

CHAPTER II

LITERATURE REVIEW

2.1 Motivation for Carbon Dioxide Capture

Greenhouse-gases emission from growing population, cultivation and industrialization causes many problems especially global climate change. This phenomena is caused by primary greenhouse gases consisting of carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), water vapor (H₂O), ozone (O₃) and chlorofluorocarbons (CFC's) as shown in Figure 2.1. Department of Energy in U.S showed global warming potential (GWP) of some greenhouse gases in times of CO₂ as shown in Table 2.1. Chlorofluocarbons has high amount of GWP (high trapping of heat) but the emission of chlorofluocarbons in year 1990-2010 is less than CO₂ emission (EPA, 2010). Thus, Carbon dioxide is clearly a major greenhouse gas that contributes to global warming. Currently, CO₂ capture technologies are significantly needed for lowering CO₂ concentration before releasing to the atmosphere. The details of CO₂ capture technologies are existed in the next section.

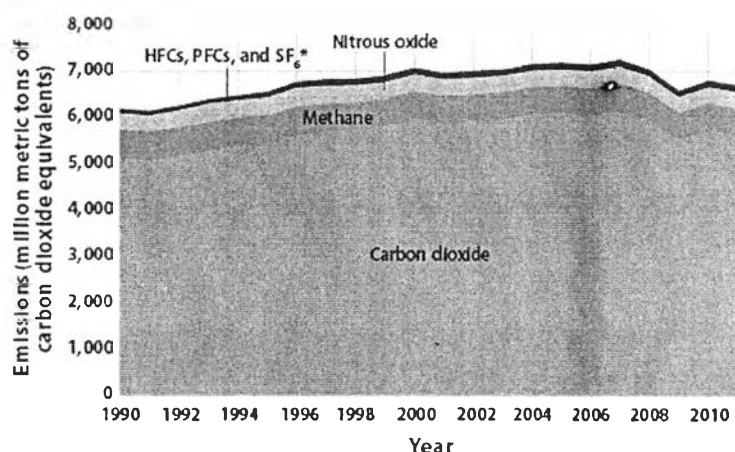


Figure 2.1 Emissions of carbon dioxide, methane, nitrous oxide, and several fluorinated gases in the United States from 1990 to 2011 (EPA, 2013)

Table 2.1 Global warming potential of primary greenhouse gases (NETL, 2011)

Greenhouse Gas	Chemical Formula	Global Warming Potential [Time Horizon]	
		20 years	100 years
Carbon Dioxide	CO ₂	1	1
Methane	CH ₄	42-70	16-26
Nitrous Oxide	N ₂ O	280	310
Hydrofluorocarbons	HFCs	460-9,100	140-11,700
Perfluorocarbon	PFCs	4,400-6,200	6,500-23,900
Sulphur Hexafluoride	SF ₆	16,300	23,900

2.2 Carbon Dioxide Capture Systems

The first step in the sequestration of carbon dioxide is the separation and capture of CO₂ from power plant flue gas and other stationary sources. CO₂ capture systems are divided into these three categories (Figure 2.2).

- Post Combustion Capture (PCC) from the flue gas of combustion-based plants
- Pre Combustion Capture from Syngas in Gasification based plants
- Oxy Combustion – the direct combustion of fuel with O₂
- Industrial Processes

2.2.1 Post Combustion Carbon Dioxide Capture System

A post-combustion system capture CO₂ from the flue gases produced by the combustion of the primary fuel such as coal, gas, biomass in air. These systems normally use a liquid solvent to capture the small amount of CO₂ (typically 3-15 percent by volume) in a flue gas at low temperature, low pressure (near atmospheric pressure) and low CO₂ concentration. These separation processes are already used on

a large scale to remove CO₂ from natural gas. Thus, these systems use large equipment size and high capital cost (IPCC, 2005).

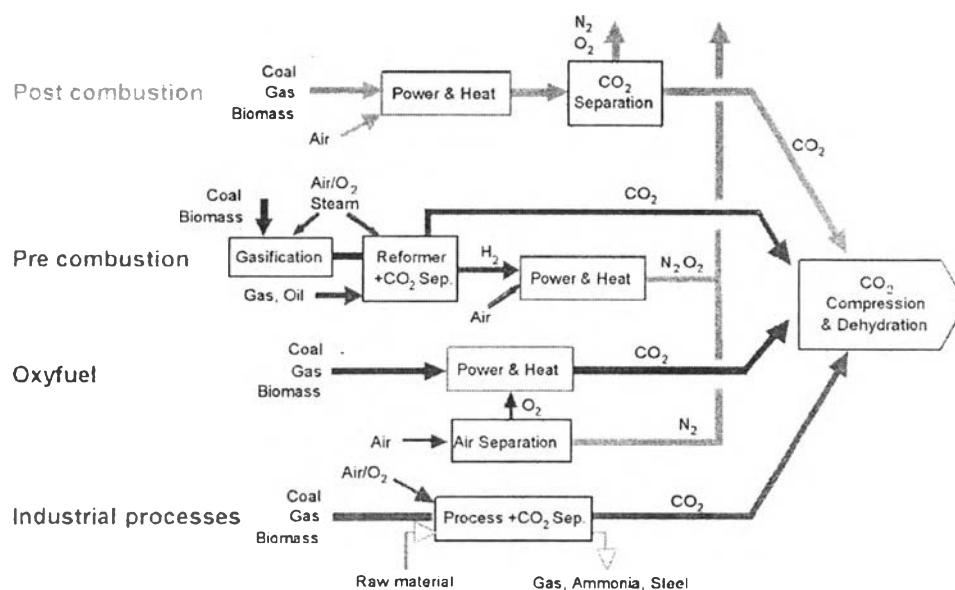


Figure 2.2 Overview of CO₂ capture processes and systems (IPCC, 2005).

There are four main methods for post-combustion CO₂ capture for flue gas.

