

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Global Warming

Global warming caused by the greenhouse effect has become a worldwide concern. With industrialization and population growth, the greenhouse gas (GHG) emissions derived from human activities have dramatically increased over the last 200 years. The desire to alleviate the problem has resulted in serious environmental concerns deriving from the need to reduce GHG emissions from industrial sources. Therefore, the international response to mitigate global warming was to ratify the Kyoto Protocol, in Japan in December 1997. Industrialized countries have agreed to cut the CO<sub>2</sub> emissions down to approximately 5 % less than the emission in 1990, in a five year period from 2008 to 2012. The regulations on CO<sub>2</sub> emissions are coming in the near future (Kyoto Protocol, 2009). Because CO<sub>2</sub> accounts for the largest portion of the world's annual emission of GHG, which contributes to 9-26 %, it has become a major target for reduction (Kiehl *et al.*, 1997).

#### 2.2 CO<sub>2</sub> Generation

##### 2.2.1 Source of CO<sub>2</sub>

The primary natural processes that release CO<sub>2</sub> into the atmosphere (sources) and that remove CO<sub>2</sub> from the atmosphere (sinks) are as follows:

- Animal and plant respiration, by which oxygen and nutrients are converted into CO<sub>2</sub> and energy, and plant photosynthesis, by which CO<sub>2</sub> is removed from the atmosphere and stored as carbon in plant biomass.
- Ocean-atmosphere exchange, in which the oceans absorb and release CO<sub>2</sub> at the sea surface.
- Volcanic eruptions, which release carbon from rocks deep in the Earth's crust (this source is very small).

A variety of human activities lead to the emission (sources) and removal (sinks) of CO<sub>2</sub>.

- The largest source of global CO<sub>2</sub> emissions is the combustion of fossil fuels, such as coal, oil, and gas, in power plants, automobiles, industrial facilities, and other sources.

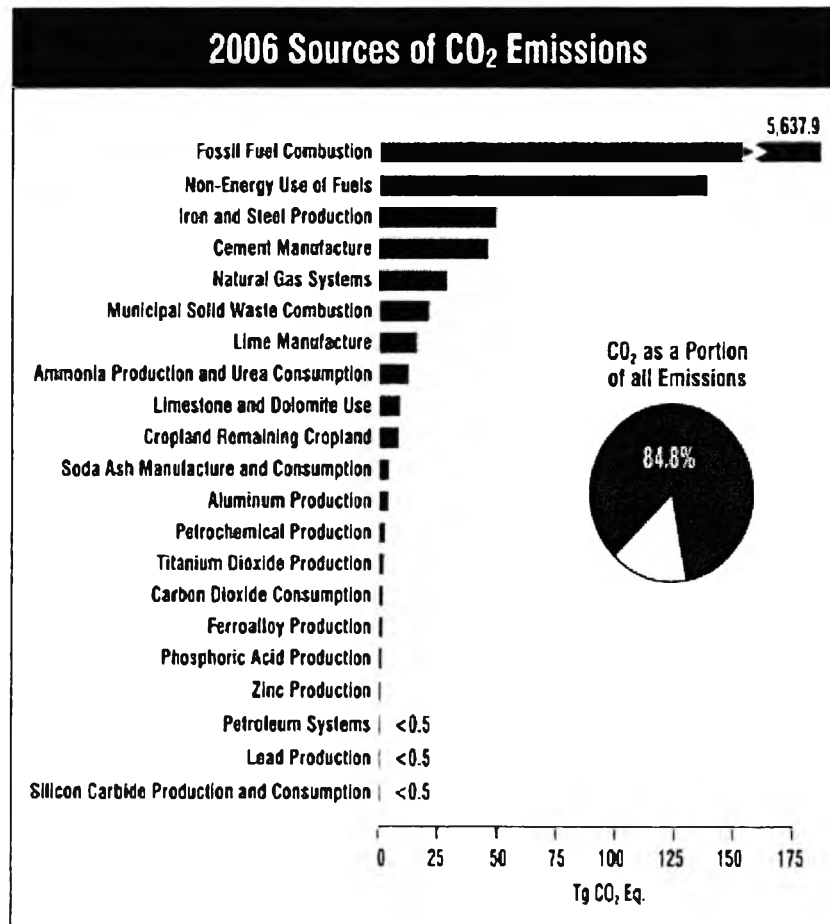
- A number of specialized industrial production processes and product uses, such as mineral production, metal production, and the use of petroleum-based products, can also lead to CO<sub>2</sub> emissions.

