CARBON DIOXIDE ABSORPTION INTO AQUEOUS AMMONIA IN A HOLLOW FIBER MEMBRANE CONTACTOR

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By

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Zheng Cui, candidate for the degree of Doctor of Philosophy in Industrial Systems Engineering, has presented a thesis titled, *Carbon Dioxide Absorption into Aqueous Ammonia in a Hollow Fiber Membrane Contactor*, in an oral examination held on June 6, 2016. 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

Chemical absorption has been considered as a promising technology for carbon dioxide (CO₂) capture from different industrial waste gases. However, this technology has not been widely commercialized due to its high capital and operational costs, especially the cost for solvent regeneration. Studies have been focused on developing more efficient gas/liquid contactors or superior solvents that require less energy for regeneration. Aqueous ammonia (NH₃) has been recently studied as a CO₂ absorption solvent in many traditional gas/liquid contactors due to its lower cost and low energy requirement for solvent regeneration compared to traditional amine solutions. Since membrane contactors offer more advantages than traditional gas/liquid contactors, it could be more efficient and economic to capture CO₂ using aqueous ammonia as a solvent in a membrane contactor. However, little research has been reported in this field.

The main objective of this research is to investigate the CO₂ absorption performance of aqueous ammonia in a hollow fiber membrane contactor. In order to achieve this research goal, a number of lab-scale CO₂ absorption experiments were conducted using aqueous ammonia and monoethanolamine (MEA) as absorption solvents in a membrane contactor fitted with polytetrafluoroethylene (PTFE) hollow fiber membranes at ambient temperatures. The CO₂ absorption performance was evaluated in terms of the volumetric overall mass transfer coefficient ($K_{Ga}$) under different operating parameters. The absorption performance of aqueous ammonia was compared to that of MEA solvent under the same experimental conditions. The long-term membrane stability was evaluated by continuously running the CO₂ absorption experiments using aqueous ammonia as a solvent for up to ten hours.
The experimental results indicated that aqueous ammonia can be used to absorb CO₂ in a membrane contactor fitted with hollow fiber PTFE membranes. At ambient temperatures, the values of $K_G a_v$ ranged from 0.025 to 0.069 mol/m³-s-kPa. The parametric impacts on CO₂ absorption performance are similar to those of traditional amine-based absorption columns. Although the reactivity of aqueous ammonia is moderately lower than MEA, the $K_G a_v$ value of aqueous ammonia is the same order of magnitude as that of MEA. Aqueous ammonia can achieve a performance comparable to MEA solvent at the maximum liquid flow rates in the experiments. Long-term stability tests showed the absorption performance of aqueous ammonia remained constant within the first hour and then gradually decreased over time. Precipitation of ammonium salts was observed on the membrane surface on the shell side, which caused membrane fouling.

This thesis also developed a 2D mathematical model to simulate the CO₂ absorption process with aqueous ammonia in the hollow fiber membrane contactor. The model was based on a steady-state material balance and was solved using COMSOL Multiphysics®. The model can generate concentration profiles and flux vectors of transported species in the gas phase, the membrane, and the liquid phase. The model was verified by comparing the simulation results to the experimental results. The simulation results indicated the PTFE membranes were partially wetted during the absorption experiments. The percentages of membrane wetting ranged from 0.5% to 70%. The model was used to analyze the impact of membrane wetting. According to the simulation results, the absorption flux of CO₂ can significantly decrease when just a small portion of the membrane is wetted. However, once the membrane has been wetted, even just partially, the absorption rate only decreases slightly as the wetting percentage increases.
ACKNOWLEDGEMENTS

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Finally, I wish to deeply thank my parents and my parents-in law for their endless support over these years. And lastly, I would like to thank my wife, my son and my daughter. Their great love has endorsed me the strength to overcome many difficulties and made this thesis possible.
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NOMENCLATURE

A  gas-liquid interfacial area, m^2
a_v  Specific area of the contactor, m^2/m^3
C_{A\text{-}g,\text{i}}  concentration of reactant A in the gas phase, mol/m^3
C_{B,0}  concentration of reactant B at the inlet of liquid phase, mol/m^3
C_{CO_2\text{-}G}  concentration of CO_2 in the shell, mol/m^3
C_{CO_2\text{-}G\text{-}mem}  concentration of CO_2 in the gas phase in the partially-wetted membrane, mol/m^3
C_{CO_2\text{-}l}  concentration of CO_2 in the liquid phase, mol/m^3
C_{CO_2\text{-}L\text{-}mem}  concentration of CO_2 in the liquid phase in the partially-wetted membrane, mol/m^3
C_{CO_2\text{-}mem}  concentration of CO_2 in the non-wetted membrane, mol/m^3
C_{i}  concentration of species i, mol/m^3
C_{i\text{-}L}  concentration of species i in the tube, mol/m^3
C_{i\text{-}L\text{-}mem}  concentration of species i in the liquid phase in the partially-wetted membrane, mol/m^3
C_{IN\text{-}G}  concentration of CO_2 in the gas inlet, mol/m^3
C_{IN\text{-}L}  concentration of CO_2 in the liquid inlet, mol/m^3
C_{in\text{-}G}  initial concentration of CO_2 in the shell side, mol/m^3
C_{in\text{-}t}  initial concentration of species i in the tube side, mol/m^3
C_{Int\text{-}A}  concentration of A in liquid at the gas/liquid interface, mol/m^3
C_{L\text{-}A}  concentration of A in liquid phase, mol/m^3
C_{OUT\text{-}G}  concentration of CO_2 in the gas outlet, mol/m^3
C_{OUT\text{-}L}  concentration of CO_2 in the liquid outlet, mol/m^3
\( \text{Cs-L} \) concentration of species other than CO\(_2\) in the tube, mol/m\(^3\)

\( \text{Cs-mem} \) concentration of species other than CO\(_2\) in the liquid phase in the partially-wetted membrane, mol/m\(^3\)

\( \text{Cs-tube} \) concentration of species other than CO\(_2\) in the tube, mol/m\(^3\)

\( \text{d} \) average membrane fiber diameter, m

\( \text{D}_A \) diffusion coefficient of reactant A, m\(^2\)/s

\( \text{D}_B \) diffusion coefficient of reactant B, m\(^2\)/s

\( \text{d'In} \) logarithmic mean diameters of wetted membrane, m

\( \text{D}_{CO2-G} \) diffusion coefficient of CO\(_2\) in the gas phase in the shell, m\(^2\)/s

\( \text{D}_{CO2-G-mem} \) diffusion coefficient of CO\(_2\) in the gas phase in the partially-wetted membrane, m\(^2\)/s

\( \text{D}_{CO2-H2O} \) diffusion coefficient of CO\(_2\) in the water, m\(^2\)/s

\( \text{D}_{CO2-mem} \) diffusion coefficient of CO\(_2\) in the non-wetted membrane, m\(^2\)/s

\( \text{D}_{CO2-NH3} \) diffusion coefficient of CO\(_2\) in the aqueous ammonia, m\(^2\)/s

\( \text{d}_e \) hydraulic diameter, m

\( \text{D}_{G,eff} \) effective diffusion coefficient of gas in the gas-filled membrane pores, m\(^2\)/s

\( \text{d}_i \) inner diameter of membrane fibers, m

\( \text{D}_i \) diffusion coefficient of species i, m\(^2\)/s

\( \text{D}_{i-L} \) diffusion coefficient of species i in the tube, m\(^2\)/s

\( \text{D}_{i-L-mem} \) diffusion coefficient of species i in the liquid phase in the partially-wetted membrane, m\(^2\)/s

\( \text{d}_{is} \) inner diameter of the shell tube, m

\( \text{D}_K \) Knudsen diffusion coefficient, m\(^2\)/s

\( \text{d}_{ln} \) logarithmic mean diameter of non-wetted membranes, m
\( d_{ln} \) logarithmic mean diameter of wetted membranes, m

\( D_M \) molecular diffusion coefficient, m\(^2\)/s

\( d_{max} \) maximum membrane pore size, m

\( D_{NH_3-H_2O} \) diffusion coefficient of NH\(_3\) in the water, m\(^2\)/s

\( d_o \) outer diameter of membranes, m

\( d_p \) membrane pore diameter, m

\( E \) enhancement factor

\( E^*_{\infty} \) asymptotic infinite enhancement factor

\( G_I \) inert gas flow rate, mol/m\(^2\)-s

\( G \) total gas flow rate in the membrane system, m\(^3\)/s

\( H \) Henry’s law constant

\( Ha^* \) dimensionless Hatta number

\( J \) absorption flux/rate, mol/m\(^2\)-s

\( k \) reaction rate constant, m\(^3\)/mol-s

\( K \) equilibrium constant

\( k_G \) gas phase mass transfer coefficient, mol/m\(^2\)-s-kPa

\( K_G \) overall gas phase mass transfer coefficient, mol/m\(^2\)-s-kPa

\( K_G^{a_v} \) volumetric overall mass transfer coefficient, mol/m\(^3\)-s-kPa

\( k_L \) liquid phase mass transfer coefficient, m/s

\( K_L \) overall liquid phase mass transfer coefficient, m/s

\( k_M \) gas-filled portion membrane mass transfer coefficient, m/s

\( k'_M \) liquid-filled portion membrane mass transfer coefficient, m/s

\( k_{OH^-} \) reaction rate constant for CO\(_2\) hydration, m\(^3\)/mol-s

\( L \) length of membrane fibers, m

\( m \) physical solubility of reactant A, mol/mol
n  number of hollow fibers in the membrane module
n_i  amount of specie i, mol
N_i  flux of transported species i, mol/m^2-s
φ  volume void fraction of the membrane contactor module
P  total pressure, kPa
Q_L  liquid flow rate, m^3/s
q  exponent in Equation 2.27
R  universal gas constant
r  radial coordinate, m
R_{CO2}  overall reaction rate, mol/s
R_{CO2-NH3}  reaction rate of CO_2 and NH_3, mol/s
R_{CO2-OH^-}  reaction rate of CO_2 and OH^-, mol/s
r_e  effective shell radius, m
R_i  reaction rate of transported species i, mol/s
r_i  inner membrane fiber radius, m
R_{i-mem}  reaction rate of species i in the membrane, mol/s
r_m  inner radius of membrane module, m
r_o  outer radius of membrane fibers, m
r_w  wetting portion of the membrane, m
S_{N_2O-H_2O}  solubility of N_2O in water, mol/mol
S_{N_2O-NH_3}  solubility of N_2O in the diluted aqueous ammonia, mol/mol
S_{CO2}  solubility of CO_2 in the absorption liquid, mol/mol
S_{CO2-H_2O}  solubility of CO_2 in the water, mol/mol
S_{CO2-NH_3}  solubility of CO_2 in the diluted aqueous ammonia, mol/mol
T  temperature, K
t  time, s

$V$  axial velocity of species i along the length of membrane fibers, m/s

$V_i$  volume of solution i or specie i, m$^3$

$v$  diffusion volume of simple molecules

$v_B$  stoichiometric coefficient of B

$V_G$  axial gas velocity on the shell side, m/s

$\bar{V}_G$  average gas velocity in the shell side, m/s

$V_L$  axial velocity in the tube, m/s

$\bar{V}_L$  average axial velocity in the tube, m/s

$W$  molecular weight

$w, t$  partial reaction orders in Equation 2.26

$x$  wetting percentage

$Y$  mole ratio of CO$_2$ in the gas bulk

$y$  mole fraction of CO$_2$ in the membrane system

$y^*_{G}$  mole fraction of CO$_2$ in equilibrium with concentration of CO$_2$ in the liquid phase at the gas/liquid interface

$y_{G}$  mole fraction of CO$_2$ in the gas phase

$y_{G,A}$  mole fraction of A in the gas phase

$y_{Int,A}$  mole fraction of A in the gas at the gas/liquid interface

$Z$  effective membrane length, m

$z$  axial coordinate, m

**Abbreviations**

app  approximation
<table>
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<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>CCS</td>
<td>carbon capture and storage</td>
</tr>
<tr>
<td>CETI</td>
<td>Clean Energy Technologies Institute</td>
</tr>
<tr>
<td>CORAL</td>
<td>CO₂ removal absorption liquid</td>
</tr>
<tr>
<td>E</td>
<td>enhancement factor</td>
</tr>
<tr>
<td>Eq</td>
<td>equivalent</td>
</tr>
<tr>
<td>GHG</td>
<td>greenhouse gas</td>
</tr>
<tr>
<td>Gz</td>
<td>Graetz number</td>
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<tr>
<td>HFCs</td>
<td>hydrofluorocarbons</td>
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<tr>
<td>KPS</td>
<td>Kværner process systems</td>
</tr>
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<td>MWe</td>
<td>megawatt electric</td>
</tr>
<tr>
<td>P</td>
<td>partially wetted</td>
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<td>PDMS</td>
<td>polydimethylsiloxane</td>
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<td>polyethylene</td>
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<tr>
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<td>polytetrafluoroethylene</td>
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<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
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<td>PVDF</td>
<td>polyvinylidene fluoride</td>
</tr>
<tr>
<td>PZ</td>
<td>piperazine</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>RE</td>
<td>relative error</td>
</tr>
<tr>
<td>Sc</td>
<td>Schmidt number</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
</tbody>
</table>
SF$_6$  sulphur hexafluoride
Sh  Sherwood number
TEA  triethanolamine

**Greek Letters**

$\tau$  membrane tortuosity
$
\phi$
  packing density, %
$
\Delta C_{LM}$  logarithmic mean concentration difference of CO$_2$ at the inlet and outlet, mol/m$^3$

$\Delta p$  breakthrough pressure, kPa

$a_{CO2}$  CO$_2$ loading of the solution, mol/mol

$\alpha$  exponent for Reynolds number

$\beta$  exponent for Schmidt number

$\gamma$  exponent in Equation 2.24

$\delta$  membrane thickness, m

$\epsilon$  membrane porosity, %

$\theta$  empirical value in Equation 2.35 and 2.36

$\theta$  contact angle of the liquid with solid surface

$\mu$  viscosity, kPa-s

$\nu$  liquid velocity, m/s

$\sigma$  decrease rate, %

$\sigma_L$  liquid surface tension, mN/m

$\phi$  volume void fraction of the membrane contactor module

$\chi_{NH3}$  molar fraction of NH$_3$ in the aqueous ammonia

$\Omega_p$, $\Omega_D$  collision integrals
CHAPTER 1: INTRODUCTION AND RESEARCH OBJECTIVE

1.1 Introduction

Greenhouse gas (GHG) emissions have been generally considered as the major cause for climate change. Most GHG emissions result from the anthropogenic activities, such as energy production and consumption, waste disposal, agriculture, industrial processes and solvent and other product use. In Canada, as shown in Figure 1.1, stationary combustion sources in the energy sector were the largest GHG emitters compared to others. They emitted 309 megatonnes of CO$_2$ equivalent (Mt CO$_2$eq) in 2012, nearly doubled the second largest emitters, transport. In the stationary combustion sources, coal fired power plants were the major GHG emission contributor. Greenhouse gases mainly include CO$_2$, methane (CH$_4$), nitrous oxide (N$_2$O), sulphur hexafluoride (SF$_6$), perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs). Although the relative contribution of CO$_2$ emission to climate change is lower than the others, its annual emission quantity is much higher. According to Environment Canada (as seen in Figure 1.2), Canada’s CO$_2$ emission in 2012 accounted for 79% of total GHG emissions, which is about six times higher than other GHG emissions (Environment Canada, 2014). Therefore, current major research efforts for reducing GHG emissions have been focusing on the development of carbon capture technologies, especially for existing stationary combustion sources.

A wide range of technologies are available for CO$_2$ capture from stationary combustion sources. They can be classified into three categories: post-combustion capture, pre-combustion capture and denitrogenated conversion. The principles of separation include: absorption, adsorption, membranes, cryogenic, carbon extraction,
Figure 1.1: Canada’s GHG Emissions by Sector in 2012

(Environment Canada, 2014)
Figure 1.2: Canada’s GHG emissions in 2012
(Environment Canada, 2014)
biotechnology and energy conversion (Feron and Hendriks, 2005). Table 1.1 compares four major mature technologies, i.e., absorption, adsorption, membrane separation and cryogenic (Rao et al., 2004). MacDowell et al., 2010, indicated there were three technologies applicable for near future commercialization, including post-combustion CO$_2$ absorption using chemical solvents, oxyfuel combustion, and calcium looping technologies. Among them, chemical absorption is the most mature technology for CO$_2$ capture. During this process, CO$_2$ is counter-currently contacted and absorbed by a chemical solvent in a gas/liquid contacting device. This technology has been developed and commercially applied for acid gas removal in natural gas processing and refineries for many years. A common process is the amine-based absorption process, which uses alkanolamine solutions as the absorbent to capture CO$_2$ in a packed column. The reactive nature of this technology is typically suited for capturing CO$_2$ from dilute and low-pressure gas streams, such as power plant flue gases. It can be relatively easy to retrofit at the back end of an existing stationary power plant, but the associated capital and operational costs are considerable. Some amine-based absorption processes are commercially available, such as the Kerr-McGee/ABB Lummus Crest Process, Fluor Daniel’s ECON-AMINE process and Mitsubishi KS-1 process from Kansai Electric Power and Mitsubishi Heavy Industries (Barchas and Davis, 1992; Sander and Mariz, 1992; Mimura et al., 1995; Chapel et al., 1999).

In the oxyfuel combustion process, the nitrogen (N$_2$) in the combustion air is removed in an air separation unit prior to the fuel combustion. As a result, the fuel is combusted in a mixture of recycled flue gas (mainly CO$_2$) and oxygen (O$_2$). This differs from the chemical absorption process since the exhausted flue gas is almost
Table 1.1: Comparison of four major CO₂ capture technologies
(Rao et al., 2004)

<table>
<thead>
<tr>
<th>Technology</th>
<th>Contacting Device</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
</table>
| Absorption    | Physical Absorber and Regenerator Physical Solvent | Less energy requirement  
Less gaseous impurities interference to the solvents | High operating pressure requirement  
Only suitable for gas streams containing high level of CO₂ |
| Chemical      | Absorber and Regenerator Chemical Solvent    | Operates at atmospheric conditions and ordinary temperature  
Suitable even for dilute CO₂ streams  
Proved commercially available technology | Large energy penalty for solvent regeneration  
Significant solvent losses due to degradation and vaporization |
| Adsorption    | Adsorber beds                               | Commercial available gas separation process | Low removal capacity and CO₂ selectivity of available adsorbents |
| Membranes     | Membrane filters                            | Space efficient  
Easy to scale-up | Requires high operating pressures  
Lower product purity |
| Cryogenics    | Refrigeration and distillation devices      | Direct production of liquid CO₂ | Large energy requirements for refrigeration |
pure CO₂, which can be used for carbon capture and storage (CCS) without any purification. The major cost of this technology depends on the air separation process. Cryogenic air separation can produce large quantities of O₂ with a low cost and energy penalty. The oxyfuel combustion process has been tested by several companies including Vattenfall, Doosan Babcock and Air Liquide (MacDowell et al., 2010).

Another research interest focused on the calcium looping technology. Similar to chemical absorption technology, it consists of two continuous steps: CO₂ absorption and sorbent regeneration. But instead of using a liquid solvent, this technology uses solid calcium oxide (CaO) to react with CO₂ and form solid calcium carbonate (CaCO₃) in the carbonator. Then the CaCO₃ is regenerated to produce CO₂ in the calciner. The typical operation temperatures are about 923 K for carbonation and 1023 K for calcinations (Ströhle et al., 2009). In order to produce a pure stream of CO₂, O₂ from an air separation unit is supplied to the calciner to increase the temperature up to 1173 K. The advantage of this technology is the low cost of CaO, which can be derived from limestone. At present, several pilot-scale post-combustion calcium looping projects are being studied in Europe and North America (Hawthorne et al., 2011, Diego et al., 2016; Symonds et al., 2016).

1.2 Chemical Absorption Process for CO₂ Capture

Current research interests and pilot-scale studies mainly focused on the post-combustion CO₂ absorption by using chemical solvents. This technology is well suited for CO₂ capture from existing fixed stationary combustion emitters, such as coal-fired power plants, which can be retrofitted to the end of pipe of plants with ease.
CO\textsubscript{2} in the gas stream reacts with the solvent and forms soluble products through effective gas-liquid contacting. The mass transfer process is driven by a concentration gradient, instead of pressure difference. This makes chemical absorption suitable for treating flue gas, which is normally emitted at atmospheric conditions and contains low CO\textsubscript{2} levels. A basic flow scheme for a typical amine-based CO\textsubscript{2} absorption process is given in Figure 1.3. The feed gas containing CO\textsubscript{2} enters the bottom of absorber and flows upward. Inside the absorber, the feed gas counter-currently contacts with the lean absorption solution, which is flowing downward from the top of absorber. Through a series of complex chemical reactions, CO\textsubscript{2} is absorbed from the gas stream to the liquid solution. As a result, the treated gas stream leaves the top of absorber. The rich solution loaded with CO\textsubscript{2} exits from the bottom of the absorber and then is heated in a rich-lean heat exchanger prior to entering near the top of regenerator. At the bottom of regenerator, the rich solution is heated to boiling for releasing the absorbed CO\textsubscript{2}. The regenerated solution with a high temperature passes through the rich-lean heat exchanger to heat the rich solution and is reused as a solvent in the absorber. At the top of regenerator the water and solvent vapors are condensed and returned to the system to make up the solvent losses.

A successful design of chemical absorption process needs to consider two major aspects: the absorber and the absorption solvent. The purpose of the absorber is to increase the contacting surface area between the gas stream and the liquid solution thereby facilitating the mass transfer of chemical species. Several contacting devices have been developed including spray columns, tray towers, random or structured packed columns, and so on. Among them, the structured packed columns have the most successful applications. However, CO\textsubscript{2} capture in the packed columns is energy
Figure 1.3: A basic flow scheme for amine-based CO$_2$ absorption process
intensive and the gas and liquid flow velocities in packed columns are limited due to frequent operating problems, such as flooding, channelling, foaming and entrainment (Kumar, 2002; Cui and deMontigny, 2013). Besides absorbers, the other significant factor affecting the performance of chemical absorption process is the chemical solvent since reversible chemical reactions greatly enhance CO$_2$ absorption performance. In 1930, Robert patented the use of amines as absorbents for acid gas capture (Robert, 1930). Since then, a number of amines have been developed such as MEA, Diethanolamine (DEA), Triethanolamine (TEA), Methyl-diethanolamine (MDEA), Diisopropanolamine (DIPA) and 2-amino-2-methyl-1-propanol (AMP), 2-((2-aminoethyl)amino)ethanol (AEEA), 2-(diethylamino) ethanol (DEEA), 4-diethylamino-2-butanol (DEAB), and so on. Structural formulas of these amines are given in Table 1.2. MEA is the most popular amine due to its high absorption capacity and reactivity. The principle reactions during the absorption of CO$_2$ into the MEA solution are (Kohl and Nielsen, 1997),

\[
2RNH_2 + CO_2 + H_2O \leftrightarrow (RNH_3)_2CO_3 \quad (1.1)
\]

\[
(RNH_3)_2CO_3 + CO_2 + H_2O \leftrightarrow 2RNH_3HCO_3 \quad (1.2)
\]

\[
2RNH_2 + CO_2 \leftrightarrow RNHCOONH_3R \quad (1.3)
\]

where \( R \) stands for \(-C_2H_5OH\). Since these reactions are reversible, absorbents will be used repeatedly by heating them in a regenerator after the CO$_2$ absorption. There are more than 30 pilot-scale plants that have studied amine-based absorption and desorption processes for CO$_2$ capture from coal-fired power plants at 0.1 to 33 megawatt electric (MWe) (Boot-Handford et al., 2014). Companies such as Dow, RWE npower, Alstom, PGE, E.ON, Hitachi and Endesa have actively engaged to
Table 1.2: Structural formulas of alkanolamines 
(Kohl and Nielsen, 1997; Ma’mun et al., 2006; Maneeintr et al., 2009; Xu et al., 2013)

<table>
<thead>
<tr>
<th>Solvent Name</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>HO-NH2</td>
</tr>
<tr>
<td>Diethanolamine (DEA)</td>
<td>HO-N-H-OH</td>
</tr>
<tr>
<td>Triethanolamine (TEA)</td>
<td>HO-N-OH-OH</td>
</tr>
<tr>
<td>Methyl-diethanolamine (MDEA)</td>
<td>CH3-N-H-OH</td>
</tr>
<tr>
<td>Dihydroxypropanolamine (DIPA)</td>
<td>HO-N-H-OH</td>
</tr>
<tr>
<td>2-Aminomethyl-1-propanol (AMP)</td>
<td>HO-C4H9-NH2</td>
</tr>
<tr>
<td>2-((2-Aminoethyl)amino)ethanol (AEEA)</td>
<td>HO-N-C2H5-NH2</td>
</tr>
<tr>
<td>2-(Diethylamino)ethanol (DEEA)</td>
<td>N-C2H5-OH</td>
</tr>
<tr>
<td>4-Diethylamino-2-butanol (DEAB)</td>
<td>N-C2H5-OH</td>
</tr>
</tbody>
</table>
research and develop this technology. Located in the PC Compostilla, Spain, Endesa’s amine-based pilot-scale plant can treat 0.22 m³/s of flue gases. Another example is RWE’s amine-based CO₂ capture unit at the Didcot combustion test facility, which is capable to remove up to one tonne CO₂ per day (MacDowell et al., 2010). The world’s first commercial-scale CCS project is the SaskPower’s Boundary Dam Project located in the Estevan of Saskatchewan, Canada. This project rebuilt the aging Unit #3 at the Boundary Dam Power Station with a fully integrated amine-based carbon capture system. This carbon capture system has the potential to capture approximately one million tonnes CO₂ per year for CCS (SaskPower, 2015).

