MOLECULAR SIMULATION STUDIES OF HEXAMETHYLENEDIAMINE (HMDA) ABSORPTION PROCESS FOR CO_2 CAPTURE

MOHAMAD HAFIZ ZULKARNAIN BIN AZMAN

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UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

Carbon dioxide, CO_2 capture by absorption with aqueous alkanolamines is considered an important technology for reducing CO_2 emissions and global climate changes. The main objective of this work is to study the effect of temperature on intermolecular interaction of 1, 6-Hexamethylenediamine (HMDA) absorption process for CO_2 capture by using molecular dynamic (MD) simulation technique. The simulation was performed under condition NVE (200 ps) and NPT (500 ps) ensembles in material studio version 7.1. Two different temperature are used which are 313K and 333K for tertiary system (HMDA + CO_2 + water, H_2O). In this study, radial distribution function (RDF) and mean square displacement (MSD) are used to analyze intermolecular interaction exist in the system and self diffusion coefficient. According to the results, the possibility interaction or g(r) values of Ow-Hw (hydrogen bond) at 313K and 333K are (1.75 Å, 19.75) and (1.75 Å, 38.39). Meanwhile, g(r) value for intermolecular interaction of Nhmda-Cco2 (carbamate formation) are (3.75 Å, 2.43) and (4.75 Å, 2.61) at temperature 313K and 333K. Besides that, the value of self diffusion at 313K and 333K for HMDA and CO_2 are (7.585E-07 m^2/s, 2.5475E-06 m^2/s) and (7.6495E-07 m^2/s, 2.7542E-06 m^2/s) respectively. Based on the result, it found that the temperature 333K show higher result for intermolecular interaction and self diffusion coefficient compared to temperature 313K. It can be seen that, the result of this simulation is obey the theory which is as the temperature increase, the self diffusion coefficient and the g(r) value for intermolecular interaction also higher.

ABSTRAK

Penangkapan CO_2 melalui penyerapan dengan alkanolamines berair dianggap satu teknologi yang penting untuk mengurangkan penyebaran CO_2 dan perubahan iklim global. Objektif utama kajian ini adalah untuk mengkaji kesan suhu ke atas interaksi antara molekul daripada 1,6-Hexamethylenediamine (HMDA) proses penyerapan untuk penangkapan CO_2 dengan menggunakan teknik simulasi dinamik molekul (MD). Simulasi ini dilakukan di bawah keadaan NVE (200 ps) dan NPT (500 ps) berkumpulan dalam studio versi 7.1. Dua suhu yang berbeza digunakan iaitu 313K dan 333K untuk sistem tertinggi (HMDA + CO2 + air, H2O). Dalam kajian ini, fungsi taburan jejarian (RDF) dan min anjakan persegi (MSD) digunakan untuk menganalisis interaksi antara molekul wujud dalam sistem dan diri pekali resapan. Menurut keputusan , interaksi kemungkinan atau g (r) Nilai untuk Ow-Hw (bon hydrogen) di 313K dan 333K adalah (1.75 Å, 19.75) dan (1.75 Å, 38,39). Sementara itu, g (r) nilai untuk interaksi antara molekul antara amina dan karbon dalam Nhmda-Cco2 (perbentukan karbamat) adalah (3.75 Å, 2.43) dan (4.75 Å, 2.61) pada suhu 313K and 333K. Selain itu, penyebaran nilai diri di 313K dan 333K untuk HMDA dan CO_2 adalah (7.585E-07 m2 / s, 2.5475E-06 m2 / s) dan (7.6495E-07 m2 / s, 2.7542E-06 m2 / s) masing-masing. Suhu 333K menunjukkan keputusan lebih tinggi untuk interaksi intermolecular dan pekali resapan analisis berbanding dengan suhu 313K. Berdasarkan keputusan, simulasi ini mematuhi teori yang mana sebagai peningkatan suhu, pekali resapan dan nilai g(r) untuk interaksi intermolecular juga lebih tinggi.