- The emissions caused by the transportation of goods and people. People traveling (by car, plane, train, etc.) are examples of direct emissions since people can choose where they are going and by what method.

- Carbon sequestration is the process, by which growing trees and plants absorb or remove CO<sub>2</sub> from the atmosphere and turn it into biomass (e.g. wood, leaves, etc.). Deforestation, conversely, can lead to significant levels of CO<sub>2</sub> emissions in some countries.

- CO<sub>2</sub> can be captured from power plants and industrial facilities before it is released into the atmosphere, and then injected deep underground.

Figure 2.1 below displays a breakdown of sources of CO<sub>2</sub> emissions in the U.S. in 2006. It can be clearly seen that by far, the largest source is fossil fuel combustion.



**Figure 2.1** Sources of CO<sub>2</sub> emissions in the U.S. in 2006, where y-axis units are teragrams of CO<sub>2</sub> equivalent (U.S. Greenhouse Gas Emissions Inventory, 2006).

### 2.2.2 Flue Gas Characteristics

Flue gases emitted from medium to large sources are generally at or slightly above atmospheric pressure. They typically contain 3-15 % (by volume) of CO<sub>2</sub>. For example, flue gas from a coal-fired power plant typically contains about 14 % CO<sub>2</sub>, 5 % O<sub>2</sub>, and 81 % N<sub>2</sub>. Flue gas from a natural gas turbine is even leaner in CO<sub>2</sub>, but higher in O<sub>2</sub>, with a typical composition of 4 % CO<sub>2</sub>, 15 % O<sub>2</sub>, and 81 % N<sub>2</sub>. Typical trace contaminants found in flue gas include sulfur oxides (SO<sub>x</sub>), nitrogen

oxides (NO<sub>x</sub>), and particulates. Their levels vary widely, depending on fuel composition, combustion system, operating system, and operating conditions. For example, the flue gas of a coal-fired power plant contains 300-3,000 ppm SO<sub>x</sub>, 100-1,000 ppm NO<sub>x</sub>, and 1,000-10,000 mg/m<sup>3</sup> particulate matter. Natural gas firing significantly lowers the contaminant levels to less than 1 ppm SO<sub>x</sub>, 100-500 ppm NO<sub>x</sub>, and to around 10 mg/m<sup>3</sup> particulate matter.

## 2.3 CO<sub>2</sub> Removal Processes

There are various technologies being used to separate CO<sub>2</sub> from the flue gas released from conventional fossil fuel combustion. These include adsorption, membrane, and cryogenic liquefaction processes, as well as both physical and chemical absorption processes.

### 2.3.1 Adsorption Processes

The adsorption process comes with close to 2,000 plants worldwide using the process for CO<sub>2</sub> removal. The process can be applied in two modes of operation: pressure swing adsorption (PSA) and temperature swing adsorption (TSA). PSA is one of the most known industrial processes for gas separation. PSA technology has already been suggested for the removal of CO<sub>2</sub> from gaseous streams containing CH<sub>4</sub>. The most important decision in any adsorption-based technology is the adsorbent selection. Zeolites are microporous materials that adsorb CO<sub>2</sub> strongly, suggesting that these materials can be used in PSA processes. Zeolites have proved to have better performance than activated carbons in the PSA separation of CO<sub>2</sub> from flue gases (Cavenati *et al.*, 2006). In addition, TSA uses alumina and zeolite adsorbents for natural gas purification. Only the zeolite removes CO<sub>2</sub> along with other contaminants from natural gas via physisorption while other contaminants besides CO<sub>2</sub> are removed by the alumina (Petrochemical Processes Handbook, 2003).

