio, low-pressure drop across the absorber, and good uniform distribution of the gas (Naami, 2012). A lower pressure drop allows for easy flow of both fluids within the column and prevents flooding of the liquid within the column. A higher pressure drop will mean more energy is required to compressing the CO$_2$. Fernandes et al. (2009) studied structured packing and discovered that the high surface area in this packing increases the mass transfer efficiencies. However, channelling, a major issue with packed columns, may occur at low liquid flow rates. In the conventional CO$_2$ Post combustion capture process, the feed gas is first supplied to the saturator where the gas is saturated with water before entering the
absorption column. In the absorption column, the gas contacts a lean amine (amine with low CO$_2$ concentration) where mass transfer across the gas into the liquid occurs. The liquid-rich CO$_2$ exits the absorption column as well as the treated gas. The rich solvent goes through a lean rich heat exchanger to exchange heat with the lean amine from the desorber. The rich amine is supplied to the desorption column where heat is applied to desorb the CO$_2$. The solvent leaves the desorption column to the reboiler where more heat is applied. This produces a much leaner amine solution and a gas mixture of CO$_2$ and water vapour. This gas mixture enters the desorption column as it contacts the incoming solvent and aids in heating up and desorbing CO$_2$ from the solvent yet to enter the reboiler. The reboiler operates at temperatures above 120°C and pressures of 2bars and above. A novel technology presented in this work uses a heater instead of a reboiler. The heater is located between the lean/rich heat exchanger and the desorption column. The heater heats the amine from the lean-rich heat exchanger to temperatures below 100°C. The aim of this was to provide an alternative heating source (liquid water) instead of steam capable of desorbing CO$_2$ from the solvent.

1.4 Catalyst Aided CO$_2$ capture

The is a high reboiler duty leading to a higher energy penalty of the capture plant integrated with a power plant. A method of process improvement suggested by Idem et al. (2017) involves the installation of catalyst in the absorption and desorption columns to further improve the capture process through enhanced CO$_2$ amine kinetics and mass transfer. The catalyst is used to increase the rate of reaction between the CO$_2$ and amine.
Solid catalyst is the most common catalyst application in fluid reaction due to the ease of separation after the reaction. Many sustainable catalysts supports have been developed particularly for CO₂ gas applications (Mazlee, 2016). Solid catalysts have advantages over liquid catalysts in the construction of efficient and environmentally benign processes (Ono, 2015). The simplified mechanism of solid catalyst involves three main processes. First, the reactants adsorb onto the catalyst active site, the reaction occurs and the product desorbs from the catalyst surface. There are several solid catalysts used in the reaction but the two-important catalyst for CO₂ capture are solid acid and solid base catalyst.

For the amine CO₂ absorption process, two reactions occur according to the zwitterion mechanism. These include CO₂ reaction with the amine to produce the zwitterion molecule in an electron transfer process. The zwitterion molecule reacts with any base in a hydrogen ion (H⁺ proton) abstraction process to form a carbamate molecule. The mechanism is only different for tertiary amines where the CO₂ reacts with the amine and water in a single step process to form bicarbonate ions and water. The two-step zwitterion reaction mechanism has been identified as a base catalysed reaction (Danckwerts, P., 1979). Base-catalysed reactions are initiated by acid–base interactions in which the catalysts act as base and the reactant, in this case CO₂, act as acid. The reverse is true for acid catalysed reactions.

The desorption reaction also involves two main reactions. The abstraction of a hydrogen (H⁺) proton (deprotonation) from a protonated amine, followed by the reaction between the abstracted proton and carbamate to form CO₂ and free amine. Protonated amine is formed when the amine reacts with the zwitterion molecule during the absorption
reaction. The two-step desorption reaction mechanism has been identified as an acid catalysed reaction (Shi et al., (2014)).

1.4.1 Solid Acid Catalyst

A solid acid catalyst performs the role of an acid in an acid-base catalysed reaction. A solid acid catalyst can be either a Bronsted or Lewis acid catalyst. A Bronsted solid acid catalyst, like a Bronsted acid, is a catalyst with active site which donates protons in a reaction. Lewis acid catalyst has active site that accepts an electron from reactants during the reaction. The acids are regenerated after proton transfer on the completion of the reaction making it ready as acids for further reactions. In the desorption process, the most energy intensive reaction identified as the rate determining step involves the proton abstraction from the protonated amine (Shi et al., 2014). This makes the Bronsted acid catalyst the most suitable catalyst as it promotes the H⁺ proton transfer. The solid acid catalyst for acid-base reactions include specific zeolites like ZSM-5, MCM-22 and chabazite, metal oxides like Al₂O₃, SiO₂ and TiO₂. Solid acid catalyst application in CO₂ capture was first proposed by Idem et al. (2006). Pilot plant studies for a number of solid acid catalyst including HZSM-5, γ-Al₂O₃ and HY was carried out by Osei et al. (2016) and Akachuku et al. (2016). Results showed the improvement in the use of these solid acid catalyst for the desorption process. HZSM-5 is a solid acid catalyst with predominantly Bronsted acid sites. The HZSM-5 catalyst donates its H⁺ proton in the deprotonation reaction of the protonated amine. On the other hand, γ-Al₂O₃ is a catalyst with predominant Lewis acid sites.
Solid acid catalysts have been applied in the field of low-grade biodiesel production (Mansir et al. 2016). In solid acid catalysis, the acid strength, number of acid sites and type of acid site are parameters considered when selecting a suitable solid acid catalyst. The major drawback to the use of these catalysts is deactivation caused by impurities in the feed and mass transfer limitation on the access to active sites.

1.4.2 Solid Base Catalyst

Solid base catalysts are the opposite of solid acid catalyst as the active sites perform the role of a base in base catalysed reaction. A solid base catalyst with its active site acting as proton acceptor is referred to as Bronsted base catalyst whiles that acting as an electron donor referred to as Lewis base catalyst. In CO$_2$ absorption into amine, the electron transfer process of CO$_2$ reacting with the amine has also been identified as the rate determining step (Caplow, M., 1968). This makes a base catalyst that is capable of donating a lone pair electron (i.e. a Lewis base catalyst) the most suitable for increasing the reactivity between the CO$_2$ and amine. The Lewis base catalyst first donates a lone pair of electrons from its anion to the CO$_2$ molecule by bonding loosely with CO$_2$ and allowing more contact time for the reaction with amine which makes the CO$_2$ more susceptible to the amine.

Most research has been focused on solid acid catalyst due to its vast application in the petroleum industry and refinery (Ono et al. 2010). A number of solid base catalysts have been identified including metal oxides like MgO, CaO and BaO. The strongly base site is generated by removal of water and carbon dioxide by pre-treatment at high temperature from the surface (Hattori, 2003). Alkali compounds on a support like KOH/
γ-Al₂O₃ as well as alkali metals on a support which includes Na/MgO, K/MgO and K/γ-Al₂O₃. Ono et al. (2010) reported the strength of the solid acid catalyst as Hemmett number whiles that of solid base catalyst was reported as H_acidity. The few publications on the application of these solid base catalyst on CO₂ capture includes a patent by Idem et al. (2012) and a recent work by Shi et al. (2015). A number of these catalyst were tested and results showed their effect on the application in the CO₂ amine reaction to produce carbamate, bicarbonate and protonated amine. Results show that solid base catalyst is capable of increasing the rate of reaction between the CO₂ and the amine. This work started with the screening and selection of a number of the solid base catalysts. Similar to solid acid catalysts, base characteristics like the basic strength, number of base sites and type of base site aid in the selection of a suitable basic catalyst. Deactivation of the catalyst is one drawback for using catalysts. Solid-base catalysts, therefore, offer environmentally benign and more economical pathways for CO₂ capture.

1.5 Mass transfer Performance

The overall mass transfer coefficient represents the constant of proportionality between the mass transfer rate or flux and its driving force. Therefore, for a specific or constant driving force, the rate at which a component moves across a gas or liquid film will depend on the overall mass transfer coefficient. A high value will mean a faster rate of mass transfer within that system for that specific driving force. More essentially, the height of the design separation units (Absorption and desorption columns) is inversely proportional to the overall mass transfer coefficient. This also means a high mass transfer coefficient will result in a shorter absorption/desorption column. The overall mass transfer
coefficient can be written in terms of either the gas side or the liquid side however, it is advisable to write in terms of the film of higher resistance as that will result in the largest possible column height to result in such a separation (worst case scenario).

1.6 Research Problem

There are two main challenges that CO$_2$ capture by post combustion poses. These include improving the carbon capture efficiency of the process as well as a reduction in the energy required for the solvent regeneration. The target of research is to investigate the processes that help improve the carbon capture efficiency which will result in avoiding the charges posed on CO$_2$ emission (carbon tax). The energy required for the desorption of CO$_2$ also needs to be reduced since it accounts for 80% of the total operating cost. Investigations on increasing capture efficiency in the absorber showed strong correlations to the process in the desorber when reactive solvents used are recycled (Sakwattananpong et al., 2005). It is therefore essential to investigate trends that lead to an increase in CO$_2$ capture so to avoid carbon tax. Most research into the capture of CO$_2$ has been delineated into two main area, the solvent improvement and process optimisation. Current research challenge under solvent improvement is finding a suitable solvent capable of improving the capture efficiency of CO$_2$. Previous solvent selection criteria used random selection however, current research by Narku-Tetteh et al. (2017) developed a solvent selection criterion based on selected properties on the solvent. The challenge is linking all the physical and chemical properties of the solvent to its performance. Viscosity is one major challenge to selecting a suitable solvent. Increasing the solvent concentration increases solvent viscosity which limits performance. Current researches are aimed at selecting
novel solvents as well their blends that can perform well in both desorption and absorption. A less viscous solution that is capable of achieving 90% in other to avoid the carbon tax is currently being researched.

The desorption of CO$_2$ from amine is an energy intensive process. Finding solutions to the high energy requirement of desorption continues to be the major challenge. The energy required in desorbing CO$_2$ from an amine takes about 80% of the total operating cost and it accounts for the energy penalty from its integration with power plants. It is therefore essential to minimising the energy required to desorb a ton of CO$_2$ which is the focus of research now. This high energy requirement, usually referred to as the reboiler heat duty is essentially a sum of the sensible heat for raising the temperature of CO$_2$-loaded solution (known as the rich solution) to the boiling point, heat of reaction for breaking the chemical bonds between CO$_2$ and the solvent, and heat of vaporization responsible for generating water vapor required for regeneration. Several approaches are being tested to reduce the energy penalty of solvent regeneration. On the solvent improvement side, tertiary as well as hindered amines capable producing bicarbonates which require less energy to breakdown are being research on currently. Current research technology into solvent improvement is focused on selecting a suitable solvent as well as their blend capable of achieving a high absorption efficiency but with less energy required. This includes bi-solvent and tri-solvent blends of amines. The concept of mixing solvents with favourable absorption characteristics and desirable desorption features has seen to the reduction of the energy for regeneration considerably. Another aspect of improving the capture of CO$_2$ is process improvement where the conventional capture process is modified to bring the desired capture efficiency. Less attention has been received in this
section due to the ease in solvent improvement as compared to a modification to the capture process. One such modification is with the use a heater in place of the reboiler. The intention here is to use liquid water instead of steam in providing heat to the amine. Since this process is aimed at reducing the energy penalty for the capture of CO₂, the solvent for desorption is heated to temperatures below 100°C (lower than the conventional process of 120°C). The desorption performance is lowered at this temperature which allows for the application of catalyst to aid the further desorption of CO₂ from the amine. Potential savings were recognised when modifications were made with the application of solid catalyst in the desorption process. (Osei et al., 2016).

### 1.7 Research objectives

The overall objectives of this research are as follows:

1. Synthesize and screen a number of solid base catalyst application in the absorption of CO₂ into an amine solvent. The experiment to screen the catalyst was performed in a semi-batch experimental setup.

2. Validate the laboratory scale pilot plant setup using 5M MEA aqueous solvent with HZSM-5 catalyst. The results are compared with previous works by Akachuku et al. (2016) under similar experimental conditions including the application of HZSM-5, a desorption catalyst.

3. Screen a number of aqueous amine solvents including 5M MEA, 7M blend of MEA/MDEA and a 4M blend of BEA/AMP. This work is also required to validate
the work done by Narku-Tetteh et al. (2017) in selecting a suitable solvent for CO₂ capture.

4. Perform general as well as mass transfer performance studies on selected solvents whiles evaluating the effects of the selected absorber catalyst in increasing the absorption rate or mass transfer rate of CO₂ into the amine.

5. To determine the physical properties of both unloaded and loaded solutions of different BEA/AMP blended ratios and develop a model for Henrys law constant, density and viscosity of the blended ratios.

6. To perform a comprehensive mass transfer study on the application of both the HZSM-5 and the developed absorption catalyst on BEA/AMP. Mass transfer models are developed relating mass transfer coefficient to independent performance parameters.

7. Perform parametric studies to develop the most dependant parameter on mass transfer of CO₂ into an amine.

8. Emission studies to determine the components of gas emissions as a result of possible amine degradation.

1.8 Thesis outline

This thesis is structured in chapters as follows. The first, Chapter 1, gives a general overview of the thesis in introduction highlighting all the relevant points of this work including justification for this field of research. Chapter 2 provides a comprehensive literature review of the research problems touching on all important works done in the same field. This chapter also looks at the progression in terms catalytic absorption and
desorption. Chapter 3 provides details on the experiments and experimental section. Chapter 4 looks at the results which describes mass transfer performance for CO$_2$ absorption in the conventional amine: MEA and MDEA, and the new chemical solvent blend of BEA/AMP in a method to screen out a suitable solvent. The results of screening solid base catalyst are included in this section. Chapter 5 looks at a comprehensive parametric and an economic analysis of the capture process. Chapter 6 looks at the catalyst deactivation studies of 10%K/MgO. Chapter 7 includes statistical analysis on the capture process which includes the use of the catalyst. This includes both catalytic and parametric statistical analysis. Chapter 8 looks at physical properties of the mixed solvent system BEA/AMP. The section includes solubility data, Henry's law constant, the density of loaded and unloaded solution. Finally, chapter 9 gives the conclusion with constructive recommendations for the catalyst aided capture process.
CHAPTER 2: THEORY AND LITERATURE REVIEW

2.1 Theory of Chemical absorption

Chemical absorption is a field of separation which deals with the chemical interactions between a gas and an absorbing liquid. The separation of an essential component in the gas into a chemical solvent is with the contact between the two fluids. The chemical interaction between the soluble gas and its absorbing liquid allows for more of the soluble gas to enter the liquid by means of providing a higher concentration gradient across both fluids and a reduction in the film resistances. Chemical absorption has become the most widely used process in most industrial sectors including chemical manufacturing, petroleum and natural gas industries as well as cement production industries. CO$_2$ absorption using alkanol amines have been researched and implemented on a large scale. Alkanol amines are the most popular absorbents used to remove CO$_2$ from process gas streams (Narku tetteh et al., 2017). The most commonly used solvent is monoethanolamine (MEA) because it has a faster rate of reaction with CO$_2$ than other secondary or tertiary amines. This allows absorption to take place in a smaller column. Most of the research in this area focuses on the absorption of CO$_2$ into the conventional solvent of aqueous MEA.

Astarita, in 1960, pioneered studies into the absorption of CO$_2$ in aqueous solutions of MEA using a laminar jet absorber. The laminar jet provided an essential knowledge of an increase in both the absorption and kinetic rates with the use of a chemical solvent in comparison to its physical absorption. This work was also replicated using a disc type absorption column. Freguia and Rochelle (2004) also investigated the absorption of CO$_2$ into 30wt% MEA in a packed column. Sensitivity analysis was also performed on the process variables to find optimum operating conditions. Results showed that the process
parameters like absorber height and solvent all affect the mass transfer rate of absorption which is eventually translated into the heat duty in the desorption column. An increase in the height of the absorber by 20% showed a reduction in the reboiler duty of 5%. Whitman and Davis (1924) absorbed CO$_2$ using a 15-plate tower with one bubble cap per plate using sodium carbonate solution as an absorbent and observed a low absorption efficiency, below 65% which was attributed to the low performance of plate absorbers. Subsequent works, therefore, focused on the use of packed columns for CO$_2$ absorption. Tan et al. (2012) also investigated the factors affecting CO$_2$ absorption efficiency in a packed column as a means of promoting efficient gases and liquids contact. Results showed the increase in absorption performance with using MEA over NaOH, structured packing over random packing and an increase in the liquid flow rate. Yeh et al. (2001) finally confirmed the improvement in the absorption performance with a structured packing material.

### 2.2 Theory of Chemical Desorption

Desorption studies have received less focus in research for CO$_2$ capture. The desorption process is the most important section of the post-combustion capture due to the high energy consumption for the regeneration of the chemical solvent (Zhang et al. 2014). The desorption section also includes the mechanism for providing heat to regenerate the loaded solvent as well as a mechanism to initiate a separation of the two phases. The energy for the regeneration accounts for about 80% of the total operating cost (Shi et al., 2014b). Astarita and Savage (1980) first looked at the mechanism of desorption about absorption. This work looked at the basic points of difference between chemical absorption and desorption and identified the points to which the two processes can be related.
However, Landeau (1992) concluded that when all reactants enter the reactor as components of the reaction phase, desorption cannot be viewed as the mirror image of absorption as earlier publishers have done. This practically makes the desorption process of primary importance. Astarita and Savage (1980a) developed a complete analytical solution for the film theory model for desorption accompanied by an instantaneous, reversible chemical reaction which is the reality of desorption conditions industrially. The widely used mechanism of CO₂ desorption is a packed desorption column coupled with a reboiler unit located at the bottom of the column.

Recent regeneration studies have been presented by Gao et al. (2017). In this study, the heat of regeneration of CO₂ from rich monoethanolamine (MEA)-methanol solvent was evaluated in a pilot-plant stripper packed with Sulzer packing BX500, Mellapack packing Y500 and Pall rings. The effect of using two different solvents was investigated between MEA-methanol and aqueous MEA solvent to evaluate the potential for MEA-methanol's application in the industrial CO₂ capture process. Also, the effects of several operating parameters of the desorption column consisting of rich CO₂ loading (0.25–0.52 mol/mol), rich solvent flow rate (21.2–51.4 L/h), rich solvent temperature (40–60°C) and regeneration temperature (68–74°C) on the regeneration performance of the stripper were studied. Results from this work showed that methanol enhanced the desorption process. An increase in rich CO₂ loading ranging from 0.25 to 0.52 molCO₂/mol amine resulted in a decrease of regeneration heat duty. This was attributed to the desorption of CO₂ from a leaner rich loading requiring more stripping steam to produce enough driving force for desorption to take place. Also, Sulzer DX packing had the least regeneration heat duty due to its high contacting area providing an effective mass transfer of the CO₂ in the gas phase.
and also the structured packing has higher surface area than random packing resulting in a faster mass transfer rate in the desorption column.

Most works of desorption employ the use of a reboiler as the heating source. However, works by (Akachuku et al., 2016; Osei et al., 2016; Decardi Nelson et al., 2016) employed the use of a heater instead of a reboiler located between the lean-rich heat exchanger and desorption column. The purpose of this was to provide an alternative lower temperature (below 95°C) of regeneration and as well increase the regeneration rate by employing a catalyst in the desorption column. Results of this showed a slightly higher heat duty as less CO₂ is produced from the heater configuration. However, the complete elimination of the reboiler and the introduction of a catalyst coupled with the total elimination of steam required initially to heat solvent above 100°C creates an essential technological advancement as the possible energy penalty from an integrated power plant is heavily reduced.

2.3 Amine Solvents for CO₂ capture

MEA is the most used conventional of all the amines applied in the capture of CO₂. Most of the amines used in the conventional absorption for CO₂ were derived from their commercial use in natural gas where amine-based processes have been utilised for the removal of acid gas impurities from process gas streams. (Strigle 1987; Kohl and Nielsen, 1997). Primary amine like MEA and secondary amines like diethanolamine DEA react rapidly with CO₂ to form carbamates. However, the heat of absorption with respect to carbamate is high resulting in a high regeneration energy.
Aroonwilas et al. (1999) studied aqueous solutions of sodium hydroxide (NaOH), monoethanolamine (MEA), and 2-amino-2methyl-1-propanol (AMP) employed as absorption solvents. Results in terms of the mass transfer coefficient confirmed earlier work done by Dubois et al. (2009) also investigated absorption of CO₂ using aqueous solutions of MDEA and MEA. Results showed that tertiary amines are the slowest of reactions between the CO₂ and the amine which is attributed to its reaction mechanism to producing bicarbonate instead of carbamate. However, desorption studies also showed a high performance of the MDEA due to ease in desorbing bicarbonate than carbamate. Veawab et al. (2004) also investigated CO₂ absorption into various aqueous alkanolamines including monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA). Results on the absorption performance of the test solutions were in the following order: MEA > DEA > DIPA > MDEA. Generally, the results showed a higher absorption of primary amines followed by secondary amines, and then finally the tertiary amines. The OH⁻ group has an electron withdrawing effect which reduces the basic strength of the amine (Narku-Tetteh et al., 2016). This is the specific reason for the higher absorption rate of MEA (a single OH⁻ group) over DEA (two OH⁻ groups). DIPA is a tertiary amine with a long chain OH⁻ group.

Narku-Tetteh et al. (2017) also investigated the effect of alkanol chain length and showed that the longer the chain is from the amino group, the less the electron withdrawing effect, and hence the higher the reactivity. This is the case for DIPA over MDEA both of which are tertiary amines. Barzargli et al. (2009) also investigated CO₂ absorption into aqueous solutions of DEA, MDEA and AMP. The result showed AMP is the most reactive of all amines as a primary amine. Each solvent investigated showed a unique performance.
Chakravarty et al. (2000) investigated the effect of blending the solvents with the purpose of maximising the effect of each component from the blend. Studies of a blend between MEA and MDEA were investigated. The results showed an increase in the overall performance with the addition of the MDEA tertiary amine to the MEA. In the absorber, the MEA in the blend at the top of the column serves to remove residual CO$_2$ from the gas while throughout the rest of the column MDEA does a bulk removal job. Also, improved desorption performance was observed with the MDEA as it forms bicarbonate, easier to desorption compared to MEA. Dawodu et al. (1994) also investigated the solubility of CO$_2$ in blends of MDEA+MEA, MDEA+DEA and compare to a single amine of MDEA. Results showed that the performance is of the order MDEA+MEA > MDEA+DEA > MDEA. This confirmed previous works as the blend performance superseded the single blend. The absorption improvement with the addition of MEA confirms the knowledge that a solvent component in a blend improves the performance of the other component. Recent blend studies are considering diamines such as piperazine and cyclic monoamines such as piperidine and its alkanolamine derivatives (Adeosun et al., 2013). Mandal et al. (2001) also studied the CO$_2$ absorption into aqueous blends of MDEA and MEA as well as AMP. The results showed that the addition of a little concentration of MEA to an aqueous solution of MDEA significantly increased the rate of absorption for both solvents. Setameteekul et al. (2008) studied mixtures of MEA-MDEA in CO$_2$ absorption for coal-fired power plants and was deduced that the energy consumption for regenerating CO$_2$ is reduced significantly when a suitable concentration of MDEA is added to MEA.
Current studies have looked at blends and tri-blends of solvents with the purpose of developing a suitable solvent blend for the post-combustion capture study. Nwaoha et al. (2016) investigated a novel tri-solvent blend between methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and diethylenetriamine (DETA). This work uniquely selected a tri solvent blend to address the issue of viscosity affecting the rate of absorption and eventually its efficiency. The AMP– MDEA – DETA tri-solvent blends showed higher performance as compared to 5 kmol/m³ MEA in terms of equilibrium CO₂ loadings, absorption capacities, initial desorption rates, cyclic loadings, cyclic capacities and regeneration energies.

Barzagli et al. (2009) also investigated the performance of several amine solvents including butyl ethanolamine (BEA). Results showed the superior performance of the BEA over the aqueous solution of MEA. This was attributed to the high basic strength of BEA. Narku-Tetteh et al. (2016) also investigated the same BEA amine solvent. Results from their work also confirmed the high absorption performance as well as desorption performance and attributed it to the presence of the alkyl group on the BEA. The alkyl group provides a more stable carbamate formation and eventually results in a high absorption rate. However, the high viscosity of BEA and AMP limits the application of high concentrations in the post-combustion capture.

All published literature on the amine solvents and their blend confirms the increase in CO₂ capture performance with the appropriate solvent blends. In this work, there are four amines of primary interest, namely, MEA, MDEA, BEA and AMP.
Figure 2.3-1: Reaction pathways of primary, secondary, tertiary and sterically hindered amines (Nwaoha et al., 2016)

Figure 2.3-2: Chemical structure of amines used.
2.4 Catalytic Absorption

Levenspiel (1999) identified the mechanism of gas absorption with a catalyst involved. This was an extension of the two-film theory as it applies to gas-liquid mass transfer. The soluble gas first transports through the entire gas bulk across the gas film by the action of concentration gradient. The gas then at the gas-liquid interface dissolves in the liquid by its solubility in the liquid. Within the liquid, both reactants, the reacting gas from the gas film and the reacting liquid component must diffuse to the catalyst surface for reaction to occur. The catalyst diffusion and surface reaction begin with the transport of both reacting components across a liquid film around the catalyst pellet followed by pore diffusion of these components through the pores of the catalyst to the catalyst active site for surface reaction. Therefore, the catalyst introduces two new resistances to mass transfer: solid-liquid film resistance and pore diffusion resistance, in addition to the original gas film and liquid film mass transfer resistances.

The process of improving both the absorption and desorption process with the application of a catalyst is intended to increase the mass transfer rate by enhancing the reactivity between the solvent and CO$_2$. The amine-CO$_2$ reaction has been identified to be catalysed by a base catalyst by Idem et al. (2011). It has been identified by Caplow (1968) that the rate limiting step for CO$_2$ absorption reaction based on the zwitterion mechanism is the first reaction step which is zwitterion formation. The second reaction has been identified to occur instantaneously. According to Astarita et al. (2004) and Danckwerts et al. (1987), any component that has an O$^2-$ or OH$^-$ groups has a potential to work as a base catalyst. The strength of several solid base catalysts was reported in literature (Ono et al., 2010).
The method of first selecting the suitable catalyst was based on these reported basic strengths. The Hₐ acidity function is the most used characterisation tool for the solid base catalyst according to Ono et al. (2010). This method was initially applied to characterize acid solution, similar to the Hammetts acidity function, Hₒ. Tanabe in 2010 proposed to use the H⁻ scale as a measure of the strength of solid base catalyst. The H⁻ acidity function is defined as a measure of the ability of the basic solution to abstract a proton from an acidic neutral solute. The catalysts for the screening process were selected from a list of high Hₐ acidity function. The activity of basic catalyst is based either on accepting protons (Bronsted base) or accepting lone pairs electrons (Lewis base). The rate determining step for CO₂ amine reaction as identified by the first reaction, forming zwitterion, is an electron transfer process. Therefore, a catalyst with the ability of interacting with the reactant through an electron transfer is preferred. This is the case for a Lewis base catalyst.