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LIST OF ABBREVIATIONS

a_i	Acceleration
$\frac{d^2 r_i}{dt^2}$	Change of position
∇_i	3 dimensions
f_i or $\dot{p}$	Force
m_i	Mass of particle
∇_i	3 dimensions
$V(r_i)$	Potential energy respect to particle position
t	Time
r_i	Position
N_α	Number of particles inside the simulation box
δt	Time step
<...>	Ensemble average and time origins in MD simulation
α	Slope
D	Diffusion coefficient

Greek

Å	Amstrong
E	Energy
N	Number of mole
P	Pressure
T	Temperature
V	Volume

LIST OF ABBREVIATIONS

ACIA	Arctic climate impact assessment
PBC	Periodic boundry conditions
CCS	Carbon capture and storage
COMPASS	Condensed-phase Optimized Molecular Potentials for Atom simulation
CO_2	Carbon dioxide
° C	degree celsius
GHG	greenhouse gas
Gt	Gigatons
HMDA	Hexamethylenediamine
IPCC	Intergorvenmental panel on climate change
MSD	Mean square displacement
MD	Melocular dynamics
MDEA	Methydiaethanolamine
MEA	Monoethanolamine
RDF	Radial distribution function
H_2O	Water

1 INTRODUCTION

1.1 Motivation and statement of problem

According to United Nations Panel, emissions of greenhouse gases were causing in global warming up to 5.8 ° C over the next 100 years if it not overcome yet (IPCC, 2001). Carbon dioxide (CO_2) is the one of greenhouse gas and it emission will cause the climate change. Climate change refers to a change of climate that is attributed directly or indirectly from the human activity that could affects the composition of the global atmosphere (IEA, 2010). According to IPCC(2001) it is almost certain that emissions of greenhouse gases will result in the planet becoming warmer, disappearing glaciers, loss of biodiversity and rising sea levels. This is supported by the Arctic Climate Impact Assessment Report (ACIA, 2004).

Figure 1-1 show CO_2 from the fossil fuel is the primary contributor in greenhouse gas that produces from the human activities compare with other source of gas. This trend will continue to grow until 40.2 Gigaton (Gt) by 2030 (IEA, 2010). Therefore, CO_2 capture and storage (CCS) is the best of approach to reduce CO_2 emission and it is considered as a critical technology for reducing atmospheric emissions of CO_2 (Folger, 2013). CCS is consisting with three step processes which are including CO_2 capture, transportation of CO_2 and geological storage or sequestration (Li et al., 2011). Generally, there are three effective options for CO_2 capture such as pre combustion process, oxy fuel combustion and post combustion (Drager et al., 2012)

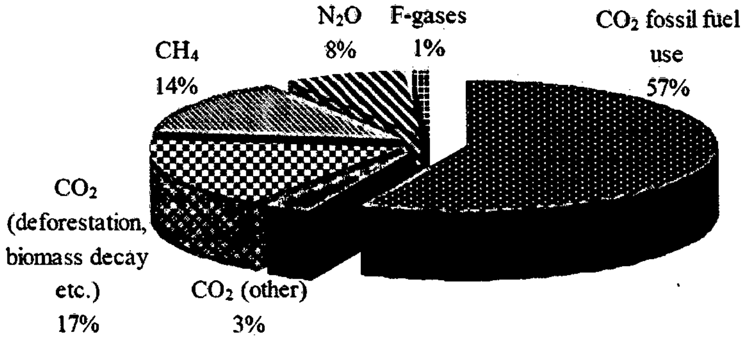

Figure 1-1: Different greenhouse gases in total global emissions in 2004 (Source: IPCC, 2007)

The increasing emissions of CO_2 were already believed to be affecting the climate change (IEA, 2012). In order to reducing this problem, there are many technologies that available for separation and capture CO_2 from gas streams, although they have not been designed for power plant scale operations. These technologies were based on different physical and chemical processes such as chemical and physical absorption, adsorption, membrane separation and other biological absorption (Kohl and Nielsen, 1997). The choice of a suitable technology depends on the characteristics of the flue gas stream, which is depend mainly on the power plant technology (Rao and Rubin, 2002).

In this study, the computer simulation technique applied was the molecular dynamics (MD) simulation. According to Maginn and Elliott (2010), MD is a powerful tool to help comprehend and reveal intermolecular interaction behaviour between the solute and the solvent molecules during the carbon capture process. The solute and solvent used in this study are CO_2 and 1, 6 Hexamethylenediamine, HMDA + water, H_2O. It also the best approach chosen to study and enhances the molecular distribution of the system inside the absorption solution (Farmahini, 2010). The concept of Newton's second law will be used to simulate the dynamic aspect of the system. In addition, the coordinate system will be used to calculate the radial distribution function (RDF), and self diffusion coefficient which could be used to describe the molecular interaction behaviour during CO_2 captures (Adam et al., 2014).

1.2 Objectives

The objective in this research is:

- To study the effect of the temperatures on intermolecular interaction of 1, 6-Hexamethylenediamine (HMDA) and CO_2 in absorption process by using molecular dynamic (MD) simulation technique.