### 2.3.2 Membranes Processes

Membrane gas separation, especially CO<sub>2</sub> separation, has been known since the 1980s. Membrane separation is used both in the petrochemical industry and in the cleaning of natural gas before transport. The use of polymer membranes in the 1980s contributed to the commercial success of this separation technique in comparison to absorption processes or cryogenic fractionation. However, the main task of the CH<sub>4</sub> used in those cases was to recover H<sub>2</sub> and CO<sub>2</sub> from CH<sub>4</sub>. In addition, these processes proceeded at high pressures. In contrast, the main goal of the membranes used in the flue gas system is the separation of CO<sub>2</sub> from N<sub>2</sub> at ambient pressure. Within the last several years, dynamic developments in membrane technology for CO<sub>2</sub>/N<sub>2</sub> separation have occurred. The use of highly selective materials, especially polymers, has allowed for production of membranes with selectivity over 200 and even up to 400. Simultaneously, an increasingly high packing density, expressed in square meters of membrane per cubic meter of the installation, can enable a relatively small separation installation (Kotowicz *et al.*, 2010). Polymers that have been studied for membrane materials include polyacetylenes, polyaniline, poly(arylene ether)s, polyarylates, polycarbonates, polyetherimides, poly(ethylene oxide), polyimides, poly(phenylene ether), poly(pyrrolone)s, and polysulfones.

### 2.3.3 Cryogenic Liquefaction Processes

By reducing the temperature of the natural gas stream, CO<sub>2</sub> will liquefy at temperatures much higher than CH<sub>4</sub>, thereby being removed in an intermediate step. This is an attractive technology when natural gas is going to be transported in the form of liquefied natural gas (LNG). This process has the additional advantage of separating water and CO<sub>2</sub>. Approximately 25 % of the natural gas produced in the world is transported as LNG, since the volume is reduced around 600 times (Cavenati *et al.*, 2006). Liquefaction technology of CO<sub>2</sub> is still limited to streams with high CO<sub>2</sub> concentration and not viable for streams containing low amount of CO<sub>2</sub> (White *et al.*, 2003). Currently, only ethanol, H<sub>2</sub>, syngas, and NH<sub>3</sub> productions utilize the cryogenic liquefaction technology.

#### 2.3.4 Physical and Chemical Absorption Processes

About 2,500 plants worldwide apply the absorption technique to remove CO<sub>2</sub>. The process using amine-based solutions has been commercialized to remove CO<sub>2</sub> from natural gas for 60 years. It is considered as the most mature CO<sub>2</sub> removal process. The process can be divided into two categories: chemical and physical. The processes, where the solvent chemically reacts with the dissolved CO<sub>2</sub>, are referred to as chemical absorption processes. For these applications, alkanolamines are commonly used as reactive absorbents. In contrast, physical absorption processes are the ones, where the solvent only interacts physically with the dissolved CO<sub>2</sub>. A solvent is used as an absorbent with thermodynamic properties such that the relative absorption of CO<sub>2</sub> is favored over the other components of the gas mixture. Some commonly used physical solvents are methanol and glycol ethers (Ritter and Ebner, 2004). In addition, the absorption process is also applied to remove CO<sub>2</sub> from syngas and NH<sub>3</sub> production using hot carbonate or monoethanolamine. A number of elements involved in the absorption process have been studied, including absorbent modification, process design improvement, and process operation optimization.

All of these four CO<sub>2</sub> removal processes are commercially important. However, chemical absorption, e.g. with amine-type absorbents, is well suited for CO<sub>2</sub> recovery from flue gas. The chemical reaction between CO<sub>2</sub> and amines greatly enhances the driving force for the separation, even at low partial pressures of CO<sub>2</sub>. The costs of this technology are relatively insensitive to the feed CO<sub>2</sub> content. Consequently, chemical absorption with amines provides the most cost-effective means of directly obtaining high purity (> 99 %) CO<sub>2</sub> vapor from flue gases in a single step (Charkravarty *et al.*, 1985).

