



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 CO₂ emissions down to approximately 5 % less than the emission in 1990, in a five year period from 2008 to 2012 (Kyoto Protocol, 2009). Because CO₂ 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 CO₂ Generation

2.2.1 Source of CO₂

A variety of human activities lead to the emission (sources) and removal (sinks) of CO₂:

- The largest source of global CO₂ 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 CO₂ emissions.

- Carbon sequestration is the process, by which growing trees and plants absorb or remove CO₂ from the atmosphere and turn it into biomass (e.g. wood, leaves, etc.). Deforestation, conversely, can lead to significant levels of CO₂ emissions in some countries.
- CO₂ 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 CO₂ emissions in the U.S. in 2006. It can be clearly seen that by far, the largest source is fossil fuel combustion.

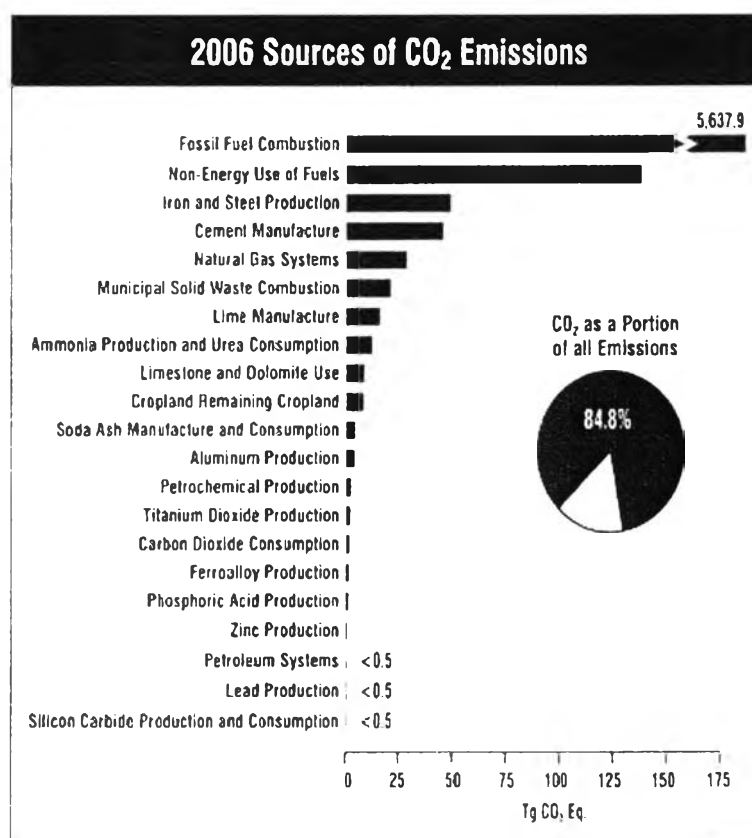


Figure 2.1 Sources of CO₂ emissions in the U.S. in 2006, where y-axis units are teragrams of CO₂ equivalent (U.S. Greenhouse Gas Emissions Inventory, 2006).

2.2.2 Flue Gas Characteristics

Flue gases emitted from medium to large point sources are generally at or slightly above atmospheric pressure. They typically contain 3-15 % (by volume) of CO₂. For example, flue gas from a coal-fired power plant typically contains about 14 % CO₂, 5 % O₂, and 81 % N₂. Flue gas from a natural gas turbine is even leaner in CO₂, but higher in O₂, with a typical composition of 4 % CO₂, 15 % O₂, and 81 % N₂. Typical trace contaminants found in flue gas include sulfur oxides (SO_x), nitrogen oxides (NO_x), 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_x, 100-1,000 ppm NO_x, and 1,000-10,000 mg/m³ particulate matter. Natural gas firing significantly lowers the contaminant levels to less than 1 ppm SO_x, 100-500 ppm NO_x, and to around 10 mg/m³ particulate matter.

2.3 CO₂ Removal Processes

As we have known, there are various technologies being used to separate CO₂ 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 CO₂ 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 CO₂ from gaseous streams containing CH₄. The most important decision in any adsorption-based technology is the adsorbent selection. Zeolites are microporous materials that adsorb CO₂ 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 CO₂ from flue gases (Cavenati *et al.*, 2006). In addition, TSA uses alumina and zeolite adsorbents for natural gas purification. Only the zeolite removes CO₂ along with other contaminants from natural gas via physisorption while other contaminants besides CO₂ are removed by the alumina (Petrochemical Processes Handbook, 2003).