The use of an inorganic catalyst to speed up the rate of reaction of CO₂ in aqueous solutions was studied by Augugliaro et al. (1987) who investigated the absorption of CO₂ in potassium carbonate-bicarbonate buffer solution with arsenious ion as catalyst. Idem et al. (2011) first proposed the use of heterogeneous catalysis in CO₂ capture for amine systems. Phan et al. (2014) also investigated the application of an inorganic catalyst to the process of post-combustion capture using alkanolamines. The kinetic investigation for the application of inorganic oxoanion catalyst including arsenite, arsenate, phosphate and borate shows the increase in the absorption kinetic rate.

Shi et al. (2017) investigated the effect of MgCO₃ and CaCO₃ as a potential catalyst for CO₂ capture. The result shows an increase in the absorption rate and a reduction in the time to reach equilibrium as the catalyst is introduced. This was attributed to the Lewis
base effect of both catalysts contributing more to the increase in absorption rate. A 14-28% increase for CaCO$_3$ and an 11-28% increase for MgCO$_3$ was observed. This was attributed to the presence of Lewis base site on both catalyst. Non-catalytic DEA showed 18mins for the absorption plot to taper of, indicating an approach to chemical equilibrium. With the addition of both CaCO$_3$ and MgCO$_3$ to the aqueous 1M DEA, this time reduced to 14mins for both DEA+CaCO$_3$ and 16 mins for DEA+MgCO$_3$. Cao et al. (2017) studied the effect of MgCO$_3$ on CO$_2$ absorption using amine and confirmed previous studies showing the increase in CO$_2$ absorption in MEA solvent. This work examines a number of Solid base catalyst for the application of CO$_2$ capture.

2.4.1 Lewis base catalytic activity

There are a number of catalyst reported to having Lewis base sites which includes most oxygen containing compounds like K/MgO, CaCO$_3$ and Ca(OH)$_2$. The activity of K/MgO, an alkaline metal promoted catalyst whose mechanism is similar to the other oxygen carrying catalyst, is discussed. The alkaline metal potassium (K) serves as a promoter to increasing the base sites on MgO. The K is more electropositive than the Mg hence destabilize and weaken the bond between the Mg and the O. The O$^{2-}$ from the weakened bond has the ability to donate electrons to CO$_2$. The electron transfer from the oxygen carrying base catalyst, leads to a series of bond formation and breaking in other to form the carbamate molecule from a reaction between the CO$_2$ and amine. Ono et al. (2010) reported on the base strength of the O$^{2-}$ in MgO. The presence of base sites on most oxygen carry catalyst serves as a basis for selection. Similar, the other oxygen
carrying compounds have also been reported as having both medium and strong base site due the presence of the $O^{2-}$ anion (Ono et al., 2010).

Jiménez et al. (2006) investigated the basic strength of K/MgO as catalyst for soot combustion and explained three major roles of the potassium on the MgO as (a) increase in surface oxygen concentration, (b) weakening of the Mg–O bonds with migration of oxygen species to the surface, and (c) reduction of the stability of carbamates formed in presence of K.

2.4.2 Bronsted base catalytic activity

A Bronsted base catalyst accepts an H+ proton from the zwitterion molecule for the formation of carbamate. The catalyst however, donates this proton to the amine molecule for the formation of protonated amine. This reaction occurs instantaneously hence, a catalytic effect is not seen. Di Cosimo et al. (1998) investigated the Catalytic Conversion of Ethanol on Mg-Al Hydrotalcite. Results from this work confirms the catalytic activity of the hydrotalcite in dehydrogenation of the ethanol (accepting two H+ ions) to form ethylene.
2.5 Catalytic Desorption

The process of catalytic desorption takes place in tri-phase, gas-liquid and solid. The mechanism for the catalytic desorption is deduced from the catalytic absorption process. It is essential to identify the products of absorption which includes carbamate, bicarbonate and protonated amine. These are the reactants for the desorption reaction.

First, the carbamate and bicarbonate in the liquid phase moves through the liquid film around the catalyst and diffuses through the catalyst pores to adsorb on the active site of the catalyst. The reaction occurs on the active site of the catalyst producing free amine and CO\(_2\). Both desorb from the active site, diffuses out of the pores to the liquid film. The free CO\(_2\) then transports out of the liquid film into the gas film and gas phase eventually due to the high concentration gradient created. Idem et al. (2011) proposed the use of a solid acid catalyst for the desorption process to reduce the energy required for desorption since it accounts for 80% of the total operating cost of a capture plant. Shi et al. (2011) developed a molecular potential energy surface (PES) diagrams of the deprotonation of a protonated amine to explain the energy requirement for the desorption reaction. The deprotonation reaction was found to be the most energy-requiring of all the desorption reaction making it the rate determining step. Experiments were conducted for CO\(_2\) desorption using single and blended amines which included MEA, MEA–MDEA, MEA–DEAB, with and without solid acid catalysts (\(\gamma\)-Al\(_2\)O\(_3\) or HZSM-5) at a desorber bed temperature ranging between 75–95 °C. The results showed that the CO\(_2\) stripping performance in terms of heat duty decreased in the order: MEA–DEAB with HZSM-5 (38%) > MEA–DEAB with - \(\gamma\)-Al\(_2\)O\(_3\) (40%) > MEA–DEAB with no catalyst (51%) > MEA with HZSM-5 (65%) > MEA with - \(\gamma\)-Al\(_2\)O\(_3\) (73%) > MEA–MDEA with - \(\gamma\)-Al\(_2\)O\(_3\)
no catalyst (74%), all relative to MEA with no catalyst (100%). Generally, the results showed that the use of a catalyst positively reduces the heat energy required to desorb CO₂ from the amine. The role of each catalyst is unique but their common role is to speed up the rate of desorption reaction by either providing a proton (HZSM-5) for the reaction or accepting an electron (γ-Al₂O₃) or doing both. This result implied that the use of solid acid catalysts could result in a reduction in the size of the desorption column as well as a reduction in the heat duty during solvent regeneration.

The use of desorption catalyst is intended to lower the lean amine loading exiting the desorption column. The lean amine serves as the feed for absorption in the absorption column. A lower lean loading will result in a higher CO₂ efficiency leading to the reduction of the absorption column height.

Osei et al. (2016) performed mass transfer studies on a catalyst-aided desorption of CO₂ using HZSM-5 and γ-Al₂O₃ for MEA and a blend of MEA/MDEA on a bench scale pilot plant. Results showed the increase in desorption rate which translates to a high CO₂ desorption efficiency. The introduction of the catalyst decreased the heat duty of the system as more CO₂ was produced (Srisang et al., 2016). Both catalysts showed positive results in reducing the heat duty of the system however, the HZSM-5 showed more superior performance. This was attributed to the role of HZSM-5 as a Bronsted acid catalyst over γ-Al₂O₃ as a Lewis acid catalyst and the rate determining step of the desorption reaction being the deprotonation (removal of H⁺ proton) of the protonated amine, AmineH⁺. The same trend was seen when using either the single MEA solvent or the solvent blend of MEA/MDEA. Liu et al. (2017) also investigated the effect of three solid acid catalyst, H-ZSM-5, MCM-41 and SO₄²⁻/ZrO₂ on several single and blended
amines including MEA, MEA-DEEA (2-diethylamino ethanol), MEAMDEA (methyltriethanolamine), MEA-1DMA2P (1-dimethylamino-2 propanol)) to determine the respective roles of catalyst and solvent in heat duty and CO₂ desorption rate. The result of this work shows the high desorption performance of the three catalysts showed the trend: H-ZSM-5 > MCM-41 > SO₄²⁻/ZrO₂ for all solvent system. This was attributed to the high Bronsted to Lewis acid site ratio of HZSM-5 coupled with the high mesoporous surface area in spite of its low total base site in comparison with the MCM-41 and SO₄²⁻/ZrO₂ catalyst. This work also confirms other works on HZSM-5 desorption performance (Osei et al., 2016).

2.5.1 HZSM-5 catalyst Role

Zeolite catalysts are known for their unique pore size which makes them suitable as shape selective catalyst. They have high surface area and are crystalline in nature (Akachuku et al. 2016). HZSM-5 catalyst has been reported as having Bronsted acid site. (Shi et al., 2014). HZSM-5 readily donates its H⁺ proton for the break down of both carbamate and bicarbonate. The recovery of the proton is from the deprotonation of the protonated amine, considered to be the rate-determining step. The bicarbonate also performs a similar role in recovering a proton from the protonated amine and supplying it to the breakdown of the carbamate or using it to break down and release CO₂ and water.
2.5.2 γ-Al_2O_3 catalyst Role

γ-Al_2O_3 is considered as an amphoteric catalyst. Its desired textural properties, such as surface area, pore volume, and pore-size distribution, and its acid/base characteristics are mainly owed to surface chemical composition, local microstructure, and phase composition. (Samain et al., 2014). The activity of the catalyst depends highly on the specific region of the solvent namely the rich and lean solvent region. In the rich solvent region, the γ-Al_2O_3 catalyst assumes an acidic role. The catalyst attacks the carbamate directly. This mechanism is such that the catalyst accepts lone pair electron from the last oxygen on the carbamate molecule. This results in its breakdown to release CO_2 directly without accepting a proton from the amine (protonated amine). This mechanism is similar to catalytic activity of Lewis acids. In the lean region the catalyst behaves as a Bronsted acid catalyst by first accepting protons from the protonated amine and later donating it to the carbamate for further breakdown. Unlike HZSM-5, the γ-Al_2O_3 accepts the proton first by virtue of its basic role and donates it due to its acidic role. Bicarbonate and H_2O in the solution performs similar role to the γ-Al_2O_3 catalyst in the lean region however, the γ-Al_2O_3 role is more predominant (Osei et al., 2016). The γ-Al_2O_3 playing the role of both an acid and a base makes it an amphoteric catalyst. It has also been explained how the catalyst can perform both Bronsted and Lewis acid roles.

2.6 Physical Properties

Physical Properties of amine solvents are an essential part of amine studies as it provides essential data for mass transfer, heat transfer and kinetic study. How the solvents
respond to changes in temperature, pressure, CO₂ loading and solvent concentration is an important information for modelling and simulation process. These physical properties allow for more rigorous analysis in its pilot plant application as performance can be directly linked to solvent property. It is also essential for the selection of a suitable solvent as the suitability of the solvent links directly to its property. The physical properties including solvent viscosity, density, diffusivity and solubility with and without CO₂. Physical properties are also essential for the design of process design equipment in the sizing of equipment. CO₂ absorption favours solvents with less viscosity and high solubility. This is particularly one major reason for blending highly viscose solvents with the less viscose for better performance. However, some physical properties of this catalyst are available. Physical properties of single pure and aqueous solvent have received much attention.

2.7 Mass transfer performance

2.7.1 Absorption efficiency

The CO₂ removal efficiency which represents the amount of CO₂ absorbed by the amine, is computed from three main methods:

1. The CO₂ removed from the gas

\[
\frac{F_{\text{in}}^{\text{CO}_2} - F_{\text{out}}^{\text{CO}_2}}{F_{\text{in}}^{\text{CO}_2}} \times 100\% \quad (2.7 - 1)
\]
Where $F_{CO_2}^{in}$ is the flowrate of CO$_2$ in the feed gas, given as mol/s. $F_{CO_2}^{out}$ as the flowrate of CO$_2$ in the exit gas. $F_{CO_2}^{in} - F_{CO_2}^{out}$ represents the amount of CO$_2$ removed from the gas phase.

2. The CO$_2$ absorbed by the liquid solvent

In this case $F_{CO_2}^{in} - F_{CO_2}^{out}$ would be the amount that the amine has absorbed.

3. The amount of CO$_2$ produced from the amine regeneration

The $F_{CO_2}^{in} - F_{CO_2}^{out}$ is obtained from the amount of CO$_2$ produced from the amine regeneration.

An average of all these methods for the CO$_2$ removal efficiency is usually taken.

2.7.2 Cyclic Capacity

The cyclic capacity for the amine is calculated by;

$$\alpha_{cyclic\ capacity} = \alpha_{rich\ loading} - \alpha_{rich\ loading}$$

Where $\alpha_{rich\ loading}$ and $\alpha_{lean\ loading}$ represents the rich and lean amine loading as mol CO$_2$/mol of amine. Here the cyclic capacity $\alpha_{cyclic\ capacity}$ is also mol CO$_2$/mol amine. The cyclic capacity is represented in terms of kg of CO$_2$/hr as follows;

$$\dot{m}_{cyclic\ capacity} = \alpha_{cyclic\ capacity} \times C_{amine} \times \dot{V}_{amine}$$
Where \( C_{\text{amine}} \) represents the amine concentration as mol/L, \( \dot{V}_{\text{amine}} \) as the volumetric flowrate of amine solvent in terms L/hr and \( \dot{m}_{\text{cyclic capacity}} \), the cyclic capacity as kg CO\(_2\)/hr.

### 2.7.3 Mass transfer coefficient

The derivations are based on a cross section of the column, dZ. The mass flux of component A (\( N_A \)) across the gas−liquid interface at steady state can be represented in terms of the gas-side mass transfer coefficient (\( k_G \)) and driving force (\( y_{A,G} - y_{A,l} \)) as follows:

\[
N_A = k_G P (y_{A,G} - y_{A,l})
\] (2.7-3)

where P represents the total pressure of the system and \( y_{A,G} \) and \( y_{A,l} \) represent the mole fraction of component A in gas bulk and gas interphase respectively. The gas mass transfer coefficient \( k_G \) is difficult to measure because of the change in the interfacial area with varying gas flow rates in the packed columns. Instead, the overall mass transfer coefficient for the gas phase (\( K_G \)) is often used. Mass transfer coefficient represents is a diffusion rate constant that relates the mass transfer rate and concentration change as driving force. This can be presented in terms of Henry's law constant (H) and enhancement factor (E) as follows:

\[
\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{E k_L}
\] (2.7-4)
The overall volumetric mass transfer resistance in terms of the gas side \( \frac{1}{K_G a_v} \) and liquid side \( \frac{1}{K_L a_v} \) from the two-film theory modified to include the solid resistance is shown below:

\[
\frac{1}{K_G a_v} = \frac{1}{k_G a_v} + \frac{H}{k_L a_v E} + \frac{1}{k_s a} \tag{2.7 - 5}
\]

\[
\frac{1}{K_L a_v} = \frac{1}{Hk_G a_v} + \frac{1}{k_L a_v E} + \frac{1}{k_s a} \tag{2.7 - 6}
\]

Where \( k_s a \) represent the solid resistance.

The mass transfer rate is expressed in terms of the bulk gas composition as it is difficult to measure the CO\(_2\) composition at the interface.

\[
N_A = K_G P (y_{A,G} - y_A^*) \tag{2.7-7}
\]

where \( y_A^* \) is the mole fraction of component A in the gas phase in equilibrium with the concentration of A in the bulk liquid.

The difficulty in measuring the interfacial area forces the above expression to be expressed in terms of per unit volume, not interfacial area, by the introduction of \( a_v \) which is defined as the ratio of the interfacial area to the packing volume

\[
K_G a_v = \frac{N_A a_v}{P (y_{A,G} - y_A^*)} \tag{2.7-8}
\]

Considering an element of the absorption column with height \( dZ \), in Figure 2.7-1 and 2.7-2, the mass balance of component A is given as
\[ N_A a_v S dZ = G_1 d\left(Y_{A,G}\right) \]  

(2.7-9)

where \( Y_{A,G} \) represents the mole ratio of component A in the bulk gas, \( G_1 \) the molar inert flow rate (total gas without component A) and \( S \) the cross-sectional area of the column.

This gives

\[ K_G a_v \times S \times P(y_{A,G} - y^*_A) dZ = G_1 d\left(Y_{A,G}\right) \]  

(2.7-10)

\[ Y_{A,G} = \frac{y_{AG}}{1-y_{AG}} \]  

(2.7-11)

Differentiating gives

\[ dY_{A,G} = d\left(\frac{y_{AG}}{1-y_{AG}}\right) = \frac{dy_{AG}}{(1-y_{AG})^2} \]  

(2.7-12)

Simplifying and integrating gives

\[ K_G a_v = \frac{G_1}{S} x \int_{y_{AG,1}}^{y_{AG,2}} \frac{dy_{AG}}{(1-y_{AG})^2(y_{AG}-y^*_A)} \]  

(2.7-13)

Similarly, a material balance on the desorption column, using the overall liquid side mass transfer coefficient, \( K_L a_v \), gives

\[ N_A = K_L a_v \rho_m (x_{AL} - x_{A}^*) \]  

(2.7-14)

Going through same derivations as \( K_G a_v \) gives

\[ K_L a_v = \frac{L_1}{\rho_m Z} x \int_{x_{AL,1}}^{x_{AL,2}} \frac{dx_{AL}}{(1-x_{AL})^2(x_{AL}-x_{A}^*)} \]  

(2.7-15)

where \( L_1 \) is the molar inert liquid flowrate, \( \rho_m \) the molar density of the solution, \( x_{AL} \) the bulk liquid mole fraction of component A and \( x_{A}^* \) the bulk liquid mole fraction of component A in equilibrium with the bulk gas. Due to the lack of sample points along the
desorber column, according to Osei et al. (2016), the expression in Equation (2.7-13) was simplified as follows:

\[ K_L a_v = \frac{l_A}{l_mz} x \sum_{i=1}^{n} \frac{\Delta x_{iAL}}{(1-x_{iAL})^2(x_{iAL}^*-x_A^*)^2} \]  

(2.7-16)

The accent represents log mean average values.

\( x_A^* \) represents the physical composition of the CO\(_2\) gas in the liquid in equilibrium with the gas phase composition. This is calculated as according to the Henrys law:

\[ P_{CO2} = He C_T x_A^* \]  

(2.7 – 17)

\[ y_{CO2}P = He C_T x_A^* \]  

(2.7 – 18)

Where \( P_{CO2} \) is the partial pressure of CO\(_2\) in the gas phase, Pa. \( He \) the Henrys law constants, Pa. m\(^3\)/mol. \( C_T \) the total concentration, mol/m\(^3\) and \( x_A^* \) the equilibrium composition in the liquid. The Henrys constant is obtained from the physical solubility experiment. The partial pressure of the CO\(_2\) in the gas phase of the desorber is obtained from the Raoult’s law:

\[ y_{H2O}P = P_{H2O}^v \times x_{H2O} \]  

(2.7 – 17)

\[ P = y_{CO2}P + y_{H2O}P \]  

(2.7 – 18)

The mole fraction of the H\(_2\)O is first determined using its vapour pressure in the Raoult’s law expression. Since the composition of the gas phase is CO\(_2\) and H\(_2\)O only, that of the CO\(_2\) is also computed from the above equation. With \( y_{CO2}, P \) and Henrys law constant, the \( x_A^* \) is computed.
2.8 Interfacial Area for mass transfer

The interfacial area with the introduction of catalyst is computed as in equation (2.8-1)

\[ R_A a = a[A^*] \left( \frac{2}{M+1} D_A k_{mn} [A^*]^{m-1} [B_o]^n \right)^{1/2} \]  

(Lee et al., 2013)

\([A^*]\) is the equilibrium solubility from the Henrys law constant. \(m\) and \(n\) are the reaction rate orders with respect to the CO\(_2\) and free amine respectively. \(D_A\) is the physical diffusivity of CO\(_2\) in the 4M blend solvent of BEA/AMP estimated from the viscosity of the 2M BEA-2M AMP solvent. \(R_Aa\) is the rate of absorption of CO\(_2\) by the BEA/AMP solvent. The porosity of the catalyst introduces an added physical increase in the interfacial area as well as an increase in the rate of chemical reaction. Having determined all these parameters and making the interfacial area (\(a\), \(m^2/m^3\)) the subject of the above equation gives equation (2.8-2)

\[ a = \frac{R_A a}{[A^*] \left( \frac{2}{M+1} D_A k_{mn} [A^*]^{m-1} [B_o]^n \right)^{1/2}} \]  

(2.8 – 2)

2.9 Kinetics of solvents

The four solvents of interest which are MEA, MDEA, BEA and AMP falls into different amine groups and therefore the kinetics of their interaction with CO\(_2\) is necessary for both catalysis studies and mass transfer. The understanding of the kinetics of each solvent component is key to explaining the reaction pathway and the relative rates of absorption of the amines. The MEA and AMP are primary amines which have fast kinetics.
However, AMP is a hindered amine with unstable carbamate formation resulting in a slightly slower reaction rate than MEA. BEA is a secondary amine which has fast kinetics but slower than corresponding primary amines. The presence of the alkyl group enhances its reaction performance beyond most secondary amines. Finally, MDEA, a tertiary amine reacts with amine the slowest. The slow reaction of AMP and MDEA is countered by their fast desorption kinetics. The evaluation of their reaction mechanism are given below.

MEA Zwitterion formation

\[ MEA + CO_2 \leftrightarrow MEA^+COO^- \]  \hspace{1cm} (2.9-1)

Carbamate formation from MEA

\[ MEACOO^- + H_2O \leftrightarrow MEACOO^- + H_3O^+ \]  \hspace{1cm} (2.9-2)

\[ MEA^+COO^- + OH^- \leftrightarrow MEACOO^- + H_2O \]  \hspace{1cm} (2.9-3)

\[ MEA^+COO^- + MEA \leftrightarrow MEACOO^- + MEAH^+ \]  \hspace{1cm} (2.9-4)

\[ MEA^+COO^- + HCO_3^- \leftrightarrow MEACOO^- + H_2CO_3 \]  \hspace{1cm} (2.9-5)

\[ MEA^+COO^- + CO_3^{2-} \leftrightarrow MEACOO^- + HCO_3^- \]  \hspace{1cm} (2.9-6)

\[ MEA + H_2O \leftrightarrow MEAH^+ + OH^- \]  \hspace{1cm} (2.9-7)

\[ MEA + H^+ \leftrightarrow MEAH^+ \]  \hspace{1cm} (2.9-8)

\[ MEAH^+ + OH^- \leftrightarrow MEA + H_2O \]  \hspace{1cm} (2.9-9)

\[ MEACOO^- + H_2O \leftrightarrow MEA + HCO_3^- \]  \hspace{1cm} (2.9-10)

AMP and BEA Zwitterion formation:

\[ AMP + CO_2 \leftrightarrow AMP^+COO^- \]  \hspace{1cm} (2.9-11)
\[ BEA + CO_2 \Leftrightarrow BEA^+COO^- \]  

Carbamate formation from AMP and BEA

\[ AMP^+COO^- + H_2O \Leftrightarrow AMPCOO^- + H_3O^+ \]  
\[ BEA^+COO^- + H_2O \Leftrightarrow BEACOO^- + H_3O^+ \]  
\[ AMP^+COO^- + OH^- \Leftrightarrow AMPCOO^- + H_2O \]  
\[ BEA^+COO^- + OH^- \Leftrightarrow BEACOO^- + H_2O \]  
\[ AMP^+COO^- + AMP \Leftrightarrow AMPCOO^- + AMPH^+ \]  
\[ BEA^+COO^- + BEA \Leftrightarrow BEACOO^- + BEAH^+ \]  
\[ AMP^+COO^- + HCO_3^- \Leftrightarrow AMPCOO^- + H_2CO_3 \]  
\[ BEA^+COO^- + HCO_3^- \Leftrightarrow BEACOO^- + H_2CO_3 \]  
\[ AMP^+COO^- + CO_3^{2-} \Leftrightarrow AMPCOO^- + HCO_3^- \]  
\[ BEA^+COO^- + CO_3^{2-} \Leftrightarrow BEACOO^- + HCO_3^- \]

AMP and BEA amine protonation

\[ AMP + H_2O \Leftrightarrow AMPH^+ + OH^- \]  
\[ BEA + H_2O \Leftrightarrow BEAH^+ + OH^- \]  
\[ AMP + H^+ \Leftrightarrow AMPH^+ \]  
\[ BEA + H^+ \Leftrightarrow BEAH^+ \]

AMP and BEA amine deprotonation

\[ AMPH^+ + OH^- \Leftrightarrow AMP + H_2O \]  
\[ BEAH^+ + OH^- \Leftrightarrow BEA + H_2O \]
\[ AMPH^+ + H_2O \Leftrightarrow AMP + H_3O^+ \quad (2.9-29) \]
\[ BEAH^+ + H_2O \Leftrightarrow BEA + H_3O^+ \quad (2.9-30) \]

Carbamate hydrolysis
\[ AMPCOO^- + H_2O \Leftrightarrow AMP + HCO_3^- \quad (2.9-31) \]
\[ BEACOO^- + H_2O \Leftrightarrow BEA + HCO_3^- \quad (2.9-32) \]

MDEA kinetics
\[ MDEA + CO_2 + H_2O \Leftrightarrow MDEAH^+ + HCO_3^- \quad (2.9-33) \]
\[ MDEAH^+ + H_2O \Leftrightarrow MDEA + H_3O^+ \quad (2.9-34) \]

All the above reactions are considered reversible. The desorption kinetics is obtained from the reverse of all the absorption reaction steps. MDEA, a tertiary amine, undergoes a different mechanism from the zwitterion procedure. The speeds of these reactions determine how fast or slow the amine combines with the CO₂.
CHAPTER 3: EXPERIMENTAL SECTION

This experimental section describes all the experiments carried out for my work on the extensive mass transfer study of the application of solid catalysts in CO$_2$ capture. It is divided into four main experiments. The first was the solid base catalyst selection, synthesis and characterisation. Screening for a suitable catalyst was carried out using a semi-batch scale absorption unit. The next was the screening for a suitable solvent using a bench scale pilot plant setup. In order to extensively study the mass transfer of CO$_2$ into the selected solvent, the physical properties which includes density, viscosity and solubility of solvent were measured. The physical solubility was measured in order to create a link between solvent property and CO$_2$ mass transfer performance. The third part of this study was performed on a bench scale pilot plant to extensively study the effects of several performance parameters on mass transfer of CO$_2$. Finally, the combined effect of the most suitable solvent, catalyst and other operating conditions on the emissions of volatile organic components (from amine degradation) was investigated. In this experiment, the essential components of amine degradation and volatile emissions are identified.