Currently, the major disadvantage of this technology is its considerable capital and operational cost. The application of this technology may lead to net efficiency penalties between 8.7% and 12% for coal-fired power generation (Finkenrath, 2011). Regeneration of solvents requires large energy consumption in the regenerator (Tock and Maréchal, 2015). In addition, several technical problems may occur during the amine-based absorption process. For example, the amine solvent is susceptible to thermal and oxidative degradation, which results in an additional cost associated with solvent make-up. It has been reported that the amine consumption rate can range between 350 and 2000 g/ton CO₂ (Bailey and Feron, 2005).

1.3 Hollow Fiber Membrane Contactors

Gas/liquid membrane contactors have become a promising alternative to traditional absorption columns for CO₂ capture in recent years (Mansourizadeh, 2012; Naim et al., 2012, Masoumi et al., 2016, Zhao et al., 2016). Compared to traditional membrane separation technology, gas/liquid membrane contactors are equipped with
hydrophobic hollow fiber membranes and offer a much higher selectivity by combining chemical absorption with membrane separation technology (Feron et al., 1992). Figure 1.4 shows the absorption process of a gas into a liquid through hollow fiber membranes. The hollow fiber membranes in the gas/liquid membrane contactor provide a barrier to separate the gas and liquid phases. In the ideal condition, the gas diffuses into the membrane pores and reacts with the liquid at the surface of membrane pores on the liquid side. The driving force for gas separation is a concentration gradient, and the absorption liquid provides the selectivity.

Membrane contactors exploit the advantages of traditional absorption columns while minimizing or eliminating some disadvantages of existing technologies. They have the following major advantages over traditional absorption contactors:

1) Junnasaksri, 2010, compared the specific contacting areas of different absorption contactors. As shown in Table 1.3, hollow fiber membrane contactors offer the highest surface area per volume ratio when compared with other absorption contactors. As a result, the membrane contactors can achieve faster mass transfer rates and the size of contactor can be considerably reduced (Junnasaksri, 2010). Research results indicated the CO$_2$ absorption performance in a membrane contactor can be up to nine times higher than a packed column (Rangwala, 1996; deMontigny et al., 2005). As an added benefit, the size of the membrane contactor may be up to 75% smaller than a packed column (Hoff and Svendsen, 2013);

2) The interfacial contacting area for mass transfer is easy to determine, which equals the total effective membrane surface area related to the porosity on the membrane surface;
Figure 1.4: Gas absorption process through hollow fiber membranes
### Table 1.3: Specific surface areas of gas/liquid contactors

(Junnasaksri, 2010)

<table>
<thead>
<tr>
<th>Contactor</th>
<th>Specific Surface Area (m²/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray column</td>
<td>1-10</td>
</tr>
<tr>
<td>Tray column</td>
<td>10-100</td>
</tr>
<tr>
<td>Mechanically agitated column</td>
<td>50-150</td>
</tr>
<tr>
<td>Bubble Column</td>
<td>100-800</td>
</tr>
<tr>
<td>Packed column</td>
<td>10-800</td>
</tr>
<tr>
<td>Membrane contactor</td>
<td>500-3000</td>
</tr>
</tbody>
</table>
3) The gas and liquid streams are separated by the hollow fiber membranes, which allow independent control of gas and liquid flow velocities. Common operating problems in traditional absorption contactors can be eliminated, such as flooding, channeling, foaming, and entrainment; and

4) The scaleup of a membrane contactor is relatively straightforward due to its modularity.

1.4 Research Limitations and Objective

In the past decade, aqueous ammonia has been studied as an alternative solvent to alkanolamine solutions for CO$_2$ absorption (Wang et al., 2011; Zhu et al., 2011; Qi et al., 2013; Zeng et al., 2013; Hanak et al., 2015; Jongpitisub et al., 2015; Li et al., 2015; Sutter et al, 2015; Yu and Wang, 2015; Zhang and Guo, 2015; Ma et al., 2016; Yu et al., 2016). Earlier studies focused on the chilled ammonia process. In this process, NH$_3$ reacts with CO$_2$ at low temperatures, typically from 0 to 293 K (Bak et al., 2015). This low temperature reduces the NH$_3$ loss due to its vaporization at an ambient condition. The main advantage of this technology over traditional amine-based absorption processes is its significant low energy consumption in the solvent regeneration process (Thomsen and Rasmussen, 1999). However, at low operating temperatures, precipitation of solids, such as ammonium bicarbonate (NH$_4$HCO$_3$), may occur in the absorber and the absorption performance is restricted due to the low reactivity (Sutter et al., 2015). Recently, researchers have studied the process at elevated temperatures. Qing et al., 2011, investigated CO$_2$ absorption efficiency by using aqueous ammonia in a packed column and a spray column at temperatures between 293 K and 328 K. Their experimental results indicated the suitable temperature is 308 K for the packed column. Darde et al., 2011, studied the
absorption rate of CO$_2$ by using aqueous ammonia (1-10% by weight) in a wetted-wall column from 279 K to 304 K. Their results indicated the absorption rate of CO$_2$ when using 10% aqueous ammonia is comparable with that by using 30% MEA solution at 314 K. Yu and Wang, 2015 studied the energy requirement of a whole CO$_2$ capture process, including CO$_2$ absorption, CO$_2$ regeneration, CO$_2$ compression, NH$_3$ abatement and NH$_3$ recovery process. Their simulation results indicated the NH$_3$ recovery process played a significant role in the total energy consumption for CO$_2$ capture. Previous results showed many advantages of aqueous ammonia as the absorption solvent over MEA, including (Yeh and Bai, 1999; McLarnon and Duncan, 2009; Han et al., 2013):

1) Much lower cost;
2) Higher CO$_2$ absorption capacity, up to 1.20 g CO$_2$/g NH$_3$;
3) No degradation and corrosion problems;
4) Capable to capture multi-pollutants, especially sulfur dioxide (SO$_2$) and nitrogen oxides (NO$_x$);
5) Less energy requirement for regenerating the solvent if necessary; and
6) The absorption products (mainly NH$_4$HCO$_3$) can be used as fertilizers in some developing countries, which will significantly reduce the CO$_2$ capture cost since the solvent regeneration process can be avoided.

However, a major disadvantage of using aqueous ammonia as an absorption solvent is the NH$_3$ loss due to its low vapor pressure. Water washing can be an effective measure to reduce the NH$_3$ emissions from the absorption liquid. However, this NH$_3$ abatement process requires additional energy consumption. Another effective measure is pH management. Research indicated a low NH$_3$ concentration or low temperature leads to low NH$_3$ vaporization (Pellegrini et al., 2010). Since
aqueous ammonia has many advantages over the MEA solvent, it has recently been studied as a CO₂ absorbent in packed columns, spray columns, and wetted wall reactors. However, there are little research works that studied CO₂ capture using aqueous ammonia in a hollow fiber membrane contactor (Mehdipour et al., 2014; Molina and Bouallou, 2015). Since aqueous ammonia offers a comparable absorption rate and several advantages compared to traditional MEA solution, development of an ammonia-based membrane absorption process may provide higher CO₂ absorption efficiency with a less capture cost than the traditional amine-based CO₂ absorption technology. Thus, detailed research work is required to examine the feasibility and study the potential technical problems of ammonia-based membrane absorption technology. Therefore, the objective of this research is to carry out a comprehensive study on the CO₂ absorption into aqueous ammonia by using a hollow fiber membrane contactor. The overall research work completed the following five tasks:

**Task 1:** Examined the feasibility of CO₂ absorption into aqueous ammonia in a used PTFE hollow fiber membrane contactor. Makhloufi et al., 2014, reported CO₂ absorption into aqueous ammonia achieved an unstable performance in a hollow fiber membrane contactor equipped with polypropylene (PP) membranes. Therefore, it was important to run a preliminary test with aqueous ammonia to evaluate the CO₂ absorption performance with the PTFE membranes, which are more hydrophobic;

**Task 2: Completed a full set of CO₂ absorption experiments using aqueous ammonia in a membrane contactor equipped with new PTFE membranes.** The impacts of various operating parameters on the CO₂ absorption performance were investigated including NH₃ concentration, liquid flow rate, CO₂ solution loading, and inlet CO₂ partial pressure.
Additionally, the long-term CO₂ absorption performance was investigated by continuously running the absorption experiments for up to ten hours;

**Task 3:** Conducted CO₂ absorption experiments with MEA solutions by using the same PTFE membrane contactor under the same experimental conditions of Task 2. The CO₂ absorption performance of aqueous ammonia and MEA was compared in terms of overall mass transfer coefficient;

**Task 4:** Developed a mathematical model to simulate the behavior of CO₂ absorption into aqueous ammonia in a hollow fiber membrane contactor. The mathematical model was essentially derived from the steady state material balance in the membrane contactor system. It can accurately predict the experimental results and be useful for scaling up the system.

**Task 5:** Verified the mathematical model using experimental results obtained in Task 2 under the non-wetted and partially wetted membrane conditions. The mathematical model was also used to evaluate the impact of membrane wetting on the CO₂ absorption performance.

The remainder of this thesis includes six chapters. Chapter 2 is a literature review of hollow fiber membrane technology for CO₂ capture. Chapter 3 introduces the detailed experimental setup and procedures. Experimental results are presented and discussed in Chapter 4. A mathematical model is developed in Chapter 5. Chapter 6 validates the mathematical model with the experimental results and discusses the impact of membrane wetting on the CO₂ absorption performance. A final conclusion and future recommendation are given in Chapter 7. The experimental data and simulation results are presented at the end of the thesis.
CHAPTER 2: A REVIEW OF MEMBRANE ABSORPTION SYSTEMS

2.1 Mass Transfer for Gas Absorption

Mass transfer happens when one component in a mixture migrates between different phases or through a same phase due to a concentration gradient (Strigle, 1987). Gas absorption into a liquid occurs when gaseous components transfer from a gas-phase to a liquid-phase. Several theories can describe the gas absorption process, such as film theory, penetration theory, surface renewal theory and boundary layer theory (Ahmad and Ramli, 2013). Due to the simplicity and similar accuracy to others, film theory, introduced by Whitman, 1923, has been widely adopted for many gas absorption studies.

Film theory assumes a gaseous component transfers into a liquid bulk through two thin films by molecular diffusion. As shown in Figure 2.1, the gas and liquid films are separated by a gas/liquid interface. Mass transfer is driven by concentration difference. The resistance to mass transfer only exists in the gas and liquid films. The overall mass transfer rate can be mathematically determined by the individual mass transfer coefficient and concentration difference in the gas or liquid phase (Kohl and Nielsen, 1997):

\[
N_A = k_G \Delta P (y_{G,A} - y_{int,A}) = k_L (C_{int,A} - C_{L,A})
\]  

(2.1)

At the interface, the gas and liquid phases are in equilibrium and their relationship complies with Henry’s Law:

\[
P y_{int,A} = H C_{int,A}
\]  

(2.2)
Figure 2.1: An illustration of film theory

(Adapted from deMontigny, 2004)
Since it is difficult to determine $k_G$ and $k_L$ values when designing an absorption device, an overall gas/liquid mass transfer coefficient is often applied (Kohl and Nielsen, 1997). Equation 2.1 can be rewritten:

$$N_A = K_G\left(P_{y_{G,A}} - HC_{L,A}\right) = K_L\left(\frac{P_{y_{G,A}}}{H} - C_{L,A}\right) \quad (2.3)$$

The overall mass transfer coefficients have the following relationships with the individual mass transfer coefficients:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L} \quad (2.4)$$

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Hk_G} \quad (2.5)$$

The mass transfer rate of gas absorption can be greatly enhanced by chemical reactions between the solute and solvent in the liquid phase. The contribution of chemical reactions to the mass transfer can be determined by the enhancement factor (E), which is the ratio of absorption flux with chemical reactions to the absorption flux with physical absorption. For a chemical absorption process, Equation 2.3 can be written:

$$N_A = K_G\left(P_{y_{G,A}} - HC_{L,A}\right) = EK_L\left(\frac{P_{y_{G,A}}}{H} - C_{L,A}\right) \quad (2.6)$$

Similar to traditional gas absorption process, mass transfer occurs during the absorption process of CO$_2$ in a hollow fiber membrane contactor. The major difference is the presence of hollow fiber membranes, which separates the gas and liquid phases. As shown in Figure 2.2, the absorption process includes three continuous steps: CO$_2$ diffuses through the gas film; continuously diffuses through
Figure 2.2: Absorption process in the hollow fiber membrane contactor
(Adapted from deMontigny, 2004)
membrane pores; and dissolves and/or diffuses into the liquid film with/without chemical reactions (Li and Chen, 2005). The presence of membrane fibers in the system adds an additional mass transfer resistance. Under some particular operating conditions, the membrane pores may be wetted by the absorption liquid during the CO₂ absorption process. Therefore, the $K_G d_v$ can be expressed as three modes of operation including non-wetted, wetted or partially wetted (Kreulen et al., 1993; Kumar et al., 2003; Mavroudi et al., 2003; Atchariyawut et al., 2006; Drioli et al., 2006; Boucif et al., 2008; Franco et al., 2009; Khaisri et al., 2009; Khaisri et al., 2010):

Non-wetted mode:

$$\frac{1}{K_G d_i} = \frac{H}{E k_L d_i} + \frac{1}{k_M d_{in}} + \frac{1}{k_G d_o}$$  \hspace{1cm} (2.7)

$$\frac{1}{K_L d_i} = \frac{1}{Ek_L d_i} + \frac{1}{H k_M d_{in}} + \frac{1}{H k_G d_o}$$  \hspace{1cm} (2.8)

Wetted mode:

$$\frac{1}{K_G d_o} = \frac{H}{E k_L d_i} + \frac{H}{E k_M' d_{in}} + \frac{1}{k_G d_o}$$  \hspace{1cm} (2.9)

$$\frac{1}{K_L d_o} = \frac{1}{E k_L d_i} + \frac{H}{E k_M' d_{in}} + \frac{1}{H k_G d_o}$$  \hspace{1cm} (2.10)

Partially wetted mode:

$$\frac{1}{K_G d_{int}} = \frac{H}{E k_L d_i} + \frac{H}{E k_M' d_{in}} + \frac{1}{k_M d_{in}} + \frac{1}{k_G d_o}$$  \hspace{1cm} (2.11)

$$\frac{1}{K_G d_{int}} = \frac{H}{E k_L d_i} + \frac{H}{E k_M' d_{in}} + \frac{1}{H k_M d_{in}} + \frac{1}{H k_G d_o}$$  \hspace{1cm} (2.12)
2.1.1 Overall Mass Transfer Coefficient

In a hollow fiber membrane contactor, the membranes separate the gas and liquid flows and provide a constant gas-liquid interfacial area, which depends on the total membrane surface area and membrane porosity. Thus it is much easier to determine its $K_{GA_v}$ value of membrane contractors than traditional packed columns. If the fluids flowing in both the tube and shell sides are assumed as ideal plug flows, the average driving force in either tube side or shell side is the log-mean concentration difference of the CO$_2$ solute (Yeon et al., 2003). Thus the overall liquid-phase mass transfer coefficient can be evaluated as (Mavroudi et al., 2003; Wang et al., 2005; Atchariyawut et al., 2008; Khaisri et al., 2009; Chen et al., 2010):

$$K_L = \left(\frac{Q_L}{A}\right)\left(\frac{C_{OUT_L} - C_{IN_L}}{\Delta C_{LM}}\right)$$  \hspace{1cm} (2.13)

$\Delta C_{LM}$ is the log-mean concentration difference of the CO$_2$ solute in the liquid phase. It can be calculated as:

$$\Delta C_{LM} = \frac{(H C_{IN,G} - C_{OUT,L}) - (H C_{OUT,G} - C_{IN,L})}{\ln\left(\frac{H C_{IN,G} - C_{OUT,L}}{H C_{OUT,G} - C_{IN,L}}\right)}$$  \hspace{1cm} (2.14)

deMontigny, 2004, manufactured a lab-scale hollow fiber membrane contactor and compared with a packed column for CO$_2$ absorption by using alkanolamine solutions. In his study, the overall gas-phase mass transfer coefficient was determined by adopting a standard method used for CO$_2$ absorption in a packed column. It can be calculated as follows,

$$K_G a_v = \frac{g_i}{p(y_G - y^*_{G})} \frac{dy}{dz}$$  \hspace{1cm} (2.15)

$Y$ is the mole ratio of CO$_2$ in the gas phase, which can be determined by:
y^*_{G} is the mole fraction of CO₂ in equilibrium with concentration of CO₂ in the liquid phase at the gas/liquid membrane interface. For a fast chemical reaction, it is essentially zero since CO₂ is quickly consumed by reacting with the absorption solvent. The concentration gradient \((dY/dL)\) can be obtained from the slope of the measured CO₂ concentration profile in the gas phase by plotting the mole ratio \(Y\) against the column height. A simple empirical approach was also developed for a small size hollow fiber membrane contactor since it is too small to accurately generate a CO₂ concentration profile. It assumes the overall volumetric mass transfer coefficient is constant in the absorption system and can be represented in the form of a log-mean driving force (deMontigny, 2004):

\[
K_G a_Y = \frac{G_I (Y_B - Y_T)}{ZP (y_G - y_G^*)_{LM}} \tag{2.17}
\]

\[
(y_G - y_G^*)_{LM} = \frac{(y_G - y_G^*)_B - (y_G - y_G^*)_T}{ln(y_G - y_G^*)_B - ln(y_G - y_G^*)_T} \tag{2.18}
\]

The subscripts \(B\) and \(T\) represent the bottom and top of the membrane contactor. Khaisri et al., 2009, successfully compared the membrane resistance and absorption performance of three different membranes in a hollow fiber membrane contactor by using the above empirical approach.

**2.1.2 Mass Transfer Coefficient on the Tube Side**

Prediction of mass transfer coefficient is important for designing mass transfer equipment. Including membrane contactors, the individual mass transfer coefficient was often estimated from a general correlation equation related to the Schmidt
number \((Sc)\), Sherwood number \((Sh)\), and Reynolds number \((Re)\) as follows (Gabelman and Hwang, 1999; Mavroudi et al., 2006):

\[
Sh \propto Re^{\alpha}Sc^{\beta}f(\text{geometry})
\]

Several similar correlations have been established based on the above general correlation equation to predict the mass transfer coefficient on the tube side of the membrane contactor. For example, the tube side mass transfer coefficient of \(\text{CO}_2\) can be calculated by adopting the well-known Leveque’s solution from heat transfer. Considering the very small diameter of membrane fibers, it is assumed that equilibrium exists at the gas/liquid interface and the liquid flow is a fully developed laminar flow. When the liquid flows in the fiber without chemical reactions, the general correlation can be expressed in two cases (Kreulen et al., 1993; Mansourizadeh and Ismail, 2009):

For \(G_z > 20\):

\[
Sh = \frac{k_{1d}}{D} = 1.62 \left( \frac{d}{D} Re Sc \right)^{0.33} = 1.62 G_z^{0.33}
\]

(2.20)

For \(G_z < 10\):

\[
Sh = \frac{k_{1d}}{D} = 3.67
\]

(2.21)

where \(G_z\) is Graetz number. Kreulen et al., 1993, gave another general correlation through curve fitting:

\[
Sh = \frac{k_{1d}}{D} = \sqrt[3]{3.67^3 + 1.62^3 G_z}
\]

(2.22)
Equation 2.22 is also valid in the range of Graetz numbers not covered by Equations 2.20 and 2.21. Qi and Cussler, 1985, used a similar correlation for physical absorption in the case of $Re < 200$:

$$Sh = 1.86 \left( \frac{d}{z} Re Sc \right)^{\frac{1}{3}}$$  \hspace{1cm} (2.23)

Some researchers found that the liquid flow on the tube side is often non-uniform at low flows due to the polydispersity in hollow fiber diameter. As a result, the above Graetz-Leveque correlations may overestimate the tube-side mass transfer coefficient (McLarnon and Duncan, 2009; Zhu et al., 2011).

### 2.1.3 Mass Transfer Coefficient on the Shell Side

Mass transfer on the shell side of a membrane contactor is still not clearly understood due to various membrane module properties. Many empirical or fundamental correlations have been proposed for calculating the shell-side mass transfer coefficient of various parallel-flow membrane modules. Table 2.1 summarizes the shell-side mass transfer correlations for CO$_2$ absorption in a hollow fiber membrane contactor (Park et al., 2008). Zheng et al., 2003, compared the correlation results from other researchers and indicated the correlation results from Yang and Cussler, 1986, Wickramasinghe et al., 1992, and Wu and Chen, 2000, were relatively close to their results. They also suggested that the correlation difference in form is possibly due to the polydispersity of fiber diameters, irregularity of fiber spacing, the fiber movement during operation, the influence of the module wall, and the inlet and outlet effects (Zheng et al., 2003). The general physical mass transfer correlation for parallel flow can be expressed in the following form:

$$Sh \propto f(\phi) \left( \frac{d}{z} \right)^{\gamma} Re^{\alpha} Sc^{\beta}$$  \hspace{1cm} (2.24)
Table 2.1: The shell-side mass transfer correlations for CO$_2$ absorption in a hollow fiber membrane contactor

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Packing Density (%)</th>
<th>Reynolds Number</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Sh=1.25(Re_d/Z)^{0.93}Sc^{0.33}$</td>
<td>3, 26</td>
<td>0-1000</td>
<td>Yang &amp; Cussler, 1986</td>
</tr>
<tr>
<td>$Sh=0.019Gz$</td>
<td>70</td>
<td>Gz&lt;60</td>
<td>Wickramasinghe et al., 1992</td>
</tr>
<tr>
<td>$Sh=(0.53-0.58\phi)(Re)^{0.53}Sc^{0.33}$</td>
<td>32-76</td>
<td>20-350</td>
<td>Costello et al., 1993</td>
</tr>
<tr>
<td>$Sh=0.41(1/N)(d_i/d_o)^2(d_o/Z)^{0.25}Re^{0.33}Sc^{0.33}$</td>
<td>5.06-15.7</td>
<td>10-300</td>
<td>Nii &amp; Takeuchi, 1994</td>
</tr>
<tr>
<td>$Sh=0.39Re^{0.59}Sc^{0.33}$</td>
<td>-</td>
<td>1.4-5.3</td>
<td>Ferreira et al., 1998</td>
</tr>
<tr>
<td>$Sh=(0.3045\phi^2-0.3421\phi+0.0015)Re^{0.9}Sc^{0.33}$</td>
<td>8.4, 30.2, 50.2, 70.2</td>
<td>32-1287</td>
<td>Wu &amp; Chen, 2000</td>
</tr>
<tr>
<td>$Sh=(0.163+0.27\phi)Gz^{0.60}$</td>
<td>20, 30, 40, 50</td>
<td>178-1194</td>
<td>Zheng et al., 2003</td>
</tr>
<tr>
<td>$Sh=0.34Re^{0.67}Sc^{0.33}$</td>
<td>-</td>
<td>&lt;12.45</td>
<td>Mavroudi et al., 2006</td>
</tr>
</tbody>
</table>
The general correlation indicates that the module packing density has an impact on the mass transfer coefficient as it affects the flow condition on the shell side. Apparently, increasing the packing density could lead to a larger mass transfer interfacial area, thus increasing the mass transfer rate. However, experimental and analytical results indicated that the observed mass transfer coefficient decreases as the packing density increases up to 50% (Wu and Chen, 2000). The decreased mass transfer coefficient is possible due to the channelling effect and dead zone in the module. The correlation results have a similar trend as the observed results, but greatly underestimated the mass transfer coefficient at low packing densities. The empirical correlations were developed based on an ideal axial and laminar flow in the shell side, but omitting the possible presence of entry and transverse flow at low packing density, which may increase the mass transfer rate (Costello et al., 1993; Wu and Chen, 2000). Lipnizki and Field, 2001, developed a set of mass transfer correlations by considering entrance effects of the hydrodynamic and of the concentration profile. Their rigorous correlations can be applied for examining the design performance of membrane modules in both laminar flow and turbulent flow.

2.1.4 Mass Transfer with Chemical Reactions

Chemical solvents are much preferred for gas absorption than physical solvents since chemical reactions between the chemical absorbent and the gas component can greatly enhance the mass transfer rate in the liquid phase. Mass transfer rate is determined by rate of diffusion of the gaseous component through both films adjacent to the gas/liquid interface (Lewis and Whitman, 1924). A higher diffusion rate means less mass transfer resistance, i.e., a higher mass transfer rate. Normally the diffusion coefficients in the gas phase are much higher than the
diffusion coefficients in the liquid phase. Therefore, mass transfer in the liquid film is
the controlled process and determines the overall mass transfer rate of gas absorption
in the absence of chemical reactions. However, in the presence of chemical reactions
in the liquid film the gas component transferred to the liquid phase can be depleted by
reacting with the chemical solvent. Thus the mass transfer resistance in the liquid
film can be greatly reduced. For the chemical absorption process, the gas phase mass
transfer process may actually determine the overall mass transfer rate (Kreulen et al.,
1993).

The contribution of chemical reactions to the mass transfer rate can be
described by enhancement factor. It is the ratio of absorption flux in the presence of
chemical reactions to the absorption flux in the presence of physical absorption only:

\[ E = \frac{J_{chem}}{J_{phy}} \]  

(2.25)

The enhancement factor is defined based on an assumption that the driving force for
mass transfer is identical when a chemical reaction is present or absent in the liquid
phase. In order to evaluate the efficiency of a membrane contactor, this parameter
needs to be determined accurately by either approximate solution or exact numerical
solution of the mass transfer model.