## 2.4 Chemical Absorption with Alkanolamines

Chemical absorption with alkanolamines has been generally used in many processes, such as natural gas sweetening and H<sub>2</sub> production for the rejection of CO<sub>2</sub>. However, in these applications, the CO<sub>2</sub> partial pressure is significantly greater than that in flue gas applications. Several alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), diglycolamine (DGA), triethanolamine (TEA), and other sterically hindered amines, have found commercial uses. The most recognized amine of the latter class is 2-amino-2-methyl-1-propanol (AMP). The particular choice of alkanolamine is primarily dictated by the requirements of the specific application (Aroonwilas and Vaewab, 2004).

### 2.4.1 Alkanolamine Solution

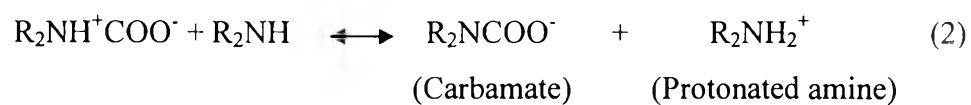
Alkanolamines have been found to effectively capture CO<sub>2</sub> from gas stream. They have been extensively used for decades in gas-treating unit. One of the advantage of alkanolamines is that, structurally, they contain at least one hydroxyl group, which helps to reduce vapor pressure and also to increase their solubilities in aqueous solution (Kohl and Reisenfeld, 1985). The amino group provides sufficient alkalinity to absorb CO<sub>2</sub>.

Alkanolamines can be categorized into three classes: primary, secondary, and tertiary amines. The classification is based on the number of substituting groups attached to the nitrogen atom of the molecule. Table 1 shows common primary amines, e.g. monoethanolamine (MEA) and diglycolamine (DGA); secondary amines, e.g. diethanolamine (DEA) and diisopropanolamine (DIPA); and tertiary amines, e.g. triethanolamine (TEA) and methyldiethanolamine (MDEA).

**Table 2.1** Structural formulas of common alkanolamines (Kohl and Reisenfeld, 1985)

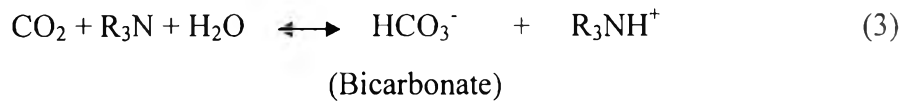
1. Primary amine	
$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{O}-\text{C}-\text{C}-\text{N} \\   \quad   \quad \diagup \quad \diagdown \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{O}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{N} \\   \quad   \quad   \quad   \quad \diagup \quad \diagdown \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
MEA	DGA
2. Secondary amine	
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{O}-\text{C}-\text{C}-\text{N}-\text{C}-\text{C}-\text{O}-\text{H} \\   \quad   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{N}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \quad   \quad   \quad   \\ \text{H} \quad \text{OH} \quad \text{H} \quad \text{H} \quad \text{OH} \quad \text{H} \end{array}$
DEA	DIPA
3. Tertiary amine	
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{OH}-\text{C}-\text{C}-\text{N}-\text{C}-\text{C}-\text{OH} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{OH} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{HO}-\text{C}-\text{C}-\text{N}-\text{C}-\text{C}-\text{OH} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$
TEA	MDEA

Typically, primary and secondary amines react to form a carbamate species, and the reaction may or may not proceed through an intermediate called the zwitterions.





Tertiary amines cannot form a carbamate species, because they do not have hydrogen attached to the nitrogen atom. Typically, the tertiary amines react according to equation 3.



As described by Kohl and Nielsen (1997), primary and secondary amines usually react faster than tertiary amines, and CO<sub>2</sub> has higher heats of absorption in these amines. Heats of reaction at 15 °C and unloaded conditions are approximately 20.3 and 14.8 kcal/mole for MEA and MDEA, respectively. Among many amines, MEA is the most widely used because MEA has the highest alkalinity; hence, it reacts most rapidly with CO<sub>2</sub>. As well, it can be reclaimed with ease from contaminated solution. Mechanism of CO<sub>2</sub> absorption into alkanolamine solution is complex and not totally understood (Astarita *et al.*, 1983). However, a general mechanism proposed several decades ago could represent the absorption process.