- Absorption
- Adsorption
- Cryogenic separation
- Membrane separation

2.2.1.1 Absorption

Previously, a number of absorption processes that used in many industrial were physical and chemical absorption

2.2.1.1.1 Physical Absorption

Physical absorption of CO₂ has been one of the method that used in many country for a long time. This method used physical solvent to attach CO₂ out of flue gases without chemical reaction. Physical absorption was based on Henry's law. Regeneration section can be regenerated by using heat, pressure

reduction or both. This process normally occurs at high CO₂ partial pressure. Main energy consumption usually take place from flue gases pressurization. Therefore, physical absorption is not economical for flue gases streams with CO₂ partial pressure lower than 15 %vol. Selexol and Rectisol is normally used as a physical solvent in the industry.

2.2.1.1.2 Chemical Absorption

Chemical absorption of CO₂ occurred by chemical reaction of CO₂ with chemical solvent to form intermediate compound. This intermediate compounds should have weak bond in their compound in order to easily break out in regeneration section for minimizing energy usage. The chemical absorption has high selectivity to capture CO₂. Thus, a relatively pure CO₂ stream could be achieved. Presently, these Technique are widely applied to many industries.

2.2.1.2 Adsorption

Adsorption is another method that can be used to capture carbon dioxide produced from industry. This process used packed solid particle such as activated carbon, alumina, metallic oxides, zeolites etc. for attachment of gases or liquid to their surface. The flue gas streams to be treated should have high CO₂ concentrations because of typical adsorbent has low selectivity (Satish *et al.*, 2013).

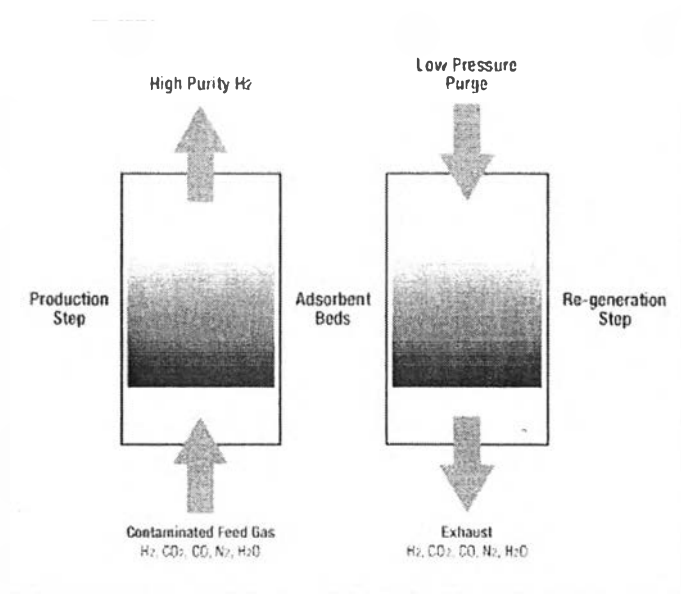


Figure 2.3 Conventional pressure swing adsorption schematic chart (XEBEC).

2.2.1.3. Cryogenic Separation

Cryogenic separation is operated at extremely low temperature and high pressure to separate components according to their different boiling temperatures. This method is widely used commercially for purification of CO₂ from streams by condensation. Flue gas entering the cryogenic system relies on the assumption that all components of the flue gas are removed except for the nitrogen and carbon dioxide prior to cooling. Triple point of carbon dioxide (5.2 bar and -56.6 celsius) is used to separate condensed CO₂ leaving out of nitrogen gas. The advantage of this technique is capturing highly concentrated liquid carbon dioxide, but energy requirement for cooling system is high, resulting in tremendous capital cost.

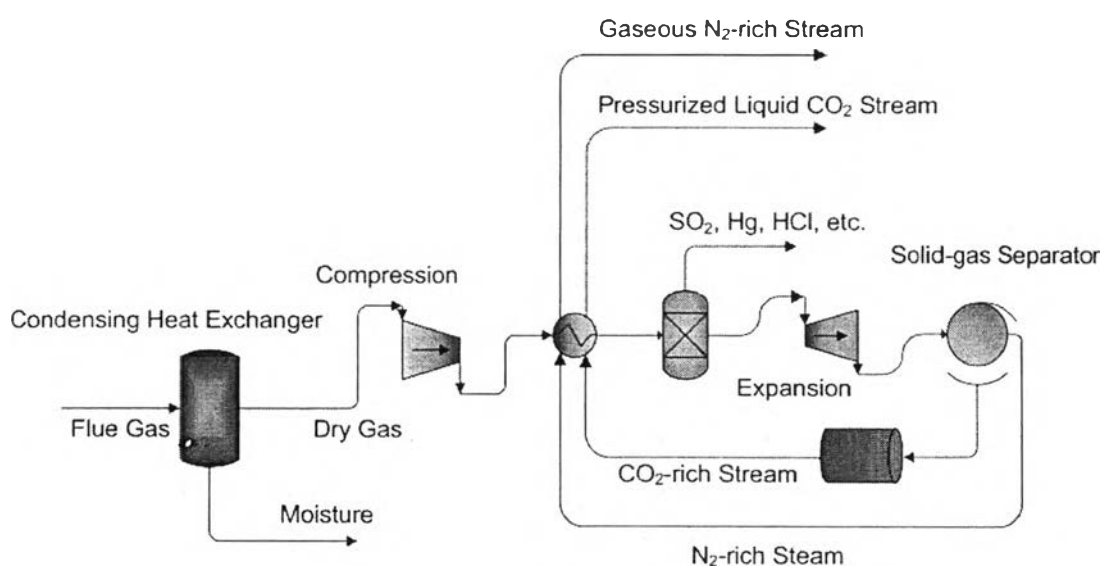


Figure 2.4 Simple schematic diagram of the cryogenic carbon capture (CCC) process (Stephanie *et al.*, 2010).

2.2.1.4 Membrane Separation

In general, Membrane separation operated in two type including membrane absorption and membrane-based separation

2.2.1.4.1 Membrane Absorption

Membrane in this process acts as contactor between gas stream and absorbent. Operation technique requires pressures on liquid and gas sides equal to CO₂ going through the membrane. Efficiency of this separation depends on CO₂ partial pressure.

2.2.1.4.2 Membrane-based Separation

This technique used partial pressure as a driving force to separate CO₂. Selectivity of this process is achieved by membrane themselves. Permeation rates based on molecular sizes or diffusion coefficients in membrane material. Nonetheless, selectivity of this process is still low (Satish *et al.*, 2013). Previously, some researchers used multistage membrane to earn more efficiency but cost of this process is relatively high (Chakravati *et al.*, 2011).