1.3 Scope of this research

The scopes of this research are:

- Radial distribution function (RDF) is used to study the intermolecular interaction for tertiary system (HMDA + water + CO_2) by using MD simulation at temperature 313K and 333K.

- The optimum molecular interaction will be determined by observing the highest intermolecular interaction between molecular while simulating the absorption process at different temperature.
- Mean square displacement (MSD) is used to determine the self diffusion coefficient of HMDA and CO_2 inside the simulation system at temperature 313K and 333K.

1.4 Main contribution of this work

The increasing emissions of CO_2 got higher attention by all peoples in this world. Due to this challenge, many researches and investigations have been made by experimental or simulation to find the efficient solution to solve this problem. In this research, the best option to reduce the emission of CO_2 is by capture CO_2 before it release to the atmosphere. The common process to capture CO_2 in industries is by using amine based absorption in post combustion process. The typical solvents used to absorb CO_2 are Monoethanolamine (MEA), Methydiaethanolamine (MDEA) and etc. However, the solvent that commonly used also have the disadvantages in terms of corrosion, cost and properties. The purpose of this thesis is to provide the information in term simulation data for the new solvent which is HMDA. The selection of HMDA solvent in this study due to its ability is comparable with MEA solvents and has the potential to be used as new solvent for carbon capture (Singh, 2011).

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provide a description of sequences in carbon capture process (CCS). It sequences was started from CO_2 produced from fossil fuels burning until storage option. A general description has been made inside this chapter about gas purification process and amine based absorption. Besides that, this thesis also provides the detail explanation in MD simulation in term of forcefield, interactions consist in the simulation and ensembles.

Chapter 3 give the review the general description about the material studio software that was used. Besides that, this chapter also provide the explanation in methodology to perform the MD simulation from start until analysis of the result simulation.

Chapter 4 give the review about the analysis of the results from the MD simulation. The results are analyzed by radial distribution function (RDF) plot and mean square displacement (MSD) plot. From RDF plot, the probability of finding a particle at distance, r from the reference particle that completely in random distribution inside the simulation box at the same density could be identify. Meanwhile, MSD is used to determine the self diffusions for HMDA and CO_2 molecules. In addition, the brief conclusion has been made from the comparison of self diffusion with other literature (Singh, 2011).

Chapter 5 is about the conclusion and future work from this study. Conclusion is made based on the objective of this study. It found that, the objective is reached to study the effect of the temperature on intermolecular interaction of HMDA and CO_2 in absorption process by using molecular dynamic (MD) simulation technique. Besides that, further study is required to be done to improve the carbon capture system.

2 LITERATURE REVIEW

2.1 Overview

Carbon storage and capture (CCS) is the best approaches to reduce quantity of CO_2 in the atmosphere. CCS is involved capturing, transporting and storing of CO_2 as shown in Figure 2-1. CO_2 is produced from power generation, cement production, steel mills and other large point sources does not anymore enter the atmosphere, but it is withdrawn before. The aim of this research is to study the effect of temperature on intermolecular interaction between HMDA and CO_2 in absorption process by using molecular dynamic (MD) simulation software. According to Maginn and Elliott (2010), MD simulation is the best approach chosen to study and enhance the molecular distribution of the system inside the absorption solution and observe the intermolecular interaction between solute and solvent in the simulation system. Furthermore, the dynamic modelling and process simulation is very valuable tool for investigating the effects of flexible operation on the capture carbon facility in industry (Lawal et al., 2010). It also could be assuming as a virtual laboratory (Rapaport, 2004).

2.2 Introduction

This chapter explain about carbon capture and storage (CCS) and molecular dynamic simulation (MD). The aim of this chapter was to review the fundamental science of the carbon capture process, absorption process and the simulation technique.

2.3 Carbon capture and storage (CCS)

Global climate change was the critical issue with major international concern and the focus of proposed mitigation policy measures in the United States and elsewhere. In this context, the technology of CCS has received higher attention over the past decade as a potential method of reducing atmospheric emissions of CO_2. In 2007 for instance, CCS was accepted as a climate change mitigation possibility within the Kyoto Protocol, on top of national regulations (IEA, 2012; Bertinelli et al., 2014).

