FOAMING BEHAVIOUR OF PRIMARY, SECONDARY AND TERTIARY AQUEOUS SOLUTION OF AMINE FOR THE REMOVAL OF CARBON DIOXIDE

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ABSTRAK

Dalam pembelajaran ini memfokus pada kesan penggunaan berlainan jenis amine untuk menyahbuang gas berasid melalui buih. Buih berasal daripada ribuan gas menggelembung. Gelembung-gelembung terbentuk apabila lapisan cecair merangkumi gas. penyelidikan ini untuk menyiasat tingkahlaku buih ke atas berlainan kes untuk amine pertama (monoethanolamine, MEA), kedua (diethanolamine, DEA) dan ketiga (methyldiethanolamine, MDEA) melalui kesan oleh kepekatan, suhu dan kekotoran. Kesan daripada semua parameter akan dinilai berdasarkan ketinggian buih yang terbentuk dan mase untuk buih pecah. Nitrogen gas (N_2) akan digunakan dalam eksperimen ini sebagai gas gelembung. Beberapa analisa telah membuat hipotesis yang telah ditetapkan berdasarkan setiap kes yang dikaji. Hipotesis untuk pembelajaran ini ialah semakin tinggi kepekataan campuran akan mengurangkan buih. Hipotesis lain pula semakin tinggi suhu campuran MEA dan DEA juga akan mengurangkan buih. Kesan kekotoran terhadap pementukan buih telah diklasifikasikan seperti berikut: iron sulphide, untuk campuran MDEA buih akan berkurang; sodium chloride, untuk campuran MDEA kecenderungan pembentukan buih juga berkurangan; methanol, buih turut berkurang dalam campuran MDEA. Ini menunjukkan iron sulphide merupakan paling mempengaruhi pencemaaran dalam pembentukan buih untuk kepekatan yang sama untuk semua kekotoran yang dikaji.

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ABSTRACT

This study is focusing on the effect by the usage of different amine in order to remove acid gases that is foaming. Foam is made up of thousands of gas filled bubbles. Bubbles are formed when a liquid film encapsulates gas. This research is to investigate the foaming behaviour on the different cases for the primary (monoethanolamine, MEA), secondary (diethanolamine, DEA) and tertiary (methyldiethanolamine, MDEA) amine on the effect of concentration, temperature and impurities. Effect of all this parameters will be evaluated based on height of foam and collapse time of foam. Nitrogen gas (N_2) will be used in this experiments as bubble gas. For this work several hypothesis has been set according to respectively cases. The hypothesis of this study is a higher solution concentration of MEA will reduce the foaminess. Other hypothesis is a higher solution temperature of MEA and DEA will reduce the foaminess also. Effects of impurities toward foaming formation are classified as following: iron sulphide, for MDEA solution foaming decrease; sodium chloride, for MDEA solution tendency for formation of foam decrease; methanol, foaming decrease in MDEA solution. It is apparently iron sulphide meet the most influential contaminants to the foam formation at the same concentrations of all impurities studied.

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LIST OF ABBREVIATIONS

C

CO_2	Carbon Dioxide

D

DEA	Diethanolamine

F

FeS	Iron sulfide

H

H_2S	Hydrogen sulfide

M

MEA	Monoethanolamine
MDEA	Methyldiethanolamine

O

N_2	Nitrogen
NG	Natural gas
NaCl	Sodium Chloride

CHAPTER 1

INTRODUCTION

1.1 Overview on Natural gas

Natural gas is a mixture of hydrocarbon gas which consists primarily of methane about 90% of the total volume and varying amounts of other hydrocarbons as well as non-hydrocarbon gases. It consists of considerable amounts of carbon dioxide, and hydrogen sulphide, sulfur dioxide and nitrogen oxide, etc., along with less quantities of carbon monoxide, and other reactive hydrocarbons. Natural gas can be considered as the cleanest as evidence in Table 1.1.

Table 1.1 Fossil Fuel Emission Levels Pounds per Billion Btu of Energy Input

Pollutant	Natural gas	Oil	Coal
Carbon Dioxide	117,000	164,000	208,000
Carbon Monoxide	40	33	208
Nitrogen Oxides	92	448	457
Sulfur Dioxide	1	1,122	2,591
Particulates	7	84	2,744
Mercury	0	0.007	0.016

Source: EIA – Natural Gas Issues and Trends 1998

Natural gas is believed to be the most important energy source. The abundance of natural gas coupled with its environmental soundness and multiple applications across all sectors, means that natural gas will continue to play an increasingly important role in meeting demand for energy. In general, there are two primary sources that determine the demand for natural gas, which are the short term demand and the long term demand.