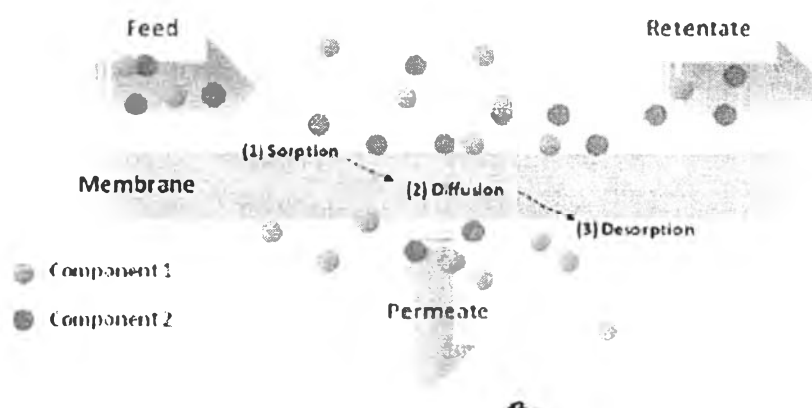


Figure 2.5 Simple schematic of membrane separation (Asia Pacific Biotech).

Table 2.2 Advantages and disadvantages of each technologies for CO₂ separation

CO ₂ Separation Technology	Advantages	Disadvantages
Absorption	<ul style="list-style-type: none"> - Recycling of the sorbent - Non dependence on human operators 	<ul style="list-style-type: none"> - Corrosion of carbon steel facilities due to oxygen - Degradation of the solvent due to SO_x and NO_x

Table 2.2 (con't) Advantages and disadvantages of each technologies for CO₂ separation

CO ₂ separation technology	Advantages	Disadvantages
Adsorption	<ul style="list-style-type: none"> - Recycling of the sorbent - High operation flexibility 	<ul style="list-style-type: none"> - Not able to handle large concentrations of CO₂ - Adsorption also of gases smaller than CO₂
Cryogenic	<ul style="list-style-type: none"> - Recycling of the sorbent - High operation flexibility 	<ul style="list-style-type: none"> - Not able to handle large concentrations of CO₂ - Adsorption also of gases smaller than CO₂
Membrane systems	<ul style="list-style-type: none"> - No moving parts and modularity - Instantaneous response to variations 	<ul style="list-style-type: none"> - Current low selectivity of membrane material - Limitation on the suitable operating temperature

Table 2.3 Comparison among the four units as function of feed and product conditions

	Absorption	Adsorption	Cryogenic	Membrane Systems
CO₂ in the feed, (% mole)	>5	>10	>5	>15
CO₂ purity, %	>95	75-90	99.99	80-95
CO₂ recovery, %	80-95	80-95	99.99	60-80
Energy requirement, MJ/kgCO₂	4-6	5-8	6-10	0.5-6

2.2.2 Pre-Combustion Carbon Dioxide Capture System

The technology for pre-combustion is widely applied in fertilizer, chemical, gaseous fuel (H₂, CH₄), and power production. Pre-combustion capture system or carbon oxide capture before combustion normally used to remove CO₂ after

gasification or steam reforming. Typically produced CO₂ of these process is 5-15 bar and can be separated produced CO₂ by using many method. Absorption by physical solvent is recommended to operate in this regime.

2.2.3 Oxy-Combustion Carbon Dioxide Capture System

In oxy-fuel combustion, the fuel is combusted in pure oxygen without containing nitrogen gas. The flue gas from this combustion contain mainly carbon dioxide and water vapor. Condensed carbon dioxide is achieved by cooling system and then separated liquefied carbon dioxide out of water vapor. The main concerns of the oxyfuel-combustion process are the cost and energy penalty related to its high oxygen requirement (Neda *et al.*, 2012).

2.3 Solvents for Chemical Absorption Systems

Carbon dioxide capture process by amine-based is widely used in oil and gas industry. Normally, amine-based is used to capture carbon dioxide from flue gas in post-combustion process. Carbon dioxide is separated out of flue gases by chemical reaction between aqueous amine and carbon dioxide to form soluble carbamate salt. This chemical reaction is reversible process that can be reversed while applied heat or pressure to the system. Amine can also recycle back to use again in close-loop system and carbon dioxide is stored in suitable conditional tank that waiting for using in other applications.

Amines that can be used in carbon dioxide capture process is categorized as primary, secondary and tertiary amines. Classification of their name are classified by number of carbon attached to nitrogen functional group. The most commonly used amines in carbon dioxide capture are Monoethano-lamine (MEA), Diethanolamine (DEA), Methyldiethanolamine (MDEA), Diisopro-panolamine (DIPA) and Diglycolamine (DGA) as shown in Figure 2.6.

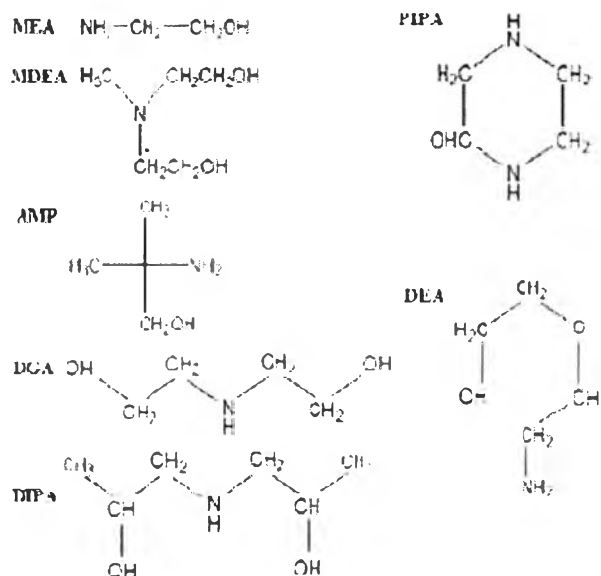


Figure 2.6 Chemical structures of amine commonly used in carbon dioxide capture.

Different structure of amines have some advantages and disadvantages. Amines structure that used in capturing CO_2 depends on performance, cost and proper properties for those systems.