3.1 Laboratory Health and Safety Precautions

The CO$_2$ capture process requires essential health and safety precautions that allows for safe environment in order to achieving the required target of removing CO$_2$ from the flue gas. The basic lab safety precautions taken are outlined below.
i. Personal Protective Equipment (PPE) including lab coat, safety goggles, hand gloves and safety shoes were used during experimental runs in the lab.

ii. Chemicals were properly labelled and stored in their appropriate cabinets according to WHMIS requirements

iii. All gas cylinders were properly secured with clamps so to avoid them from being knocked over when in use and capped and chained on appropriate carts when transported.

iv. Chemical spills were dealt with immediately and if safe to do so using standard procedures whilst broken glassware were collected and stored in their appropriate containment

v. Work areas were kept clean and free of obstructions; equipment and chemicals were stored properly to ensure good housekeeping

vi. Laboratory fume hoods were used to contain and exhaust toxic, offensive and flammable vapours when mixing chemicals in the laboratory.

For the specific health issues, emissions from post-combustion CO₂ capture plants using amine solution may affect the human health and environment. Amines themselves are known to have specific toxicity mechanisms against aquatic organisms and some degraded amines, such as nitrosamines, may also pose risks to the human health. Amines are carcinogenic and therefore proper handling is required. The use of appropriate gloves is essential. The use of emission specific nose masks is essential to avoiding the inhalation of the volatile organic matter emitted which are products of amine degradation.
Amine carry over from the absorber and stripper is another health risk concern. This process leaves the environment saturated with aerosols of amine and poses serious health issues when inhaled. Mitigation approach includes; A high efficient water wash section above each column. And a high efficient demister.

Another concern is the safe disposal of waste amine solvent. The waste amine needs to be pumped out of the columns first and then stored in waste sample containers an well labelled. Also, the waste water from the pre-scrubbing of the gas stream is also efficiently stored and deposed in waste water drains or stored for wastewater treatment.

3.2. Materials and Equipment

3.2.1 Chemicals and Catalyst Synthesis

The catalysts selected for solid base catalyst screening were K/MgO, Cs$_2$O/$\alpha$-Al$_2$O$_3$, Ca(OH)$_2$, BaCO$_3$, Cs$_2$O/$\gamma$-Al$_2$O$_3$, Hydrotalcite and CaCO$_3$ These catalysts were selected on the basis their basic strength reported as H_acidity, the ability of the catalyst to abstract a proton from a proton as well as its ability to donate an electron in an acid base reaction (Ono et al. 2010). Chemicals for preparing each catalyst are listed in table 3.2-1.
Table 3.2.-1: Selected solid base catalysts and their precursors

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/MgO</td>
<td>KOH and Mg(OH)$_2$</td>
</tr>
<tr>
<td>Cs$_2$O/$\alpha$-Al$_2$O$_3$</td>
<td>Cesium Acetate and $\alpha$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>Ca(OH)$_2$</td>
</tr>
<tr>
<td>BaCO$_3$</td>
<td>BaCO$_3$</td>
</tr>
<tr>
<td>Cs$_2$O/$\gamma$-Al$_2$O$_3$</td>
<td>Cesium Acetate and $\gamma$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>Mg-Al Hydrotalcite</td>
<td>Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>CaCO$_3$</td>
</tr>
</tbody>
</table>
Cesium Acetate was purchased from Sigma-Aldrich Co., Canada, and both \( \alpha \)-alumina and \( \gamma \)-alumina from Zeochem, USA. Potassium hydroxide and magnesium hydroxide also purchased from Sigma-Aldrich Co., Canada, 98% purity. Aluminum nitrate nonahydrate and magnesium nitrate hexahydrate as catalyst precursors were also purchased from Sigma Aldrich with 98% purity. Also, NaOH and Na\(_2\)CO\(_3\) as precipitating agents for hydrotalcite were purchased from Fisher Scientific (≥98%). CaCO\(_3\) and BaCO\(_3\) were purchased from Sigma Aldrich as well. Ca(OH)\(_2\) from Fisher Scientific (≥98%). HZSM-5 zeolite catalyst with a silica to alumina (Si/Al) ratio of 19 was purchased from Zibo Yinghe Chemical Co., Ltd, Zibo City, China. Solid catalyst binder, colloidal silica, was purchased from Sigma Aldrich and used to maintain the mechanical strength of the synthesized catalyst.

3.3 Catalyst Preparation

3.3.1 Cs\(_2\)O/\( \alpha \)-Al\(_2\)O\(_3\) and Cs\(_2\)O/ \( \gamma \)-Al\(_2\)O\(_3\)

Both catalysts were prepared in reference to work done by Gorzawski et al. (1999), for the preparation of superbases. The preparation procedure was modified to suit current experimental conditions. Both \( \alpha \)-Al\(_2\)O\(_3\) and \( \gamma \)-Al\(_2\)O\(_3\) were first obtained in pellets form. These pellets were crushed into powder, to increase the surface area for the impregnation of the active metal on the catalyst surface.

The crushed alumina was first heated to 500°C at constant stirring hydrothermally for 2h. The slurry solution was then allowed to cool. The catalyst was dried for 12 hours. Caesium acetate was impregnation at 8 wt.% of the catalyst support. After the addition of
caesium acetate, the mixture was stirred for 2 h. As a final treatment, the catalyst was calcined at 900°C for decomposition of the acetate and activation of the catalyst. The final catalysts Cs$_2$O/α-Al$_2$O$_3$ was pelletized to obtain a particle size of 4.25-4.6 mm.

3.3.2 K/MgO

This catalyst was prepared by the incipient wetness method. Commercial available Mg(OH)$_2$ purchased from Sigma Aldrich was used in the preparation of the support. The Mg(OH)$_2$ was first calcined at 600°C for 2 hours to produce MgO. Then the catalyst was allowed to cool for 1 hour. A solution of KOH was prepared with concentration intended to give a final composition of the K, the active metal/promoter, as 1 mol% over the support. The prepared slurry was dried for 12 hours and later calcined at 600°C for 2 hours. The final catalyst was pelletized to obtain a particle size of 4.25-4.6 mm.

3.3.3 Mg-Al Hydrotalcite

Mg-Al hydrotalcite was prepared from coprecipitation produced by mixing two solutions: solution A containing 603.98g of Mg(NO$_3$)$_2$·6H$_2$O and 662.38g of Al(NO$_3$)$_3$·9H$_2$O, solution B containing 294.80g of NaOH and 24.40g of Na$_2$CO$_3$ dissolved in 2L of distilled water. Both solutions were coadded at a rate of 1 mL/min under a vigorous mechanical stirring at room temperature. The precipitate was left at 333 K for 16 h. The hydrotalcite formed was filtered and washed until the pH of the filtrate was 7. The resultant solid was dried at 333 K for 12 h. The hydrotalcite was activated by calcination at 873 K for 6 h. The solid was then cooled to room temperature and rehydrated to activate
the catalyst before use. Rehydration of calcined hydrotalcite (HTc) was carried out by directly adding 10ml of water on the calcined hydrotalcite just before application in the semi-batch absorption experiment.

3.4 Catalyst Characterisation

3.4.1 Temperature Program Desorption (TPD)

The TPD experiment was used to measure the total number of base sites as well as the basic strength for each sample. The TPD of each catalyst was measured using a CHEMBET 3000 from Quantachrome model with a TCD Detector type. The samples were initially exposed to a stream of pure helium while the furnace temperature was gradually increased to 250°C at 10°C/min ramping. After 2 hours of maintaining the temperature, the temperature of the system was reduced to 30°C still in a flow of helium. The helium was switched off and a 3% of CO₂ (N₂ balance) gas flowed at 30ml/min for 60 min. This allowed adsorption of CO₂ to take place on the base sites. The helium was switched back on whiles the temperature of the sample was increased gradually to 800°C. The TPD analysis began simultaneously as the temperature increased. In CO₂ TPD, the low temperature desorption (50-150°C) peak corresponds to CO₂ adsorbed on the weak base sites (OH groups) while the peak in intermediate temperature range and at high temperature (150-650°C) represent CO₂ adsorptions on the medium strength (O²⁻ ions) and strong strength basic (O²⁻ ions) sites, respectively (Di Cosimo et al., 1998)
3.4.2 The Brunauer-Emmett-Teller (BET) Surface Area, Pore Volume, and Average Pore Size Measurements

The (BET) surface area, pore volume, and average pore size measurements were obtained using an adsorption Micromeritics ASAP 2020 instrument. The adsorption of nitrogen gas on the catalyst surface was used in estimating the BET surface area. The instrument used for analysis is BET ASAP 2020 from Micromeritics, Georgia, USA. The sample is degassed at 150°C for 5 hours. BJH method is used to calculate adsorption and desorption of surface area, pore volume, and pore size. 46 relative pressure points are recorded to give Isotherm plot. Nitrogen gas is used during analysis.

3.4.4 Powder X-ray Diffraction

The powder X-Ray Diffraction experiments were performed on a Rigaku Ultima IV X-Ray Diffractometer, equipped with a Cu source (1.54056 Å), a CBO optical, and a Scintillation Counter detector. The measurements were carried out on the Multipurpose Attachment in the Para focusing mode, with a Kβ filter (Ni foils) inserted into the receiving slit box. 2θ was scanned from 5° to 80°, with a scan rate of 5° per minute.

3.4.4 Scanning electron microscope (SEM)

The surface morphology of the prepared catalyst samples was investigated by scanning electron microscopy (SEM) using a JEOL 5600 132-10 electron probe microanalyzer with an active area of 10mm². The samples were initially crushed to obtain
powdery catalyst and then loaded into the specimen chamber. Beams were generated based on the accelerating voltage of 150kV. The positioning of the beam was controlled by the computer software and micrographs were finally acquired.

### 3.5 Semi-batch Absorption Experiment

Reagent grade butyl ethanolamine (≥98%), 2-amino-2-methyl-1-propanol (≥99%) and 1 N hydrochloric acid (HCl), were purchased from Sigma-Aldrich Co., Canada. The gas cylinders used were supplied by Praxair Inc., Regina, Canada. This included pure CO\(_2\), pure N\(_2\) as well as premixed 15% CO\(_2\) (N\(_2\) balance) ±0.5 %. A mass flow meter (Electronic AALBORG GFM171 with a range of 0–500 mL/min with accuracy ±1%, and a hot plate from Fischer Scientific Company were used. A three-neck glass flask with a mercury ball thermometer and a gas diffusor connected was used.

The absorption experiment was performed at 45±2°C using the setup in Figure 3.4-1. The procedure used was similar to that reported by Narku-Tetteh et al. (2017). The setup was modified to include a stainless-steel basket that contained the catalyst. The apparatus consisted of a three-necked round-bottomed flask with a condenser installed at the middle neck, a thermometer at one neck for amine solution temperature measurement, and a gas dispersion tube on the other neck for supplying the feed gas. At the start of the experiment, a concentration of 4M BEA-AMP biblend (2:2) molar ratio was prepared and the concentration confirmed by titration with 1N HCl using the Chittick apparatus. At the start of the experiment, the solvent of a known volume (500 mL) was poured into the flask. The experiment was performed with and without a catalyst. In the case of catalytic runs, a
known weight (50 g) of catalyst was measured and placed in the basket and suspended in the flask such that it was completely immersed in the solution yet not touching the bottom of the flask so as to allow the stirrer to rotate freely at the bottom. The flask was then immersed in a preheated oil bath and allowed to reach the desired absorption temperature. Then, a premixed gas (15% CO₂ and 85% N₂) at a flow rate of 650 mL/min (±5 accuracy) was then bubbled into the solution through the dispersion tube. Samples were then taken at time intervals of 5 min (starting from 0 min after reaching the desired temperature) for the first hour, and then 30 min interval until equilibrium was reached. The CO₂ loading of each sample was determined by titration using the Chittick apparatus. A plot of loading versus time was generated and the initial absorption rate was determined by finding the slope of the linear part of the absorption profile. In the case of the blank run (no catalyst), the same procedure was followed but with no catalyst in the basket. Table 3.5-1 shows the experimental conditions used in the semi-batch run. The end of the experiment was marked by the constant CO₂ loading of the amine (equilibrium) after 2 hours.
Figure 3.5-1: Semi batch absorption Setup
Table 3.5-1: The operating conditions of the semi-batch experiments

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow rate</td>
<td>650 mLpm</td>
</tr>
<tr>
<td>Liquid volume</td>
<td>500 mL</td>
</tr>
<tr>
<td>Absorption temperature</td>
<td>45°C</td>
</tr>
<tr>
<td>CO₂ in the feed gas</td>
<td>15%</td>
</tr>
<tr>
<td>Catalyst weight</td>
<td>50 g</td>
</tr>
<tr>
<td>Catalyst investigated</td>
<td>K/MgO, Cs₂O/α-Al₂O₃, Ca(OH)₂, BaCO₃, Cs₂O/γ-Al₂O₃, Hydrotalcite, CaCO₃</td>
</tr>
</tbody>
</table>
3.6 The physical solubility of CO₂ (N₂O analogy)

The experimental setup used for determining N₂O solubility was similar to work done by Seema T. (2012). The solubility experiment was performed in a rotary-type 600 ml stainless steel autoclave reactor (model Parr 5500, Parr Instrument Co., Moline, IL) connected to a controller (model Parr 4843, Parr Instrument Co., Moline, IL) as shown in Figure 3.6-1. The reactor consisted of a variable-speed impeller, a heating mantle, a cooling coil, a gas feed port, a thermocouple, and a pressure transducer. Initially, the amine solution was degassed using an ultrasonic bath (VWR model 75D, VWR international, ON, Canada), and then 300 ml of the degassed amine solution was introduced into the reactor. The desired temperature was set and controlled by the controller and then the vacuum was turned on. After shutting down the vacuum pump, the liquid was under a certain pressure due to liquid vaporization. The pressure, Pᵥ (kPa), was measured at equilibrium. Then, a certain amount of N₂O (n₅₂₋₀; kmol) was fed to the reactor. The amount of N₂O was determined by measuring the pressure in the reactor before N₂O injection (P₁; kPa) and after N₂O injection (P₂; kPa).

\[
n_{N_2O} = \left( P_2 - P_1 \right) \frac{V_g}{Z_{N_2O}RT}
\]  

(3.6 − 1)

Where Vₙ is the volume of the gas in reactor (m³), R is the gas constant, and Z₅₂₋₀ is compressibility factors of N₂O. Equilibrium is reached when the N₂O pressure doesn’t change after 12 hours. After the system had reached equilibrium, the equilibrium pressure (Pₑ; kPa) was measured.

The equipment and calculation procedure for the N₂O solubility were validated with 5M MEA within a temperature range of 298 K to 343 K. The experimental results are
in good agreement with the literature works (Ma’mun et al., 2011 and Tsai et al., 2000) with an absolute average deviation (AAD) of 1.5% and 1.3% respectively, which confirms that the N₂O solubility data obtained from this work are accurate.
Figure 3.6-1: Autoclave reactor for the determination of Henrys Law constant (Seema T., 2011)
3.7 Pilot Plant Experiment

The solvents used: butylethanolamine (≥98%), 2-amino-2-methyl-1-propanol (≥99%), monoethanolamine (≥99%), and methyl diethanolamine (≥99%) were purchased from Sigma-Aldrich Co., Canada. Titrations using 1 N hydrochloric acids (HCl), was also purchased from Sigma-Aldrich. 100% CO₂ and N₂ were purchased from Praxair Inc., Regina. The CO₂ gas analyzer was purchased from (NOVA analytical system Inc.). Gas analyzer calibrations were done using pure N₂ gas and 15% CO₂ (N₂ balance) also acquired from Praxair Inc., Regina. Stainless steel LDX Sulzer structured packing with outside diameter of 0.047 m was provided by Sulzer Chemtech Ltd. Temperatures were recorded using J-type thermocouples from Cole Parmer, Canada. Concentrated H₂SO₄ (98% purity) was purchased from Fisher scientific as an impinger solution for the emissions analysis.

The set-up describing the experimental system is shown in Figure 3.7-1. The system comprises two stainless steel columns lagged with each measuring 3.5ft (1.067 m) in height and having an internal diameter of 2 inches (0.0508 m). Both columns were equipped with 5.08 cm LDX Sulzer structured packing arrangement. For the desorption column arrangement, a 0.18 m height of a 5.08 cm Sulzer LDX structured packing placed at the top and bottom of the column serving primarily as support, aiding solvent distribution and also as an efficient mass transfer medium. A 0.051 m height 6 mm marble that sits on top and bottom of the catalyst bed serving as support for the bed. A 0.51 m height 3 mm diameter marble, randomly mixed with the desired mass of catalyst for each experimental condition. The absorber column was arranged in an alternating bed of Sulzer LDX structured packing and K/MgO (absorption catalyst). This comprised of seven 5.08 cm LDX Sulzer packings and six 8.9 cm layers of catalyst. This was done to minimize
pressure drop, flooding and liquid carryover within the absorption column. Both column internal arrangements are shown in Figure 3.7-2.

A typical experimental run begins with the lean amine solvent. The desired concentration and flow rate of amine was fed from the storage tank to the top of the absorber column via a variable-speed gear pump. The amine lean in CO\textsubscript{2} flowed through the absorption column with the idea of contacting feed gas rich in CO\textsubscript{2} counter-currently and leaves at the bottom of the column. The amine leaving the absorption column was pumped through a lean rich heat exchanger intended to exchange heat with the hot lean amine from the desorption column. After flowing through the lean-rich heat exchanger, the amine was further heated by an external heater to the desired amine temperature for desorption. The heating fluid for this heater was glycerol which heats up the rich amine prior to entering the desorber. The amine after flowing through the desorption column left as lean amine. This amine then flows through the lean-rich heat exchanger and then through a cooler to further reduce its temperature prior to entering the absorption column. Once amine solvent circulation was set, a mixture of CO\textsubscript{2} and N\textsubscript{2} gas at the appropriate CO\textsubscript{2} concentration of 15% was introduced to the bottom of the absorber column and monitored by a gas flow meter. The lean amine contacts counter-currently the gas feed from the bottom of the column. Treated gas leaves the top of the column while the rich amine solvent leaves the absorber bottom and exchanges heat with the hot lean amine stream leaving from the bottom of the desorber. The rich amine entering the desorption column contacts the catalytic desorber bed, where further desorption was enhanced by the catalyst bed. A condenser was employed to cool the CO\textsubscript{2} product gas leaving the top of the desorption column to remove any entrained water. The product gas is dried. The
internal arrangement absorber catalyst is shown in Figure 3.7-2. Here the catalyst was supported by structured packing only and was segmented to prevent a high pressure drop within the column leading to column flooding. The duration of an experimental run was between 5 to 7 hours. The end of the experiment was marked by the thermal stability within the absorption column, indicating that the solution entering the absorber was at a constant CO$_2$ concentration taking all other conditions to be constant. At this point, the CO$_2$ concentrations in the gas phase and temperature profile were measured along the height of the column using the IR gas analyzer and thermocouples respectively. Also, samples were taken from the bottom of both columns to determine the rich and lean CO$_2$ loadings (liquid phase CO$_2$ concentrations). The CO$_2$ loadings and concentrations were determined from titration using a Chittack apparatus. A mass balance error calculation was done to determine the validity of each run. The calculation compared the quantity of CO$_2$ removed from the gas phase to the CO$_2$ quantity added to the liquid phase. A value of 10% or less was considered a valid run.

The glycerol flowrate and mass of CO$_2$ produced were measured and used in determining the heat duty. Also, the gas phase concentration profile and liquid phase concentrations (CO$_2$ loading) were also measured and used to determine the overall mass transfer coefficients ($K_{L,a,v}$ and $K_{G,a,v}$) as well as the chemical rates of CO$_2$ absorption and desorption. Table 2 shows the operating conditions used in the pilot plant experiments. Detailed conditions for the parametric analysis has been represented in the appendix (table A.1-1).
Table 3.7-1: The operating conditions used in the pilot plant solvent screening experiment

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent used</td>
<td>5M MEA, 7M MEA/MDEA, 2M BEA-2M AMP</td>
</tr>
<tr>
<td>Solvent flowrate</td>
<td>1.83 m³/m²h</td>
</tr>
<tr>
<td>Absorber/Desorber cross sectional area</td>
<td>0.00206 m²</td>
</tr>
<tr>
<td>Feed Gas flow rate</td>
<td>19.30 kmol/m³h</td>
</tr>
<tr>
<td>CO₂ in the feed gas</td>
<td>15%</td>
</tr>
<tr>
<td>Desorber amine inlet Temperature</td>
<td>87°C</td>
</tr>
<tr>
<td>Desorber Catalyst</td>
<td>HZSM-5 (Si/Al =19)</td>
</tr>
<tr>
<td>Desorber Catalyst weight</td>
<td>150g</td>
</tr>
</tbody>
</table>
Figure 3.7-1: Schematic representation of the experimental set-up for CO$_2$ removal (Srisang et al. 2016)
Table 3.7-2: The operating conditions used in the pilot plant studies on comprehensive mass transfer

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent used</td>
<td>2M BEA-2M AMP</td>
</tr>
<tr>
<td>Solvent flowrate</td>
<td>1.53-2.14 m³/m²h</td>
</tr>
<tr>
<td>Feed Gas flow rate</td>
<td>12.6-25.5 kmol/m²h</td>
</tr>
<tr>
<td>CO₂ in the feed gas</td>
<td>15%</td>
</tr>
<tr>
<td>Desorber bed temperature</td>
<td>75, 85, 95°C</td>
</tr>
<tr>
<td>Desorber Catalyst</td>
<td>HZSM-5 (Si/Al =19)</td>
</tr>
<tr>
<td>Desorber Catalyst weight</td>
<td>150g</td>
</tr>
<tr>
<td>Absorption catalyst</td>
<td>K/MgO</td>
</tr>
<tr>
<td>Absorption catalyst Weight</td>
<td>0, 50, 100, 150g</td>
</tr>
<tr>
<td>Amine inlet temperature into absorber</td>
<td>20, 30, 40°C</td>
</tr>
</tbody>
</table>
Figure 3.7-2: Column Packing and catalyst bed arrangement for absorber and desorber
3.8 Volatile Organic Matter Emissions experiment

The pilot plant setup as described earlier served as the basis for the emission setup. The only modification is that the off-gas from the absorber unit was connected directly to a 4 impinger system as shown from Figure 3.8-1. The first and second impingers contained 300ml of a 0.1N H₂SO₄ solution each. The third and fourth impinger contained distilled water, 300ml each. The method of analysis was adapted from the EPA analysis for ammonia. The impinger samples were analysed as well as the amine solutions using a GCMS by taking 3ml of each solution. The feed gas for the emissions experiment, as feed to the pilot plant setup, was also modified to include oxygen with 15% CO₂ and 7% O₂ (balance N₂). Operation was similar to pilot plant operation described earlier.
Figure 3.8-1: Volatile organic matter emissions setup
CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Catalyst Characterisation Results

4.1.1 Temperature program desorption TPD

The temperature programmed desorption of CO$_2$ indicates the catalyst strength, the base strength of the catalyst and the amount of base sites. The base strength corresponds to the temperature for the TPD peaks while the amount of base sites corresponds to the area under the TPD peaks. The CO$_2$ TPD shows various active sites for the CO$_2$ adsorption on MgO. The results for the catalyst samples have been shown in the Figure 4.1-2. In CO$_2$ TPD, the low temperature desorption (50-150°C) peak corresponds to CO$_2$ adsorbed on the weak base sites (OH groups) while the peak in intermediate temperature range (150-650°C) and at higher temperatures (above 650°C) represent CO$_2$ adsorptions on the medium and strong base (O$^{2-}$ ions) sites, respectively (Di Cosimo et al., 1998). The results from Figure 4.1-2 shows the different peaks for five catalysts Cs$_2$O/$\gamma$-Al$_2$O$_3$, Ca(OH)$_2$, Cs$_2$O/$\alpha$-Al$_2$O$_3$, Mg-Al hydrotalcite and 1%K/MgO. For Cs$_2$O/$\gamma$-Al$_2$O$_3$, two major peaks are observed. The first, observed at 500 °C corresponding to a medium strength site and the other peak observed at 800 °C for the strong sites. Comparing with the other samples, Cs$_2$O/$\gamma$-Al$_2$O$_3$ has the strongest medium site and strong base sites. It however has the least number of base sites from the height of its peak. Ca(OH)$_2$ TPD plots gave a single peak corresponding to a strong site. The high base strength of Cs$_2$O/$\gamma$-Al$_2$O$_3$, Ca(OH)$_2$, Cs$_2$O/$\alpha$-Al$_2$O$_3$ can be attributed to ease to which oxygen makes electros available for bonding with CO$_2$. The number of base sites was also high for that of Cs$_2$O/$\gamma$-Al$_2$O$_3$, from a height of 100 signal.
Results on Cs$_2$O/α-Al$_2$O$_3$, Hydrotalcite and 1%K/MgO catalyst shows multiple peaks corresponding to weak and medium base sites. However, the positions of the peaks indicate the relative strength of the base site. This follows Cs$_2$O/α-Al$_2$O$_3$<Hydrotalcite < 1%K/MgO for the basic strength. The peak height for these catalysts which corresponds to the amount of base sites also follows Cs$_2$O/α-Al$_2$O$_3$<Hydrotalcite < 1%K/MgO. The peak for K/MgO has strong base sites but has the highest amount of base sites. The performance of the catalyst however depends on both the strength of the base sites as well as the number of the base sites. In general, the trend for the amount of base sites follows Cs$_2$O/γ-Al$_2$O$_3$<Ca(OH)$_2$< Cs$_2$O/α-Al$_2$O$_3$<Hydrotalcite < 1%K/MgO. K/MgO indicated a high number of base sites despite its low surface area. For the strength of base sites, obtained trend follows Cs$_2$O/α-Al$_2$O$_3$<Hydrotalcite < 1%K/MgO< Cs$_2$O/γ-Al$_2$O$_3$<Ca(OH)$_2$.