The short term demand includes the weather, fuel switching as well as the current economy while the long term demand includes the residential, commercial, industrial, electric generation and transportation sector demands. There are many reasons for the long term expected increase in natural gas demand. The productions of natural gas have been increasing gradually over the years to meet the global demand for natural gas in various sectors. As can be seen, demand for all types of energy, except nuclear and hydro power, is expected to increase over the next 20 years. This general upswing can be attributed to the expected general growth of the economy and population, as well use of personal technologies such as computers, smart phones and music devices increasing day by day.

1.2 Overview on Carbon Dioxide

The impurities in a gas stream of natural gas usually consisting of carbon dioxide (CO_2), hydrogen sulfide (H_2S) and COS and was known as acid gases. One of the main acid gases is produced in large quantities by many important industries such as fossil fuel fired power plant, steel production, chemical and petrochemical manufacturing, cement production and natural gas purification. Acid gas that has to be removed from natural gas is CO_2.

The presence of CO_2 in natural gas reduces the fuel value of natural gas and an acidic component, whereas the presence of H_2S increases the toxicity. Environmental concerns, such as global climate change, are now one of the most important and challenging environmental issues facing the world community and have motivated intensive research on CO_2 capture and sequestration. Carbon dioxide is currently responsible for over 60% of the enhanced greenhouse effect. Therefore, CO_2 knows to be a major contributor in global climate change.

It is usually desirable to remove acid gas due to the corrosion problem, lowering the heating value of natural gas and other operational problem. Removal of the contaminant is required for reason of safety, corrosion control, gas and/or liquid product specification, to prevent freeze-out at low temperature, to decrease compression cost, to prevent poisoning of catalyst in downstream facilities and to meet environmental requirement. The process to remove CO_2 is called gas conditioning or treating. This process is generally referred to the process of removing or actually reducing the amount of acid gases until to an acceptable limit.

In principle, various methods could be used for the removal of CO_2. Rao and Rubin (2002) stated that a wide range of technologies currently exist for separation and capture of CO_2 from gas streams. There are a few processes in removing CO_2, namely absorption based on chemical solvent, absorption based on physical solvent, by adsorption and by gas permeation. CO_2 was also produced for other industrial application such as carbonation of brine, welding as inert gas, food and beverage carbonation, dry ice, urea production and soda ash industry.

Since CO_2 is the main product during the combustion of natural gas, it can cause serious and challenging environment concern facing the world community especially the greenhouse effect that can contribute to global warming. CO_2 is currently responsible for over 60% of the enhanced greenhouse gases, methane (CH_4) contributes 20% and the remaining 20% is caused by nitrous oxide (N_2O), a number of industrial gases and ozone is shown in Figure 1.1. Global climate change has a long time issue with implications in different areas, such as, climate, environment, economy, society, politics, technology, institution, etc.