Approximate solution of the mass transfer model is based on the selected
traditional mass transfer theory, such as film theory, penetration theory and surface
renewal theory. All these theories assume that the liquid bulk should be completely
mixed closed to the mass transfer zone and no velocity gradient in the mass transfer
zone. Therefore, the dimensionless Hatta number and infinite enhancement factor
used in these approximate solutions are based on the conditions in the liquid bulk.
However, this assumption depends on the gas-liquid contact time. When the gas-liquid contact time is long enough, the mass transfer zone can extend up to the axis of the fiber and the centerline concentration may be disturbed. In the case of short gas-liquid contacting time, the penetration depth of gaseous component in the liquid phase is short compared to fiber radius. As a result, the liquid near the axis of the fiber can be considered mostly undisturbed, which is similar to the bulk liquid infinitely far from the gas/liquid interface in traditional mass transfer models (Kumar et al., 2003). The concentration of absorbent in the liquid phase at the axis is the same as its concentration at the fiber inlet (Li and Chen, 2005). In such a case, the dimensionless Hatta number and asymptotic enhancement factor for a membrane fiber can be determined according to the surface renewal theory and the conditions at the liquid inlet (Kumar et al., 2003):

\[ Ha^* = \sqrt{\frac{k_{w,t} D_A C_{A,B}^{w-1} C_{B,D}^t}{k_L}} \]  

(2.26)

For mass transfer in the presence of an irreversible chemical reaction, the asymptotic infinite enhancement factor is calculated by:

\[ E_{\infty}^* = (1 + \frac{C_{B,D}}{v_{Bm} C_{A,B} D_A}) \frac{C_{D_A}}{D_B} q \]  

(2.27)

where \( w \) and \( t \) are the partial reaction orders with respect to A and B; \( q \) is a factor dependent on the selected mass transfer model.

Kumar et al., 2003, developed the explicit approximate solution of Decoursey based on Danckwert’s surface renewal theory for an irreversible second-order chemical reaction. The enhancement factor can be determined by using the dimensionless Hatta number and asymptotic enhancement factor:
They compared their approximate solutions with the exact numerical results and experimentally measured values of the enhancement factor. The approximate solution was found as accurate as others when the $G_z$ number is greater than 120 or even lower. However, for very low values of $G_z$ number, the driving force for mass transfer is not identical for both physical and chemical absorption. Thus the approximate solution for the enhancement factor needs to be corrected in order to improve its accuracy.

The approximate solution has limited applications for determination of enhancement factor. Especially for the membrane module with a very small fiber diameter, the real conditions in the liquid bulk cannot usually meet the assumption of traditional mass transfer theories. As a result, the liquid bulk in the tube is not completely mixed and the velocity gradient exists in the liquid bulk, which decreases the accuracy of the approximation solution. Another method for determining enhancement factor is the numerical solution of the mass transfer model. Different from traditional contactors, the absorption process in a membrane contactor can be well simulated by using a serial of differential mass balance equations for the transferred species. Enhancement factor can be accurately determined by numerically solving these differential mass balance equations. Compared to numerical solution, the approximate solution is a more convenient approach; but the numerical solution has a broader application and offers more accurate results for determination of enhancement factor.
2.1.5 Membrane Mass Transfer Coefficient

During the operation of gas absorption, the membrane pores can be filled by either gas or liquid. When the membrane pores are filled with gas completely, the membrane is non-wetted. The non-wetted membrane is preferred for gas absorption due to its low membrane mass transfer resistance. However, the liquid may penetrate into the membrane pores and cause the membrane partially or completely wetted. Therefore, the membrane mass transfer coefficient depends on the status of the membrane during the absorption operation. In the ideal condition, i.e., the non-wetted membrane operation, the membrane mass transfer coefficient can be estimated by using the effective diffusion coefficient of gas in the gas-filled membrane pores \( (D_{G,e_{ff}}) \) and the membrane properties as follows (Qi and Cussler, 1985),

\[
k_{M} = \frac{D_{G,e_{ff}}E}{\tau\delta} \quad (2.29)
\]

The effective diffusion coefficient is determined by molecular and Knudsen diffusion coefficients:

\[
\frac{1}{D_{G,e_{ff}}} = \frac{1}{D_{M}} + \frac{1}{D_{K}} \quad (2.30)
\]

The molecular diffusion coefficient of gas in the membrane can be estimated from the kinetic gas theory (Mavroudi et al., 2006; Reid et al., 1987):

\[
D_{M} = 1200 \left( \frac{RT}{W_{P}} \right) \left( \frac{\Omega_{\mu}}{\Omega_{D}} \right) \mu \quad (2.31)
\]

The collision integrals \( \Omega_{\mu} \) and \( \Omega_{D} \) are dimensionless functions of temperature. They can be obtained from the empirical equations (Reid et al., 1987). The Knudsen diffusion coefficient depends on the membrane pore radius \( (r_{p}) \) and can be calculated by using the following equation (Henley et al., 2011):
In the case of wetted membrane operation, the membrane pores are completely filled with absorption liquid. The membrane mass transfer coefficient is determined by the CO\textsubscript{2} diffusion coefficient into the liquid. Khaisri et al., 2010, adapted Equation 2.29 to calculate the mass transfer coefficient of wetted membrane:

\[ 100D_k = 0.485d_p\left(\frac{T}{W_{CO_2}}\right)^{0.5} \]  

(2.32)

When the membrane is partially wetted, the membrane has both gas-filled and liquid-filled pores. Accordingly, the partially wetted membrane mass transfer resistance consists of non-wetted and wetted membrane mass transfer resistance. And the mass transfer coefficient can be calculated as follows (Rangwala, 1996):

\[ k'_M = \frac{D_{LE}}{\tau\delta_{wetted}} \]  

(2.33)

where \( x \) is the average fractional distance of penetration of liquid in the membrane pores (wetting percentage).

The Wilson plot method is another effective technique for determining the membrane mass transfer coefficient by using the experimental results. It was firstly applied to estimate the resistance to heat transfer by Wilson (Diao et al., 2004). Since heat transfer is analogous to mass transfer, the Wilson plot method has been introduced to determine the individual mass transfer resistance (Viegas et al., 1998). The Wilson plot equation can be obtained by simplifying the Equation 2.7 and 2.8 as follows (Khaisri, 2009),

\[ \frac{1}{k_G} = C_{CO_2}l v^{-q} + d_i\left(\frac{1}{k_{M_{in}}} + \frac{1}{k_{Gd_o}}\right) \]  

(2.35)
The Wilson plot can be made with \(1/K_G\) or \(1/K_L\) versus \(\nu^{-\varphi}\). \(\nu\) is the liquid velocity. \(\varphi\) is an empirical value, which need to be assumed first in order to obtain a best straight line. According to the Wilson plot equation, the membrane mass transfer resistance and gas phase mass transfer resistance can be determined from the y interception of the plot. Since the gas phase mass transfer resistance can be estimated by using an empirical mass transfer correlation, the membrane mass transfer resistance can be effectively determined by using the Wilson plot method. For CO\(_2\) absorption in a hollow fiber membrane contactor, the gas phase mass transfer resistance is much smaller and negligible compared to the liquid and membrane mass transfer resistance (Rangwala, 1996). So the membrane mass transfer resistance can be determined by the Wilson plot method directly (Khaisri et al., 2009).

2.2 Membrane Module Design

In general hollow fiber membranes inside the membrane contactor are packed in a parallel arrangement within the shell (Yu et al., 2011). In this structure, the packing of membrane fibers is usually random. This random packing structure can lead to a non-uniform fiber distribution on the shell side of membrane module, causing possible liquid bypassing and channelling when the liquid flows on the shell side of the module. Additionally, the liquid flow in the tube is severely restricted because of the small inner diameter of membrane fibers. As a result, the random packing and limited liquid flow can deteriorate the mass transfer performance of membrane contactors. Thus, membrane module design is a significant factor for affecting the efficiency of membrane gas absorption process. In real applications of
membrane contactors for CO₂ absorption, it is necessary to obtain a large membrane contact area to facilitate mass transfer. In addition to considering increasing the membrane length and diameter, the design of membrane cascade systems may be a good option for achieving the desired contact area (Boributh et al., 2011; Boributh et al., 2012).

To date researchers designed and tested various types of membrane modules in order to increase the mass transfer performance (Albo et al., 2010; Junnasaksri, 2010; Mulukutla et al., 2015; Cai et al., 2016). The major membrane module designs include the spacing of the fibers, the packing density of membrane fibers, and the relative two-phase fluid flow directions on the shell and tube sides, such as parallel and cross flows. Some current research results on the overall mass transfer rate/coefficient for CO₂ absorption in gas/liquid membrane contactors are summarized in Table 2.2. According to the relative flow direction of both fluids in the membrane system, membrane modules can be classified as parallel flow or cross flow modules.

2.2.1 Parallel flow modules

Parallel flow modules are mostly adopted in designing hollow fiber membrane contactors for CO₂ capture because they are relatively easy to make and suitable for predicting mass transfer rates (Dindore et al., 2004; Lu et al., 2005; Yeon et al., 2005; Gong et al., 2006; Yan et al., 2007; Yan et al., 2008; Zhang et al., 2009; Weifeng et al., 2010; Franco et al., 2012; Makhloufi et al., 2014; Masoumi et al., 2014; Zhang et al., 2014; Rahim et al., 2015; Zaidiza et al., 2015; Fashandi et al., 2016). A schematic diagram for a parallel flow module is given in Figure 2.3. In such a module, the gas phase flow is parallel to the liquid phase flow, which is on the
Table 2.2: Current research on the overall mass transfer rate/coefficient for CO₂ absorption in gas/liquid membrane contactors

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Flow direction</th>
<th>Gas component</th>
<th>Liquid component</th>
<th>Lumen side</th>
<th>Overall mass transfer rate/coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>Counter-current</td>
<td>N₂+CO₂</td>
<td>Piperazine activated glycine salt solution</td>
<td>Gas</td>
<td>1.3-2.4×10⁻⁴ m/s</td>
<td>Lu et al., 2010</td>
</tr>
<tr>
<td>PVDF</td>
<td>Counter-current</td>
<td>CO₂</td>
<td>NaOH</td>
<td>Gas</td>
<td>3.0-3.6×10⁻³ mol/m²·s</td>
<td>Mansourizadeh et al., 2010</td>
</tr>
<tr>
<td>PTFE</td>
<td>Counter-current</td>
<td>N₂+CO₂</td>
<td>Potassium glycinate</td>
<td>Liquid</td>
<td>3.89-7.78×10⁻⁴ mol/m²·s</td>
<td>Eslami et al., 2011</td>
</tr>
<tr>
<td>PP</td>
<td>Counter-current</td>
<td>N₂+CO₂</td>
<td>N-methylmonoethanolamine +AMP</td>
<td>Gas</td>
<td>1.25-2.50 ×10⁻⁴ m/s</td>
<td>Lu et al., 2011</td>
</tr>
<tr>
<td>PVDF</td>
<td>Counter-current</td>
<td>CO₂</td>
<td>Pure water</td>
<td>Gas</td>
<td>1.00-6.22×10⁻⁴ m/s</td>
<td>Naim and Ismail, 2013</td>
</tr>
<tr>
<td>PTFE</td>
<td>Counter-current; concurrent</td>
<td>N₂+CO₂</td>
<td>2-amino-2-hydroxymethyl-1,3-propanediol + piperazine aqueous</td>
<td>Liquid</td>
<td>1.67×10⁻⁴ -1.30 ×10⁻³ mol/m²·s</td>
<td>Bougie et al., 2014</td>
</tr>
<tr>
<td>Modified aluminum oxide hollow fiber membranes</td>
<td>Counter-current</td>
<td>N₂+CO₂</td>
<td>Pure water</td>
<td>Liquid</td>
<td>7.8×10⁻⁴ mol/m²·s</td>
<td>Lee et al., 2015</td>
</tr>
<tr>
<td>Fluoroalkylsilane-modified silica aerogel tubular membrane</td>
<td>Counter-current</td>
<td>N₂+CO₂</td>
<td>2-amino-2-methyl-1-propanal/piperazine amine</td>
<td>Gas</td>
<td>0.6×10⁻³ mol/m²·s</td>
<td>Lin et al., 2015</td>
</tr>
<tr>
<td>Poly(vinyl chloride) (PVC)</td>
<td>Counter-current</td>
<td>CO₂</td>
<td>Pure water</td>
<td>Gas</td>
<td>6.54×10⁻⁵ -2.29×10⁻³ m/s</td>
<td>Fashandi et al., 2016</td>
</tr>
</tbody>
</table>
Figure 2.3: A schematic diagram for a parallel flow module
opposite side of the membrane fibers. The relative flow direction of both fluids is concurrent or counter-current. Experimental results indicated that the counter-current flow is preferred since it offers averagely 20% higher mass transfer rate than the concurrent flow (deMontigny et al., 2006). The configuration of this module is preferred when mass transfer only depends on the membrane itself or the boundary layer inside the membrane fibers (Wang and Cussler, 1993). When mass transfer is primarily controlled by the boundary layer outside of the membrane fibers, such as the liquid flows in the shell side, parallel flow modules offer moderate mass transfer performance. The mass transfer process for CO₂ capture in a hollow fiber membrane contactor is generally controlled by the liquid phase when the membrane is not wetted. Therefore, parallel flow modules offer less efficiency than cross flow modules when the absorption liquid flows in the shell side of the membrane module.

2.2.2 Cross Flow Modules

The cross-flow module was firstly investigated for gas treating processes by Yang and Cussler in 1986. They studied the stripping of O₂ and CO₂ from water into N₂ by using hollow fiber membrane contactors with two types of geometric designs including a parallel flow module and a cross flow module. In their study, the theoretical mechanism responsible for controlling the mass transfer rate has been discussed and the mass transfer correlations for designing membrane modules were reported. However, the mass transfer performance of each module design was not studied in detail. Wickramasinghe et al., 1992, conducted a followed research by comparing a number of commercially available cross-flow membrane modules with a cylindrical parallel flow module based on equal flow per membrane area and equal flow per module volume. Their experimental results indicated that the cross-flow
modules were at least ten times more efficient than the parallel flow module. Their conclusion was further approved by Jansen et al., 1994. This higher mass transfer efficiency of cross-flow modules attributes to the reduced liquid channeling and increasing local turbulence level on the shell side (Dindore and Versteeg, 2005). As a result, many researchers designed and evaluated various cross-flow hollow fiber membrane contractors for CO₂ capture (Bhaumik et al., 1998; Albo et al., 2010; Cai et al., 2016).

TNO of the Netherlands developed and patented a cross-flow membrane module design as shown in Figure 2.4 (Jansen et al., 1994; Feron and Jansen, 1995; Feron and Jansen, 2002). In this membrane module the gas stream flows on the shell side perpendicular to the fibers and the absorption liquid flows in the membrane fibers. In this schematic, the overall relative flow of two phases in the module is countercurrent, but the shell-side flow to a single fiber is cross-flow. The benefits of this design include high mass transfer efficiency, low pressure drop, and easy scale-up. This cross flow module was successfully applied in a pilot plant for CO₂ capture from flue gases. Although the cross-flow module performs better than the parallel flow module, the mass transfer analysis of this module is relatively complicated due to the concentration changes of both fluids in the direction of flow and the direction perpendicular to flow. Dindore et al., 2005, from the University of Twente designed another similar cross-flow module and tested it for CO₂ absorption by using physical and chemical solvents. Heat transfer analysis in cross flow heat exchangers was adapted to describe the mass transfer process for this cross-flow gas/liquid membrane module. The simulation results of the analytical model were in good agreement with the experimental results. Junnasaksri, 2010, designed another type of cross-flow membrane module by installing baffles on the shell side of a parallel flow module.
Figure 2.4: A schematic diagram for a rectangular cross flow module

(Feron and Jansen, 2002)
As shown in Figure 2.5, the presence of baffles can prevent the shell-side fluid flowing parallel to the tube-side flow and generate a shell-side flow normal to the membrane surface. He evaluated this cross-flow module by capturing CO₂ from a mixture of CO₂ and air and compared its performance with a similar (unbaffled) module with no baffles. In his cross-flow membrane module, the gas stream flowed on the shell side and liquid entered the contactor on the tube side. The integration of baffles into the module was intended to improve the gas flow by converting a parallel flow into a cross flow. However, a small improvement of 5% in the overall mass transfer coefficient was obtained when compared with an unbaffled module under the same operating conditions (Junnasaksri, 2010). Such a minor improvement is due to the little impact of the gas phase on the overall mass transfer performance. Liqui-Cel® membrane contactor from Membrana, Germany is a commercially available baffled hollow fiber membrane contactor. It adapts baffles to offer a shell-side cross flow and can yield a high liquid-phase mass transfer coefficient. The initial development of this module is for de-aeration of liquids such as removal of CO₂ from water. Currently this membrane contactor has been utilized for lab-scale CO₂ absorption from simulated flue gases (Mavroudi et al., 2003, 2006; Porcheron and Drozdz, 2009).

### 2.3 Membrane Wetting

Three modes of operation for CO₂ absorption in hollow fiber membrane contactors were reported previously depending on the status of membranes, including non-wetted, completely wetted, and partially wetted. In the non-wetted mode, the membrane pores keep completely filled with gas over a prolonged period of operation time. In the completely or partially wetted mode, total or partial membrane pores are
Figure 2.5: A schematic diagram for a baffled hollow fiber membrane contactor

(Junmasaksri, 2010)
gradually filled with the absorption liquid. The mass transfer resistance caused by the liquid-filled membrane pores is much higher than that caused by the gas-filled membrane pores. As a consequence, occurring of membrane wetting can lead to a significant drop of overall mass transfer performance and deteriorate the long-term operation stability of hollow fiber membrane contactors (Wang et al., 2005; Lin et al., 2016). Mavroudi et al., 2006, studied the change of mass transfer resistance over time by absorbing CO₂ into water in a PP hollow fiber membrane module. Their experimental and simulation results indicated the mass transfer resistance from the liquid-filled membrane pores could account for more than 98% of the total membrane resistance and 20% - 50% of total resistance to absorption when only 13% of the membrane pores were wetted. Rajabzadeh et al., 2013, developed a mathematical model to simulate CO₂ absorption into MEA solutions using a PTFE hollow fiber membrane contactor under the non-wetted and wetted mode of operation. Simulation results showed when the membrane pores were only 10% wetted the gas absorption flux may decrease to 23% of the initial flux. Thus, the membrane-based CO₂ absorption should be preferably operated in the non-wetted membrane mode since it has a much lower membrane mass transfer resistance compared to the wetted modes.

In general hydrophobic membranes such as PTFE, PP, Polyethylene (PE) and Polyvinylidene fluoride (PVDF) as well as organic solvents with low surface tensions were selected for CO₂ absorption in hollow fiber membrane contactors. Large amounts of research work on membrane-based CO₂ absorption had focused on the membrane wetting studies. Most results demonstrated that membrane wetting cannot be completely prevented over a prolonged periods of operation (Rangwala, 1996; Yeon et al., 2003; Dindore et al., 2004; Zhang et al., 2008; Wang et al., 2013; Wang et al., 2014; Hashemifard et al., 2015). Rongwong et al., 2009, investigated the
PVDF membrane wetting potential by testing various single and mixed amine solutions including MEA, DEA, and AMP. Their results showed that neither single nor mixed solvents can avoid wetting the membrane over 12 days of operation. Wang et al., 2013, tested both PP and PVDF hollow fiber membranes for CO₂ absorption with MEA solution. Analysis from Wilson Plot method suggested the membrane resistance increased by 160% and 290% for PP and PVDF membrane systems after a 30-day operation. Khaisri et al., 2010, studied CO₂ absorption into MEA solutions using PTFE hollow fiber membranes by developing a mathematical model based on a partially wetted mode. Their model proposed the percentage of membrane wetting should be less than 40%. If membrane wetting exceeds this threshold the membrane cartridges should be replaced in order to maintain the best performance for CO₂ absorption. Membrane wetting can easily occur in the membrane-based absorption process to significantly deteriorate the overall mass transfer performance. Therefore, it has been significant impedance to the large scale long-term industrial application of membrane contactors for CO₂ absorption. Currently, a number of researchers dedicated to investigate the mechanism of membrane wetting and develop efficient methods for avoiding or mitigating membrane wetting.

2.3.1 Mechanism of Membrane Wetting

The membrane-solvent interaction was generally considered as the main reason for membrane wetting. However, the detailed mechanism of membrane wetting is still unclear because of the complexity of membrane-solvent interaction. Different explanations for membrane wetting had been proposed for different membrane module systems. The major discrepancy of these explanations is if the membrane wetting is caused by chemical reactions or physical interaction between the
membrane material and solvents. Wang et al., 2004, investigated the impact of DEA solution on the PP membrane surface morphology and surface tension. Their results suggested that membrane wetting may be due to possible chemical reactions between the PP membranes and DEA which change the surface tension of the membranes and decrease their hydrophobicity. Franco et al., 2008, also made a similar conclusion by contacting PP membranes with MEA solutions for CO₂ absorption from a CO₂/air stream. However, some researchers believed membrane wetting is only due to the physical interaction between the membrane pores and solvents (Wang et al., 2014). Rangwala, 1996, reported the membrane surface hydrophobicity was possibly modified by the penetration of trace impurities and ionic species in the solvent into the membrane pores. Lv et al., 2010, investigated the membrane wetting by immersing PP hollow fibers in the aqueous MEA, MDEA, and deionized water for up to 90 days, respectively. According to the characterization analysis of the membrane samples, they proposed an absorption-swelling wetting mechanism, in which the absorbent molecules penetrate into the membrane surface, leading to a swelling of the membrane pores. As a result, the membrane surface hydrophobicity is reduced significantly. They recommended that improving membrane surface hydrophobicity maybe effective for avoiding the occurrence of membrane wetting. Mansourizadeh et al., 2010, tested PVDF membranes for CO₂ absorption into water and NaOH solutions. They observed the phenomena of membrane wetting in the chemical absorption and attributed it to the possible membrane pore enlargement which was caused by the physical interaction between the chemical solvent and PVDF membranes.
2.3.2 Membrane Wetting Prevention

As discussed above, membrane wetting can be caused by the physical interaction or chemical reactions between the absorption solvents and membrane materials. If absorption liquids have a relatively high surface tension, such as water or inorganic solvents, they do not easily wet the commonly used hydrophobic membranes such as PTFE and PP over a prolonged operating time (Franken et al., 1987). However, the gas absorption in a membrane contactor usually adopts organic solvents which have been successfully applied in the traditional natural gas treatment process, such as alkanolamines. These solvents are easy to wet the hydrophobic membranes gradually since they have a lower surface tension than water. Therefore, the ease of membrane wetting (membrane wettability) depends on the properties of the membrane material and absorption solvent as well as their mutual interaction. The impacts of membrane and absorption solvent on membrane wetting can be determined by the surface tension of the liquid, contact angle of the liquid with the membrane, and membrane pore diameter (Kumar et al., 2002). In addition, the operating conditions of membrane contactors can affect the membrane wettability. For a given membrane module system, the absorption liquid may penetrate and wet the membrane pores due to a high pressure applied on the liquid. Kumar, 2002, determined the minimum pressure to be applied on the liquid phase to enter the membrane pores (breakthrough pressure) by using the Laplace-Young equation:

\[ \Delta p = -\frac{4\sigma_L \cos \theta}{d_{max}} \]  

(2.37)

Membrane wettability depends on the balance between the applied pressure on the liquid phase and the calculated breakthrough pressure. If the liquid-phase pressure is higher than the breakthrough pressure, the membrane is prone to wet gradually. So a
high breakthrough pressure is preferred since it allows the membrane contactor to operate at a wide range of liquid-phase pressures without wetting the membrane. As indicated in Equation (2.37), three strategies can increase the breakthrough pressure, including selection of an absorption liquid with a high surface tension, using the membrane with a small pore diameter, and increasing the cosine of contact angle of liquid with the membrane (Li and Chen, 2005). Current research work mainly focused on solvent screening, membrane surface treatment, and membrane manufacturing.

2.3.2.1 Solvent Screening

Researchers have studied various inorganic and organic solvents for CO₂ absorption in hydrophobic hollow fiber membrane contactors. Inorganic solvents such as deionized water, NaOH, and potassium carbonate (K₂CO₃) have high surface tensions and do not easily wet common hydrophobic membranes (Qi and Cussler, 1985; Franken et al., 1987; Dindore et al., 2005). However, their CO₂ absorption performance is much lower than traditional organic solvents used in the gas processing operation (Nii and Takeuchi, 1994). Alkanolamine solutions are the most commonly used organic absorption liquids for CO₂ absorption in hollow fiber membrane contactors since they offer high absorption performance and require moderate energy for solvent regeneration. However, their surface tensions and breakthrough pressures are lower compared to water (Li and Chen, 2005). As a result, they are prone to wet hydrophobic membranes including PP, PE, PVDF and even PTFE. Another issue is that alkanolamines may be degraded by reacting with other components in the gas streams, such as SO₂ in the flue gas. These degradation products may absorb into the PP membranes and reduce the hydrophobicity of the
membrane, eventually resulting in membrane wetting (Franco et al., 2009). To date, this issue has not been researched in detail.