4.1.2 BET Surface Area and Porosity

The effect of varying the promoter concentration (% K) on the MgO catalyst was investigated. The K promotes the electron density around the MgO thereby improving its catalytic role in CO$_2$-amine reaction. The aim of this BET experiment was to show how catalyst surface area, pore volume and pore size changes as the promoter concentration increased. The result is tabulated below. Result on table 4.1-1 shows the reduction in surface area and pore volume as the K percentage increases and is attributed to the non-dispersion of the active metal on the catalyst surface causing agglomeration on the catalyst surface. An increase in the amount of promoter reduced the catalyst surface dispersion leading to a collapse of the catalyst pores. A low BET surface area is very characteristic
of MgO catalyst. Jiménez et al. (2006) investigated the surface area of K/MgO using different catalyst precursors and reported the surface area as 27 m²/g. This confirms our low surface area and pore volumes obtained. This result confirms that potassium introduction diminishes the surface area in comparison with pure MgO (Jiménez et al., 2006).

4.1.3 Powder X-ray Diffraction (XRD)

XRD was performed for all catalyst to confirm their composition as well as crystalline size. Both the synthesized and commercially obtained catalyst were characterised by this method. To identify the species in each catalyst, a reference paper with similar characterisation method was used. The results for the K/MgO catalyst revealed the presence of KOH as well as MgO with high peak intensities. The observed peak phases included Mg(OH)₂, MgO and KOH. Mg(OH)₂ in the prepared catalyst was due to the partial rehydration of the prepared MgO back to Mg(OH)₂ by moisture. However, its peak intensity is low. The KOH also indicates below 100% calcination to K obtain. The peak intensity was highest for MgO indicating its high concentration and confirming the catalyst prepared. Increasing the K percentage on the MgO resulted in an increase in KOH peak intensity from Figure 4.1-4 indicating the increase in KOH amount on the catalyst. XRD of Cs₂O/α-Al₂O₃ and Cs₂O/γ-Al₂O₃ also showed peaks of α-Al₂O₃ and γ-Al₂O₃ respectively as the highest peaks. Cs₂O peak was obtained. Both had little but significant amount of each type of alumina with the dominant corresponding to the catalyst type. After XRD of the Mg-Al hydrotalcite, results showed four main peaks with each corresponding to hydrotalcite, MgO, brucite and gibbsite. The highest peak
corresponding the hydrotalcite (HT). Finally, XRD of the commercially obtained catalysts including CaCO$_3$, Ca(OH)$_2$ and BaCO$_3$ were also obtained. The peaks for each of those samples corresponded with the content. However, Ca(OH)$_2$ showed peaks of both Ca(OH)$_2$ and CaCO$_3$. The carbonate compound is believed to be as a result of impurities.

4.1.4 Scanning electron microscopy (SEM)

The morphology of varying potassium (K) promoter concentration on MgO was also investigated. This work investigated the effect of potassium (K) on the catalyst surface dispersion. The results of this work showed that as the catalyst promoter concentration increased the catalyst surface dispersion reduced resulting in the formation of lumps and clusters of the catalyst surface. The Figure 4.1-5 showed the different SEM graphs with a particle size of 100nm. Diez et al. (2006) investigated the effect of increasing the Li percentage on MgO using SEM. Result showed a flake morphology of unpromoted MgO after SEM analysis which confirmed result of this work for the MgO. It was discovered that the increase in active metal concentration resulted in the crystal size increase, the drop of surface area and pore volume, as well as the morphological changes toward a smoother appearance as the Li content increases and was attributed to particle agglomeration (ununiform active particle distribution). Sahu et al. (2015) also investigated the effect of KOH % on MgO using SEM. Results showed the change in morphology as KOH percentage increased due to the catalyst surface agglomeration. This confirmed the different morphologies as the K% increases. Results from Figure 4.1-6 showed an increase in the porosity of the catalyst (a less flaky structure) when the K percentage on the catalyst increased from 0 to 3%. This can be attributed to a well distributed K concentration as the
catalyst pores increases from 0 to 3% K. An increased catalyst pore volume results in more accessible catalyst sites and therefore allowed for a more distributed potassium on the catalyst site. Beyond 3% K, results showed a gradual increase K agglomeration on the catalyst surface which is seen as a flaky structure. This can be attributed to the further increase in K percentage resulting in the blockage of these pores, eventually resulting in the collapsing of the pores and catalyst sintering. This was confirmed with the results on BET surface area which showed a big drop in surface area and pore volume as the %K increased beyond 3%.

The SEM plots for the absorber catalyst screened on the semi batch setup was also investigated. The result also showed a more porous structure for the K/MgO, Ca(OH)_2 and Cs_2O/α-Al_2O_3 catalysts. This is consistent with their performance in influencing the absorption of CO_2 by the amine as was seen in the semi batch screening section of this work. The other catalyst samples showed a highly flaky structure which is a result of non-dispersion of the catalyst particles also consistent with its low performance in semi batch experimental setup.
Figure 4.1-1: XRD pattern for different promoter (K) concentration on MgO
Figure 4.1-2: TPD plots for Cs$_2$O/$\gamma$-Al$_2$O$_3$, Ca(OH)$_2$, Cs$_2$O/$\alpha$-Al$_2$O$_3$, Mg-Al Hydrotalcite and 1%K/MgO
Figure 4.1-3: XRD plot for Cs$_2$O/γ-Al$_2$O$_3$

Figure 4.1-4: XRD plot for Cs$_2$O/α-Al$_2$O$_3$
Figure 4.1-5: XRD plot for BaCO$_3$, Ca(OH)$_2$, CaCO$_3$ and Hydrotalcite
Figure 4.1-6: SEM graphs for different promoter (K) concentration on MgO
Figure 4.1-7: SEM graphs for Cs$_2$O/$\alpha$-Al$_2$O$_3$, Ca(OH)$_2$, BaCO$_3$, Cs$_2$O/$\gamma$-Al$_2$O$_3$, Hydrotalcite, CaCO$_3$
Table 4.1-1: BET analysis for different promoter (K) concentration on MgO

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area, m²/g</th>
<th>BET Pore Volume, cm³/g</th>
<th>BET Pore Size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>43.49</td>
<td>0.21</td>
<td>19.78</td>
</tr>
<tr>
<td>0.5% K/MgO</td>
<td>59.50</td>
<td>0.31</td>
<td>21.09</td>
</tr>
<tr>
<td>1% K/MgO</td>
<td>63.33</td>
<td>0.27</td>
<td>17.076</td>
</tr>
<tr>
<td>3% K/MgO</td>
<td>69.75</td>
<td>0.13</td>
<td>7.40</td>
</tr>
<tr>
<td>5% K/MgO</td>
<td>10.00</td>
<td>0.042</td>
<td>16.95</td>
</tr>
<tr>
<td>10% K/MgO</td>
<td>4.194.19</td>
<td>0.012</td>
<td>11.41</td>
</tr>
</tbody>
</table>
4.2 Solid base catalyst screening on a Semi-Batch Absorption setup

The results on the semi batch experiment for the screening of the solid base catalysts was represented in Figure 3.4-1. The catalytic performance was evaluated on influence to increasing the CO$_2$ loading in amine. For the non-catalytic process, the experiment included the presence and absence of the blank catalyst basket. This was done to alleviate or access any contribution if any, by the metal mesh. The results showed no contribution from the metal mesh. The suitable solid base catalyst was selected on their basic strength reported as H$_{\text{acidity}}$ (ability of the catalyst to donate an electron or abstract a proton from reaction). Ono et al. (2010) reported on H$_{\text{acidity}}$ of a number of solid base catalyst, grouped as superbases. At the end of the experiment, a plot of CO$_2$ loading in the amine verses time showed the various catalytic performances in the absorption of CO$_2$. Result generally showed the increase in the rate of absorption as the catalyst was introduced. Also, the initial absorption rates (slope of linear section of CO$_2$ amine loading vs time plot) for the catalytic effect were evaluated to represent how fast the reaction proceeds. This is particularly important as it results in a faster mass transfer and reduction in the column height. In order to access each contribution effectively, the linear portion of each plot was taken from time zero to 240 min. Beyond this, the plot starts tapering off as the solvent is approaching its equilibrium loading. The work of the solid base catalyst is to increase the rate of the reaction between the CO$_2$ and the Amine by providing an alternative reaction pathway.

The K/MgO catalyst was reported as having Lewis base sites by Ono et al. (2010). The K is more electropositive than the Mg hence destabilizes and weakens the bond between the Mg and the O. The O$^{2-}$ from the weakened bond donates electrons to CO$_2$
forming a bond between the catalyst and CO$_2$. The bond formed between the catalyst and the CO$_2$ violates carbons octet rule, making it unstable and causing the breakdown of one of the CO$_2$ double bonds between carbon and Oxygen (C=O). This puts a partial charge on the oxygen (from the C=O) and makes the CO$_2$ molecule more reactive to the amine. The nitrogen of the amine now donates its lone electrons to the catalyst-CO$_2$ bond and eventually breaks the bond between the catalyst and CO$_2$. The newly formed compound between the amine and the CO$_2$ represents the zwitterion molecule. The original role of the amine is to bond with CO$_2$ and break the carbon oxygen double bond to form the zwitterion molecule. The catalyst therefore initiates the carbon double bond breakage (an energy requiring process) leaving the amine with the single role of donating its lone pair electrons. The K promoter destabilises the bond between the Mg and O thereby increasing the amount of O$^{2-}$ Lewis base sites. Magnesium oxide is an active catalyst for the hydrogenation of 1,3-butadiene. It is also reported of the acid sites on the Mg$^{2+}$ (Ono et al. 2010). Another role of the K is to poison these acid sites. The activity for the MgO catalyst is similar to most O$^{2-}$ containing catalysts like CaCO$_3$, BaCO$_3$ and Ca(OH)$_2$. The high basic strength of each of the catalyst was confirmed with TPD.

All except the hydrotalcite have been reported to be solid base catalysts with Bronsted sites by Ono et al. (2010). The caesium which is an alkaline earth metal forms a weak bond between it and the oxygen as it is for most transition metal compounds. This allows the easy breaking of the bond between them and makes the ease of electron transfer from the catalyst to the CO$_2$ molecule. The catalyst electron donation allows for faster formation of the zwitterion, the rate determining step of the absorption process. The support of the Cs$_2$O, the $\alpha$-Al$_2$O$_3$ has also been reported to have some base sites which goes to further improve the basicity of the catalyst. The Cs$_2$O/ $\gamma$-Al$_2$O$_3$ showed a lower
performance when compared to the Cs$_2$O/α-Al$_2$O$_3$. This can be attributed to the hydrothermal treatment of the α-Al$_2$O$_3$ creating a higher surface area in addition to the catalytic activity of α-Al$_2$O$_3$ when compared with the γ-Al$_2$O$_3$. The difference in surface area accounts for the higher performance of the α-Al$_2$O$_3$ over the γ-Al$_2$O$_3$ as seen in the results.

The carbonates of calcium and barium CaCO$_3$, BaCO$_3$ were also reported to have Lewis base sites just like the Cs$_2$O. These carbonates have 3 molecules of oxygen ions O$^{2-}$ and as a result more electrons are available on the O$^{2-}$ ion increasing the electron donating effect of the catalyst and ability to form multiple bonds with CO$_2$ resulting in multiple zwitterion formation. The lower surface area of the MgO however lowers the performance against its basic strength of the catalyst as compared with the high surface area of the hydrated α-Al$_2$O$_3$. The Hydrotalcite catalyst however donates one of its H$^+$ ions from one of the H$_2$O molecules. The problem however is that the reaction requiring the proton proceed spontaneously. The catalyst however recovers the H$^+$ ion from the abundant H$_2$O molecules in the solution. The result of the low contribution of the catalyst on the extent of the reaction is seen in the low absorption rate similar to that of the blank solution. The Ca(OH)$_2$ was also screened. The results also showed a higher performance on the absorption rate. This is as a result of the number of O$^{2-}$ molecules available for reaction. The catalyst having two oxygen ions means more electrons are available for the zwitterion formation by bonding with two CO$_2$ molecules. Generally, a sum of the vacant O$^{2-}$ ions on the catalyst surface, BET surface area and pore volume accounts for the improved absorption performance when compared with blank system.
Figure 4.2-1: A plot of the amine loading against time for the semi batch experiment

Figure 4.2-2: Rate of absorption plot for Cs2O/α-alumina
Figure 4.2-3: Rate of absorption plot for blank system

Figure 4.2-4: Rate of absorption plot for BaCO$_3$
Figure 4.2-5: Rate of absorption plot for CaCO₃

Figure 4.2-6: Rate of absorption for K/MgO
Figure 4.2-7: Rate of absorption plot for Hydrotalcite

Figure 4.2-8: Rate of absorption plot for Ca(OH)$_2$
The initial absorption rate was computed from the slope of the linear portions and divided by the volume of solvent. These results are represented in a table 4.2-1. The initial absorption rate calculation showed a high for Cs2O/α-Al2O3, Ca(OH)2 and K/MgO however the selection of the suitable catalyst considering the hydrodynamics of the absorption column was based on the mechanical strength of the catalyst. A test of the catalyst mechanical strength after the reaction showed K/MgO as a suitable pilot plant catalyst as it maintained its shape and strength even after the absorption experiment. However, the Cs2O/α-Al2O3 catalyst didn’t show much mechanical strength as the catalyst easily disintegrates into powder after the absorption reaction. The K/MgO was selected as a result. Further pilot plant studies on the K/MgO catalyst was carried out. Further catalyst stability tests were carried out to improve the mechanical strength of K/MgO with employing both γ-Al2O3 and colloidal silica as catalyst binders. Results showed no contribution from these binders on the original catalytic effect of K/MgO on amine loading. However, the colloidal silica showed a significant mechanical improvement over the γ-Al2O3.

Figure 4.2-9: Rate of absorption plot for Cs2O/γ-alumina
Table 4.2-1: Semi batch experimental results (initial absorption rate)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial absorption rate (mol/L.min) $\times 10^3$</th>
<th>Percentage (% increase from blank)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/MgO</td>
<td>5.80</td>
<td>10.69%</td>
</tr>
<tr>
<td>Cs$_2$O/$\alpha$-Al$_2$O$_3$</td>
<td>5.92</td>
<td>12.98%</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>5.84</td>
<td>11.45%</td>
</tr>
<tr>
<td>BaCO$_3$</td>
<td>5.6</td>
<td>6.87%</td>
</tr>
<tr>
<td>Cs$_2$O/$\gamma$-Al$_2$O$_3$</td>
<td>5.48</td>
<td>4.68%</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>5.4</td>
<td>3.05%</td>
</tr>
<tr>
<td>Blank</td>
<td>5.24</td>
<td>0.00%</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>4.9</td>
<td>-8.40%</td>
</tr>
</tbody>
</table>
4.3 Possible K/MgO catalytic mechanism

Step 1: An oxygen containing catalyst donates a lone pair of electrons to CO$_2$

Step 2: C=O bond breaking and electron transfer onto O

Step 3: Nitrogen now donates its electrons to the carbon which breaks and forms N-C bond of the zwitterion
In this mechanism, K/MgO provides electron is as a result of bond destabilising between magnesium and oxygen bond (Mg-O) and makes electrons available for bonding with CO$_2$. K is more electropositive than Mg, hence destabilizes and weakens the bond between Mg and O. The O$^-$ from the weakened bond donates electrons to CO$_2$ thereby forming a bond between the catalyst and CO$_2$ (step 1). The bond formed violates the carbon octet rule, making it unstable and causing the breakdown of one of the double bonds between carbon and oxygen (C=O) (step 2). This puts a partial charge on the oxygen (from the C=O) and makes the CO$_2$ molecule more reactive to the amine. The nitrogen of the amine now donates its lone electrons to the catalyst-CO$_2$ bond and eventually breaks the bond between the catalyst and CO$_2$. The newly formed compound between the amine and CO$_2$ represents the zwitterion molecule (step 3).

4.4 Physical Solubility Experiment

4.4.1 Effect of temperature on physical Solubility of BEA/AMP

The physical solubility of CO$_2$ in the bi-blend solvent of BEA-AMP was evaluated and compared to the conventional solvent of 5M MEA. The results of the Henrys law constant for N$_2$O and CO$_2$ in water were obtained from the correlations developed by Versteeg and Swaaij, (1988). The trend from Figure s 4.4-1 to 4.4-3 shows a decrease in the physical solubility (increase in Henrys Law constant) of the N$_2$O gas as the temperature increases. This can be explained by the increase in the chemical activity as the temperature increases. The dissolution of the N$_2$O within the amine is an exothermic process just like that of CO$_2$. In exothermic processes, increasing the temperature decreases the solubility of the solute. Increasing temperature introduces more heat into the system. So according
to Le Chatelier’s Principle, the system will adjust to this excess in heat energy by inhibiting the dissolution of the N$_2$O gas. The physical solubility of the gas was seen to be small (high Henry’s law constant), hence, the need for the chemical reactivity with the amine. The experiment was validated with 5M MEA. The result showed good agreement with the work done by Ma’mun et al. (2014) with an AAD of 1.5%.

The physical solubility of CO$_2$ in the 2M BEA-2M AMP solvent was compared to that of 5M MEA shown in Figure 4.4-5. The result shows a lower Henry’s law constant at the various temperatures with 2M BEA-2M AMP. This is due to the low solvent-solvent interaction of the BEA-AMP solvent resulting in a higher solubility of the gas even though the viscosity of the 2M BEA-2M AMP is higher than that of 5M MEA as reported in the literature (Narku-Tetteh et al., 2017). Viscosity plays an important role in determining the physical solubility of a gas. The higher the viscosity, the lower the physical solubility. Finally, from Figure 4.4-4, a correlation was developed for the Henrys law constant of N$_2$O in the 2M BEA-2M AMP solution. The validity of the correlation was confirmed with the experimental results in a parity plot (Figure 4.4-6). The results show a strong correlation with the experimental work with an AAD of 1.02%.
Figure 4.4-1: Henry’s Law constant of N₂O in water at different temperatures

Figure 4.4-2: Henry’s Law constant of CO₂ in water at different temperatures
Figure 4.4-3: Henry’s Law Constant Validation with CO$_2$ in MEA against 1000/T (at different temperatures).

Figure 4.4-4: Henry’s Law constant plot of N$_2$O in 2.0M BEA/2.0M AMP against 1000/T (at different temperatures).
Figure 4.4-5: Henry’s Law constant CO$_2$ in 2.0M BEA/2.0M AMP compared with 5M MEA at different temperatures.

Figure 4.4-6: Parity plot for the Henrys Law constant of N$_2$O in the 2M BEA-2M AMP biblend solvent

AAD 1.02%
Fitting the Henrys law constant equation of N$_2$O to the arhenius equation (equation 4.4-1);

\[ H_{N2O-BEA/AMP} = a \exp\left(-\frac{b}{T}\right) \]  \hspace{1cm} (4.4-1)

Linearizing gives

\[ \ln(H_{N2O-BEA/AMP}) = \ln(a) + \frac{-b}{T} \]  \hspace{1cm} (4.4-2)

From Figure 4.4-4, a plot of \( \ln H_{N2O-BEA/AMP} \) as against \(-1/T\) gives

\ln a = 13.364 (intercept)

b = 1552.1 (slope)

a = \( e^{13.364} = 0.64 \times 10^6 \)

Therefore,

\[ H_{N2O-BEA/AMP} = 0.64 \times 10^6 \exp\left(-\frac{1552.1}{T}\right) \]  \hspace{1cm} (4.4-3)

4.5 Pilot plant setup Validation

An experiment to validate the pilot plant experimental setup was conducted with a 5M MEA solution with and without HZSM-5 catalyst (150g) at different desorption bed temperatures. Results are compared with works done by Akachuku et al. (2016). The experimental conditions are given in table 4.5-1.
Table 4.5-1: Pilot plant experimental conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent used</td>
<td>5M MEA,</td>
</tr>
<tr>
<td>Solvent flowrate</td>
<td>1.83 m³/m²h</td>
</tr>
<tr>
<td>Feed Gas flow rate</td>
<td>19.6 kmol/m²h</td>
</tr>
<tr>
<td>CO₂ in the feed gas</td>
<td>15%</td>
</tr>
<tr>
<td>Desorber amine inlet Temperature</td>
<td>85°C</td>
</tr>
<tr>
<td>Desorber Catalyst</td>
<td>HZSM-5 (Si/Al =19)</td>
</tr>
<tr>
<td>Desorber Catalyst weight</td>
<td>150g</td>
</tr>
</tbody>
</table>
The results showed good agreement with previous work (Osei et al. 2016) in terms of temperature and concentration profile along the absorption column. The temperature profile of both works explained the reaction scheme with the highest reaction point corresponding to the point of the biggest bulge. The exothermic reaction between the CO\textsubscript{2} and the amine results in the temperature increase along the column. However, the lowest temperatures at the top and bottom of the absorber column corresponded to minimum reaction as well as low temperature of the inlet amine. The gradual build up of temperature as the reaction proceeds from the amine inlet point is evident in the profile. The concentration profile also gives account of the amine CO\textsubscript{2} reactivity and how it affects mass transfer. An increase in the rate of reaction between CO\textsubscript{2} and the amine will result in a high enhancement factor, reducing the liquid film resistance and allowing for a faster mass transfer rate. The concentration profile shows the reduction of CO\textsubscript{2} concentration as the feed gas flows from the bottom of the column to the top as it contacts amine.
Figure 4.5-1: Concentration profile of the absorption column

Figure 4.5-2: Temperature profile of the absorption column
Figure 4.5-3: Temperature profile of the desorption column
The possible variation in temperature profile was attributed to the slight variations in the feed gas and amine inlet temperatures to absorber as well as experimental errors, which are beyond the control of this experiment. Nonetheless, an AAD of 0.447% indicates high correlation with previous work. AAD of 1.85% for the concentration profile as well as the temperature profile validates the pilot plant experimental setup to be used for further studies. The temperature profile of the desorption column showed the gradual drop in temperature as the CO$_2$ gets desorbed from the solution (an endothermic process). When compared with previous work an AAD of 1.82% also validated the use of the desorption column for mass transfer studies. The effect of different amine solvents was investigated.

4.6 Solvent effect on mass transfer

The solvent screening experiment was performed to select the best solvent for the CO$_2$ absorption unit using the lab scale pilot plant. The solvents screened included 5M MEA, a 7M bblend of MEA/MDEA (5:2 ratio) and a 4M bblend of BEA/AMP (2:2 ratio).

The results on the temperature profile for the different solvent is shown in Figure 4.6-1. From the results, the highest temperature bulge was obtained for the BEA/AMP despite its lower molarity indicating higher reactivity. This can be explained based on the structure of the solvent. The AMP is a sterically hindered amine. These types of amine form very unstable carbamates from the reaction with CO$_2$. The unstable carbamate easily hydrolyses to bicarbonate and in so doing, frees up more amine for reaction. This is the
major reason for the high absorption capacity of the amine given as 1mol of CO₂ per 1 mol of AMP.

The AMP, a primary amine is also very reactive and hence produces more unstable carbamates which eventually breaks down to the bicarbonate (Narku-Tetteh et al., 2017). The unstable nature of the carbamate is also enhanced at elevated temperatures during desorption. The BEA has a long chain alkyl group. This alkyl groups have been reported by Narku-Tetteh et al., (2017) to be responsible for the high reactivity of the solvent. The alkyl group present on the BEA increases the basicity of the solvent by inducing the transfer of electron from the nitrogen ion to the alkyl group. The longer the alkyl chain, the stronger the electrons abstraction is. The process of electron transfer from the nitrogen to the alkyl group is by electronegativity as the more electronegative, the alkyl group, abstract the electron from the nitrogen ion. The increase in the basic strength from the transfer of electrons results in an increase in the reactivity of the solvent. The BEA also has its long chain group further away from the ammonia molecule making it a bit less stable but more reactive than the AMP. The BEA also has one OH⁻ group. The OH⁻ group is reported to reduce the reactivity of the solvent but its presence also allows for the easy hydrolysis with water during the preparation of its aqueous solution. A single OH⁻ ion has very little has less negative effect on the amines reactivity than the MDEA which has two OH⁻ ion (diethanol).

In the case of the MEA/MDEA blend, the MEA, a primary amine, reacts very fast with the CO₂ gas. However, the MEA forms less of bicarbonate but more of carbamate. The carbamates require more energy to breakdown as compared to the bicarbonates (Shi et al., 2014b). This results in a higher lean loading produced at the desorption column.
Since the capture process is cyclic, the reactivity is also reduced. The capacity for CO\textsubscript{2} absorption is also lower than the AMP with a value of 0.5 mol/mol of amine due to the formation of stable carbamates and less free amine become available. The MDEA, a tertiary amine forms only bicarbonates which are easy to breakdown during desorption. The addition of the MDEA to the conventional 5M MEA was intended to improve its desorption process by enhancing the formation of more bicarbonate. The MDEA solvent blend adds two important ions for CO\textsubscript{2} desorption, a higher concentration of HCO\textsuperscript{3−} ion and MDEAH\textsuperscript{+} ion to the MEA-CO\textsubscript{2}-H\textsubscript{2}O system. The MDEAH\textsuperscript{+} performs the basic role in a quaternary system in CO\textsubscript{2} desorption process of its blend. It does this by reducing the MEAH\textsuperscript{+} energy requirement of the deprotonation. H\textsubscript{2}O acts as the base during the deprotonation process in the absence of MDEA. This is an energy intensive process particularly due to the low basicity of the H\textsubscript{2}O. Shi et al. (2014) further explained using the energy diagram the energy saving when MEAH\textsuperscript{+} donates its proton to MDEAH\textsuperscript{+} instead of donating to H\textsubscript{2}O during solvent regeneration.