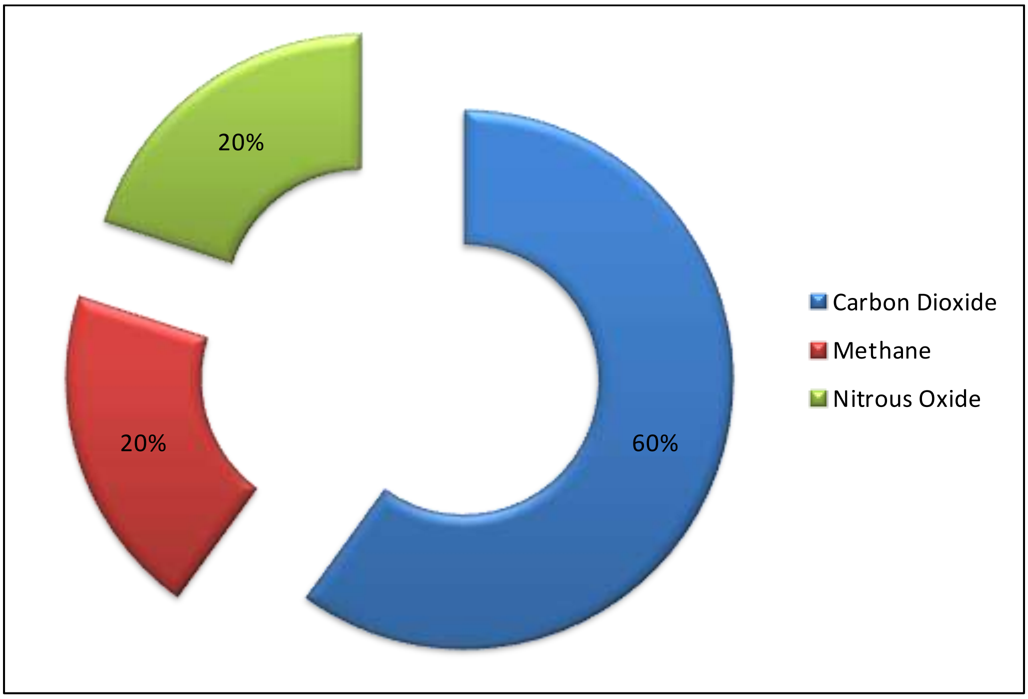


Figure 1.1 Contribution of Greenhouse Gas

Scientific evidence strongly suggests that increased levels of greenhouse gas may lead to higher temperature and cause climate change on a global scale. Various climate models estimate that the global average temperature may rise about 1.4°C - 5.8°C by the year 2100 (Williams, 2002). An estimate during January 2008 showed that the natural gas reserves in Malaysia were at 88.0 trillion standard cubic feet (tscf) or 14.67 billion barrels of oil equivalent, approximately three times the size of crude oil reserves (5.46 billion barrel). The distribution of gas reserves in Malaysia is shown in Figure 1.2.

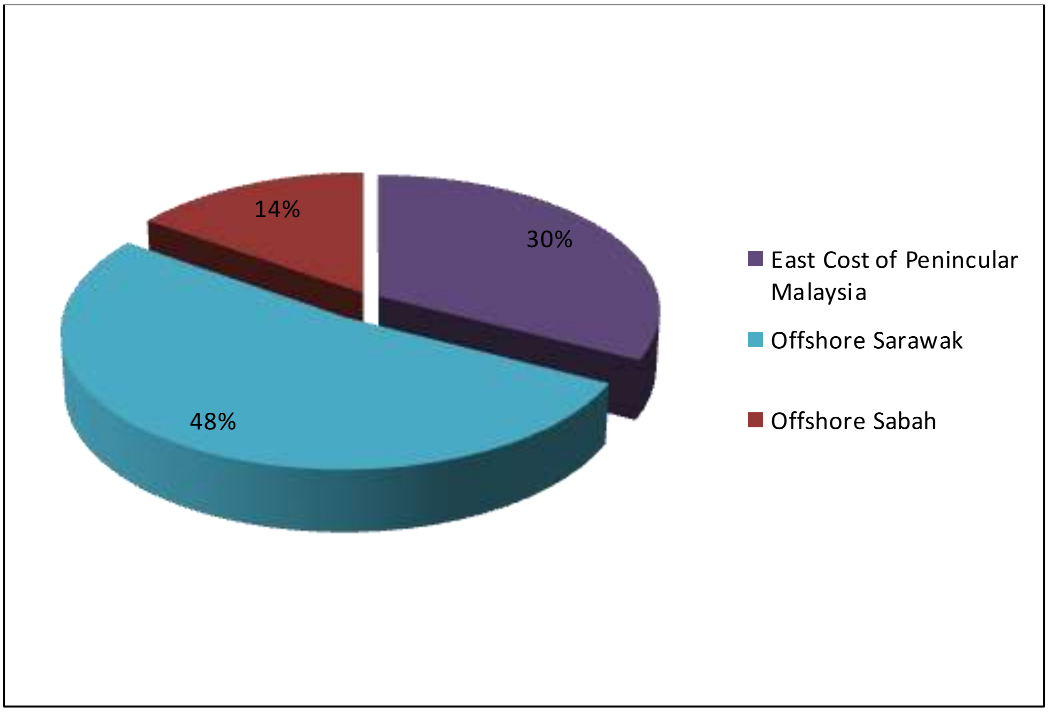


Figure 1.2: Malaysia natural gas reserves

(*Source: www.gasmalaysia.com*)