2.3.2 Membranes Processes

Membrane gas separation, especially CO₂ 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 CH₄ used in those cases was to recover H₂ and CO₂ from CH₄. 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 CO₂ from N₂ at ambient pressure. Within the last several years, dynamic developments in membrane technology for CO₂/N₂ 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, CO₂ will liquefy at temperatures much higher than CH₄, 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 CO₂. 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 CO₂ is still limited to streams with high CO₂ concentration and not viable for streams containing low amount of CO₂ (White *et al.*, 2003). Currently, only ethanol, H₂, syngas, and NH₃ 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 CO₂. The process using amine-based solutions has been commercialized to remove CO₂ from natural gas for 60 years. It is considered as the most mature CO₂ removal process. The process can be divided into two categories: chemical and physical. The processes, where the solvent chemically reacts with the dissolved CO₂, 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 CO₂. A solvent is used as an absorbent with thermodynamic properties such that the relative absorption of CO₂ 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 CO₂ from syngas and NH₃ 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 CO₂ removal processes are commercially important. However, chemical absorption, e.g. with amine-type absorbents, is well suited for CO₂ recovery from flue gas. The chemical reaction between CO₂ and amines greatly enhances the driving force for the separation, even at low partial pressures of CO₂. The costs of this technology are relatively insensitive to the feed CO₂ content.

Consequently, chemical absorption with amines provides the most cost-effective means of directly obtaining high purity (> 99 %) CO₂ 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 H₂ production for the rejection of CO₂. However, in these applications, the CO₂ 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

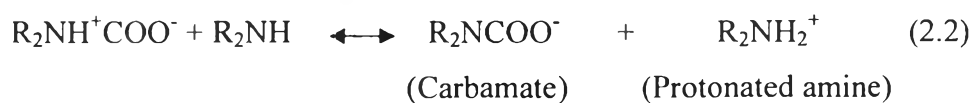
Alkanolamines have been found to effectively capture CO₂ from gas stream. They have been extensively used for decades in gas-treating unit. One of the advantage of alkanolamines is that, structurally, they contain at least one hydroxyl group, which helps to reduce vapor pressure and also to increase their solubilities in aqueous solution (Kohl and Reisenfeld, 1985). The amino group provides sufficient alkalinity to absorb CO₂.

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 2.1 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).

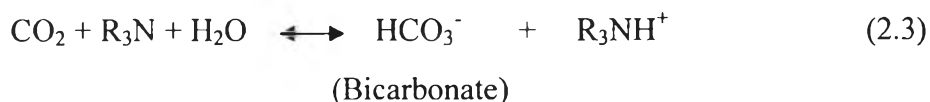
Table 2.1 Structural formulas of common alkanolamines (Kohl and Reisenfeld, 1985)

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

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 (Equations 2.1 and 2.2).



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 2.3.



As described by Kohl and Nielsen (1997), primary and secondary amines usually react faster than tertiary amines, and CO₂ 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 CO₂. As well, it can be reclaimed with ease from contaminated solution. Mechanism of CO₂ 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 CO₂ 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 (O₂), has the highest corrosivity among commercially 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 2.2.

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 (CS₂), SO₂, SO₃, and O₂, 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 H₂S per 100 standard cubic feet (SCF) at very low H₂S partial pressures. When MEA is used, essentially all of the CO₂ must be absorbed to produce gas, which meets the quarter grain H₂S specification. Since the heat of reaction for MEA is about 825 BTU/lb CO₂, a feed gas containing high concentrations of CO₂ will cause either extremely high reboiler duty or poor acid gas stripping. The heat of reaction for MEA with H₂S 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 CS₂ 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 H₂S and CO₂, 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 H₂S and will permit a significant fraction of the CO₂ 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 H₂S/CO₂ feed gas ratio > 1 would probably rule out any chance of significant CO₂ slippage while producing 1/4 grain H₂S/100 SCF sales gas. The heat of reaction for DEA with CO₂ is 653 BTU/lb, which is about 25 % less than for MEA. The heat of reaction of DEA with H₂S 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 CO₂ and 522 BTU/lb H₂S), higher resistance to degradation, fewer corrosion problems, and higher selectivity toward H₂S in the presence of CO₂. 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 CO₂ 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 H₂S in the presence of CO₂. At high CO₂/H₂S ratios, a major portion of the CO₂ can be slipped through the absorber and into the sales gas while removing most of the H₂S. The enhanced selectivity of MDEA for H₂S results from the inability of tertiary amines to form a carbamate with CO₂. MDEA does not have a hydrogen attached to the nitrogen and cannot react directly with CO₂ to form carbamate. The CO₂ reaction can only occur after the CO₂ 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 Mixed Amines

Mixtures of amines are generally mixtures of MDEA and DEA or MEA, and are used to enhance CO₂ removal by MDEA. Such mixtures are referred to as MDEA-based amines with DEA or MEA as the secondary amine generally comprises less than 20 % of the total amine on a molar basis. At lower

concentrations of MEA and DEA, the overall amine concentration can be as high as 55 wt.% without the implementation of exotic metal equipment.