There are three factors worldwide interest in CCS method. One of them is the increasing of agreement that large reductions in global CO_2 emissions really required to avoid serious climate change impacts (Biello, 2007). Secondly is the reduction of CO_2 cannot be achieved easily by using less energy or replacing fossil fuels with alternative energy sources that emit little or no CO_2 (IEA 2009). Finally, CCS is the strategic choice that could lower of other GHG reduction measures and significantly lowers the cost of mitigating climate change (IEA, 2012). Most of study also has affirmed that by 2030 and beyond, CCS was the major component of a cost effective portfolio of emission reduction strategies (IPCC 2007).

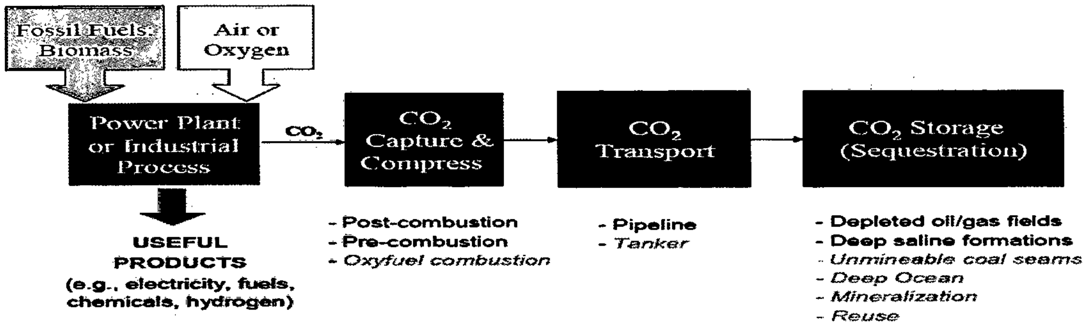

Figure 2-1: The carbon capture and storage (CCS) process
(Source: Folger, 2013)

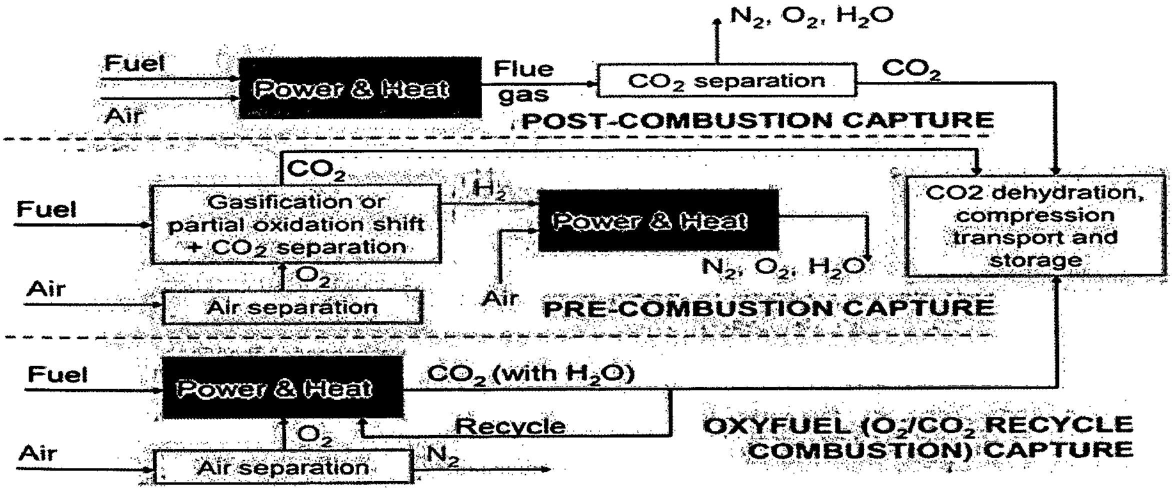

Figure 2-2: Principles of three main CO2 capture options
(Source: Gibbins and Chalmers, 2008; Jordal et al., 2005)

CCS could be defined as a system of technologies that contain CO_2 capture, transportation of CO_2 and geological storage or sequestration (Sigh, 2011). In Figure 2-2, there are three options that commonly used to capture CO_2 generated from fossil fuel energy conversions which are post combustion capture, pre combustion capture and oxy fuel combustion (Pires et al., 2011; Figueroa et al., 2008). In addition, Figure 2-2 also show the different operating principles for the three main technologies currently proposed for CO_2 capture (Jordal et al., 2005):

- In post combustion capture, a new final processing stage was applied to remove most of the CO_2 from the combustion products just before it was released to atmosphere (Gibbins and Chalmers, 2008). The most commercially advanced methods were used is wet scrubbing with aqueous amine solutions to separate and capture the CO_2 (Rao and Rubin, 2002).