Primary alkanolamine such as MEA is one of most commercial alkanolamine that used for carbon dioxide capture and acid removal process. Advantages of this amine are low molecular weight, low cost, low viscosity and high absorption rate. But MEA still have some drawbacks which are high solvent losses, high regeneration energy and severe corrosion.

Secondary alkanolamine such as DEA is another choice for carbon dioxide capture. Advantages of this amine are less corrosion, lower regeneration energy, lower solvent losses while compared with monoethanolamine. Drawback of this solvent is lower reaction rate.

Tertiary alkanolamine such as MDEA is used in specific carbon dioxide capture. Advantages are less corrosion, low solvent losses, high selectivity for CO_2 and low energy required for regeneration but also have some disadvantages which is low reaction rate. Thus, High circulation rate should be used to comprehensive this problem.

Table 2.4 Property comparison among primary, secondary and tertiary alkanolamine

Amines	Reaction rate constant (mol/L.s)	Heat of reaction (kJ/mol CO ₂)	Stoichiometric	CO ₂ loading
Monoethanolamine (MEA)	7,000	90	0.5	0.4
Diethanolamine (DEA)	1,000	80	0.5	0.4
Methyldiethanolamine (MDEA)	7	60	1.0	0.5

2.4 Carbon dioxide capture process by monoethanolamine (MEA)

Monoethanolamine as a feasible solvent is the most effective system for carbon dioxide capture in post-combustion. Figure 2.7 shows simple amine scrubbing system for carbon dioxide capture.

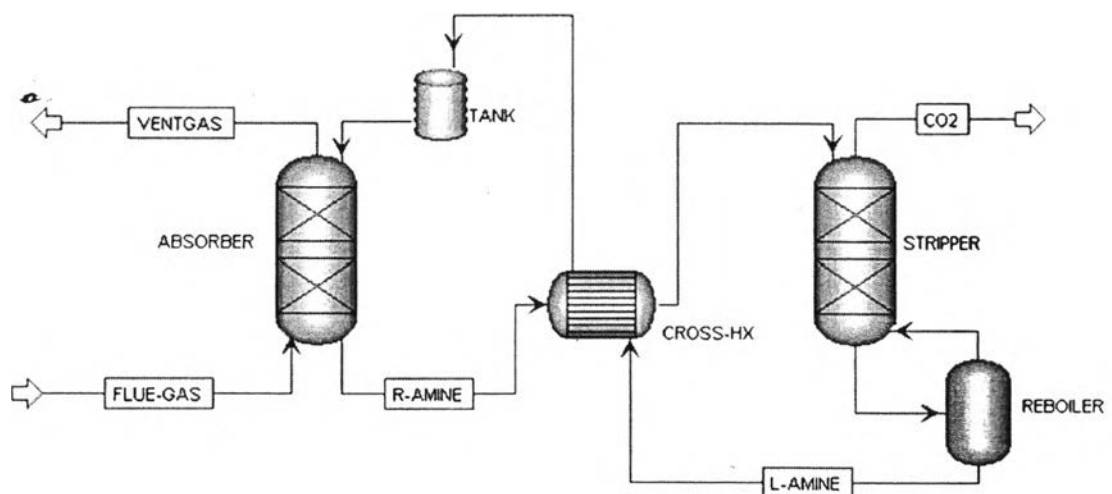


Figure 2.7 Simple process flow diagram of an amine absorption process (Noorlisa *et al.*, 2012).

Cooled flue gas (38-50 °C) from post-combustion enters on absorber at atmospheric or higher pressure. Restrictions of absorption column are minimum temperature used should be above condensation point of gas and freezing point of absorbent. The flue gas entering the column moved upward countercurrent with lean-amine solvent that moved downward from the top of the column. After treating process, before treated flue gas exit to the surrounding some process has water scrubber that removed trace of MEA for achieving low amount of MEA contaminant. Rich-amine solution at the bottom of the column is pumped through rich-lean heat exchanger to preheat cold stream for minimize energy usage in the system. In regeneration section, rich-amine that contain large amount of CO₂ enter to stripping column for separating CO₂ in amine solution. Hot steam from reboiler is used for carbon dioxide desorption process in stripping column. Condenser is used for remove trace of water back to stripping column before carbon dioxide gas go through storage section. Finally, lean-amine is pumped through rich-lean heat exchange for cooling down lean-amine and recycled back to absorber.

During economical and environmental concerns, amine-based (MEA) carbon dioxide capture process has high energy usage in regeneration section and high amount of volatile solvent components that damaged to surrounding. Thus, ionic liquids that has low volatility and superior properties have been investigated as alternative absorbent for CO₂ capture.

2.5 Carbon dioxide capture process by aqueous ammonia

Aqueous ammonia has considered as one of alternative absorbent for CO₂ capture. The flow sheet development was divided into two parts including CO₂ capture system and ammonia abatement system as shown in Figure 2.8. CO₂ capture system, was designed to capture CO₂ about 90 % by volume from the flue gas. The flow sheet was optimized by varying the concentration of ammonia solution and CO₂ lean loading of ammonia solution. Then, 98 % by weight of CO₂ purity entering storage section was specified by varying reflux ratio (mass), distillation rate and liquid holdup in stripping section. For ammonia abatement system, it was used to recycle the volatilized ammonia and also minimize ammonia vent to atmosphere due to restriction of

loss of ionic liquid can negligible. Therefore, ionic liquids retain quantitatively in the system and act as a green solvent.

