การดูดซึมก๊าซคาร์บอนไดออกไซด์ด้วยสารละลายของไดเมทิลอะมิโนเอทานอลในน้ำ

นายธนภัทร ลือมั่นคง

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2556
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย
The abstract and full text of theses from the academic year 2011 in Chulalongkorn University Intellectual Repository (CUIR)
are the thesis authors' files submitted through the University Graduate School.

CARBON DIOXIDE ABSORPTION IN AQUEOUS SOLUTION OF DIMETHYLAMINOETHANOL

Mr. Thanaphat Luemunkong

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2013

Copyright of Chulalongkorn University

Thesis Title	CARBON DIOXIDE ABSORPTION IN AQUEOUS SOLUTION OF DIMETHYLAMINOETHANOL
By	Mr. Thanaphat Luemunkong
Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor Tawatchai Charinpanitkul, D.Eng.
Thesis Co-Advisor	Kreangkrai Maneeintr, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Engineering

(Professor Bundhit Eua-arporn, Ph.D.)

THESIS COMMITTEE

....Chairman

(Professor Suttichai Assabumrungrat, Ph.D.)

....Thesis Advisor

(Associate Professor Tawatchai Charinpanitkul, D.Eng.)

....Thesis Co-Advisor

(Kreangkrai Maneeintr, Ph.D.)

....Examiner

(Pimporn Ponpesh, Ph.D.)

....External Examiner

(Ruktai Prurapark, Ph.D.)

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

ธนภัทร ลือมั่นคง : การดูดซึมก๊าซคาร์บอนไดออกไซด์ด้วยสารละลายของไดเมทิลอะมิโนเอทานอลในน้ำ. (CARBON DIOXIDE ABSORPTION IN AQUEOUS SOLUTION OF DIMETHYLAMINOETHANOL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.ธวัชชัย ชรินพาณิชกุล, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: อ. ดร.เกรียงไกร มณีอินทร์, , หน้า.

การดูดซึมทางเคมีโดยใช้สารละลายเอมีนนับเป็นวิธีหนึ่งที่เหมาะสมสำหรับการจับเก็บก๊าซคาร์บอนไดออกไซด์ที่ถูกปล่อยออกจากโรงไฟฟ้า ในปัจจุบัน สารละลายโมโนเอทาโนลามีน (MEA) และสารละลายเมทิลไดเอทาโนลามีน (MDEA) เป็นสารละลายที่ใช้ในเชิงพานิชย์อย่างกว้างขวาง เนื่องจากประสิทธิภาพการดูดซึมก๊าซคาร์บอนไดออกไซด์ที่ดี อย่างไรก็ตาม สารละลายทั้งสองชนิดนี้ยังมีข้อจำกัด อาทิเช่น การใช้พลังงานในการดูดซึมและการนำสารละลายมาใช้ใหม่ที่สูง และการกัดกร่อนที่รุนแรง เป็นต้น ในงานวิจัยนี้จึงสนใจที่จะศึกษาการดูดซึมก๊าซคาร์บอนไดออกไซด์ด้วยสารละลายไดเมทิลอะมิโนเอทานอล (DMAE) ที่สภาวะต่างๆ และเปรียบเทียบผลการทดลองกับสารละลาย MEA และ MDEA โดยสภาวะการทดลองที่ศึกษา ได้แก่ ความเข้มข้นของสารละลาย ในช่วง 3 ถึง 5 โมลาร์ ความดันย่อยของก๊าซคาร์บอนไดออกไซด์ในช่วง 5 15 30 50 75 และ 100 กิโลพาสคาล และอุณหภูมิที่ใช้ดูดซึมในช่วง 30 40 60 และ 80 องศาเซลเซียส ผลการวิจัยแสดงให้เห็นว่า สารละลาย DMAE สามารถดูดซึมก๊าซคาร์บอนไดออกไซด์ได้ดีกว่าสารละลาย MEA และ MDEA นอกจากนี้ สารละลาย DMAE ยังให้ค่าความจุวัฏจักร (cyclic capacity) ที่สูงกว่า กล่าวคือ สูงกว่าสารละลาย MEA 241% และสูงกว่าสารละลาย MDEA 12% ดังนั้น จึงสรุปได้ว่า สารละลาย DMAE มีสมรรถนะในการดูดซึมก๊าซคาร์บอนไดออกไซด์ที่ดีกว่าสารละลาย MEA และ MDEA และจะช่วยลดการใช้พลังงานในการดูดซึมและการนำสารละลายกลับมาใช้ใหม่รวมทั้งลดค่าใช้จ่ายโดยรวมของระบบได้

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก	....
ปีการศึกษา	2556	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม	....

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

5570216621 : MAJOR CHEMICAL ENGINEERING
KEYWORDS: CARBON DIOXIDE CAPTURED / ABSORPTION / DIMETHYLAMINOETHANOL / CYCLIC CAPACITY / FLUE GAS

THANAPHAT LUEMUNKONG: CARBON DIOXIDE ABSORPTION IN AQUEOUS SOLUTION OF DIMETHYLAMINOETHANOL. ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng., CO-ADVISOR: KREANGKRAI MANEEINTR, Ph.D., pp.

Amine-based carbon capturing processes have widely been utilized in fossil-fired power plants which are regarded as a large stationary source of carbon dioxide emission. Monoethanolamine (MEA) and methyldiethanolamine (MDEA) aqueous solution are the alkanolamine used commercially because of their great absorption performance. However, there still are some major drawbacks, such as high energy consumption and low cyclic capacity for MEA and low absorption rate for MDEA. Consequently, exploration of novel solvent is of interest to compensate of such drawbacks. In this work, solubility of carbon dioxide in a novel promising solvent, Dimethylaminoethanol (DMAE) was examined under various experimental conditions in comparison with those of MEA and MDEA. The effect of solvents concentration was studied and varied in a range of 3, 4 and 5 molar. Influence of carbon dioxide content in simulated flue gas was examined by varying carbon dioxide partial pressure in a range of 5 - 100 kPa. Furthermore, effect of temperature was also investigated at 30, 40, 60 and 80 degrees Celsius. It was found that DMAE exhibited outstanding performance on carbon dioxide loading over both MEA and MDEA. Furthermore, DMAE could provide the greater average cyclic capacity than MEA for 241% and the greater average cyclic capacity than MDEA for 12%.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Department: Chemical Engineering Student's Signature ....
Field of Study: Chemical Engineering Advisor's Signature ....
Academic Year: 2013 Co-Advisor's Signature ....

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

ACKNOWLEDGEMENTS

I am very grateful to my thesis advisor, Assoc. Prof. Dr.Tawatchai Charinpanitkul, Department of Chemical Engineering, Chulalongkorn University, for his advice, encouragement and kindness.

I would also like to thank Kreangkrai Maneeintr, Ph.D., as the co-advisor, Professor Suttichai Assabumrungrat, Ph.D., as the chairman, Pimporn Ponpesh, Ph.D., as the internal examiner and Ruktai Prurapark, Ph.D., as the external examiner for their comments and participation in the committee.

Thanks to my friends in the Center of Excellence in Particle Technology (CEPT), Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University and all of my friends for friendship, encouragement and their assistance all the time.

Finally, I would like to extremely express my highest gratitude to my parents and my family for their unconditional support.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

CONTENTS

Page

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Page

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

LIST OF TABLE

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

LIST OF FIGURE

Page

Page

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

CHAPTER I

INTRODUCTION

1.1 Background and motivation

Since the industrial revolution, humans have known how to generate power from steam by burning fuels such as biomasses, coals and also petroleum products. This activity has led to an increase in concentration of anthropogenic Greenhouse Gases (GHGs) such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). According to the amount of emitted greenhouse gases, carbon dioxide accounted for about 76.7%, which takes a major part of all greenhouse gases emission [1]. Consequently, an increase of carbon dioxide concentration in the atmosphere is likely to enhancing the effect of climate change, which the one of the most concerned environmental issues nowadays.

Greenhouse gases, such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), are the gases that generally exist in the atmosphere and able to trap heat that radiate from the sun or emit from the earth surface. This mechanism is the natural greenhouse effect, which makes the suitable temperature of earth surface. However, an increasing concentration of anthropogenic greenhouse gases in atmosphere especially carbon dioxide, which takes the major part of global anthropogenic greenhouse gases emissions, results in the increasing the amount of heat absorbed in the atmosphere and releasing this amount of heat to the earth in the night. Global warming is the consequence of this phenomenon which enhances the greenhouse effect and makes the increasing of the earth average surface temperature, in the other words, this makes the global warmer. Therefore, to deal with this problem, CO_2 which discharged from various sources must be carefully controlled.

CHULALONGKORN UNIVERSITY

1.2 Uses and effects of carbon dioxide (CO_2)

Carbon dioxide (CO_2) is normally produced from the combustion of coal or hydrocarbons, the fermentation and the breathing of humans and animals. CO_2, as the chemical, is used in several ways such as an ingredient in the production of urea and methanol, the carbonation in beverages such as soft drinks, mineral water or beer in the food and beverage industry and the enhancing oil recovery process which recover more oil and petroleum from petroleum reservoirs. Inversely, the major drawback of CO_2 is the main greenhouse gas that impacts to environment by causing climate change and global warming [1, 2].

1.3 CO_2 emission sources

There are several sources of CO_2 emission. Among them, power generation sector, which generates the electricity by burning the fossil fuels such as coal and natural gas to produce steam, is one of the major anthropogenic sources of CO_2 emission. According to the figure 1.1 and 1.2, power generation sectors emit CO_2 to the atmosphere, for 41.7% of all emitting sources in Thailand [3] and for 25.9% of all global emitting sources [1] in form of flue gas—the gas exhaust from the combustion process. Although fossil fuel-power plants produce a large number of CO_2 that will impact to our environment, they still play an important role in effectively serve the energy supply since its great efficiency and flexibility to operate at variety demands [4]. Therefore, in order to achieve the equivalent point of the effective way of energy supply and the friendly way to conserving the environment, the CO_2 capture is required to apply to power generation.

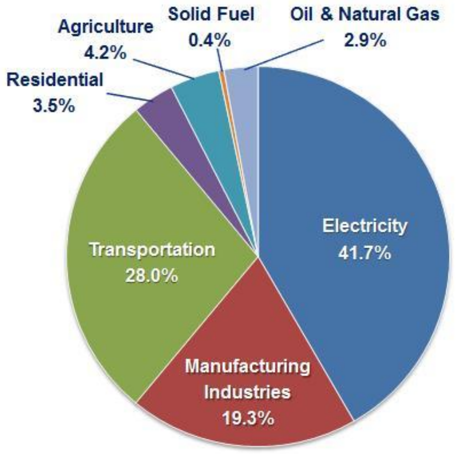


Figure 1.1 Greenhouse gases emissions from the energy sector in CO_2 equivalent [3]

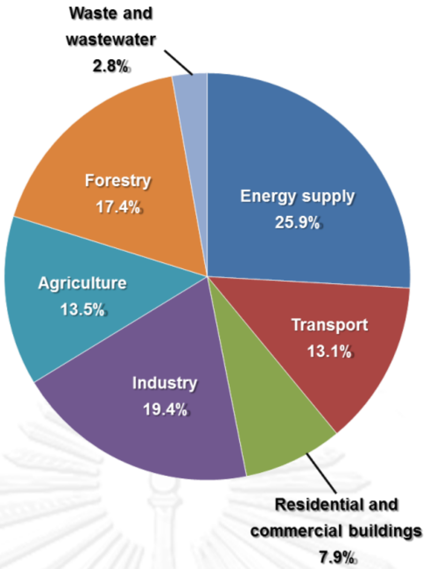


Figure 1.2 Share of different sectors in total anthropogenic GHG emissions in 2004 in terms of CO_2 equivalent [1]

1.4 Flue gas characteristics from fossil-fired power plants

Flue gas, as mentioned earlier, is referred to the gas exhaust from the combustion process. Characteristics of flue gas from coal fired and natural gas fired power plant are provided in table 1.1.

Table 1.1 Flue gas characteristics from coal fired and natural gas power plant [5]

Characteristic	Power plant type	
	Natural gas	Coal fired
CO_2 concentration (%v/v)	5-10	12-18
Flue gas pressure (MPa)	0.1	0.1

Power generation is the source that emits the enormous amount of CO_2 to environment via flue gas; therefore, applying the CO_2 capture system is strongly necessary for reduces the environmental issues. The purpose of CO_2 capture is to produce a concentrated stream of CO_2 at high pressure that can readily be transported to a storage site (CO_2 storage). Based on the process or power plant application, there are three main approaches for capturing the CO_2 generated from a primary fossil fuel (coal, natural gas or oil), biomass, or mixtures of these fuels: post-combustion capture, pre-combustion capture and oxyfuel process [2, 4, 5].

1) *Post-combustion systems* separate CO_2 from the flue gases produced by the combustion of the primary fuel in air. These systems normally use a liquid solvent to capture the small fraction of CO_2 (typically 3–15% by volume) present in a flue gas stream in which the main constituent is nitrogen (from air). For a modern pulverized coal (PC) power plant or a natural gas combined cycle (NGCC) power plant, current post-combustion capture systems would typically employ an organic solvent such as monoethanolamine (MEA).

2) *Pre-combustion systems* process the primary fuel in a reactor with steam and air or oxygen to produce a mixture consisting mainly of carbon monoxide (CO) and hydrogen (H_2) that well known in synthesis gas. Additional hydrogen, together with CO_2, is produced via the reaction of carbon monoxide with steam in a second reactor or a shift reactor. The resulting mixture of hydrogen and CO_2 can then be separated into a CO_2 gas stream, and a stream of hydrogen. If the CO_2 is stored, the hydrogen is a carbon-free energy carrier that can be combusted to generate power and/or heat. Although the initial fuel conversion steps are more elaborate and costly than in post-combustion systems, the high concentrations of CO_2 produced by the shift reactor (typically 15 to 60% by volume on a dry basis) and the high pressures often encountered in these applications are more favorable for CO_2 separation. Pre-combustion would be used at power plants that employ integrated gasification combined cycle (IGCC) technology.

3) *Oxyfuel combustion systems* use oxygen instead of air for combustion of the primary fuel to produce a flue gas that is mainly water vapor and CO_2. This results in a flue gas with high CO_2 concentrations (greater than 80% by volume). The water vapor is then removed by cooling and compressing the gas stream. Oxyfuel combustion requires the upstream separation of oxygen from air, with a purity of 95–99% oxygen assumed in most current designs. Further treatment of the flue gas may be needed to remove air pollutants and non-condensed gases (such as nitrogen) from the flue gas before the CO_2 is sent to storage. As a method of CO_2 capture in boilers, oxyfuel combustion systems are in the demonstration phase [5]. Oxyfuel systems are also being studied in gas turbine systems, but conceptual designs for such applications are still in the research phase [5].

Post-combustion capture is advantageous over the other two approaches in that it as a flexible operation and can directly merge with the existing fossil fuel-power plants without any changes in the upstream systems [2, 4, 5].

1.5 Flue gas control technologies

Selecting the optimum technologies to implement the capturing of CO_2 is based on the characteristics of the flue gas emitted from fossil fuel-power plants such as pressure of flue gas, partial pressure of CO_2 in the flue gas stream and the purity of desire CO_2 product and also based on the economic considerations, for example, capital and operating costs of the process and cost of additives necessary to overcome fouling and corrosion [2, 6]. The technologies which can be applied to the post-combustion capture are absorption, adsorption, cryogenic and membranes.

1.5.1 Chemical and physical absorption

The basic concept of absorption is the transfer of a soluble gas phase to a liquid phase. Consider the gas treating system, chemical and physical absorption processes are commonly used in the petroleum, natural gas treatment and chemical industries. Absorption process also plays an important role in CO_2 separation since its high absorption performance.

In chemical absorption system, the absorbents or solvents react to the dissolved gases and capture them. In the other words, the reaction between solvents and dissolved gases increase the absorption rate resulting in chemical absorption is the process that more suitable for operate at low target gas partial pressure in the gas stream like the CO_2 in the flue gas from fossil fired-power plant. In order to regenerate the solvents, heat is applied to these solvents and the captured gases will be released then the regenerated solvents can be brought to an absorption column to re-absorb CO_2 again.

In contrast, unlike chemical solvents, absorption in physical solvents depends only upon the solubility of target gases in physical solvents. This refers that physical absorption systems will be used when the high target gas partial pressure is introduced since the weaker bond between absorbed gases and solvent comparing with chemical absorption system. Solvents regeneration is achieved by applying heat reduce the pressure or both.

1.5.2 Adsorption process

Adsorption process refers to the selective concentration of one or more components of a gas at the surface of a microporous solid. The mixture of adsorbed components is called the adsorbate, and the microporous solid is the adsorbent. Selective gas adsorption depends on temperature, partial pressures, surface forces and adsorbent pore size. The attractive forces holding the adsorbate on the adsorbent are weaker than those of chemical bonds, and the adsorbate can generally be released (desorbed) in a manner analogous to the stripping of an absorbed component from solution by raising the temperature in temperature swing adsorption (TSA) or reducing the partial pressure of the component in the gas phase in the pressure swing adsorption (PSA) or passing a low-voltage electric current through the adsorbent in electric swing adsorption (ESA). When an adsorbed component reacts chemically with the solid, the operation is called chemisorption and desorption is generally not possible.