MDEA-based mixtures are normally used to increase the CO₂ pickup in cases, where the MDEA is allowing too much CO₂ to slip overhead in the absorber. Spiking the MDEA with MEA or DEA to achieve the desired CO₂ pickup is often advantageous over a complete amine switch-out to a DEA or MEA system because the MDEA regenerator reboiler may be undersized for the DEA or MEA system. Amine mixtures are particularly useful for lower pressure applications since the MDEA becomes less capable of picking up sufficient CO₂ to meet pipeline specifications at lower pressures. At higher pressures, amine mixtures appear to have little or no advantage over MDEA. Mixed amines are also useful for cases, where the CO₂ content the feed gas is increasing over time due to field aging (Polasek and Bullin, 2006). The development of solvents aims at selecting the alternative solvents to replace the single MEA, which should provide the equivalent or greater CO₂ absorption rate, higher CO₂ loading capacity, and lower regeneration energy consumption than MEA (Shuiping *et al.*, 2009).

2.4.1.5 Sterically Hindered Amines

Sartori and Savage (1983) stated that sterically hindered amines have unique capacity and rate advantages in CO₂ absorption processes. It has been reported that the sterically hindered amine solutions can be desorbed to a greater extent than their non-substituted counterparts, thus producing a leaner solution, which will result in a greater mass transfer upon reabsorption (Sartori and Savage, 1983).

2-Amino-2-methyl-1-propanol (AMP) is the R-dimethylated derivative of MEA. Its structural formula is shown in Figure 2.2. It has been reported that when AMP reacts with CO₂, no carbamate is observed in solution, with almost total hydrolysis to bicarbonate. The CO₂ solubilities in AMP solutions are higher than those for MEA solutions at 40 °C but lower at 80 °C. These facts suggest that AMP has the potential to be a superior absorber of CO₂ at low temperature and a superior desorber of CO₂ at the higher temperatures. It is also claimed that such

amines exhibit superior degradation resistance in comparison to those, which are unsubstituted (Tontiwachwuthikal *et al.*, 1991).

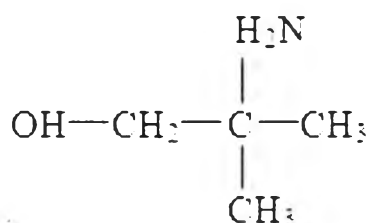


Figure 2.2 Structural formula of 2-amino-2-methyl-1-propanol (AMP).

Recently, apart from AMP, many studies have been developing other new sterically hindered amines to use in the CO₂ absorption process, such as 2-amino-2-methyl-1,3-propanediol (AMPD), and 2-amino-2-ethyl-1,3-propanediol (AEPD), which are a primary hindered amine; and methylaminoethanol (MAE), ethylaminoethanol (EAE), and *n*-butylaminoethanol (BAE), which are secondary hindered amines.

2.4.1.6 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 2.3. 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 non-ideality of PZ in solution. Increasing the concentration of PZ in solution allows for increased solvent capacity and faster kinetics (Freeman *et al.*, 2009).

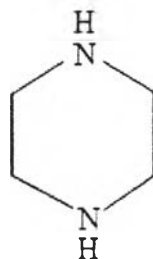


Figure 2.3 Structural formula of piperazine (PZ).

From the above mentioned information, there are several different amines that have been proposed for separate the CO₂. But, MEA is chosen as the current solvent of choice for flue gas treatment because its high capacity for CO₂, 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.

2.5 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 CO₂ 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 CO₂ 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 CO₂ 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 H₂S and CO₂ 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 CO₂ and high temperature. Since only primary and secondary alkanolamines form carbamates with CO₂, 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 O₂. It produces oxidized fragments of the solvent, such as organic acids and ammonia, and is expected to occur in the presence of dissolved O₂ in the liquid holdup at the bottom of the absorber. Since flue gas contains 5 % O₂, oxidative degradation can be significant. Neither CO₂ 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

Mandal *et al.* (2001) examined the removal of CO₂ by absorption in mixed amines: aqueous MDEA-MEA and AMP-MEA solutions. It has been found that the addition of a small amount of MEA to an aqueous solution of MDEA or AMP significantly increased the enhancement factor and rate of absorption for both solvents, while the enhancement was found to be relatively higher for CO₂ absorption into AMP-MEA-H₂O system than into MDEA-MEA-H₂O system. This established the importance of the blended amine solvent of AMP-MEA as a potential alternative besides MDEA-MEA for CO₂ absorption.