In general, MEA has the highest CO<sub>2</sub> separation rate, which should lead to relatively low overall costs. However, MEA requires a large amount of energy for regeneration, degrades most rapidly in the presence of oxygen (O<sub>2</sub>), has the highest corrosivity among commercial amines, and has a substantially higher vapor pressure than other alkanolamines, resulting in significant vaporization and solvent losses.

As different operating conditions are tested and proven with a particular amine, they become accepted on an industry-wide basis. Thus, each amine has a currently "accepted" range of process conditions and parameters associated with it. These "accepted" conditions and parameters are discussed below. Some of the typical operating conditions for common amines are summarized in Table 2.

**Table 2.2** Typical operating conditions and data for amines (Polasek and Bullin, 2006)

	Amine:	MEA	DEA	DGA	MDEA
Solution strength, wt. %		15-20	25-35	50-70	20-50
Acid gas loading, mole/mole (carbon steel)		0.3-0.35	0.3-0.35	0.3-0.35	Unlimited
Ability to selectively absorb $H_2S$	No	Under Limited Conditions	No	Under Most Conditions	

#### 2.4.1.1 Monoethanolamine (MEA)

MEA is generally used as a 10 to 20 wt.% solution in water. Due to corrosion problems, the acid gas loading is usually limited to 0.3 to 0.35 moles acid gas per mole of amine for carbon steel equipment. Loadings as high as 0.7 to 0.9 mole/mole have been used in stainless steel equipment with no corrosion problems. Although MEA itself is not considered to be particularly corrosive, its degradation products are extremely corrosive. MEA reacts with oxidizing agents, such as carbonyl sulfide (COS), carbon disulfide (CS<sub>2</sub>), SO<sub>2</sub>, SO<sub>3</sub>, and O<sub>2</sub>, to form the soluble products, which must be removed from the circulating system to avoid serious corrosion problems. Degradation or deactivation of MEA also lowers the effective amine concentration, but fortunately a reclaimer can recovery most of deactivated amine.

Since MEA is a primary amine, it has a high pH, which enables MEA solutions to produce a sweetened gas product containing less than 1/4 grain H<sub>2</sub>S per 100 standard cubic feet (SCF) at very low H<sub>2</sub>S partial pressures. When MEA is used, essentially all of the CO<sub>2</sub> must be absorbed to produce gas, which meets the quarter grain H<sub>2</sub>S specification. Since the heat of reaction for MEA is about 825 BTU/lb CO<sub>2</sub>, a feed gas containing high concentrations of CO<sub>2</sub> will cause either extremely high reboiler duty or poor acid gas stripping. The heat of reaction for MEA with H<sub>2</sub>S is 550 BTU/lb. Note that the heat of reaction for all amines is a function of loading and other conditions and usually varies by only 50 to 60 BTU/lb up to about 0.5 mole/mole total acid gas loadings. Above this loading, the heat of

reaction varies considerably and should be calculated as a function of loading (Polasek and Bullin, 2006).