Adsorption process, however, may not be attractive for large-scale CO_2 removal of flue gas from power plant because of low capacity and selective to adsorb CO_2 but combination with another technology may be the better choice.

1.5.3 Cryogenics

Cryogenic separation is widely used in commercial for purification of high concentration of CO_2 (generally more than 50%) from the gas stream. It is not appropriately used for gases consist of dilute CO_2 concentration especially flue gas from power plant since the amount of energy required for refrigeration is uneconomic for the plant. The advantage of this system is the direct production of liquid CO_2 which facilitate to economic transport such as via ship or pipeline. The most promising applications for cryogenics are expected to be for separation of CO_2 in pre-combustion or oxyfuel process which the input gas contains a high concentration of CO_2.

1.5.4 Membrane

A membrane is a barrier film that allows selective and specific permeation under suitable condition. Membrane is now a relatively new technology in the field of gas purification. In this process, polymeric membranes separate gases by selective permeation of one or more gaseous components from one side of a membrane barrier to the other side. The components dissolve in the polymer at one surface and are transported across the membrane as the result of a concentration gradient. The concentration gradient is maintained by a high partial pressure of the key components in the gas on one side of the membrane barrier and a low partial pressure on the other side. Although membrane permeation is still a minor factor in the field of gas purification, it is rapidly finding new applications.

In summary, considering the characteristics of each CO_2 capture technologies, chemical absorption process is found to be the most suitable technology to remove CO_2 due to the low partial pressure of CO_2 in the flue gas stream (about 10-15 %v/v of CO_2), physical absorption processes become less competitive to chemical absorption processes because the capture capacity strongly depends on partial pressure while the absorbent used in chemical absorption processes is favored to capture CO_2 at lower partial pressure [2, 6]. Flue gas from fossil fuel-power plants does not only have low CO_2 partial pressure but also has numerous amount of emitted gas. These make the other technologies (adsorption, cryogenic and membranes) are less attractive because they prefer the higher partial pressure of CO_2 in the gas stream [2, 4, 6].

In terms of chemical absorption system, an alkanolamine species such as monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) are the organic amine based chemical absorbent (solvent) that have proved to be of commercial interest for CO_2 capture since its good performance [6]. However, they still have some major drawbacks, for example, corrosion in the presence of O_2 and other impurities, high degradation rates from reaction with SO_2 and NO_2 and the large amount of energy required to absorbent regeneration [2, 6].

In this study, the development of new novel promising chemical solvent, Dimethylaminoethanol (DMAE), which can eliminate the drawbacks of the old commercial solvents and enhance the efficiency of CO_2 capture, is desired. The solubility of CO_2 in this DMAE solvent and the optimum conditions to capture CO_2 will be investigated and discussed.

1.6 Research objective

The major objective of this work is to investigate the solubility of CO_2 in a novel promising solvent, DMAE, under various experimental conditions in comparison with commercial solvents which are MEA and MDEA.

1.7 Research scope

The scope of this research includes the following topics.

1.7.1 Absorption of CO_2 in the new solvent is conducted at various following conditions.

- Solvent concentration is varied at 3, 4 and 5 molar.
- Partial pressure of CO_2 is varied at 5, 15, 30, 50, 75 and 100 kPa.
- Temperature is varied at 30, 40, 60 and 80°C.
- Types of solution used are MEA, MDEA and DMAE.

1.7.2 The solubility of CO_2 in the new solvent is examined by titration of the solvent with the 1.0 M standard aqueous HCl solution.

1.8 Research contributions

This research is able to evaluate the CO_2 capture performance of the new solvent via the measuring solubility parameter of CO_2 in this DMAE solvent comparing to the commercial solvents and also investigate the effect of various conditions. Additionally, if this new solvent gives the excellent ability in CO_2 capture, it will hope to be improved to uses as a commercial solvent.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

CHAPTER II

THEORY AND LITERATURE REVIEWS

In the previous chapter, background of CO_2 emission scenario and control technologies was discussed. Then, this chapter will present in the related theories of absorption process, which is the chosen technology for coping with CO_2 emitted from the large source like fossil-based power plant, and basic concept of absorption and absorbent types. Furthermore, data of new absorbent studies gathered from various research works are also enclosed and summarized in the literature review section.

2.1 Absorption process

2.1.1 Basic concept of absorption process

Absorption is utilized to separate the impurities, contaminants, pollutants, or catalyst poisons from a gas stream and also recover valuable chemicals. Thus, the species which are desired may be all components, some of the components or only the component that will be transferred into liquid phase. Oppositely, when liquid mixture is contacted with a gas to selectively remove components by mass transfer from the liquid to the gas phase, this called stripping or desorption. Strippers are frequently coupled with absorbers to permit regeneration and recycle of the absorbent.

Generally, absorption involves mass transfer of the component(s) between two phases: gas and liquid. The component in gas to be absorbed, which is given as A, diffuses from the bulk gas into a thin stagnant gas film then through a thin film of liquid B. Thus, a process of absorption of A into liquid B takes place, without vaporization of B, and there is no resistance to mass transfer of A in the gas phase, because it is pure A. At the interface, phase equilibrium is assumed, so the concentration of A at the interface, cAi, is related to the partial pressure of A at the interface, p_A, by a solubility relation like Henry's law, $c_{Ai} = H_A p_A$. In the liquid film of thickness, δ, molecular diffusion occurs with a driving force of $c_{Ai} - c_{Ab}$, where c_{Ab} is the bulk-average concentration of A in the liquid. Since the film is assumed to be very thin, all of the diffusing A is assumed to pass through the film and into the bulk liquid. Figure 2.1 is an illustration of this mechanism.

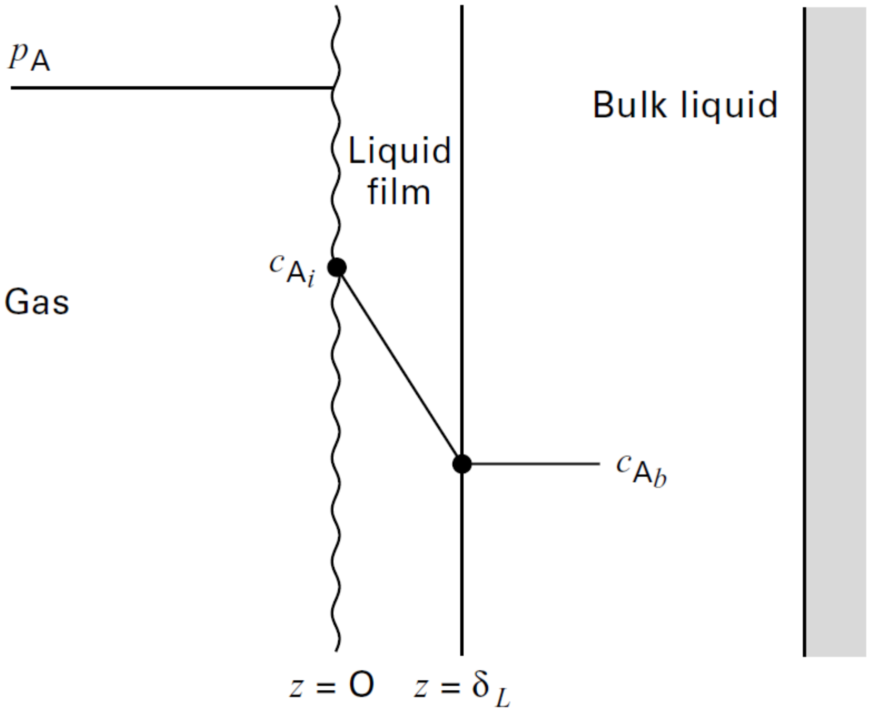


Figure 2.1 Film theory for mass transfer from a fluid–fluid interface into a liquid phase [7]

2.1.2 Types of absorption

As mentioned in Chapter I, absorption process is the most reasonable method to deal with CO_2 in flue gas from fossil-based power plant. Types of absorption process, based on the nature of the interaction between acid gas and solvent, are chemical absorption and physical absorption. The most important key of absorption performance is the solvent, which can be categorized in the same fashion of the absorption types: chemical solvent and physical solvent. Therefore, to obtain the best absorption performance, using the most effective solvent must be applied. The desired characteristics of that solvent are: high solubility of acid gas, high water solubility, high reaction rate, high thermal and chemical stability, low structure material corrosion rate, low cost and low environmental impact [6]. In this section, the two types of CO_2 absorption process and their solvents will be further discussed.

Chulalongkorn University

Chemical absorption: this type of absorption, the absorbate component in the gaseous phase dissolves and reacts chemically with the absorbent species in the liquid phase is the idea of the chemical absorption. After the absorption reaction, the characteristic of the chemical product depends upon the absorbent used. The kind of the absorbent that can release the absorbate is accounted to be the reversible absorbent while the other is accounted to be the irreversible absorbent. Practically, the reversible absorbent is preferable to the other one since it can be regenerated and brought back to use again.

Physical absorption: the component being absorbed by physical absorption is more soluble in the liquid absorbent than other components of the gas stream. However, it does not react chemically with the absorbent. The equilibrium concentration of the absorbate in the liquid phase is strongly dependent on the partial pressure in the gas phase. In the other words, the suitable condition for absorption using the physical solvent is the process that consists of high partial pressure of acid gas component in the flue gas stream. Therefore, when the large fraction of acid gas in the gas stream is presented, to capture it, chemical absorption may be applied, however, to regenerate the solvent, chemical solvent requires more heat to purify itself. This leads to higher energy consumption comparing with physical absorption, which only applies the pressure-driven to absorb or desorb the acid gas [6].

2.1.3 Process description of absorption

Figure 2.2 indicates a flow diagram of an acid-gas absorption process system. Flue gas containing CO_2 is fed at the bottom of the absorber column then flows upward and counter-currently contacts with the lean absorber solution which flows downward from the top of absorber. CO_2 in the flue gas is removed by dissolves and reacts with absorber solution then the solution becomes rich solution. The gases that are not dissolve or react with the absorber exit at the top of the absorber and become treated gas. The rich solution leaves at the bottom of absorber and passes through the heat exchanger. In this unit, the rich solution obtain the heat from regenerated lean solvent, which become itself warmer, then enters at the top of the regeneration column.

CO_2 which is absorbed in the rich solvent is stripped by steam and then the vapor mixture is fed to a condenser which is located at the top of the regenerator to collect the condensed water and solvent back to the regenerator. The regenerated solution becomes the lean solvent and leaves out the regenerator. The lean solvent then cooled itself when passes through the heat exchanger and fed to the top of absorber to capture CO_2 again.

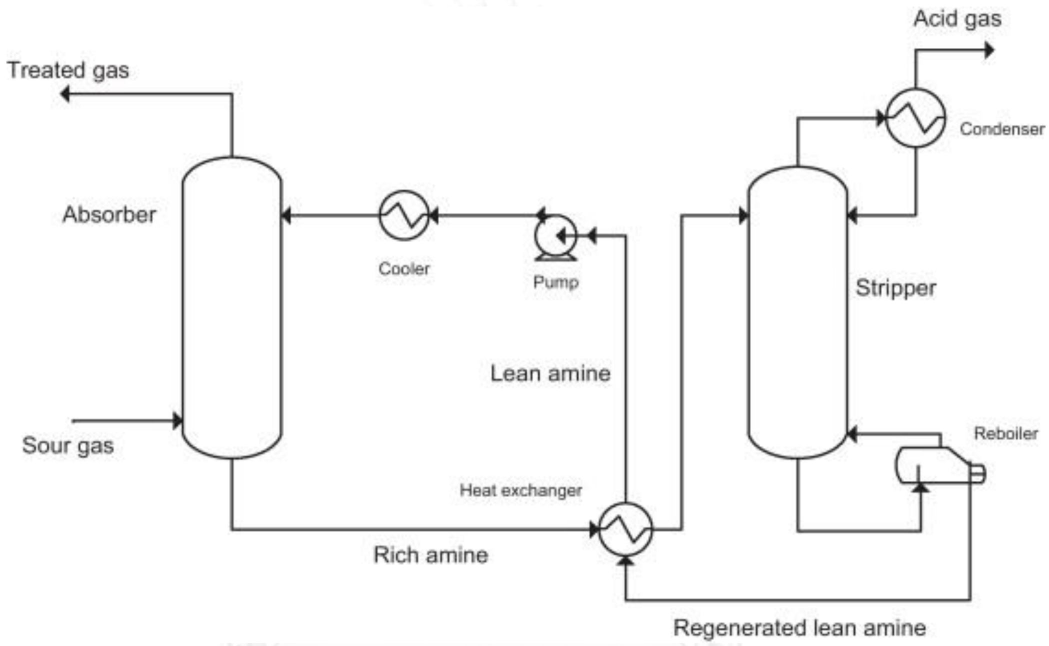


Figure 2.2 Process flow diagram of a conventional acid-gas capture process

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

2.2 Solvents used in absorption process

2.2.1 Solvents for chemical absorption

Amine solutions have been used in chemical absorption process for a long decade to capture CO_2 from various industrial sections such as power generation, natural gas treatment or chemical industry. Generally, one molecule of amine comprise of one hydroxyl group and one amino group. Each functional group affects the properties of amine that the hydroxyl group reduces the itself vapor pressure and provides more solubility in water, for the amino group, it mainly functions to absorb the dissolved CO_2 in the solution [6]. Furthermore, amines can be categorized by their molecular structure. Firstly, primary amines are the amines that two hydrogen atoms attach to a nitrogen atom directly. Monoethanolamine (MEA) and 2-(2-aminoethoxy) ethanol (DGA) are classified in this category. Next, secondary amines such as diethanolamine (DEA) and diisopropanolamine (DIPA) have only a hydrogen atom attaches to the nitrogen atom. Finally, triethanolamine (TEA) and methyldiethanolamine (MDEA) are examples of amines called tertiary amines which no hydrogen atom attaches to the nitrogen atom.

As chemical solvent, in order to capture CO_2 in gas stream, a set of principal reactions between amine solution and CO_2 involving in this mechanism can be following represented in terms of a primary amine, such as monoethanolamine (MEA) [6].

Ionization of water

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (1)$$

Hydrolysis and ionization of dissolved CO_2

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^- \qquad (2)$$

Dissociation of bicarbonate ion

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad (3)$$

Protonation of alkanolamine

$$RNH_2 + H^+ \rightleftharpoons RNH_3^+ \qquad (4)$$

Carbamate formation

$$RNH_2 + CO_2 \rightleftharpoons RNHCOO^- + H^+ \qquad (5)$$

Reactions (1) through (5) not only relate specifically to primary amines like MEA, but can also be applied to secondary amines like DEA by suitably modifying the amine formula. This makes the CO_2 capture capacity limited to approximately 0.5 mole of CO_2 per mole of amine because the carbamate ion has high stability but low rate of hydrolysis itself to bicarbonate. On the other hand, because there is no hydrogen atom attached with nitrogen atom of amine group, tertiary amine solutions can undergo only reactions (1) through (4), but cannot react directly with CO_2 to form carbamates by reaction (5). Consequently, the solubility of CO_2 can theoretically reach to one mole of CO_2 per mole of amine. However, the reaction between tertiary amine and CO_2 can only undergo via reaction (3) which results in slower CO_2 capture in this solvent.

CHULALONGKORN UNIVERSITY

Generally, the equilibrium concentrations of CO_2 in solution is proportional to their partial pressures in the gas phase, therefore, reactions (2), (3), and (5) are driven to the right by increased acid gas partial pressure. The reaction equilibria are also sensitive to temperature, causing the vapor pressures of absorbed acid gases to increase rapidly as the temperature is increased. As a result it is possible to strip absorbed gases from amine solutions by the application of heat.

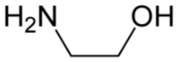
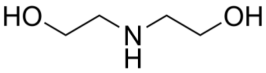
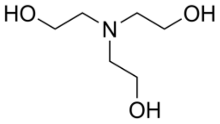
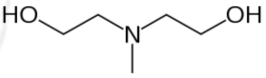
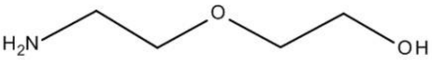
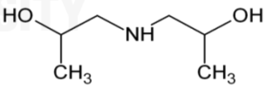
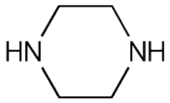
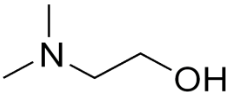
Some examples uses of alkanolamines such as MEA and MDEA which are utilized as the commercial chemical solvent are briefly presented as follows [6].