- Pre combustion process is the process involves separating and capture CO_2 before the fuel was burned and it is applied on IGCC power plants (Padurean et al., 2012). Pre combustion rate was based on the production of syngas, removal of CO_2 and combustion of H_2 (Steeneveldt et al.,2006). It also known oxymoron because CO_2 was obviously not normally available for capture prior to combustion, as CO_2 was a product of coal combustion, not a natural precursor (Gibbins and Chalmers, 2008).

- Oxy fuel combustion. This process was involved by combustion of a fuel with oxygen in nitrogen free environment to produce a flue or exhaust gas consisting essentially of CO_2 and H_2O. The concept of oxy fuel combustion was proposed by Abraham in the context of providing a CO_2 rich flue gas for enhanced oil recovery (Abraham et al., 1982).

Amongst these technologies, post combustion capture was considered to be one of the most mature capture technologies, since there was a good experience and reputation of this type of technology within many other industrial applications (Singh, 2011). Table 2-1 provides a summary of the inherent advantages and disadvantages of each of these technologies.

Table 2-1: Advantages and disadvantages of different CO2 approaches

Type of process	Advantages	Barriers to implementation
Post combustion	• Applicable to the majority of existing coal fired power plants	Flue gas was: • Dilute in CO_2 • At ambient pressure

	• Modification technology option	Resulting in • Low CO_2 partial pressure • Required higher performance for high capture level • Production CO_2 not follow sequestration requirement
Pre combustion	Synthesis gas was • Concentrated in CO_2 • High pressure Resulting in • Higher CO_2 partial pressure • Increased driving force of separation CO_2 • More technologies available for separation CO_2	• Applicable mainly to the new plants • Obstacle to commercial application of this process • Availability of equipment • Cost of equipment • Advance supporting system required
Oxy combustion	• Flue gas with higher CO_2 concentration • Modification and repowering option	• Required large pure O_2 production • Required cooled CO_2 to maintain temperature fuel material

Source: (Figueroa et al., 2008)

Once the CO_2 is captured, CO_2 would need to be transported to the storage site by the pipeline, motor carriers, railway and water carriers in early of CCS demonstration projects and in regions with inadequate storage (Rao and Rubin, 2002; Sigh, 2011). Figure 2-3 show the transportation and storage of CO_2 by the industrials. There are three pathways of storage options:

- Ocean storage

  This was process involves the dilution of captured CO_2 into ocean waters or the collection of CO_2 in pools at the ocean floor. It requires careful assessment of the environmental impact of putting massive quantities of CO_2 into the ocean (Tamburri et al., 2000).

- Underground injection

  Geological storage involves the underground injection of CO_2. CO_2 was compressed from a gas into a supercritical fluid or a liquid and injected into underground storage reservoirs, such as oil or gas wells, or saline aquifers (Bachu et al., 2000).

- Mineralization

  CO_2 was reacted with minerals to produce rock formations and it offers the opportunity of permanent and safe storage on a virtually unlimited scale (Lackner and Brennan, 2009).

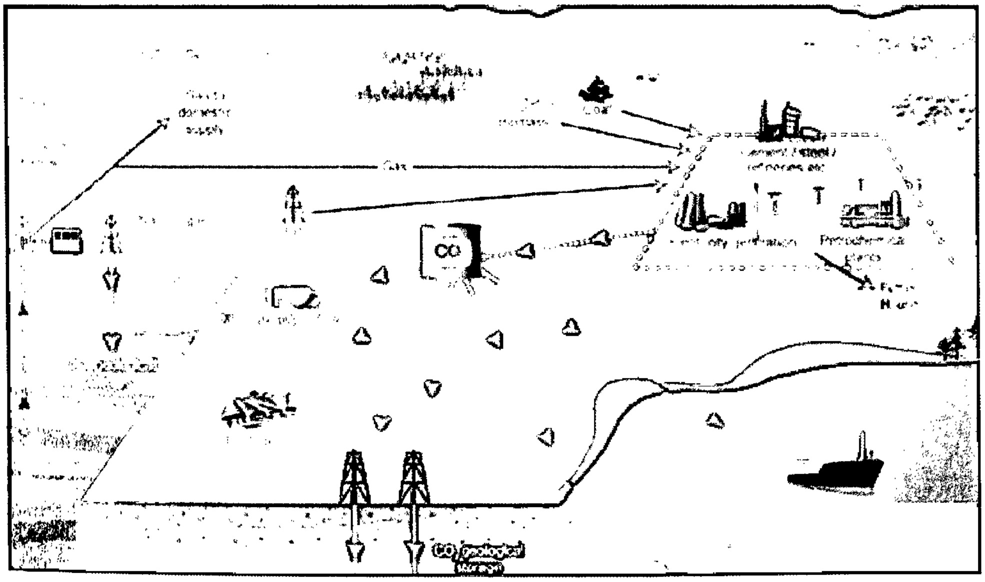

Figure 2-3: Transportation and storage of CO2
(Source: IEA, 2012)

