CHARTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Sources of CO_2 Capture

Minimization of global CO_2 emissions has continued to take center stage of several international conferences due to its adverse effects in the environment and contribution to climate change. From 2012 global emissions, International Energy Agency (2014) stated that coal and crude oil contributed most of the fuel emitted CO_2 when compared to natural gas (Figure 2.1), while electricity generation contributed the most in terms of emissions by sector (Figure 2.2). Considering the fact that coal is cheap and readily available in large quantities globally, it will most likely continue to be the preferred fuel for power generation for decades to come (Tontiwachwuthikul *et al.*, 2011).

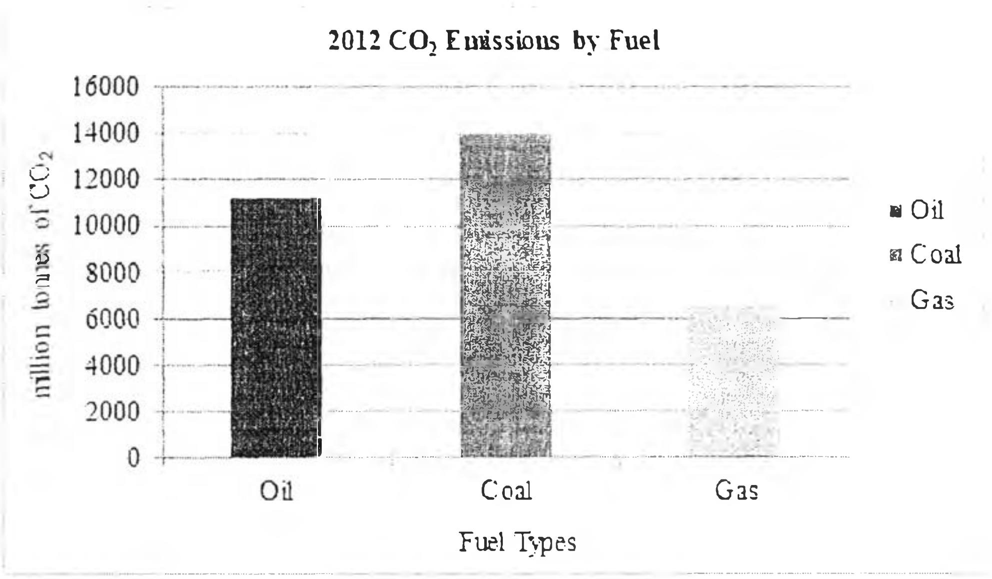
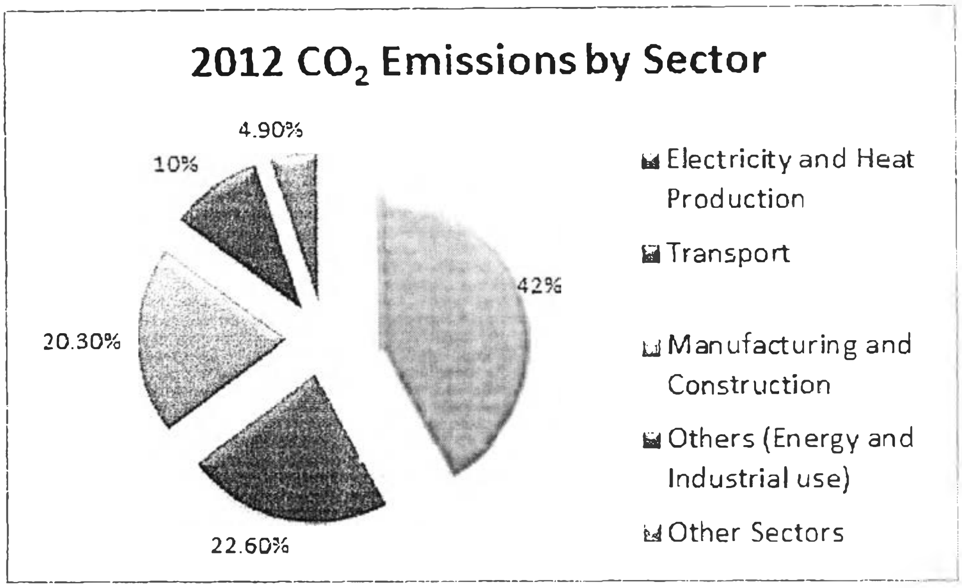


Figure 2.1 Annual CO_2 emissions by fuel type (IEA, 2014).



Note: Other sectors include residential

Figure 2.2 2012 CO_2 emissions by sector (IEA, 2014).

The greater the emissions of greenhouse gases, the greater the warming and danger of the accompanying consequences (International Energy Agency, 2013). These consequences cover rise in sea levels, extreme weather conditions, and increase in both human diseases and mortality rate (International Energy Agency, 2013). Carbon capture and storage is now being believed to be the major and viable solution to reducing atmospheric CO_2 levels in the short term. Luis and Van der Bruggen (2013) pointed that this technology will include the capture, transportation, storage, and possible utilization of CO_2. Figure 2.3 depicts an entire value chain of CO_2 capture, storage and utilization.

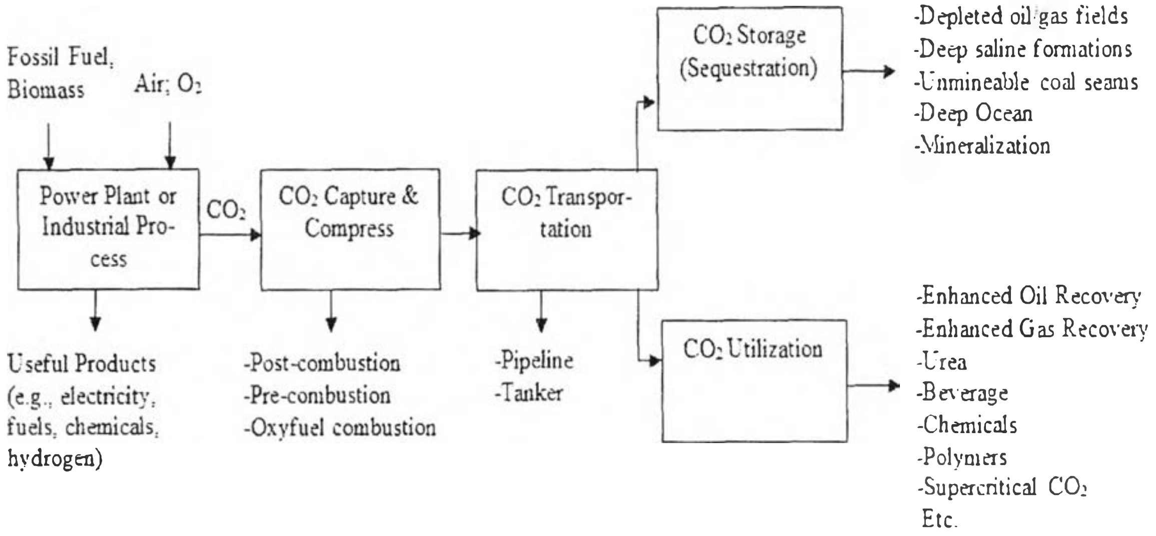


Figure 2.3 Schematic of a carbon capture storage and utilization system (modified from Rubin *et al.*, 2012; Li *et al.*, 2013).

Carbon capture from large point exhaust sources like fossil fuel fired power plants, chemical and petrochemical production, steel and cement production, and natural gas purification, will go a long way in reducing these problems (Chowdhury *et al.*, 2013). Figure 2.4 shows the various sources where CO_2 are emitted and can be captured.