Monoethanolamine (MEA): MEA aqueous solution has widely been used almost exclusively for many years for the removal of acid gases like H_2S and CO_2 from natural and synthesis gases. Moreover, it is still the chosen solvent for gas stream which containing low H_2S and CO_2 concentrations and has no minor contaminants such as COS and CS_2. In addition, MEA-based absorption also preferred when the pressure of the gas to be treated is low and maximum removal of the acid gases is required. The outstanding advantages of MEA include low molecular weight resulting in high solution capacity at moderate concentrations, high alkalinity and fast kinetics. However, the drawbacks of using MEA still remain. For instance, when the gas stream contains COS and CS_2, the formation of irreversible reaction products with these compounds will takes place and resulting in excessive chemical losses. Furthermore, MEA solution is more corrosive than other amines especially the amine concentrations exceed 20% and the solutions are highly loaded with acid gas. Another one of the major problems of MEA system is high heat of reaction with H_2S and CO_2 which leads to higher energy requirements for regeneration of the solution.

Methyldiethanolamine (MDEA): MDEA solution has become utilized particularly in the purification of non-hydrocarbon gases such as the products from coal gasification processes. This tertiary amine also applied in the process in which selective absorption of hydrogen sulfide in the presence of carbon dioxide, especially in cases where the ratio of carbon dioxide to hydrogen sulfide is very high. Because of its low vapor pressure, MDEA can be used in concentrations up to 60 wt% in aqueous solutions without appreciable evaporation losses. Furthermore, MDEA is highly resistant to thermal and chemical degradation, is essentially noncorrosive, has low specific heat and heats of reaction with H_2S and CO_2, finally, is able to miscible with hydrocarbons.

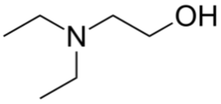
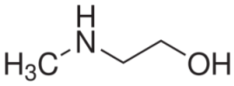
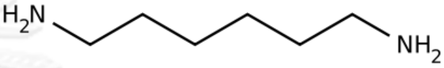
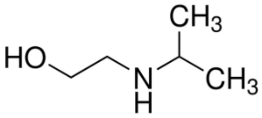
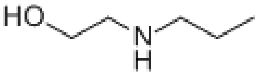
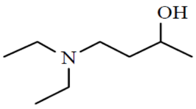
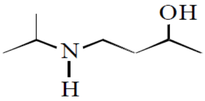
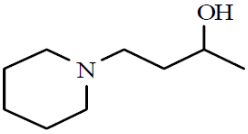
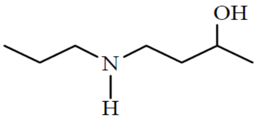
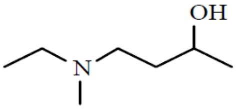
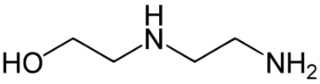
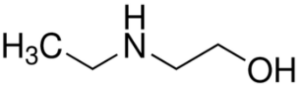
Since their highly reactive capture of CO_2 and ability in regeneration of amine process are widely used of these amines especially of MEA. The problems, however, such as corrosion and energy required penalty are still the main classical issues of amine-based absorption plants which need to be solved [2, 6]. Consequently, there are various proposed methods to mitigate or fix those problems. One of the answers is inventing the new amines to replace the conventional used amine. This topic will be further discussed in the literature review section. The chemical solvents including new solvents which mentioned in this work are summarized in table 2.1

Table 2.1 Summary of amine solvents name and their molecular structure

Absorbents name	Molecular weight	Amine type	Molecular structure
Monoethanolamine (MEA)	61.08	Primary	
Diethanolamine (DEA)	105.14	Secondary	
Triethanolamine (TEA)	149.19	Tertiary	
Methyldiethanolamine (MDEA)	119.17	Tertiary	
2-(2-aminoethoxy) ethanol (DGA)	105.14	Primary	
Diisopropanolamine (DIPA)	133.19	Secondary	
Piperazine (PZ)	86.13	Sterically hindered amine	
2-Dimethylamino-ethanol (DMAE)	89.14	Tertiary	

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Table 2.1 Summary of amine solvents name and their molecular structure (con't)

Absorbents name	Molecular weight	Amine type	Molecular structure
2-Diethylamino-ethanol (DEAE)	117.19	Tertiary	
2-Methylamino-ethanol or *N*-Methylethanolamine	75.11	Secondary	
1,6-Hexanediamine	116.20	Diamine	
2-(isopropylamino) ethanol (IPAE)	103.16	Secondary	
2-(propyl amino) ethanol (PAE)	103.16	Secondary	
4-diethylamino-2-butanol	145.24	Tertiary	
4-isopropylamino-2-butanol	117.00	Secondary	
4-piperidino-2-butanol	152.24	Tertiary	
4-propylamino-2-butanol	131.25	Secondary	
4-(ethyl-methyl-amino)-2-butanol	131.25	Tertiary	
2-(2-amino-ethylamino) ethanol (AEEA)	104.15	Secondary	
2-(ethylamino) ethanol (EMEA)	89.14	Secondary	

In addition to using alkanolamine solutions as chemical solvent, alkaline processes are also utilized to remove CO_2 in the gas stream. Solutions such as carbonates and hydroxide of potassium and sodium and aqueous ammonia are used especially potassium carbonate (K_2CO_3). However, due to the low rate of reaction between CO_2 and alkaline solution at room temperature, increasing temperature and using promoters are applied to increase the rate of acid gas absorption and mass transfer [6]. The good example is Benfield process or Hot Potassium Carbonate process that uses hot solution of potassium carbonate as CO_2 removal absorbent. The process operates at high temperature range for 70 to 120°C and high pressure about 3,000 kPa. Diethanolamine (DEA) is a promoter commonly used in this process [6].. Furthermore, other various promoter types of hot potassium process are also proposed such as MEA [8], boric acid [9] and activated carbon particles [10].

2.2.2 Solvents for physical absorption

There are several types of physical solvent that utilized to remove acid gas. Water was the one that proposed to be a physical absorbent but it does not become a practically use since the low solubility of acid gas such as CO_2 or H_2S. The various solvents, which are the organic chemicals, are later proposed such as methanol that used in Rectisol process, propylene carbonate (PC) used in Fluor Solvent process and dimethyl ether of polyethylene glycol (DMPEG) used in SELEXOL process. Some physical solvent processes can be seen in table 2.3. Like chemical absorbents, physical absorbents, however, have some restrictions, for example, the solvent must have a large number of acid gas solubility greater than water, low viscosity, low or none metals corrosion rate and nonreactive with all components in the gas stream. Finally, their cost must be acceptable [6].

CHULALONGKORN UNIVERSITY

Table 2.2 Solvents for physical absorption [6]

Process name	Solvent	Process licensor
Simple physical solvents		
Fluor Solvent	Propylene carbonate (PC)	Fluor Daniel
SELEXOL	Dimethyl ether of polyethylene glycol (DMPEG)	Union Carbide
Sepasolv MPE	Methyl isopropyl ether of polyethylene glycol (MPE)	Badische (BASF)
Purisol	N-Methyl-2-pyrrolidone (NWP)	Lurgi
Rectisol	Methanol	Lurgi and Linde AG
Ifpexol	Methanol	Institut Franqais du Pitrole (IFP)
Estasolvan	Tributyl phosphate	IFP/Uhde
Methylcyanoacetate	Methylcyanoacetate	Unocal
Mixed physical/chemical solvents		
Sulfinol	Sulfolane and DIPA or MDEA	Shell Oil/SIPM
Amisol	Methanol and secondary alkylamine	Lurgi
Selefining	Undisclosed physical solvent and tertiary amine	Snamprogetti

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

2.2.3 Mixed chemical-physical solvents

The key point of mixing chemical and physical solvents together is to obtain the advantages from using both solutions. This is particularly true for the system that the characteristics of gas stream are unconventional or extra degree of acid gases removal is needed. The major examples of the mixed chemical-physical solvents process such as Sulfinol process, Amisol process and Selefining process will be next presented [6].

Sulfinol processs: In Sulfinol process (licensed by the Shell Oil Company and SIPM), the chemical solvents used are usually alkanolamine such as diisopropanolamine (DIPA) or methyldiethanolamine (MDEA), and water. The role of chemical solvent is to purify the process gas to achieve desired levels. Meanwhile, the physical solvent, which mainly consists of sulfolane (tetrahydrothiophene dioxide), remove the bulk of the acid gas from the gas stream. The Sulfinol solvent enhances the solution capacity, especially when the gas stream to be treated is at high pressure and the acidic components are present in high concentrations. The Sulfinol process also has demonstrated its ability to achieve high efficiency removal of other impurities like COS, mercaptans, and other organic sulfur compounds. In terms of acid gases removal, The Sulfinol process can meet the requirement for deep CO_2 removal to 50 ppm for LNG plants, as well as the opposite extreme of bulk CO_2 removal using flash regeneration. The applications of the process has found in many fields such as treatment of natural, refinery, and synthesis gases.

Amisol process: The process was developed by Lurgi GmbH. In this process, methanol is used as physical solvent while MEA and DEA were first used as chemical solvent. However, alphatic alkylamines consist of diisopropylamine (DIPAM) and diethylamine (DETA) have later been used because they have greater chemical stability, higher acid gas loading, high H_2S selectivity, easier regeneration (including a lower reboiler temperature), soluble in water and higher volatility. The Amisol process can be used for either selective desulfurization or complete removal of CO_2, H_2S, COS, and other organic sulfur compounds, especially for sulfur and CO_2 which can be removed to less than 0.1 ppm and less than 5 ppm respectively.

Selefining process: This process was developed by Snamprogetti SpA of Milan, Italy, for selectively removing H_2S from natural and synthesis gases also containing CO_2. The Selefining solvent consists of an undisclosed physical solvent and a tertiary amine. The combination of the Selefining solution promotes selective H_2S removal by mixing the tertiary amine with a physical solvent instead of with water results in the hydration of CO_2 in the solution is still retarded because H_2S can react directly with tertiary amines without the requirement for water. This makes the process able to control the CO_2 removal by adjusting the water content of the solution.

2.3 Literature review

The chemical solvents that have been commercially used to remove CO_2 for very long decades are categorized in the organic amine group [2]. These organic amines can generally be classified themselves by the structure into primary, secondary and tertiary amines. Especially monoethanolamine (MEA), which is the primary amine, provides an effective removal of CO_2 in the power plants and natural gas treatment since its highly reactive to CO_2 and its available technology [6]. Consequently, as the widely used of MEA, there were a number of published VLE data of aqueous MEA solution and CO_2 which are illustrated in the table 2.3. Furthermore, table 2.3 also show solubility data of CO_2 in other amine solvents.

According to the table 2.3, back to over 20 years, researchers including with Jones et al. [11], Lee et al. [12], Jou et al. [13-15], Isaac et al. [16], Yeh et al. [17], Bishnoi et al. [18] and Kadiwala et al. [19] mainly focused on the study of solubility of CO_2 at a varieties of temperature, CO_2 partial pressure, solvent type and solvent concentration in only the lab scale. While the recent researchers, for example, Schäffer et al. [20] and Sonderby et al. [21] studied the solubility of CO_2 in the MEA solution by the same fashion but scaled them up to the pilot scale.

Although a lot of MEA is being used in the existing CO_2 removal plants and a lot of published data of MEA nowadays, the problems of using MEA and other amines as previously mentioned in the introduction section are still exist [2]. Consequently, there are some researchers who invented the several methods to solve such the problems. For instance, Choi et al. [22] presented aqueous blended solutions of MEA and 2-amino-2-methyl-1-propanol (AMP) to enhance absorption characteristics. Taib and Murugesan [23] proposed new hybrid solvents comprised of bis(2-hydroxyethyl) ammonium acetate (bheea) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) mixed with water/aqueous solutions of MEA for improve the absorption of CO_2. Shim et al. [24] suggested KoSol-2, the new sterically hindered amine for the CO_2 removal improvement. Jung et al. [25] introduced an advanced configuration of MEA process which improved the heat exchanger system to reduce the reboiler heat requirement for solvent regeneration.

Table 2.3 Solubility data for CO_2 in various aqueous amine solutions

Researcher	Solvent	Temperature (°C)	CO_2 partial Pressure	Solvent Concentration
Jones et.al. [11]	MEA	40-140	1-7000 (mmHg)	15.3 (wt%)
Lee et.al. [12]	MEA	40,100	0.1-1000 (psia)	2.5, 5.0 (normality)
Jou et.al. [14]	MEA	0, 25, 40, 60, 80, 100, 120 and 150	200-20000 (kPa)	30 (wt%)
Schäffer et.al. [20]	MEA	30-95	15.2 (kPa)	20-70 (wt%)
Sonderby et.al. [21]	MEA	ambient	10.1 (kPa)	30 (wt%)
Yeh et al. [17]	MEA	10-40	8-16 (kPa)	7-35 (wt%)
Isaac et.al. [16]	DIPA	40,100	2-5991 (kPa)	2.5 (kmol/m^3)
Jou et.al. [13]	MDEA	40-120	0.001-6600 (kPa)	1.0, 2.0, 4.28 (kmol/m^3)
Jou et.al. [15]	TEA	50, 75, 100	100-5490 (kPa)	2.0, 3.5, 5.0 (mol/dm^3)
Yeh et al. [17]	NH_3	10-40	8-16 (kPa)	7-35 (wt%)
Bishnoi et al. [18]	PZ	25-60	30-40000 (kPa)	0.2, 0.6 (mol/dm^3)
Kadiwala et al. [19]	PZ	40, 70	200-6500 (kPa)	0.3, 1.2 (mol/dm^3)

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

However, absorbents still play a main role for the CO_2 removal performance of absorption process. In order to improve this performance, the problems of using commercial absorbents could be solved. Therefore, in this work, it is a good opportunity to investigate the properties of the new solvent such as CO_2 solubility which expected to provide the solution that could solve the absorbent issues.

Besides using and studying of commercial amines such as MEA as absorbent, other new amines have also been studied. Table 2.4 illustrates the CO_2 capture data of new various types of amine.

DMAE, which regarded as a new promising solvent for CO_2 removing in this work, was previously examined for its CO_2 solubility by the number of researchers but lack of a comprehensive operating condition range [26-28]. Their interesting results are shown as follows. Chowdhury et al. [26] investigated CO_2 capture properties such as absorption rates, CO_2 loadings, cyclic capacities, and heats of reaction for the absorbents with 24 tertiary amine absorbents compared with the conventional absorbent, MDEA. Each amine was used at 30wt% concentrations and was scrubbed with 20% CO_2 and 80% N_2 gas mixture a flow rate of 700 mL/min. The scrubbing process was conducted in water bath at 40 °C and 60 minutes duration time. Then CO_2 was regenerated from the absorbent for 60 min by moved the amine to another water bath at 70 °C. Consider the results of 2-dimethylamino-ethanol (DMAE) which illustrated that the CO_2 absorption amount and absorption rate of DMAE was higher than that of MDEA but the cyclic capacity of DMAE was slightly lower than MDEA. In summary, this study provides a good indication in CO_2 absorption performance of DMAE although the results show DMAE the lower cyclic capacity than that of MDEA.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

Table 2.4 Solubility data for CO_2 in new various aqueous amine solutions

Researcher	Solvent	Temperature (°C)	CO_2 partial Pressure	Solvent Concentration
Chowdhury et al. [26]	DMAE	40	20 (kPa)	30 (wt%)
Puxty et al. [27]	DMAE	40	15 (kPa)	30 (wt%)
Daneshvar et al. [28]	DMAE	16-32	-	1.11 - 3.24 (mol/dm^3)
Chowdhury et al. [26]	DEAE	40	20 (kPa)	30 (wt%)
Yamada et al. [29]	IPAE	40, 100 and 120	5 kPa to 0.2 MPa	30 (wt%)
	PAE			
Haider et al. [30]	N-Methylethanolamine	30, 40 and 60	1-100 (kPa)	1.0, 2.0 and 4.0 (mol/dm^3)
Singh et al. [31]	1,6-Hexanediamine	30	1-40 (kPa)	2.55 (mol/dm^3)
Maneeintr et al. [32]	4-diethylamino-2-butanol	40, 60 and 80	15 and 100 (kPa)	3 (mol/dm^3)
	4-isopropylamino-2-butanol			
	4-piperidino-2-butanol			
	4-propylamino-2-butanol			
	4-(ethyl-methyl-amino)-2-butanol			
Ma’mun et al. [33]	AEEA	40 and 120	10 (kPa)	2.99 (mol/dm^3)
	EMEA			

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

Puxty et al. [27] also studied the CO_2 absorption capacity of aqueous amine solutions for 76 different amines including the reference compound MEA, and compared their performance to MEA. Those 76 amines including with primary, secondary, and tertiary amines were initially tested by using isothermal gravimetric analysis (IGA) to obtain the CO_2 solubility and CO_2 absorption rate. The IGA method was performed at 40°C isothermal, 30% w/w amine concentration, 15% CO_2 by volume and ambient pressure. Amines that showed good CO_2 absorption ability in IGA method were then tested with the macro-scale CO_2 absorption which conducted at CO_2 concentration of 13% by volume and the same amine concentration and system pressure. According from their results, there were 24 amines which were selected from IGA method to be further tested in macro-scale CO_2 absorption. Among of those amines, there were seven types of amines which showed outstanding CO_2 absorption capacity performance including with 2-dimethylamino-ethanol (DMAE). The findings showed that DMAE achieved capacity in CO_2 capturing better than the predicted value which stated in terms of pK_a. These findings also agree with the results of the previous researchers, Chowdhury et al. [26], who investigated the CO_2 capture performance of 24 tertiary amines. Moreover, the authors also suggested that DMAE and another selected six amines share a common molecular structure, a hydroxyl group within 2 or 3 carbons of the amine functionality. In the other words, the molecular structural form of amines could affect the CO_2 capture performance and this might advantage to DMAE. In addition, this conclusion conforms to the study of Yamada et al. [29]. In conclusion, DMAE could potentially be utilized as one of the new solvent because of the great CO_2 capture capacity.