This blend of MEA/MDEA demonstrated to be better than the conventional 5M MEA. The increase in the total molarity is a factor for the increase performance as against the 5M MEA. This means more free amines were available and hence more CO\textsubscript{2} reacted. The issue with the high molarity is put to bed when comparing the 7M MEA/MDEA blend with the 2M BEA-2M AMP. Mass transfer is enhanced with chemical reaction by the reduction of the liquid film resistance and an increase in concentration gradient. This is evident from the concentration profile of the absorber in Figure 4.6-2, which shows the highest drop for the 2M BEA-2M AMP solvent over the 7M MEA-MDEA and 5M MEA.
Under absorber performance, Figure 4.6-3 shows the CO₂ removal efficiencies for the different solvents while Figure 4.6-4 reveals the amine cyclic capacity for the different solvents with respect to the pilot plant experiment. From these Figures, the BEA-AMP solvent recorded a 111.33% increase in the CO₂ removal efficiency and a 150% increase in amine cyclic capacity over the base 5M MEA solvent confirming the high mass transfer performance of the BEA-AMP solvent. Figure 4.6-5 also shows the various desorption performances for the different solvents, recorded as CO₂ desorption efficiency. The desorption performance from Figure 4.6-5 showed a 139% increase in desorption efficiency with BEA-AMP blend confirming the superior performance of AMP in desorption. Figure 4.6-6 and Figure 4.6-7 shows overall mass transfer coefficient, \( K_{Ga_v} \) and \( K_{La_v} \) plots respectively, for the different solvent systems. The overall mass transfer coefficient validates the improvement with the BEA-AMP solvent from a 101% and 239% increase in \( K_{Ga_v} \) and \( K_{La_v} \) over the base 5M MEA solvent. This can be compared with 7M MEA-MDEA blend which had 7% and 8% increase, respectively, in \( K_{Ga_v} \) and \( K_{La_v} \) over the base 5M MEA solvent.
Figure 4.6-1: Absorber temperature profiles for different solvent systems for non-catalytic (blank) process

Figure 4.6-2: Absorber concentration profiles for different solvent systems for non-catalytic (blank) process
Figure 4.6-3: Catalyst (HZSM-5) effect on CO₂ removal efficiency as a function of solvent

Figure 4.6-4: Catalyst (HZSM-5) effect on amine cyclic capacity as a function of solvent
Figure 4.6-5: Catalyst (HZSM-5) effect on CO$_2$ desorption efficiency as a function of solvent.

Figure 4.6-6: Catalyst (HZSM-5) effect on the overall mass transfer coefficient ($K_{GAV}$) for absorption as a function of solvent.
Figure 4.6-7: Catalyst (HZSM-5) effect on overall mass transfer coefficient ($K_{Lav}$) for desorption as a function of solvent.
4.7 Effect of HZSM-5 catalyst on mass transfer

The use of HZSM-5 as a desorption catalyst on post combustion pilot plant studies has been reported by Akachuku et al. (2017). Zeolite catalysts are known for their unique pore size which makes them suitable as shape selective catalyst. They have high surface area as well as being crystalline (Akachuku et al., 2017). Figure 4.7-1 shows the concentration profile for the different solvent systems with and without HZSM-5 catalyst. The result shows the reduction in the gas phase CO₂ concentration of the absorber with the introduction of HZSM-5 in the desorber. The HZSM-5 catalyst reduces the lean amine loading from the desorption column. The reduced lean loading leads to more CO₂ absorption in the absorption column producing a much leaner CO₂ gas phase concentration. The concentration profile from Figure 4.7-2 also compares the catalyst aided desorption for the different solvent systems. Result shows the highest mass transfer performance for BEA-AMP bi-blend with HZSM-5, similar to results for the non-catalytic (blank) system. The concentration profile also confirms the reactivity of BEA-AMP bi-blend resulting in a high mass transfer of CO₂, similar to the non-catalytic system. The results from the absorption efficiency, cyclic capacity and overall mass transfer coefficient in Figure s 4.6-3 to 4.6-6 shows a significant improvement which can be explained from the catalytic role in desorption.

The HZSM-5 catalyst donates its H⁺ ion first from its active site to the carbamate which reacts to form free amine and release the CO₂. The catalyst also donates part of its H⁺ protons to the breakdown of HCO₃⁻ as well (Shi et al., 2014b). The catalyst becomes a conjugate base after donating its proton making it capable of accepting back an H⁺ proton. The catalyst recovers its H⁺ ion from the protonated amine thereby breaking and lowering
the energy barrier for the release of CO₂. This results in more CO₂ production and translates to a much lower lean loading shown in table 4.7-1. The lean loading confirms the benefit of HZSM-5 in improving the desorption process. The lower lean amine loading has a direct effect on the CO₂ removal efficiency, shown in Figure 4.6-3, as more free and active amine molecules are available for reaction. Therefore, this explains the increase in desorption performance (Figure 4.6.5) leading to a corresponding increase in absorption performance with the addition of HZSM-5 catalyst in the desorber.

Figure 4.6-3 shows a 23.8% absorption efficiency increase from the base case of no catalyst in both columns. The lower lean amine loading has a direct effect on the CO₂ removal efficiency, shown in Figure 4.6-3, as more free and active amine molecules are available for reaction. The catalytic contribution of HZSM-5 in improving the amine cyclic capacity for the different solvents were evaluated as shown in Figure 4.6-4. For the 2M BEA-2M AMP blend, a 27.8% increase was observed from the base case of no catalyst in both columns. Similarly, the HZSM-5 contribution on 5M MEA and the 5M MEA-2M MDEA blend were 37.6 and 37.0 % increase in amine cyclic capacity respectively. The high contribution of the catalyst on the 5M MEA and 5M MEA-2M MDEA blend as compared to the 2M BEA-2M AMP blend can be attributed to the high concentration of free and active amine for reaction as well as their original low solvent performance, allowing for the HZSM-5 catalyst to make a significant contribution in increased reactivity. This therefore explains the increase in desorption performance (Figure 4.6-5) leading to a corresponding increase in absorption performance with the addition of HZSM-5 catalyst in the desorber.
For the overall mass transfer coefficient (Figure s 4.6-6 and 4.6-7), a 38.7% $K_{Ga}$ and 23.6 % $K_{La}$ increase with the HZSM-5 catalyst on 2M BEA-2M AMP blend and a higher HZSM-5 catalytic contribution for the 5M MEA and 5M MEA-2M MDEA was obtained. The increased rate of mass transfer as the concentration gradient across the film increases will result in a much lower column height required. This is significant since column design accounts for more than 17% of the total design cost of the CO$_2$ capture plant (Shi et al., 2014).
Figure 4.7-2: Absorber concentration profile for different solvent systems with and without 150g HZSM-5 catalyst

Figure 4.7-2: Absorber concentration profile for different solvent systems with 150g HZSM-5 catalyst
Table 4.7-1: The desorption column lean amine loading (mol of CO$_2$/mol of amine)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Non-catalytic</th>
<th>HZSM-5 in desorber</th>
</tr>
</thead>
<tbody>
<tr>
<td>5M MEA</td>
<td>0.42</td>
<td>0.41</td>
</tr>
<tr>
<td>7M MEA-MDEA</td>
<td>0.35</td>
<td>0.32</td>
</tr>
<tr>
<td>2M BEA- 2M AMP</td>
<td>0.33</td>
<td>0.30</td>
</tr>
</tbody>
</table>
4.8 Effect of K/MgO catalyst on mass transfer

The selected solid base catalyst K/MgO was investigated in its application in the absorption column. The desorption column was loaded with 150g HZSM-5 while the effect of introducing 150g of K/MgO in the absorption column was evaluated. The results were evaluated in terms of absorption efficiency, amine cyclic capacity and overall mass transfer coefficients which showed improvement with the use a solid base catalyst in conjunction with a solid acid catalyst. As explained earlier, the two reactions involved in the CO$_2$ reaction with amine includes the electron transfer step to form zwitterion (rate determining step) and carbamate formation from zwitterion deprotonation, which occurs spontaneously (Shi et al., 2014). As such a Lewis base catalyst capable of donating electrons is desired.

K/MgO catalyst has been reported as having Lewis base sites (ono et al. 2010). The original role of the amine is to bond with CO$_2$ and break the carbon oxygen double bond to form the zwitterion molecule. The catalyst therefore initiates the carbon double bond breakage (an energy requiring process) leaving the amine with the single role of donating its lone pair electrons. The K promoter destabilises the bond between Mg and O thereby increasing the amount of O$^2-$ Lewis basic sites. Also, magnesium oxide is an active catalyst for hydrogenation of 1,3-butadiene. It has been reported that Mg$^{2+}$ has acid sites which are responsible for reduction in catalytic base performance of the K/MgO (Ono et al., 2010). Thus, another role of K is to poison these acid sites. The increase in the rate of reaction also results in a higher driving force for mass transfer as the concentration of free CO$_2$ in the liquid reduced. All these result in a faster rate of mass transfer. The electron
donating ability of the K/MgO catalyst also results in a higher rich loading as more CO\textsubscript{2} gets absorbed into the amine. In addition, the cyclic capacity also increased.

The temperature profile for the application of both catalysts on the novel solvent of 2M BEA-2M AMP is shown in Figure 4.8-1. The result demonstrates the progression of improvements in absorption of CO\textsubscript{2} when both catalysts are placed in the absorption and desorption columns. The catalyst weight used was 150g of HZSM-5 based on previous studies (Akachuku et al., 2016). An initial weight of 150g of the K/MgO was used in a test case for the pilot plant experiment to assess the improvement on CO\textsubscript{2} absorption into amine. The concentration profile from Figure 4.8-2 shows higher CO\textsubscript{2} absorption when both catalysts were employed with the lowest CO\textsubscript{2} exit concentration for this catalyst configuration. Figure 4.8-3 shows the effect of K/MgO on rich amine loading. Results from Figure 4.8-3 confirm improvements in CO\textsubscript{2} absorption as well as an increase in amine loading resulting from K/MgO catalyst influencing the absorption of CO\textsubscript{2}.

For the application of both catalysts on the 2M BEA-2M AMP, Figure 4.8-4 shows a 23.7% increase in absorption efficiency with HZSM-5 catalyst alone while a 47.3% increase was obtained with both K/MgO in the absorber and HZSM-5 in the desorber as compared with the base case of no catalyst in both columns. From Figure 4.8-5, HZSM-5 catalyst alone gave a 27.8% increase in cyclic capacity whereas a 57.02% increase was obtained with both K/MgO in the absorber and HZSM-5 in the desorber as compared with the base case of no catalyst in both columns. For the overall mass transfer coefficient (Figure s 4.8-6 and 4.8-7), a 38.7% K\textsubscript{Ga} and 23.6% K\textsubscript{La} increases were obtained with HZSM-5 catalyst alone while 95% K\textsubscript{Ga} and 45% K\textsubscript{La} increases were obtained with both K/MgO and HZSM-5, also as compared with the base case of no catalyst in both columns.
Figure 4.8-1: Temperature profiles for 4M BEA-AMP with different configurations of K/MgO in absorber and HZSM-5 in the desorber
Figure 4.8-2: Concentration profiles for 4M BEA-AMP with different configurations of K/MgO in absorber and HZSM-5 in desorber

Figure 4.8-3: Effect of K/MgO catalyst on rich amine loading
Figure 4.8-4: Effect of catalyst configuration on CO₂ removal efficiency
Figure 4.8-5: Effect of catalyst configuration on amine cyclic capacity

Figure 4.8-6: Effect of catalyst configuration on $K_{Ga_v}$ of Absorber
Figure 4.8-7: Effect of catalyst configuration on $K_{L,a}$ of desorber
4.9 Effect of the absorber catalyst (K/MgO) weight on mass transfer performance

The effect of absorber catalyst weight at different absorber inlet lean amine loadings were examined. Three different lean amine loadings (LAL) of 0.2, 0.33 and 0.42 mol CO$_2$/mol corresponding to operating and keeping the desorption column temperature at 95°C, 85°C and 75°C respectively were studied. From Figures 4.9-1 to 4.9-4, It is observed that an increase in the absorption catalyst weight generally results in an increase in the mass transfer performance in terms of $K_{GA}$ of the absorber and $K_{LA}$ of the desorber. Also, the decrease in the lean amine loading shows an increase in mass transfer performance as more free active amine molecules become available for reaction.

Results from Figure 4.9-2 shows the effect of increasing the K/MgO catalyst weight on CO$_2$ removal efficiency from the gas mixer. From the results, an increase in the weight of K/MgO in the absorption column resulted in an increase in the CO$_2$ removal efficiency. This can be attributed to the increase in reaction rate as the catalyst weight increases. The increase in catalyst weight results in an increase in the total active catalyst sites available for reaction. The amount of active site and total surface area of the active site increases with the increased catalyst weight. This, therefore, results in an increase in the CO$_2$ and amine reactivity on the catalyst active site.

The increase in reaction rate creates a higher concentration gradient as free CO$_2$ in the liquid is consumed at a faster rate. This increased concentration gradient serves as the driving force for mass transfer and is directly proportional to the rate of transfer. Most importantly, the increase in reactivity results in an increase in the enhancement factor. The enhancement factor, which is a ratio of the absorption rate of CO$_2$ due to reaction to the physical absorption of CO$_2$ by the same solvent and conditions, results in a decrease in the
liquid film resistance, seen from equations 2.8-1 and 2.8-2. The combined effect of an increase in reaction rate resulting in a decrease in liquid film transfer resistance and an increase in concentration gradient accounts for the increased performance with the increase in catalyst weight. Figure 4.9-2 shows the catalyst weight effect on the amine cyclic capacity. Similarly, the increase in the CO$_2$ removal efficiency translates to a higher cyclic of the amine as it absorbs more CO$_2$. The increased catalytic surface area also provides an added area for mass transfer. Mass transfer proceeds by the wetting of the catalyst surface area, similar to mass transfer on random or structured packing.

In summary the external mass transfer comprising of both the gas and liquid film transfer is enhanced with the introduction of the catalyst as against the internal mass transfer of the catalyst. The presence of a catalyst however introduces a solid film resistance. This resistance is made up of the pore diffusivity and catalyst surface reaction. The catalyst introduces an internal mass transfer resistance (due to the pore diffusivity).

The increase in the overall mass transfer coefficients ($K_{Ga_v}$) of absorber and ($K_{La_v}$) of desorber as a factor of the improved mass transfer is shown in Figures 4.9-3 and 4.9-4 respectively. From Figure 4.9-3, at 0.33 mol of CO$_2$/mol amine, an increase of 17.8% for $K_{Ga_v}$ was observed for 50g K/MgO, 33.1% $K_{Ga_v}$ increase for 100g K/MgO, 40.6% $K_{Ga_v}$ increase for 150g K/MgO and a 42.0% $K_{Ga_v}$ increase for 170g K/MgO when compared to no catalyst in absorber (0g K/MgO).

Similarly, from Figure 4.9-4 and at 0.33 mol CO$_2$/mol amine (lean amine loading to the absorber), an increase of 0.6% for $K_{La_v}$ was observed for 50g K/MgO, 12.8% $K_{La_v}$ increase for 100g K/MgO, 16.7% $K_{La_v}$ increase for 150g K/MgO and a 19.6% $K_{La_v}$ increase for 170g K/MgO when compared to no catalyst in absorber (0g K/MgO).
corresponding increase in $K_{L}A_v$ can be attributed to the increase in the desorption or regeneration rate. The increase in the amount of CO$_2$ absorbed by the amine leads to a high desorption rate as the CO$_2$-loaded solvent becomes more unstable at higher loading. This makes the amine easier to regenerate at the higher loadings, evident from the Figure 4.9-4. Also, it is easier to generate water vapour for the richer amine solution leading to a high concentration gradient as a driving force for mass transfer. Nonetheless, an increase in the catalyst weight results in an increase in both mass transfer coefficients which leads to a decrease in the heights of both columns.

Generally, we observe a higher catalytic performance when the CO$_2$ loading of the amine is highest. This can be attributed to the increase in the solvent effect as the lean loading reduces. The decrease in the lean loading results in more free amines available for reaction. This therefore promotes reaction within the liquid phase, referred to as the solvent effect, and reduces catalyst influence (surface reaction of the catalyst). 170g served as the limit as further increase in the catalyst weight resulted in column flooding and liquid carry over, affecting the hydrodynamics of the absorber.
Figure 4.9-1: Concentration profile for the effect of absorber catalyst (K/MgO) weight at amine inlet loading to the absorption column of A) 0.42 mol of CO$_2$/mol of amine B) 0.33 mol of CO$_2$/mol of amine
Figure 4.9-2: Effect of the absorber catalyst (K/MgO) weight on CO₂ removal efficiency and cyclic capacity at different absorber lean amine loadings (LAL) 0.42, 0.33 and 0.2 mol of CO₂/mol of amine.

Figure 4.9-3: Effect of the absorber catalyst (K/MgO) weight on overall mass transfer coefficient ($K_{Gav}$) of the absorption column at different absorber lean amine loadings (LAL) 0.42, 0.33 and 0.2 mol of CO₂/mol of amine.
Figure 4.9-4: Effect of the absorber catalyst (K/MgO) weight on Overall mass transfer coefficient ($K_{LAV}$) of the desorption column at different absorber lean amine loadings (LAL) 0.42, 0.33 and 0.2 mol of CO$_2$/mol of amine
4.10 Effect of desorption bed temperature on desorption mass transfer.

The effect of varying the desorption bed temperature on the mass transfer performance of both columns was investigated and reported in Figures 4.10-1 to 4.10-3. The temperature of the catalyst/structured packing bed was varied at 95°C, 85°C and 75°C. From results, an increase in the desorption temperature resulted in a lower lean loading. The increase in the desorption bed and inlet temperature of the amine to the absorber results in an increase in the kinetic energy of the molecules of the carbamate, bicarbonate and protonated amine. This results in an increase in the desorption reaction rate to produce CO₂ as the reaction is highly endothermic (positive temperature influence). This leads to a high concentration of free CO₂ in the amine solution which produces a high concentration gradient, and hence, a high rate of mass transfer. The increase in the desorption reaction rate also leads to an increase in the interfacial area between the gas and liquid film which results in a reduction in the resistances in both films all resulting in a faster mass transfer rate. The viscosity of the solvent is also affected by the increase in temperature. The viscosity of the amine solution also reduces as temperature increases. This also leads to a faster rate of mass transfer from the liquid to gas as the viscosity of the solvent reduces.

Another key parameter is the physical solubility of CO₂ within the liquid which also reduces. The reduction in the physical solubility results in an unstable rich loaded amine solution and therefore serves as a driving force for mass transfer from the liquid in the gas phase. Finally, an increase in the desorption temperature also results in an increase in the amount of water vapour in the gas phase. This leads to a lower composition of CO₂
in the gas and hence a high driving force or concentration gradient for transport from the liquid into the gas.

Figures (4.10-1, 4.10-2, 4.10-3) shows the performance with increasing desorption bed temperature. The increase in desorption temperature decreased as the catalyst weight increased signifying the increase in catalytic effect as against the desorption temperature effect on the CO₂ absorption process.

Figures 4.10-1 and 4.10-2 shows the effect of K/MgO on CO₂ desorption efficiency from the gas mixer and amine cyclic capacity respectively, at different absorber catalyst weights. From Figure 4.10-1 and at a catalyst weight of 50g K/MgO, a 72.5% increase in CO₂ desorption efficiency from 75 to 85°C desorption bed temperature, 33% increase from 85 °C to 95 °C desorption bed temperature was obtained. At a catalyst weight of 150g K/MgO, a 64.4% increase in CO₂ desorption efficiency from 75 to 85°C desorption bed temperature, 26.6% increase from 85 °C to 95°C desorption bed temperature was obtained. From Figure 4.10-2 and at a catalyst weight of 50g K/MgO, a 66.5% increase in amine cyclic capacity from 75 to 85°C desorption bed temperature, 20% increase from 85 °C to 95 °C desorption bed temperature was obtained. At a catalyst weight of 150g K/MgO, a 73.5% amine cyclic capacity increase from 75 to 85°C desorption bed temperature, 10% increase from 85 °C to 95 °C desorption bed temperature was obtained. For the corresponding mass transfer performance, from Figure 4.10-3, a 73.6% increase in K_LaV from 75 to 85°C desorption bed temperature at a catalyst weight of 50g 46.6% increase from 85 °C to 95°C was obtained. A 70% increase in K_LaV from 75 to 85°C desorption bed temperature at a catalyst weight of 150g, 37.4% increase from 85 °C to 95 °C was obtained.
After analysis of the heat duty for the system (a ratio of the amount of energy required in heating the solution to the required temperature to the amount of CO\textsubscript{2} produced) showed an 85°C the least regeneration energy from figure 4.10-4. Results also showed the reduction in the catalyst performance as the desorption temperature increases. The high desorption bed temperature results in a lower lean loading.
Figure 4.10-1: Effect of the desorption bed temperature on CO₂ desorption efficiency at different absorber catalyst (K/MgO) weight.

Figure 4.10-2: Effect of the desorption bed temperature on CO₂ cyclic capacity at different absorber catalyst (K/MgO) weight.
Figure 4.10-3: Effect of the desorption bed temperature (DBT) on Overall mass transfer coefficient ($K_{L}a_{V}$) of the desorption column at different absorber catalyst (K/MgO) weight.

Figure 4.10-4: Effect of the desorption bed temperature (DBT) on amine regeneration energy at different absorber catalyst (K/MgO) weight.
4.11 Effect of the lean amine loading on the absorption mass transfer

The effect of lean amines loading generated from the increase in desorption temperature on the absorption rate were investigated from Figures 4.11-1. The CO$_2$ loading is an important parameter because it changes along the height of the column and can be considered as a dynamic parameter, whereas other parameters, such as solution concentration and liquid flow rate, are static parameters (Naami A., 2012). The amines with a much leaner loading resulted in a higher mass transfer of CO$_2$ in the amine.

From the temperature profile (Figure 4.11-1), the lowest lean amine loading resulted in the biggest bulge and average temperature. This can be attributed to the amount of free amine available at these lean loadings. As the solvent lean loading decreases, the amount of free amines available for reaction increases. Therefore, results in a faster rate of reaction between the CO$_2$ and the amine. The temperature bulge explains the increase in the reaction as a faster reaction will result in a higher temperature of the solution. This is due to fact that the reaction between the CO$_2$ and the amine is an exothermic reaction. The increase in the rate of reaction as explained earlier results in a lower mass transfer resistance between the gas and liquid, a high mass transfer area and a high concentration gradient all influencing the increase in the mass transfer rate.

Also, viscosity which is a less likely effect, increases with increase in loading. Therefore, the lower loadings have lower liquid viscosities and as a result, an increase in the mass transfer rate from the gas to the liquid. The trend for increase in desorption temperature and an increase in catalyst weight resulting in a higher mass transfer rate is seen across all field of mass transfer including the cyclic capacity, absorption efficiency and the overall mass transfer coefficient of both absorption and desorption columns.
The concentration profile from Figure 4.11-2 shows higher CO₂ absorption with the lowest lean amine loading (0.20 mol CO₂/mol amine) with the lowest CO₂ exit concentration. This confirms the improvement in the mass transfer performance as the lean amine loading for the absorber inlet was reduced.

Figure 4.11-3 shows the effect of lean amine loading on CO₂ removal efficiency from the gas feed mixer, at different absorber catalyst weights. From Figure 4.11-3 and at a catalyst weight of 150g K/MgO, a 69.10% increase in CO₂ removal efficiency from 0.42 to 0.33 mol CO₂/mol amine (lean loading of amine to absorber), 8.5% increase from 0.33 to 0.20 mol CO₂/mol amine was obtained. A 113% increase in $K_{Gav}$ from 0.42 to 0.33 lean amine loading (LAL) at a K/MgO catalyst weight of 150g was obtained. However, a decrease in LAL from 0.33 to 0.2 resulted in a 15% increase in $K_{Gav}$. 
Figure 4.11-1: Effect of absorber lean amine loading on the temperature profile of absorber at 150g K/MgO

Figure 4.11-2: Effect of absorber lean amine loading on the concentration profile of absorber at 150g K/MgO
Figure 4.11-3: Effect of absorber lean amine loading on CO₂ removal efficiency at different absorber catalyst (K/MgO) weight.

Figure 4.11-4: Effect of absorber lean amine loading on overall mass transfer coefficient ($K_{Gav}$) of the absorption column at different absorber catalyst (K/MgO) weight
4.12 Effect of solvent flowrate on mass transfer

The effect of varying the solvent flowrate into both columns were investigated within the range from 1.5 m$^3$/m$^2$h to 2.2 m$^3$/m$^2$h shown in Figures 4.12-1 to 4.12-3. From the results, an increase in the amine flowrate resulted in an increase in free active amine available to react with the CO$_2$ for the absorption mass transfer. As explained earlier, this results in the increase in mass transfer and the increase in the absorption mass transfer area. Much energy however is required to increase the temperature of the solvent as the flowrate increases. The amount of CO$_2$ production in the desorber section also increases resulting in a higher cyclic capacity and a high mass transfer performance for desorption. Also, the increase in the liquid flowrate increase the Reynolds number of the solvent. The Reynolds number is an essential parameter indirectly related to the liquid film resistance. Therefore, an increase in its value greatly reduced the liquid film resistance and the overall resistance as well.

It can therefore be inferred that an increase in the solvent flowrate increases the liquid film mass transfer coefficient which greatly increases the overall mass transfer coefficient as their directly related. The flowrate increase also increases the liquid wetting area of the structured packing which results in a higher mass transfer area for transfer. Also, an increase in the solvent flowrate increases the amount of free amines available for reaction thereby increasing the rate of mass transfer by increasing the enhancement factor and reducing the liquid film resistance. The solvent flowrate increase the amount of free amine molecules in the system becoming larger and the system having more capacity to absorb CO$_2$ the gas feed. At high inlet amine flowrates, the solvent effect supersedes the
catalyst effect and as a result, increasing the catalyst weight doesn’t show any significant improvement.

Figure 4.12-1 showed the combined effect of solvent flowrate on CO$_2$ removal efficiency and amine cyclic capacity, at different absorber catalyst weights. From Figure 4.12-1 and at a catalyst weight of 150g K/MgO, a 31.9% increase in CO$_2$ removal efficiency from 1.53 to 1.83 m$^3$/m$^2$h solvent flowrate, 1.0% increase from 1.83 to 2.14 m$^3$/m$^2$h was obtained. From Figures 4.12-2 54.2% increase in $K_{Gav}$ from 1.53 to 1.83 m$^2$/m$^3$h solvent flowrate at a K/MgO catalyst weight of 150g was obtained, 5.2% $K_{Gav}$ increase from 1.83 to 2.14 m$^3$/m$^2$h was obtained. From Figures 4.12-3 35.8% increase in $K_{Lav}$ from 1.53 to 1.83 m$^3$/m$^2$h solvent flowrate at a K/MgO catalyst weight of 150g was obtained, 8.7% $K_{Lav}$ increase from 1.83 to 2.14 m$^3$/m$^2$h was obtained.
Figure 4.12-1: Effect of the solvent flowrate on CO₂ removal efficiency and cyclic capacity at different absorber catalyst (K/MgO) weight

Figure 4.12-2: Effect of the solvent flowrate on overall mass transfer coefficient ($K_{Gav}$) of the absorption column at different absorber catalyst (K/MgO) weight
Figure 4.12-3: Effect of the solvent flowrate on Overall mass transfer coefficient ($K_{LaV}$) of the desorption column at different absorber catalyst (K/MgO) weight.
4.13 Effect of Absorber lean amine inlet temperature

The effect of increasing the lean amine inlet temperature to the absorber was investigated at 20, 30 at 40°C. Results from Figure (4.13-1, 4.13-2, 4.13-3) showed an increase in the lean amine temperature to the absorber reduces the mass transfer performance of the absorber. This can be explained based on the CO₂ amine reactivity. The reaction between CO₂ and the amine is reported to be an exothermic reaction (Carsonet al., 2000; Gabrielsen et al., 2005). Therefore, an increase in the lean amine temperature is seen to reduce the reaction rate of CO₂ and amine. From Le Chatelier's principle, as the temperature of the reactant as well as the reaction temperature increases, the equilibrium shifts to the reversible reaction that favours the endothermic reaction direction (temperature increase favouring direction) whereas a decrease in the inlet or reaction temperature of the amine shifts the equilibrium to favour the exothermic reaction direction (temperature decrease favouring direction).