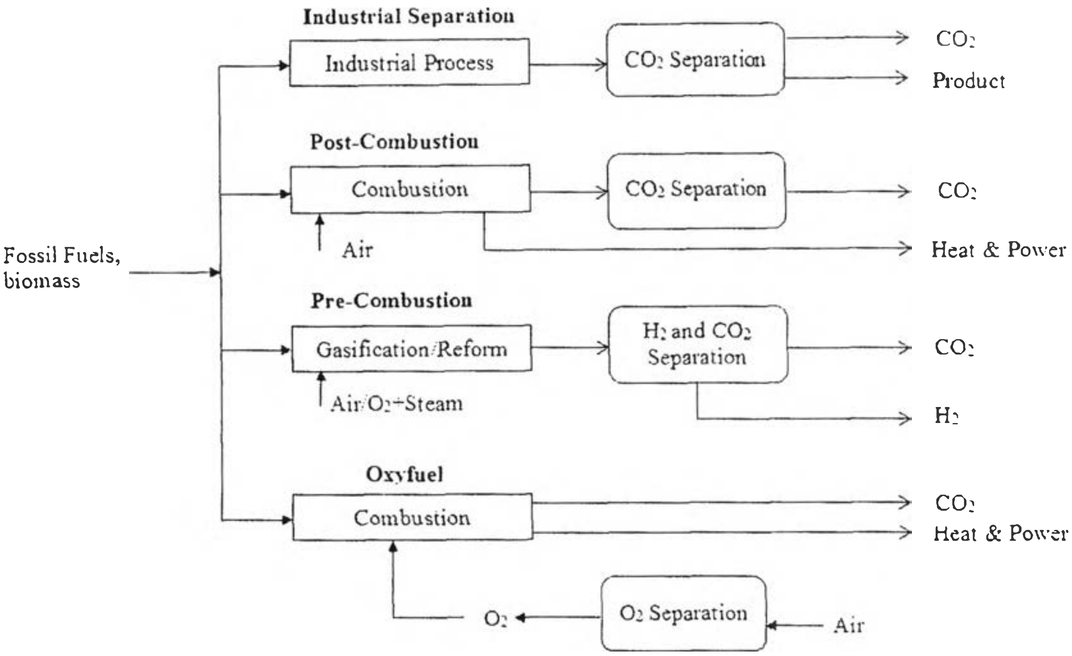


Figure 2.4 Sources of CO_2 capture (Tontiwachwuthikul *et al.*, 2012).

2.1.1 Post-combustion Capture

In this process CO_2 is released from combusting fossil fuels/biomass with air, and the produced CO_2 can be recovered from the produced flue gas. This is a major technology in fossil fuel fired power plants. The flue gas CO_2 concentration from post-combustion process is usually between 12 - 15 % for coal fired power plants and 3 – 8 % for natural gas fired power plants (Rubin, 2008; National Energy Technology Laboratory, 2013; Halmann and Steinberg, 1998; Alie *et al.*, 2005; Singh *et al.*, 2003; Mondal *et al.*, 2012). The flue gas is at atmospheric pressure thereby creating a technical issue for cost effective development of advanced CO_2 capture processes (Figueroa *et al.*, 2008). Figueroa *et al.* (2008) stated that irrespective of this challenge, CO_2 capture from post-combustion process has the highest near-term possibility for minimizing GHG emissions. This is due to its ease to be retrofitted to existing units that generate two-thirds of the CO_2 emissions in the power generation sector. Figure 2.4 shows the process scheme of post-combustion CO_2 capture.

2.1.2 Pre-combustion Capture

In this process, the CO_2 is captured from the gas stream before the fuel is combusted (Figueroa *et al.*, 2008). According to Yang *et al.* (2008) fuels are first converted into CO_2 and H_2 mixture via natural gas reforming or coal gasification process and the subsequent shift-reaction. The produced CO_2 is then captured and the H_2 can then be burned in a gas turbine. The viability of integrating a CO_2 capture in this process will depend on the CO_2 concentration. High CO_2 concentrations in the syngas will make CO_2 capture less expensive when compared with post-combustion capture (Mondal *et al.*, 2012). Figure 2.4 depicts the pre-combustion process.

2.1.3 Oxyfuel Combustion

This oxy-fuel process is another viable approach to capturing CO_2 from flue gas. The idea is to modify the combustion process in other to have high CO_2 concentration (Figueroa *et al.*, 2008). Instead of combusting with air, pure or nearly pure oxygen (greater than 95 %) is used (Mondal *et al.*, 2012). The flue gas stream from this process contains mainly CO_2 and water vapor. The water vapor can be separated from the CO_2 through condensation, and the nearly pure CO_2 can be further purified at a low cost. The CO_2 content in the dry flue gas is usually in the range of 70 – 90 % which depends largely on the type of fuel used (Mondal *et al.*, 2012). Table 2.1 highlighted the merits and demerits of CO_2 capture processes.

2.1.4 Industrial Separation

This involves CO_2 capture from various industrial processes ranging from natural gas processing, to cement and steel production, refinery and petrochemical processes etc. Alie *et al.* (2005) also stated that the CO_2 concentration in flue gas from cement plant could be as high as 25 %.

Table 2.1 Merits and De-merits of CO_2 Capture Sources (Olajire, 2010; National Energy Technology Laboratory, 2013; Figueroa *et al.*, 2008)

Capture Sources	**Merits**	**Demerits**
Post-Combustion	• It can be easily retrofitted to existing power-plant designs. • Offers extra NO_x and SO_x removal.	• High energy requirement due to regeneration of solvent and CO_2 compression to pipeline pressure. • Solvent loss • Possible trace impurities in the flue gas will reduce the efficient CO_2 removal process.
Pre-Combustion	• Emissions are very low. • The synthesis gas is at high pressure and rich in CO_2. • The high pressure of the synthesis gas reduces costs and energy load requirements for CO_2 compression.	• It requires cooling of gas to capture CO_2. • High cost of equipment's. • There's loss of efficiency in the water-gas shift section. • It's mainly applicable to new plants.
Oxyfuel	• The lack of nitrogen excludes NO_x emissions. This is due to the use of pure oxygen instead of air for the combustion. • Reduced volume of the gas and hence the size of plant. • The CO_2 concentration is very high in the flue gas.	• Involves large cryogenic O2 production requirement which will be cost prohibitive and energy intensive. • Using pure oxygen for combustion is quite complicated. This could also lead to reduction in process efficiency.

2.2 CO_2 Separation and Capture Technologies

Depending on the process, there are several CO_2 capture technologies that can be applied, which includes absorption, adsorption, membranes, cryogenics, or even a combination of these as highlighted in Figure 2.5 (Tontiwachwuthikul *et al.*, 2011). Considering the available CO_2 capture technologies, regenerable amine solvents is the most matured and promising technology (Metz *et al.*, 2005; Rao and Rubin, 2002). Liang *et al.* (2011) also forecast that in the nearest future, post-combustion CO_2 capture from fossil fuel fired power plants using chemical absorption (utilizing amines) appears to be the most matured. However, regenerable amine solvents are accompanied with high energy of regeneration, and this accounts for about 70 - 80 % of the plant operational cost (Aaron and Tsouris, 2005). Several other challenges covering solvent degradation (thermal, chemical and oxidative), equipment corrosion, solvent loss (vaporization) also taken into consideration during chemical absorption of CO_2 with amines.

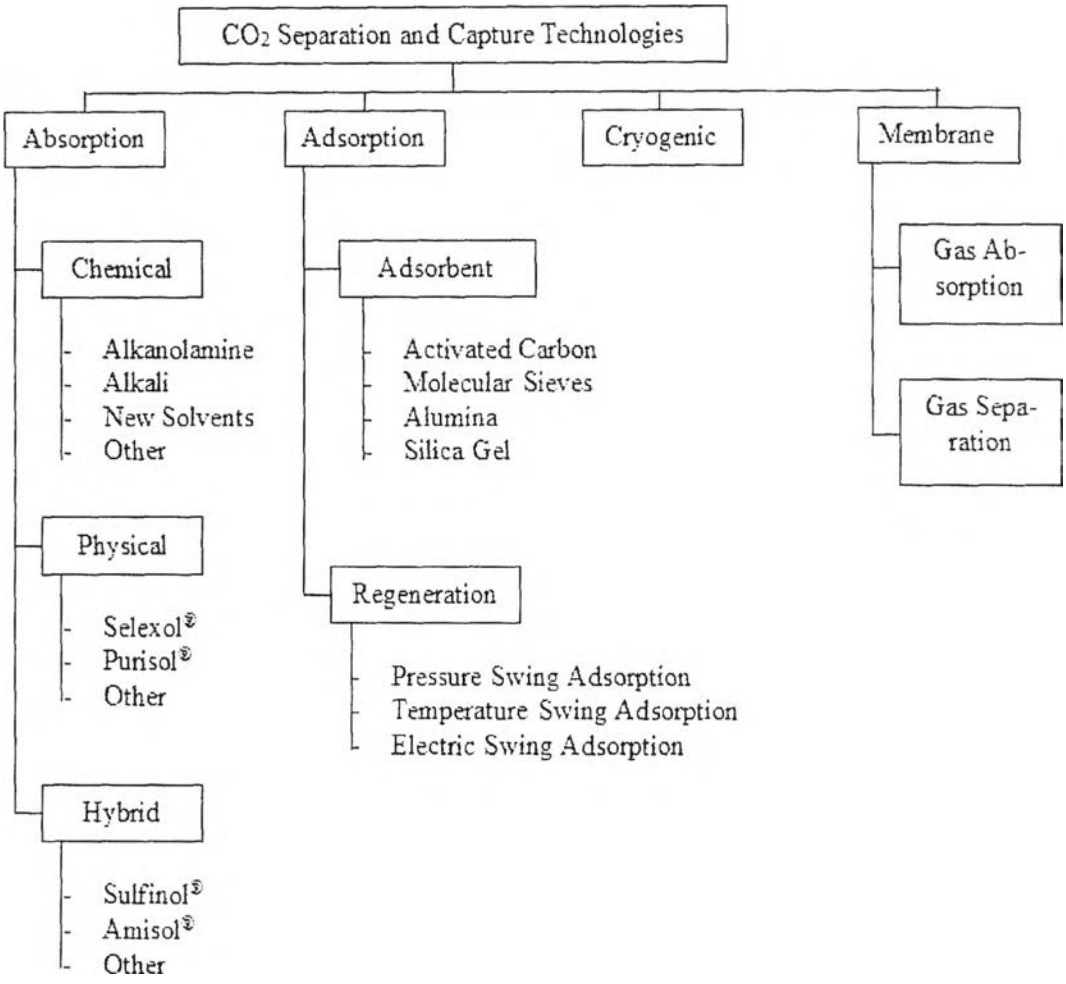


Figure 2.5 Schematic of CO_2 separation and capture technologies.