Although the key property that is desired in the study of new solvent is the CO_2 capture performance, the stability is also one of the characteristic that should be considered. Because the regeneration column in typical CO_2 absorption process, where the CO_2 will be stripped off from the solvent by steam, normally operates at the temperature up to 140°C [6, 34], solvent degradation could occur and result in promoting corrosion as well as cause viscosity changes and foaming. Moreover, oxygen containing in flue gas can oxidize the amine in both the absorber and the regenerator then result in the loss of amine and environmental impact of the degradation products. These problems will especially be more severe in case of the solution loaded with CO_2.

To prevent this degradation, the solvent, therefore, should have chemical and thermal stability when experiences such regeneration condition. There are consequently some of studies that researched in this topic such as thermal and chemical stability [34-36],and the degradation mechanism [37, 38]. Focused to the thermal and chemical stability of solvent, the study of Eide-Haugmo et al. [35] investigated thermal and chemical stability of eleven amines including MEA, MDEA and DMAE. The 30 wt% amines were all tested by stored in the 316 SS metal cylinders at 135°C for 5 weeks. The degree of degradation is presented as percentage loss of amine. Their findings stated that in terms of no CO_2 loaded in the solvent, MEA and MDEA showed no degradation while DMAE indicated some degradation about 10% amine losses. Inversely, both MEA and MDEA had higher degradation comparing to DMAE in case of CO_2 presented in the amines for 0.5 mole CO_2/mole amine with degree of degradation of 55%, 35% and 30% for MEA, MDEA and DMAE respectively. In the other words, DMAE had higher chemical and thermal stability than MEA and MDEA especially loaded with CO_2 in the solution.

In contrast, while the chemical and thermal stability of solvent is desired, an environmental impact of amine is the topic that should also be concerned. This could occur when the solvent accidentally spills while operating the process or emits through the cleaned exhaust gas as volatile solvent or in the form of an aerosol. The solution must be able to naturally degrade to avoid the chemical buildup when this emission takes place. Researchers who deeply studied in the biodegradation of amines are various [35, 39, 40]. Considered to biodegradability of DMAE, back to the Eide-Haugmo et al. [35] work, their work performed by following a marine biodegradation test which according to OECD guideline 306. The findings stated that DMAE was biodegradable with degree of degradation of 70% for with and without the CO_2 loading while MEA and MDEA had lower biodegradability with the maximum degree of degradation of 25% and smaller than 5%, respectively. The higher ability of biodegradation of DMAE comparing to MEA and MDEA advantages for the absorption process that emphasize to the environment issues.

According to these literatures, alkanolamine solutions are still attractive solvents for CO_2 removal process. In this study, DMAE is proposed to be a one of the promising candidates in the absorption of CO_2 since the high performance of the acid gas removal and good properties of amine compound.

CHAPTER III

EXPERIMENTAL

This chapter mainly describes in the topic which including with the materials and chemicals used, experimental procedure and finally the analytical method of CO_2 loading.

3.1 Materials and chemicals

In this study, AALBORG GFM17 flowmeters are used to measure N_2 and CO_2 mass flow and are calibrated by Agilent Technology ADM100 Universal Mass Flowmeter with flow range of 0.5 to 1,000 mL/min and accuracy of ±3% of reading. To control the absorption temperature, the saturation cells and reactors are put in Memmert water bath with a temperature range of 0-100°C and water temperature is uniformed by Lauda water circulator. A schematic apparatus is shown in Fig. 3.1.

In terms of chemicals used, MEA is purchased from Sigma Aldrich with 99% purity, DMAE is purchased from Fluka (98%) and hydrochloric acid (HCl) with a purity of 99% is purchased from Fisher Scientific. N_2 (99.5%) and CO_2 (99.9%) are purchased from Praxair (Thailand). All of aqueous solutions are prepared by distilled water and all chemicals and gases are directly used without further purification.

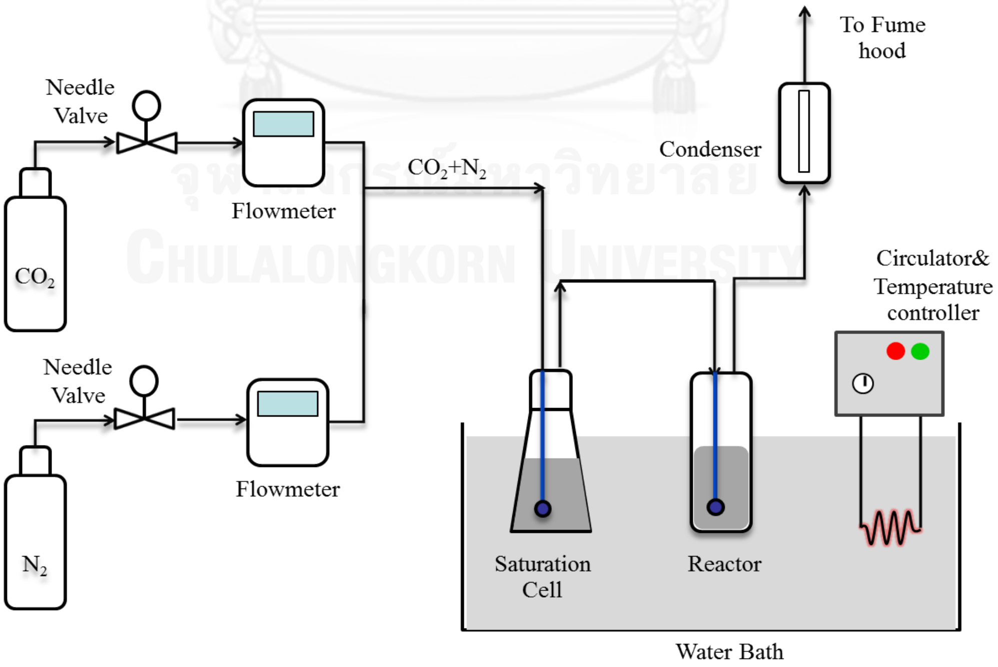


Figure 3.1 Experiment apparatus of solubility study of CO_2

3.2 Experimental procedure

This section describes the method for investigating the effects of various operating conditions to the CO_2 capture performance of solvents interested. The conditions involved are summarized in table 3.1.

Table 3.1 Summary of operating conditions for solubility study

Operating condition	**Value**
Solvent concentration (molar)	3, 4 and 5
Partial pressure of CO_2 (kPa)	5, 15, 30, 50, 75 and 100
Absorption temperature ($^{\circ}C$)	30, 40, 60 and 80
Solvent type	MEA, MDEA and DMAE

Before performing the solubility study of CO_2, temperature and solvent concentration were initially set at the desired value. Then the experiment will conduct by following procedure. First, at the desired solvent concentration and temperature, the CO_2 and N_2 gas mixture was blended and adjusted the gas flow rate until the desired CO_2 partial pressure has been reached. The gas mixture was introduced to the system through the flow meter and saturated with moisture content in the saturation cell to maintain to solution concentration. After that, the wetted gas mixture was bubbled through the amine solution in the reactor cell, where the CO_2 is absorbed. The unreacted gas then eventually exhausted. The gas was sent to the condenser to recover moisture in the gas stream before being vented to the fume hood. The experiment was performed under atmospheric pressure.

In order to ensure that equilibrium was reached, the system was kept in operation for 14–16 hours until the parameter such as temperature, partial pressure and solution concentration were constant, especially CO_2 loading which was determined at the difference value of ±0.05 mol CO_2/mol amine. The liquid sample was then taken for 3 times to analyze the average CO_2 loading at the equilibrium state by titration method.

CHULALONGKORN UNIVERSITY

3.3 Analyze

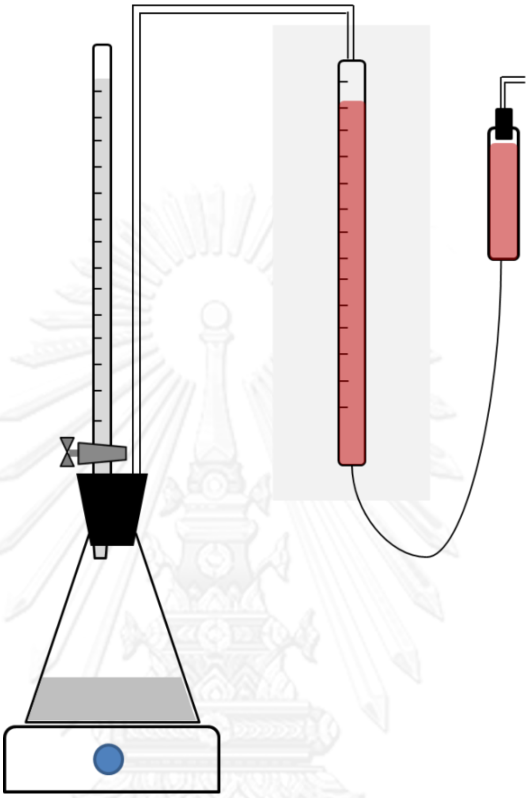


Figure 3.2 CO_2 loading analyzer

The CO_2 loading of the solvents is the parameter which indicates the CO_2 absorption ability of the solvent. Figure 3.2 shows the CO_2 loading analyzer. The following section presents the procedure which states how to determine this CO_2 loading. At first, the solution was precisely sampled by 2 mL pipette. The solution of 1.0 M HCl was then used to measure the concentration of liquid sample by titration method. This concentration was finally converted to mole of liquid sample. The amount of CO_2 that emitted from the reaction between acid and amine sample was all collected and calculated in mole with respected to room temperature (25°C). The ratio of mole CO_2 per mole of amine sample represents the CO_2 loading.

CHAPTER IV

RESULTS AND DISCUSSION

Motivation and method of CO_2 solubility study in an aqueous solution of dimethylaminoethanol (DMAE) have been described in the former chapters. In this chapter, after performing the experiment, measurement of CO_2 absorption and effect of each variable will be intensively discussed and compared to the commercially used solvents like monoethanolamine (MEA) and methyldiethanolamine (MDEA). Moreover, equipment verification results are also reported in this section.

4.1 Equipment verification

As a new established experimental setup, equipment verification was therefore conducted to verify the reliability of this setup and also the procedure that was applied in this work. The verification was performed at MEA concentration of 5 molar, temperatures of 40, 60 and 80°C and CO_2 partial pressure ranging from 5 to 100 kPa. The CO_2 solubility results obtained from the current apparatus were compared to the results from previously published literatures [12, 29, 41, 42] at the same experimental conditions. These results are illustrated in Figure 4.1 through 4.3.

Figure 4.1 through 4.3 state the solubility of CO_2 at 40, 60 and 80°C respectively. They also clearly show that our solubility data agree well with those of the reference literatures. Furthermore, an average absolute deviation (%AAD) [43] and the maximum absolute deviation when compared to Shen and Li [41] measurement are 2.75% and 11.05% respectively. This can be concluded that the equipment and procedure which are used in this work are sufficiently reliable to perform other experimental conditions with the acceptable deviation.

Chulalongkorn University

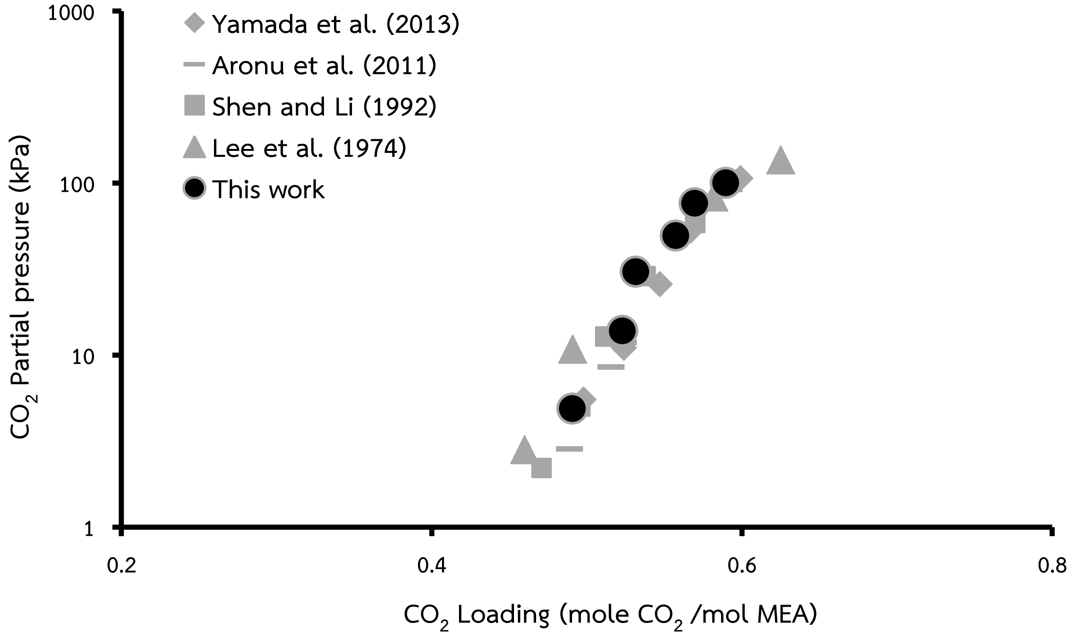


Figure 4.1 Comparison of CO_2 solubility in 5M MEA between the results from this work and reference literatures at 40°C

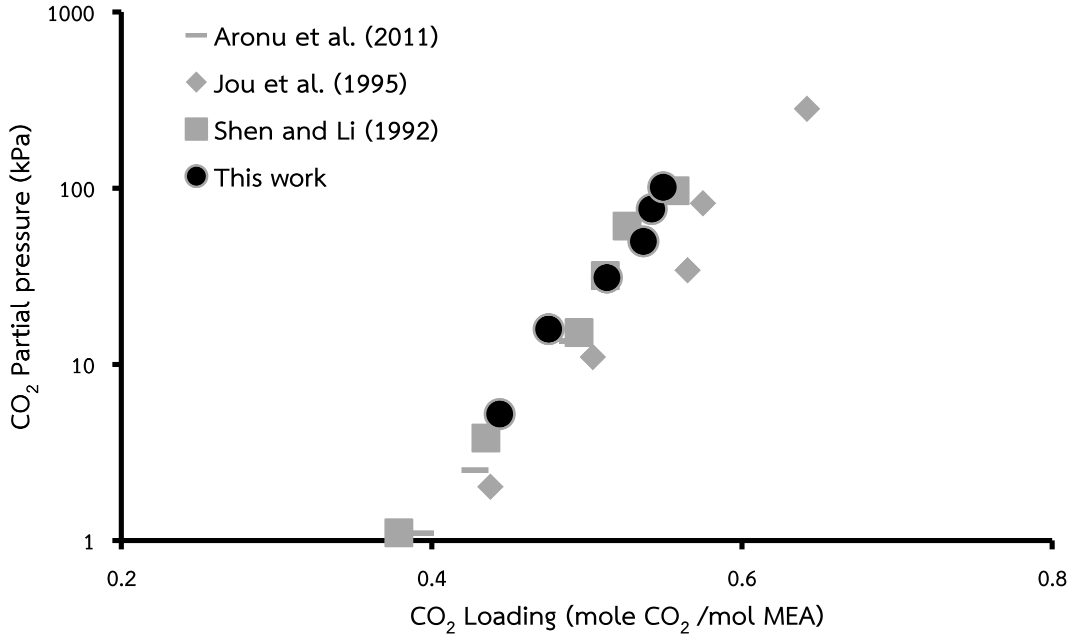


Figure 4.2 Comparison of CO_2 solubility in 5M MEA between the results from this work and reference literatures at 60°C

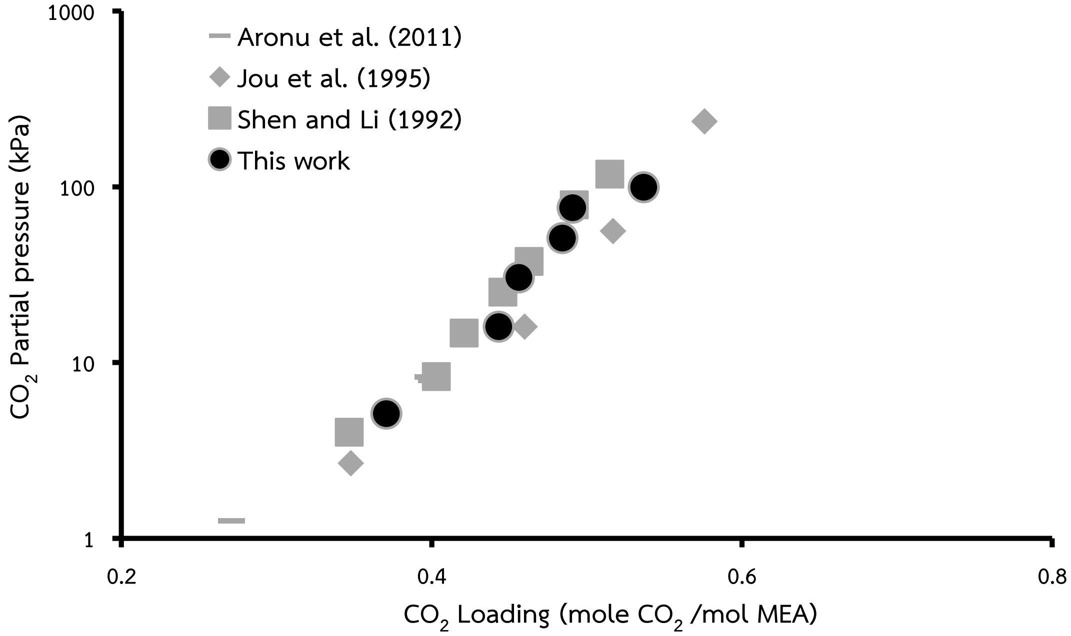


Figure 4.3 Comparison of CO_2 solubility in 5M MEA between the results from this work and reference literatures at 80°C

The deviation of this equipment mainly comes from errors in measurement of CO_2 volume that is emitted from the liquid sample during CO_2 loading analysis. In the other words, because volume of the acid gas is temperature-sensitive, the difference of temperature between experimental condition and CO_2 loading determination may be the main cause of changing in the gas volume.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

4.2 CO_2 solubility results

The effects of interested variables to the CO_2 solubility are shown in this section. The findings are categorized to the topics as follow.