1.3 Overview of Foaming

Few problems has arises when using the common amine as the absorption solvent in industry such as the health hazards, sales contact and corrosion problems and foaming tendency. In this study, foaming tendency will be investigate using different type of amine for different concentration, temperature and impurities. Foaming is a mass of bubbles form of air or gas in a matrix of liquid film, especially an accumulation of fine, frothy bubbles formed in or on the surface of a liquid, as from agitation or fermentation. Bubbles will form when a liquid film encapsules gas (Phul, 2001). Foaming is one of severe problem in CO_2 absorption process. This is due to many causes such as suspended solid, condensed hydrocarbons, amine-degradation products and foreign matter from corrosion inhibitors, from grease or from contaminants in the water.

Despite having relatively high solubility of CO_2, the usage of amine solutions can has many drawbacks such as foaming. In a way to reduce foaming, the elements such as concentration, temperature and impurities must be controlled by continuous research.

1.4 Objectives

The following are the objectives of this research:

- To investigate the forming tendency on primary, secondary and tertiary amine.
- To study the effect of temperature-dependence on the foaming behaviour.
- To study the forming behaviour on amine solution with the presence of different type of impurities.

1.5 Scope of research

The scope of the present research is to identify the suitable amines on the characteristic of foam behaviour for the effective capture of CO_2. The chemicals used in this research are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). The first case is the study on the primary (MEA), secondary (DEA) and tertiary (MDEA) amine solution on the foam behaviour. In this case, all aqueous solution will be varied in terms of its concentration from 20% to 100% by volume of amines. The concentration with the lowest foam tendency will be choosing for the study on temperature-dependence. The temperatures that will be use are varied from 40°C to 70°C. The best results on the foaming tendency from the temperature-dependency investigation will be used for the investigation on the presence of impurities. Different type of impurities will be used which are iron sulphide and sodium chloride.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Alkanolamine

Amines are organic compounds that contain nitrogen and are basic. An amine is a compound in which one or more of the hydrogen atoms in ammonia have been replaced by an organic functional group which is hydrogen groups. Amines are generally weak bases. Furthermore, most amines are organic bases. Recently a new class of amines, which is sterically hindered amines, has been introduced as commercially attractive to remove acid gases. The effect of hydrocarbon and organic acids on the absorbent over conventional amines such as MEA, DEA, DIPA, MDEA, etc., and as rate promoters for the hot carbonate process has been studied by Sartori & Savage, 1978, 1983; Say et al., 1984; Brown, Chludzinski, Clem, & Goldstein, 1984; Kohl & Nielsen, 1997.

Alkanolamines are the most commonly used chemical absorbents for the removal of acidic gases today. Recent economic studies by Desideri and Corbelli, (1998) indicate that the process will also remain competitive in the future. A chemical need to be used as a commercial absorbent must have high net cyclic capacity, high absorption rate for CO_2, and good chemical stability. Therefore, the CO_2 reaction with alkanolamines is of considerable importance. A wide range of technologies currently exist for separation and capture of CO_2 from gas streams.

Absorption is a separation process in which soluble components of a gaseous mixture dissolve in absorption liquid. There are two main types of absorption processes; one based on physical solubility (physical absorption), and the other based on chemical reactions between solute and solvent (chemical absorption). Absorption with amine-based absorbents is the most common technology for CO_2 removal today. The common alkanolamine used in industry are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) in order to remove acid gas in natural gas. Based on Kohl and Riesenfeld, (1985) the alkanolamine is a common chemical absorbent used in refineries. Miguel Ángel et al. (2011) stated that mixtures of two or more alkanolamines (primary or secondary with tertiary alkanolamine) have been used to improve the efficiency of the purification processes. The commonly used absorbents for CO_2 removal from gas mixtures in industry are aqueous solutions of alkanolamines such as monoethanolamine (MEA) and diethanolamine (DEA). The gas is contacted with the amine solution, which preferentially absorbs the CO_2. The amine solution is then heated and almost pure CO_2 is released from the stripper.