2.2.1 Absorption Process

The absorption process refers to the transfer of a gas phase component into a liquid phase in which it is soluble in. Absorption is undeniably the only most significant operation of CO_2 capture processes (Kohl and Nielsen, 1997). It involves a chemical reaction between the gas phase to be removed and liquid phase, which is achieved at high pressure and low temperature. Desorption (stripping or regeneration) is the opposite of absorption which is achieved at low pressure (mostly atmospheric pressure) and high temperature, and simply used to recover the chemical solvent used for CO_2 capture for easy recycling.

CO_2 capture in an absorption process can be done by either a chemical or physical solvent. For physical solvents, there's no chemical reaction between the gas phase to be captured and the liquid solvent. The physical solvents have affinity for the absorbed gas phase, and the solvent is recovered by gradual pressure reduction. Absorption with physical solvents occurs at high CO_2 partial pressures. Due to this fact, physical absorption is not economical for gas streams with CO_2 partial pressures lower than 15 vol% (Wang *et al.*, 2011). There are several existing commercial processes such as Selexol Process, Rectisol Process, Purisol Process, Morphysorb Process, and Fluor process (Yu *et al.*, 2012a).

2.2.2 Adsorption Process

Carbon dioxide capture using solid adsorption process is considered one of the most promising technologies for carbon capture and storage (Spigarelli and Kawatra, 2013). In adsorption process, there is a selective concentration of one or more gas components (to be adsorbed) at the surface of a micro-porous solid. The adsorbed component(s) is called the adsorbate, while the micro-porous solid the adsorbent (Kohl and Nielsen, 1997). The activity of the adsorbent is recovered either by heat application through temperature swing adsorption, TSA or by pressure reduction known as pressure swing adsorption, PSA (Wang *et al.*, 2011).

Adsorption process utilizes an activated carbon, molecular sieves, alumina or silica gel. Their choices will depend on the feed gas compositions, pressure, temperature, and purity level of the sweet gas.

2.2.3 Cryogenic Process

CO_2 capture can also be achieved through cryogenic process by condensation. CO_2 condenses at -56.6 °C at atmospheric pressure (Wang *et al.*, 2011). Although the cryogenic process is commercially applied in capturing CO_2 from gas streams with high concentrations of CO_2 (greater than 50 – 70 %), it has not been used in large CO_2 capture from flue gas streams (Shimekit and Mukhtar, 2012). This is due to low concentrations of CO_2 in flue gas that makes it not economical. Once oxyfuel combustion process matures, this process will best suit it for CO_2 capture.

2.2.4 Membrane

In the membrane process, polymeric membranes are utilized to separate gas components by permeation (selective) of one or more of its components from one side of the membrane to the other side (Kohl and Nielsen, 1997). The rate of permeation would be on the basis of the relative sizes of the molecules of the gas component(s) or due to the diffusion coefficients in the membrane material. According to Wang *et al.* (2011) the permeation driving force is the partial pressure differential of the components at either side of the membrane.

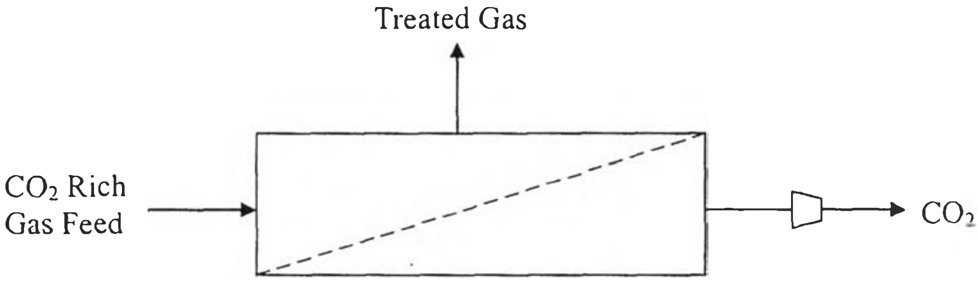


Figure 2.6 Simplified Membrane Unit (modified from Peters *et al.*, 2011).

Table 2.2 shows the comparison between the CO_2 separation and capture technologies.

Table 2.2 Comparison of CO_2 separation and capture technologies (Spigarelli and Kawatra, 2013; Rubin *et al.*, 2012; Shimekit and Mukhtar, 2012)

Techniques	Merits	Demerits
Absorption	• It is usually used for efficient (50-100%) technologies for the capture of acid gases (CO_2 and H_2S). • Cost of solvent is reasonable. • Very high purity to ppm levels.	• At very high partial pressures, physical solvents are preferred to chemical solvents. • Chemical solvents require massive regeneration energy.
Adsorption	• Possess high CO_2 adsorption capacity and surface area contact. • Stability and durability of the adsorption and desorption cycle.	• Captured CO_2 purity is lower compared to absorption process. • Relatively single pure product.
Membrane	• No steam load requirement. • No chemical requirement. • Stable at high pressure. • Products recovery is high. • Less impact on environmental. • Simplicity, mobility, versatility, low capital investment and operation.	• Membranes tend to be more suitable for high pressure processes such as IGCC. • High selectivity requirement (due to CO_2 concentration and low pressure ratio). • Feed gas pre-treatment is required. • Requirement of multiple stages and recycle streams. • Permeate recompression needed. • Moderate purity of treated gas due to trade-off with product purity.
Cryogenics	• Compared to other processes, its CO_2 recovery is relatively high. • Relatively high purity products.	• Regeneration energy is high. • It's not economical to apply as very small units.

2.3 Chemical Absorption

Figure 2.7 shows a typical and conventional process flow diagram of CO_2 chemical absorption process. The feed gas to be treated (which contains CO_2) is sent to the absorber through the bottom. Due to gravity, the feed gas flows upward through the absorber and counter current to the stream of lean chemical solvent which is flowing downwards from the top. As mass transfer occurs at the absorber, the lean chemical solvent gradually heats up giving rise to a temperature bulge in the absorber. The location of the temperature bulge in the absorber will depend on the reactivity of the chemical solvent (heat of reaction), chemical solvent and flue gas flow rates and the CO_2 composition in the gas phase (Razi *et al.*, 2013). For MEA-CO_2 systems, the temperature bulge occurs towards the top stage of the absorber (Razi *et al.*, 2013). The temperature inside the absorber is typically between 40 °C and 60 °C (Wang *et al.*, 2011; Chowdhury *et al.*, 2013). The CO_2 rich solvent from the bottom of the absorber exchanges heat with the hot lean solvent from the stripper bottom. The hot rich chemical solvent is then sent to the top of the stripper where it is regenerated at high temperatures between 100 - 120 °C (Wang *et al.*, 2011; Chowdhury *et al.*, 2013). The lean solvent from the stripper bottom, after partial cooling in the rich/lean heat exchanger, is further cooled with either water or air, and sent into the top section of the absorber to complete the cycle (Kohl and Nielsen, 1997).

CO_2 that is stripped from the rich solvent in the stripper is cooled to condense a major portion of the water vapour and chemical solvent that is carried over. This condensed water vapor is continually refluxed to the stripper at a point above the incoming rich solvent to both minimize amine losses and reduce significant increase in the amine concentration of the rich amine solution (Kohl and Nielsen, 1997). The reboiler provides the necessary heat of stripping required to effectively remove almost all the captured CO_2 from the rich solvent. Steam or heating oil is usually used for this purpose, depending on their availability and cost consideration.