Amino acid salts have become promising solvents which are able to efficiently avoid membrane wetting during the CO$_2$ absorption process (Kumar et al., 2002; Yan et al., 2007; Simons et al., 2010; Han et al., 2013). In 2002, TNO firstly patented a range of new absorption liquids named CORAL (CO$_2$ Removal Absorption Liquid). These advanced new absorption liquids were developed based on amino acid salts. Experimental results revealed that they possessed a similar CO$_2$ absorption performance to alkanolamines but without wetting PP membranes (Feron and Jansen, 1997). Their research work stimulated a number of researchers to examine amino acid salts either as absorption liquids or promoters in alkanolamine solutions for CO$_2$ absorption in hollow fiber membrane contactors (Kumar et al., 2002; Simons et al., 2010; Han et al., 2013). Glycinate solutions including sodium glycinate (SG) and potassium glycinate (PG) are the most popular amino acid salts used as absorption solvents for CO$_2$ absorption in membrane contactors (Portugal et al., 2007; Lu et al., 2009; Zhang et al., 2009; Weifeng et al., 2010; Eslami et al., 2011). PG has a considerable high CO$_2$ absorption capacity and a lower potential to wet membranes due to its higher surface tension than water, aqueous MEA and MDEA solutions (Yan et al., 2007; Portugal et al., 2009). A 10 wt% aqueous SG solution was found to offer even higher absorption capacity than MEA, MDEA and AMP (Song et al., 2006). Zhang et al., 2009, compared the performance of PG, MEA and MDEA by capturing CO$_2$ from flue gases using a PP membrane contactor. Their experimental results showed the CO$_2$ absorption performance of PG was better than MEA and MDEA under the same operating conditions. Rongwong et al., 2009, mixed SG with MEA solution and examined the performance of this mixed solvent in a PVDF membrane.
contactor. The addition of SG improved the CO$_2$ absorption flux and significantly mitigated the extent of membrane wetting.

Some researchers also examined several composite solvents based on the glycinate solution for CO$_2$ absorption in hydrophobic hollow fiber membrane contactors (Lu et al., 2009; Lu et al., 2010; Weifeng et al., 2010). For example, an activating chemical piperazine (PZ) was added into the glycinate salt solution which was examined for CO$_2$ absorption in a membrane contactor. Experimental and simulation results indicated that the overall mass transfer coefficient with the PZ activated glycinate salt solution was much higher than that of single glycinate salt solution (Lu et al., 2009; Lu et al., 2010). In addition to amino acid salts, AMP and PZ were also added into alkanolamine solutions as a promoter for CO$_2$ capture in hollow fiber membrane contactors (Mandal et al., 2003; Yeon et al., 2004; Lu et al., 2005; Lu et al., 2007; Lin et al., 2009; Chen et al., 2010). Experimental results found that the addition of either AMP or PZ in the MDEA solutions can efficiently enhance the mass transfer of CO$_2$ in a hollow fiber module even a little amount was added (Lu et al., 2007). PZ is more effective in increasing the mass transfer than AMP. However, no experimental results have shown that the composite solvents are able to help prevent membrane wetting.

2.3.2.2 Membrane Surface Modification and Manufacturing

In general, hydrophobic membranes including PTFE, PP, PE and PVDF have been widely examined for CO$_2$ absorption in hollow fiber membrane modules. Experimental results from Khaisri et al., 2009, showed that the PTFE membranes has a superior CO$_2$ absorption performance to the other three members. For a long-term operating study, PTFE membranes was able to remain a stable absorption
performance over 60 hours without being wetted by absorption liquids. However, commercially available PTFE membranes are usually made in relatively large diameters and expensive. Therefore, the economic feasibility of CO$_2$ absorption by using PTFE membranes is limited, especially when compared to traditional packed columns.

Compared to PTFE membranes, PP membranes are commercially available at affordable costs and in a wide range of diameters. PP membranes in CO$_2$ membrane absorption systems can initially maintain a stable and comparable performance to PTFE membranes. However, a number of experiments found that their performance would drop rapidly and greatly over a prolonged period of operation due to membrane wetting (Rangwala, 1996; Wang et al., 2004; Wang et al., 2005; Mavroudi et al., 2006; Franco et al., 2008; Lv et al., 2010). In order to reduce or prevent PP membrane wetting researchers attempted to add a superior hydrophobic surface coating on the PP membranes (Lv et al., 2012). Franco et al., 2012, successfully fabricated coated PP membranes sputtered with an ultrathin PTFE surface in a radio frequency plasma reactor and examined their CO$_2$ absorption performance in MEA solutions. The coated PP membranes showed a superior performance to the untreated PP membranes for at least 45 hours of operating time. After twenty-five days of operation the treated membranes became partially wetted. But the extent of the wetting was still relatively low compared to the plain PP membranes and the mass transfer performance of the coated PP membranes was found comparable to the PTFE membranes. Nguyen et al., 2011, developed a dense skin composite PP membrane by coating with two glassy polymers including Teflon AF 2400 and poly(1-(trimethylsilyl)-1-propyne. This composite PP membrane was examined for CO$_2$ absorption from a gas mixture by using MEA solutions. Results revealed that the dense skin provided an effective
wetting protection for PP membrane without significantly scarifying the mass transfer rate. Two novel composite hollow fiber membranes were manufactured by coating a thin layer of poly(4-methyl-2-pentyne) and a Teflon-AF on PP membranes, respectively (Chabanon et al., 2011). The membrane wetting resistance of these two composite membranes was examined by continuously absorbing CO₂ in the MEA solution over 1000 hours and compared with PTFE and PP membranes. Results showed that the composite membranes initially had a lower CO₂ absorption flux when compared to the PP and PTFE membranes. This decreased performance is reasonable and attributed to the extra mass transfer resistance imposed by their hydrophobic dense skins. Interestingly, due to the gradual wetting of PP and PTFE membranes by the solvent, the absorption flux of the composite membranes became comparable to PTFE membranes and even significantly exceeded the PP membranes over 500 hours of operation. This type of behavior further confirmed the effective protection of dense skins on PP membrane wetting.

Recently many researchers manufactured and examined PVDF membranes for CO₂ absorption in hollow fiber membrane contactors since they have relatively high hydrophobicity and reasonable costs. Most of the PVDF hollow fiber membranes were made through the wet/dry phase inversion method. The addition of different non-solvent promoters in the spinning dope may change the membrane structure and performance. Lithium chloride (LiCl) can be used as a non-solvent additive in the polymer dope for PVDF membrane manufacturing (Mansourizadeh and Ismail, 2010; Mansourizadeh et al., 2010). Mansourizadeh and Ismail, 2011, examined the morphology, gas permeation and mass transfer resistance of the prepared PVDF membranes and tested for CO₂ absorption in the distilled water. They reported that CO₂ flux of prepared PVDF membranes can be up to 68% higher than plain PVDF
membranes. Although the CO₂ flux of the PVDF membranes was gradually decreased by 23% during the initial 26 hours, afterwards a constant stability of performance can be achieved for over 140 hours of the operation. A number of other polymer dope additives have been investigated for manufacturing PVDF membranes with different structures (Atchariyawut et al., 2006; Ismail and Mansourizadeh, 2010; Mansourizadeh et al., 2010; Mansourizadeh and Ismail, 2011). For example, glycerol, phosphoric acid, ethanol, and polyethylene glycol (PEG-400) were examined as additives in the polymer dope to manufacture PVDF membranes (Mansourizadeh and Ismail, 2011). The morphology examination of the prepared PVDF membranes discovered an almost sponge-like membrane structure in the PVDF membranes with PEG-400, glycerol, or phosphoric acid as an additive, while a finger/sponge-like structure in the PVDF membranes with ethanol as an additive. Results from physical absorption of CO₂ showed that the CO₂ flux in PVDF/glycerol membranes was superior to the other manufactured membranes. Atchariyawut et al., 2006, manufactured PVDF membranes by using N-methyl-2-pyrrolidone and three different additives, including distilled water, phosphorous acid, and glycerol, respectively. A gas-liquid membrane contactor equipped with the manufactured PVDF membranes was examined for pure CO₂ absorption in the distilled water. An observed constant CO₂ flux of three PVDF membranes over 15 days of operation indicated the prepared PVDF membranes have a long-term effective resistance to membrane wetting. The CO₂ absorption flux increased in the order of phosphorous acid > glycerol > distilled water. Another research compared the PVDF membranes with phosphoric acid as an additive with the PVDF membranes prepared with lithium chloride monohydrate (LiCl·H₂O) as additive. The former could achieve over 30% higher CO₂ absorption
flux in the distilled water than the latter as well as the commercial PTFE membranes (Mansourizadeh et al., 2010).

Lastly, some researchers have found that internal coagulants also have a great impact on membrane structure and absorption performance via the phase inversion method. Xu et al., 2008, selected three different internal coagulants to fabricate PVDF membranes, which includes water, ethanol-water, and dimethylacetamide (DMAc)-water solutions. The examination of the membrane cross-sections by scanning electron microscopy (SEM) indicated the membrane thickness and structure of the inner skin layer may be different when using different internal coagulants. Using of the DMAc-water solutions as a coagulant can form PVDF membranes with an inner skinless surface, which had a comparable CO₂ absorption performance to PTFE membranes. In addition, Feng et al., 2011, confirmed that the inner skinless surface of PVDF membranes had a higher gas permeation rate and lower membrane resistance than membranes with a double skin structure. However, researchers also found the deformation issues of PVDF membranes when contacting with NaOH at high pH values (Alchikh et al., 2010). Two factors were attributed to the deformation of PVDF: a high stress and a high pH of solution. However, neither single factor was found to cause the membrane deformation (Hinksman et al., 2000).

2.4 Reaction Mechanisms of CO₂ Absorption with Alkaline Solvents

Absorption solvents for CO₂ absorption can be classified as physical solvents and chemical solvents. Chemical solvents are generally preferred since they have much higher absorption capacities and faster absorption rates compared to the physical solvents due to their rapid chemical reactions. Since CO₂ is an acid gas, these chemical solvents are generally alkaline solutions.
Alkanolamine solutions have been widely used as chemical solvents for almost eighty-five years in the acid gas treating industry since they have high reactivity and absorption capacities (Zhao et al., 2012). Based on the replacement of the hydrogen molecule on the nitrogen atom alkanolamines can be grouped into three classifications: primary, secondary and tertiary amines. Primary amines and secondary amines have rapid reactions with CO$_2$ to form carbamates. But they have moderate CO$_2$ loading capacities up to 0.5 mol of CO$_2$ per mol of amine (Versteeg and Rubin, 2011). Their regeneration costs are relatively high because their energy demands for CO$_2$ desorption is high. While tertiary amines mainly react with CO$_2$ to form bicarbonates through the CO$_2$ hydrolysis reaction with low reaction heat released. Thus they have lower reactivity with CO$_2$ but lower regeneration costs than primary and secondary amines. The maximum CO$_2$ loading capacity of tertiary amines is 1.0 mol of CO$_2$ per mol of amine (Versteeg and Rubin, 2011).

Aqueous ammonia has recently become a promising alternative to alkanolamine solutions for CO$_2$ capture due to its several advantages, including a low cost, a high absorption capacity, a low energy demand for solvent regeneration, and no corrosion and degradation problems. In 2008, Gal developed a chilled ammonia process for CO$_2$ capture from various combustion gases (Niu et al., 2013). This process is similar to the traditional CO$_2$ absorption process, but uses aqueous ammonia as an absorption solvent instead of alkanolamine solutions. The operating temperature is typically limited in the range of 0-283 K for preventing NH$_3$ losses from evaporation (Niu et al., 2013). However, these low temperatures restrict the reactivity and absorption capacity of aqueous ammonia. Recently, the aqueous ammonia process has been widely studied. In this process, CO$_2$ absorption into aqueous ammonia was carried out at room temperatures, typically 298-313 K.
(Bandyopadhyay, 2011). At room temperatures, the absorption capacity of NH$_3$ solvents was found over two times higher than those of MEA solvents (Bai and Yeh, 1997).

### 2.4.1 Reaction Mechanism between CO$_2$ and MEA

MEA is a primary amine, which has been widely applied for various acid gas removal processes in the world. In 1990, 40% CO$_2$ separation industries used MEA as an absorption solvent (Ahn et al., 2011). The zwitterion mechanism originally proposed by Caplow in 1968 has been generally accepted for explaining the reactions between MEA and CO$_2$ (Linnenberg et al., 2012; Mondal et al., 2012). The zwitterion mechanism mainly includes two steps: formation of zwitterion and deprotonation of zwitterion. Based on the zwitterion mechanism, Aboudheir, 2002, summarized all possible reactions between MEA and CO$_2$:

**Step 1:** MEA ($RNH_2$) reacts with CO$_2$ to form a zwitterion as an intermediate:

\[
CO_2 + RNH_2 \xrightarrow{k_{3,2}} RNH_2^+COO^- \quad (2.38)
\]

where the ethanol component of MEA, which is $-\text{CH}_2\text{CH}_2\text{OH}$, is defined as R.

**Step 2:** The zwitterion deprotonates by a base or bases in the solution resulting in carbamate formation. The contribution of each base to the overall reaction rate relies on the concentration and strength of the base (Zhang and Guo, 2013). The major bases, contributing to the deprotonation of the zwitterion in the MEA solution, include MEA itself, hydroxide and water:

\[
RNH_2^+COO^- + RNH_2 \xrightarrow{k_{3,2}} RNH_3^+ + RNHCOO^- \quad (2.39)
\]

\[
RNH_2^+COO^- + H_2O \xrightarrow{k_{3,3}} H_3^+O + RNHCOO^- \quad (2.40)
\]
Since CO\textsubscript{2} loaded MEA solutions were used in the most CO\textsubscript{2} absorption studies, the contributions of bicarbonate and carbonate in the solution are possibly significant. Thus these species should be accounted as base for zwitterion deprotonation:

\[
RNH\textsubscript{2}\textsuperscript{+}COO\textsuperscript{-} + OH\textsuperscript{-} \rightleftharpoons H\textsubscript{2}O + RNHCOO\textsuperscript{-} \quad (2.41)
\]

\[
RNH\textsubscript{2}\textsuperscript{+}COO\textsuperscript{-} + HCO\textsubscript{3}\textsuperscript{-} \rightleftharpoons H\textsubscript{2}CO\textsubscript{3} + RNHCOO\textsuperscript{-} \quad (2.42)
\]

\[
RNH\textsubscript{2}\textsuperscript{+}COO\textsuperscript{-} + CO\textsubscript{3}\textsuperscript{2-} \rightleftharpoons HCO\textsubscript{3}^- + RNHCOO\textsuperscript{-} \quad (2.43)
\]

In the mean time, there are a number of other reactions occurring during the CO\textsubscript{2} absorption in the MEA solution. They are presented as follows:

**Water ionization:**

\[
2H\textsubscript{2}O \rightleftharpoons OH\textsuperscript{-} + H\textsubscript{3}O^+ \quad (2.44)
\]

**Dissociation of dissolved CO\textsubscript{2} and bicarbonate:**

\[
CO\textsubscript{2} + 2H\textsubscript{2}O \rightleftharpoons HCO\textsubscript{3}^- + H\textsubscript{3}O^+ \quad (2.45)
\]

\[
HCO\textsubscript{3}^- + H\textsubscript{2}O \rightleftharpoons CO\textsubscript{3}\textsuperscript{2-} + H\textsubscript{3}O^+ \quad (2.46)
\]

**Bicarbonate formation:**

\[
CO\textsubscript{2} + OH\textsuperscript{-} \rightleftharpoons HCO\textsubscript{3}^- \quad (2.47)
\]

**Reversion of carbamate to bicarbonate (hydrolysis reaction)**

\[
RNHCOO\textsuperscript{-} + H\textsubscript{2}O \rightleftharpoons RNH\textsubscript{2} + HCO\textsubscript{3}^- \quad (2.48)
\]

**Dissociation of protonated MEA:**
where $K$ is the equilibrium constant, $k_i$ and $k_{-i}$ is the forward and reverse rate coefficient for reaction $i$, respectively.

2.4.2 Reaction Mechanism between CO$_2$ and NH$_3$

The overall reaction rate of CO$_2$ absorption in the aqueous ammonia is determined by two reactions: bicarbonate formation between CO$_2$ and hydroxide ion, and reaction between CO$_2$ and NH$_3$ (Derks and Versteeg, 2009). The reaction between CO$_2$ and NH$_3$ is similar to the one between CO$_2$ and MEA, which is via the zwitterion mechanism. At first, CO$_2$ reacts with NH$_3$ to form a zwitterion. Next, the zwitterion is deprotonated by bases in the solution. In the aqueous ammonia, water and NH$_3$ were considered as dominant bases, which contribute to the zwitterion deprotonation (Qin et al., 2010; Darde et al., 2011). The reactions for CO$_2$ absorption in the aqueous ammonia can be expressed as following:

The formation of bicarbonate:

$$CO_2 + OH^- \overset{k_{10}}{\rightleftharpoons} HCO_3^- \tag{2.47}$$

Reaction of NH$_3$ and CO$_2$ to form a zwitterion as an intermediate:

$$CO_2 + NH_3 \overset{k_{13}}{\rightleftharpoons} NH_3^+COO^- \tag{2.50}$$

Deprotonation of zwitterion by the dominant bases in the solution:

$$NH_3^+COO^- + NH_3 \overset{k_{14}}{\rightleftharpoons} NH_2COO^- + NH_4^+ \tag{2.51}$$
2.5 Scale-Up of the Membrane Gas Absorption Technology

CO₂ absorption using membrane technology has been extensively studied at the bench scale level. This technology has been approved to have a higher absorption performance than traditional packed columns under the same operating condition. However, many experimental studies revealed that hollow fiber membranes may be partially or completely wetted during the CO₂ absorption process, resulting in a significant and rapid reduction of CO₂ absorption performance and deterioration of the long-term stability of membrane operation. Thus membrane wetting is the major obstacle for the commercial application of this technology. Several pilot-scale studies had been carried out for CO₂ absorption from various industrial waste gases by using the membrane contactor technology, such as natural gas and flue gas. They were all successful in operation and reported positive results as well as some practical problems.

Starting from 1992, Kværner Process Systems (KPS) has begun to design gas/liquid membrane contactors and develop efficient process simulation tools for different applications by working with many collaborators in the world. KPS designed a gas/liquid membrane contactor at the Statoil Gas Terminal at Kårst φ, K-Lab for exhaust gas treatment from a gas turbine on an offshore installation. This pilot-scale unit had been successfully operated for 7000 hours from autumn 1998 to August 2001. 85% (54.2 g/s) of the CO₂ was removed from the exhaust gas, which had a flow rate of 725 g/s. By comparing to the conventional amine treating process, the membrane contactor technology could potentially save 35-40% of the capital cost.
and 38-42% of the operational costs (Falk-Pedersen et al., 2005). A pilot scale membrane contactor has also been tested for natural gas treatment at a large gas terminal in Scotland. An activated MDEA solution was used as an absorption solvent and eight different membrane modules were tested. The longest testing time for one module was about 5000 hours from January to October in 1999. No decrease in the membrane performance was observed during all testing periods. Similar results have been achieved from another pilot-scale test by KPS at the Shell/Tejas Gas Fandango gas plant in Texas. Natural gas with 6% CO₂ was treated in a gas/liquid membrane contactor by using a physical solvent over twenty weeks’ operation.

Besides KPS, a number of pilot-scale membrane absorption contactors have been designed and tested for CO₂ capture from simulated or even real flue gas. Yan et al., 2007, built a hollow fiber membrane contactor with 1.0 m module length and 7000 PP membrane fibers. Three absorbents including MEA, MDEA and PG were examined to absorb CO₂ from a gas mixture in this contactor. The experimental results showed the aqueous PG solution could maintain 90% of CO₂ removal efficiency for 40 hours and has a better performance than MEA and MDEA solutions under the same operating condition.

Some issues were also occurred and reported during the scale-up studies of membrane contactor technology. Cooperative Research Centre for Greenhouse Gas Technology (CO2CRC) has built a pilot-scale gas/liquid membrane contactor for capturing CO₂ from real flue gas, which was generated from a coal fired power station. This pilot study tested three commercially available membranes including PP, PTFE and Polydimethylsiloxane (PDMS) and an amino acid based PuraTreat™ F solvent. The experiment results indicated that this membrane absorption system could also
efficiently absorb Nitrogen oxides (NOx) into the solvent. However, the porous PP and PTFE membranes were significantly wetted during the pilot-scale study due to the difficulty in controlling the membrane pressure differential (Scholes et al., 2014). Chabanon et al., 2014, conducted both lab-scale and pilot-scale experiments for absorbing CO$_2$ into MEA solvents by using PTFE membrane contactors. They developed a 2D mathematical model based on the lab-scale membrane module. By validating the simulation results with the experimental results, they found that this simple model could not agree well with the pilot-scale experimental results. They believed that the mal-distribution of the flows around and inside of the fibers and remarkable temperature rise over the length of the fibers have great impacts on the CO$_2$ absorption performance in the large scale system and has to be considered in the simulation model. These previous studies indicated the scale-up of a hollow fiber membrane contactor might not as easy as straightforward. Further detailed scale-up studies are necessary.
CHAPTER 3: EXPERIMENTAL SETUP AND PROCEDURES

3.1 Experimental Setup

A large amount of experiments were conducted to investigate the absorption performance of CO₂ into aqueous ammonia using a hollow fiber membrane contactor. The experimental work consisted of three parts: (1) tested the compatibility among the NH₃ solvent, membrane material and membrane cartridge sealant; (2) investigated CO₂ absorption performance into aqueous ammonia under different operating parameters; and (3) tested and compared the CO₂ absorption performance of aqueous ammonia and MEA under the same experimental condition. In order to complete the experimental work, a lab-scale gas absorption membrane system was designed and built in the Clean Energy Technologies Institute (CETI) at the University of Regina. A schematic diagram of the experimental setup is shown in Figure 3.1. A picture of the experimental system is given in Figure 3.2. The experimental setup consists of the following:

1) A hollow fiber membrane contactor, in which CO₂ in the gas stream was absorbed by the liquid solvent;

2) Two mass flow controllers (Aalborg, United States) for controlling CO₂ and air flow rates, respectively. They were calibrated with a Humonics Outflows 650 soap flow meter (Sigma-Aldrich, United States);

3) A gas mixer for mixing the air and CO₂;

4) A gas filter for removing any impurities at the inlet of the gas phase;
Figure 3.1: A schematic diagram of experimental setup for the gas absorption membrane system
Figure 3.2: A picture of gas absorption experimental setup
5) Two solution containers (0.01 m³) for containing lean and rich solutions, respectively;

6) A digital gear pump (Cole-Parmer, United States) for delivering the solution in the system; and,

7) An IR CO₂ analyzer (Model 302 WP) from Nova Analytical Systems Inc. for CO₂ concentration measurement with a testing range of 0.0% to 20.0% by volume.

The outlet gas stream from the membrane contactor may contain gaseous NH₃, which may interfere with the CO₂ measurement accuracy of the IR analyzer. Thus one 0.25×10⁻³ m³ Erlenmeyer flask was placed prior to the IR analyzer for treating gaseous NH₃ in the treated gas stream. The Erlenmeyer flask contains a 0.1×10⁻³ m³ 40% sulfuric acid (H₂SO₄) solution for removing gaseous NH₃.

3.2 Membrane Contactor

This study adopted the gas absorption membrane module originally designed by deMontigny, 2004. This module offers removable membrane cartridges and provides a number of gas, liquid and temperature sampling points along the height of the module. Figure 3.3 shows the schematic layout of a single membrane module. This module was made from acrylic since it is chemically compatible with alkanolamine solutions and allows visible observation of internal shell side activity as well as inspection of the membrane conditions. The inner and outer diameters of the module are 0.028 and 0.034 m, respectively. A membrane cartridge was inserted into the module and sealed at both ends with 0.028 m rubber O-rings. Previous
Figure 3.3: A Schematic layout of a single membrane module
experimental results indicated the liquid flowing in the tube offers a higher absorption flux than that in the shell side (Junnasaksri, 2010). Thus in all experiments of this study the liquid solvent flowed in the tube from the bottom to the top of the column and the gas flowed counter-currently in the shell side. In addition, this module can be connected to additional modules through its flanges to add capacity. Figure 3.4 shows the layout of two serial membrane modules. In this system, the gas phase flows from one module to the other module in the shell side via the gas bypass tubing.

Previous studies have tested three types of hollow fiber membrane materials including PTFE, PP and PVDF using this membrane contactor (deMontigny, 2004; Khaisri, 2009). In this study PTFE membranes were selected for CO$_2$ absorption into aqueous ammonia since they offer the largest inner diameter and more durable performance compared to the others. The characteristics of the PTFE membranes are shown in Table 3.1. The membrane cartridge was made by potting each end of PTFE membranes to an acrylic disc. In order to ensure no leaking between the lumen side and shell side, the membranes were potted by applying an epoxy resin (Loctite E-60NC Hysol® epoxy). The detailed procedure of membrane potting can be referred from deMontigny, 2004.

3.3 Materials

A number of chemicals were purchased and used for the CO$_2$ absorption experiment. The mixed gas stream included air and CO$_2$. The absorption solvents were aqueous MEA and aqueous ammonia. 100 mol/m$^3$ hydrochloric acid (HCl) and methyl orange were used for liquid sample titration and CO$_2$ loading analysis. 40% H$_2$SO$_4$ solution was used to remove gaseous NH$_3$ from the treated gas stream.
Figure 3.4: A layout of two serial membrane modules
Table 3.1: Characteristics of the PTFE membrane

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Outer diameter ($\times 10^{-3}$ m)</th>
<th>Inner diameter ($\times 10^{-3}$ m)</th>
<th>Length (m)</th>
<th>Porosity (%)</th>
<th>Mean pore size ($\times 10^{-7}$ m)</th>
<th>Fibers per module</th>
</tr>
</thead>
<tbody>
<tr>
<td>Markel Corporation (United States)</td>
<td>1.920</td>
<td>1.499</td>
<td>0.122</td>
<td>0.34</td>
<td>2.57</td>
<td>57</td>
</tr>
</tbody>
</table>
Aqueous solutions of these chemicals were prepared to desired concentrations by diluting with de-ionized water provided in the laboratory. The CO₂ loadings were prepared by dissolving appropriate amount of NH₄HCO₃ solids into aqueous ammonia. Properties of these chemicals are presented in Table 3.2.