Other than that, Frazier and Kohl, (1950) said the alkanolamines of prime significance include monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA) as well as the use of aqueous solutions of *N*-methyldiethanolamine (MDEA) help to accomplish selective removal of acid gases. For economic reasons, the absorbents must have a low solvent cost, a high net cyclic capacity and high reaction/absorption rate for CO_2 and must be an energy saving solvent. Table 2.1 shows the boiling points of some amines.

Physical properties of amines

Boiling points

Table 2.1 Boiling points of amines

Type	Formula	Boiling point (°C)
primary	CH_3NH_2	-6.3
primary	$CH_3CH_2NH_2$	16.6
primary	$CH_3CH_2CH_2NH_2$	48.6
secondary	$(CH_3)_2NH$	7.4
tertiary	$(CH_3)_3NH$	3.5

2.1.1 Primary amine

In primary amines, there is only one of the hydrogen atoms in the ammonia molecule has been replaced. That means that the formula of the primary amine will be RNH2 where "R" is an alkyl group. The example shows the formula such as:

i. $CH_3\text{-}NH_2$

ii. $CH_3\text{-}CH_2\text{-}NH_2$

iii. $CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_2$

Thee et al. (2012) said aqueous solutions of both carbonate and amines, mainly monoethanolamine (MEA), are widely used in CO_2 removal processes. Schäffer et al. (2012) also claimed that aqueous solutions of monoethanolamine (MEA) has been commonly used for the existing amine scrubbing processes because of its high reaction kinetics during CO_2 absorption. Moreover, the degradation rate of each type of amine is important for primary amines such as MEA significantly greater than those of tertiary and hindered amines reported by Dawodu and Meisen, 1996. The absorber is operates at between 30 and 60°C by Dumee et al. (2012). Chowdhury et al. (2009) stated that absorption rate of alkanolamines is dependent on the nitrogen substituent feature as MEA reacts faster than DEA and MDEA. The properties of MEA are shown in Table 2.2 while in Table 2.3 are the advantages and disadvantages of MEA.

Table 2.2 Properties of MEA

Molecular formula	C_2H_7NO
Molar mass	61.08g/mol
Mol file	141-43-5mol
Melting point	10.3°C
Boiling point	170.8°C
Density	1.01g/mL at 25°C
Vapor density	2.1 (vs air)
Vapor pressure	0.1kPa (20°C)
Water soluibility	Miscible

Table 2.3 Advantages and Disadvantages of MEA

Advantages	Disadvantages
- high reactivity	- high enthalpy of reaction with CO_2
- low solvent cost	- high desorber energy consumption
- low molecular weight	- high the formation of a stable carbanate
- high absorbing capacity on a mass basis	- high formation of degradation products with COS or oxygen bearing gases
- high reasonable thermal stability	- inability to remove mercaptans
- high thermal degardation rate	- vaporization losses
	- more corrosive

Table 2.4 below contains literature citations from 1960s to the present, for various temperature or temperature ranges of the experiments, MEA concentrations or concentrations ranges, and experimental techniques used.

Table 2.4 Literature data on the reaction between CO_2 and MEA

(Sources: A. Aboudheir et al., 2008)

Referance	T (K)	[MEA]mol/dm3	Experimental Technique
Alvarez-Fuster et al. (1980)	293	0.2-2.0	Wetted wall column
Donaldson and Nguyen (1980)	298	0.03-0.08	Membranes method
Laddha and Danckwert (1981)	298	0.49-1.71	Stirred cell reactor
Peny and Ritter (1983)	278-303	0-0.06	Stopped flow method
Sada et al. (1985)	303	0.5-2.0	Stirred cell reactor
Barth et al. (1986)	293	0.02-0.05	Stopped flow method
Barth et al. (1986)	298	0.02-0.05	Stopped flow method
Crooks and Donnellan (1989)	298	0.02-0.06	Stopped flow method
Alper (1990)	278-298	0-0.45	Stopped flow method
Little et al. (1992)	318	0-3.2	Stirred cell, numerical
Little et al. (1992)	333	0-3.2	Stirred cell, numerical
Hagewiesche et al. (1995)	313	0	Laminar jet, numerical
Versteeg et al. (1996)	Literature	Literature	Literature Data
Xiao et al. (2000)	303	0.1-0.4	Wetted wall column
Xiao et al. (2000)	308	0.1-0.4	Wetted wall column
Xiao et al. (2000)	313	0.1-0.4	Wetted wall column
Horng and Li (2002)	303-313	0.1-0.5	Wetted wall column