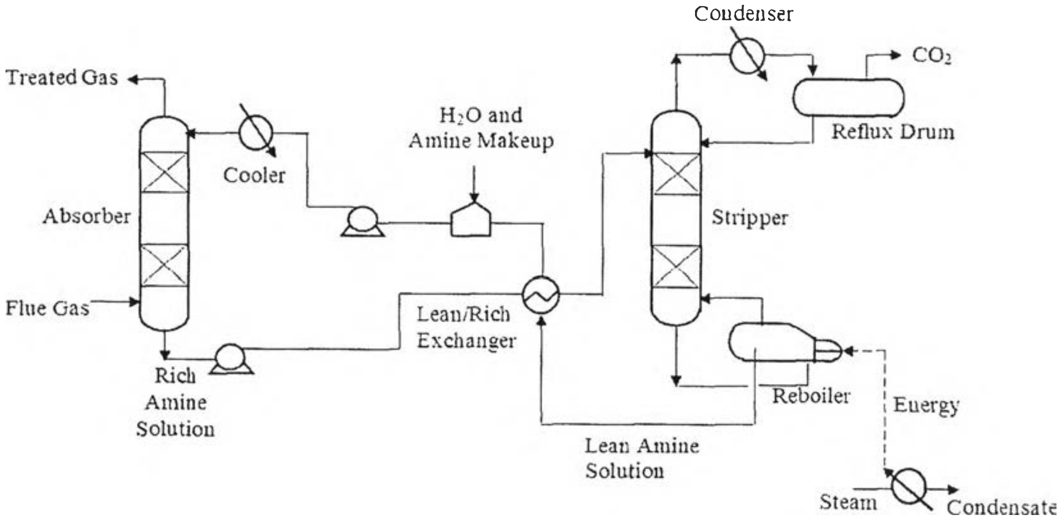


Figure 2.7 Typical process flow diagram of CO_2 chemical absorption.

2.3.1 Alkanolamine Solutions

Alkanolamines for acid gas (H_2S and CO_2) treating was first discovered by Bottoms in 1930, and since then several research reports and solvent developments have evolved. Alkanolamines contain an amino group (N), hydroxyl group (OH), and alkane group (R-C-H). The amino group provides the necessary alkalinity for the chemical reaction with the CO_2 and the hydroxyl group gives it the solubility characteristics with water and lowers the vapor pressure (Kohl and Nielsen, 1997; Yildirim *et al.*, 2012). The alkane group separates the hydroxyl group (OH^-) and that of the amine thereby providing chemical stability. In addition, in the work of Chowdhury *et al.* (2009) methyl group (alkane group) in the amine structure can decrease its heat of reaction and as well increase its initial rate of absorption and capacity

2.3.1.1 Primary Amines

Primary amines react with CO_2 forming a stable carbamate. This carbamate formation limits the theoretical capacity of primary amines to 0.5 mol CO_2/ mol amine (Chowdhury *et al.*, 2013). The reaction between primary amines and CO_2 can be explained using the zwitterion and termolecular mechanism.

Zwitterion Mechanism

The reaction between CO_2 and primary amines has been generally described and accepted using the two-step zwitterion mechanism. This mechanism was first introduced by Caplow in 1968 and later re-introduced by Danckwerts in 1979. The first step involves the formation of an intermediate zwitterion seen in Equation 2.1.

$$RNH_2 + CO_2 \leftrightarrow RNH_2^+COO^- \qquad 2.1$$

$$RNH_2^+COO^- + B \leftrightarrow RNHCOO^- + BH^+ \qquad 2.2$$

In the second step, the zwitterion is de-protonated by a base (B) producing carbamate as seen in Equation 2.2. This base can be either or a combination of H_2O, amine, and OH^- as shown in Equations 2.3 – 2.5 (Pei *et al.*, 2008; Vaidya and Kenig, 2007; Saha *et al.*, 1996).

$$RNH_2^+COO^- + RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+ \qquad 2.3$$

$$RNH_2^+COO^- + H_2O \leftrightarrow RNHCOO^- + H_3O^+ \qquad 2.4$$

$$RNH_2^+COO^- + OH^- \leftrightarrow RNHCOO^- + H_2O \qquad 2.5$$

Tong *et al.* (2013) stated that the rate of de-protonation strongly depends on the basicity of the base and hence by the pH of the amine solution. Versteeg and van Swaaij (1988) stated that for aqueous solutions of amine, the effect of the hydroxyl ion (OH^-) is minimal because of its very low concentration and may be neglected without any significant error. In aqueous amine solutions, the amine itself has been considered as the only base (Equation 2.3) as proposed by Laddha and Danckwerts (1981).

Further reactions involving carbamate hydrolysis in primary amines have also been documented by Sartori and Savage (1983) as displayed in Equation 2.6. They further concluded that, though carbamate formation is the major reaction for primary amines, a certain amount of carbamate hydrolysis also takes place. This carbamate hydrolysis slightly increases the theoretical CO_2 loading above 0.5 mol CO_2/ mol amine. Carbamate hydrolysis form bicarbonate and produces free amine to further react with additional CO_2.

$$RNHCOO^- + H_2O \leftrightarrow RNH_2 + HCO_3^- \qquad 2.6$$

As revealed by Xu *et al.* (1996) in aqueous amine systems the amine dissociates to form protonated amine and hydroxyl ion (Equation 2.7) thereby favoring bicarbonate formation. Other reactions are the reaction of CO_2 with water and hydroxyl ion (Equations 2.8–2.9) to form bicarbonate, but are considered negligible (Tong *et al.*, 2013), as well as carbonate formation (Equation 2.10).

$$RNH_2 + H_2O \leftrightarrow RNH_3^+ + OH^- \qquad 2.7$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \qquad 2.8$$

$$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^- \qquad 2.9$$

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \qquad 2.10$$

Termolecular Mechanism

The single-step termolecular mechanism is another alternative way of describing the reaction between primary amines and CO_2. It was first introduced by Crooks and Donnellan (1989) and later revisited by da Silva and Svendsen (2004). They assumed that the amine simultaneously react with one mole of CO_2 and the base (B) seen in Equation 2.11.

$$RNH_2 + CO_2 + B \leftrightarrow RNHCOO^- + RNH_3^+ \qquad 2.11$$

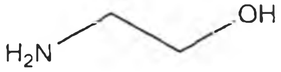
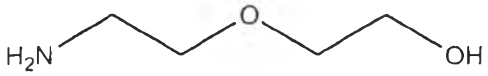
This reaction does not produce zwitterion rather it proceeds in a single step through a loosely-bound encounter complex as the intermediate. This complex breaks up to form reactant molecules (CO_2 and amine), while it's small fraction reacts with a second molecule of the amine or a water molecule (as the base) to give ionic products like carbamates (Sutar *et al.*, 2012; Vaidya and Kenig, 2010). Vaidya and Kenig (2010) also suggest that H_2O, OH^-, amine and other bases if present in the amine solution will influence the reaction (Equation 2.11) in parallel. According to (Siemieniec *et al.*, 2011), the validity of this mechanism is questionable because from the likelihood standpoint, it's near impossible that three molecules will be able to meet and react every time.

Some other properties of primary amines are high vapor pressure compared to the other amines (Table 2.3). This results in significant solution losses through vaporization (Mokhatab *et al.*, 2012). This challenge usually can be reduced by installing a simple water wash at the top exit of the absorber to recover all vaporized solvent from the treated flue gas stream. Monoethanolamine (MEA) and diglycolamine (DGA) are the two available primary alkanolamines (Table 2.4). For the capture of CO_2 from flue gases 30 wt% (5 M) MEA is widely used and it regarded as the benchmark amine solvent (Rao and Rubin, 2002). Other properties of MEA range from high vapor pressure resulting to losses due to vaporization, high reaction kinetics, and degradation due to the presence of carbonyl sulphide (COS), carbon disulphide (CS_2), SO_x NO_x and oxygen (O_2). The high energy of regeneration (3.7 – 4 GJ/ton CO_2) for MEA has made it very expensive for the capture of CO_2 (Alie *et al.*, 2005; Abu-Zahra., 2007; Adeosun *et al.*, 2013; Pires *et al.*, 2011; Singh *et al.*, 2003).

Table 2.3 Properties of alkanolamines (Yildirim *et al.*, 2012)

Primary Amines	Secondary Amines	Tertiary Amines
High	Enthalpy of reaction ←	Low
High	Enthalpy of vaporization ←	Low
High	Reaction rate ←	Low
High	Corrosivity ←	Low
Low	CO_2 loading →	High

Table 2.4 Most common types of primary amines

Primary Amine	Acronym	Chemical/Skeletal Structure
Monoethanolamine	MEA	
Diglycolamine	DGA	

2.3.1.2 *Secondary Amines*

Secondary amines have lower reactivity than primary amines (Table 2.3). It also experiences lower solvent loss due to lower vapor pressure. They also form carbamates like primary amines which theoretically limit their capacity to 0.5 mol CO_2/ mol amine (Chowdhury *et al.*, 2013).