2.4 Gas purification processes

CO_2 usually exists in a mixture of gases and it should be separated in order to be used or stored. This gas is produced from by product of many commercial processes such as ammonia and hydrogen plants, flue gases from the combustion of fossil fuels, lime kiln operation, sodium phosphate manufacture and industrial fermentation (Herzog and Golomb, 2004). In addition, CO_2 also useful in food and beverage production, chemical manufacturing, oil and gas recovery and many other processes.

The selection of technique for separation and capture CO_2 is depends on many factors such as partial pressure of CO_2 in any stream, extent of CO_2 recovery, sensitivity to impurities such as acid gases, particulates, purity of CO_2 and corrosion that could affect our product (White et al., 2003). Based on Figure 2-4, CO_2 separation and capture technique could be classified into the following categories (Gupta et al., 2003; Bui et al., 2014; Herzog and Golomb, 2004):

- **Chemical or physical absorption**

  Chemical or physical absorption is refers to the transfer of a soluble component from a gas phase to a liquid phase (Abharchaei, 2010). This process is one of the most important operations of gas liquid mass transfer. The reaction of gaseous species between liquids and suspended solid particles in liquids was considered as a special case of absorption. These processes were widely used in petroleum, natural gas and chemical industries for separation of CO_2 producing from coal or gases (Micek, 2010). The solvent capacity of an absorbed gas is based on the function of its partial pressure.

- **Cryogenics**

  Cryogenic separation is widely used commercially for removal of CO_2 from stream contains higher CO_2 (Gupta et al., 2003). This purification process is applied using principle of separation based on cooling and condensation, and usually used in liquid separations for a long time (Li et al., 2011). Unfortunately, this technique was not suitable for CO_2 capture. It is because this technique required higher energy demand which is considered unreasonable for practical application.

- **Membrane**

  Membrane is a new technology for gas purification and involves separation of gases by polymeric membranes (Yang et al., 2008). Generally, membrane is made of from polymers or ceramics and could be used to effectively sieve out CO_2 from gas streams. The gaseous component penetrates to the other side of the membrane considering the selectivity of the membrane to the certain component (Abharchaei, 2010). Membrane found into two categories which are membrane gas absorption and gas separation membrane. The examples of membranes for CO_2 separation are polymeric, inorganic, Carbon, Alumina and Silica membranes (Favre, 2011).

- **Microbial or Algae**

  Apart from physical and chemical methods, biological methods have also been proposed for CO_2 separation. Algal bio fixation of CO_2 in photo bioreactors was the suitable example because it has recently gained great interest in CO_2 capture (Kumar et al., 2010). Furthermore, various studies have been performed, in order to determine the excellent microalgae strain. In many cases, cyanobacteria, especially Anabaena sp. have been reported to meet with considerable success (Uddipto et al., 2010).

- **Adsorption**

  According to Abharchaei (2010), adsorption defined as the selective concentration of one or more components of a gas (adsorbate) at the surface of a micro porous solid (adsorbent). This process is start when a gas accumulates on the surface of a solid or a liquid which known as the adsorbent and the accumulated gas was called the adsorbate. (Yazaydin et al., 2009). Adsorption systems operate in a three step cycle: adsorb of CO_2 from mixture gas, purge to remove impure gases and evacuate to remove CO_2 (Abanades et al.,2004). Adsorption process is categories into Physisorption, chemisorptions and desorption (Lu et al., 2008; Valer et al.,2005).