3.4 Experimental procedure and analysis

The CO₂ absorption experiments were implemented by contacting the gas with the liquid in the hollow fiber membrane contactor. As shown in Figure 3.2 above, the mixed gas stream was first introduced to the top of the membrane contactor where it flowed downward and exited at the bottom of the membrane contactor. Then the treated gas stream passed through a 0.15×10⁻³ m³ 40 wt% H₂SO₄ scrubber to remove gaseous NH₃ before entering the CO₂ IR analyzer. The IR analyzer was used to measure the outlet CO₂ concentration in the gas stream over time. Once the outlet CO₂ concentration was steady, a prepared absorption solution was pumped to the bottom of the membrane contactor and counter-currently contacted with the gas stream. The solution flowed upward and left at the top of contactor. For all the experiments, the absorption liquid flowed in the tube and the gas stream flowed in the shell side. The inlet liquid samples were collected in the lean solution container before each experiment. The outlet liquid samples were withdrawn at the liquid sampling point at the top of the membrane contactor. The gaseous and liquid samples were only taken when the system reached a steady-state condition, in which the outlet CO₂ concentrations remained constant over time. The experimental conditions are presented in Table 3.3.
Table 3.2: Properties of chemicals used in the CO\textsubscript{2} absorption experiment

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>/</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Carbon dioxide (CO\textsubscript{2})</td>
<td>99.5%</td>
<td>Praxair</td>
</tr>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>≥99%</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Aqueous ammonia</td>
<td>28-30%</td>
<td>VWR</td>
</tr>
<tr>
<td>Ammonia bicarbonate (NH\textsubscript{4}HCO\textsubscript{3})</td>
<td>≥99%</td>
<td>VWR</td>
</tr>
<tr>
<td>Hydrochloric acid (HCl)</td>
<td>1000 mol/m\textsuperscript{3}</td>
<td>VWR</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>0.1 wt.%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Sulfuric acid (H\textsubscript{2}SO\textsubscript{4})</td>
<td>95-98%</td>
<td>VWR</td>
</tr>
</tbody>
</table>
Table 3.3: Experimental conditions for CO$_2$ absorption

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>294.15, 294.65, 295.15</td>
</tr>
<tr>
<td>Inert gas flow rate ($\times 10^{-5} \text{ m}^3/\text{s}$)</td>
<td>5.0</td>
</tr>
<tr>
<td>Inlet partial pressure of CO$_2$ (%)</td>
<td>10%, 15%, 20%</td>
</tr>
<tr>
<td>Liquid flow rate ($\times 10^{-6} \text{ m}^3/\text{s}$)</td>
<td>0.55 - 3.8</td>
</tr>
<tr>
<td>Concentration of NH$_3$ ($\times 10^3 \text{ mol/m}^3$)</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>Inlet CO$_2$ loading (mol CO$_2$/mol NH$_3$)</td>
<td>0.10, 0.20, 0.30</td>
</tr>
</tbody>
</table>
A standard titration method was used to determine the concentration of NH₃ in a known volume of liquid sample. HCl acid (1000 mol/m³) was used as a titrant with methyl orange as an indicator. The NH₃ concentration was calculated as follows:

\[ C_{NH₃} = \frac{C_{HCl} \times V_{HCl}}{V_{NH₃}} \]  

(3.1)

The CO₂ loading of liquid samples was determined by using a CO₂ loading measurement apparatus as shown in Figure 3.5. The testing procedure was modified according to the procedure outlined by the Association of Official Analytical Chemist (Horwitz et al., 1975). At the beginning of the test, set the displacement solution in the leveling bulb to the zero position. A 3.0×10⁻⁶ m³ liquid sample was added into 5×10⁻⁵ m³ deionized water in a 0.25×10⁻³ m³ flask. The flask was sealed by a rubber stopper and the diluted sample was quickly titrated with 5×10⁻⁶ m³ 40 wt% H₂SO₄. After titration, the flask was gently shaken by hand several times. Then the sample was stirred for five minutes to release all of absorbed CO₂ into a gas burette. While the sample was stirring, the leveling bulb was lowered to decrease the pressure of the gas burette. Once the agitation was completed, the leveling bulb was adjusted to the same level as the liquid inside the graduated gas burette and the volume of released gas was recorded. The amount of CO₂ absorbed in the liquid sample was obtained according to the recorded volume in the gas burette before and after the acid titration. The liquid sample must be diluted first and the measurement process must be as quick as possible to minimize the effect of NH₃ vaporization on the measurement accuracy. The CO₂ loading was determined according to the following equation:

\[ \alpha_{CO₂} = \frac{n_{CO₂}}{n_{NH₃}} = \frac{V_{CO₂} \times 1000 \times 273.15}{22.414 \times T \times C_{NH₃} \times V_{NH₃}} \]  

(3.2)
Figure 3.5: CO$_2$ loading measurement apparatus
Four NH₃ solutions with known CO₂ loadings were prepared and tested by following the above CO₂ loading test procedure to check the testing accuracy. Relative errors (RE) were calculated as following:

\[ RE = \frac{|\text{Measured CO}_2 \text{ loading} - \text{Known CO}_2 \text{ loading}|}{\text{Known CO}_2 \text{ loading}} \times 100\% \]  

(3.3)

As shown in Table 3.4, relative errors are less than 2%. Thus this test procedure is valid and accurate for the CO₂ loading measurement.

The validity of each experimental result was verified by using Equation (3.4) to check the mass balance of CO₂ in the system. Ideally, the amount of CO₂ absorbed into the liquid should be the same as that removed from the gas stream. However, experimental errors always occur. Considering the impact of strong vaporization of NH₃ at ambient temperatures, experimental results within a mass balance error of ±10% were accepted as valid.

\[ \text{Mass balance error} = \frac{\text{Absorbed CO}_2 - \text{Removed CO}_2}{\text{Absorbed CO}_2} \times 100\% \]  

(3.4)

3.5 Data Analysis

The CO₂ absorption performance was evaluated by using the \( K_G a_v \). Since the single membrane module is very small, it is hard to accurately determine the profile of concentration gradient \( (dY/dZ) \) of Equation (2.15). The empirical approach was adopted to calculate the average \( K_G a_v \) for a single membrane module by assuming the \( K_G a_v \) to be constant along the length of the module. It is represented in terms of a log-mean driving force (deMontigny, 2004):

\[ K_G a_v = \frac{g_i (Y_B - Y_T)}{Z_P (Y_T - y_G)_{IM}} \]  

(2.17)
\[ (y_G - y_G^*)_{\text{Im}} = \frac{(y_G - y_G^*)_B - (y_G - y_G^*)_T}{\ln \frac{(y_G - y_G^*)_B}{(y_G - y_G^*)_T}} \] (2.18)

The subscripts \( B \) and \( T \) refer to the bottom and top of the membrane module.

### 3.6 Laboratory Safety

All experiments were carried out at the membrane absorption laboratory of University of Regina. The laboratory is equipped with an air ventilation system to minimize the exposure to odoriferous or toxic substances and a plumbed emergency shower and eyewash. Prior to starting the experiment, the Chemical and Laboratory Safety Training and the Workplace Hazardous Material Information System Training were taken. The university laboratory health and safety acts and regulations were complied while conducting the experimental work in the laboratory. Personal protective equipments were used, including safety goggles, fully covered lab coats, chemical protective gloves, and safety footwear. Aqueous ammonia is a solution of \( \text{NH}_3 \) in water with a strong pungent odor. The \( \text{NH}_3 \) vapor is toxic and irritating. Thus preparation of \( \text{NH}_3 \) and MEA solutions was conducted in a closed fume hood. Liquid wastes were collected in 0.01 m\(^3\) waste containers and sent to the Science Store for proper waste disposal. Accidental chemical spills were cleaned up immediately and properly by using a laboratory spill kit, and reported to the laboratory manager.
Table 3.4: Relative errors of CO₂ loading tests

<table>
<thead>
<tr>
<th>Concentration of NH₃ (×10³ mol/m³)</th>
<th>Known CO₂ loading (mol/mol)</th>
<th>Measured CO₂ loading (mol/mol)</th>
<th>RE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>0.276</td>
<td>0.275</td>
<td>0.36</td>
</tr>
<tr>
<td>1.29</td>
<td>0.293</td>
<td>0.288</td>
<td>1.71</td>
</tr>
<tr>
<td>2.54</td>
<td>0.100</td>
<td>0.100</td>
<td>0.00</td>
</tr>
<tr>
<td>3.74</td>
<td>0.186</td>
<td>0.188</td>
<td>1.08</td>
</tr>
</tbody>
</table>
4.1 Description of the Experimental Program

The objective of this experimental work was to study the performance of aqueous ammonia as a solvent for CO$_2$ absorption in a PTFE hollow fiber membrane contactor. The experimental work consisted of three tasks. Task 1 was the feasibility study of CO$_2$ absorption into the aqueous ammonia in a previously used PTFE membrane contactor. This work explored the capability of CO$_2$ absorption into the aqueous ammonia in the PTFE membrane contactor, which established a solid foundation for further more detailed experimental and numerical studies. Task 2 studied the mass transfer performance of CO$_2$ absorption into the aqueous ammonia in the PTFE membrane contactor. In this task a brand new membrane cartridge was fabricated in the laboratory and used for all experiments. A number of CO$_2$ absorption experiments were conducted by varying several operating parameters, including inlet CO$_2$ partial pressure, liquid velocities, solvent concentration, and CO$_2$ solution loading. A study of long-term membrane operation was also conducted to investigate the performance stability of CO$_2$ absorption into aqueous ammonia in the PTFE membrane contactor. In Task 3, MEA solvents were used for CO$_2$ absorption under the same operating condition as NH$_3$ solvents. The MEA solvent functioned as a benchmark to compare and assess the absorption performance of the aqueous ammonia. An example of experimental results is given in Table 4.1. The following sections discuss the experimental results in detail.
Table 4.1: An example of experimental log

<table>
<thead>
<tr>
<th>Description</th>
<th>PTFE (N01)</th>
<th>PTFE (N02)</th>
<th>PTFE (N03)</th>
<th>PTFE (N04)</th>
<th>PTFE (N05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>295.15</td>
<td>295.15</td>
<td>295.15</td>
<td>295.15</td>
<td>295.15</td>
</tr>
<tr>
<td>Inert Gas Flow Rate ($\times 10^{-3}$ m$^3$/s)</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>CO$_2$ Flow Rate ($\times 10^{-6}$ m$^3$/s)</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>NH$_3$ Concentration ($\times 10^3$ mol/m$^3$)</td>
<td>2.02</td>
<td>2.02</td>
<td>2.02</td>
<td>2.02</td>
<td>2.02</td>
</tr>
<tr>
<td>Liquid Flow Rate ($\times 10^{-6}$ m$^3$/s)</td>
<td>0.55</td>
<td>1.42</td>
<td>2.25</td>
<td>3.11</td>
<td>3.81</td>
</tr>
<tr>
<td>Inlet CO$_2$ concentration (%)</td>
<td>10.10</td>
<td>10.10</td>
<td>10.10</td>
<td>10.10</td>
<td>10.10</td>
</tr>
<tr>
<td>Outlet CO$_2$ concentration (%)</td>
<td>8.99</td>
<td>8.86</td>
<td>8.83</td>
<td>8.74</td>
<td>8.65</td>
</tr>
<tr>
<td>Inlet CO$_2$ loading (mol/mol)</td>
<td>0.102</td>
<td>0.102</td>
<td>0.102</td>
<td>0.102</td>
<td>0.102</td>
</tr>
<tr>
<td>Outlet CO$_2$ loading (mol/mol)</td>
<td>0.127</td>
<td>0.115</td>
<td>0.110</td>
<td>0.109</td>
<td>0.108</td>
</tr>
<tr>
<td>Mass Balance Error (%)</td>
<td>-8.88</td>
<td>8.69</td>
<td>-3.09</td>
<td>5.88</td>
<td>7.09</td>
</tr>
</tbody>
</table>
4.2 Feasibility Study

Makhloifi et al., 2014, studied the feasibility of CO\(_2\) absorption into aqueous ammonia in a PP hollow fiber membrane contactor. Their experimental results showed the micro-porous PP membranes could not maintain a stable CO\(_2\) absorption performance. This performance failure was caused by precipitation of ammonium salt in the membrane which blocks the membrane pores. Thus, at the beginning of this study, a number of experiments were carried out to examine the feasibility of CO\(_2\) absorption into the aqueous ammonia in a PTFE hollow fiber membrane contactor.

Firstly, a used membrane cartridge as shown in Figure 4.1 was adopted to test the compatibility among the membrane material, the sealant, and the aqueous ammonia. A schematic layout of a single membrane cartridge is given in Figure 4.2. As shown in Figure 4.2, the membrane cartridge consisted of PTFE membranes and two acrylic discs. Both ends of membrane fibers were potted through the holes of the acrylic discs by using an epoxy sealant (Loctite E-60NC Hysol® epoxy). This Loctite E-60NC Hysol® epoxy has been proven resistant to alkanolamine solutions (deMontigny, 2004). One end of this membrane cartridge was immersed in a highly concentrated NH\(_3\) solution (8.5×10\(^3\) mol/m\(^3\)) in a 0.25×10\(^{-3}\) m\(^3\) beaker at 295.15 K. Observation of the membrane cartridge shows no physical changes even though the end of the membrane cartridge was in contact with aqueous ammonia for 48 hours. This visual inspection indicated that the membrane cartridge including the acrylic disc, Loctite E-60NC Hysol® epoxy, and PTFE membranes were resistant to the aqueous ammonia. Therefore, it was concluded that the PTFE membrane and Loctite E-60NC Hysol® epoxy were compatible with aqueous ammonia and could be used for making new membrane cartridges for subsequent experiments.
Figure 4.1: A picture of a single membrane cartridge
Figure 4.2: A schematic layout of a single membrane cartridge
Before making a new membrane cartridge, the feasibility of CO₂ absorption into aqueous ammonia was evaluated by using the previously used PTFE membrane cartridge. The CO₂ absorption experiments were conducted with 0.97×10³ mol/m³ aqueous ammonia in the PTFE membrane contactor at a room temperature (295.15 K). Since deMontigny, 2004, demonstrated that mass transfer is higher when the absorption liquid flows in the tube side rather than the shell side, the aqueous ammonia in this experimental work flowed in the tube side. The initial CO₂ loading of solution was zero. The inert gas stream was air with a flow rate of 6.1×10⁻⁵ m³/s. The inlet CO₂ concentration was 20% by volume. The experimental results indicated that the aqueous ammonia can offer a stable performance for CO₂ absorption in the PTFE membrane contactor. As shown in Figure 4.3, \( K_G a \) values ranged from 0.07 to 0.12 mol/m³-s-kPa as the liquid flow rate was increased from 1.05×10⁻⁶ to 3.15×10⁻⁶ m³/s. However, during the course of absorption experiment, it was observed that aqueous ammonia in the tube gradually permeated through the membrane pores to the shell side at the top of some membrane fibers. This phenomenon indicated that the PTFE membranes were partially wetted. The reason for membrane wetting is due to the significant reduction of hydrophobicity of the used PTFE membranes since they have been directly contacted with various organic solvents in a large number of experiments in the past, such as MEA and AMP. Previous works have revealed that wetted membranes would result in a significant reduction of CO₂ absorption performance (Rangwala, 1996; Khaisri et al., 2010). Therefore, it was concluded that this previously used PTFE membrane cartridge could not be used for evaluating the CO₂ absorption performance of aqueous ammonia.
Figure 4.3: Experimental test of CO₂ absorption into aqueous ammonia in a PTFE membrane contactor

(NH₃ concentration: 0.97×10³ mol/m³, air flow velocity: 6.1×10⁻⁵ m³/s, inlet CO₂ percentage: 20%, temperature: 295.15 K)
4.3 Impact of Operating Parameters on the \( K_{Ga} \)

The feasibility study has demonstrated that aqueous ammonia can absorb CO\(_2\) in a micro-porous PTFE membrane contactor at a room temperature. However, the CO\(_2\) absorption performance was deteriorated due to significant membrane wetting. In order to evaluate the CO\(_2\) absorption performance, a brand new hollow fiber membrane module was built and adopted for all subsequent experimental studies.

According to previous studies, operating parameters had significant impacts on the CO\(_2\) absorption performance in various gas/liquid contacting devices, such as packed columns, spray columns or hollow fiber membrane contactors (Aroonwilas, 2001; Cui et al., 2010). Thus, impact of operating parameters on the CO\(_2\) absorption performance must be evaluated in order to design an efficient gas/liquid membrane absorption system. In this study, several operating parameters including the inlet CO\(_2\) partial pressure, liquid flow velocity, liquid concentration, and CO\(_2\) loading in the solution were evaluated by conducting a number of CO\(_2\) absorption experiments in a brand new PTFE membrane contactor.

4.3.1 Inlet CO\(_2\) Partial Pressure

The effect of inlet CO\(_2\) partial pressure was examined by conducting CO\(_2\) absorption experiments at three different inlet CO\(_2\) partial pressures including 10 kPa, 15 kPa, and 20 kPa. In the experiments the liquid flow rates ranged from 5.51×10\(^{-7}\) to 3.83×10\(^{-6}\) m\(^3\)/s. The NH\(_3\) solvent used in the experiments was 2.0×10\(^3\) mol/m\(^3\) with a CO\(_2\) loading of 0.1 mol/mol.
The experiment results indicated that the inlet CO₂ partial pressure has a great impact on the overall mass transfer performance of the PTFE membrane contactor. As seen in Figure 4.4, at a given liquid flow rate the $K_{Ga_v}$ value decreased as the inlet partial pressure of CO₂ increased from 10 kPa to 20 kPa. Figure 4.5 shows a much clearer trend by plotting the $K_{Ga_v}$ against the inlet partial pressure of CO₂. This trend holds true at different values of liquid flow rates. A number of researchers have observed a similar trend in their CO₂ absorption experiments (Strigle, 1987; Aroonwilas and Tontiwachwuthikul, 1997; Kuntz, 2006; Zeng et al., 2011). During the CO₂ absorption process in the hollow fiber membrane contactor, the driving force for CO₂ absorption is the CO₂ concentration gradient between the gas and liquid phases. As shown in Figure 2.2, increasing the driving force by raising the inlet CO₂ partial pressure will allow more CO₂ to transfer from the gas bulk to the gas/liquid interface, leading to an increase in the overall mass-transfer rate of CO₂. However, the overall mass transfer process is mainly controlled by the chemical reaction at the gas/liquid contacting interface and the concentration of available solvent in the liquid phase. Generally the diffusion of species in the liquid phase is relatively lower than that in the gas phase. Thus the increase of the overall mass transfer rate is restricted by the limited diffusion rate of solvent molecules in the liquid phase. The $K_{Ga_v}$ value represents the overall mass transfer rate per unit driving force. Although increasing the inlet CO₂ partial pressure leads to an increase of overall mass transfer rate, the increase in driving force has a greater influence when compared to the increase of
Figure 4.4: Effect of inlet partial pressure of CO\textsubscript{2} at different liquid flow rates

(NH\textsubscript{3} concentration: 2.0×10\textsuperscript{3} mol/m\textsuperscript{3}, air flow velocity: 5.0×10\textsuperscript{-5} m\textsuperscript{3}/s,
CO\textsubscript{2} loading: 0.1 mol/mol, temperature: 295.15K)
Figure 4.5: Relationship between the $K_G a_v$ and the inlet partial pressure of CO$_2$
mass transfer rate. Thus the $K_G a_v$ value decreased as the inlet CO$_2$ partial pressure increased.

4.3.2 Liquid Flow Rate

A number of experiments have been conducted to examine the effect of liquid flow rate on the CO$_2$ absorption performance of the hollow fiber membrane contactor. The flow rates of aqueous ammonia in the tube were ranged from $5.5 \times 10^{-7}$ to $3.8 \times 10^{-6}$ m$^3$/s. The concentration of NH$_3$ solvent was $2.0 \times 10^3$ mol/m$^3$ with a CO$_2$ loading of 0.1 mol/mol.

Figure 4.6 shows the effect of liquid flow rate on the $K_G a_v$ at different inlet CO$_2$ partial pressures. It is clear that an increase in the liquid flow rate leads to an increase in $K_G a_v$ values. This trend also holds true for all other experimental conditions. Since the reaction between CO$_2$ and NH$_3$ is fast (Derks and Versteeg, 2009), the overall mass transfer rate of CO$_2$ depends on the amount of CO$_2$ transferred from the gas bulk to the gas/liquid interface and the available reactive NH$_3$ molecules at the interface. When increasing the liquid flow rate, the boundary layer thickness of the liquid phase is decreased, causing a decreased liquid-phase mass transfer resistance. As a result, more NH$_3$ molecules are diffused to and available for the reaction with CO$_2$ at the gas/liquid contacting interface. Therefore, the $K_G a_v$ value increased as the liquid flow rate increased. The same relationship between the $K_G a_v$ and the liquid flow rate was observed in a packed column since both contactors are based on the same gas absorption principle (deMontigny, 2004).
Figure 4.6: Effect of liquid flow rate at different inlet CO\textsubscript{2} partial pressures

(NH\textsubscript{3} concentration: 2.0×10\textsuperscript{3} mol/m\textsuperscript{3}, air flow velocity: 5.0×10\textsuperscript{-5} m\textsuperscript{3}/s,
CO\textsubscript{2} loading: 0.1 mol/mol, temperature: 295.15 K)
4.3.3 Liquid Concentration

The major disadvantage of aqueous ammonia used for CO$_2$ absorption is the NH$_3$ vaporization due to its high vapor pressure at a room temperature. Using a high concentrated aqueous ammonia as an absorption solvent will lead to a higher amount of gaseous NH$_3$ slip into the treated gas stream, which means a higher rate of NH$_3$ loss during the CO$_2$ absorption process. In addition, research results revealed that when the NH$_3$ concentration is higher than 4.0×10$^3$ mol/m$^3$, an increase in NH$_3$ concentration has a slight effect on the CO$_2$ removal efficiency but it may aggravate the NH$_3$ loss (Qi et al., 2013). Thus in this study the effect of NH$_3$ concentration on the $K_{Ga}$ was investigated by using aqueous ammonia with a low concentration in order to mitigate the NH$_3$ loss as much as possible during the membrane absorption process. In the experiments the concentrations of NH$_3$ were 1.0×10$^3$, 2.0×10$^3$ and 3.0×10$^3$ mol/m$^3$. The CO$_2$ partial pressure was 15 kPa. The CO$_2$ loading of solution was 0.1 mol/mol. The liquid flow rates increased from 5.9×10$^{-7}$ to 3.8×10$^{-6}$ m$^3$/s.

As shown in Figure 4.7, the $K_{Ga}$ value increases as the NH$_3$ concentration increases from 1.0×10$^3$ to 3.0×10$^3$ mol/m$^3$ at a given liquid flow rate. This behavior can be better demonstrated by plotting the $K_{Ga}$ against the NH$_3$ concentration as shown in Figure 4.8. Similar to the traditional alknolamine solvents, an increase of NH$_3$ concentration yields a greater amount of reactive NH$_3$ molecules to diffuse to the gas/liquid contacting interface and available for the reaction with CO$_2$. As a result, the enhancement factor is increased. The $K_{Ga}$ value increases as the enhancement factor is increased.
Figure 4.7: Effect of NH\textsubscript{3} concentration at different liquid flow rates

(Air flow velocity: 5.0\times10^{-5} \text{ m}^3/\text{s}, inlet CO\textsubscript{2} percentage: 15\%; CO\textsubscript{2} loading: 0.1 \text{ mol/mol}, temperature: 294.65 K)
Figure 4.8: Relationship between the $K_{G\alpha v}$ and the concentration of NH$_3$
4.3.4 CO₂ Loading in the Solution

Normally the CO₂ absorption process requires the regeneration of the absorption liquid by heating the rich solution to release the absorbed CO₂ from the solvent. A number of studies have demonstrated that CO₂ loading in the lean solution had a significant effect on the CO₂ absorption performance in various types of absorbers (Setameteekul et al., 2008; Kuntz and Aroonwilas, 2009). Thus this study examined the CO₂ absorption performance by increasing the CO₂ solution loading from 0.1 to 0.3 mol/mol. The concentration of NH₃ was 1.0×10³ mol/m³. The CO₂ partial pressure was 15 kPa. The liquid flow rate ranged from 5.9×10⁻⁷ to 3.8×10⁻⁶ m³/s.

An increase of CO₂ loading reduces the amount of reactive NH₃ molecules in the liquid bulk, then resulting in a fewer amount of active NH₃ molecules to diffuse to and react with CO₂ at the gas/liquid contacting interface. As a result, the enhancement factor is decreased, which leads to a decreased $K_{Gav}$ value. As expected, Figure 4.9 showed that the $K_{Gav}$ value decreases as the CO₂ loading increases.