The reaction mechanisms of secondary amines are also described using both the two-step zwitterion mechanism (Caplow, 1968; Danckwerts, 1979) of primary amines as shown in Equations 2.1-2.10 and the single-step termolecular mechanism shown in Equation 2.11 (Crooks and Donnellan, 1989; da Silva and Svendsen, 2004). Siemieniec *et al.* (2011) stated that the most widely used interpretation for the reaction between CO_2 and secondary amines solutions is the zwitterion mechanism (Siemieniec *et al.*, 2011). Secondary amines are represented by the Equations 2.12-2.13 (Little *et al.*, 1992) for the zwitterion mechanism.

$$R_2NH + CO_2 \leftrightarrow R_2NH^+COO^- \qquad 2.12$$

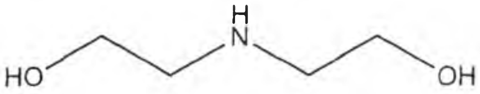
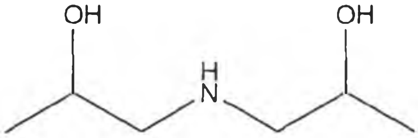
$$R_2NH^+COO^- + B \leftrightarrow R_2NCOO^- + BH^+ \qquad 2.13$$

The de-protonation of the zwitterion can come from any base (B) in the solution like H_2O, amine, OH^- (Versteeg and van Swaaij, 1988; Siemieniec *et al.*, 2011).

The two most popular secondary alkanolamines are diethanolamine (DEA) and diisopropanolamine (DIPA). Their chemical structures are shown in Table 2.5.

It's good to also note that COS, O_2, and CS_2 may irreversibly degrade DEA. Another advantage of DEA is that its heat of reaction with CO_2 (70 kJ/mol) is lower than 85 kJ/mol of MEA (Rolker and Seiler, 2011). DIPA possess selectivity for H_2S, though not as high as tertiary amines as described by GPSA (2004). It is mostly used in Europe for removing CO_2, H_2S and COS from refinery gases and liquids (Kohl and Nielsen, 1997). The major DIPA technology is the ADIP process licensed by Shell.

Table 2.5 Most common types of secondary amines

Primary Amine	**Acronym**	**Chemical/Skeletal Structure**
Diethanolamine	DEA	
Diisopropanolamine	DIPA	

2.3.1.3 Tertiary Amines

In tertiary amines, lack of free hydrogen atom attached to the amino group prevents it from forming a carbamate, but rather bicarbonate (Table 2.6). Therefore, the removal of CO_2 by tertiary amines can only follow the slow route to bicarbonate (GPSA, 2004). The three carbon atoms attached to the amino group provides it with more chemical stability. More so, the slow route to bicarbonates theoretically allows at equilibrium a chemical loading ratio of 1 mol CO_2 / mole of amine (Chowdhury *et al.*, 2013).

Base-Catalysed Hydration Mechanism

On the reaction pathway, Donaldson and Nguyen (1980) proposed and satisfactorily described CO_2 and tertiary amine reaction using the base-catalysis mechanism. They further stated that tertiary amines cannot directly react with CO_2 due to the base catalytic effect on the hydration of CO_2, and proposed the reaction as shown in Equation 2.14.

$$R_3N + H_2O + CO_2 \rightarrow R_3NH^+ + HCO_3^- \qquad 2.14$$

Several other researchers (Blauwhoff *et al.*, 1984; Barth *et al.*, 1984; Yu *et al.*, 1985; Tomcej and Otto, 1989; Crooks and Donnellan, 1990) who experimentally studied MDEA and TEA support this mechanism.

Other reactions (Equations 2.8-2.9) also occur in aqueous tertiary amine solutions (Crooks and Donnellan, 1990). Also, in aqueous solutions amine dissociation reaction may occur as seen in Equation 2.15 (Vaidya and Kenig, 2007; Filburn *et al.*, 2005).

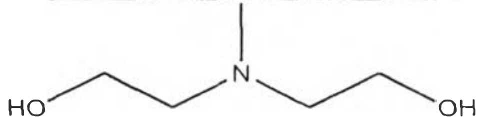
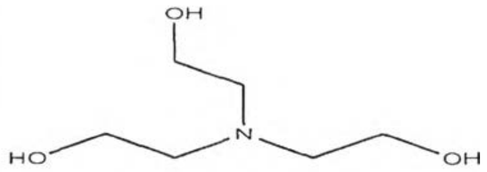
$$R_3N + H_2O \leftrightarrow R_3NH^+ + OH^- \qquad 2.15$$

Filburn *et al.* (2005) revealed that in aqueous amine solutions the OH^- is an intermediate in their CO_2 capture mechanism. According to Little *et al.* (1990); Kierzkowska-Pawlak and Chacuk (2010) the reaction between CO_2 and OH^- (Equation 2.8) may have significant contribution to the reaction rate. On the other hand, Rinker *et al.* (1995) stated that neglecting the CO_2 and OH^- reaction can result in large errors for the MDEA-catalyzed hydrolysis reaction, especially at the higher temperatures.

In addition, from the regeneration standpoint, tertiary amines require less heat energy than primary and secondary amines due to the formation of bicarbonate and not carbamate (Filburn *et al.*, 2005). However, its low reaction rates of CO_2 absorption make them difficult to use for CO_2 gas removal from flue gas (Chowdhury *et al.*, 2013). Examples of tertiary amines are methyldiethanolamine (MDEA) and triethanolamine (TEA). Table 2.6 shows most common types of tertiary amines.

MDEA have other advantages over primary and secondary amines which includes lower vapor pressure and high resistance to degradation (Polasek and Bullin, 2006). It also has lower heats of reaction (60 kJ/mol) than both primary and secondary alkanolamines (Rolker and Seiler, 2011).

Table 2.6 Most common types of tertiary amines

Tertiary Amine	Acronym	Chemical/Skeletal Structure
Methyldiethanolamine	MDEA	
Triethanolamine	TEA	

2.3.2 Sterically Hindered Amines

The concept of hindered amine is based on increasing the solvent capacity and reducing carbamate formation/stability. It can be achieved by slowing down the formation of carbamate by providing a steric hindrance. This is done by attaching a bulky substitute group adjacent to the amino molecule (Sartori and Savage, 1983). According to Chakma (1999) bulkier substitutes produces less stable carbamate. The most common primary sterically hindered amine is 2-amino-2-methyl-1-propanol (AMP).

As a primary amine, the reaction mechanism of AMP and CO_2 can also be described using the two-step zwitterion mechanism (Xu *et al.*, 1996; Pei *et al.*, 2008; Tong *et al.*, 2013). Several chemical reactions take place during the CO_2 solubility into aqueous solutions of AMP. Aqueous AMP solutions dissociates forming OH^- and protonated AMP, which increases the solution pH and also favors bicarbonate formation similar to those seen in Equations 2.7-2.8 (Xu *et al.*, 1996; Tong *et al.*, 2013).

The major CO_2 – AMP chemical reactions that take place involves the formation of a carbamate which rapidly hydrolyzes to bicarbonate, releasing free amine molecules to further react with CO_2 as shown in Equation 2.16 (Xu *et al.*, 1996; Sartori and Savage, 1983; Tontiwachwuthikul *et al.*, 1991; Sharma, 1964; Sharma, 1965; Tong *et al.*, 2013):

$$RNHCOO^- + H_2O \leftrightarrow RNH_2 + HCO_3^- \qquad 2.16$$

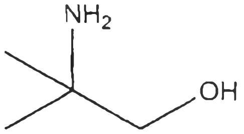
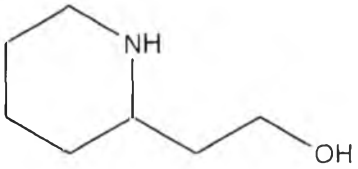
The steric hindrance of AMP (Table 2.7) makes the carbamate unstable which rapidly hydrolyzes to bicarbonate (Xu *et al.*, 1996; Sartori and Savage, 1983; Tontiwachwuthikul *et al.*, 1991). In 1992, Xu *et al.* measured the concentration of the AMP carbamate and discovered it to be only of the order of 10^{-4} of the AMP concentration. This verification confirms that the carbamate of sterically hindered amines like AMP may rapidly undergo hydrolysis, leading to the formation of bicarbonates and free amine molecules increasing the theoretical capacity to 1 mol CO_2/ mol AMP. This also increases the bicarbonate and carbamate molar concentration ratio. Xu *et al.* (1996); Vaidya and Kenig (2007) stated that the effect of Equation 2.8

on the rate of absorption will depend on the hydroxyl ion concentration in the amine solution.