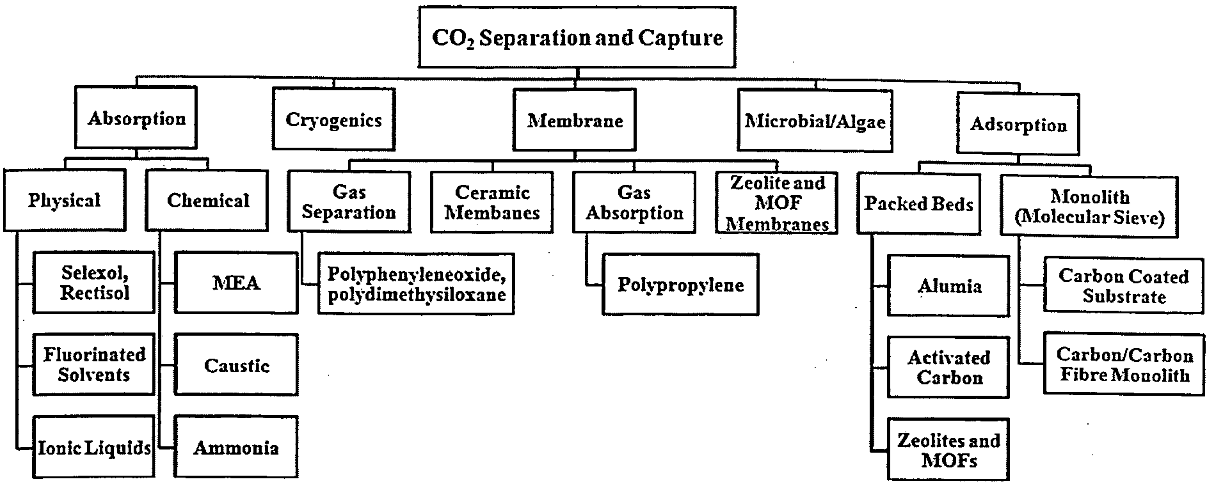

Figure 2-4: Different technologies and associated materials for CO_2 separation and capture
(Source: Li et al., 2011; Rao and Rubin, 2002)

The present thesis deals with chemical solvent absorption to capture CO_2. Today, this technology is the most important in post combustion CO_2 capture process (Bui et al., 2014). The available process for CO_2 capture also represents the most efficient technology for capturing CO_2. This part reflects technological maturity, the technology having been introduced for natural gas sweetening as early as 1930 (Kohl and Nielsen, 1997). Furthermore, it has been used in small scale removal of CO_2 from exhaust gas. Chemical absorption is one of the technologies that could be fairly easily installed; whereas many other technologies involve new forms of power plant technology. Various researches have been made to develop the different technologies, and improvements were likely to change the relative performance of different technologies. Recent investigations have been made by several authors (Santos, 2013; Davidson, 2007). Based on their investigation, researchers suggested that chemical absorption of CO_2 was likely to remain a highly competitive technology for CO_2 capture in the future.

2.5 *CO_2 absorption by amine based*

Separations of CO_2 by using amine based solvent have been implemented since the 1930s for applications such as natural gas purification. In the present chapter a general explanation will be made of the CO_2 capture technology and the nature of available experimental data for the process will be taken from the textbook “Gas Purification” (Kohl and Nielsen, 1997). Figure 2-5 illustrates the instruments commonly used for CO_2 capture in industries.

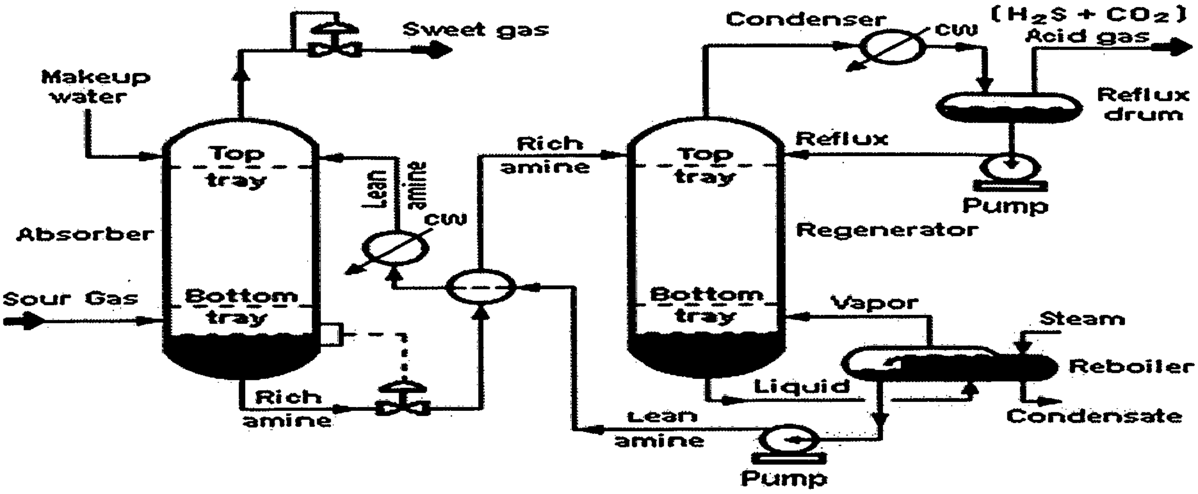

Figure 2-5: A typical process flow diagram for separation and CO_2 capture from industrial effluents using amine solutions
(Source: Zhao et al., 2010)

A cooled exhaust gas is feed into the bottom of the absorber column. Inside the column, the gas rises from the bottom and meets with a counter current liquid stream. The CO_2 absorbs and reacts with components in the liquid, and CO_2 in gas stream was gradually reduced while moving up the column. (Radosz et al., 2008).