#### *2.4.1.2 Diethanolamine (DEA)*

DEA is most commonly used in a 25 to 35 wt.% range. The total acid gas loading for DEA is also limited to 0.3 to 0.35 mole/mole for carbon steel equipment. DEA can safely be loaded to equilibrium (~1 mole/mole) when using stainless steel equipment or when using inhibitors. The degradation products of DEA are much less corrosive than those of MEA. Exposure to oxygen forms corrosive acids and COS, and CS<sub>2</sub> may react irreversibly with DEA to some extent. DEA is not reclaimable in most units because at atmospheric pressure, it decomposes below its boiling point, and vacuum reclaimers have proved operationally unreliable. Since DEA is a secondary alkanolamine, it has a reduced affinity for H<sub>2</sub>S and CO<sub>2</sub> and may not be able to produce pipeline specification gas for some low pressure gas streams. In general, as the gas pressure is lowered, the stripping steam must be increased, or a split flow design must be used. In some cases, even these measures will not suffice, and another solvent must be used. Under some conditions, such as low pressure and a liquid residence time on the tray of about 2 s, DEA is selective toward H<sub>2</sub>S and will permit a significant fraction of the CO<sub>2</sub> to remain in the sales gas. In this particular case, selective absorption was not desired, but was encountered due to a low contactor pressure of 11 psig and a short liquid residence time on the trays. An H<sub>2</sub>S/CO<sub>2</sub> feed gas ratio > 1 would probably rule out any chance of significant CO<sub>2</sub> slippage while producing 1/4 grain H<sub>2</sub>S/100 SCF sales gas. The heat of reaction for DEA with CO<sub>2</sub> is 653 BTU/lb, which is about 25 % less than for MEA. The heat of reaction of DEA with H<sub>2</sub>S is 511 BTU/lb (Polasek and Bullin, 2006)

#### *2.4.1.3 Methyldiethanolamine (MDEA)*

An accepted set of operating conditions has not been as firmly established for MDEA as for the previously mentioned amines. This has been due to the flexibility and versatility of MDEA and the resulting wide range of applications.

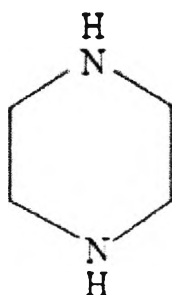
Although the range of operating conditions for MDEA is expanding, the present range of successful applications will be discussed below.

MDEA is commonly used in a 20 to 50 wt.% range. Lower wt.% solutions are typically used in very low pressure for high selectivity applications. Due to considerably reduced corrosion problems, acid gas loadings as high as 0.7 to 0.8 mole/mole are practical in carbon steel equipment. Higher loadings may be possible with few problems. Exposure of MDEA to oxygen forms corrosive acids, which if not removed from the system, can result in the buildup of iron sulfide in the system. MDEA has several distinct advantages over primary and secondary amines, which include lower vapor pressure, lower heats of reaction (600 BTU/lb CO<sub>2</sub> and 522 BTU/lb H<sub>2</sub>S), higher resistance to degradation, fewer corrosion problems, and higher selectivity toward H<sub>2</sub>S in the presence of CO<sub>2</sub>. Depending on the application, some of the advantages have special significance. For example, due to its lower heat of reaction, MDEA can be employed in pressure swing plants for bulk CO<sub>2</sub> removal. In a pressure swing plant, the rich amine is merely flashed at or near atmospheric pressure, and little or no heat is added for stripping. At the present time, the overwhelming advantage that MDEA possesses over the other amines is that it is readily selective toward H<sub>2</sub>S in the presence of CO<sub>2</sub>. At high CO<sub>2</sub>/H<sub>2</sub>S ratios, a major portion of the CO<sub>2</sub> can be slipped through the absorber and into the sales gas while removing most of the H<sub>2</sub>S. The enhanced selectivity of MDEA for H<sub>2</sub>S results from the inability of tertiary amines to form a carbamate with CO<sub>2</sub>. MDEA does not have a hydrogen attached to the nitrogen and cannot react directly with CO<sub>2</sub> to form carbamate. The CO<sub>2</sub> reaction can only occur after the CO<sub>2</sub> dissolves in water to form a bicarbonate ion, which then undergoes an acid-base reaction with the amine (Polasek and Bullin, 2006).

#### *2.4.1.4 Other Amines*

Piperazine (PZ) or diethylenediamine is a diamine that has previously been studied as a promoter for amine systems to improve absorption kinetics, such as MEA/PZ and MDEA/PZ blends. Its structural formula is shown in Figure 2. The concentration of PZ when used as a promoter has been low between 0.5 and 2.5 M PZ, because PZ is not highly soluble. Given the nature and magnitude of absorption/stripping systems, any possibility of precipitation ruled out PZ for use

at concentrations above its room temperature solubility. Additionally, the boiling point of PZ (146.5 °C) is lower than that of MEA (170 °C), indicating the possibility for higher volatility. Recent work has indicated that the volatility of PZ is comparable to that of MEA due to the no ideality of PZ in solution. Increasing the concentration of PZ in solution allows for increased solvent capacity and faster kinetics (Freeman *et al.*, 2009).