This can be extended to our study of increase in lean amine temperature. The decrease in performance as the temperature increases indicates the increase in the reaction rate of the reverse process where carbamates, bicarbonate and protonated amine reacts to produce back the free CO₂. The forward reaction rate between the CO₂ and the amine reduces as the temperature increases as a result of the equilibrium temperature shift. At low lean amine inlet temperatures, the temperature effect supersedes the catalyst effect and as a result, increasing the catalyst weight does not show any significant improvement.

Figure 4.13-1 shows the effect of absorber amine inlet temperature on CO₂ removal efficiency and amine cyclic capacity, at different absorber catalyst weights. From Figure 4.13-1 and at a catalyst weight of 150g K/MgO, a 1.5% increase in CO₂ removal efficiency
by lowering the amine inlet temperature from 30°C to 20°C, 22.1% increase by lowering the amine inlet temperature 40°C to 30°C was obtained. From Figures 4.13-2, a 6.6% increase in \( K_{GaV} \) by lowering the amine inlet temperature from 30°C to 20°C at a K/MgO catalyst weight of 150g was obtained, 22.7% \( K_{GaV} \) increase from 40°C to 30°C was obtained. From Figures 4.13-3, a 3.7% increase in \( K_{GaV} \) by lowering the amine inlet temperature from 30°C to 20°C at a K/MgO catalyst weight of 150g, 22.7% \( K_{LaV} \) increase from 40°C to 30°C was obtained.
Figure 4.13-1: Effect of the absorber lean amine inlet temperature on CO₂ removal efficiency and cyclic capacity at different absorber catalyst (K/MgO) weight

Figure 4.13-2: Effect of the absorber lean amine inlet temperature on overall mass transfer coefficient ($K_{Gav}$) of the absorption column at different absorber catalyst (K/MgO) weight
Figure 4.13-3: Effect of the absorber lean amine inlet temperature on Overall mass transfer coefficient ($K_{LaV}$) of the desorption column at different absorber catalyst (K/MgO) weight
4.14 Effect of BEA/AMP blend ratio on mass transfer performance

The effect of varying the solvent blend ratio between the BEA and AMP were investigated. Four blends investigated were BEA/AMP (2M:2M), BEA/AMP (2.5M:1.5M), BEA/AMP (1.5M:2.5M) and BEA/AMP (3M:1M). The results in Figures (4.14-1, 4.14-2, 4.14-3) showed an increase in the performance as the concentration of the AMP increased in the solvent blend. The performance of AMP over BEA can be attributed to the individual chemical structure of AMP and BEA as well as its physical properties like viscosity and diffusivity. As explained earlier, the AMP is a steric hindered amine. The steric hinderance is a distinct property of branched chain hydrocarbons where the reaction between the CO\textsubscript{2} and the amine results in a highly unstable carbamate formation. The high unstable nature of the carbamate results in the further breakdown in the absorber to form bicarbonate. This therefore frees up more amine to react with the CO\textsubscript{2}. The BEA molecule has an alkyl group, known to be responsible for its high base strength. The alkyl group gives BEA a high reactivity among other secondary amines. The presence of a single OH\textsuperscript{-} ion on the hydrocarbon is also responsible for its high reactivity.

Most importantly, BEA solvent has a high viscosity and low absorption capacity, in comparison with AMP, which goes against the absorption performance. The alkyl group on the amine also gives BEA a slight edge over AMP in absorption performance. The sole presence of the bicarbonate in AMP solvent and the high unstable carbamate at the desorption temperature results in its easy breakdown. Shi et al. (2014) showed that the energy required to breakdown bicarbonate to release CO\textsubscript{2} is much less than a stable carbamate which is what the BEA brings. Narku-Tetteh et al. (2016) showed that AMP performs better than BEA in desorption.
Increasing the ratio of BEA in the blend results in an increase in the total solvent viscosity, lowering of the total solvent capacity and desorption performance of the blend. A high viscosity introduces mass transfer limitation. The advantage of BEA in the blend is its high reactivity as well as low heat of reaction particularly for secondary amines in comparison to primary amines. At high AMP composition in the blend, the solvent effect supersedes the catalyst effect and as a result, increasing the catalyst weight does not show any significant improvement. The highest performance was obtained from the highest AMP concentration in the blend of (1.5M:2.5M). However, that blend ratio revealed the precipitation of AMP at that high concentration (2.5M). Therefore, a blend ratio of 2M:2M was selected.
Figure 4.14-1: Effect of the BEA/AMP blend ratio on CO₂ removal efficiency and cyclic capacity at different absorber catalyst (K/MgO) weight

Figure 4.14-2: Effect of BEA/AMP blend ratio on overall mass transfer coefficient (K_{GaV}) of the absorption column at different absorber catalyst (K/MgO) weight
Figure 4.14-3: Effect of BEA/AMP blend ratio on Overall mass transfer coefficient ($K_{LaV}$) of the desorption column at different absorber catalyst (K/MgO) weight
4.15 Effect of Inlet gas flowrate on mass transfer performance

Results from Figures 4.15-1, 4.15-2 and 4.15-3 shows an increase in the mass transfer performance with the increase in feed gas flowrate. The composition was kept at 15% CO₂ with nitrogen as balance. The increase in the gas flowrate increases the concentration gradient between the gas and liquid film which eventually results in a faster mass transfer. The increase in the gas flowrate also results in an increase in its Reynolds number of the gas and just like the liquid flowrate, leads to a reduction in the gas film resistance. The reaction rate between the CO₂ the amine increases with the increase in concentration gradient and lower gas film resistance. This leads to a higher interfacial area for mass transfer between the gas and liquid film resulting in an eventual reduction in the liquid film resistance in terms of the enhancement factor. The effect of the gas flowrate was selected at a low K/MgO weight of 50g to maximise the effect of the gas flowrate.

From Figures 4.15-2 and 4.15-3, at 50g of K/MgO, as the gas flowrate increased from 12.67 kmol/m²h to 19.3 kmol/m²h, the K_{Ga} and K_{La} values increased by 191.1% and 5.2%. respectively. For a gas flowrate increase from 19.3 kmol/m²h to 25.5 kmol/m²h, the K_{Ga} and K_{La} increased by 78.8% and 4.10%. respectively. The high increase in the K_{Ga} as the gas flowrate changes signifies the dependence of the rate of CO₂ absorption on the gas side resistance.
Figure 4.15-1: Effect of Inlet gas flowrate as Kmol/m\(^2\)hr on CO\(_2\) removal efficiency and cyclic capacity at 50g catalyst (K/MgO) weight

Figure 4.15-2: Effect of Inlet gas flowrate as Kmol/m\(^2\)hr on overall mass transfer coefficient (K\(_{GaV}\)) of the absorption column at 50g absorber catalyst (K/MgO) weight
Figure 4.15-3: Effect of Inlet gas flowrate as Kmol/m²hr on overall mass transfer coefficient ($K_{LaV}$) of the desorption column at 50g absorber catalyst (K/MgO) weight
4.16 Effect of potassium concentration (K%) over MgO on mass transfer performance

The role of the increased promoter concentration was investigated. The catalyst role is mainly performed by the MgO with K acting as promoter in destabilizing the bond between the Mg-O. This allows more of the shared electrons between the Mg and O to be drawn more unto the \( \text{O}^{2-} \) ion as the more electronegative ion. The increase in the electron density around the \( \text{O}^{2-} \) allows it to attack and donate a pair of these electrons to the \( \text{CO}_2 \). Amine now reacts faster with the \( \text{CO}_2 \) in the electron transfer step to form the intermediate zwitterion molecule. As it has been identified, the rate determining step of the \( \text{CO}_2 \) amine reaction is the electron transfer step of zwitterion formation. As such, the catalyst needed to increase the rate of the slowest reaction is an electron transfer promoting catalyst, identified previously as a Lewis base catalyst. Another role of the K on the MgO is that it poisons the acid site created by the \( \text{Mg}^{2+} \) as a result of bond destabilizing or weakening. In the absence of K on the MgO, the bond between MgO fails to destabilize, and therefore, there is no electron transfer between the catalyst and the amine. As much as the presence of the K influences the catalytic role positively, increasing the percentage beyond a specific amount will result in an increase in the non-dispersion on the MgO catalyst surface as observed under catalyst characterisation. This prevents the accessibility of the catalyst surface for the surface electron transfer reaction. Too much of the K also results in the agglomeration of the K on the catalyst surface and blockage of the pores of the catalyst. MgO is known to have a small surface area therefore even a slight block in its pores can greatly affect its performance. From the results, increasing the K percentage from 0 to 1% saw an increase in its mass transfer performance which is attributed to its bond weakening and acid sites poisoning as well as its good dispersion on the surface of the catalyst. Going
beyond 1% results in the pore blockage and reduction in its mass transfer performance eventually.

Also, as explained earlier, increasing the K percentage beyond the 1% sees a reduction in the pore volume as well as the surface area. The CO₂ therefore is unable to fully access the active sites to promote a reaction. At 10% K, a drop in BET surface area, pore volume and pore size all results in a lower mass transfer performance. This therefore points out that an eventual increase in the chemical role of K on the catalyst as it promotes electron density around the surface O²⁻ comes against a reduction in the physical properties like surface area and pore volume of the catalyst. The highest performance in terms of mass transfer is achieved with K % on the MgO as 1% from Figures 4.16-1 to 4.16-3.
Figure 4.16-1: Effect of potassium concentration (K%) over MgO on CO₂ removal efficiency and cyclic capacity at 150g absorber catalyst (K/MgO) weight

Figure 4.16-2: Effect of potassium concentration (K%) over MgO on overall mass transfer coefficient ($K_{GAV}$) of the absorption column at 150g absorber catalyst (K/MgO) weight
Figure 4.16-3: Effect of potassium concentration (K%) over MgO on Overall mass transfer coefficient ($K_{Lav}$) of the desorption column at 150g absorber catalyst (K/MgO) weight
4.17 Combined effect of HZSM-5 and γ-Al₂O₃ catalyst on mass transfer

This part of the work sorts to investigate the effect of mixing two different solid acid catalyst for the desorption of CO₂ from rich solvent and evaluate their performance. HZSM-5, a type of zeolite, and γ-Al₂O₃ an amphoteric catalyst were both experimented on by introducing different ratios of the two catalyst in the desorption column. The role of the HZSM-5 as a Bronsted acid catalyst has been explained earlier as providing a proton for the deprotonation of amine. Shi et al. (2014b) identified the deprotonation of the protonated amine as the rate determining step and most energy intensive step. The work of the HZSM-5, a protonated zeolite, is to donate its H⁺ proton first to the breakdown of carbamate and bicarbonate to release the CO₂ as explained earlier. It recovers this proton from deprotonating the protonated amine. This therefore breaks the energy chain to release the CO₂ and lowers the energy level for the release of CO₂. The γ-Al₂O₃, an amphoteric catalyst can either behave as a Lewis acid where it attacks the carbamate directly to release CO₂ or assume the role of Bronsted acid catalyst where it can accept protons from the protonated amine and donate it to either the water molecule forming H₃O⁺. The H₃O⁺ reacts directly with the carbamate and the bicarbonate to release the CO₂. The bicarbonate also has a similar role in accepting protons from the protonated amine due to its high basicity and donating it to the H₂O molecule to form H₃O⁺. The bicarbonate however can utilize the accepted proton for itself and react to release the CO₂ directly. The role of the alumina depends on the solvents loading. In the rich loading region (desorption condition) the acidic role of the alumina is seen where the catalyst attacks the carbamate molecule directly. The Al ion attaches to the third O of the carbamate in an electron sharing. The O ion donates the shared electron between it and the catalyst. This makes the carbamate
unstable and with the supply of heat, drives the breaking down of the carbamate to release CO$_2$ and free amine.

In the lean solvent region, the catalyst acts as both basic and acid in accepting the protons from the protonated amine and donating to the H$_3$O$^+$ as explain earlier. This is similar to the role of HCO$_3^-$ during the desorption reaction. Generally, there is a drop in the performance with the introduction of the alumina in the catalyst blend ratio. This is due to the lower performance of the alumina during the desorption process (rich region). The Lewis acid role of the alumina is prevalent at this point as against the Bronsted acid activity of the HZSM-5. Shi et al. (2014a) identified the deprotonation as the rate determining step requiring the Bronsted activity of the HZSM-5. There are two main factors affected by the hybrid mixing of the HZSM-5 and γ-Al$_2$O$_3$ according Liang et al. (2015). These are: (1) Bronsted/Lewis ratio which determines which mechanism is predominant, and (2) the mesoporous surface area of the combined catalyst, which determines the fraction of the acid sites that is available for reaction. In this work, Liang et al. (2015) related the product of the mesoporous surface area (MSA) and Bronsted to Lewis sites (B/L) to the CO$_2$ desorption rate in MEA solvent.

Results showed an increase in desorption rate with increase in value of the product which was inferred that the more Bronsted acid sites relative to Lewis acid sites that are exposed to the catalyst surface for the reaction, the better the performance of the catalyst for solvent regeneration. The introduction of the alumina according to Liang et, (2015) lowers the combined Bronsted/Lewis acid activity as explained earlier. However, the overall mesoporous surface area increases as a part of the HZSM-5 is replaced by the γ-Al$_2$O$_3$ (γ-Al$_2$O$_3$ having the higher mesoporous surface area). Increasing the γ-Al$_2$O$_3$
percentage in the hybrid catalyst from 25% to 75% shows an increase in performance. This is due to the increase in the mesoporous surface area but not so significant reduction in the B/L catalytic activity resulting in a higher value of their product. Also, the HZSM-5 in the hybrid catalyst combined with the temperature effect is able to lower the solvent loading to the lean loading region. Within the lean loading region, the effect of the γ-Al₂O₃ is strongest where it tries to further reduce the loading by acting as a Bronsted acid catalyst just like HZSM-5. This is confirmed by 100% γ-Al₂O₃ where the effect of the HZSM-5 is absent. This leaves the alumina in its rich solvent region resulting in a Lewis activity. Generally, the performance of the hybrid catalyst performed worse than pure H-ZSM-5 and can attributed to its lower (B/L)*(MSA).
Figure 4.17-1: Combined effect of HZSM-5 and γ-Al₂O₃ catalyst on CO₂ removal efficiency at 150g catalyst (K/MgO) weight and 150g of mixed desorption catalyst weight.

Figure 4.17-2: Combined effect of HZSM-5 and γ-Al₂O₃ catalyst on cyclic capacity at 150g catalyst (K/MgO) weight and 150g of mixed desorption catalyst weight.
Figure 4.17-3: Combined effect of HZSM-5 and γ-Al₂O₃ catalyst on overall mass transfer coefficient (K_{GaV}) of the absorption column at 150g catalyst (K/MgO) weight and 150g of mixed desorption catalyst weight.

Figure 4.17-4: Combined effect of HZSM-5 and γ-Al₂O₃ catalyst on overall mass transfer coefficient (K_{LaV}) of the desorption column at 150g catalyst (K/MgO) weight and 150g of mixed desorption catalyst weight.
4.18 Effect of catalyst weight and lean amine inlet loading on the gas liquid interfacial area

The effect of increasing the catalyst weight and lean amine inlet loading to the absorber on the mass transfer area between the gas and liquid film was also investigated. A correlation developed by Lee et al. (2013) for determining the mass transfer area between the gas and liquid film was employed. This interfacial area can increase by either the chemical reactivity within the liquid or by an external surface provided for by a catalyst. Therefore, the physical effect of the increased catalyst weight and varying lean amine loading on the gas liquid interfacial area was investigated.

As observed, the increase in the catalyst weight results in an increase in the interfacial area for mass transfer. This can be attributed to the resultant increase in the surface area of the catalyst as the weight increases. An increase in the catalyst weight leads to an increase in the total active sites available for reaction which results in an increase in the reaction rate between CO₂ and amine (the chemical effect of the catalyst). An increase in the catalyst weight also results in an increase in the total surface area of the catalyst, which promotes mass transfer through physical transfer (physical effect of catalyst) through an added area for mass transfer. Mass transfer proceeds by the wetting of the catalyst surface area, similar to mass transfer on random or structured packing. As explained earlier, the sum of the reactivity effect (chemical effect) and interfacial area increase (physical effect) results in the increase in mass transfer rate and a higher mass transfer coefficient. The interfacial area is indirectly proportional to the mass transfer resistance. This results in the reduction of the mass transfer resistance in each film as the interfacial area increases. Similarly, the decrease in lean amine loading to the absorber
allows for more free and active amine to react with the CO$_2$ resulting in an increased reactivity. The interfacial area can also increase either by an increase in reactivity or the provision of an added surface area by the catalyst. The lean amine loading results in an increase in the reactivity which leads to an increase in the interfacial area. The increased reactivity allows more of the CO$_2$ to cross from one phase to another leading to an increase in the mass transfer area. The increased reactivity therefore results in an increase in interfacial area leading to an increase in mass transfer performance.

The interfacial area is therefore affected by an increase in reactivity between the CO$_2$ and the BEA/AMP blend as well as an increase in the surface area provided by the catalyst. However, without an increase in reactivity for application of the catalyst, the improvement in mass transfer can be said to be solely due to the surface area provided by the catalyst. The increase in the rate of mass transfer which is a combined effect of the rate of reactivity (chemical effect of catalyst) and surface area provided by catalyst (physical effect of catalyst) was therefore computed and compared with its physical catalytic role in providing a surface area for mass transfer. A 43% increase in rate of mass transfer after the addition of 150g of K/MgO catalyst in absorber as compared to the 24% increase in interfacial area (the result of an added catalytic surface area), suggests that the interfacial area is not the sole reason for the increase in absorption efficiency; it also includes the increase in the rate of reaction. However, knowledge of the interfacial area for mass transfer helps to determine the most appropriate way to optimize the rate of catalytic mass transfer, either physically or chemically.

The results also show a general increase in the interfacial area as the lean loading of the amine to the absorber decreased which resulted in an increase in reactions rate.
Figure 4.18-1: Effect of catalyst weight and lean amine inlet loading on the gas liquid interfacial area
4.19 Determination of the film controlling mass transfer

An experiment was conducted to determine the film controlling mass transfer. 100% CO₂ was supplied into the absorption column. The 100% CO₂ eliminated any resistance in the gas film, and therefore, any resistance obtained for the blank system can be attributed to the liquid film resistance. For the blank system,

\[
\frac{1}{K_G a_v} = \frac{1}{k_G a_v} + \frac{H}{E k_L a_v} \quad (4.19 - 1)
\]

At the 100% CO₂, \( \frac{1}{k_G} \), the gas film resistance =0. Therefore,

\[
\frac{1}{K_G a_v} = \frac{H}{E k_L a_v} \quad (4.19 - 2)
\]

The \( K_G a_v \) calculated for an experimental run of 100% CO₂ was 1.399 kmol/m³.kPa.hr

Hence,

\[
\frac{H}{E k_L a_v} = \frac{1}{1.399} = 0.714 \, m^3.kPa.hr/kmol \quad (4.19 - 3)
\]

Now the \( K_G a_v \) calculated for an experimental run of 15% CO₂ under the same conditions as the 100% CO₂ was 0.120 kmol/m³.kPa.hr. The liquid resistance was taken as 0.714 \( m^3.kPa.hr/kmol \)

From equation 4.19-1

\[
\frac{1}{0.120} = \frac{1}{k_G a_v} + 0.714
\]

Calculating for \( \frac{1}{k_G a_v} \), gives 7.62 \( m^3.kPa.hr/kmol \)
This result indicates that majority of the resistance resides in the gas film as it controls the mass transfer across both films. Knowledge of this helps research to be focused on improving factors that affect the gas film mass transfer. The controlling effect of the gas film was further confirmed in the parametric sensitivity analysis of this work.
4.20 Results on the volatile organic matter emissions.

Results of qualitative GC MS analysis on the two impinger solutions (0.1 N H$_2$SO$_4$ and H$_2$O) are shown in Figures 4.20-1 for the 0.1 N H$_2$SO$_4$ and 4.20-2 for the H$_2$O. Figures 4.20-1 and 4.20-2 shows a plot of GC MS peak intensity against retention time. Results indicated the presence of essential components like ammonia, acetone and ethanol as volatile components from amine degradation. Ammonia is formed from the reaction of primary and secondary amines with half of a mole of O$_2$ gas (Lepaumier et al. 2009). This also forms formaldehyde. Acetone, a derivative of acetic acid, is formed from the conversion of acetic acid. Ethanol is believed to also be a derivative of amine degradation which releases ethanol as a by-product (Lepaumier et al. 2009). This result was in agreement with literature (Lepaumier et al. 2009) on the oxidative degradation of amines however, the influence of the catalyst on the identified emission components is not known.
Figure 4.20-1: GC MS analysis on 0.1N H₂SO₄ impinger solution

Figure 4.20-2: GC MS analysis on H₂O impinger solution
The parametric analysis of the various performance parameters varied were investigated to identify the most controlling. The first was to normalise the data set for each effect within the range of 0-1. Parametric sensitivity analysis is integral in the optimizing process plant operation because it allows the contribution of various process parameters on the plant efficiency to be determined and quantified (Nwaoha et al., 2017). Considering the fact that each parameter had different units, these parameters were normalised within the range of 0-1 as mentioned above, to have a unified scale.

\[
X_{\text{norm}} = \frac{X - X_{\text{min}}}{X_{\text{max}} - X_{\text{min}}} \quad (5.1 - 1)
\]

Where \(X_{\text{min}}\) and \(X_{\text{max}}\) corresponds to the minimum and maximum values for that independent parameter, for example, the variation of desorber bed temperature from 75°C to 95 with the 75 as minimum and 95 as maximum. \(X\) corresponds to the parameter being considered. A plot of the normalized independent process parameters (x–axis) were generated in a graph against their overall mass transfer coefficient of the absorber as the dependent process parameter (y–axis). The aim of the graph is to reveal the relationship with the dependant parameters, either linear, exponential or polynomial. In order to evaluate each terms contribution, the slope of each plot was taken. For power, exponential or polynomial plots, the slope at adjacent points was evaluated from the derivative of the plot equation. A single slope was generated by computing the log mean average of these adjacent points. Due to the number of varied parameters of this work, a single plot of all parameters would be clumsy. However, the individual parameters slopes are presented in a table as well as the log mean average slope. For example, the plot for the effect of
absorber catalyst weight has three different plots, each corresponding to a different desorption bed temperature as was varied alongside. Therefore, the overall slope for absorber catalyst weight was computed by first calculating the slope of the adjacent points of each line plot. Next, a log mean average was computed for that line as well as other lines that are under variation of absorber catalyst weight. Finally, a log mean average for the slope of each line is evaluated to obtain a single slope for absorber catalyst weight. The values corresponding to this calculation are presented in the table 5.1-1.
Table 5.1-1: tabulated results on parametric sensitivity analysis

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<td>Effect of desorber bed temperature</td>
<td>Plots</td>
<td>Plot lines</td>
<td>slope of line</td>
<td>Average Slope</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.035</td>
<td></td>
<td>0.061</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.058</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.042</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.064</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>0.075</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effect of solvent flowrate</td>
<td>Plots</td>
<td>Plot lines</td>
<td>slope of line</td>
<td>Average Slope</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.096</td>
<td></td>
<td>0.098</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.102</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.095</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.097</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effect of lean amine inlet temperature</td>
<td>Plots</td>
<td>Plot lines</td>
<td>slope of line</td>
<td>Average Slope</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.038</td>
<td></td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.027</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.027</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>150</td>
<td>0.032</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effect of solvent composition</td>
<td>Plots</td>
<td>Plot lines</td>
<td>slope of line</td>
<td>Average Slope</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.080</td>
<td></td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.093</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.071</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.060</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effect of Gas flowrate</td>
<td>Plots</td>
<td>Plot line</td>
<td>slope of line</td>
<td>Average Slope</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.20</td>
<td></td>
<td>0.20</td>
</tr>
<tr>
<td>Effect of % K on MgO</td>
<td>Plots</td>
<td>Plot line</td>
<td>slope of line</td>
<td>Average Slope</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.25</td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>Effect of Effect of desorber hybrid catalyst (HZSM-5 and gamma alumina)</td>
<td>Plots</td>
<td>Plot line</td>
<td>slope of line</td>
<td>Average Slope</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.083</td>
<td></td>
<td>0.083</td>
</tr>
</tbody>
</table>
From the table 5.1-1, the effect of the %K on MgO is obtained as the highest contributing performance parameter. This is mainly due the sudden and rapid fall in performance as the %K on MgO was increased beyond 1%. The results shown earlier sees the performance of both columns fall below that of blank or no catalyst in the absorber as the percentage increases to 5%. This means that, increasing the K% on MgO can seriously reduce the performance and therefore an optimum K% of 1% should be used. Another reason for the decrease in performance below the blank is the drop in kinetic activity as well as the physical characteristics of the catalyst (pore volume and Surface area). This leads to the catalyst not being able to provide enough surface area for kinetics mainly due to the reduction in surface area and pore volume. The structured packing shows to provide a better mass transfer surface area for no catalyst in the absorber than the 5% and 10% K promoted catalyst.