4.2.1 Effect of types of solvent used

Solvents investigated in this study were MEA, MDEA and DMAE. Figure 4.4 illustrates the performance on CO_2 removal of difference solvent types at 3M and 40°C. Among these solutions, DMAE shows the most preferable in CO_2 solubility at all entire range of CO_2 partial pressure in terms of absorption capacity. For MEA, it is concluded that CO_2 loading in DMAE has more sensitivity to CO_2 concentration. It can be seen that when the partial pressure of CO_2 is increased, the amount of captured CO_2 of DMAE is increased more rapidly than MEA. Moreover, this advantages to DMAE over MEA that its performance is also increased when the CO_2 partial pressure is increased. In case of MDEA and DMAE, they show the similar trend of the CO_2 partial pressure and CO_2 loading relationship because both of them have a mutual molecular structure form, which is the tertiary amine. Furthermore, the reason that explains why DMAE has greater number of CO_2 loading than the others was suggested by Puxty et al. [27] and Yamada et al. [29]. They both indicated that DMAE has a distinctive molecular structure which may advantage to CO_2 capture performance.

Moreover, Table 4.1 and 4.2 show the CO_2 solubility data at each CO_2 partial pressure with 3M and 40°C operating condition. The CO_2 partial pressure is stated in the unit of kPa and α represents the CO_2 loading in solution with the unit of mole CO_2 per mole amine. The results also clearly indicate that DMAE performs better CO_2 removal ability than both MEA and MDEA, with the average and maximum percent difference of CO_2 loading of 23.63% and 38.79% respectively higher than MEA and 49.35% and 114.66% higher than MDEA. This is particular true when the CO_2 partial pressure is higher than 5 kPa.

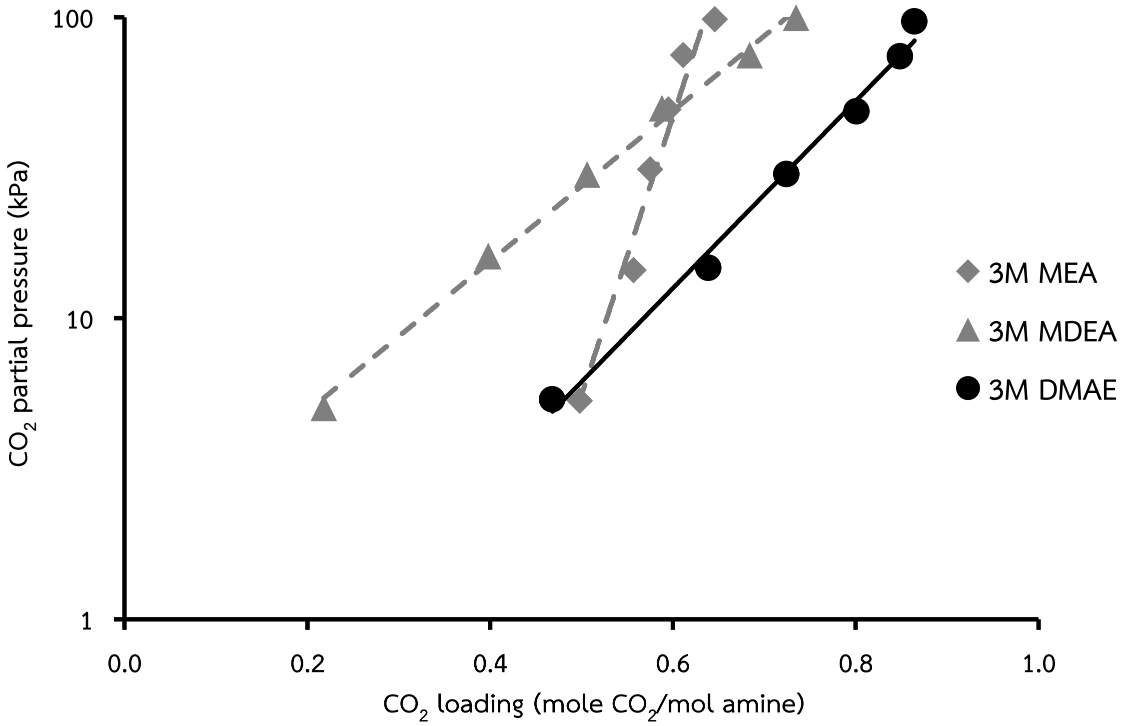


Figure 4.4 Solubility of CO_2 in 3M MEA, MDEA and DMAE at 40°C

Table 4.1 Details of solubility results of 3M MEA and DMAE at 40°C

MEA		DMAE		CO_2 loading difference	%Difference
P_{CO_2}	α	P_{CO_2}	α		
5.32	0.498	5.37	0.468	-0.030	-6.06
14.43	0.557	14.68	0.639	0.082	14.71
31.21	0.575	30.08	0.724	0.149	25.94
49.40	0.595	48.61	0.801	0.206	34.56
74.77	0.611	74.18	0.849	0.237	38.79
98.56	0.646	96.68	0.864	0.218	33.82

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Table 4.2 Details of solubility results of 3M MDEA and DMAE at 40°C

MDEA		DMAE		CO_2 loading difference	%Difference
P_{CO_2}	α	P_{CO_2}	α		
5.04	0.218	5.37	0.468	0.250	114.66
16.08	0.398	14.68	0.639	0.241	60.49
30.01	0.506	30.08	0.724	0.218	43.10
49.87	0.588	48.61	0.801	0.213	36.21
74.90	0.684	74.18	0.849	0.164	24.00
99.78	0.735	96.68	0.864	0.130	17.65

According to the results, the outstanding performance in CO_2 removal of DMAE has advantages over the others competitors in terms of CO_2 loading in the power plant flue gas condition range. This is the significant evidence indicating that a new promising solvent like DMAE is capable for replacing the conventional solvents like MEA and MDEA.

4.2.2 Effect of CO_2 partial pressure

The partial pressure of CO_2 studied in this work covers the range of typical amount of CO_2 emitted from fossil-based power plants. Figure 4.5 is the re-plotted of Figure 4.4 to illustrate the effect of CO_2 partial pressure to the CO_2 solubility. For all solutions, the solubility of CO_2 is a direct proportional to the partial pressure of itself at equilibrium state. In other words, increasing the CO_2 partial pressure is likely to enhance the driving force of CO_2 in gas phase transferring to liquid phase. Thus, the higher of CO_2 partial pressure in gas phase is applied, the higher amount of CO_2 is to be captured. This conforms to the thermodynamic relation like Henry’s Law.

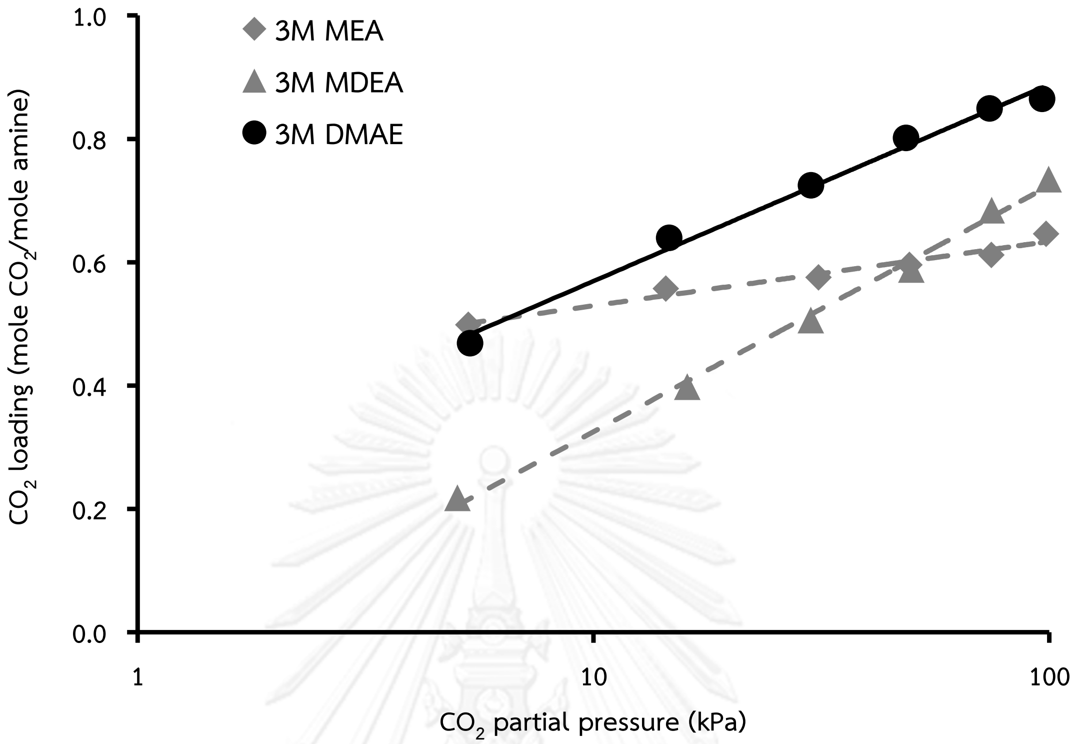


Figure 4.5 Sensitivity of CO_2 loading on the acid gas partial pressure of the solvents re-plotted from Figure 4.4

Like Figure 4.4, Figure 4.5 also emphasizes that DMAE has a greater ability in CO_2 absorption than both MEA and MDEA. With the 237% and 85% increasing in CO_2 loading from 5 kPa to 100 kPa of MDEA and MEA, respectively, also indicate the good ability in CO_2 removal while MEA presents only 30% increased. Moreover, the CO_2 solubility sensitivity on changing of CO_2 partial pressure for each solvent is also illustrated. The slope of the trend line is the key evidence that indicates the sensitivity of the solvents that the greater slope of the solvent, the greater in sensitivity. This sensitivity is the useful ability which notifies us how broad of CO_2 concentration range can be used with a good performance.

4.2.3 Effect of solvent concentration

Concentration of solvent is one of the most essential factors which are considered in acid gas capturing process designing and capital cost estimating. Figure 4.6 shows the effect of solvent concentration to the CO_2 solubility. The figure indicates the data at the operating condition of 3, 4 and 5 molar concentration of DMAE and 40°C absorption temperature. The findings illustrate that the CO_2 loading at 5M concentration is less than at 4 and 3M concentration. In the other words, as the solution concentration is increased, the CO_2 loading is oppositely decreased. Table 4.3 also shows details of the CO_2 solubility at each points of CO_2 partial pressure.

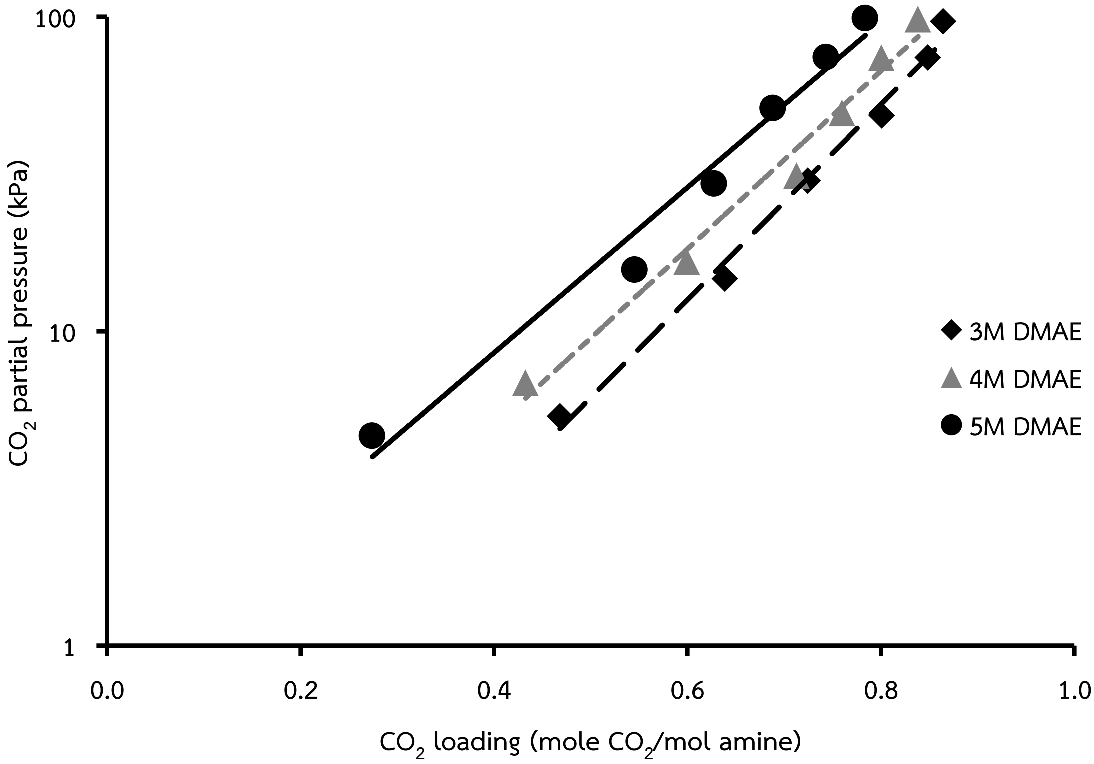


Figure 4.6 CO_2 loading of 3, 4 and 5M DMEA concentration at 40°C

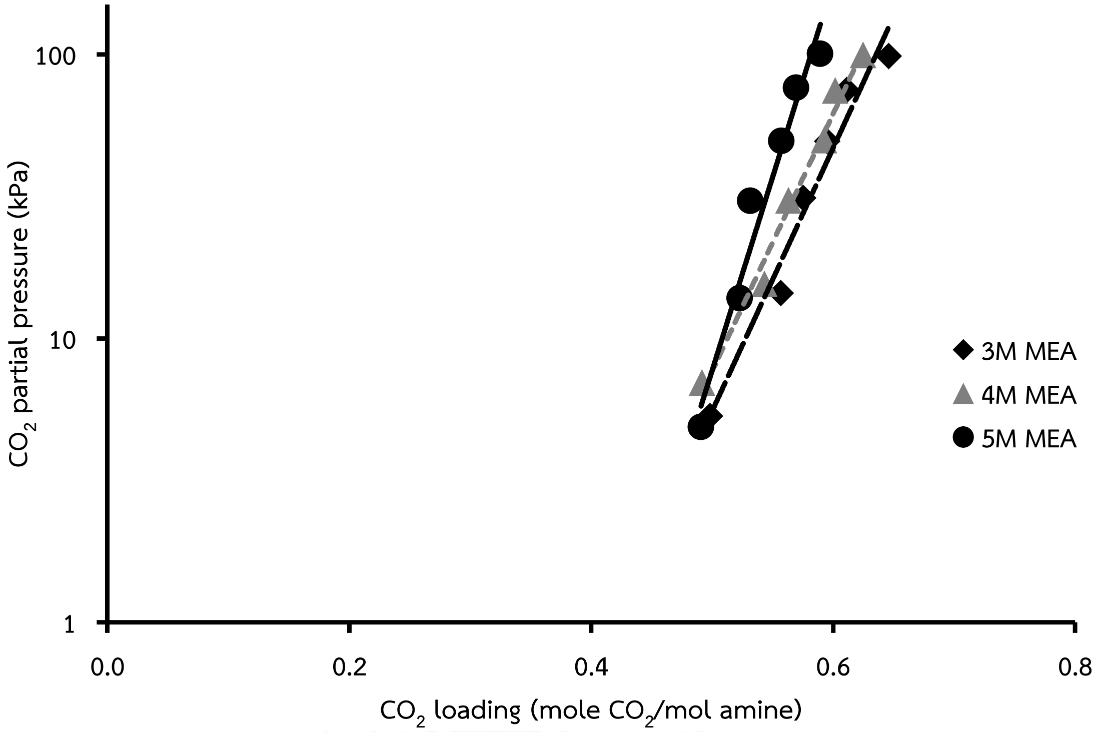


Figure 4.7 CO_2 loading of 3, 4 and 5M MEA concentration at 40°C

Theoretically, considered in an amine-based absorption process, increasing of solvent concentration is resulting in increasing of the mole of unreacted amine or free amine per unit volume. According to Figure 4.6, the results may contradict to the postulation that the CO_2 loading should be increased as much as the solution concentration increased. The feasible explanation of this phenomenon is that the mole of CO_2 in the solution is actually increased when the solution concentration is increased. However, it should be reminded that the amount of captured CO_2 in the solvent is reported in terms of CO_2 loading, which states the ratio of mole of CO_2 and mole of amine. Increasing the concentration of solvent is likely to increase the mole of solvent. Although the increasing of mole of captured CO_2 as well as the solvent concentration, the mole of solvent is also developed but in the higher rate. Consequently, this affects to the mole of CO_2 per mole of solvent ratio, or CO_2 loading, that it will be decreased when the solution concentration is increased.