**Figure 2.2** Structural formula of piperazine (PZ).

From the above mentioned information, there are several different amines that have been proposed for separating the CO<sub>2</sub>. MEA is chosen as the current solvent of choice for flue gas treatment because of its high capacity for CO<sub>2</sub>, fast reaction kinetics, and high removal efficiencies. However, the operating cost of the absorption process using MEA is prohibitively high, mainly because of (i) the significant amount of energy required for solvent regeneration and (ii) severe operational problems, such as corrosion and solvent degradation.

#### 2.4.1.5 Mixed Amines

Most frequently, the removal of CO<sub>2</sub> from various industrial gas streams is done by the regenerative chemical absorption into aqueous solutions of alkanolamines. Commercially available alkanolamine solvents for these processes are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). Recently, there is a growing interest in the use of piperazine (PZ)-activated aqueous MDEA for gas treating processes in order to achieve higher overall reaction rate for CO<sub>2</sub> and reduced regeneration energy requirement. Activated methyldiethanolamine (MDEA) solutions have been used in the CO<sub>2</sub> removal process successfully. Piperazine (PZ) is more effective than other traditional

activators, such as monoethanolamine (MEA), diethanolamine (DEA), etc (Appl *et al.*, 1982).

## 2.5 Amine Degradation

A significant problem with the MEA absorption technique in its current form is the degradation of the amine over time. The by-products of MEA degradation are known to decrease the efficiency of CO<sub>2</sub> capture and have also been implicated in the corrosion of machinery. In order to compensate for this degradation, current facilities include distillation of the amine to remove by-products while continuously adding fresh amine to the system. Unfortunately, this leads to increased material and waste disposal costs. In addition, degradation processes have forced the use of lower concentrations of MEA (< 20 %), leading to larger overall equipment size, higher solvent circulation rate, and therefore increased energy requirements for CO<sub>2</sub> regeneration from the rich amine. This increased energy requirement is especially significant since it increases the parasitic load on the power plant, leading to increased fuel consumption, higher maintenance costs, and (ironically) increased CO<sub>2</sub> production relative to the power output of the plant (Strazisar *et al.*, 2002).

Most sour gas processing facilities use chemical absorption using alkanolamines (or amines in short) to separate H<sub>2</sub>S and CO<sub>2</sub> from the raw gas. Normally, the amine processes are cycles of absorption and desorption in order to permit the use of the absorbent. Due to the closed loop nature of these processes, non-regenerable contaminants tend to accumulate and can cause major reduction in efficiencies and operational problems (Abdi and Meisen., 2001). Degradation of MEA in a flue gas stream can be classified into three different types, depending on its products, mechanisms, and conditions. They are:

- Carbamate polymerization is the most common degradation mechanism. It requires CO<sub>2</sub> and high temperature. Since only primary and secondary alkanolamines form carbamates with CO<sub>2</sub>, tertiary amines do not undergo this type of degradation reaction. The degradation products resulting from the carbamate polymerization are usually of high molecular weight.

- Oxidative degradation requires  $O_2$ . It produces oxidized fragments of the solvent, such as organic acids and ammonia, and is expected to occur in the presence of dissolved  $O_2$  in the liquid holdup at the bottom of the absorber. Since flue gas contains 5 %  $O_2$ , oxidative degradation can be significant. Neither  $CO_2$  nor high temperature is required in this case.

- Thermal degradation is not commonly encountered since it involves high temperatures than 205 °C; therefore, it is the least well studied.