The next most controlling parameters were the gas flowrate and followed by lean amine flowrate. The gas flowrate controlling the performance of the absorption confirms the highest resistance in the gas film. The liquid flowrate rate controlling over other parameters tells us of its high resistance in terms of mass transfer but still less than that of the gas side. Also, the liquid provides more free amine for reaction and hence promotes reaction within the liquid. Reaction occurring in the liquid reduces the liquid film resistance considerably making it less than the gas resistance. Next is the effect of desorption catalyst hybrid. The hybrid catalyst saw the substitution of part of the HZSM-5 with gamma alumina. The parametric analysis shows that the substitution of HZSM-5 catalyst affected the performance as the alumina is unable to perform at par mainly due to the HZSM-5 role as a Bronsted acid catalyst and gamma alumina as a Lewis acid catalyst as explained earlier. This parameter mainly affects the kinetics as it results in the a much
leaner amine to the absorber for reaction. The solvent composition results show it to be a less controlling parameter. This is due to the fact that an increase in AMP concentration in the blend ratio improves the solvent viscosity, solvent capacity and desorption property. According to work done by Narku-Tetteh et al. (2017) AMP has a lower solvent viscosity and higher solvent capacity as compared to BEA. An increase in the AMP ratio in the blend should therefore result in a lower solvent viscosity and a higher overall solvent capacity. These effects however are unable to greatly impact the performance as mass transfer of CO$_2$ from gas to liquid sees a slight improvement. The slight increase in performance can be attributed to lowering of the solvent viscosity. The effect of the desorption bed temperature and absorber catalyst weight are both low as they affect the kinetics of CO$_2$ reaction with solvent. Therefore, the optimisation of the capture process should be as follows:

1. Parameters that affect CO$_2$ mass transfer into the liquid, gas film resistance (gas flowrate) and gas -liquid interface (catalyst surface area).
2. Parameters that affect liquid film resistance and mass transfer area (Liquid flowrate)
3. Parameters that affect reactivity within the liquid by increasing the amount of free amines (desorption catalyst type and bed temperature)
4. Parameters that affect reactivity within the amine by increasing the rate of reaction (absorber catalyst weight and the lean amine inlet temperature).

Considering the steps above, mass transfer of CO$_2$ (steps 1 and 2) controls the absorption performance above amount of reactant (step 3) followed by rate of reaction (step 4). Result from Figure 5.1-1 showed a plot of the effect of various performance
parameters on $K_{Gav}$. The condition used was to keep only the performance parameter varying and normalised with whiles selecting the optimum value for the other performance parameters. This didn’t change the trend of the above results shown in table 5.1-1. The slopes of the individual lines are shown on the plot.
Figure 5.1-1: Parametric sensitivity plot for varying performance parameters
5.2 Techno economic analysis on the catalyst aided Capture process

A simple economic analysis was performed for the catalyst process to access the cost reduction or increase with varying the process parameters. The cost was computed in terms of the CAD per kg of CO₂ produced for a specific configuration. The first was the cost of energy required for that specific process integration which was expressed as kJ per CO₂ produced. An assumption was made such that, the energy provided for regeneration was sourced from a low-pressure steam turbine. This therefore allowed for the costing of the regeneration energy in terms of how much energy from low pressure steam required to produce that need regeneration energy. The cost of steam in terms of the kJ of regeneration energy needed was adapted from Turton et al. (2012) as $16.8/GJ of steam. Secondly, the cost of solvent, carbon tax of CO₂ emitted, cost of structured parking, cost of HZSM-5 and cost of K/MgO required was computed and expressed as Canadian dollars per kg of CO₂ produced. The solvent cost was gotten from the sigma Aldrich, as technical grade and expressed as CAD per gram. The carbon tax used was obtained from the Canadian carbon tax which was given as $50/ton of CO₂ emitted at 2022 (Government of Canada, 2018). The HZSM-5 cost used was obtained from Zibo Yinghe Chemical Co. The K/MgO catalyst cost was calculated on the amount of precursor required for a catalyst weight. The Cost of the structured packing was obtained from Sulzer Chemtech Canada Inc. for Sulzer LDX.
Table 5.2-1: Unit cost (CAD $) of operation for the Capture process

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>CAD $</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEA</td>
<td>1 Litre</td>
<td>57</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>AMP</td>
<td>1 Litre</td>
<td>68.15</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>MEA</td>
<td>1 Litre</td>
<td>48.325</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>MDEA</td>
<td>1 Litre</td>
<td>47.54</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>K/MgO</td>
<td>gram</td>
<td>0.181</td>
<td>Sigma Aldrich (Precursors)</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>gram</td>
<td>0.13</td>
<td>Zibo Yinghe Chemical Co.</td>
</tr>
<tr>
<td>Carbon tax</td>
<td>kg of CO$_2$ emitted</td>
<td>0.05</td>
<td>Government of Canada, 2018</td>
</tr>
<tr>
<td>Structured packing</td>
<td>1 piece</td>
<td>375</td>
<td>Sulzer Chemtech Canada Inc.</td>
</tr>
<tr>
<td>Regeneration energy</td>
<td>GJ of low pressure steam</td>
<td>16.8</td>
<td>Turton et al. (2012)</td>
</tr>
</tbody>
</table>
| Catalyst regeneration energy | 1 kWh              | 0.14  | Saskpower (2018) Available from [https://www.saskpower.com/accounts-and-services/billing/power-rates/power-supply-rates]
Figure 5.2-1: Total cost (CAD $) per kg CO₂ captured for the different solvent systems

Figure 5.2-2: Total cost (CAD $) for the different performance parameters
From Figure 5.2-1, result shows the total cost for the effect of the different solvent systems as well as HZSM-5 on the operating cost for the carbon capture. Here, the total cost required for switching from MEA to MEA/MDEA then to the novel solvent of BEA/AMP was evaluated. The total cost comprised of amine cost, the carbon tax, cost of structured packing, cost of HZSM-5 and cost of K/MgO. An assumption of 12 months before 10% of the solvent is replaced and 6 months before the catalyst is replaced was made as the worst-case scenario. The results showed a low total cost per kg of CO₂ captured for the BEA/AMP solvent as against the MEA and MEA/MDEA biblend solvents. This is attributed to the high capture efficiency of the 2M BEA-2M AMP solvent in comparison with the other solvent even though the cost per litre of the BEA and AMP has shown to be higher than that of MEA and MDEA (table 5.2-1). The initial cost of the solvent is therefore offset by the increase in the CO₂ captured. Generally, the introduction of HZSM-5 introduces an extra cost as against an improved desorption efficiency. For all solvents, a decrease in the total cost per kg of CO₂ produced was observed with the introduction of the HZSM-5 catalyst. This implied that the added cost of the HZSM-5 catalyst was offset by the increase in amount of the CO₂ captured. The catalytic process still demonstrates the BEA/AMP solvent as the most economical over the other solvents.

Figure 5.2-2 shows the plot for total cost involved after varying the performance parameters for the BEA/AMP solvent. The results from the total cost per kg of CO₂ captured showed the lowest with the introduction of the absorber catalyst as against increasing the solvent flowrate, gas flowrate, increasing the desorber bed temperature or reducing the inlet temperature to the absorber. This can also be attributed first to the reduction in total cost as the catalyst replaces a number of the structured packing. In comparison, the cost of a structured packing was more as compared to the K/MgO catalyst.
occupying the same volume in the column. This therefore points the cost reduction with
the introduction of catalyst in place of the structured packing. Secondly, the introduction
of the K/MgO catalyst results in a high production of CO$_2$ when compared with the other
performance parameters. Both a reduction in the total cost for capture and an increase in
the amount of CO$_2$ captured is desired for a reduced total cost per kg of CO$_2$ captured. The
total cost for increasing the desorber temperature to 95°C shows a lower total cost per kg
of CO$_2$ captured. This can be attributed to the high production of CO$_2$ against a high energy
input. The increase of gas flowrate is however limited by the hydrodynamics of the
column. Increasing the gas flowrate can result in liquid hold up or even liquid flooding the
column. The highest total cost was achieved when the inlet temperature to the absorber
was reduced to 20°C as well as increasing the solvent flowrate to 70ml per minute. For the
reduced amine inlet temperature, the lean amine solution leaving the desorption column
requires further cooling to a temperature suitable for absorption. This is an energy
requiring process. In this work, we looked at lowering the temperature from 57°C to three
different temperature s, 40°C, 30°C and 20°C. Results showed the low capture efficiency
when the amine inlet temperature to the absorber was high and the high capture efficiency
of CO$_2$ when the amine inlet temperature to the absorber was lowest as observed from
Figure 5.2-2. However, less energy is required when lowering the solvent temperature
from 56°C to 40°C and highest when reducing the temperature from 56°C to 20°C. This
meant that the increase in CO$_2$ captured wasn’t able to offset the increase in total cost for
reducing the absorber amine inlet temperature to 20°C. This is attributed to the high energy
required to further cool the solvent prior to entering the desorption column as against the
high capture efficiency for the 20°C amine inlet temperature to the absorber. This means
lowering the temperature is less economical in reducing the total cost/ kg of CO$_2$ captured.
Increasing the solvent flowrate showed a significant increase in the total cost as results on the CO₂ capture showed no significant improvement when the solvent flowrate was increased against the increased total cost of the added solvent amount. This therefore resulted in the high total cost per kg of CO₂ captured. In addition, an increase in solvent flowrate has the potential of causing column flooding within the columns just like the increase in gas flowrate which affects the hydrodynamics of the column.
CHAPTER 6: K/MgO CATALYST STABILITY STUDIES

The catalyst stability studies were performed using XRD plots of 1%K/MgO before the pilot plant experiment and after the experiment. The XRD was performed to identify the species of the catalyst which were represented at the various peaks. Figure 6.1-1 shows the different peaks for fresh 1%K/MgO as against spent 1%K/MgO. From the results, it was observed that the majority peak for the fresh catalyst corresponded to MgO whiles that of the spent catalyst corresponded to Mg(OH)$_2$. This meant during the reaction, most the MgO was rehydrated to Mg(OH)$_2$ due to the presence of the water in the solvent and gas feed respectively. The water in effect doesn’t deactivate the catalyst as the activity of the catalyst is found on the lattice surface O$^2-$ produced and promoted by the presence of the promoter. The only effect of the water is proposed to be the reduction of the active site for CO$_2$ and amine reaction.
Figure 6.1-1: XRD plot for freshly prepared (K/MgO) catalyst

Figure 6.1-2: XRD plot for used 1% K/MgO catalyst
CHAPTER 7: STATISTICAL ANALYSIS

7.1 Catalytic Statistical Analysis

The property of the catalyst as all other process parameters are kept constant is also evaluated to give the direct contribution of the catalyst to the mass transfer performance of process. Within the absorption column, the variation in $K\%$ introduces several properties of the catalyst. Minitab 17 was used to analyse and develop a multiple regression correlation for the $K_{Gav}$ of the absorber.
Table 7.1-1: predicting $K_{GaV}$ from BET surface area, pore volume and pore size

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area, m²/g</th>
<th>BET Pore Volume, cm³/g</th>
<th>BET Pore Size, nm</th>
<th>$K_{GaV}$ Kmol/m³.kPa.hr</th>
<th>predicted $K_{GaV}$ Kmol/m³.kPa.hr</th>
<th>AAD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>43.49</td>
<td>0.22</td>
<td>19.78</td>
<td>0.083</td>
<td>0.094</td>
<td>13.49%</td>
</tr>
<tr>
<td>0.5% K/MgO</td>
<td>59.50</td>
<td>0.31</td>
<td>21.08</td>
<td>0.094</td>
<td>0.12</td>
<td>33.27%</td>
</tr>
<tr>
<td>1% K/MgO</td>
<td>63.33</td>
<td>0.27</td>
<td>17.08</td>
<td>0.17</td>
<td>0.12</td>
<td>28.67%</td>
</tr>
<tr>
<td>3% K/MgO</td>
<td>69.75</td>
<td>0.13</td>
<td>7.40</td>
<td>0.082</td>
<td>0.095</td>
<td>15.34%</td>
</tr>
<tr>
<td>5% K/MgO</td>
<td>10.00</td>
<td>0.042</td>
<td>16.95</td>
<td>0.057</td>
<td>0.046</td>
<td>19.28%</td>
</tr>
<tr>
<td>10% K/MgO</td>
<td>4.194.19</td>
<td>0.012</td>
<td>11.41</td>
<td>0.053</td>
<td>0.059</td>
<td>10.64%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average AAD</td>
<td>20.11%</td>
</tr>
</tbody>
</table>
The linear correlation fitted to the data is

\[ K_{GaV} = k + a \times (\text{BET Surface Area}) + b \times (\text{Pore Volume}) + c \times (\text{Pore Size}). \]

After multiple regression on both Excel and Minitab gives the correlation.

\[ K_{GaV} = 0.105 - 0.00052 \times (\text{BET Surface Area}) + 0.45 \times (\text{Pore Volume}) - 0.0043 \times (\text{Pore Size}). \]

The ability of the model in predicting the experimental value was also investigated. This was done by comparing the predicted \( K_{GaV} \) from the above correlation with experimental. From the regression analysis, the statistical errors associated with each parameter lies within the range of 0.4-0.7 for prob t. The prob t indicates the significance of the estimated parameter. The high values obtained indicates that the variables attached to these estimates are either irrelevant in predicting the \( K_{GaV} \) or the selected linear correlation for that particular term is invalid. The high error values indicate the inability of the physical properties of the catalyst (surface area and pore volume) in predicting the \( K_{GaV} \). This means the chemical property of the K/MgO catalyst is more prevalent over its physical properties like surface area and pore volume. As well, more rigorous models can be developed for the BET surface area as well as the pore volume to predict the mass transfer coefficient in terms of the physical parameters. From table 7.1-1, the AAD for the predicted \( K_{GaV} \) correlation in terms of the catalyst physical property was 20.11% with a 57.15%. 
7.2 Empirical predictive correlation for $K_{GaV}$ and $K_{LaV}$ of blended BEA-AMP

The absorption column requires $k_{GaV}$ and $k_{LaV}$ to effectively design the both absorption and desorption columns. (Liang et al., 2011). The only way to obtain the overall mass transfer coefficient is experimentally making it time consuming and expensive for a packed column. Dey and Aroonwilas (2009) proposed a predictive correlation for blended AMP-MEA. The model was tested with the experimental mass transfer data of blended AMP-MEA in a laboratory scale absorption column packed with DX structural packing. Results showed good agreement between the predictive and experimental mass transfer coefficients. The Minitab 18 software was used to analyse the data. The developed predictive correlation shows the dependence of parameters on the mass transfer coefficient.

\[
K_{GaV} = 70.767 + ((-96.28 \times (\text{Lean Amine Loading}^2))) + ((0.00035 \times (\text{Lean Amine inlet temp}^2))) + ((-0.000015 \times (\text{K/MgO Catalyst weight}^2))) + ((0.012 \times (\text{Des bed temperature}^2))) + (0.00039 \times (\text{k% on MgO}^2)) + ((0.0000085 \times (\text{HZSM - 5/ alumina comp}^2))) + ((0.0016 \times (\text{BEA/AMP}))) + ((66.06 \times (\text{Lean Amine Loading}))) + (\text{Liquid flowrate} \times (0.0067)) + ((-0.024 \times (\text{Lean Amine inlet temp}))) + (\text{gas flowrate} \times (0.020)) + ((0.00054 \times (\text{K/MgO Catalyst weight}))) + ((-2.01 \times (\text{Des bed temperature}))) + ((0.000073 \times (\text{des catalyst weight}))) + ((-0.011 \times (\text{k% on MgO}))) + ((-0.00020 \times (\text{HZSM5/ alumina comp})))
\]

(7.2-1)
\[ K_L a_v = -0.476 - 0.0661 \times \textit{solvent blend ratio} - 3.081 \times \]

\[ \textit{Lean Amine Loading} + 0.021 \times \textit{Liquid flowrate} - 0.0083 \times \]

\[ \textit{temperature inlet} + 0.0095 \times \textit{gas flowrate} + 0.00093 \times k/ \]

\[ \textit{MgO Catalyst weight} + 0.011 \times \textit{Des bed temperature} + 0.000621 \times \]

\[ \textit{des catalyst weight} - 0.05278 \times k\% \text{ on MgO} + 0.003253 \times HZSM - 5/ \]

\[ \textit{alumina comp} \quad (7.2-2) \]

A parity plot of the above equation is shown below with a degree of correlation of 92.13\% and an AAD of 8.2\% for \( k_{Gav} \). A 90\% degree of correlation and an AAD of 7\% for \( k_{Lav} \). Th high deviation value of \( k_{Gav} \) suggest that a linear correlation is not best in representing the correlation for the various performance parameters. This is not the case for \( k_{Lav} \) which shows a good linear correlation with the performance parameters.
Figure 7.2-1: Parity plot for predicted $K_{GaV}$ against experimental $K_{GaV}$

Figure 7.2-2: Parity plot for predicted $K_{LaV}$ against experimental $K_{LaV}$
CHAPTER 8: THE PHYSICAL PROPERTIES OF THE DIFFERENT BLEND RATIOs OF BEA: AMP

8.1 Unloaded solvents

Generally, we observed a decrease in the viscosity when temperature increased. For the different solvent systems, an increase in the concentration of BEA resulted in a higher viscous solution which is attributed to the high viscosity of BEA in comparison with AMP. For density, AMP has a higher density (0.91g/cm$^3$) as compared to BEA (0.891g/cm$^3$) which results in a higher solvent density as the AMP concentration increases.
Figure 8.1-1: Solvent viscosities for the different solvent blend ratios at different solvent temperatures.

Figure 8.1-2: Solvent densities for the different solvent blend ratios at different solvent temperatures.
8.2 Loaded Solvents

For the loaded samples, the introduction of CO$_2$ causes both the dynamic viscosity and density to increase. This is attributed to the gas liquid interaction. When a mole of CO$_2$ enters the liquid, it interacts with the liquid in a way that prevents other CO$_2$ gas molecules from entering solution.
Figure 8.2-1: 1.5M BEA/2.5M AMP Solvent densities for the different amine CO₂ loadings at different solvent temperatures.

Figure 8.2-2: 1.5M BEA/2.5M AMP Solvent viscosity for the different amine CO₂ loadings at different solvent temperatures
Figure 8.2-3: 2.0M BEA/2.0M AMP Solvent densities for the different amine CO\textsubscript{2} loadings at different solvent temperatures.

Figure 8.2-4: 2.0M BEA/2.0M AMP Solvent viscosities for the different amine CO\textsubscript{2} loadings at different solvent temperatures.
Figure 8.2-5: 2.5M BEA/1.5M AMP Solvent densities for the different amine CO$_2$ loadings at different solvent temperatures

Figure 8.2-5: 2.5M BEA/1.5M AMP Solvent viscosities for the different amine CO$_2$ loadings at different solvent temperatures
Figure 8.2-5: 3.0M BEA/1.0M AMP Solvent densities for the different amine CO₂ loadings at different solvent temperatures

Figure 8.2-5: 3.0M BEA/1.0M AMP Solvent viscosities for the different amine CO₂ loadings at different solvent temperatures
CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

This work has demonstrated in a great measure the effect of solvent and catalyst on mass transfer performance. The increase in the mass transfer coefficient is greatly seen with the introduction of catalyst. This study looked at both the solvent improvement as well as process improvement of the capture process.

Under the solvent improvement, 2M BEA-2M AMP blend showed significant increase in CO$_2$ removal efficiency as well as for both $K_{GAV}$ and $K_{LAV}$. A 78% increase in $K_{GAV}$ of the absorber results in the reduction in the height of the column significantly. The $K_{LAV}$ of the desorber also saw a significant increase with introduction of the novel solvent as against 5M MEA and 7M MEA/MDEA blend. This served as a basis among other results like heat duty and kinetic rate for the selection of novel solvent for our study.

For Process improvement, a build up of previous studies (Shi et al., 2014; Osei et al., 2016) saw the introduction of HZSM-5 into the desorption column. This proved significant in increasing the CO$_2$ removal efficiency and mass transfer rate with the catalyst from the desorption column. The addition of HZSM-5 provided an alternate pathway with a lower activation energy for a substantial amount of desorption to occur. This was evident in the high desorption rate as well as low lean amine loading. A 78% increase in $K_{LAV}$ of the desorber resulted in the reduction in the height of the column significantly. The indirect effect of the increased desorption rate results on different lean amine loading on $K_{GAV}$ of the absorber also saw a 39% increase against a 26% increase in kinetic rate and an 18% decrease in heat duty.
Further process improvement saw the introduction of an absorber catalyst to help increase the capture efficiency within the BEA/AMP solvent. The influence of K/MgO on the rate of CO₂ absorption into amines was found to be superior over other solid base catalysts tested. The overall mass transfer coefficient increase of 39% with the HZSM-5 and 95% with both HZSM-5 and K/MgO catalyst was observed for $K_{GA}$ of the absorber with the 4M BEA-AMP biblend. The overall mass transfer coefficient increases of 22% with the HZSM-5 and 45% with both HZSM-5 and K/MgO catalyst is observed for $K_{LV}$ of the desorber.

The extensive study of the effects of K/MgO catalyst weight, Amine concentration in the blend, amine loading, solvent flowrate, gas flowrate and desorption bed temperature all showed a significant increase in both $K_{GA}$ and $K_{LV}$ as these parameters are increased. However, the effect of gas flowrate, solvent flowrate and absorber catalyst weight showed higher effects from a parametric sensitivity analysis. Results on the effect of amine inlet temperature to the absorber showed a reduction in performance as the temperature of the amine to the absorber increased. The interfacial area increased with the catalyst was seen to be lower than the overall increase in mass transfer performance. This confirmed that the catalyst does not only increase the interfacial area, its physical effect, but also an increase in the reactivity. A correlation was developed in predicting the mass transfer coefficients with an AAD of below 10%.

Finally, an economic analysis based on the power requirement or energy penalty for the various process improvements established the use of K/MgO catalyst as the least energy penalty over an increase in solvent flowrate, gas flowrate, desorption bed temperature and a decrease in amine inlet temperature for the absorber. Overall, employing
the use of catalyst shows a tremendous increase in the mass transfer performance which greatly reduces the height and eventually the unit cost of manufacturing the absorption and desorption columns as well. Employing the absorber catalyst had shown a significant and cost-effective capture technology improvement over increase in either gas flowrate, liquid flowrate or desorption bed temperature.

### 9.2 Recommendations

1. First this study has shown that the performance of the catalyst doesn’t only depend on the basic strength but also on the catalyst surface area. Therefore, it becomes important for further screening studies in improving or selecting a catalyst that has both high surface area as well as high basic strength.

2. Under solvent improvement, it would be essential to run solvent degradation studies on the selected solvent as well as potential solvents. The effect these process parameters on the influence of solvent degradation for the novel solvents needs to be established. The effect of these catalyst on the solvent degradation should be investigated.

3. An extensive parametric effect on the quantitative emissions of volatile organic matter as products of amine degradation should be studied as a build up of the work done in this study which identified essential products from the emission of volatile organic matter.

4. For process improvement, the catalyst deactivation studies should be performed in-situ to determine to time on stream of the catalyst.
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### APPENDIX A

Table A.1-1: Detailed experimental condition

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent used</td>
<td>2M BEA-2M AMP</td>
</tr>
<tr>
<td>Solvent flowrate, m³/m²h</td>
<td>1.83 1.53-2.14 1.83 1.83 1.83 1.83 1.83 1.83</td>
</tr>
<tr>
<td>Feed Gas flowrate kmol/m²h</td>
<td>19.3 19.3 19.3 19.3 12.6-25.5 19.3 12.6-25.5</td>
</tr>
<tr>
<td>CO₂ in the feed gas, %</td>
<td>15 15 15 15 15 15 15 15</td>
</tr>
<tr>
<td></td>
<td>75, 85, 95</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Desorber bed temperature, °C</td>
<td></td>
</tr>
<tr>
<td>Desorber catalyst</td>
<td>HZSM-5</td>
</tr>
<tr>
<td>Desorber catalyst weight, g</td>
<td>150g</td>
</tr>
<tr>
<td>Absorber catalyst</td>
<td>1% K/MgO</td>
</tr>
<tr>
<td>Absorber catalyst weight, g</td>
<td>0, 50, 100, 150, 170</td>
</tr>
<tr>
<td>Amine inlet temperature into absorber, °C</td>
<td>30</td>
</tr>
</tbody>
</table>
Figure A.1-1: Picture of pilot plant setup
A.2: Detailed experimental condition

A.2.1: Semi Batch Experimental setup

Table A.2-1: The operating conditions of the semi-batch experiments

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow rate</td>
<td>650 mLpm</td>
</tr>
<tr>
<td>Liquid volume</td>
<td>500 mL</td>
</tr>
<tr>
<td>Absorption temperature</td>
<td>45°C</td>
</tr>
<tr>
<td>CO₂ in the feed gas</td>
<td>15%</td>
</tr>
<tr>
<td>Catalyst weight</td>
<td>50 g</td>
</tr>
<tr>
<td>Catalyst investigated</td>
<td>K/MgO, Cs₂O/α-Al₂O₃, Ca(OH)₂, BaCO₃, Cs₂O/γ-Al₂O₃, Hydrotalcite, CaCO₃</td>
</tr>
</tbody>
</table>
A.2.2: Pilot plant experimental Condition

Table A.2-2: The operating conditions used in the pilot plant studies on comprehensive mass transfer

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent used</td>
<td>2M BEA-2M AMP, 5M MEA, 7M MEA/MDEA</td>
</tr>
<tr>
<td>Solvent flowrate</td>
<td>50, 60, 70 ml/min</td>
</tr>
<tr>
<td>Feed Gas flow rate</td>
<td>10, 15, 20 SLPM</td>
</tr>
<tr>
<td>CO$_2$ in the feed gas</td>
<td>15%, 100%</td>
</tr>
<tr>
<td>Desorber bed temperature</td>
<td>75, 85, 95$^\circ$C</td>
</tr>
<tr>
<td>Desorber Catalyst</td>
<td>HZSM-5 (Si/Al =19), $\gamma$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>Desorber Catalyst weight</td>
<td>150g</td>
</tr>
<tr>
<td>Absorber catalyst</td>
<td>K/MgO</td>
</tr>
<tr>
<td>Absorber catalyst weight</td>
<td>0, 50, 100, 150, 170g</td>
</tr>
<tr>
<td>Amine inlet temperature into absorber</td>
<td>20, 30, 40$^\circ$C</td>
</tr>
</tbody>
</table>
A.3: Feed gas and Amine solvent preparation and verification.

The feed gas mixture containing 15(by vol) % CO$_2$ gas was prepared by combining 100% CO$_2$ and 100% N$_2$ gas to obtain a specific total flowrate. The gas mixture obtained is validated with an IR CO$_2$ Analyser (purchased from Nova Analytical Systems Inc. with a ±2% error). A solvent of the desired concentration was prepared using a solution preparation method by mass. A 2-litre solution of desired concentration is prepared by measuring a calculated mass of stock solution and mixing with de-ionized water to the mark of a 2L flat bottom flask. The concentration of the solvent was validated by titrating with 1N hydrochloric acid solution using methyl orange indicator.