Table 4.3 Solubility data of DMAE and MEA at 40°C and 3, 4 and 5M concentration

Solvent type	3 Molar		4 Molar		5 Molar	
	P_{CO_2}	α	P_{CO_2}	α	P_{CO_2}	α
DMAE	5.37	0.468	6.87	0.433	5.19	0.211
	14.68	0.639	16.66	0.599	15.08	0.545
	30.08	0.724	31.25	0.713	28.97	0.593
	48.61	0.801	49.51	0.760	51.22	0.688
	74.18	0.849	74.11	0.801	75.56	0.744
	96.68	0.864	98.22	0.838	100.42	0.784
MEA	5.32	0.498	6.98	0.492	4.87	0.491
	14.43	0.557	15.55	0.543	13.82	0.523
	31.21	0.575	30.62	0.563	30.44	0.532
	49.40	0.595	49.88	0.593	49.52	0.557
	74.77	0.611	74.64	0.602	76.14	0.570
	98.56	0.646	99.65	0.625	100.33	0.590

Another possible reason that explains this result was proposed by Schäffer et al. [20]. They gave the suggestion that the difference in the water content of each amine solvent concentration may be the reason of this mechanism. At high amine concentration, the water content of the solution decreases as well as the number of mole of water per mole of amine decreases. According to Equations (2)-(5) in Chapter II, the equilibrium of reaction shifts back from bicarbonate formation to increase water. This leads to lower CO_2 loadings at high solvent concentrations (low water content).

In summary, in order to achieve the highest performance in removal of the low pressure of CO_2 in power plant flue gas, it is sufficient to use the solvent concentration at 3 molar. In addition, using high solvent concentration may experience some of physical property issues [43]. Moreover, the economic viewpoint is also considered because when the higher solution concentration is used, the higher in capital and operating cost must be applied. The conclusion is also true in case of MEA and can be seen in Figure 4.7.

4.2.4 Effect of temperature

In terms of thermodynamics, temperature is the main role that affects the equilibrium of CO_2 capture capacity. The effects of temperature on CO_2 solubility derived from the experimental conditions of 30, 40 60 and 80°C temperature, 3M solvent concentration and three types of solution are shown in the Figure 4.8 through 4.10, which present the results for MEA, MDEA and DMAE, respectively.

From these Figure, it is clearly illustrated that the solubility of CO_2 is conversely proportional to the absorption temperature for all kinds of solvents. It can be observed that the results at lower temperature have higher CO_2 loading when comparing to the results at higher temperature. The decreasing in CO_2 loading when increasing the system temperature can be explained that when the acid gas that dissolves in the solution gains a large amount of kinetic energy at high temperature. This results in the increasing amount of the escaping gas from liquid phase and eventually reduces the CO_2 content in the solvent.

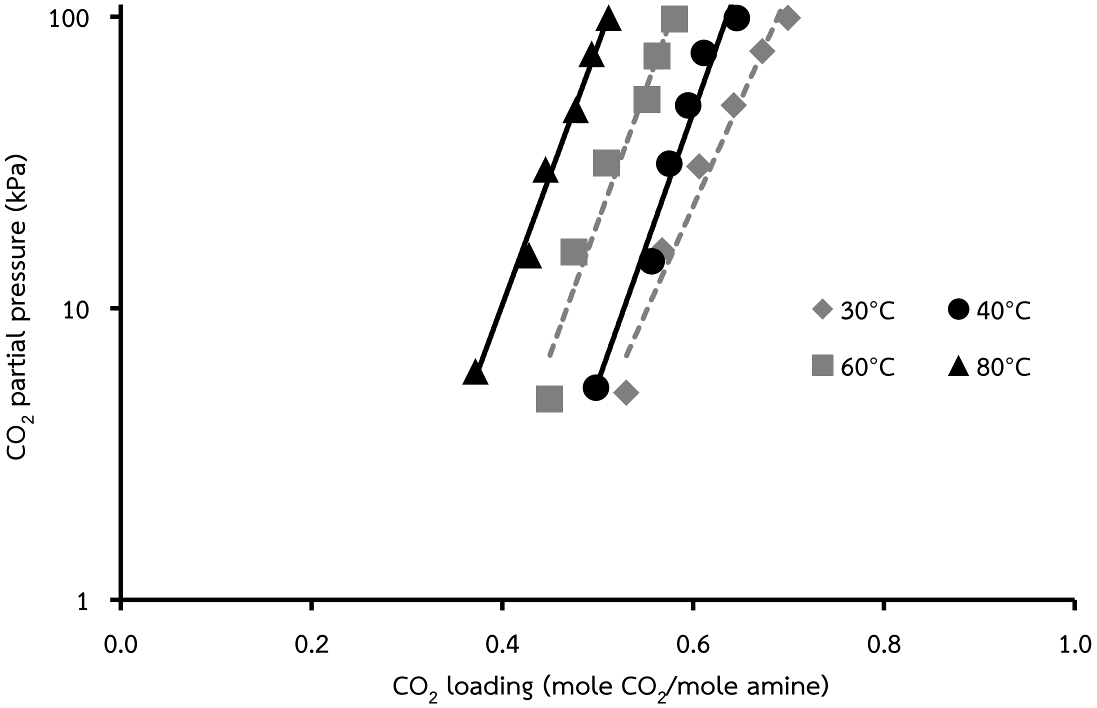


Figure 4.8 Effect of temperature to CO_2 loading at 3M MEA concentration

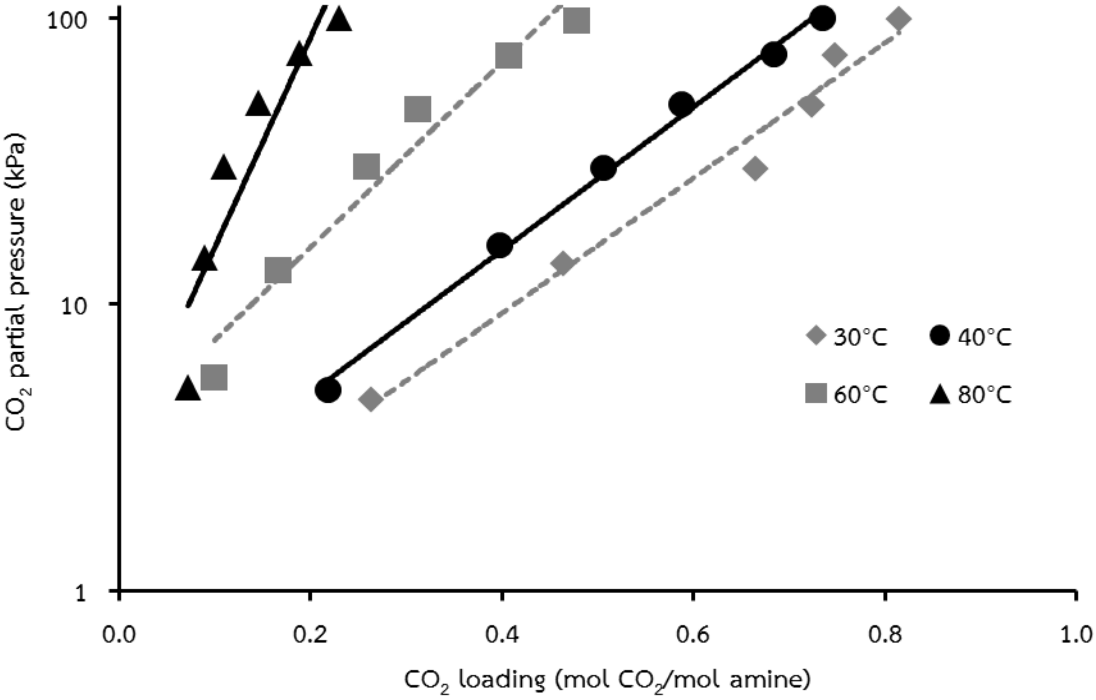


Figure 4.9 Effect of temperature to CO$_2$ loading at 3M MDEA concentration

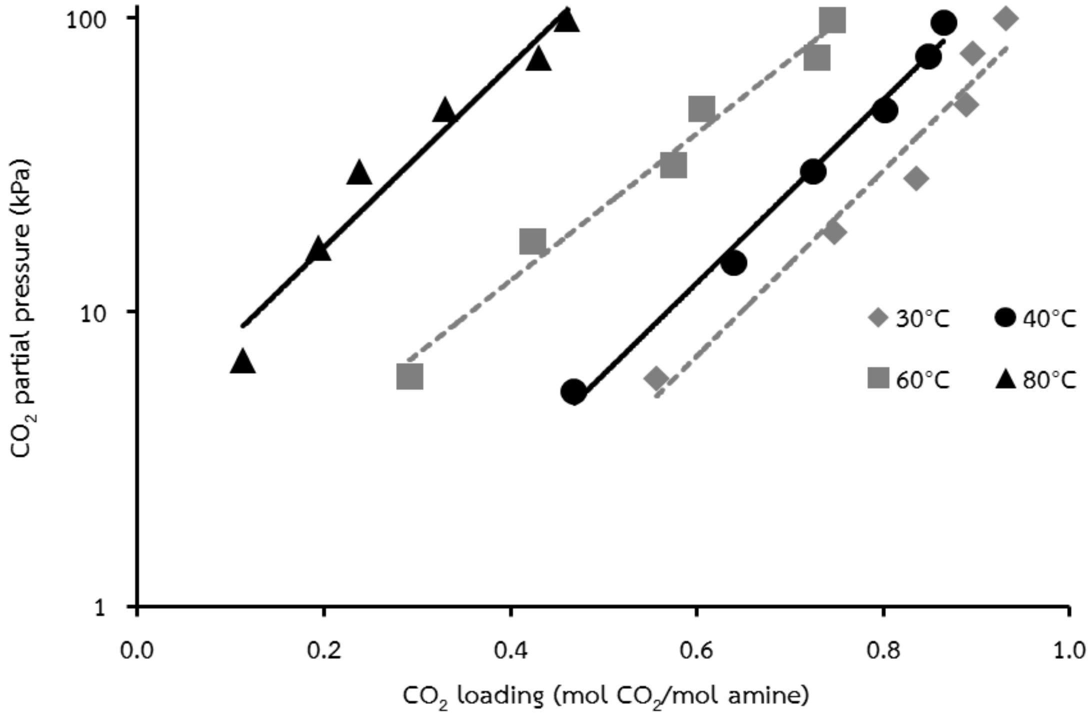


Figure 4.10 Effect of temperature to CO$_2$ loading at 3M DMAE concentration

According to Figure 4.8 through 4.10, they state the different CO_2 capturing behaviors of each solvent. Moreover, Table 4.4 also shows the solubility data at each point of various operating conditions. For MEA in the Figure 4.8, the CO_2 solubility results at the various temperatures are stayed closest compared with the other two solvents. The explanation is made when the primary amine solutions like MEA react with dissolved CO_2, they form the complex substance called carbamate ions which relatively stable [6]. Thus, although the temperature is increased, the carbamate ions still exist and do not release CO_2 out. This consequently results in remaining of CO_2 loading in the solution. However, in case of the solution of tertiary amines like MDEA and DMAE illustrated in Figure 4.9 and 4.10, they cannot form the carbamate ions while capturing CO_2. This leads to the easier in the CO_2 stripping off and eventually left lower CO_2 content in the amine molecule [6]. For summary, the two tertiary amines benefit over MEA that they have a greater in cyclic capacity, which will be further discussed in the next section.

Table 4.4 Solubility data of 3M MEA, MDEA and DMAE at 30, 40, 60 and 80°C

Solvent type	30°C		40°C		60°C		80°C	
	P_{CO_2}	α	P_{CO_2}	α	P_{CO_2}	α	P_{CO_2}	α
MEA	5.12	0.530	5.32	0.498	4.87	0.450	6.06	0.372
	15.78	0.568	14.43	0.557	15.53	0.475	15.18	0.428
	30.59	0.606	31.21	0.575	31.36	0.510	29.93	0.445
	49.56	0.643	49.40	0.595	51.68	0.552	47.84	0.477
	76.00	0.673	74.77	0.611	73.00	0.563	74.38	0.494
	98.80	0.700	98.56	0.646	97.83	0.581	98.94	0.512
MDEA	4.64	0.264	5.04	0.218	5.56	0.100	5.11	0.072
	13.87	0.464	16.08	0.398	13.14	0.166	14.47	0.090
	29.55	0.666	30.01	0.506	30.14	0.259	30.25	0.110
	49.68	0.725	49.87	0.588	48.02	0.312	50.62	0.146
	74.05	0.748	74.90	0.684	73.63	0.408	75.28	0.189
	99.06	0.815	99.78	0.735	97.67	0.478	99.93	0.230

Table 4.4 Solubility data of 3M MEA, MDEA and DMAE at 30, 40, 60 and 80°C (con't)

Solvent type	30°C		40°C		60°C		80°C	
	P_{CO_2}	α	P_{CO_2}	α	P_{CO_2}	α	P_{CO_2}	α
DMAE	5.90	0.557	5.37	0.468	6.06	0.292	6.85	0.113
	18.64	0.747	14.68	0.639	17.35	0.424	16.45	0.194
	28.33	0.835	30.08	0.724	31.52	0.575	30.10	0.239
	50.47	0.890	48.61	0.801	49.01	0.605	49.03	0.331
	75.69	0.897	74.18	0.849	73.50	0.728	73.20	0.430
	98.89	0.932	96.68	0.864	97.92	0.746	98.96	0.461

In general, the reactions between solvents used in chemical absorption process and the gas to be absorbed, CO_2 for this study, are reversible reaction which means that the CO_2 loosely reacts with the solvents. Inversely, the absorbed gas can also finally be released. Then those free solvents will be brought to re-absorb again. In order to release the captured CO_2 from the solvent, heat from steam is generally applied. This mechanism is normally called desorption or stripping. In the other words, absorption and stripping are utilized the principle of temperature that effects to the amount of captured CO_2 for carbon capture systems.

Considered to our work, since Thailand is the country that locates in the tropical zone, temperature of 30°C is reasonably used to be a representative of the room temperature instead of 25°C. However, the existing absorption plants that operate today utilize the absorption temperature at 40°C to supply heat of reaction of solvent and CO_2, especially for MEA plants, and to compensate the temperature-raised for tropical countries. Temperature of 60°C is used to identify the trend of changing in temperature between 40°C and 80°C. Finally, 80°C temperature is represented as stripping temperature. The reason for choosing this temperature because if the new solvent can strip CO_2 out well at this temperature, it is better that the lower temperature could be used although the stripping temperature in the existing plants normally operates at 120-140°C.

According to Figure 4.11, at CO_2 partial pressure of 15 kPa, which is an average CO_2 partial pressure emitted from coal-fired power plant [5], and solvent concentration of 3M, the relationships between temperature and CO_2 loading of each solution are illustrated. The solubility of CO_2 in MDEA and DMAE solution are rapidly decreased with an increasing in absorption temperature. In addition, the CO_2 loading of MEA is also decreased under the same fashion in those of MDEA and DMAE but lower amount of CO_2. In the other words, MDEA and DMAE have more sensitivity to temperature than MEA in which their CO_2 loading can be great changed while changing the temperature.