Vaidya and Kenig (2007) also Equations 2.3-2.5 also take place in AMP-CO_2 reaction (based on the zwitterion mechanism). For sterically hindered amine (like AMP), the zwitterion will react more easily with water than the amine and bicarbonate formation takes place (Vaidya and Kenig, 2007). Regarding Equation 2.5, Versteeg and van Swaaij (1988) claimed that the contribution of the hydroxyl ion is only minor due to its low concentration and may be ignored without any significant error.

Commercial technologies are Flexorb SE and Flexorb PS. Other researchers (Roberts and Mather, 1988; Teng and Mather, 1990) also investigated the CO_2 absorption capacity of AMP. 2-Piperidineethanol (PE) is an example of a secondary sterically hindered amine (Sartori and Savage, 1983). Table 2.7 displays some types of sterically hindered amines.

Table 2.7 Sterically hindered amines

Hindered Amine	Acronym	Chemical/Skeletal Structure
2-Amino-2-Methyl-1-Propanol	AMP	
2-Piperidineethanol	PE	

2.3.3 Polyamines

Polyamines have been found to have very good absorption capacity and high reaction kinetics. This is largely due to the presence of multiple amino groups. Piperazine (PZ) is the most common and commercially available polyamine.

According to several researchers (Optimized Gas Treating Inc., 2008; Bishnoi and Rochelle, 2000; Derks *et al.*, 2006; Samanta and Bandyopadhyay, 2007; Plaza and Rochelle, 2011; Freeman *et al.*, 2010b; Yildirim *et al.*, 2012; Dugas and Rochelle, 2009), the major merits of PZ are below;

- At equivalent CO_2 partial pressure, its absorption and desorption rate is 2-3 times faster than MEA.
- It contains two reactive amino groups (diamine) per molecule, which both can easily get attached to CO_2. This therefore gives it high capacity to carry CO_2 equivalent to 1 mol CO_2/mol PZ.

Therefore, the proposed mechanism for the reaction between CO_2 with PZ involves the formation of a zwitterion seen in Equation 2.17 (Conway *et al.*, 2013). This is then followed by the de-protonation of the zwitterion by a base (B) to produce PZ-carbamate and protonated base shown in Equation 2.18 (Derks *et al.*, 2006).

$$PZ + CO_2 \leftrightarrow H^+PZCOO^- \quad 2.17$$

$$PZ + CO_2 + B \leftrightarrow PZCOO^- + BH^+ \quad 2.18$$

Any base present in the solution may contribute to the de-protonation of the zwitterion (Caplow, 1968; Danckwerts, 1979). According to Derks *et al.* (2006), the base present in solution aqueous PZ solution is PZ, $PZCOO^-$, H_2O, OH^-, PZH^+ and they will all contribute towards the de-protonation. The contribution of each base would depend on its concentration as well as how strong a base it is (Hagewiesche *et al.*, 1995; Bishnoi, 2000). The possible PZ – CO_2 – H_2O reactions are shown in Equations 2.19 – 2.24 (Derks *et al.*, 2006; Gupta *et al.*, 2013; Bishnoi and Rochelle, 2000; Dash and Bandyopadhyay, 2013).

$$PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+ \quad 2.19$$

$$H^+PZCOO^- + H_2O \leftrightarrow PZCOO^- + H_3O^+ \quad 2.20$$

$$PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+ \qquad 2.21$$

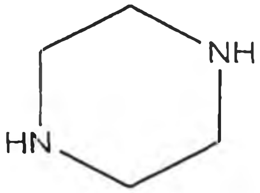
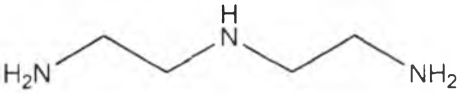
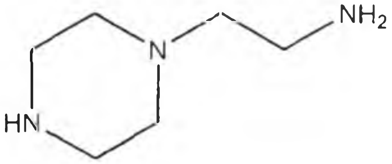
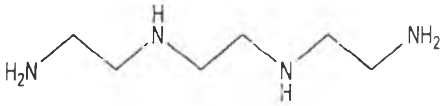
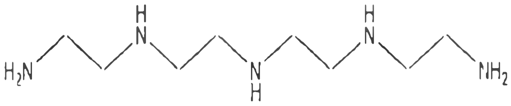
Xu *et al.* (1996) confirmed that in aqueous amine solutions the amine dissociates to form protonated amine and hydroxyl ion (Equation 2.7) which promotes bicarbonate formation, similar to the Equations 2.8-2.10. For PZ which contains two secondary amino groups (Table 2.8) it will form mono-protonated PZ and di-protonated PZ seen in Equations 2.24-2.25 (Conway *et al.*, 2013; Gupta *et al.*, 2013; Ermatchkov *et al.*, 2003; Ermatchkov and Maurer, 2011; Derks *et al.*, 2010).

$$PZH_2^{2+} + H_2O \leftrightarrow PZH^+ + H_3O^+ \qquad 2.22$$

$$PZH^+ + H_2O \leftrightarrow PZ + H_3O^+ \qquad 2.23$$

Many other polyamines (Table 2.8) like ethylenediamine (EDA), 3-methylaminopropylamine (MAPA), diethylenetriamine (DETA), N-2-Aminoethyl-Piperazine (AEP), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) are currently being researched on and also tested in pilot plants (Zhou *et al.*, 2010; Brúder and Svendsen, 2012; Hartono *et al.*, 2009; Du *et al.*, 2013; Esmaeili and Roozbehani, 2014).

Table 2.8 Skeletal structure of other polyamines

Polyamine	Acronym	Chemical/Skeletal Structure
Piperazine	PZ	
Ethylenediamine	EDA	
Methylaminopropylamine	MAPA	
Diethylenetriamine	DETA	
N-2-Aminoethyl-Piperazine or 2-(1-Piperazinyl)ethylamine	AEP or PZEA	
Triethylenetetramine	TETA	
Tetraethylenepentamine	TEPA	

2.3.4 Blended/Mixed Amines

Chakravarty *et al.* (1985) first proposed blending amines to utilize the advantages of each amine solvent. Most often, due to the high absorption capacity and superior chemical stability of tertiary amines and sterically hindered amines, they are often blended with primary, secondary, polyamines which possess far better reaction kinetics. For instance, blending a primary or secondary alkanolamine with a tertiary alkanolamine bulk removal of CO_2 is easily achieved while the cost of regeneration is reduced. For instance, in 2006, Idem *et al.* stated that utilizing MEA - MDEA binary blend will greatly minimize the heat duty when compared to using MEA alone an industrial CO_2 capture plant. In addition, Oyenekan and Rochelle (2007) suggested that tertiary amine (MDEA) solvents promoted by PZ offered energy savings between 15 – 22 %. This success in blending binary amines is gradually leading to ternary and quartenary amine blends. Haghtalab *et al.* (2014); Esmaeili and Roozbehani (2014) have investigated ternary and quartenary amine blends respectively.

2.3.4.1 Binary Amine Blends

Binary (Bi-solvent) blends of amines have existed for several decades and are commercially available (like MDEA - PZ) and are currently researched for better combinations. Examples are MDEA- MEA, MDEA - DEA, MDEA - PZ, AMP - PZ, AMP - MEA. The above listed are binary blends of commercial amines. Several other binary blends of newly developed amines are currently been studied in the laboratory and pilot plant.

2.3.4.1.1 MDEA Blends

MDEA as a tertiary amine have superior CO_2 absorption capacity compared to other amines, but have the slowest reaction kinetics. Researchers then started promoting/activating MDEA using amines with faster reaction kinetics, like the primary, secondary and polyamines. Below is a highlight of common MDEA blends. MDEA have been activated with piperazine (MDEA-PZ) to utilize their various merits which is high absorption capacity and high reaction kinetics. This technology was first introduced by BASF gmbh (Germany), and since the license expired, several other companies have produced this combination. Researchers in the academia and industry have also continued to study more about this blend to further increase and optimize its functions. Najibi and Maleki (2013); Mudhasakul *et al.*, (2013); Ermatchkov and Maurer, (2011); Closmann *et al.*, (2009); Ali and Aroua (2004) have all studied CO_2 capture either experimentally or through simulation model.

Another interesting combination that has drawn wide research is the MDEA-MEA blends. MEA which is a primary amine boast of excellent reaction kinetics too, though it's lower than piperazine. Sema *et al.* (2012) researched the mass transfer and kinetics of this blend, while Dawodu and Meisen (1994); Austgen *et al.* (1991); Mandal *et al.* (2001) investigated CO_2 absorption capability of this blend.