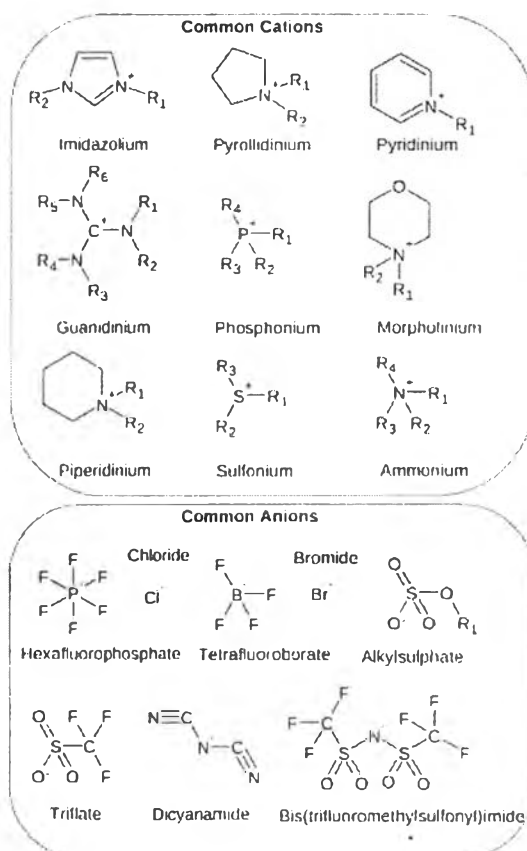


Figure 2.9 Commonly used anions and cations of ionic liquids (Mahinder *et al.*, 2012)

In addition, properties of ionic liquids depend on the combination between the cation and the anion. Type of the cation has strong impact on stability of ionic liquid, while the type of anion is responsible of the impact on chemistry and functionality (such as gas solubility).

Nowadays, Carbon dioxide capture process by ionic liquid has been investigated by some researchers (Jessica *et al.*, 2012). Ionic liquids still have some drawbacks such as high viscosity, high cost that cannot be used in the industry. Therefore, Advantages of ionic liquid and aqueous amine might combined together to earn superior properties that beneficially purposed for carbon dioxide capture process.

2.7 Carbon dioxide capture process by aqueous MEA and ionic liquids solution

Aqueous MEA and ionic liquids solution is another application for carbon dioxide capture process. This system used advantages of MEA and ionic liquid as shown in previous section and solved viscosity problem of ionic liquids. MEA in ionic liquid can act as supporting solvent while IL can also act as supporting solvent. From both resulted, responsibility depends on CO₂ loading of each aqueous solution which one has higher CO₂ loading behaving as a supporting solvent. Anyway, MEA and ionic liquid solution has higher CO₂ loading and lower viscosity when compared with pure ILs aqueous solution (Malyanah *et al.*, 2012).

Therefore, MEA, aqueous ammonia and ionic liquids solution for carbon dioxide capture process are obviously interested for many researchers. From this reason, simulation process of MEA, aqueous ammonia and ionic liquids for carbon dioxide capture will investigate in this study in order to find energy usage in regeneration section and capital cost of this system and then compare with MEA-based.

2.8 Literature Review

Amine-based especially monoethanolamine (MEA) is widely used to capture carbon dioxide from post-combustion system (PC). Many researcher are trying to find out additional technologies or superior conditions to manipulate MEA-based carbon dioxide capture. However, carbon dioxide capture by using MEA-based still have some drawback, e.g., high volatility, high corrosion and high energy usage in regeneration section (Stefan *et al.*, 2012).

Ionic liquids are chosen as alternative absorbents for carbon dioxide capture from PC. As a result, ILs have some favorable properties, e.g., low volatility, high thermal and chemical stability and tenability (Afshin *et al.*, 2011), (Zhang *et al.*, 2012).

Jessica B. *et al.* (2012) studies comparison of CO₂ absorption in imidazolium based ionic liquids with different anions, [BF₄]⁻, [NTf₂]⁻, [B(CN)₄]⁻, [CF₃SO₃]⁻, [FAP]⁻ and [OAc]⁻ (as shown in Figure 2.10), the result showed that very low Henry's law constants of 8.33 bar ([emim][OAc]) and 9.29 bar ([bmim][OAc]) when compared

to another anions. Significantly, very low value of Henry's law constants inferred to high CO₂ solubility.

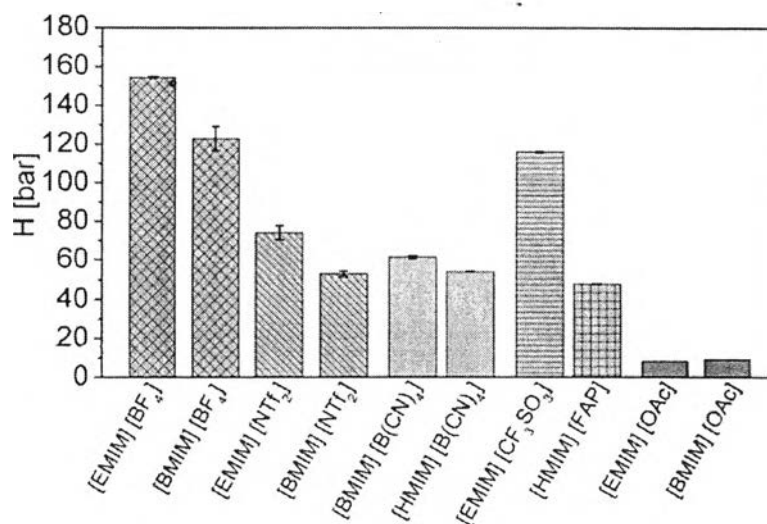


Figure 2.10 Henry's law constant of CO₂ in imidazolium based ionic liquids at 60°C [OAc]⁻ in comparison to [BF₄]⁻, [NTf₂]⁻, [B(CN)₄]⁻, [CF₃SO₃]⁻ and [FAP]⁻.

Furthermore, this literature review showed that equilibrium pressure up to 1 bar only chemical absorption will be occurred. And at higher equilibrium pressure than 1 bar physical absorption of saturated ionic liquid is dominant. Besides, this review showed CO₂ capture mechanism on carboxylate formation in Figure 2.11.

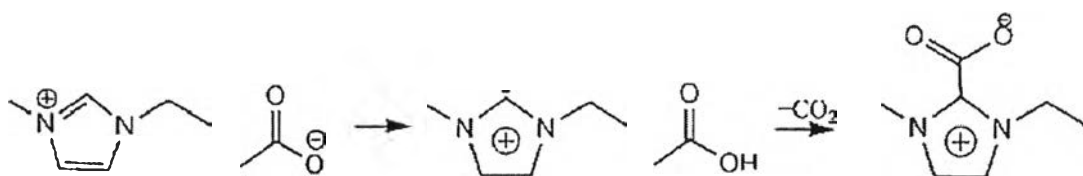


Figure 2.11 Carbon dioxide capture mechanism by carboxylate formation.