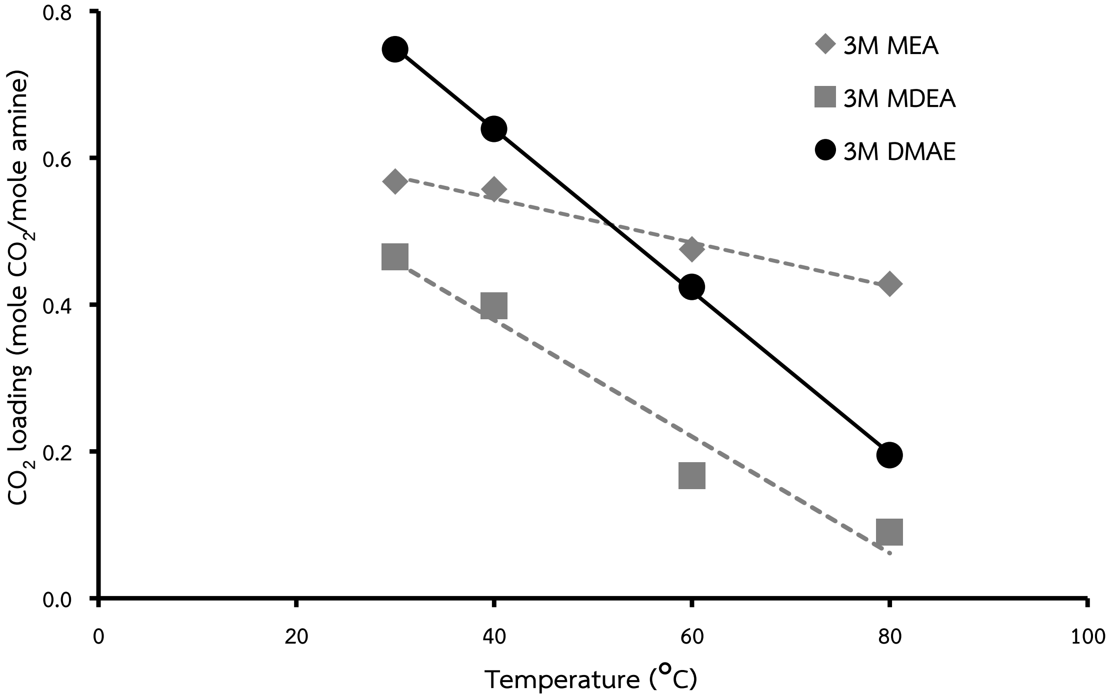


Figure 4.11 Trend of temperature to CO_2 loading at 15 kPa CO_2 partial pressure and 3M solvent concentration

Chulalongkorn University

4.3 Cyclic capacity study

Considered in a chemical absorption of acid gas using amine solution, the processes usually involve both absorption and acid gas stripping (or solvent regeneration). Especially for CO_2 containing in flue gas from power plant, absorbent or solvent must achieve the various abilities to deal with this emitted CO_2. One of the most important abilities of the solvents is cyclic capacity.

Cyclic capacity is defined as the difference in equilibrium CO_2 loading at the absorption condition and CO_2 loading at the regeneration condition. It is noted that CO_2 loading is derived from moles of absorbed CO_2 per one mole of the solvent. As mentioned earlier, the absorption and regeneration condition are identified by operating temperature, which are 40 and 80°C for absorption and regeneration condition respectively. Therefore, temperature is the main role that impact to cyclic capacity of the solvent.

Cyclic capacity is the key factor that should be concerned when designing the process. It affects to the design of solvent circulation rate, solvent concentration, solvent type and also energy consumption in the system.

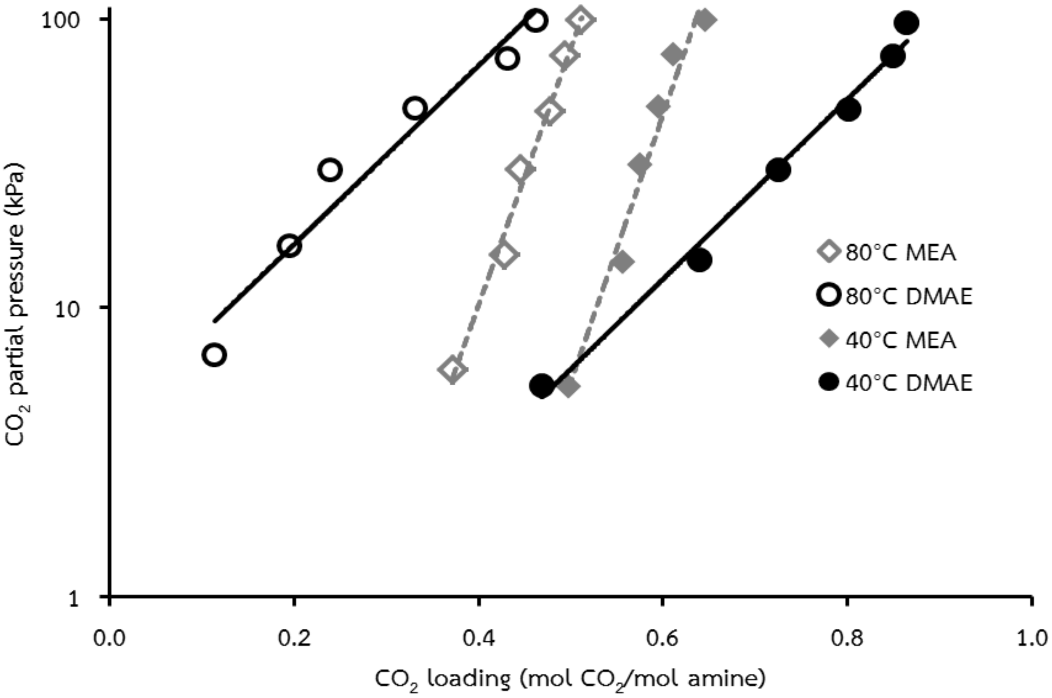


Figure 4.12 Comparison of cyclic capacity between 3M MEA and DMAE

The results of cyclic capacity study are obtained at 3M solvent concentration and temperature at 40 and 80°C. The comparison of cyclic capacity between DMAE and MEA and MDEA are shown on the Figure 4.12 and 4.13 and also Table 4.5 and 4.6.

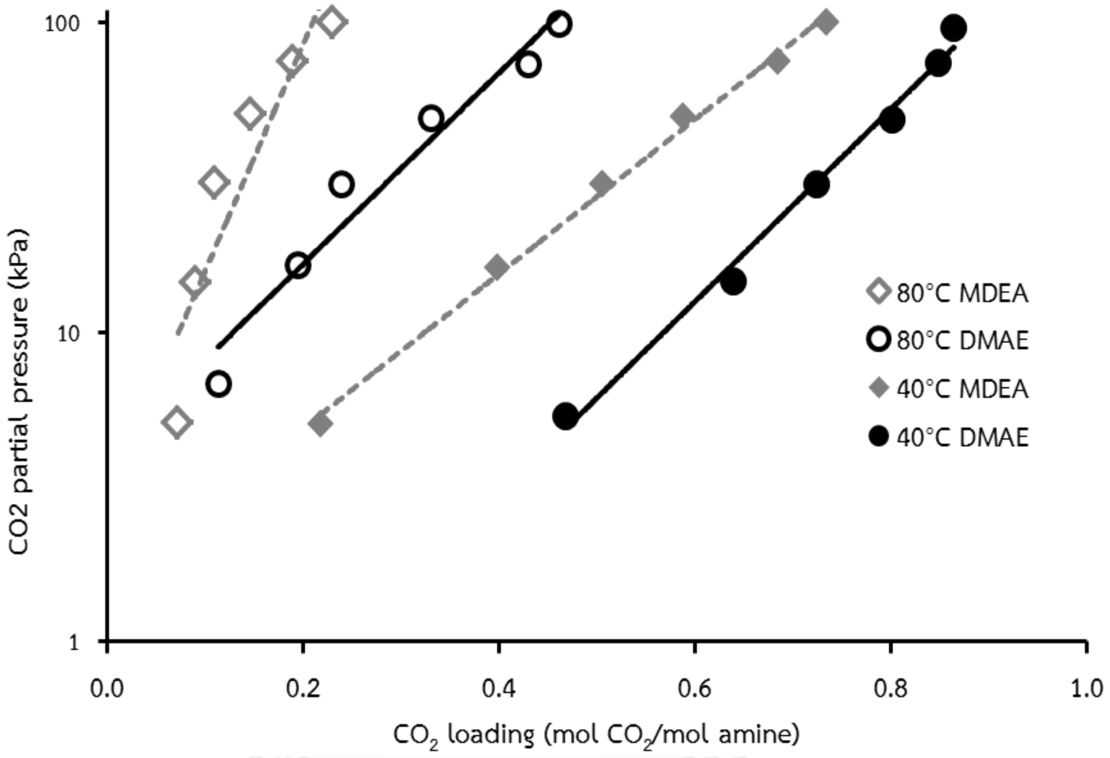


Figure 4.13 Comparison of cyclic capacity between 3M MDEA and DMAE

Table 4.5 Details of cyclic capacity comparison between 3M MEA and DMAE

Solvent type	40°C		80°C		Cyclic capacity
	P_{CO_2}	α	P_{CO_2}	α	
MEA	5.32	0.498	6.06	0.372	0.126
	14.43	0.557	15.18	0.428	0.129
	31.21	0.575	29.93	0.445	0.130
	49.40	0.595	47.84	0.477	0.118
	74.77	0.611	74.38	0.494	0.118
	98.56	0.646	98.94	0.512	0.134

Table 4.5 Details of cyclic capacity comparison between 3M MEA and DMAE (con’t)

Solvent type	40°C		80°C		Cyclic capacity
	P_{CO_2}	α	P_{CO_2}	α	
DMAE	5.37	0.468	6.85	0.113	0.355
	14.68	0.639	16.45	0.194	0.445
	30.08	0.724	30.10	0.239	0.486
	48.61	0.801	49.03	0.331	0.470
	74.18	0.849	73.20	0.430	0.418
	96.68	0.864	98.96	0.461	0.403

Table 4.6 Details of cyclic capacity comparison between 3M MDEA and DMAE

Solvent type	40°C		80°C		Cyclic capacity
	P_{CO_2}	α	P_{CO_2}	α	
MDEA	5.04	0.218	5.11	0.072	0.146
	16.08	0.398	14.47	0.090	0.308
	30.01	0.506	30.25	0.110	0.397
	49.87	0.588	50.62	0.146	0.442
	74.90	0.684	75.28	0.189	0.496
	99.78	0.735	99.93	0.230	0.505
DMAE	5.37	0.468	6.85	0.113	0.355
	14.68	0.639	16.45	0.194	0.445
	30.08	0.724	30.10	0.239	0.486
	48.61	0.801	49.03	0.331	0.470
	74.18	0.849	73.20	0.430	0.418
	96.68	0.864	98.96	0.461	0.403

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

According to Figure 4.12 and Table 4.5, the results show that at 40°C, DMAE can provide a higher CO_2 loading when compared with MEA at all entire CO_2 partial pressure. Furthermore, at high temperature of 80°C, CO_2 loading obtained from DMAE becomes conversely lower than MEA. This can be concluded that DMAE has a greater cyclic capacity compared with that of MEA, thus making DMAE having advantage over MEA for CO_2 capturing performance with the increasing of average cyclic capacity of 241%. The reasons that explain why DMAE has greater CO_2 capturing performance are stated in the previous section. In addition, because DMAE could be regenerated to lower CO_2 loading at the same temperature of MEA, the lower require energy consumption for solvent regeneration can also be achieved. Moreover, the larger cyclic capacity of DMAE can also reduce the solvent circulation rate in the process since it has high capture capacity. In summary, the greater performance of DMAE over MEA can increase the overall efficiency of absorption process and would eventually result in lower overall capital cost.

Furthermore, the comparison of cyclic capacity between MDEA and DMAE are also illustrated in Figure 4.13 and Table 4.6. The results indicate that at absorption condition, DMAE shows higher ability in CO_2 loading than those of MDEA for all range of CO_2 partial pressure. However, MDEA provides lower CO_2 solubility at regeneration condition. Considering the cyclic capacity of both solvents, DMAE presents an advantage over MDEA for greater in average cyclic capacity of 12%. Therefore, although DMAE gives lower performance in regeneration step to MDEA, it can benefit over MDEA in the absorption and cyclic capacity competition.

Eventually, according to the experimental results and the conclusions provided above, DMAE presents the preferable ability in CO_2 capture over both MEA and MDEA as initially proposed in various aspects such as outstanding absorption amount, great sensitivity to partial pressure and temperature and also larger cyclic capacity. In conclusion, DMAE can potentially be used or developed in the larger scale and may hopefully reduce the operating cost and also makes the carbon capture processes become more attractive.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this work, the solubility of the new promising solvent applied for chemical absorption, Dimethylaminoethanol (DMAE), was investigated using lab-scale carbon dioxide absorption apparatus. The operating conditions used are following described. First, types of chemical absorption solvents were monoethanolamine (MEA), methyldiethanolamine (MDEA) and dimethylaminoethanol (DMAE). Second, solvent concentrations were 3, 4 and 5 molar. Next, CO_2 partial pressure was used in the range of 5, 15, 30, 50, 75 and 100 kPa. Finally, temperatures were used at 30, 40, 60 and 80°C.

In order to verify the reliability of this setup and also the procedure that was applied in this work, equipment verification was therefore conducted. The verification was performed at MEA concentration of 5 molar, temperatures of 40, 60 and 80°C and CO_2 partial pressure ranging from 5 to 100 kPa. The equipment and procedure are sufficiently reliable to perform other experimental conditions with an average absolute deviation (%AAD) and the maximum absolute deviation when compared to Shen and Li of 2.67% and 11.05% respectively.

The effect of solvents used is considered at 3 molar solvents concentration and 40°C absorption temperature. Among the all solutions, DMAE shows the most preferable in CO_2 solubility for all entire range of CO_2 partial pressure with average %difference of CO2 loading of 23.63% higher than MEA and 49.35% higher than MDEA. Comparing to MEA, the CO_2 loading of DMAE is significantly changed depending on CO_2 partial pressure. This can be seen that when the partial pressure of CO_2 is increased, the amount of captured CO_2 of DMAE is increased more rapidly than MEA. For MDEA and DMAE, they show the similar trend of the CO_2 partial pressure and CO_2 loading relationship because both of them have a mutual molecular structure form, which is the tertiary amine. However, DMAE still gives a better CO_2 capture performance than MDEA. For summary, the outstanding in CO_2 removal ability promotes DMAE to advantage over MEA and MDEA solvents and makes DMAE more attractive solvent for CO_2 capture system.

As previously mentioned, the effect of CO_2 partial pressure to the solubility of CO_2 is a direct proportional to the partial pressure of itself at equilibrium state. In the other words, increasing the CO_2 partial pressure is likely to enlarge the driving force of CO_2 in gas phase transferring to liquid phase. Thus, the higher of CO_2 partial pressure in gas phase is applied, the higher amount of CO_2 is to be captured. At CO_2 partial pressure of 5 to 30 kPa which is the power plant flue gas condition, DMAE also presents higher CO_2 solubility than the others solutions. Therefore, the conclusion that using DMAE as chemical solvent for CO_2 absorption is better than MEA and MDEA is still true especially the CO_2 from power plants.

The effect of solvent concentration illustrates that the operating condition of 3, 4 and 5 molar concentration of DMAE and 40°C absorption temperature. The findings show that the CO_2 loading at 5 molar concentration is less than at 3 molar concentration. In the other words, as the solution concentration is increased, the CO_2 loading is oppositely decreased. This also agrees with the CO_2 loading results of MEA at the same range of concentration. In this study, it can be summarized that 3 molar is the best appropriate for CO_2 removal since this uses lower amount of concentrated amines and prevents the issues like corrosion and physical properties changing.

Furthermore, the effect of temperature is indicated that the solubility of CO_2 is conversely proportional to the absorption temperature for all solution types. It can be observed that the CO_2 solubility at lower temperature has higher CO_2 loading when comparing to the CO_2 solubility at higher temperature. The decreasing in CO_2 loading when increasing the system temperature can be applied to strip CO_2 off the rich solvent and then brings the low CO_2 content solvent, or lean solvent, back to absorb the emitted CO_2 again. Temperature of 40 and 80°C are used as absorption and regeneration temperature, respectively. This will be connected to describe another one parameter, cyclic capacity.

Cyclic capacity is the key factor that should be concerned when designing the process. The cyclic capacity of all solvents was obtained at 3 molar solvent concentration and temperature at 40 and 80°C. The results indicate that DMAE gives a greater average cyclic capacity up to 241% and 12% when comparing with MEA and MDEA at the same absorption and regeneration conditions. This makes DMAE requires lower temperature in solution regeneration than both MEA and MDEA which result in lower operating cost of the CO_2 removal process.