It is also important to note that the CO₂ loading at different liquid flow rates has a different degree of effect on the $K_{Gav}$ value at the same concentration of NH₃. Figure 4.10 clearly indicates the different extent of effects of CO₂ loading on the $K_{Gav}$ at different liquid flow rates. It is clear that the $K_{Gav}$ value is less affected by the CO₂ loading at a low liquid flow rate compared to that at a high liquid flow rate. This phenomenon can be explained by considering the relationship of two factors including the liquid phase mass transfer resistance and available reactive NH₃ molecules at the gas/liquid contacting interface. As discussed earlier, the liquid phase mass transfer resistance at a high liquid flow rate is lower than that at a low liquid flow rate.
Figure 4.9: Effect of CO₂ loading at different liquid flow rates

(NH₃ concentration: 1.0×10³ mol/m³, air flow velocity: 5.0×10⁻⁵ m³/s,
inlet CO₂ percentage: 15%, temperature: 294.65 K)
Figure 4.10: Relationship between the $K_{Ga}$ and the CO$_2$ solution loading

"Figure 4.10: Relationship between the $K_{Ga}$ and the CO$_2$ solution loading"
Thus changing the CO$_2$ loading at a low liquid flow rate will generate a less amount of reactive NH$_3$ molecules to diffuse to the gas/liquid contacting interface due to the high mass transfer resistance compared to that at a high liquid flow rate with a low mass transfer resistance. Therefore, the effect of CO$_2$ loading on the $K_Ga_v$ value at a high liquid flow rate is much more significant than that at a low liquid flow rate due to the difference of the liquid-phase mass transfer resistance.

### 4.4 Performance Comparison of NH$_3$ Solvent with MEA Solvent

The CO$_2$ absorption rates of aqueous ammonia were compared with traditional alkanolamine solutions such as MEA, MDEA, and AMP in many types of gas/liquid contactors (Dave et al., 2009; Gonzalez-Garza et al., 2009; Puxty et al., 2010). However, no experimental work has compared their CO$_2$ absorption performance in a hollow fiber membrane contactor. Earlier experimental results have demonstrated that aqueous ammonia solution was able to absorb CO$_2$ in a PTFE membrane contactor. In order to compare the absorption performance of the MEA and aqueous ammonia, CO$_2$ absorption experiments using MEA as a solvent were conducted under the same experimental condition as the previous ammonia-based membrane absorption experiments. In the experiments, the MEA solutions with 1.0×10$^3$ mol/m$^3$ and 2.0×10$^3$ mol/m$^3$ were studied, respectively. The CO$_2$ partial pressure was 15 kPa. The CO$_2$ solution loading was 0.1 mol/mol. The liquid flow rate was varied from 5.3×10$^{-7}$ to 3.9×10$^{-6}$ m$^3$/s.

As seen in Figure 4.11 and 4.12, the $K_Ga_v$ value of MEA solvent is higher than that of NH$_3$ solvent. This is due to the difference in reactivity of NH$_3$ and MEA with CO$_2$. In order to compare the reactivity of NH$_3$ and MEA with CO$_2$, the second-order
Figure 4.11: Comparison of CO₂ absorption performance of 1.0 × 10³ mol/m³ aqueous ammonia and MEA

(Solvent concentration: 1.0 × 10³ mol/m³, air flow velocity: 5.0 × 10⁻⁵ m³/s, inlet CO₂ percentage: 15%, CO₂ loading: 0.1 mol/mol, temperature: 294.65 K)
Figure 4.12: Comparison of CO$_2$ absorption performance of 2.0×10$^3$ mol/m$^3$ aqueous ammonia and MEA

(Solvent concentration: 2.0×10$^3$ mol/m$^3$, air flow velocity: 5.0×10$^{-5}$ m$^3$/s, inlet CO$_2$ percentage: 15%, CO$_2$ loading: 0.1 mol/mol, temperature: 294.65 K)
reaction rate constants \((k_2)\) are derived by using the Equation 4.1 and Equation 4.2 
(Alper, 1990; Puxty et al., 2010) and the reaction rate constants of \(\text{NH}_3\) and MEA are presented in Table 4.2 at different temperatures.

\[
k_{2,\text{NH}_3} = 0.915 \times e^{-\frac{61000 \times 0.6 (1/283)}{R}}
\]  
(4.1)

\[
k_{2,\text{MEA}} = 8.51 \times 10^8 \times e^{-\frac{5617}{T}}
\]  
(4.2)

According to Table 4.2, the reaction rate constant of \(\text{NH}_3\) is much lower than that of MEA at the same temperature. For example, the reaction rate constant of \(\text{NH}_3\) at 293 K is 1.8 times lower than that of MEA. Due to the lower reactivity of \(\text{NH}_3\), the \(K_{GA_v}\) value of aqueous ammonia is less than that of MEA. Figure 4.11 and 4.12 also indicate that the \(K_{GA_v}\) value of aqueous ammonia gets much closer to that of MEA as the liquid flow rate increases. In particular, at the solvent concentration of \(2.0 \times 10^3\) mol/m\(^3\) the \(K_{GA_v}\) value of aqueous ammonia is only 2% less than that of MEA at the maximum liquid flow rate \((3.9 \times 10^{-6} \text{ m}^3/\text{s})\). This is probably due to a higher concentration of reactive \(\text{NH}_3\) at the gas/liquid contacting interface compared to that of MEA as the liquid flow rate increases. As a result relatively more reactive \(\text{NH}_3\) molecules react with \(\text{CO}_2\) at the gas/liquid interface than MEA. Although the reaction rate constant of aqueous ammonia is less than that of MEA, a higher concentration of reactive \(\text{NH}_3\) makes the overall absorption rate of \(\text{NH}_3\) with \(\text{CO}_2\) close to that of MEA. By comparing the \(K_{GA_v}\) values of aqueous ammonia and MEA, it can be concluded that the \(K_{GA_v}\) value of \(\text{NH}_3\) with \(\text{CO}_2\) is in the same order of magnitude as MEA. In this respect, aqueous ammonia could be a promising alternative to traditional amines for \(\text{CO}_2\) capture in the hollow fiber membrane contactor.
Table 4.2: Second-order reaction rate constants ($k_2$) of NH$_3$ and MEA with CO$_2$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k_{2, NH_3}$ (m$^3$/mol-s)</th>
<th>$k_{2, MEA}$ (m$^3$/mol-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>278</td>
<td>0.574</td>
<td>1.429</td>
</tr>
<tr>
<td>283</td>
<td>0.915</td>
<td>2.042</td>
</tr>
<tr>
<td>293</td>
<td>2.217</td>
<td>4.020</td>
</tr>
</tbody>
</table>
4.5 Long-term Operation Performance

The long-term performance of membrane absorption systems has been investigated and reported by many researchers. Previous experimental results indicated that the membrane absorption performance may be significantly deteriorated due to membrane wetting over a prolonged operation time (Wang et al., 2005; Rongwong et al., 2009). Wang et al., 2005, indicated that the reduction of overall CO\textsubscript{2} absorption rate may reach up to 20% even if only 5% of the membrane pores were wetted. Therefore, it is necessary to experimentally evaluate the long-term CO\textsubscript{2} absorption performance of aqueous ammonia in the PTFE membrane contactor. In this study, two different concentrations of NH\textsubscript{3} solutions (1.0×10\textsuperscript{3} mol/m\textsuperscript{3} and 2.0×10\textsuperscript{3} mol/m\textsuperscript{3}) were used for continuously absorbing CO\textsubscript{2} in the PTFE membrane contactor in seven and ten hours, respectively. During the experiment, the outlet CO\textsubscript{2} concentration was recorded over time. The inlet CO\textsubscript{2} partial pressure was 15 kPa. The liquid flow rate was 3.2×10\textsuperscript{-7} m\textsuperscript{3}/s for the 1.0×10\textsuperscript{3} mol/m\textsuperscript{3} NH\textsubscript{3} solution and 3.5×10\textsuperscript{-7} m\textsuperscript{3}/s for the 2.0×10\textsuperscript{3} mol/m\textsuperscript{3} NH\textsubscript{3} solution. The NH\textsubscript{3} solution flowed in the membrane fibers of the system.

The experimental result is shown in Figure 4.13. Both 1.0×10\textsuperscript{3} mol/m\textsuperscript{3} and 2.0×10\textsuperscript{3} mol/m\textsuperscript{3} NH\textsubscript{3} solutions were observed a similar trend of CO\textsubscript{2} absorption performance over a prolonged operating time. During the absorption process, the $K_Ga_V$ value has maintained constant within the first hour and then gradually decreased as time. The decrease rate ($\sigma$) of $K_Ga_V$ value was calculated by using the following equation:

$$\sigma = \frac{K_Ga'_V - K_Ga_V(t)}{K_Ga_V'} \times 100\%$$  \hspace{1cm} (4.3)
Figure 4.13: Long-term performance of aqueous ammonia in the PTFE membrane contactor

(Air flow velocity: $5.0 \times 10^{-5}$ m$^3$/s, inlet CO$_2$ percentage: 15%, CO$_2$ loading: 0.1 mol/mol, temperature: 295.15 K)
where, $K_G a_v (t)$ is the measured value of $K_G a_v$ as time; $K_G a_v'$ is the constant value of $K_G a_v$ within the first hour. The decrease rate of the $K_G a_v$ value is shown in Figure 4.14 plotted against time. As shown in the figure, the $K_G a_v$ value has decreased by 36% for the $2.0 \times 10^3$ mol/m$^3$ NH$_3$ solution after seven hours and 45% for the $1.0 \times 10^3$ mol/m$^3$ NH$_3$ solution after ten hours. After three hours of operation, at the same operation time (for example, at the seventh hour), the $K_G a_v$ value was decreased by 34% for the $1.0 \times 10^3$ mol/m$^3$ NH$_3$ solution while 36% for the $2.0 \times 10^3$ mol/m$^3$ NH$_3$ solution, which indicates that the $K_G a_v$ value of the $2.0 \times 10^3$ mol/m$^3$ NH$_3$ solution decreased much more quickly than that of the $1.0 \times 10^3$ mol/m$^3$ NH$_3$ solution.

As seen in Figure 4.15, visual observation confirmed that this decreased performance over time was caused by the ammonium salt precipitation inside of the membrane pores and on the membrane surface of the module shell side. The precipitation of ammonium salts was due to the high NH$_3$ vaporization from the liquid phase to the gas phase and caused a serious membrane fouling problem. In addition, the precipitation of ammonium salts on the membranes may reduce the hydrophobicity of the membrane surface and further facilitate the membrane wetting. As a result, the membrane’s performance was degraded gradually due to membrane fouling and membrane wetting. A similar observation of ammonium salt precipitation has been reported by Makhloufi et al., 2014. A PP hollow fiber membrane contactor was tested to absorb CO$_2$ by using aqueous ammonia (1, 3, 5% by weight) at 294K. CO$_2$ removal efficiency was found to continuously decrease with time due to the precipitation of ammonium salts within the membrane pores and on the tube side of the fibers. A dense skin membrane was designed and manufactured which can limit the NH$_3$ permeation through the membrane pores. Experimental results indicated that this dense skin membrane module can offer stable absorption performances over time.
Figure 4.14: The decrease rate of $K_Ca_v$ values over time
Figure 4.15: A picture of ammonium salt precipitation
Another effective method may use chemical inhibitors to mitigate the NH$_3$ loss from the absorption solution. Research has been studied a number of inhibitors for CO$_2$ absorption, such as glycerol, ethylene glycol, and isoamyl alcohol (Seo et al., 2012). Experimental results showed the NH$_3$ loss could be reduced up to 50% by adding even 1% by weight these inhibitors into aqueous ammonia. However, the CO$_2$ absorption rate may decrease due to the bonding effect between NH$_3$ and the hydroxyl group of the inhibitors in the solution.
CHAPTER 5: DEVELOPMENT OF MATHEMATICAL MODELING

5.1 Concept of Mathematical Modeling

A comprehensive two dimensional (2D) mathematical model was developed in order to simulate the CO$_2$ absorption into aqueous ammonia in the PTFE membrane contactor. Mass transfer in the hollow fiber membrane absorption system takes place through three regions, including the gas phase, the membrane, and the liquid phase. The 2D mathematical model was derived from the steady state material balances of the transferred species within these three regions. As shown in Figure 5.1, the 2D mathematical model is developed for a single hollow membrane fiber, in which the absorption liquid flows in the tube while the gas mixture containing CO$_2$ and N$_2$ flows counter-currently on the shell side. The model is assumed to comply with the following assumptions:

- No angular gradients and use an axisymmetrical approximation;
- The gas stream obeys the idea gas behavior;
- The absorption process is an isothermal and steady state process;
- Axial diffusion is negligible compared to shell or tube side convective flows;
- The liquid pressure drop is negligible in the tube;
- Fully developed laminar velocity profiles on both tube and shell sides;
- Constant liquid absorbent viscosity and gas diffusivity.
Figure 5.1: A schematic diagram of a single partial hollow membrane fiber
5.2 Steady State Material Balance

During the CO₂ absorption process in the hollow fiber membrane system, species are transported via diffusion, chemical reaction and/or convection in the gas phase, the membrane, and the liquid phase. The general continuity equation for each transported species during the simultaneous mass transfer and chemical reaction in a reactive absorption system can be expressed as the following equation:

\[
\frac{\partial C_i}{\partial t} = -\nabla \cdot N_i + R_i
\]  

(5.1)

where \(C_i\), \(N_i\), and \(R_i\) are the concentration, flux, and reaction rate of transported species \(i\) along the length of the membrane, respectively. The flux of species \(i\) can be determined by Fick’s law of diffusion:

\[
N_i = -D_i \nabla C_i + C_i V
\]  

(5.2)

where \(D_i\) is the diffusion coefficient of species \(i\); \(V\) is the axial velocity of species \(i\) along the length of membrane fiber. By combing Equation (5.1) and (5.2), the overall steady state material balance including the effects of chemical reaction, diffusion, and convection is given as follows:

\[
\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i - \nabla \cdot C_i V + R_i
\]  

(5.3)

5.2.1 Material Balance in the Liquid Phase

On the tube side of the membrane module system, species \(i\) is transported by molecular diffusion, convection, and chemical reaction. Thus, the steady state material balance for transport of species \(i\) can be written as:

\[
D_{i-L} \left[ \frac{\partial^2 c_{i-L}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{i-L}}{\partial r} + \frac{\partial^2 c_{i-L}}{\partial z^2} \right] + R_i = V_L \frac{\partial c_{i-L}}{\partial z}
\]  

(5.4)
where $D_{i-L}$ is the diffusion coefficient of any species in the tube; $C_{i-L}$ is the concentration of any species in the tube; $R_i$ is the reaction rate of any species in the liquid phase; $V_L$ is the axial flow velocity of liquid in the tube. Assume the velocity distribution in the tube complies with Newtonian laminar flow (Bird et al., 2002):

$$V_L = 2\bar{V}_L [1 - \left( \frac{r}{r_i} \right)^2 ]$$

(5.5)

where $\bar{V}_L$ is the average axial velocity in the tube; $r_i$ is the inner fiber radius.

Boundary conditions of the liquid phase are given as:

at $z=0$,

$$C_{i-L} = C_{in-t}$$

(5.6)

Where, $C_{in-t}$ is the initial concentration of species $i$ on the tube side of the module.

at $r=0$, and for all $z$:

$$\frac{\partial C_{i-L}}{\partial r} = 0 \text{ (symmetry)}$$

(5.7)

at $r=r_i$, and for all $z$:

$$C_{CO2-L} = C_{CO2-mem} \times S_{CO2}$$

(5.8)

$$\frac{\partial C_{s-L}}{\partial r} = 0$$

(5.9)

where $C_{CO2-mem}$ is the concentration of CO$_2$ in the membrane. $S_{CO2}$ is the CO$_2$ solubility in the absorption liquid; $C_{s-L}$ is the concentration of species other than CO$_2$ in the tube.
5.2.2 Material Balance in the Gas Phase

The gas mixture containing CO$_2$ and air flows on the shell side and no reactions occur. The steady state material balance for the transport of CO$_2$ in the gas phase can be written as:

\[
D_{CO_2-G} \left[ \frac{\partial^2 C_{CO_2-G}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{CO_2-G}}{\partial r} + \frac{\partial^2 C_{CO_2-G}}{\partial z^2} \right] = V_G \frac{\partial C_{CO_2-G}}{\partial z} \quad (5.10)
\]

where $D_{CO_2-G}$ is the diffusion coefficient of CO$_2$ in the gas phase in the shell; $C_{CO_2-G}$ is the CO$_2$ concentration in the shell; $V_G$ is the axial gaseous velocity on the shell side.

According to Happel’s free surface model (Happel, 1959), only a portion of the fluid around the fiber is considered and approximated as a circular cross section as shown in Figure 5.2. Thus the velocity profile in the shell side is given as follows,

\[
V_G = 2\overline{V}_G \left[ 1 - \left( \frac{r_o}{r_e} \right)^2 \right] \times \left\{ \frac{\left( \frac{r_o}{r_e} \right)^2 - \left( \frac{r_o}{r_e} \right)^2 - \ln \left( \frac{r_o}{r_e} \right)}{3 + \left( \frac{r_o}{r_e} \right)^2 - 4\left( \frac{r_o}{r_e} \right)^2 + 4\ln \left( \frac{r_o}{r_e} \right) + 2\left( \frac{r_o}{r_e} \right)^2 + 2\ln \left( \frac{r_o}{r_e} \right)} \right\} \quad (5.11)
\]

\[
r_e = r_o \sqrt{\frac{1}{1 - \phi}} \quad (5.12)
\]

where $\overline{V}_G$ is the average gas velocity on the shell side; $r_o$ is the outer membrane fiber radius; $r_e$ is the effective shell radius; $\phi$ is the volume void fraction of the membrane contactor module, which can be calculated as follows,

\[
\phi = 1 - n \frac{r_o}{r_m} \quad (5.13)
\]

where $n$ is the number of hollow fibers in the membrane module; $r_m$ is the inner radius of the membrane module.
Figure 5.2: Circular approximation of the fluid around the fiber
Boundary conditions in the shell side are given as:

at $z=L$,

$$C_{CO2,G}=C_{in-G} \quad (5.14)$$

where, $C_{in-G}$ is the initial concentration of CO$_2$ in the shell side of the membrane module.

at $r=r_o$,

$$C_{CO2,G}=C_{CO2-mem} \quad (5.15)$$

at $r=r_e$,

$$\frac{\partial C_{CO2,G}}{\partial r} = 0 \quad (5.16)$$

where $C_{CO2-mem}$ is the concentration of CO$_2$ in the membrane in the non-wetted mode.

**5.2.3 Material Balance in the Membrane**

During the gas absorption process in the hollow fiber membrane contactor, the membrane pores may be gradually wetted by the absorption liquid. As a result, the absorption performance of membrane system will be significantly reduced. Therefore, the material balance in the membrane should consider two different operation modes, including non-wetted mode and partially wetted mode. In the membrane, the convective flow in the membrane pores is assumed negligible. Thus the convective term in Equation (5.3) is zero.

**5.2.3.1 Non-Wetted Mode of Operation**

In the non-wetted mode of membrane operation, the membrane pores are completely filled with the gas stream. Mass transfer of CO$_2$ in the membrane only
occurs through CO₂ diffusion in the membrane pores. So the steady state material balance for CO₂ in the non-wetted membrane pores can be written as:

\[ D_{CO₂-mem} \left[ \frac{\partial^2 c_{CO₂-mem}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{CO₂-mem}}{\partial r} + \frac{\partial^2 c_{CO₂-mem}}{\partial z^2} \right] = 0 \]  

(5.17)

where \( D_{CO₂-mem} \) is the diffusion coefficient of CO₂ in the non-wetted membrane pores.

Boundary conditions are given as:

at \( r=r_i \),

\[ C_{CO₂-mem}=C_{CO₂-L}/S_{CO₂} \]  

(5.18)

at \( r=r_o \),

\[ C_{CO₂-mem}=C_{CO₂-G} \]  

(5.19)

### 5.2.3.2 Partially-wetted Mode of Operation

In the case of partially-wetted mode of membrane operation, the membrane pores are partially filled by liquid and gas streams. As shown in Figure 5.3, both gas-filled and liquid-filled portions of the membrane should be considered for the steady state material balance of CO₂ in the membrane.

In the gas-filled portion of the membrane fiber mass transfer occurs through the diffusion of CO₂ in the gas phase only. Thus the steady state material balance for the transport of CO₂ in the gas-filled portion of the membrane fiber can be written as:

\[ D_{CO₂-G-mem} \left[ \frac{\partial^2 c_{CO₂-G-mem}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{CO₂-G-mem}}{\partial r} + \frac{\partial^2 c_{CO₂-G-mem}}{\partial z^2} \right] = 0 \]  

(5.20)
Figure 5.3: A schematic diagram of a partially-wetted membrane fiber
where $D_{CO_2-G\text{-membrane}}$ is the diffusion coefficient of CO$_2$ in the gas-filled portion of membrane, which equals to the $D_{CO_2\text{-membrane}}$; $C_{CO_2\text{-G\text{-mem}}}$ is the concentration of CO$_2$ in gas-filled portion of membrane.

Boundary conditions are:

at $r=r_w$, 

$$C_{CO_2\text{-G\text{-mem}}}= C_{CO_2\text{-L\text{-mem}}}/S_{CO_2}$$  \hspace{1cm} (5.21)

at $r=r_0$, 

$$C_{CO_2\text{-G\text{-membrane}}} = C_{CO_2\text{-G}}$$  \hspace{1cm} (5.22)

where $r_w$ is the wetting portion of the membrane; $C_{CO_2\text{-L\text{-mem}}}$ is the concentration of CO$_2$ in the liquid-filled portion of membrane.

In the liquid-filled portion of the membrane fiber mass transfer occurs through the diffusion of reactive species and chemical reactions. CO$_2$ diffused from the gas-filled portion of membrane fiber reacts with the absorbent in the liquid-filled portion of the membrane. Thus the steady state material balance for the transport of species $i$ inside the liquid-filled portion of membrane fiber can be written as:

$$D_{i-L\text{-mem}} \left[ \frac{\partial^2 c_{i-L\text{-mem}}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{i-L\text{-mem}}}{\partial r} + \frac{\partial^2 c_{i-L\text{-mem}}}{\partial z^2} \right] + R_{i\text{-mem}} = 0$$  \hspace{1cm} (5.23)

where $D_{i-L\text{-mem}}$ is the diffusion coefficient of species $i$ in the liquid-filled portion of membrane; $R_{i\text{-mem}}$ is the reaction rate of species $i$ in the membrane.
Boundary conditions are:

at $r=r_i$,

$$C_{i-L\text{-mem}} = C_{i-L} \tag{5.24}$$

at $r=r_w$,

$$C_{CO2-L\text{-mem}} = C_{CO2-G\text{-mem}} \times S_{CO2} \tag{5.25}$$

$$\partial C_{s\text{-mem}} / \partial r = 0 \tag{5.26}$$

where $C_{s\text{-mem}}$ is the concentration of species other than CO$_2$.

5.3 Determination of Model Parameters

5.3.1 The overall reaction rate

As discussed in Chapter 2, the overall reaction rate ($R_{CO2}$) of CO$_2$ with aqueous ammonia can be achieved by considering the following two reactions:

Reaction 1:

$$CO_2 + OH^- \overset{k_{OH^-}}{\rightleftharpoons} HCO_3^- \tag{2.47}$$

Reaction 2:

$$CO_2 + 2NH_3 \leftrightarrow NH_2COO^- + NH_4^+ \tag{5.27}$$

The reaction rate ($R_{CO2-OH^-}$) of CO$_2$ with hydroxyl ion (OH$^-$) in Equation (2.47) can be expressed as:

$$R_{CO2-OH^-} = k_{OH^-}C_{OH^-}C_{CO2} \tag{5.28}$$
where \( k_{OH^-} \) is the reaction rate constant, which can be obtained by (Pinsent et al., 1956):

\[
\log(10^3 \times k_{OH^-}) = 13.635 - \frac{2895}{T} \tag{5.29}
\]

Similar to the reaction of CO\(_2\) and MEA, the reaction between CO\(_2\) and NH\(_3\) (Reaction 2) consists of two steps:

(1) Formation of zwitterions:

\[
CO_2 + NH_3 \xrightleftharpoons[k_{13}, k_{-13}]{k_{NH_3}, k_{-NH_3}} NH_3^+COO^- \tag{2.50}
\]

(2) Zwitterions deprotonated by the bases in the solution. In the aqueous ammonia, the bases are NH\(_3\), water and OH\(^-\). However, due to the rather small contribution of OH\(^-\), only NH\(_3\) and water are considered as the dominate bases available for the zwitterions deprotonation (Darde, 2011). Thus the deprotonation of zwitterions by the dominant bases in the solution can be expressed as:

\[
NH_3^+COO^- + NH_3 \xrightleftharpoons[k_{NH_3}, k_{-NH_3}]{k_{H_2O}, k_{-H_2O}} NH_2COO^- + NH_4^+ \tag{2.51}
\]

\[
NH_3^+COO^- + H_2O \xrightleftharpoons[k_{NH_3}, k_{-NH_3}]{k_{H_2O}, k_{-H_2O}} NH_2COO^- + H_3^+O \tag{2.52}
\]

The reaction rate \( R_{CO_2-NH_3} \) of CO\(_2\) and NH\(_3\) in Reaction 2 can be obtained by using the following equation:

\[
R_{CO_2-NH_3} = \frac{c_{NH_3}c_{CO_2}}{(1/k_2) + (1/k_{H_2O})c_{H_2O}K_{NH_3}c_{NH_3}} \tag{5.30}
\]

where

\[
K_{H_2O} = \frac{k_2k_{H_2O}}{k_{-1}} \tag{5.31}
\]
The kinetic parameters of \( k_2 \), \( K_{H_2O} \), and \( K_{NH_3} \) can be determined by using the following temperature dependent correlations (Darde, 2011):

\[
k_2 = 4.9 \times \exp \left(-14000 \times \left(\frac{1}{T} - \frac{1}{283.15}\right)\right) \tag{5.33}
\]

\[
K_{H_2O} = 7.1 \times 10^{-7} \times \exp \left(-18000 \times \left(\frac{1}{T} - \frac{1}{283.15}\right)\right) \tag{5.34}
\]

\[
K_{NH_3} = 2.1 \times 10^{-4} \times \exp \left(-2200 \times \left(\frac{1}{T} - \frac{1}{283.15}\right)\right) \tag{5.35}
\]

By summing the reaction rate of \( CO_2 \) and \( NH_3 \) \( (R_{CO2-NH3}) \) and the reaction rate of \( CO_2 \) with \( OH^- \) \( (R_{CO2-OH}) \), the overall reaction rate \( (R_{CO2}) \) of \( CO_2 \) with aqueous ammonia can be expressed as:

\[
R_{CO2} = k_{OH^-}C_{OH^-}C_{CO2} + \frac{c_{NH3}c_{CO2}}{(1/k_2)+(1/K_{H_2O})c_{H_2O}+K_{NH3}c_{NH3}} \tag{5.36}
\]

The reaction rates of other reactive species including \( OH^- \) and \( NH_3 \) can be obtained according to Reactions 1 and Reaction 2 as follows,

\[
R_{OH^-} = R_{CO2-OH^-} \tag{5.37}
\]

\[
R_{NH3} = 2 \times R_{CO2-NH3} \tag{5.38}
\]

In the partially wetted mode of membrane operation, the chemical reaction occurs in the membrane. Considering the effect of membrane porosity on the reaction rate, the reaction rate in the membrane is defined as:

\[
R_{i-mem} = R_i \times \varepsilon \tag{5.39}
\]
5.3.2 Diffusion Coefficients in the Gas Phase, Liquid Phase and the Membrane

A gaseous diffusion coefficient (diffusivity) can be predicted from many kinetic theories or empirical correlations. The use of kinetic prediction methods sometimes is limited because some prediction parameters are not available for all gases. However, the empirical correlation methods normally adopt a simple format and can achieve similar success to the kinetic prediction methods. Thus, this study used an empirical correlation to calculate the diffusion coefficient of CO$_2$ in the air as follows (Cussler, 2009),

$$D_{CO_2}\rightarrow G = 10^3 \times \frac{T^{1.75} \times \left(\frac{1}{W_{\text{air}}} + \frac{1}{W_{CO_2}}\right)^{0.5} \times 101.325}{P \left(\frac{v_{air}}{v_{CO_2}}\right)^{1/3}}$$  (5.40)

where $W$ is the molecular weights. $v$ is the diffusion volume of simple molecules. $v_{\text{air}}$ is 20.1; and $v_{CO_2}$ is 26.9 (Fuller et al., 1966).