Shiflett *et al.* (2012) showed that at low CO₂ concentration (less than 20 ca. 20 mole %) reflected a strong complex formation of [bmim][Ac]-CO₂ but at high concentration (above ca. 70 mole %) reflected liquid-liquid separations (or immiscible

VLE). The best ways to observe phase behavior of [bmim][Ac]-CO₂ is to inspect the thermodynamic excess functions (excess Gibbs free energy G^E , excess enthalpy H^E and excess entropy S^E). A minimum in G^E occurred in 33 mole % of CO₂-[emim][Ac] similar to CO₂-[emim][Ac]. Furthermore, They indicated that [emim][Ac] had heat of reaction $-30.8 \pm 0.5 \text{ kJmol}^{-1}$ and compared to MEA and MDEA in water (15 mass % to 50 mass) had -50 to -80 kJmol^{-1} . Therefore, the combination of high loading capacity and low heat of reaction of [emim][Ac] is useful properties for scrubbing CO₂ from flue gas. With [acetate] as an anion, ionic liquid perform like a chemical solvent at low pressure (<0.1 MPa) and more like a physical solvent at higher pressure (>0.1 MPa). The addition of water in ionic liquid can reduce the viscosity of the solution for an industrial process. In another way, adding some water does not appear to aid in the absorption of CO₂.

Stefan *et al.* (2013) investigated effective of monoethanolamine and ionic liquid aqueous solutions for CO₂ capture. This group worker concerned high viscosity and creation of the second phase (MEA carbamate), they decided to use water as a co-solvent for reducing the viscosity. But they observed that, water inhibits the reaction between acetate anion and C(2)-H proton of an imidazolium ionic liquid as a result, it is stronger acid than C(2)-H as shown in Figure 2.11. In conclusion, addition amount of water causes decreasing in CO₂ absorption. In addition, monoethanolamine and ionic liquid aqueous solutions, MEA concentration is the largest influent on overall CO₂ loads and is 50-60 times more effective than IL or water as an absorbent. Furthermore, increasing temperature in this system resulted in decreasing CO₂ absorbed but increasing absorption rate by decreasing the viscosity.

Dean *et al.* (2008) studied RTIL-amine solutions offered beneficial advantages over commercial aqueous amine solutions, specially energy requirement for CO₂ capture. In the regeneration step, If amine-carbamate did not soluble in RTIL, heated (100 °C) and pressured can be decomplexed easily. Thermal input could be more directly to carbamate-bound CO₂, achieving energy efficiency. Furthermore, RTIL-amine solutions can uptake CO₂ 20 times greater than neat RTIL.

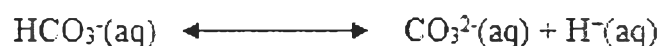
Afshin *et al.* (2011) showed that, CO₂ loading decreasing with increasing of IL concentration, especially at high temperature. Main reason of reducing of CO₂ in MDEA+ILs mixture, may be described due to decreased water that replaced by ILs

but it is still much more than neat pure ionic liquids. In case, water is main species of CO₂ absorption for using MDEA solution as shown in Figure 2.12. Furthermore, the CO₂ loading increases with increasing of CO₂ partial pressure and decreasing with increasing temperature.

Autoprotolysis of water:



Formation of bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻):



Protonation of MDEA:



Figure 2.12 Mechanism of MDEA solution for CO₂ capture system.

Zhang *et al.* (2012) studied performance of CO₂ in ionic liquid (tetramethyl ammonium glycinate [N₁₁₁₁][Gly]) and MDEA (N-metyldiethanolamine) solution. Under a certain MDEA concentration, the solution's density is quite the same value with rising IL's concentration. The viscosity of the solution greatly rises with increase in the concentration of IL or MDEA (as shown in Table 2.5). Adding small concentration of ILs into 30wt% MDEA aqueous solution caused dramatically increasing in the absorption rate of CO₂ (as shown in Figure 2.13). The influence of IL on the absorption of 40wt% and 50wt% MDEA aqueous solutions was similar to the case of 30 wt. % MDEA solution, except that the absorption rate was lower, due to the higher viscosity. Therefore, 50wt% MDEA aqueous solution is not fit for industrial CO₂ removal, since longer residence time.

Table 2.5 Density, viscosity and surface tension of varied MDEA-IL solution

MDEA (wt%)	ILs (wt%)	Density (gcm⁻³)	Viscosity (mPa s)	Surface tension (mN m⁻¹)
0	100	1.089 ^a	304 ^a	NA
30	2.5	1.02759	4.11	47.00
30	5.0	1.03041	4.57	49.32
30	7.5	1.03308	5.02	44.03
30	10.0	1.03597	5.76	45.63
30	12.5	1.03889	6.45	43.02
30	15.0	1.04130	7.22	49.51
40	2.5	1.03672	6.20	49.51
40	5.0	1.03978	7.10	50.40
40	7.5	1.04253	8.24	50.62
40	10.0	1.04526	10.1	47.85
40	12.5	1.04770	11.3	48.73
40	15.0	1.05023	12.9	47.45
50	2.5	1.04488	12.4	48.36
50	5.0	1.04719	14.2	44.61
50	7.5	1.04957	17.2	45.34
50	10.0	1.05154	19.3	26.07
50	12.5	1.05345	22.8	44.20
50	15.0	1.05512	26.5	45.51

In addition, higher concentration of IL provoked slightly increase in the absorption capacity, especially in high IL concentration. Furthermore, absorption capacity can be improved by increasing MDEA concentration but restriction is operation under low pressure (Figure 2.14).

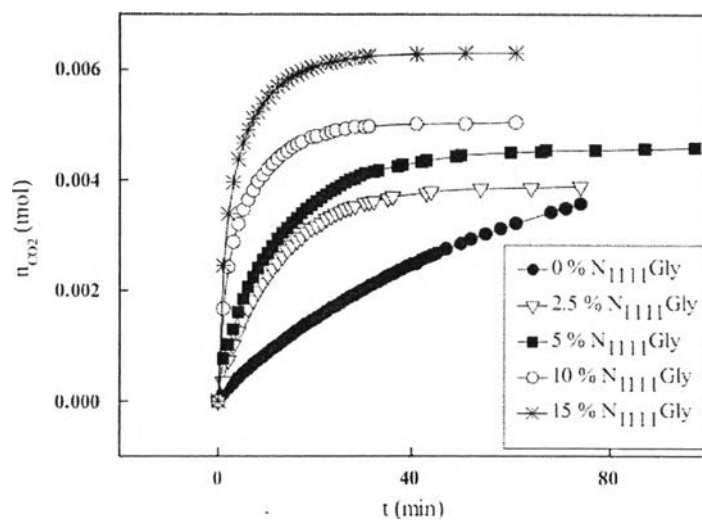


Figure 2.13 CO₂ absorption capacity vs. time for the mixed solutions of 30 wt% MDEA and [N₁₁₁₁][Gly].