At the top stream of the column, the gas with low CO_2 content was released to the atmosphere. The CO_2 content of the liquid increases as the liquid moves down the column. The liquid stream was usually at 90-95% of equilibrium with incoming exhaust gas at the column bottom. The liquid was flow out at the bottom stream and is pumped into the top of a second column, the stripper or desorber. In the stripper the temperature and pressure were set to produce chemical equilibrium in the liquid were reversed and the CO_2 was released into the gas phase. Basically, the temperature was changed by adding heat as steam in the reboiler below the stripper column. The gas phases contain only of CO_2 and steam was taken out at the top of the column. CO_2 was separated from the steam in the overhead condenser and then, CO_2 could be compressed and sent to the storage. The liquid at the bottom of the stripper column will be containing a low concentration of CO_2; and recycle again to be used for CO_2 absorption. It was sent back to the top of the absorber column. The liquid keeps circulating between absorber and stripping column to transport the CO_2 between the columns. In an industrial system, the absorber will usually be operated at temperatures around 40-55° C while the stripper will be operating at around 120 °C (Santos, 2013).

Recent researches have been made to increase the knowledge about CO_2 absorption of amine based including the research has been made by Yeh and Pennline (2001). Yeh and Pennline (2001) found that many factors could affect amine based scrubbing such as gas liquid area, structured packing and the type amine used.

2.6 Commercial solvents for CO_2 post combustion capture process

The development of amine scrubbing technology has been started for over 60 years in the chemical and oil industries for removal of hydrogen sulphide (H_2S) and CO_2 (Gupta et al, 2003). In addition, chemical absorption with alkanolamines have been used in processes such a natural gas sweetening and hydrogen production to remove CO_2 (Chakravarti et al., 2001).

Alkanolamines could be divided in four main groups: primary amines, secondary amines, and tertiary amine and these structures were containing at least one hydroxyl functional group (OH) and amino group (Yu et al., 2012). Several example of alkanolamines such as MEA (monoethanolamine), DEA (diethanolamine), MDEA (methyldiethanolamine), DIPA (diisopropanolamine), DGA (diglycolamine), TEA (triethanolamine). Another group was sterically hindered which is defined as amines for which either a primary amino group or secondary amino was attached to a tertiary or secondary carbon atom. Several examples of sterically hindered is AMP (2-Amino-2-methyl-1-propanol) and PE (2-Piperidine ethanol) (Singh, 2011; Idris and Eimer, 2014). All of these solvents have been found commercially used in industries. Figure 2-6 illustrate the molecular structure of monoethanolamine (MEA) absorbent.

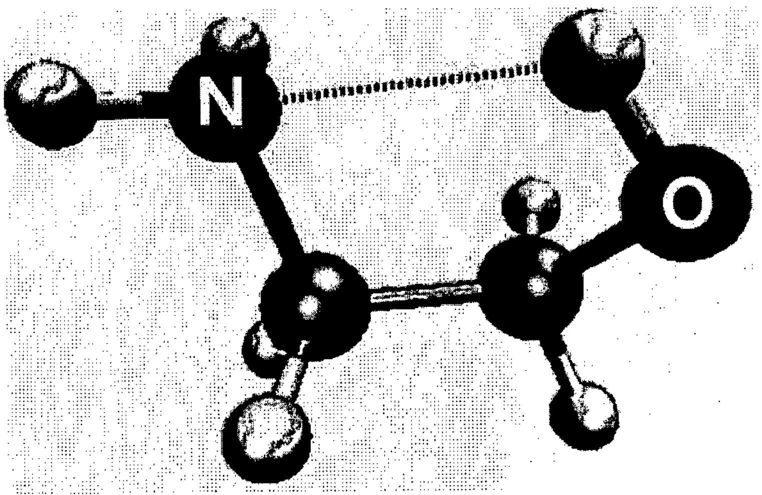

Figure 2-6: MEA (Monoethanolamine) absorbent
(Source: Yu et al., 2012).