In the liquid phase, the diffusivity of CO$_2$ in aqueous ammonia can be estimated from the solution’s viscosity by using a modified Stokes-Einstein Equation (Derks and Versteeg, 2009):

$$D_{CO_2\rightarrow NH_3} = D_{CO_2\rightarrow H_2O} \left(\frac{\mu_{H_2O}}{\mu_{NH_3}}\right)^{0.8}$$  (5.41)

where $D_{CO_2\rightarrow H_2O}$ is diffusion coefficient of CO$_2$ in the water; $\mu_{H_2O}$ and $\mu_{NH_3}$ are viscosities of water and aqueous ammonia, respectively. The diffusion coefficient of CO$_2$ in the water can be determined by (Versteeg and Van Swaalj, 1988):

$$D_{CO_2\rightarrow H_2O} = 2.35 \times 10^{-6} EXP\left(\frac{-2119}{T}\right)$$  (5.42)

Since the CO$_2$ loadings of solution tested in the experiment were low, the CO$_2$ loadings in the solution were assumed to have no impact on the viscosity of the
solution. Thus the viscosities of aqueous ammonia and water can be estimated by using the following equations (Frank et al., 1996):

\[
\mu_{NH_3} = (0.67 + 0.78\chi_{NH_3}) \times 10^{-9} \exp\left(\frac{17900}{RT}\right) \quad (5.43)
\]

\[
\mu_{H_2O} = 1.18 \times 10^{-9} \exp\left(\frac{16400}{RT}\right) \quad (5.44)
\]

where \(\chi_{NH_3}\) is the molar fraction of NH\(_3\) in the aqueous ammonia; \(R\) is the universal gas constant \((8.314 \text{ J/mol-K})\). The diffusion coefficient of NH\(_3\) in the water can be determined as follows (Frank et al., 1996):

\[
D_{NH_3-H_2O} = (1.65 + 2.47\chi_{NH_3}) \times 10^{-6} \exp\left(\frac{-16600}{RT}\right) \quad (5.45)
\]

For simplicity, the diffusion coefficient of OH\(^-\) in the NH\(_3\) solution is considered equal to the diffusion coefficient of NH\(_3\) in the water.

During the course of membrane absorption, the membrane pores may be partially filled with gas and liquid. Thus diffusion coefficients of each diffused component in the gas-filled portion of membrane pores and liquid-filled portion of membrane pores should be determined, respectively. In the liquid-filled portion of membrane pores the diffusion coefficient \((D_{i-L-mem})\) of species \(i\) is the effective diffusion coefficient, which is a function of membrane porosity \((\varepsilon)\) and tortuosity \((\tau)\):

\[
D_{i-L-mem} = \frac{D_{i-L} \varepsilon}{\tau} \quad (5.46)
\]

The tortuosity of porous membrane module can be estimated by using Equation (5.47) (Iversen et al., 1997).

\[
\tau = \frac{1}{\varepsilon} \quad (5.47)
\]
In the gas-filled portion of membrane pores, the mean free path of gas molecules cannot be negligible due to very small membrane pore sizes. The gaseous diffusion in the membrane pores is affected by the membrane fiber wall. Therefore, the diffusion coefficient of CO$_2$ in the gas-filled portion of membrane should consider molecular diffusion and Knudsen diffusion as follows,

$$
\frac{1}{D_{CO_2-G-membrane}} = \frac{1}{D_K} + \frac{1}{D_{CO_2-G}}
$$

(5.48)

where $D_K$ is the Knudsen diffusion coefficient, which can be calculated as (Henley et al., 2011):

$$
100D_K = 0.485d_p\left(\frac{T}{W_{CO_2}}\right)^{0.5}
$$

(2.32)

where $d_p$ is the membrane pore diameter.

5.3.3 Solubility of CO$_2$ in the aqueous ammonia

During the mass transfer process in the hollow fiber membrane contactor, the resistance to mass transfer only exists in the gas phase, the membrane and the liquid phase. According to the Film Theory, no mass transfer resistance presents at the gas/liquid contacting interface. Thus at the gas/liquid contacting interface the gas and liquid phases are in equilibrium and their relationship obeys Henry’ Law as follows,

$$
P_{y_{Int,A}} = HG_{Int,A}
$$

(2.2)

where $H$ is Henry’s law constant. For a gas dissolving into a liquid, Henry’s law constant can be expressed as solubility of the gas in the liquid. The solubility of a gas in a liquid is proportional to the partial pressure of that gas above the liquid, which has the same relationship as Equation (2.2).
The solubility of CO$_2$ (S$_{CO2-NH3}$) in the diluted aqueous ammonia can be estimated by using the “N$_2$O analogy” proposed by Versteeg and Van Swaalj, 1988, as follows,

$$S_{CO2-NH3} = \frac{S_{CO2-H_2O}}{S_{N2O-H_2O}} \times S_{N2O-NH3}$$  \hspace{1cm} (5.49)

The solubility of CO$_2$ and N$_2$O in water can be estimated according to the following equations, respectively (Versteeg & Van Swaaij, 1988):

$$S_{CO2-H_2O} = 3.54 \times 10^{-7}RT exp(2044/T)$$  \hspace{1cm} (5.50)

$$S_{N2O-H_2O} = 1.17 \times 10^{-7}RT exp(2284/T)$$  \hspace{1cm} (5.51)

Derks and Versteeg, 2009, measured the physical solubility of N$_2$O in the aqueous ammonia at a series of temperatures between 278.15 and 297.15 K. The concentrations of NH$_3$ were tested from 0 to 5.0×10$^3$ mol/m$^3$. According to their experimental results, the solubility of N$_2$O is hardly dependent on the tested concentration of NH$_3$ in the solution at the same temperature. In this study the concentration of aqueous ammonia is ranged from 1.0×10$^3$ to 3.0×10$^3$ mol/m$^3$. Accordingly, the solubility of N$_2$O in the aqueous ammonia in this study can be assumed constant at the same temperature. The solubility of N$_2$O in the diluted aqueous ammonia at different temperatures is estimated by a linear interpolation of the experimental data from Derks and Versteeg, 2009, and is presented at Table 5.1.

**5.4 Model Solution**

The finite element method is a numerical technique, which can find approximate solutions for partial differential equations with boundary conditions. It uses so called “finite elements” to solve the complex problem within a large physical
Table 5.1: Solubility of N$_2$O in the aqueous ammonia at different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$S_{N2O-NH3}$ (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>294.15</td>
<td>0.676</td>
</tr>
<tr>
<td>294.65</td>
<td>0.668</td>
</tr>
<tr>
<td>295.15</td>
<td>0.660</td>
</tr>
</tbody>
</table>
domain by minimizing an associated error function. COMSOL Multiphysics® software, which uses the finite element method, is an efficient tool for numerically solving partial differential equations. Accordingly, this study used the COMSOL Multiphysics® software to solve the complex steady state mathematical model developed earlier in this chapter with the finite element method.

In the COMSOL Multiphysics® model, a built-in *Transport of Diluted Species Interface* was adopted to model the evolution of all chemical species transported through diffusion and convection by implementing the mass balance. This physics interface assumes that the concentrations of all species are small compared to a solvent. As a rule of thumb, a mixture of several species is considered as a dilute solution when the concentration of the solvent is higher than 90% by mole. The *Transport of Diluted Species Interface* supports the simulation of multiple chemical species transported in an asymmetric 1D or 2D system. Considering the geometry of hollow fibers used in this study, an asymmetric 2D model was built. In the *Transport of Diluted Species Interface*, the convection and diffusion, initial values, and concentrations of transported species as well as the reaction rates and boundary conditions are defined.

The 2D mathematical model in COMSOL Multiphysics® was built via 5 steps: 1) defined model global parameters, including experimental conditions, physical and chemical parameters, and membrane module parameters; 2) defined model variables, including concentrations of all reactive species in the liquid phase, the membrane and the gas phase, 3) established the geometry of a hollow fiber as shown in Figure 5.4; 4) set up the transport of diluted species in the gas phase, the membrane and liquid phase; and 5) generated finite element meshes as shown in Figure 5.5. It is noted that the
Figure 5.4: Geometry of the hollow membrane fiber in the COMSOL Multiphysics®

(a) Non-wetted mode of membrane operation

(b) Wetted mode of membrane operation
Figure 5.5: Mapped meshing for model simulation in the COMSOL Multiphysics®
accuracy of the simulation results significantly depends on the degree of meshing, especially in some boundary domains, which include significant concentration changes. For example, close to the gas/liquid contacting boundary, a very dense meshing is applied in order to precisely determine the concentration profiles of the transported species due to chemical reaction. By using the COMSOL Multiphysics® software, the complex asymmetric 2D mathematical model can be successfully solved by considering the appropriate boundary conditions, physical and chemical properties, and reaction rate equations.
CHAPTER 6: SIMULATION RESULTS AND DISCUSSION

6.1 Model Validation

A complex 2D mathematical model was developed for simulating the mass transfer behavior of CO\textsubscript{2} absorption into the aqueous ammonia in a hollow fiber membrane contactor. This model was established based on the steady-state material balance of the gas phase, the membrane, and the liquid phase. Since the membrane may be wetted by the absorption liquid, this model was developed with two different membrane operation conditions, including a non-wetted membrane model and a partially-wetted membrane model. COMSOL Multiphysics\textsuperscript{®} software was used to solve this 2D mathematical model by inputting the inlet conditions of gas and liquid phases, membrane module parameters, and physical and chemical parameters. Each run of the simulation can generate concentration profiles and total flux vectors of transported/reactive species within the membrane absorption system, such as the concentration of CO\textsubscript{2} in the gas phase, the membrane, and the liquid phase.

In this Chapter, the developed 2D mathematical model was validated for CO\textsubscript{2} absorption into aqueous ammonia in a PTFE membrane contactor. In the model system, the liquid flows in the tube and the gas mixture flows counter-currently on the shell side. The absorption of CO\textsubscript{2} occurs through mass transfer and is enhanced by chemical reaction between CO\textsubscript{2} and NH\textsubscript{3} in the liquid phase. The verification of this model was achieved by comparing the simulation results with the prior experimental results. The simulation and experimental results were evaluated in terms of the CO\textsubscript{2} absorption rate (flux), which can be calculated as follows:

\[
J_{\text{CO}_2} = \frac{(G_{\text{in} \text{y}_{\text{in}} - G_{\text{out} \text{y}_{\text{out}}}) \times 273.15 \times 1000}{22.414 \times T \times A}
\]  

(6.1)
6.1.1 Validation of Non-Wetted Membrane Model

The non-wetted membrane model assumes that CO₂ is absorbed into the aqueous ammonia under the non-wetting mode of membrane operation. Under the non-wetted mode of membrane operation, the membrane pores are completely filled with the gas stream. CO₂ diffuses through the gas-filled membrane pores and then is absorbed by the solvent at the surface of the membrane pores on the liquid side of the membrane system. The non-wetted mode of membrane operation is generally preferred since its overall mass transfer resistance was found to be much less than that obtained under a partially-wetted mode of membrane operation (Khaisri et al., 2010).

The CO₂ absorption rates from experimental results and simulation results obtained with the non-wetted membrane model were compared. As shown in Figure 6.1, the CO₂ absorption rates from experimental results are about three times less than those from simulation results. This low experimental result indicates that the hollow fiber membrane pores were partially wetted by aqueous ammonia during the absorption process. Attributed to membrane wetting, the absorption rates of CO₂ were significantly decreased. This phenomenon holds true for all experimental results. The absorption rates of CO₂ from the experiments were up to 76% lower than those from simulation results. A parity plot made by all experimental and simulation results is given in Figure 6.2. The determination coefficient of 0.75 indicates a very low agreement between the experimental and simulation results.
Figure 6.1: Comparison of simulation results and experimental results under the non-wetted mode

(NH$_3$ concentration: 2.0×10$^3$ mol/m$^3$, air flow rate: 5.0×10$^{-5}$ m$^3$/s, inlet CO$_2$ percentage: 10%, CO$_2$ loading: 0.1 mol/mol, temperature: 295.15K)
Figure 6.2: Parity plot of the experimental and simulated CO\textsubscript{2} outlet concentration in the gas phase (non-wetted membrane model)
6.1.2 Validation of Partially-Wetted Membrane Mathematical Model

Under the partially wetted mode of membrane operation, the membrane pores were partially wetted by aqueous ammonia. As a result, the absorption rate of CO$_2$ was significantly reduced. In the partially-wetted membrane model, the extent of membrane wetting is determined by the wetting percentage ($x$) as follows:

$$x = \frac{r_w-r_i}{r_o-r_i} \times 100\%$$  \hspace{1cm} (6.2)

Since the mass transfer resistance in the membrane increases with the wetting percentage, a higher wetting percentage leads to a less absorption rate of CO$_2$. Figure 6.3 gives an example of the simulation results obtained by using the partially-wetted membrane model. As shown in the figure, the simulation results generate an excellent agreement with the experimental results. Figure 6.3 also indicates that the absorption rates of CO$_2$ from the partially-wetted membrane model are much lower than those obtained from the non-wetted membrane model. This confirms that the presence of membrane wetting greatly decreased the membrane absorption performance.

The simulation results obtained from the partially-wetted membrane model show that the membranes were partially wetted in different extents for all experiments. The wetting percentages in the partially-wetted membrane model are ranged from 0.5% to 70%. The absorption rate of CO$_2$ was decreased by 66% when only 0.5% of the membrane pores were wetted by aqueous ammonia. The occurrence of membrane wetting in the experiments was due to the high pressure applied to the liquid phase. The breakthrough pressure is the minimum pressure required on the liquid side to push the liquid phase into the membrane pores.
Figure 6.3: Comparison of simulated results and experimental results (partially-wetted membrane mode)

(NH$_3$ concentration: $2.0 \times 10^3$ mol/m$^3$, air flow rate: $5.0 \times 10^{-5}$ m$^3$/s, inlet CO$_2$ percentage: 10\%, CO$_2$ loading: 0.1 mol/mol, temperature: 295.15K)
In the experiments, the liquid phase pressure was adjusted manually by using a valve at the outlet of liquid flow. The valve was adjusted to gradually increase the liquid phase pressure until no gas was bubbling in the liquid phase. During the experiment, it was very difficult to accurately balance the pressure difference between the gas phase and liquid phase without partially wetting the membrane pores and allowing the gas bubbling in the liquid phase. When the liquid phase pressure was adjusted higher than the breakthrough pressure, the absorption liquid penetrated and partially wetted the membrane pores. A very good agreement of all experimental and simulation results is indicated in Figure 6.4 with a determination coefficient of nearly 1.0.

6.2 Concentration Profiles and Flux Vectors in the Membrane System

The concentration profiles and total flux vectors of CO$_2$ and NH$_3$ were obtained from both the non-wetted and partially-wetted membrane models. In the non-wetted model, as shown in Figure 6.5, the gas stream flows from the top of the membrane fiber ($z = L$) in the shell side where the concentration of CO$_2$ in the gas phase is highest. As the gas flows through the shell side of the module, more and more CO$_2$ is transported and absorbed into the aqueous ammonia. As a result, the concentration of CO$_2$ in the gas stream gradually decreases along the membrane fiber. However, in the liquid phase the transported CO$_2$ from the gas phase is quickly consumed by reacting with NH$_3$ at the gas/liquid contacting interface, located at the membrane surface on the liquid side. Thus the concentration of CO$_2$ in the liquid phase stays low during the CO$_2$ absorption process. The total flux vectors of CO$_2$ in the tube and shell sides are in both the $r$ and $z$ directions due to the cumulative effects of diffusion and convection. The total flux vectors in the membrane are only in the $r$ directions since only gaseous diffusion occurs in the membrane.
Figure 6.4: Parity plot of the measured and simulated CO$_2$ outlet concentration in the gas phase (partially-wetted membrane model)
Figure 6.5: Concentration and flux vectors of CO$_2$ in the model solution (non-wetted membrane model)

(NH$_3$ concentration: 2.0×10$^3$ mol/m$^3$, air flow rate: 5.0×10$^{-5}$ m$^3$/s, inlet CO$_2$ percentage: 10%, CO$_2$ loading: 0.1 mol/mol, temperature: 295.15K)
The concentration profile of NH₃ in the liquid phase is shown in Figure 6.6. Since the aqueous ammonia flows from the bottom of the membrane contactor, the concentration of NH₃ is largest at the entry of membrane fiber \((z = 0)\). At the gas/liquid contacting interface, which is the membrane surface of the liquid side \((r = r_i)\), CO₂ is dissolved in the liquid phase and reacts with NH₃. As a result, the concentration of NH₃ at the interface is minimal. However, farther from the contacting surface, the concentration of NH₃ increases due to less CO₂ being available for the reactions with NH₃ in the liquid.

In the partially-wetted membrane model, the concentration of CO₂ in the gas phase has a similar behavior to that in the non-wetted membrane model. However, the concentrations of CO₂ in the membrane and liquid phase are different. As shown in Figure 6.7, when the membrane pores were partially wetted (30%) the absorption liquid occupies 30% of the membrane pore volume. Thus the membrane is divided into two parts, the gas-filled portion and the liquid-filled portion. During the CO₂ absorption process, NH₃ diffuses from the liquid phase to the liquid-filled portion of the membrane. CO₂ diffuses from the gas phase to the gas-filled portion of the membrane. CO₂ reacts with NH₃ and is consumed in the aqueous ammonia at the gas/liquid contacting surface. The gas/liquid contacting surface in the partially-wetted membrane model is the interface between the gas-filled portion and liquid-filled portion of the membrane, whose location depends on the wetting percentage. The concentration profile of NH₃ is given in Figure 6.8. Similar to the non-wetted membrane model, the concentration of NH₃ is at a minimum at the gas/liquid contacting interface in the membrane and increases farther from the interface.
Figure 6.6: Concentration of NH$_3$ in the model solution (non-wetted membrane model)

(NH$_3$ concentration: 2.0×10$^3$ mol/m$^3$, air flow rate: 5.0×10$^{-5}$ m$^3$/s, inlet CO$_2$ percentage: 10%, CO$_2$ loading: 0.1 mol/mol, temperature: 295.15K)
Figure 6.7: Concentration and flux vectors of CO$_2$ in the model solution (partially wetted membrane model)

(NH$_3$ concentration: $2.0 \times 10^3$ mol/m$^3$, air flow rate: $5.0 \times 10^{-5}$ m$^3$/s, inlet CO$_2$ percentage: 10%, CO$_2$ loading: 0.1 mol/mol, temperature: 295.15K)
Figure 6.8: Concentration of NH₃ in the model solution (partially-wetted membrane model)

(NH₃ concentration: 2.0×10³ mol/m³, air flow rate: 5.0×10⁻⁵ m³/s, inlet CO₂ percentage: 10%, CO₂ loading: 0.1 mol/mol, temperature: 295.15K)
6.3 Axial and Radial Concentration Gradients

Figure 6.9 shows the concentrations of CO$_2$ at the gas/liquid contacting interface derived from the non-wetted membrane model and the partially-wetted membrane model, respectively. It should be noted that the gas/liquid contacting interface is located at different positions for both models. In the non-wetted membrane model the contacting surface is located at the membrane surface of the liquid side. In the partially-wetted membrane model it is located within the membrane, depending on the wetting percentage. In both models, the CO$_2$ concentration decreases almost linearly from the top of the membrane until it reaches the minimum at the gas outlet. At any position at the gas/liquid contacting interface, the CO$_2$ concentration of the non-wetted membrane model is always lower than that of partially-wetted membrane model. A similar trend is also found for the NH$_3$ concentration at the gas/liquid contacting surface as shown in Figure 6.10. The concentration of NH$_3$ at the gas/liquid contacting interface decreases as the liquid flows through the membrane fibers as more NH$_3$ is consumed by reacting with CO$_2$.

The radial concentration profile of CO$_2$ across the gas phase, the membrane, and the liquid phase at the middle of the membrane fiber (1/2L) is shown in Figure 6.11. It indicates that the concentration of CO$_2$ derived from the non-wetted membrane model barely decreases in the gas phase due to a small resistance to mass transfer. However, the concentration of CO$_2$ is decreased in the membrane due to a relatively high resistance to mass transfer in the membrane compared to the gas-phase resistance. When CO$_2$ is diffused through the membrane and contacts with aqueous ammonia at the membrane surface of the liquid side, the diffused CO$_2$ is quickly
Figure 6.9: Concentration of CO\textsubscript{2} at the gas/liquid contacting surface

(NH\textsubscript{3} concentration: 2.0\times10^3 mol/m\textsuperscript{3}, air flow rate: 5.0\times10^{-5} m\textsuperscript{3}/s, inlet CO\textsubscript{2} percentage: 10\%, CO\textsubscript{2} loading: 0.1 mol/mol, temperature: 295.15K)
Figure 6.10: Concentration of NH$_3$ at the gas/liquid contacting surface

(NH$_3$ concentration: 2.0×10$^3$ mol/m$^3$, air flow rate: 5.0×10$^{-5}$ m$^3$/s, inlet CO$_2$ percentage: 10%, CO$_2$ loading: 0.1 mol/mol, temperature: 295.15K)
Figure 6.11: Concentration of CO$_2$ at the middle of the membrane fiber (1/2$L$) 
(NH$_3$ concentration: 2.0×10$^3$ mol/m$^3$, air flow rate: 5.0×10$^{-5}$ m$^3$/s, 
inlet CO$_2$ percentage: 10%, CO$_2$ loading: 0.1 mol/mol, temperature: 
295.15K)
reacted with NH₃ and consumed in the liquid. Therefore, the concentration of CO₂ sharply decreases at the interface between the membrane and liquid phase. Similarly, the simulation results derived from the partially-wetted membrane model indicates a sharp decrease of CO₂ concentration at the interface between the gas-filled portion and liquid-filled portion of the membrane in which the diffused CO₂ reacts with NH₃ and is consumed in the liquid.

**6.4 Effect of Membrane Wetting on Membrane Absorption Performance**

Membrane wetting is a significant issue which can affect the long-term stability of membrane operation. Many research results have indicated that the hollow fiber membrane pores in the membrane system may be wetted by the absorption liquid over a prolonged operating time. The liquid intrusion into the membrane pores can significantly decrease the overall mass transfer performance and deteriorate the long-term stability of the membrane contactor. The overall mass transfer coefficient could reduce by 20% if only 5% of membrane pores were wetted (Wang et al., 2005).

In order to study the effect of membrane wetting on the ammonia-based membrane absorption process, the absorption rate of CO₂ was derived from the partially-wetted membrane model by assuming a full range of wetting percentages. An example of simulation results is given in Figure 6.12. As seen in the figure, membrane wetting can significantly decrease the CO₂ absorption performance. Even if only 5% of membrane pores have been wetted, the absorption rate of CO₂ decreased sharply. However, once the membrane pores have been partially wetted, the absorption rate of CO₂ slightly decreases as the membrane wetting percentage
Figure 6.12: Effect of wetting percentage on the membrane absorption rate

(NH$_3$ concentration: 2.0×10$^3$ mol/m$^3$, air flow rate: 5.0×10$^{-5}$ m$^3$/s,
inlet CO$_2$ percentage: 10%, CO$_2$ loading: 0.1 mol/mol, temperature: 295.15K)
increases. The relationship between the absorption rate of CO₂ and wetting percentage is close to linear. Since the membrane pores are gradually wetted over the operating time, once the membrane pores have been wetted by the absorption liquid the absorption rate of CO₂ will decrease slightly over time due to membrane wetting.