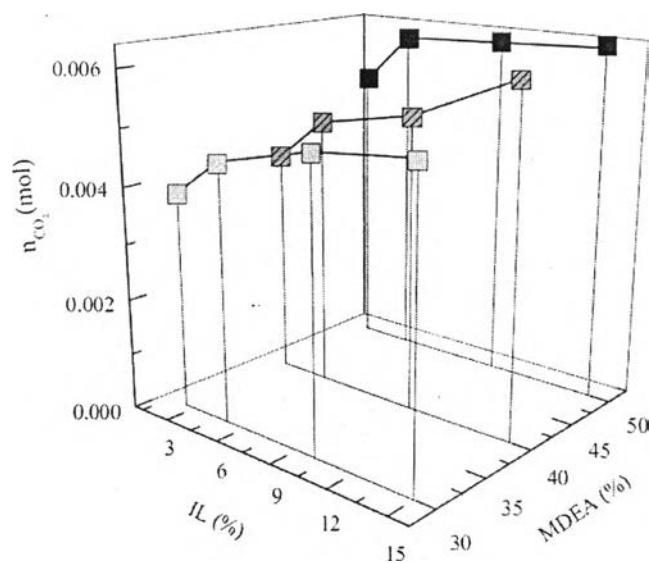


Figure 2.14 Absorption capacity of CO₂ varied by using different concentration of IL and MDEA under $P_0 = 97$ kPa.

A maximum value of apparent absorption rate was obtained at 10 wt% ILs in case of containing 30 wt% of MDEA in the solution. The result was quite the same in 40 wt% of MDEA in the solution as shown in Figure 2.15 and Figure 2.16.

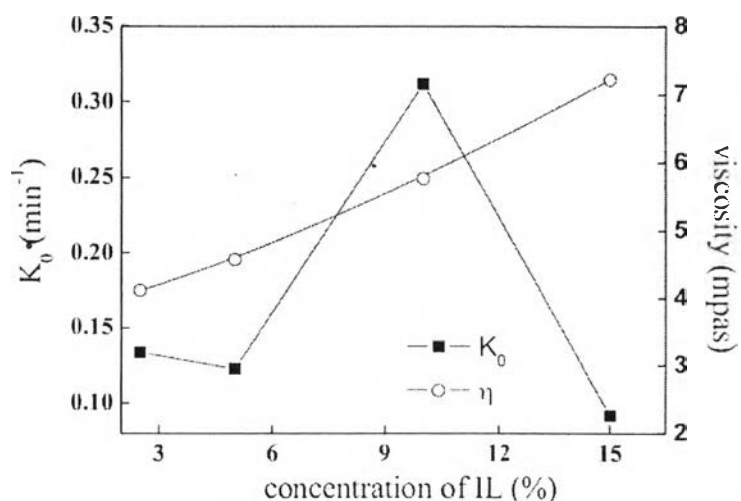


Figure 2.15 Apparent absorption rate (K_0) and viscosity (η) of mixed solutions of 30 wt% MDEA and $[\text{N}_{1111}][\text{Gly}]$.

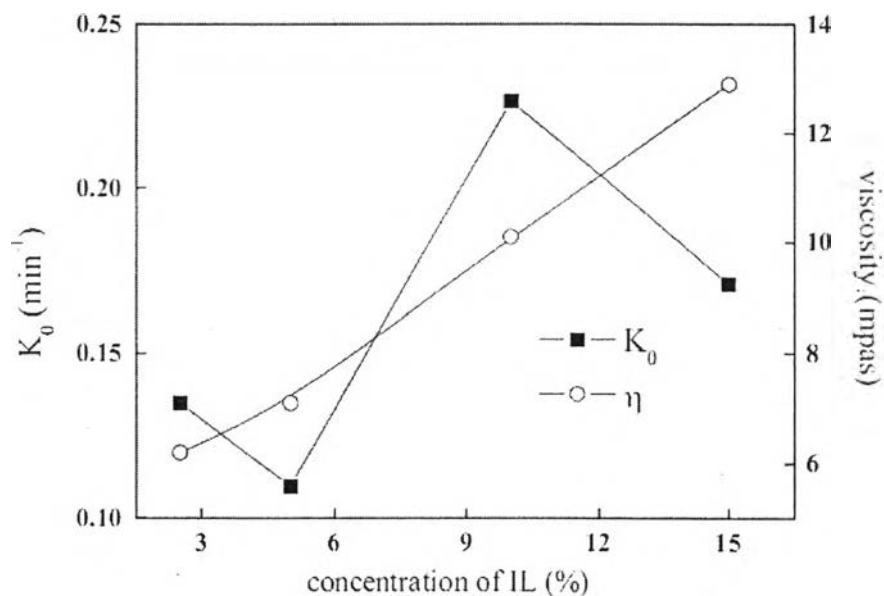


Figure 2.16 Apparent absorption rate (K_0) and viscosity (η) of mixed solutions of 40 wt% MDEA and $[\text{N}_{1111}][\text{Gly}]$.

In the last section of this literature showed that adding amount of MDEA into IL aqueous solution improved CO_2 load about 1-5 times more than IL aqueous solution. Whereas, adding amount of ILs into fixed MDEA concentration of 30 wt%

caused minor effect on CO₂ loading. From the result while, IL act as an accelerator of CO₂ absorption by forming zwitterions that transfer protons to MDEA. Therefore, IL has little influence on the absorption load.