2.1.2 Secondary amine

In a secondary amine, two of the hydrogen in an ammonia molecule has been replaced by hydrocarbon groups. The examples of secondary amine are:

i. CH_3-NH-CH_3
ii. CH_3-CH_2-NH-CH_2-CH_3

By Wang et al. (2004), DEA is a popular commercially used absorbent with two ethanol groups attached to the nitrogen atom. Secondary amines are less corrosive and require less heat to regenerate because the additional ethanol group draws most of the free electron character away from the nitrogen atom. Table 2.5 shows the properties of DEA.

Table 2.5 Properties of DEA

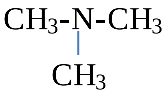
Molecular formula	$C_4H_{11}NO_2$
Molar mass	105.14g/mol
Melting point	28°C
Boiling point	217°C/150mmHg
Density	1.097g/mL at 25°C
Vapor density	3.6(vs air)
Vapor pressure	<0.98atm(100°C)

DEA is more resistant to solvent degradation and corrosion than MEA. Sutar et al., 2012 discussed that secondary alkanolamines linked to an alkyl group constitute a further class of candidate amines with good potential for gas purification. These sterically hindered amines offer high absorption capacity and reaction rates. Moreover, they are more resistant to corrosion than MEA even at high amine concentrations; besides, the regeneration energy requirement is lower than that of MEA.

2.1.3 Tertiary amine

In a tertiary amine, all of the hydrogen in an ammonia molecule have been replaced by hydrocarbon groups. You are only likely to come across simple ones where all three of the hydrocarbon groups are alkyl groups and all three are the same. For example:

i.



$$\begin{array}{c} CH_3\text{-}N\text{-}CH_3 \\ | \\ CH_3 \end{array}$$

The tertiary amine of MDEA has two ethanol groups attached to the nitrogen atom along with a methyl group. Loo et al. (2007) stated that if the costs of regeneration are taken into account, tertiary amine which is MDEA is much more attractive. Table 2.6 shows the properties of MDEA.

Table 2.6 Properties of MDEA

Molecular formula	$C_5H_{13}NO_2$
Molar mass	119.16g/mol
Mol file	105-59-9mol
Melting point	-21°C
Boiling point	246-248°C
Density	1.038g/mL at 25°C
Vapor density	4 (vs air)
Vapor pressure	0.01mmHg (20°C)
Refrective index	1.469 at 20°C
Water solubility	miscible

2.2 CO_2 Removal

In gas processing industry, impurities in natural gas such as CO_2 and H_2S need to be removed because they have own causes during the process. According to Bhide et al. (1998) natural, synthesis, and refinery of the raw gases contain acid gases such as H_2S and CO_2. Removal of acid gas from gas mixtures is very important in natural gas processing, hydrogen purification, refinery off gases treatment and synthesis gas for ammonia and methanol making. In gas absorption process there is increasing interest for the selective removal of acid gases from the raw gas stream.

Thee et al. (2012) mentions that the removal and sequestration of carbon dioxide (CO_2) from the flue gas of coal-fired power stations by aqueous absorption is being actively investigated as a technology to help mitigate global warming due to human activities. Other than that, increasing carbon dioxide emission level due to fossil fuel combustion have been shown as a cause climate changing and global average temperature rise said by Le Treut, 2003; Marchal and Chappellaz, 2004; Michard, 2008. Therefore, the research has been conducted toward capturing CO_2 from fossil fuel combustion as an approach to greenhouse gas mitigation (Pires et al., 2011; Steeneveldt et al., 2006).

CO_2 capture by chemical absorption using an aqueous solution of amine based absorbents is a common industrial process and has, in many cases, been found to be the most viable solution compared with other processes (Chowdhury et. al., 2009). While, Kohl and Nielsen, 1997 said that the use of an aqueous solution of an amine to chemically react and absorb CO_2 is the most widespread technology in the natural gas sweetening industry. CO_2 is typically recovered by a reversal of the chemical reaction between CO_2 and amine, which is induced by a temperature increase, a reduction in pressure or both said by Pires et al., 2011; Wang et al., 2011; Yang et al., 2008.