Researchers also looked into the potential of blending MDEA with DEA. DEA have better reaction kinetics than MDEA, but lower than that of MEA. Solvent losses due to volatility and also the corrosion rate are lower in DEA than in MEA. This blend type has been studied by both Adeosun and Abu-Zahra (2013); Kundu and Bandyopadhyay (2006); Glasscock *et al.* (1991).

The amine combination of MDEA-DIPA has not been left out in experimental and modeling studies. Vahidi *et al.* (2013); Zoghi *et al.* (2012); Dell'Era *et al.* (2010) each analysed its absorption capacity of CO_2.

Other MDEA blends of interest like MDEA-AMP and MDEA-DGA have both been tested by Zoghi *et al.* (2012).

2.3.4.1.2 AMP Blends

AMP as discussed in Section 2.3.2 is a primary sterically hindered amine, which was synthesized to improve its absorption capacity, reaction kinetics, and minimize degradation.

AMP-DEA has been studied by Adeosun and Abu-Zahra (2013) with blend concentration of 5 wt% DEA and 25 wt% AMP. Their research concluded that this blend combination provided better performance in terms of solvent rate, reboiler duty, and cyclic loading. Previous studies by Mandal et al (2003) have also been documented.

Tong *et al.* (2013) investigated CO_2 solubility in aqueous mixtures of AMP and PZ at temperatures ranges of 40–120 °C and at total pressures up to 460 kPa. Various solvent combinations of 25 % AMP – 5 % PZ and

20 % AMP – 10 % PZ were studied while keeping the total solvent mass fraction at 30 %. From the experimental results, the mole-ratio loading capacity of the aqueous blend of AMP - PZ still favourably competes with 30 wt% aqueous MEA: AMP-PZ blend for CO_2 capture has been extensively analysed by Yang *et al.* (2010); Dash *et al.* (2014).

The blends of AMP - MEA drew huge attention due to their special properties of high absorption capacity and high reaction kinetics. Adeosun and Abu-Zahra (2013); Dey and Aroonwilas (2009); Choi *et al.* (2009) all reported increased CO_2 absorption.

In addition to the above discussed AMP blends, another interesting blend of DIPA - AMP was reported by Haghtalab *et al.* (2014).

2.3.4.1.3 PZ Blends

In Sections 2.3.4.1.1 and 2.3.4.1.2, promoting and activating MDEA and AMP with PZ have been highlighted. It was noticed that the blends possess increased reaction kinetics. Several other researches involving PZ have been conducted and also ongoing like MEA-PZ, DEA-PZ blends etc. MEA-PZ has been studied by Nainar and Veawab (2009a) for CO_2 capture from industrial flue gas streams. Their research deduced that this blend is a cost effective way of capturing CO_2 with respect to corrosion, which is seen as one of the major challenges in a CO_2 capture plant. Other researchers like Dang and Rochelle (2003); Dugas and Rochelle (2009) have also studied MEA-PZ amine blends.

Adeosun *et al.* (2013) carried out an experiment on DEA - PZ blends at10 wt% - 20 wt% respectively. This concentration recorded higher CO_2 absorption capacity than the 0.50 mol CO_2/mol amine of 30 wt% MEA. Previous studies on DEA-PZ combination have been conducted by Mondal (2009); Benamor *et al.* (2012).

Furthermore, Haghtalab *et al.* (2014) researched the solubility of CO_2 in DIPA-PZ.

2.3.4.2 Ternary Amine Blends

Considering the success recorded by the binary amine blends, ternary blends are beginning to attract wide attention. The idea is to further utilize the potentials of three amine solvents and as well potentially minimize their individual limitations (precipitation, low reaction kinetics, degradation etc.). More insights are provided in the Section 2.5 (Related Works).

2.3.5 Hybrid Solvents

Hybrid systems are a mixture of both chemical and physical solvents. This is aimed at taking the advantages of both solvents. Commercial technologies are improved Amisol (Lurgi) which is a combination of Methanol-secondary alkylamine, Sulfinol M (Shell) a combination of MDEA-sulfolane-water, and Sulfinol D (Shell) a combination of DIPA-sulfolane-water.

Hybrid system could also be a combination of membrane-absorption processes, which also currently researched. Mohebi *et al.* (2009) modeled and simulated a hollow fiber membrane contactor and an amine solution for CO_2 and H_2S capture from $CO_2/H_2S/CH_4$ gas stream.

2.4 Amine Problems

There are various challenges facing chemical solvent absorption which have prompted researchers to both optimize solvent combinations and to develop several novel chemical solvents with the main aims below (Wang *et al.*, 2011);

- Increase solvent reactivity with CO_2– this will in turn reduce the height of the absorber.
- Reduce cost of solvent regeneration.
- Increase absorption capacity, which translates to lower solvent circulation rate.
- Reduce solvent loss due to degradation and vaporization.
- Lower environmental impact.
- Minimize solvent costs.

2.4.1 Degradation

Solvent degradation is one of the most important limitations that must be closely observed in order to retain the maximum efficiency of the process (Supap *et al.*, 2011). According to Kennard and Meisen (1985), degradation is a complex process which is affected by temperature, pressure, composition of the raw gas, concentration of the amine solution and possibly the presence of metal ions. Degradation products from chemical solvents are irreversible components generated by chemical reaction of the amine with substantial quantity of some impurities (CO_2, COS, NO_x, CS_2, SO_x) in the feed gas stream. Heat stable salts (HSS) are the nomenclature for the group of degradation products which are very difficult to regenerate under normal operating conditions of the regenerator (Supap *et al.,* 2011). This is most common in primary and secondary amines. If not removed from the system, it keeps accumulating and can cause severe problems from solvent loss to corrosion etc. This adds more capital and operational costs by installing a reclaimer near the regenerator reboiler. Degradation can also be caused by oxygen (oxidative degradation), which can enter the system from both the flue gas stream and from the amine make-up unit (Freeman, 2011; Freeman *et al.,* 2010a; Davis, 2009; Sexton, 2008). The final type of degradation is 'thermal degradation', which can occur at regeneration temperature of 120 °C. Several amines have different rates of thermal degradation. According to Freeman *et al.* (2010a) at 135 – 150 °C (temperatures above stripping temperature) concentrated solution of PZ degrades 100 times less than MEA. Also, at high temperature PZ degrades slower than AMP. Careful selection and /or blending of amines can reduce the formation of degradation products. For instance, due to degradation problem, systems with MEA have been forced to use lower concentrations which are indirectly proportional to equipment size, solvent circulation rate, and regeneration energy.

2.4.2 Vaporization Losses

In many amine systems, losses due to vaporization have been a problematic issue and a drawback, because it increases operational cost (Rao and Rubin, 2006). Excessive volatility of amine during CO_2 capture operation may result in significant economic losses and environmental impact. Losses at the top of the absorber will affect the capital cost of the water wash and also increase the make-up cost of the lost amines especially with highly expensive amine solvents (Nguyen *et al.,* 2010). At the regenerator where CO_2 stripping is achieved at high temperature, amine losses will increase the duty of the overhead cooler, condenser and reflux pump. The higher the vapor pressure and lower the boiling point of an amine, the more the losses. Since the regeneration temperature is 120 - 140 °C, amines with boiling point close to this range will be prone to more losses (Yu *et al.*, 2012a). Since the OH group reduces the vapor pressure, amines with high vapor pressure (like MEA) are blended with MDEA (lower vapor pressure) to further reduce this loss. Table 2.6 depicts ranking of primary to tertiary amines according to their rate of vaporization.

2.4.3 Solvent Reactivity

Solvent reactivity is another challenge that is worth addressing. All amines have their distinctive reactivity with CO_2 as shown in Table 2.6 for the conventional alkanolamines. Amines with more amino groups (N) will be more reactive than those with less, as is the case between EDA and DETA (Singh *et al.*, 2009). In addition, cyclic amines are also associated with higher absorption rate and absorption capacity (Singh *et al.*, 2009). According to Rayer *et al.* (2011) the level of reactivity is polyamines > cyclic amines > primary amines > secondary amines. This is the reason why the reactivity of aqueous PZ (a diamine) is more than double than MEA (Freeman *et al.*, 2009).

2.4.4 Corrosion

According to Saiwan *et al.* (2011) corrosion is a huge set back that affects the overall efficiency of the amine process. Corrosion in amine units can be caused due to high CO_2 absorption capacity, solution temperature, high solvent circulation rate (low amine concentration), and formation of heat stable salts etc. Nowadays, corrosion inhibitors are added in amines to minimize the problem. In addition, stainless steel cladding is also used in sections that are vulnerable to corrosion. This thereby increases the capital and operating costs.