Malyanah *et al.* (2012) studied solubility of CO₂ in aqueous solutions of ionic liquids (ILs) and monoethanolamine (MEA) at pressures from 100 to 1600 kPa. Result showed that, CO₂ absorption capacity decreases with increasing concentration of ILs. From the result of viscosity increased by decreasing amount of water in the mixture. In aqueous solution of IL, water content act as accelerator that driving absorption activity in CO₂ capture system. For aqueous solutions of ILs and MEA, increase in concentration up to 20 wt% in the solution increases in CO₂ loading. CO₂ loading at equilibrium is 0.9 mol CO₂/mol IL for 20 wt% of [bheaa] and 2.6 mol CO₂/mol for 20 wt% of [bmim][BF₄] under 1200 kPa and 298.15 K. This types of solvent is dominated by physical process rather than chemical process and rate of absorption of these two mixture higher than their pure solution. Physical solubility and chemical reaction can be reached by observing in proportional of solubility in varied pressure. If the solubility was increased linearly with pressure, this system might indicated in physical solubility. On one hand, If did not show direct proportion between the pressure and solubility, system might involve chemical reaction (which normally occurs when using MEA as solvent). In case of using [bheaa] as IL, increasing temperature from 298.15 to 313.15 K did not change in CO₂ loading. From the result showed that, increasing temperature can reach equilibrium earlier. In [bmim][BF₄] as IL, varied temperature at the same condition deceases the CO₂ loading due to increasing in vapour pressure with temperature.

Furthermore, they known that the solubility of CO₂ in the mixture of ILs and MEA aqueous solution also higher than the pure ILs or the conventional MEA solutions, particularly with imidazolium and hydroxyl type ILs. And compared their information with other work (as shown in Table 2.6). Result shows that, 20% [bmim][BF₄] + 20% MEA have highest CO₂ loading.

Table 2.6 Comparison with other literature data with aqueous mixtures of present ILs+MEA at pressure with highest CO₂ loading

Aqueous mixtures of ILs + alkanolamine	CO ₂ loading
20%[bheaa] + 5% MEA	0.570
20%[bheaa] + 10% MEA	0.739
20%[bheaa] + 15% MEA	1.006
20%[bheaa] + 20% MEA	1.043
20%[bmim][BF ₄] + 5% MEA	0.371
20%[bmim][BF ₄] + 10% MEA	0.634
20%[bmim][BF ₄] + 15% MEA	0.753
20%[bmim][BF ₄] + 20% MEA	1.143
15%[N ₁₁₁₁][Gly] + 15% MDEA	0.562
15%[N ₂₂₂₂][Gly] + 15% MDEA	0.643
15%[N ₁₁₁₁][Lys] + 15% MDEA	0.694
15%[N ₂₂₂₂][Lys] + 15% MDEA	0.740

Zhang *et al.* (2013) Studied rate base modeling of absorption and regeneration for CO₂ capture by aqueous ammonia solution. At first they studied effect of the flow rate and concentration of lean solvent, while increasing both parameters beneficially increased absorbed CO₂ by lean solvent but more NH₃ volatilizes into the flue gas. Besides, increasing lean solvent flow rate and concentration caused decreasing in CO₂ loading of rich solvent by NH₃ slipping pass through CO₂. Therefore, this system led to a higher regeneration energy. Ammonia aqueous based for CO₂ capture process has advantages over MEA-based such as no degradation and less corrosion. Furthermore, Stripper can operated at ambient pressure and regeneration section can operated in lower range of 85-95 °C. But this process still had some limitation such as NH₃ slip problem, crystallization of NH₄HCO₃ in condenser, great amount of supplementary energy for regeneration process, CO₂ compression, and cooling necessities. Main restriction of this system was in crystallization of NH₄HCO₃ during low temperature in condenser that affect up-scale in the industry. They observed that regeneration energy usage of this system is 3.63 MJ/kg CO₂ which is lower that reported from

Munmorah pilot plant (4-4.2 MJ/kg CO₂). The optimal operation conditions were shown in Table 2.7.

Table 2.7 Optimal condition using ammonia aqueous for CO₂ capture process

Operating condition	Value
Condenser temperature (°C)	50
Boil-up ratio	0.02
Packed height of stripper (m)	0.5
Packed diameter of stripper (m)	4.5
Re-boiler duty (kW)	63.2
Carbon dioxide flow rate (kg/hr)	62.67
Regeneration energy(MJ/kg CO ₂)	3.63

Zhang *et al.* (2013) also studied Process simulation of NH₃ abatement system for large-scale CO₂ capture using aqueous ammonia solution. NH₃ abatement system was used to minimize emission of NH₃ before going out to the atmosphere and also regenerate NH₃ back to CO₂ capture system. The result showed that, the flow rate of NH₃ slip is 1.687 kg/hr and concentration in the vent gas is 1.6 ppmv, which both can meet the NH₃ emission standards in major countries of the world. Moreover, the condenser heat duty can be totally used for CO₂ regeneration. The corresponding CO₂ regeneration energy will decrease from 3.63 MJ/kg CO₂ to 3.05 MJ/kg CO₂.

Niu *et al.* (2013) studied a novel process for capturing carbon dioxide using aqueous ammonia. First, equilibrium constants were regressed against experimental data from literatures. The regressed data were corrected to the properties data in simulation mode. Then simulated ammonia plant in Aspen plus program. The result showed that total heat duty of overall process is approximately 3000 kJ/kg CO₂ which is lower than MEA-based process about 700 kJ/kg CO₂ as shown in Table 2.8. Besides, the regeneration temperature is 85-95 °C at ambient pressure which can be supplied with low-grade thermal energy.

Table 2.8 Energy consumption comparison among different processes

Process	Reboiler heat duty kJ/kg, CO ₂	NH ₃ abatement heat duty, kJ/kg CO ₂
MEA (Darde <i>et al.</i>)	3700	-
MEA (Huang <i>et al.</i>)	3400 - 3600	-
Chilled ammonia (Darde <i>et al.</i>)	2000	-
Chilled ammonia (Mathias <i>et al.</i>)	2291	2377
Novel ammonia process (This paper)	1285	1703

Khonkaen *et al.* (2014) studied simulation of carbon dioxide capture using ionic liquid 1-ethyl-3-methylimidazolium acetate (EmimAc). EmimAc performed as a chemical absorbent in the solution with CO₂ which showed in high amount of CO₂ capacity. The result showed that, total energy requirement of EmimAc decreases 13.5% compared with MEA-based process.