## 2.6 Related Works

Si and Aroua (2004) investigated the solubilities of CO<sub>2</sub> in aqueous solutions of activated methyldiethanolamine (MDEA) for temperatures and CO<sub>2</sub> partial pressures ranging from 40 to 80°C and 0.1 to 100 KPa, respectively. Piperazine (PZ) was used as activator, with a concentration ranging from 0.01 to 0.1 M, keeping the amine total concentration in the aqueous solution at 2 M. The experimental solubility results were represented by the molar ratio of CO<sub>2</sub> per activated amine present in the liquid mixture. The addition of piperazine, as activator for MDEA, increased the solubility of CO<sub>2</sub> in the region of low CO<sub>2</sub> partial pressure compared to pure MDEA. The CO<sub>2</sub> loading increased with decreasing temperature, increasing CO<sub>2</sub> partial pressure, and increasing PZ concentration.

Aroonwilas and Vaewab (2004) investigated the characterization and comparison of the CO<sub>2</sub> absorption performance using single and blended alkanolamines: monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and their mixtures, including MEA-MDEA, DEA-MDEA, MEA-AMP, and DEA-AMP. The rank of the CO<sub>2</sub> absorption performance is therefore in accordance with the order of the reaction rate constant ( $k_2$ ), i.e. MEA > DEA > AMP > DIPA > MDEA. Among these solvents, MEA has a faster rate of reaction with CO<sub>2</sub>, but it uses high amount of energy for solvent regeneration and severe operational problems, such as corrosion and solvent degradation.

Zhang *et al.* (2008) investigated the regeneration of 2-amino-2-methyl-1-propanol (AMP) used for CO<sub>2</sub> absorption. The results showed that the sterically hindered AMP enhanced the CO<sub>2</sub> absorption capacities and regeneration efficiencies in comparison to other amines. The regeneration performance can be ranked in the following order: AMP > MDEA > DETA > DEA > MEA. Among these solvents, AMP made the carbamate less stable as compared to other primary alkanolamines, such as MEA, facilitating formation of bicarbonate through reversion of carbamate. The order of absorption capacity of different amines was DETA > AMP > MEA > DEA > MDEA.



Xu *et al.* (1992) investigated the kinetics of carbon dioxide absorption in activated methyldiethanolamine (MDEA) solutions, which contain piperazine as an activator. A little piperazine obviously improved the absorption rate. The higher the absorption temperature, the higher the contribution of piperazine to absorption rate. The reaction between piperazine and CO<sub>2</sub> is a rapid pseudo-first-order reversible reaction, and it is parallel with the reaction between MDEA and CO<sub>2</sub>.

Tobiesen and Svendsen (2006) developed a computational model for the regeneration unit of a MEA-based absorption plant for CO<sub>2</sub> removal. The desorption process using MEA is very sensitive to the reboiler temperature. There is a significant increase in reboiler duty as hydrocarbon is added to the system. However, the reboiler and desorber column temperatures are reduced significantly. The driving force for desorption is lowered, even though the acid gas is diluted throughout the desorber tower. This is due to the strong temperature dependency of the CO<sub>2</sub> partial pressure over the MEA. The amount of hexane that must be added causes the reboiler duty to increase significantly. However, an increased desorber pressure can reduce compression costs. If a reduction in reboiler temperature is required because of excessive corrosion or solvent degradation, the addition of an organic component can greatly reduce tower temperatures, however, at the expense of increased reboiler duties.

Closmann *et al.* (2009) investigated the blended methyldiethanolamine/piperazine (MDEA/PZ) solvent as an alternative for CO<sub>2</sub> capture from coal-fired power plants. MDEA/PZ offers advantages over monoethanolamine (MEA) and methyldiethanolamine (MDEA) alone because of its resistance to thermal and oxidative degradation at typical absorption/stripping conditions. The resistance to oxidative degradation follows the order: MDEA/PZ > MDEA > PZ. The formation of amides in oxidatively degraded samples can be as much as twice the amount of formate produced. The blended MDEA/PZ solvent provided greater stability than MEA (30 to 50 wt %) when tested at conditions pertinent to CO<sub>2</sub> scrubbing in flue gas. Formate production in solvents adhered to the following order: MEA > MDEA > MDEA/PZ. Amide production rates were roughly twice the formate production rates in the MDEA/PZ solvent.