Aroonwilas and Vaewab (2004) investigated the characterization and comparison of the CO₂ 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 CO₂ absorption performance is therefore in accordance with the order of the reaction rate constant, i.e. MEA > DEA > AMP > DIPA > MDEA. Among these solvents, MEA has a faster rate of reaction with CO₂, but it uses high amount of energy for solvent regeneration and severe operational problems, such as corrosion and solvent degradation. In addition, AMP and MDEA have relatively low energy consumption for solvent regeneration, leading to significant saving in process cost. So, this work further considered blending a variety of single alkanolamine, such as MDEA-based solvents and AMP-based solvents. The results showed that AMP-based solvents, especially MEA-AMP, were more effective in CO₂ absorption than MDEA-based solvents with a mixing ratio of 1:1.

Idem *et al.* (2006) studied the CO₂ capture performance of aqueous MEA and mixed MEA-MDEA solvents. The specific goal with respect to the use of mixed amines is to have a solution consisting of tertiary and primary amines or tertiary plus secondary amines that, in comparison with single amine systems, retains much of the reactivity of primary or secondary amines at similar or reduced circulation rates, but

offers low regeneration cost similar to those of tertiary amines. The results showed that a huge heat-duty reduction could be achieved by using a mixed MEA-MDEA with a mixture ratio 4:1 solution instead of a single MEA solution in an industrial environment of a CO₂ capture plant. However, this benefit was dependent on whether the chemical stability of the solvent could be maintained.

Zhang *et al.* (2008) investigated the regeneration of 2-amino-2-methyl-1-propanol (AMP) used for CO₂ absorption. The results showed that the sterically hindered AMP enhanced the CO₂ 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. The absorption rate of CO₂ into aqueous AMP was not much more ascendant than others, whereas the higher absorption capacity made it more suitable for CO₂ absorbents.

Choi *et al.* (2009) studied the removal characteristics of CO₂ by using aqueous MEA-AMP solutions in the absorption and regeneration processes and evaluated the optimum blending ratio of MEA and AMP by considering reactivity and efficiency. The sterically hindered amine, such as 2-amino-2-methyl-1-propanol (AMP), has been proposed as commercially attractive new CO₂ absorbent because of their advantages in absorption capacity, absorption rate, degradation resistance, and regeneration energy. In addition, aqueous MEA solution is the most frequently used alkanolamine absorbent owing to its high reactivity with CO₂, low solvent cost, and easy regeneration. So, the use of blends of MEA and AMP was considered to enhance the capacity and absorption rate of CO₂ even though it maintained the stripping characteristics of the sterically hindered amine. The results showed that MEA was superior to AMP in the CO₂ removal efficiency, but AMP was better than MEA in CO₂ absorption amount. In absorption/regeneration processes, reaction rate constant of blended MEA-AMP solutions increased and CO₂ loading of rich amine decreased with an increase in MEA content. On the other hand, with an increase in AMP content, the reverse results were obtained as compared to the previous results.

Samanta and Bandyopadhyay (2010) studied an experimental and theoretical investigation on the absorption of CO₂ into PZ-activated aqueous MDEA solvent. The rates of absorption of CO₂ into aqueous solutions of MDEA-PZ have been measured in a wetted wall contactor over the CO₂ partial pressure range of 2-14 kPa and temperature range of 298-313 K under atmospheric pressure. In view of industrial gas treating conditions, the absorption experiments were performed over the MDEA concentration range of 1.89-2.41 kmol m⁻³ (22-28 wt.%) along with PZ concentrations of 0.24, 0.60, and 0.95 kmol m⁻³ (2-8 wt.%), by keeping the total amine concentration in the solution at 30 wt.%. Required physicochemical properties, such as density and viscosity of aqueous amine solvents, and Henry's constant and diffusivity of CO₂ in the solvents have been determined in this work by appropriate experimental methods or estimated from available literature.

Dugas and Rochelle (2008) studied the absorption and desorption rates of CO₂ with MEA and PZ. PZ was reported to be the most promising solvent for acid gas removal as an additive (low concentration) to conventional solvents, such as MDEA and AMP, because of its high acid gas loading capacity and reaction rate. Based on their studies, they concluded that 4.6 M PZ had about 75% greater CO₂ capacity than 4.91 M MEA, and CO₂ reaction rates for PZ were shown to be 2-3 times faster than MEA solutions.