The correlation for estimating the corrosion rate of carbon steel was studied by Nainar and Veawab (2009b) using MEA-PZ solution as seen in Equation 2.24.

$$CR = \frac{0.13 \times i_{corr} \times E.W}{A \times D} \qquad 2.24$$

Where, CR is rate of corrosion in mils (thousandths of an inch) per year (mpy), i_{corr} is corrosion current density in μA/cm^2, $E.W.$ is the specimen equivalent weight, A is the specimen area in cm^2, while D is specimen density in g/cm^3.

2.4.5 Environmental Impact

Environmental impact is a very serious issue in any process, CO_2 capture inclusive. This has gained more attention and focus due to the need to monitor amine based pollutants and their toxicology, potential challenges to the environment and to human health (Thitakamol *et al.*, 2007). Amine losses up the stack may be environmentally significant by participating in atmospheric reactions to produce ozone and other toxic compounds (Nguyen *et al.*, 2010). Others can be related to waste products produced in some amine units. Such waste could range from wastewater used to wash the treated gas to recover amine solvent, incidental spills, fugitive emissions, vaporization losses (Reynolds *et al.*, 2012; Thitakamol *et al.*, 2007). Additionally, solid and aqueous wastes (like degradation products) are generated from the reclaimer (Gelowitz *et al.*, 2013; Gjernes *et al.*, 2013). These wastes must be treated under the most efficient and safest option prior to its disposal.

2.4.6 Regeneration Energy

This has drawn the most attention because energy requirement for amine regeneration accounts for about 70 - 80 % of the plant operational cost (Aaron and Tsouris, 2005). According to Alie *et al.* (2005); Abu-Zahra *et al.*, (2007); Adeosun *et al.* (2013); Pires *et al.* (2011); Singh *et al.* (2003) the energy of regeneration for MEA is between 3.7 – 4 GJ/ton CO_2 which is high and very expensive for the capture of CO_2. The total energy required for amine solution regeneration during CO_2 capture process can be estimated by Equation 2.25 (Quang *et al.*, 2013).

$$Q_{\mathrm{reg}} = Q_{\mathrm{des}} + Q_{\mathrm{sen}} + Q_{\mathrm{vap}} \qquad 2.25$$

Where Q_{reg} (GJ/ ton CO_2) is the energy of regeneration; Q_{des} (GJ/ ton CO_2) is the heat of desorption required to break the CO_2 carrying species (carbamates, bicarbonates, carbonates) formed during the CO_2 absorption (has the same value as heat of absorption); Q_{sen} (GJ/ ton CO_2) is the sensible heat that must be provided to raise the temperature of the amine solution to the regeneration temperature; while the Q_{vap} (GJ/ ton CO_2) is the latent heat of vaporization of the volatile components in the amine solution (usually includes the vaporization heat of water). In addition to regeneration energy, Pei *et al.* (2008); Cheng *et al.* (2013) also highlighted regeneration efficiency (RE) as an important parameter shown in Equations 2.26. Several factors that can increase the RE are high rich loading, increase in regeneration temperature etc.

$$RE = \left[1 - \left(\frac{\alpha CO_2\ (lean)}{\alpha CO_2\ (rich)}\right)\right] \times 100\ \% \qquad 2.26$$

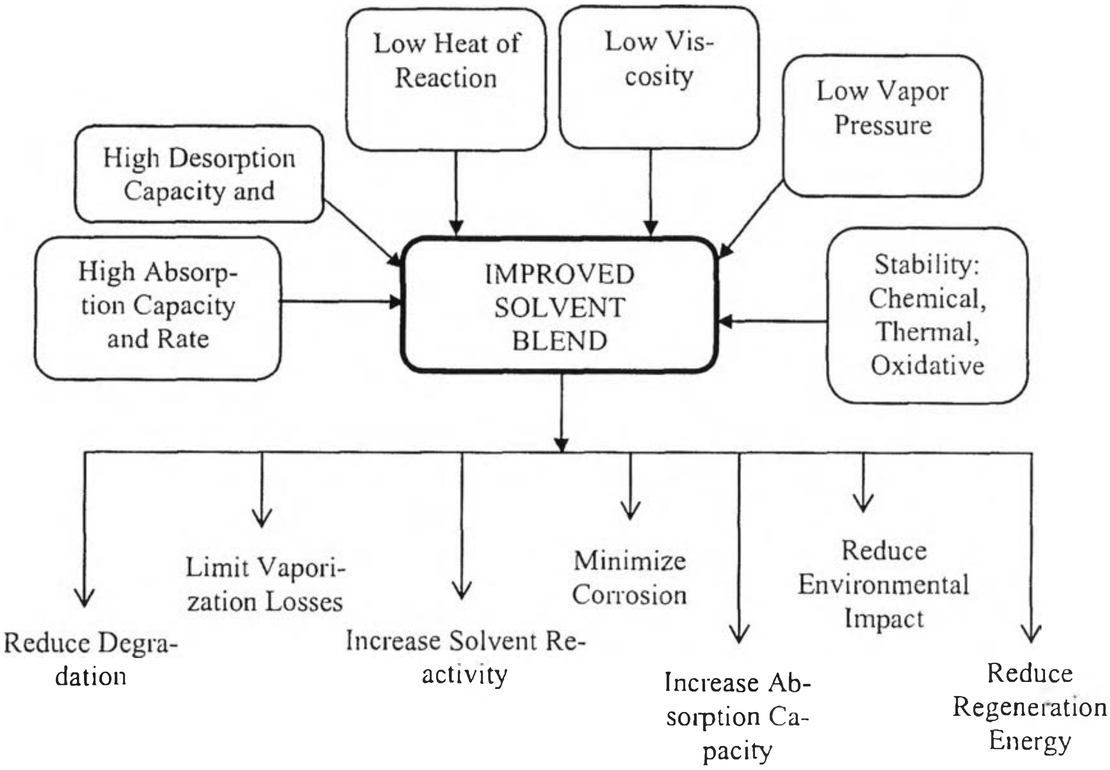
According to Shi *et al.* (2014) researchers proposed that the two significant ways of reducing regeneration heat duty to the desired value is by solvent optimization and process configuration. In terms of process configurations, split flow streams to the regenerator have been introduced to reduce the amount of energy required to remove acid gases from amine solvents (Kohl and Nielsen, 1997). Several other process configurations that reduce regeneration energy have been proposed by several researchers (Table 2.9).

Table 2.9 Several proposed CO_2 capture process configurations

Process Configuration	**Reference**
Multi pressure stripping with vapor recompression	(Jassim and Rochelle, 2006)
Split-stream with cooler	(Karimi *et al.*, 2011)
Vapor recompression	(Karimi *et al.*, 2011)
Tripled staged flash regeneration	(Plaza *et al.*, 2010)
Double matrix	(Rochelle and Oyenekan, 2008)
Two split-feeds semi-lean heat EX	(Liang, 2010)

2.5 Related Works

The success of blending binary chemical solvents is gradually leading to the blending of ternary solvents for CO_2 capture. This is aimed at further utilizing the benefits of the three chemical solvents to enhance CO_2 solubility and to also reduce the individual problems accompanying each solvent. Figure 2.8 shows different important properties desired from the optimized blended solvents.



*Others – Can be physical solvents, ionic liquids and novel solvents etc.

Figure 2.8 Several routes to an improved solvent mixture for CO_2 capture.

Related research works covering ternary amine blends are highlighted below;

Haghtalab *et al.* (2014) researched the experiment and modeling solubility of CO_2 in aqueous solutions of DIPA + AMP + PZ at high pressures of 1 – 40 bar and temperature range of 40 – 70 °C. The solvents compositions of the aqueous mixtures are: (36 wt.% DIPA - 7 wt.% AMP - 2 wt.% PZ), (30 wt.% DIPA - 10 wt.% AMP - 5 wt.% PZ), (24 wt.% DIPA - 13 wt.% AMP - 8 wt.% PZ). It was discovered the AMP - PZ blend as a promoter for the DIPA increased the CO_2 loading.

Haghtalab and Izadi (2014) studied the solubility of CO_2 + H_2S into aqueous blends of alkanolamines measured at 70 °C and total pressure range of 0.1 - 2.1 MPa. The ternary blends consist of MDEA+AMP+PZ (25+15+5) mass %, MDEA+AMP+PZ (25+10+10) mass % and MDEA+AMP+PZ (25+5+15) mass %, and the total amine mass fraction was kept at 0.45. AMP and PZ blends enhanced the CO_2 loading in the MDEA based solvent.

The research conducted by Freeman *et al.* (2013) analyzed CO_2 absorption into a new blend of piperazine (PZ), N-methylpiperazine (MPZ) and N,N'-dimethylpiperazine (DMPZ). The blend ratio considered was 3.75 m PZ/3.75 m MPZ/0.5 m DMPZ. When compared to 8m PZ and 7m MEA, this novel blend showed advantages in CO_2 capacity and CO_2 absorption rate.