The impact of membrane wetting on the CO₂ absorption rate is caused by the increase of mass transfer resistance in the membrane once the membrane pores have been wetted. As shown in Equation 2.34, when the membrane pores were partially wetted, the membrane mass transfer resistance equals to the sum of the resistance in the liquid-filled portion and gas-filled portion of the membrane:

\[
\frac{1}{k'_M} = \frac{1-x}{k_M} + \frac{x}{k_M}
\]  

(2.34)

According to Equation 2.29 and 2.33, the mass transfer resistance in the liquid-filled and gas-filled portions is determined by the effective gas phase diffusion coefficients in the membrane and liquid phase diffusion coefficient in the liquid, respectively.

\[
k_M = \frac{D_{G,\text{eff}}E}{\tau \delta}
\]  

(2.29)

\[
k'_M = \frac{D_{L}E}{\tau \delta_{\text{wetted}}}
\]  

(2.33)

Because the \(D_L\) values are generally \(10^3\) to \(10^4\) times lower than the \(D_{G,\text{eff}}\) values, the mass transfer resistance in the gas-filled portion of membrane is much lower and negligible compared to that in the liquid-filled portion of membrane. When the membrane is not wetted, the membrane pores are completely filled with the gas stream. The membrane mass transfer resistance equals to the mass transfer resistance in the gas-filled membrane. However, once only a small portion of membrane is
wetted, the membrane mass transfer resistance will be significantly increased due to
the presence of much higher resistance in the liquid-filled portion of the membrane
compared to that in the gas-filled portion of the membrane. Rearranging Equation
2.34 by combing with Equation 2.29 and Equation 2.33, the membrane mass transfer
resistance can be calculated by using the following equation:

\[
\frac{1}{k_M} = \frac{(1-x)}{D_{a,eff}} \times \frac{r_{a-l}}{\epsilon} + \frac{x}{D_L} \times \frac{r_{a-l}}{\epsilon}
\]  

(6.3)

Figure 6.13 shows the calculated membrane mass transfer resistance with
different membrane wetting percentages. It confirms that once the membrane is
wetted, the membrane mass transfer resistance is increased sharply. Therefore, the
absorption rate of CO\(_2\) decreases sharply due to the occurring of membrane wetting.

It is noted that once the membrane has been partially wetted, the absorption
rate of CO\(_2\) decreases slightly as the wetting percentage increases. When the
membrane is wetted, the membrane mass transfer resistance mainly depends on the
resistance in the liquid-filled portion of the membrane since the resistance in the gas-
filled portion of the membrane is relatively small and negligible. As seen in Figure
6.13, as the wetting percentage is higher than 30\%, the membrane mass transfer
resistance is almost linearly proportional to the membrane wetting percentage. This
indicates that the gas-filled portion membrane resistance \((\frac{(1-x)}{D_{a,eff}} \times \frac{r_{a-l}}{\epsilon})\) from
Equation 6.3 is negligible compared to the liquid filled portion of membrane
resistance \((\frac{x}{D_L} \times \frac{r_{a-l}}{\epsilon}).\)
Figure 6.13: Effect of membrane wetting on the membrane mass transfer resistance
6.5 Membrane Wetting of Long-Term Operation Performance

The long-term stability of the membrane absorption process was studied by continuously running the CO\textsubscript{2} absorption experiment in the PTFE membrane contactor for up to ten hours. As discussed earlier, the experimental results showed that the absorption rates of CO\textsubscript{2} kept constant during the first hour and then gradually decreased as time. The decreased absorption rate indicates that the membrane has been gradually wetted after one hour.

The developed 2D mathematical model was used to simulate the long-term CO\textsubscript{2} absorption performance with the non-wetted membrane model and partially-wetted membrane model. The non-wetted membrane model assumes the membrane was not wetted by aqueous ammonia, which produced the highest CO\textsubscript{2} absorption performance under the idea condition. While the partially-wetted membrane model assumes that the membrane has been gradually wetted over time, which is demonstrated as the real operating condition in the experiments.

The simulation result is given in Figure 6.14. As seen in the figure, the simulation result generated from the partially-wetted membrane model showed an excellent agreement with the experimental results when the appropriate wetting percentages were determined. The simulated CO\textsubscript{2} absorption rate generated from the non-wetted membrane model is about three times higher than that obtained from the experimental results and simulation results derived from the partially-wetted membrane model, which indicates that the membrane was wetted since the experiment has been started. In addition, Figure 6.15 shows the effect of wetting percentage on the absorption rate of CO\textsubscript{2}. The simulated CO\textsubscript{2} absorption rates with
Figure 6.14: Simulation results of long-term membrane absorption process

(NH₃ concentration: 2.0×10³ mol/m³, air flow velocity: 5.0×10⁻⁵ m³/s, inlet CO₂ percentage: 15%, CO₂ loading: 0.1 mol/mol, temperature: 295.15 K)
Figure 6.15: Effect of membrane wetting on the CO$_2$ absorption rate in a long-term membrane absorption process
different wetting percentages agreed well with the experimental results. A similar trend is obtained by comparing with the previous membrane wetting study, as shown in Figure 6.12: the CO$_2$ absorption rate from the experimental results slightly and almost linearly decreases as the wetting percentage increases.

The presence of membrane wetting is also confirmed by plotting the wetting percentage against time (shown in Figure 6.16). It shows that 25% of the membrane pore was wetted during the first hour and then the wetting percentage increased up to 89% over time. This constant membrane wetting percentage during the first hour is due to the high liquid phase pressure, which forced the liquid to penetrate into the membrane pores and wet the membrane. As the absorption process continued, more and more ammonium salts were precipitated inside of the membrane pores due to the NH$_3$ slip from the liquid phase. The precipitation of ammonium salts on the membrane pore surface decreases the hydrophobicity of the membrane surface, resulting in more serious membrane wetting, as well as leads to membrane fouling.
Figure 6.16: Wetting percentage against membrane operating time
CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

Aqueous ammonia had been studied as an absorption solvent for CO$_2$ capture in various types of gas/liquid contactors. Prior research results showed aqueous ammonia may become a promising alternative to traditional alkanolamine solvents. This research work further extended the application of aqueous ammonia as a solvent for CO$_2$ capture in a hollow fiber membrane contactor, which has been shown more efficient than traditional packed columns.

At the beginning of this study the feasibility of CO$_2$ absorption into aqueous ammonia in a hollow fiber membrane contactor was examined (Task 1). Afterwards, a number of CO$_2$ absorption experiments were carried out at ambient temperatures (around 295.15K) using aqueous ammonia as a solvent in a PTFE membrane contactor (Task 2). The absorption performance was evaluated in terms of $K_{GA_v}$. The effects of various operating conditions on the $K_{GA_v}$ were examined, including inlet CO$_2$ partial pressure, NH$_3$ concentration, liquid flow rate, and CO$_2$ loading of solution.

CO$_2$ absorption into the MEA solvents was also experimentally studied in the same operating condition as aqueous ammonia in order to compare the absorption performance of aqueous ammonia and MEA solvents (Task 3). Since membrane wetting is a critical issue affecting the stability of membrane absorption performance, a long-term stability of membrane operation was also investigated. At the end of this study, a 2D mathematical model was developed to simulate the CO$_2$ absorption into aqueous ammonia in a hollow fiber membrane contactor (Task 4). The developed mathematical model was validated with the experimental results. Using the 2D mathematical model the effect of membrane wetting on the ammonia-based CO$_2$
absorption performance was also simulated and analyzed (Task 5). The following main conclusions are summarized based on the experimental and simulation work:

I. Experimental work:

- The PTFE membrane and Loctite E-60NC Hysol epoxy were proven to be chemically resistant to aqueous ammonia.

- At an ambient temperature (295.15K) the $K_G a_v$ values of CO$_2$ absorption into aqueous ammonia in a PTFE membrane contactor ranged from 0.025 to 0.069 mol/m$^3$-s-kPa.

- The impacts of operating parameters on the CO$_2$ absorption performance have trends similar to previously tested gas/liquid absorption systems. The $K_G a_v$ value increased with liquid concentration and liquid flow rate; decreased as the inlet CO$_2$ partial pressure and CO$_2$ solution loading increased.

- Although the MEA solvent generally offered a moderately higher CO$_2$ absorption rate than aqueous ammonia due to its higher reactivity with CO$_2$, CO$_2$ absorption rate of aqueous ammonia was in the same order of magnitude as that of MEA solvent under the same experimental condition. In terms of absorption performance and solvent cost, aqueous ammonia could be a promising alternative to the traditional alkanolamine solvents.

- During long-term stability tests, the membrane absorption performance remained constant within the first hour of operation and then gradually
decreased over time due to membrane wetting and fouling. The degree of membrane wetting and fouling increased as the ammonium salt started to precipitate inside the membrane pores and on the membrane surface of the module shell side.

II. Simulation work:

- A 2D mathematical model, based on the steady-state material balance, was developed for predicting and simulating CO$_2$ absorption into aqueous ammonia in a hollow fiber membrane contactor. According to the operating conditions of membrane, the mathematical model includes a non-wetted membrane model and a partially-wetted membrane model.

- The absorption rates of CO$_2$ from the experimental results are up to 76% lower than the simulation results derived from the non-wetted membrane model. This low absorption rate indicates the membrane pores were wetted by aqueous ammonia. The simulation results derived from the partially-wetted membrane model achieved an excellent agreement with the experimental results.

- The simulation results indicate the membrane pores were partially wetted during the experiment due to a high liquid-phase pressure that forced the liquid to penetrate into the membrane pores. The membrane wetting percentages are ranged from 0.5% to 70%.
The 2D mathematical model can generate concentration profiles and flux vectors of CO$_2$ and NH$_3$ in the gas phase, the membrane, and the liquid phase.

The simulation results indicate the CO$_2$ absorption rates can significantly decrease when only a small percentage of the membrane is wetted by aqueous ammonia. Once membrane pores are wetted, the absorption rate slightly decreases as the wetting percentage increases over time.

The 2D model can accurately predict the CO$_2$ absorption performance over a prolonged operating time. The long-term simulation result reveals the percentage of membrane wetting maintained constant and was small during the first hour of operation and then slightly increased over time due to the precipitation of ammonium salt inside the membrane pores and on the membrane surface of the module shell side.

### 7.2 RECOMMENDATIONS FOR FUTURE WORK

Aqueous ammonia is a promising solvent that has a comparable CO$_2$ absorption performance and a lower cost when compared to MEA. Although this study has carried out a series of experimental and numerical studies on CO$_2$ absorption into aqueous ammonia in a PTFE membrane contactor, a great research effort is still required in order to make this new technology applicable to the industry. The following recommendations give some suggestions for future research work that needs to be considered.
One major drawback of this ammonia-based membrane absorption technology is the NH₃ slip from the absorption solvent to the treated gas stream. NH₃ slip can cause precipitation of ammonium solid in the membrane system and may cause membrane fouling and membrane wetting. In a pilot scale application, significant NH₃ slip may lead to a considerable amount of NH₃ loss and decrease the absorption efficiency. Therefore, future research work needs to focus on mitigating the NH₃ slip from aqueous ammonia as much as possible. This may be achieved by either using a selective membrane material to limit the diffusion of NH₃ or adding an inhibitor to the solvent to restrain the NH₃ slip.

The developed 2D mathematical model assumes that the NH₃ loss due to its vaporization is small and negligible since the membrane contactor used in the experiments is short in length. However, NH₃ slip is significant and should be considered in the large scale industrial application. In the large scale application, a condenser may be required at the treated gas outlet to mitigate the NH₃ loss. Future research work needs to develop a more rigorous mathematical model that considers the NH₃ slip and can accurately predict NH₃ losses during the CO₂ absorption process.
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APPENDIX A

Experimental data for CO$_2$ absorption into aqueous ammonia

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Table A.1: CO₂ absorption into aqueous ammonia (Exp 1)

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Table A.3: CO\textsubscript{2} absorption into aqueous ammonia (Exp 3)

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Table A.4: CO$_2$ absorption into aqueous ammonia (Exp 4)

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<td>9.0</td>
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Table A.5: CO₂ absorption into aqueous ammonia (Exp 5)

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Table A.6: CO$_2$ absorption into aqueous ammonia (Exp 6)

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Table A.7: CO$_2$ absorption into aqueous ammonia (Exp 7)

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<td>7.81</td>
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APPENDIX B

Experimental data for CO$_2$ absorption into aqueous MEA

Table B.1: CO$_2$ absorption into aqueous MEA (Exp 1) .......................... 198

Table B.2: CO$_2$ absorption into aqueous MEA (Exp 2) .......................... 199
Table B.1: CO$_2$ absorption into aqueous MEA (Exp 1)

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<td>9.14</td>
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APPENDIX C

Experimental data for long-term stability test

Table C.1: Membrane long-term stability test (Exp 1) ..............................201

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Table C.1: Membrane long-term stability test (Exp 1)

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Table C.5: Membrane long-term stability test (Exp 2)

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Table C.6: Membrane long-term stability test (Exp 2)

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Table C.7: Membrane long-term stability test (Exp 2)

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<td>1.00</td>
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Table C.8: Membrane long-term stability test (Exp 2)

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<td>Inert gas flow rate (×10^{-5} m³/s)</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>CO₂ flow rate (×10^{-6} m³/s)</td>
<td>8.8</td>
<td>8.8</td>
<td>8.8</td>
</tr>
<tr>
<td>NH₃ concentration (×10^{3} mol/ m³)</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Liquid flow rate (×10^{-6} m³/ s)</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Inlet CO₂ loading (mol/mol)</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Inlet CO₂ concentration (%)</td>
<td>15.05</td>
<td>15.05</td>
<td>15.05</td>
</tr>
<tr>
<td>Outlet CO₂ concentration (%)</td>
<td>14.49</td>
<td>14.58</td>
<td>14.58</td>
</tr>
</tbody>
</table>
APPENDIX D

Plotting the simulation results for ammonia-based CO₂ absorption experiments

Figure D.1: Results for aqueous ammonia experiments (10% CO₂)...

Figure D.2: Results for aqueous ammonia experiments (20% CO₂)

Figure D.3: Results for aqueous ammonia experiments (15% CO₂)

Figure D.4: Results for aqueous ammonia experiments (0.1 mol/mol)

Figure D.5: Results for aqueous ammonia experiments (0.2 mol/mol)

Figure D.6: Results for aqueous ammonia experiments (0.3 mol/mol)

Figure D.7: Results for aqueous ammonia experiments (3×10³ mol/m³)
Figure D.1: Results for aqueous ammonia experiments (10% CO₂)
Figure D.2: Results for aqueous ammonia experiments (20% CO₂)
Figure D.3: Results for aqueous ammonia experiments (15% CO$_2$)
Figure D.4: Results for aqueous ammonia experiments (0.1 mol/mol)
Figure D.5: Results for aqueous ammonia experiments (0.2 mol/mol)
Figure D.6: Results for aqueous ammonia experiments (0.3 mol/mol)
Figure D.7: Results for aqueous ammonia experiments (3×10^3 mol/m^3)
# APPENDIX E

## Material safety data sheet

### IDENTIFICATION

<table>
<thead>
<tr>
<th>Product name</th>
<th>BDH Ammonium Hydroxide 28-30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synonyms</td>
<td>Ammonia solution, Aqueous ammonia</td>
</tr>
</tbody>
</table>

### HAZARD IDENTIFICATION

<table>
<thead>
<tr>
<th>Flammability</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toxicity</td>
<td>Moderate</td>
</tr>
<tr>
<td>Body Contact</td>
<td>High</td>
</tr>
<tr>
<td>Reactivity</td>
<td>Moderate</td>
</tr>
<tr>
<td>Chronic</td>
<td>Minimum</td>
</tr>
<tr>
<td>Ingredient</td>
<td>Ammonia anhydrous liquefied</td>
</tr>
<tr>
<td>CAS number</td>
<td>7664-41-7</td>
</tr>
<tr>
<td>Classification</td>
<td>Compressed Gas, Flammable Gas, Very Toxic Material Causing Immediate and Serious Toxic Effects, Corrosive Material</td>
</tr>
<tr>
<td>Classification Code</td>
<td>A, B1, D1A, E</td>
</tr>
<tr>
<td>Risk Phrases</td>
<td>Very toxic to aquatic organisms; causes burns; harmful if swallowed; risk of serious damage to eyes.</td>
</tr>
<tr>
<td>Safety Advices</td>
<td>Keep locked up; keep out of reach of children; keep in a cool place; keep away from living quarters, keep away from food, drink and animal feeding stuffs; when using do not eat or drink; when using do no smoke; do not breathe gas/fumes/vapour/spray; in case of contact with eyes, rinse with</td>
</tr>
</tbody>
</table>
plenty of water and contact Doctor or Poisons Information Centre; After contact with skin, wash immediately with plenty of water; do not empty into drains; this material and its container must be disposed of in a safe way; wear suitable protective clothing; wear suitable gloves; wear eye/face protection; to clean the floor and all objectives contaminated by this material, use water; in case of accident or if you feel unwell immediately contact doctor or Poisons Information Centre; if swallowed, seek medical advice immediately and show this container or label; not recommended for interior use on large surface areas; dispose of this material and its container at hazardous or special waste collection point; use appreciate container to avoid environmental contamination; avoid release to the environment; if swallowed, rinse mouth with water (only if the person is conscious).

**COMPOSITION**

<table>
<thead>
<tr>
<th>CAS NO</th>
<th>7664-41-7; 7732-18-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>% weight</td>
<td>28-30; NotSpec.</td>
</tr>
<tr>
<td>Name</td>
<td>Ammonia anhydrous liquefied; water</td>
</tr>
</tbody>
</table>

**FIRST-AID MEASURES**

**Eye Contact**
If this product comes in contact with the eyes:
- Immediately hold eyelids apart and flush the eye continuously with running water.
- Ensure complete irrigation of the eye by keeping eyelids apart and away from eye and moving the eyelids by occasionally lifting the upper and lower lids.
- Continue flushing until advised to stop by the Poisons Information Centre or a doctor, or for at least 15 minutes.
- Transport to hospital or doctor without delay.
- Removal of contact lenses after an eye injury should only be undertaken by skilled personnel.

**Skin Contact**
If skin or hair contact occurs:
- Immediately flush body and clothes with large amounts of water, using safety shower if available.
- Quickly remove all contaminated clothing, including footwear.
- Wash skin and hair with running water. Continue flushing with water until advised to stop by the Poisons Information Centre.
- Transport to hospital, or doctor.

**Inhalation**
- If fumes or combustion products are inhaled remove from contaminated area.
- Lay patient down. Keep warm and rested.
- Prostheses such as false teeth, which may block airway, should be removed, where possible, prior to initiating first aid procedures.
- Apply artificial respiration if not breathing, preferably with a demand valve resuscitator, bag-valve mask device, or pocket mask as trained. Perform CPR if necessary.
- Transport to hospital, or doctor.

**Ingestion**

- For advice, contact a Poisons Information Centre or a doctor at once.
- Urgent hospital treatment is likely to be needed.
- If swallowed do NOT induce vomiting.
- If vomiting occurs, lean patient forward or place on left side (head-down position, if possible) to maintain open airway and prevent aspiration.
- Observe the patient carefully.
- Never give liquid to a person showing signs of being sleepy or with reduced awareness; i.e. becoming unconscious.
- Give water to rinse out mouth, then provide liquid slowly and as much as casualty can comfortably drink.
- Transport to hospital or doctor without delay.

---

### FIRE-FIGHTING MEASURES

<table>
<thead>
<tr>
<th>Extinguishing media</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water spray or fog.</td>
</tr>
<tr>
<td>Foam.</td>
</tr>
<tr>
<td>Dry chemical powder.</td>
</tr>
<tr>
<td>BCF (where regulations permit).</td>
</tr>
</tbody>
</table>

---

### ACCIDENTAL RELEASE MEASURES

**Minor Spills**

- Drains for storage or use areas should have retention basins for pH adjustments and dilution of spills before discharge or disposal of material.
- Check regularly for spills and leaks.
- Clean up all spills immediately.
- Avoid breathing vapours and contact with skin and eyes.
- Control personal contact with the substance, by using protective equipment.
- Contain and absorb spill with sand, earth, inert material or vermiculite.

**Major Spills**

- Clear area of personnel and move upwind.
- Alert Fire Brigade and tell them location and nature of hazard.
- Wear full body protective clothing with breathing apparatus.
- Prevent, by any means available, spillage from entering drains or water course.

---

### HANDLING AND STORAGE
| Safe handling | Contains low boiling substance: Storage in sealed containers may result in pressure buildup causing violent rupture of containers not rated appropriately.  
- Check for bulging containers.  
- Vent periodically  
- Always release caps or seals slowly to ensure slow dissipation of vapours  
- DO NOT allow clothing wet with material to stay in contact with skin  
- Avoid all personal contact, including inhalation.  
- Wear protective clothing when risk of exposure occurs.  
- Use in a well-ventilated area.  
- Avoid contact with moisture. |
| Other Information | Store in original containers.  
- Keep containers securely sealed.  
- Store in a cool, dry, well-ventilated area.  
- Store away from incompatible materials and foodstuff containers.  
- DO NOT store near acids, or oxidising agents  
- No smoking, naked lights, heat or ignition sources. |
| Suitable Container | Lined metal can, lined metal pail/ can.  
- Plastic pail.  
- Polyliner drum.  
- Packing as recommended by manufacturer.  
For low viscosity materials  
- Drums and jerricans must be of the non-removable head type.  
- Where a can is to be used as an inner package, the can must have a screwed enclosure.  
For materials with a viscosity of at least 2680 cSt. (23 °C) and solids (between 15 °C. and 40 °C.):  
- Removable head packaging;  
- Cans with friction closures and  
- low pressure tubes and cartridges may be used. |
| Storage Incompatibility | Avoid any contamination of this material as it is very reactive and any contamination is potentially hazardous  
- Avoid strong acids, acid chlorides, acid anhydrides and chloroformates.  
- Avoid contact with copper, aluminium and their alloys. |
| EXPOSURE CONTROLS | CARE: Explosive vapour air mixtures may be present on opening vessels which have contained liquid ammonia. Fatalities have occurred Engineering controls are used to remove a hazard or place a barrier between the worker and the hazard. Well-designed engineering controls can be highly effective in protecting workers and will typically be independent of worker interactions to provide this high level of protection. The basic types of engineering controls are: |
Process controls which involve changing the way a job activity or process is done to reduce the risk. Enclosure and/or isolation of emission source which keeps a selected hazard "physically" away from the worker and ventilation that strategically "adds" and "removes" air in the work environment.

### Personal Protection

<table>
<thead>
<tr>
<th></th>
<th><img src="image1" alt="Gloves" />, <img src="image2" alt="Person" />, <img src="image3" alt="Boots" />, <img src="image4" alt="Face mask" />, <img src="image5" alt="Chemical goggles" /></th>
</tr>
</thead>
</table>

### Eye and Face Protection

- Chemical goggles.
- Full face shield may be required for supplementary but never for primary protection of eyes.
- Contact lenses may pose a special hazard; soft contact lenses may absorb and concentrate irritants. A written policy document, describing the wearing of lenses or restrictions on use, should be created for each workplace or task.

### Hands/feet Protection

- Wear chemical protective gloves, e.g. PVC.
- Wear safety footwear or safety gumboots, e.g. Rubber
- When handling corrosive liquids, wear trousers or overalls outside of boots, to avoid spills entering boots.

The selection of suitable gloves does not only depend on the material, but also on further marks of quality which vary from manufacturer to manufacturer. Where the chemical is a preparation of several substances, the resistance of the glove material cannot be calculated in advance and has therefore to be checked prior to the application. The exact break through time for substances has to be obtained from the manufacturer of the protective gloves and has to be observed when making a final choice. Suitability and durability of glove type is dependent on usage.

### Other Protection

- Overalls.
- PVC Apron.
- PVC protective suit may be required if exposure severe.
- Eyewash unit.

### PHYSICAL AND CHEMICAL PROPERTIES

<table>
<thead>
<tr>
<th></th>
<th><img src="image6" alt="Chemical" />, <img src="image7" alt="Water" /></th>
</tr>
</thead>
</table>

<p>| <strong>Appearance</strong>          | Clear, colourless corrosive liquid with ammonia-like odour; mixes with water. |
| <strong>Physical state</strong>      | Liquid                                |
| <strong>Relative density</strong>    | 0.9                                   |
| <em>(Water = 1)</em>           |                                       |</p>
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (as supplied)</td>
<td>&gt;11</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>-62</td>
</tr>
<tr>
<td>Initial boiling point (°C)</td>
<td>36</td>
</tr>
<tr>
<td>Vapour pressure (kPa)</td>
<td>288</td>
</tr>
</tbody>
</table>

**DISPOSAL CONSIDERATIONS**

- Recycle wherever possible.
- Consult manufacturer for recycling options or consult local or regional waste management authority for disposal if no suitable treatment or disposal facility can be identified.
- Treat and neutralise at an approved treatment plant.
- Treatment should involve: Neutralisation with suitable dilute acid followed by: burial in a land-fill specifically licensed to accept chemical and/or pharmaceutical wastes or Incineration in a licensed apparatus (after admixture with suitable combustible material).