The IR Analyzer was calibrated with the premixed 15% CO$_2$ in N$_2$ purchased from Praxair Inc and zeroed with 100%N$_2$. The thermocouples along the column where calibrated with a trusted laboratory thermometer whilst the liquid flow meters were regularly calibrated by measuring a known volume of fluid against time.

A.4: Sample preparation of 15SLPM of feed gas containing 15(vol)% CO$_2$ (N$_2$ balance)

15% CO$_2$ gas in 15SLPM will contain 0.15(15) = 2.75 SLPM. N$_2$ =0.85(15) = 12.75 SLPM. Therefore, 12.75SLPM of N$_2$ gas is supplied initially to aid in flushing out any gas within the column after which the 2.75SLPM CO$_2$ gas is added to makeup the 15SLPM.
A.5: Sample preparation of 4M biphase solvent of BEA: AMP (2M:2M)

Calculation

Total solution volume $V_{total} = 2$ litres

For 2M BEA, the amount of BEA required in terms of mass, $m_{BEA}$ is given by

$$m_{BEA} = C_{BEA} \times V_{total} \times M_{wt, BEA}$$

(A.5-1)

The $M_{wt, BEA}$ of BEA is 117.19 g/mol and AMP is 87.14 g/mol

$$m_{BEA} = 2 \times 2 \times 117.19 = 468.76g$$

(A.5-2)

For 2M AMP, the amount of AMP required in terms of mass, $m_{AMP}$ is given by

$$m_{AMP} = C_{AMP} \times V_{total} \times M_{wt, AMP}$$

(A.5-3)

$$m_{BEA} = 2 \times 2 \times 89.14 = 356.56g$$

(A.5-4)

Therefore, 468.76g of BEA and 356.56g of AMP solution are mixed and poured into a 2L flask. Distilled water is then added to the total solution until the total volume in the flask reaches the marked 2L point.
A.6: Sampling and data collection

As stated earlier, the end of the experiment was marked by the constant temperature along the absorber and desorption column. The temperature profiles were observed using J type thermocouples connected along the columns. The thermocouples were then connected to LabVIEW, a computer software. The user interface of this LabView software is shown in Figure A.6-1. As well, plots of the absorption and desorption profiles were constantly monitored with the end of the experiment marked by a constant temperature having a straight horizontal line against time. The software records the temperature and pressure drop along the column in a form of excel data sheet. The CO₂ concentrations at the along the absorber column height were measured with the IR gas analyzer. The sample CO₂ containing gas is flowed through a gas valve along the absorber unit into the IR gas analyser where it is measured.

The solvent loading and concentration were determined by first taking 10ml of both the lean and rich amine samples and titrated against 1N HCL using a Chittick apparatus. For accuracy, the liquid loading titration was conducted at least two times. A mass balance error calculation that compares the amount of CO₂ removed from the gas phase, as measured by the IR gas analyzer, with the amount of CO₂ added into the liquid phase from the Chittick apparatus and expressed as a percentage was used as a verification of the validity of the run.
Figure A.6-1: Screenshot of LABVIEW software interface for data collection from CO2 capture plan
Table A.6-1: Sample of Collected Data of Catalytic run

<table>
<thead>
<tr>
<th></th>
<th>Inlet (FT-200)</th>
<th>Outlet (FT-900)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Flow rate Reading:</td>
<td>15.1</td>
<td>14.4</td>
</tr>
<tr>
<td>Meter Temperature:</td>
<td>23.6</td>
<td>24.1</td>
</tr>
<tr>
<td>Meter Pressure:</td>
<td>17.4</td>
<td>14.6</td>
</tr>
<tr>
<td>CO₂ Composition:</td>
<td>15.1</td>
<td>10.4</td>
</tr>
<tr>
<td>N₂ Composition:</td>
<td>84.10</td>
<td>89.6</td>
</tr>
</tbody>
</table>

**Titration**

<table>
<thead>
<tr>
<th></th>
<th><strong>Lean</strong></th>
<th><strong>Rich</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>HCL Concentration</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>HCL volume used at endpoint</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Extra HCl volume added</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>CO₂ Volume</td>
<td>42</td>
<td>53</td>
</tr>
<tr>
<td>BEA/AMP Concentration</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>molCO₂</td>
<td>0.001488</td>
<td>0.002218</td>
</tr>
<tr>
<td>CO₂ loading</td>
<td>0.37</td>
<td>0.55</td>
</tr>
</tbody>
</table>
Table A.6-2: Sample temperature and concentration data of absorption and desorption column

<table>
<thead>
<tr>
<th>Height</th>
<th>Absorber</th>
<th>Stripper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>temp</td>
<td>CO2 %</td>
</tr>
<tr>
<td>Gas outlet</td>
<td>35.89</td>
<td>5.60</td>
</tr>
<tr>
<td>42 (liquid inlet)</td>
<td>27.13</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>39.51</td>
<td>6.5</td>
</tr>
<tr>
<td>30</td>
<td>51.56</td>
<td>8.2</td>
</tr>
<tr>
<td>24</td>
<td>58.51</td>
<td>10.5</td>
</tr>
<tr>
<td>18</td>
<td>56.97</td>
<td>11.8</td>
</tr>
<tr>
<td>12</td>
<td>54.22</td>
<td>12.8</td>
</tr>
<tr>
<td>6</td>
<td>50.65</td>
<td>13.4</td>
</tr>
<tr>
<td>0</td>
<td>20.32</td>
<td>15.00</td>
</tr>
</tbody>
</table>

A.7: Sample CO₂ loading calculation

Mol CO₂, \( n_{CO₂} = \frac{V_{CO₂} \times P_{CO₂}}{M_{wCO₂}} \)  \hspace{1cm} (A.7-1)

\[
n_{CO₂} = \frac{42ml \times 1.842g/l \times 10^{-3}}{44.02g/mol} = 0.001488 \text{ mols}
\]
Mol Amine, \( n_{\text{amine}} = V_{\text{soln}} \times C_{\text{Amine}} \)  \hspace{1cm} (A.7-2)

\( V_{\text{soln}} \) corresponds to the volume of solution taken for titration, which is 1ml

\[
n_{\text{amine}} = 0.001 l \times \frac{4\text{mol}}{l} = 0.004 \text{ mol}
\]

Therefore, the loading of CO\(_2\) is given by

\[
\alpha_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{amine}}} = \frac{0.001488}{0.004} = 0.372 \text{ mol CO}_2/\text{mol amine}
\]
A.8: Henrys law constant calculation

Table A.8-1: Sample Data collected for the Henrys law constant of CO₂ in Amine experiment

<table>
<thead>
<tr>
<th></th>
<th>psi</th>
<th>pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>equilibrium Pressure of N₂O, P₁</td>
<td>8.2</td>
<td>56537.4</td>
</tr>
<tr>
<td>Initial Pressure of N₂O, P₂</td>
<td>15</td>
<td>103422</td>
</tr>
<tr>
<td>Vacuum pressure, Pᵥ</td>
<td>-2</td>
<td>-13789.6</td>
</tr>
</tbody>
</table>

Table A.8-2: Sample calculation data collected for the Henrys law constant

<table>
<thead>
<tr>
<th>Vg</th>
<th>0.0003m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>8.314 j/mol.k</td>
</tr>
<tr>
<td>T</td>
<td>303.15 K</td>
</tr>
<tr>
<td>VL</td>
<td>0.0003 m³</td>
</tr>
</tbody>
</table>
A.8.1: Sample calculation for the Henrys law constant of CO$_2$ in Amine experiment

First, the N$_2$O moles at the start of the experiment is calculated

$$n_{N_2O^1} = (P_2 - P_v) \frac{V_g}{Z_{N_2O}RT}$$

$$n_{N_2O^1} = (103422 - -13789.6) \frac{0.0003}{1.0 \times 8.314 \times 303.15} = 0.0140 \text{ mols}$$

The N$_2$O moles at the end of the experiment is calculated

$$n_{N_2O^2} = (P_1 - P_v) \frac{V_g}{Z_{N_2O}RT}$$

$$n_{N_2O^2} = (56537.4 - -13789.6) \frac{0.0003}{1.0 \times 8.314 \times 303.15} = 0.0084 \text{ mols}$$

Therefore, the amount of N$_2$O absorbed into the liquid is given by

$$n_{N_2O^L} = n_{N_2O^1} - n_{N_2O^2}$$

$$n_{N_2O^L} = 0.0140 - 0.0084 = 0.0056 \text{ mol}$$

The concentration of N$_2$O in the liquid

$$C_{N_2O} = \frac{0.0056}{0.0003} = 18.67 \text{ mol/m}^3$$

Then, the N$_2$O solubility ( $He_{N_2O}$ ; kPa m$^3$/kmol) is defined as:

$$He_{N_2O-amine} = \frac{56537.4 - -13789.6}{18.67} = 3780.82 \text{ kPa.m}^3/\text{kmol}$$
\[ He_{N_2O-water} = 8.55 \times 10^6 \exp \left[ -\frac{2284}{T} \right] \]

\[ He_{N_2O-water} = 8.55 \times 10^6 \exp \left[ -\frac{2284}{303.15} \right] = 4569.77 \text{ kPa} \cdot \text{m}^3/\text{kmol} \]

\[ He_{CO_2-water} = 2.82 \times 10^6 \exp \left[ -\frac{2044}{T} \right] \]

\[ He_{CO_2-water} = 2.82 \times 10^6 \exp \left[ -\frac{2044}{303.15} \right] = 3326.62 \text{ kPa} \cdot \text{m}^3/\text{kmol} \]

\[ He_{CO_2-amine} = He_{N_2O-amine} \times \left( \frac{He_{CO_2-water}}{He_{N_2O-water}} \right) \]

\[ He_{CO_2-amine} = 3780.82 \times \left[ \frac{3326.62}{4569.77} \right] = 2752.29 \text{ kPa} \cdot \text{m}^3/\text{kmol} \]
APPENDIX B: DETAILS OF CALCULATIONS

B.1: Sample calculation of Overall Mass Transfer Coefficient

The overall mass transfer coefficient of the gas ($K_{GaV}$) and liquid side ($K_{LaV}$) are calculated from the above data collected after an experimental run. As shown in the early section, the gas side controls the absorption side and therefore ($K_{GaV}$) is used to characterise the absorption unit. Similarly, the desorption process as controlled by the liquid side mass transfer is characterised by ($K_{LaV}$).

\[
K_{GaV} = \frac{G_1}{S} \int_{y_{A,G,1}}^{y_{A,G,2}} \frac{dy_{A,G}}{(1 - y_{A,G})^2(y_{A,G} - \hat{y}_A)}
\]

$G_1$ represents the inert gas flowrate and calculated as:

\[
G_1 = \frac{\dot{V}_{feed\,gas \times (1-y_{CO_2}^1)}}{60 \, \text{s/min} \times V_m}
\]

(\text{B.1-1})

$\dot{V}_{feed\,gas}$ is the feed gas volumetric flowrate in SLPM=15 SLPM

$y_{CO_2}^1$ is CO$_2$ composition in the feed gas =0.15

$V_m$ is the molar volume of CO$_2$ at standard conditions = 24.465 l/mol

Therefore,

\[
G_1 = \frac{15 \times (1 - 0.15)}{60 \, \text{s/min} \times 24.465} = 0.00869 \, \text{mol/s}
\]

$S$ represents the cross-sectional area of both columns, given by

\[
S = \frac{3.14 \times d^2}{4} = \frac{3.14 \times 0.0501^2}{4} = 0.001963 \, \text{m}^2
\]
$P$ is the total pressure in the column = 101.325 kPa

$K_G a_v$ is calculated for any two adjacent points along the absorber column. Therefore, $Z$ will represent that specific height which is equal to 0.1556 m.

$P$ is the total pressure in the column = 101.325 kPa

$y_{A,G,1}$ represents the inlet gas concentration and $y_{A,G,2}$ the outlet gas concentration at that section. From the table A.5-2, an inlet composition of 0.15 and the adjacent composition of 0.134 are selected.

$$K_G a_v = \frac{0.00869}{0.001963} \times \frac{101.325 \times 0.156}{0.15} \times \int_{0.134}^{0.15} \frac{dy_{A,G}}{(1-y_{A,G})^2(y_{A,G} - y_A^*)}$$

$y_A^*$ is assumed to be zero based on the assumption of a fast reaction between the CO2 and the amine.

The trapezoidal rule with a step size of 0.00001 is used to evaluate the integral expression. This gives,

$$K_G a_v = \frac{0.00869}{0.001963} \times 0.1533 = 0.0429 \text{ mol/m}^3\cdot\text{kPa.s}$$

$$K_G a_v = 0.0429 \text{ mol/m}^3\cdot\text{kPa.s} = \frac{0.0429 \times 3600}{1000} \text{kmol/m}^3\cdot\text{kPa.hr}$$

$$= 0.1546 \text{kmol/m}^3\cdot\text{kPa.hr}$$

For the liquid side mass transfer
\[ K_L a_v = \frac{L_1}{S} x \int_{x_{AL1}}^{x_{AL2}} \frac{dx_{AL}}{(1 - x_{AL})^2(x_{AL} - x_A^*)} \]

$L_1$ represents the inert liquid flowrate and calculated as:

\[ L_1 = L_{FR}(1 - x_{CO_2}) \]

$L_{FR}$ represents the solvent flowrate

$x_{CO_2}$ is the mole fraction of CO$_2$ in the rich liquid =0.0552

\[ L_{FR} = \frac{\rho_{Soln} \times 60 \times V_{FR}}{M_{Wt\_soln}} \]

$\rho_{Soln}$ represents the measured liquid solution density =1.015g/ml

$V_{FR}$ represents the volumetric flowrate =60ml/min

$M_{Wt\_soln}$ represents the solvent average molecular weight =28.33g/mol

\[ L_{FR} = \frac{1.015 \times 60 \times 60}{28.33} = \frac{128.98mol}{hr} \]

\[ L_1 = 128.98(1 - 0.0552) = \frac{121.86mol}{hr} \]

\[ S = \frac{3.14 \times d^2}{4} = \frac{3.14 \times 0.0501^2}{4} = 0.001963 \text{ m}^2 \]

$\rho_m$, the molar density of the liquid is calculated as:

\[ \rho_m = \frac{\rho_{Soln}}{M_{Wt\_soln}} = \frac{1.015}{28.33} = 0.0358 \text{ mol/ml} \]
The integral expression is computed by two ways. First by the trapezoidal rule and an expression developed by Osei et al. (2016). This was due to the lack of sample points on the desorption column

\[
\int_{x_{AL,2}}^{x_{AL,1}} \frac{dx_{AL}}{(1 - x_{AL})^2 (x_{AL} - x_A^*)} = \sum_{i=1}^{n} \frac{\Delta x_{AL}}{(1 - \bar{x}_{AL})^2 (\bar{x}_{AL} - \bar{x}_A^*)}
\]

\(x_{AL,1}\) represents the CO\(_2\) concentration in the rich amine and \(x_{AL,2}\) the CO\(_2\) concentration in the lean amine.

**B.1.1 Sample calculation of \(x_A^*\)**

\(\bar{x}_A^*\) represents the physical composition of the CO\(_2\) gas in the liquid in equilibrium with the gas phase composition. This is calculated as according to the Henrys law constant

\[y_{CO_2}P = HeC_T x_A^*\]

It is important to note that the gas phase is composed of water and CO\(_2\) within the desorber. The gas phase composition of CO\(_2\) is computed from the Raoult's law. The Raoult's law is used to compute the gas phase H\(_2\)O composition, \(y_{H2O}\)

\[y_{H2O}P = P_{H2O}^v \times x_{H2O}\]

\(P_{H2O}^v\) represent the vapour pressure of the water in the gas mixer. This was computed from the steam table. The mole fraction of water in the liquid solution, \(x_{H2O}\) is calculated. From equation x. The partial pressure of water \(y_{H2O}P\) is computed and then equation x gives partial pressure of CO\(_2\) \(y_{CO_2}P\)
\[ y_{H_2O}P = 38543.50 \times 0.86 = 33147.41 \text{ Pa} \]

\[ P = y_{CO_2}P + y_{H_2O}P \]

\[ 101325 = y_{CO_2} \times 101325 + 33147.41 \]

Solving for \( y_{CO_2} \) gives 0.67. He is the Henrys law constant of CO2 in amine at these high temperatures was out of the acceptable limit for temperature within the autoclave reactor.

Therefore the \( He_{N2O-Amine} \) correlation developed in equation \( x \) is used.

\[ He_{N2O-BEA} = 0.64 \times 10^6 \exp \left( \frac{-1552.1}{T} \right) \]

\[ He_{N2O-BEA/AMP} = 0.64 \times 10^6 \exp \left( \frac{-1552.1}{75 + 273.15} \right) = 7413.72 \]

Then the \( He_{CO_2-amine} \) is computed as before

\[ He_{N2O-water} = 8.55 \times 10^6 \exp \left( \frac{-2284}{75 + 273.15} \right) = 12101.09 \text{ kPa} \cdot \text{m}^3/\text{kmol} \]

\[ He_{CO_2-water} = 2.82 \times 10^6 \exp \left( \frac{-2044}{75 + 273.15} \right) = 7952.28 \text{ kPa} \cdot \text{m}^3/\text{kmol} \]

\[ He_{CO_2-amine} = He_{N2O-amine} \times \left[ \frac{He_{CO_2-water}}{He_{N2O-water}} \right] \]

\[ He_{CO_2-amine} = 7413.72 \times \left[ \frac{7952.28}{12101.09} \right] = 4871.35 \text{ kPa} \cdot \text{m}^3/\text{kmol} \]

From the Henrys Law constant,

\[ C_T = \frac{Total \ mols \ (BEA + AMP + water + CO_2)}{1L} \]
\[ C_T = \frac{2 + 2 + 32.63 + 2.024}{1L} = 38.654 \text{ mol/l} = 38.654 \text{ kmol/m}^3 \]

Therefore,

\[ 0.67 \times 101.325 \text{kPa} = 4871.35 \frac{\text{kPa} \cdot \text{m}^3}{\text{kmol} \times 38.654 \text{ kmol/m}^3} \times x_A^* \]

\[ x_A^* = 0.00036 \]

**B.1.2: \( K_L a_v \) sample calculation**

\[ K_L a_v = \frac{L_1}{S} \frac{d}{\rho m Z} x \int_{x_{AL,1}}^{x_{AL,2}} \frac{d x_{AL}}{(1 - x_{AL})^2 (x_{AL} - x_A^*)} \]

\[ K_L a_v = \frac{121.86 \text{ mol}}{0.001963} \frac{0.0358 \text{ mol/ml} \times 1.00 \text{ m}}{0.054} \int_{0.023}^{0.054} \frac{d x_{AL}}{(1 - x_{AL})^2 (x_{AL} - x_A^*)} \]

The integral is initially computed from trapezoidal rule

\[ K_L a_v = \frac{121.86 \text{ mol}}{0.001963 \text{ m}^2} \frac{0.0358 \text{ mol/ml} \times 1.00 \text{ m}}{1 \times 10^6 \text{ ml/m}^3 \times 0.0358 \text{ mol/ml} \times 1.00 \text{ m}} x 0.93 = 1.62 \text{ hr}^{-1} \]

The integral is computed from the correlation developed by Osei et al. (2016)

\[ \sum_{i=1}^{n} \frac{\Delta x_{AL}}{(1 - x_{AL})^2 (x_{AL} - x_A^*)} \]

\[ \bar{x}_{AL} = \frac{0.053999 - 0.22939}{\ln 0.053999 - 0.22939} = 0.03628 \]
\[ \bar{x}_A^* = 0.00012 \]

\[ \Delta x_{\bar{A}L} = 0.053999 - 0.22939 = 0.03106 \]

Therefore,

\[ \sum_{i=1}^{n} \frac{\Delta x_{\bar{A}L}}{(1 - \bar{x}_{\bar{A}L})^2(\bar{x}_{\bar{A}L} - \bar{x}_A^*)} = \frac{0.03106}{(1 - 0.03628)^2(0.03628 - 0.00012)} = 0.925 \]

This value is very close to integral computed from trapezoidal rule with a 0.5% deviation.

\[ K_L \alpha_v = \frac{121.86 \text{mol/hr}}{0.001963 \text{m}^2} \cdot \frac{1 \times 10^6 \text{ml/m}^3 \times 0.0358 \text{mol/ml} \times 1.00 \text{m} \times 0.925}{1.61 \text{hr}^{-1}} \]
Table B.1-1: Sample calculated $x_A^*$ at different desorption bed temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$x_{H_2O}$</th>
<th>$P_{H_2O}^n$</th>
<th>$\gamma_{H_2O}P$</th>
<th>$\gamma_{CO_2}$</th>
<th>He</th>
<th>$x_A^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>0.86</td>
<td>38543.50</td>
<td>33147.41</td>
<td>0.67</td>
<td>4871.95</td>
<td>0.00036</td>
</tr>
<tr>
<td>85</td>
<td>0.86</td>
<td>57808.58</td>
<td>49715.38</td>
<td>0.51</td>
<td>5384.76</td>
<td>0.00025</td>
</tr>
<tr>
<td>95</td>
<td>0.86</td>
<td>84526.4</td>
<td>72692.70</td>
<td>0.28</td>
<td>5948.07</td>
<td>0.00012</td>
</tr>
</tbody>
</table>
**B.2: $K_G a_v$ plot along the column height**

$K_G a_v$ is calculated along the height of the absorption column from any two adjacent points. A plot of the $K_G a_v$ against the height of the column from the bottom is constructed as shown in Figure B.2-1. This plot shows the non-linear relation between the height and $K_G a_v$. This is in part the reason for using log mean square in computing the average $K_G a_v$ from the absorption column. The $K_G a_v$ was seen to be highest as the top of the absorption column as the amine is leanest at that point and therefore, the absorption of CO$_2$ corresponds as highest at that point. Generally, the $K_G a_v$ remains fairly constant till about 0.6m. The increase in $K_G a_v$ above this point can be attributed also to the high mass transfer activity owing to the high reactivity at that point. However, the inconsistent drop and rise in $K_G a_v$ above 0.6m could be as a result of channelling of the solvent which reduces the mass transfer performance.
Figure B.2-1: A plot of the column height against overall mass transfer coefficient ($K_{GAV}$) between two adjacent points.
**B.3: Sample calculation of interfacial Area**

For the interfacial area calculation below is used

\[
a = \frac{R_A}{[A^*]\left(\frac{2}{M + 1} D_A k_{mn}[A^*]^{m-1}[B_0]^n\right)^{1/2}}
\]

\( R_A \) is the rate of CO\(_2\) absorption into the amine solvent 0.070 kg/hr

\( R_A \) is converted to mol/m\(^3\)s

\[
R_A = 0.070 \frac{kg \ CO_2}{hr} \times \frac{mol}{44g} \times \frac{1000g}{1kg} \times \frac{1hr}{3600s} = 4.419 \times 10^{-4} mol/s
\]

The total volume occupied by the structured packing can be calculated as

The volume of the reactor = 0.001963m\(^2\) x column height = 0.001963 x 1m = 0.001963m\(^3\)

Therefore, the rate of absorption per unit reactor volume

\[
R_A = \frac{4.419 \times 10^{-4} mol/s}{0.001963 m^3} = 0.225 \frac{mol}{s \cdot m^3}
\]

\([A^*]\), the physical equilibrium concentration CO\(_2\), is computed from the physical absorption of N\(_2\)O in the BEA/AMP blend = 18.67mol/m\(^3\)

The rate expression developed from kinetic analysis by Afari D. B. (2018) was given as:

\[
-r_{CO_2} = 7.98 \times 10^{-7} \exp \left( \frac{-3.4 \times 10^4}{RT} \right) F_A^2 F_B
\]

Where \( F_A \) and \( F_B \) represent the flowrate of CO\(_2\) and amine respectively, in mol/min. The two rate equations can be linked by unit balance as:
\[
7.98 \times 10^{-7} \exp \left( \frac{-3.4 \times 10^4}{R T} \right) F_A^{(m-1)} F_B^n \times \rho_{bulk} \times \dot{V}_{total} = k_{mn}[A^*]^{m-1}[B_0]^n
\]

Where \( \rho_{bulk} \) is the bulk density of the catalyst, 60880 g/m\(^3\) and \( \dot{V}_{total} \) is the total volumetric flowrate of all fluids entering the column. 0.02506 m\(^3\)/min.

\[
\dot{V}_{soln} = \frac{0.02506 \text{ m}^3/\text{min.}}{60 \text{s/min}} = 4.187 \times 10^{-4} \text{ m}^3/\text{min.}
\]

\( F_A = C_A^* \times \dot{V}_{soln} \quad \text{(B.3-1)} \)

\( C_A^* \) is the equilibrium concentration of CO\(_2\) in the solvent. = 18.67 mol/m\(^3\)

Therefore,

\[
F_A = 18.607 \times \frac{60 \times 10^{-6} \text{ m}^3}{\text{min}} = 0.0011 \text{ mol/ min}
\]

\( F_B = C_B \times \dot{V}_{soln} \quad \text{(B.3-2)} \)

\( C_B \) is the concentration of amine in the solvent. = 4000 mol/m\(^3\)

\[
F_B = 4000 \times \frac{60 \times 10^{-6} \text{ m}^3}{\text{min}} = 0.24 \text{ mol/ min}
\]

m and n are the orders with respect to CO\(_2\) and amine which are 2 and 1 respectively.

\[
k_{mn}[A^*]^{m-1}[B_0]^n = \left[ 7.98 \times 10^{-7} \exp \left( \frac{3.4 \times 10^4}{8.314 \times 303.15} \right) \right] \times 60880 \text{ g/m}^3 \\
\times 4.187 \times 10^{-4} = 3.869 \times 10^{-3} \text{ S}^{-1}
\]
$D_A$, the diffusivity of CO$_2$ in amine was computed from a 4M AMP solution and estimated via the stoke Einstein equation. $D_A = 5.46355 \times 10^{-10} \text{ m}^2/\text{s}$

Therefore, the interfacial area

$$a = \frac{0.225}{18.67 \text{ mol/m}^3 \left( \frac{2}{2+1} \times 5.46355 \times 10^{-10} \times 3.869 \times 10^{-3} \text{ S}^{-1} \right)^{\frac{1}{2}}} = 10151 \text{ m}^{-1}$$