5.2 Recommendations

The solubility of CO_2 is one of the solvents properties that should be investigated. However, for the new solvent, the others properties of DMAE should also be studied. For example, the kinetics data or the reaction mechanism between dissolved CO_2 and the solution, the physical properties like viscosity or density at various operating conditions, the corrosion of the solvent, thermal and chemical stability of the solvent at desired operating time and also the biodegradability are required for absorption process design.

The modification for using of this new amine is also of interest, such as, blending of such amine with other amine in the various ratios or using this solvent in the other hybrid system like amine solution promoted the membrane system.

Moreover, pilot plant and, if possible, plant scale-up studies are also necessary in order to apply this new solvent in the practical CO_2 separation process. As a result, data from every order of scale can be utilized for prediction or simulation of the CO_2 capturing phenomena.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

REFERENCES

[1] Bernstein, L., P. Bosch, O. Canziani, Z. Chen, R. Christ, O. Davidson, W. Hare, S. Huq, D. Karoly, and V. Kattsov, *Climate change 2007: synthesis report. An assessment of the Intergovernmental Panel on Climate Change.* Retrieved March, 2007. **20**: p. 2011.

[2] Gupta, M., I. Coyle, and K. Thambimuthu. *CO_2 capture technologies and opportunities in Canada*. in *1st Canadian CC&S Technology Roadmap Workshop*. 2003.

[3] Organization, T.G.G.M., *Thailand Greenhouse Gases Inventory.* 2000.

[4] Wang, M., A. Lawal, P. Stephenson, J. Sidders, and C. Ramshaw, *Post-combustion CO_2 capture with chemical absorption: A state-of-the-art review.* Chemical Engineering Research and Design, 2011. **89**(9): p. 1609-1624.

[5] Metz, B., *Carbon dioxide capture and storage: Special report of the intergovernmental panel on climate change*. 2005: Cambridge University Press.

[6] Kohl, A.L. and R. Nielsen, *Gas purification*. 1997: Gulf Professional Publishing.

[7] Henley, E.J., J.D. Seader, and D.K. Roper, *Separation process principles*. 2011: Wiley.

[8] Thee, H., Y.A. Suryaputradinata, K.A. Mumford, K.H. Smith, G.d. Silva, S.E. Kentish, and G.W. Stevens, *A kinetic and process modeling study of CO_2 capture with MEA-promoted potassium carbonate solutions.* Chemical Engineering Journal, 2012. **210**: p. 271-279.

[9] Smith, K.H., C.J. Anderson, W. Tao, K. Endo, K.A. Mumford, S.E. Kentish, A. Qader, B. Hooper, and G.W. Stevens, *Pre-combustion capture of CO_2—Results from solvent absorption pilot plant trials using 30wt% potassium carbonate and boric acid promoted potassium carbonate solvent.* International Journal of Greenhouse Gas Control, 2012. **10**: p. 64-73.

[10] Lu, S., Y. Ma, C. Zhu, and S. Shen, *The Enhancement of CO_2 Chemical Absorption by K_2CO_3 Aqueous Solution in the Presence of Activated Carbon Particles.* Chinese Journal of Chemical Engineering, 2007. **15**(6): p. 842-846.

[11] Jones, J., H. Froning, and E. Claytor Jr, *Solubility of Acidic Gases in Aqueous Monoethanolamine.* Journal of Chemical and Engineering Data, 1959. **4**(1): p. 85-92.

[12] Lee, J., F.D. Otto, and A.E. Mather, *The solubility of H_2S and CO_2 in aqueous monoethanolamine solutions.* The Canadian Journal of Chemical Engineering, 1974. **52**(6): p. 803-805.

[13] Jou F.Y., M.A.E., and Otto F.D, *Solubility of H_2S and CO_2 in aqueous methyldiethanolamine solutions.* Industrial&Engineering Chemistry Process Design and development, 1982. **21**: p. 539-544.

[14] Jou, F.Y., A.E. Mather, and F.D. Otto, *The solubility of CO_2 in a 30 mass percent monoethanolamine solution.* The Canadian Journal of Chemical Engineering, 1995. **73**(1): p. 140-147.

[15] Jou, F.-Y., F.D. Otto, and A.E. Mather, *Solubility of mixtures of hydrogen sulfide and carbon dioxide in aqueous solutions of triethanolamine.* Journal of Chemical & Engineering Data, 1996. **41**(5): p. 1181-1183.

[16] Isaac E.E., O.F.D., and Mather A.E., *The solubility of mixtures of carbon dioxide and hydrogen sulphide in an aqueous DIPA solution.* The Canadian Journal of Chemical Engineering, 1977. **55**: p. 210-212.

[17] Yeh, A.C. and H. Bai, *Comparison of ammonia and monoethanolamine solvents to reduce CO_2 greenhouse gas emissions.* Science of the total environment, 1999. **228**(2): p. 121-133.

[18] Bishnoi, S. and G.T. Rochelle, *Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility.* Chemical Engineering Science, 2000. **55**(22): p. 5531-5543.

[19] Kadiwala, S., A.V. Rayer, and A. Henni, *High pressure solubility of carbon dioxide (CO_2) in aqueous piperazine solutions.* Fluid Phase Equilibria, 2010. **292**(1): p. 20-28.

[20] Schäffer, A., K. Brechtel, and G. Scheffknecht, *Comparative study on differently concentrated aqueous solutions of MEA and TETA for CO_2 capture from flue gases.* Fuel, 2012. **101**: p. 148-153.

[21] Sønderby, T.L., K.B. Carlsen, P.L. Fosbøl, L.G. Kiørboe, and N. von Solms, *A new pilot absorber for CO_2 capture from flue gases: Measuring and modelling capture with MEA solution.* International Journal of Greenhouse Gas Control, 2013. **12**: p. 181-192.

[22] Choi, W.-J., J.-B. Seo, S.-Y. Jang, J.-H. Jung, and K.-J. Oh, *Removal characteristics of CO_2 using aqueous MEA/AMP solutions in the absorption and regeneration process.* Journal of Environmental Sciences, 2009. **21**(7): p. 907-913.

[23] Taib, M.M. and T. Murugesan, *Solubilities of CO_2 in aqueous solutions of ionic liquids (ILs) and monoethanolamine (MEA) at pressures from 100 to 1600kPa.* Chemical Engineering Journal, 2012. **181**: p. 56-62.

[24] Shim, J.-G., J.-H. Kim, J.H. Lee, and K.-R. Jang, *Highly efficient absorbents for post-combustion CO_2 capture.* Energy Procedia, 2009. **1**(1): p. 779-782.

[25] Jung, J., Y.S. Jeong, Y. Lim, C.S. Lee, and C. Han, *Advanced CO_2 Capture Process Using MEA Scrubbing: Configuration of a Split Flow and Phase Separation Heat Exchanger.* Energy Procedia, 2013. **37**: p. 1778-1784.

[26] Chowdhury, F.A., H. Yamada, T. Higashii, K. Goto, and M. Onoda, *CO_2 Capture by Tertiary Amine Absorbents: A Performance Comparison Study.* Industrial & Engineering Chemistry Research, 2013. **52**(24): p. 8323-8331.

[27] Puxty, G., R. Rowland, A. Allport, Q. Yang, M. Bown, R. Burns, M. Maeder, and M. Attalla, *Carbon dioxide postcombustion capture: A novel screening study of the carbon dioxide absorption performance of 76 amines.* Environmental science & technology, 2009. **43**(16): p. 6427-6433.

[28] Daneshvar, N., D. Salari, H. Zamzami, M. Zarei, and S. AHER, *Absorption of carbon dioxide into I) aqueous solutions of N, N-dimethylethanolamine II) aqueous blends of mono and diethanolamine with N, N-dimethylethanolamine.* Chemical and biochemical engineering quarterly, 2005. **19**(3): p. 297-302.

[29] Yamada, H., F.A. Chowdhury, K. Goto, and T. Higashii, *CO_2 solubility and species distribution in aqueous solutions of 2-(isopropylamino) ethanol and its structural isomers.* International Journal of Greenhouse Gas Control, 2013. **17**: p. 99-105.

[30] Haider, H.A., R. Yusoff, and M. Aroua, *Equilibrium solubility of carbon dioxide in 2 (methylamino) ethanol.* Fluid Phase Equilibria, 2011. **303**(2): p. 162-167.

[31] Singh, P., D. Brilman, and M.J. Groeneveld, *Evaluation of CO_2 solubility in potential aqueous amine-based solvents at low CO_2 partial pressure.* International Journal of Greenhouse Gas Control, 2011. **5**(1): p. 61-68.

[32] Maneeintr, K., R.O. Idem, P. Tontiwachwuthikul, and A.G. Wee, *Synthesis, solubilities, and cyclic capacities of amino alcohols for CO_2 capture from flue gas streams.* Energy Procedia, 2009. **1**(1): p. 1327-1334.

[33] Ma'mun, S., H.F. Svendsen, K.A. Hoff, and O. Juliussen, *Selection of new absorbents for carbon dioxide capture.* Energy Conversion and Management, 2007. **48**(1): p. 251-258.

[34] Rochelle, G.T., *Thermal degradation of amines for CO_2 capture.* Current Opinion in Chemical Engineering, 2012. **1**(2): p. 183-190.

[35] Eide-Haugmo, I., H. Lepaumier, A. Einbu, K. Vernstad, E.F. da Silva, and H.F. Svendsen, *Chemical stability and biodegradability of new solvents for CO_2 capture.* Energy Procedia, 2011. **4**: p. 1631-1636.

[36] Fredriksen, S. and K.-J. Jens, *Oxidative Degradation of Aqueous Amine Solutions of MEA, AMP, MDEA, Pz: A Review.* Energy Procedia, 2013. **37**: p. 1770-1777.

[37] Lepaumier, H., D. Picq, and P.-L. Carrette, *Degradation study of new solvents for CO_2 capture in post-combustion.* Energy Procedia, 2009. **1**(1): p. 893-900.

[38] Dumée, L., C. Scholes, G. Stevens, and S. Kentish, *Purification of aqueous amine solvents used in post combustion CO_2 capture: A review.* International Journal of Greenhouse Gas Control, 2012. **10**: p. 443-455.

[39] Eide-Haugmo, I., O.G. Brakstad, K.A. Hoff, K.R. Sørheim, E.F. da Silva, and H.F. Svendsen, *Environmental impact of amines.* Energy Procedia, 2009. **1**(1): p. 1297-1304.

[40] Brakstad, O.G., A. Booth, I. Eide-Haugmo, J.A. Skjæran, K.R. Sørheim, K. Bonaunet, S.-H. Vang, and E.F. da Silva, *Seawater biodegradation of alkanolamines used for CO_2-capture from natural gas.* International Journal of Greenhouse Gas Control, 2012. **10**: p. 271-277.

[41] Shen, K.P. and M.H. Li, *Solubility of carbon dioxide in aqueous mixtures of monoethanolamine with methyldiethanolamine.* Journal of chemical and Engineering Data, 1992. **37**(1): p. 96-100.

[42] Aronu, U.E., S. Gondal, E.T. Hessen, T. Haug-Warberg, A. Hartono, K.A. Hoff, and H.F. Svendsen, *Solubility of CO_2 in 15, 30, 45 and 60 mass% MEA from 40 to 120° C and model representation using the extended UNIQUAC framework.* Chemical engineering science, 2011. **66**(24): p. 6393-6406.

[43] Maneeintr, K., A. Henni, R.O. Idem, P. Tontiwachwuthikul, and A.G. Wee, *Physical and transport properties of aqueous amino alcohol solutions for CO_2 capture from flue gas streams.* Process Safety and Environmental Protection, 2008. **86**(4): p. 291-295.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

APPENDIX A

CALCULATION

Calculation of CO_2 loading

CO_2 loading in the amine solution was calculated by titration method using the CO_2 loading analyzer, which can be seen in Chapter III. The method include with two parts: the mole determination of solvent and captured CO_2. The mole of amine solvent was obtained by titration of exact solvent volume with standard 1 molar HCl and methyl orange as indicator. At the endpoint of the titration, the volume of HCl consumed was measured and used to calculate the concentration of the solvent by following equation A.1.

$$C_{amine} = \frac{C_{HCl}V_{HCl}}{V_{amine}} \tag{A.1}$$

Where, C_{amine} = calculated amine concentration, molar

C_{HCl} = standard HCl concentration, molar

V_{HCl} = volume of HCl consumed, cm^3

V_{amine} = volume of sampled amine, cm^3

Mole of the solvent is determined from equation A.2.

$$M_{amine} = \frac{C_{amine}V_{amine}}{1000} \tag{A.2}$$

Substituting equation A.2 by equation A.1, the solution of mole of solvent calculation is obtained and shows in equation A.3.

$$M_{amine} = \frac{V_{HCl}}{1000} \tag{A.3}$$

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

When volume of HCl is in the litre, mole of amine stands for $M_{amine} = V_{HCl}$.

Mole of CO_2 was obtained by measuring all of CO_2 volume that escaped from the amine solvent while titration was performed. CO_2 was first assumed as ideal gas. Therefore, the mole of CO_2 can be calculated at standard conditions for temperature and pressure (STP) condition and then converted to mole of CO_2 at room temperature, 298K (25°C). Equation A.4 shows the determination of mole of captured CO_2.

$$M_{CO_2} = \left(\frac{V_{CO_2}}{22.41}\right)\left(\frac{273}{298}\right) \tag{A.4}$$

Then, CO_2 loading was finally obtained from equation A.5.

$$CO_2 \text{ loading, } \alpha = \frac{M_{CO_2}}{M_{amine}} \tag{A.5}$$

Calculation of cyclic capacity

Cyclic capacity is derived from the difference in equilibrium CO_2 loading at the absorption condition and CO_2 loading at the regeneration condition, 40 and 80°C for this work respectively, and can be illustrated in equation A.6.

$$\text{Cyclic capacity} = \alpha_{absorption} - \alpha_{regeneration} \tag{A.6}$$

Calculation of CO_2 partial pressure

CO_2 partial pressure determines the flow rate of CO_2 for each experiment. Thus, at desired partial pressure of CO_2, the gas flow rate was calculated and is shown in equation A.7.

$$CO_2 \text{ flow rate, } F_{CO_2} = \frac{P_{CO_2} F_{total}}{P_{atm}} \tag{A.7}$$

Where, P_{CO_2} = CO_2 partial pressure, kPa

F_{total} = arbitrary total flow of CO_2 and N_2, ml/min

P_{atm} = atmospheric pressure, kPa

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

APPENDIX B

FLOWMETER CALIBRATION

AALBORG GFM17 flowmeters were used to measure N_2 and CO_2 mass flow and were calibrated by Agilent Technology ADM100 Universal Mass Flowmeter. The examples of calibration curve are illustrated in Figure B.1 through B.4.

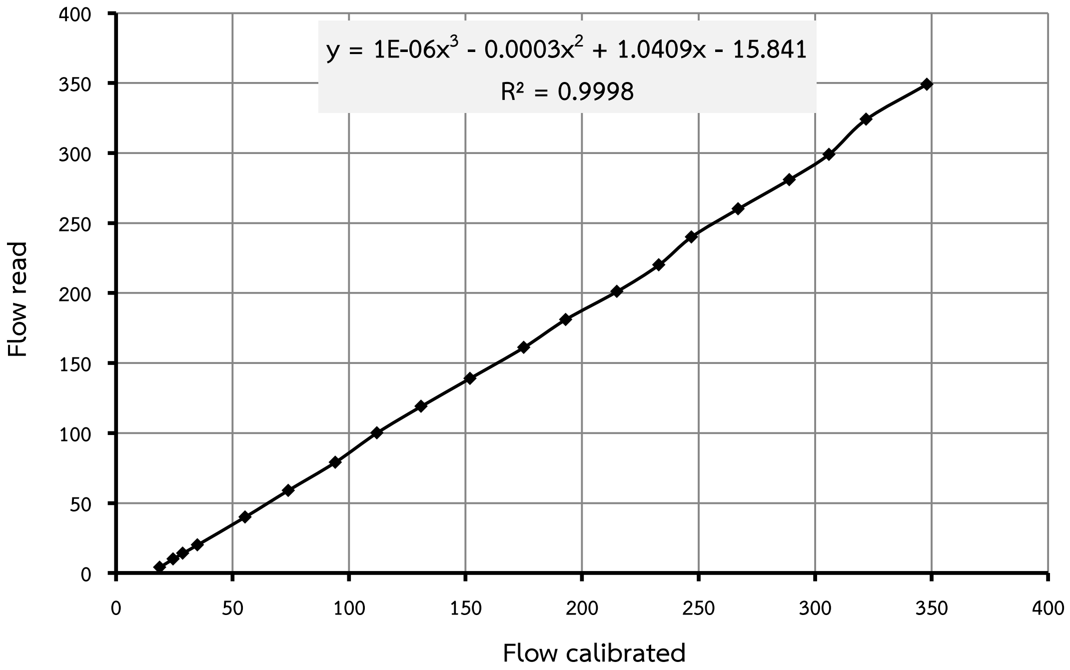


Figure B.1 Calibration curve of N_2 flowmeter in gas line 1

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

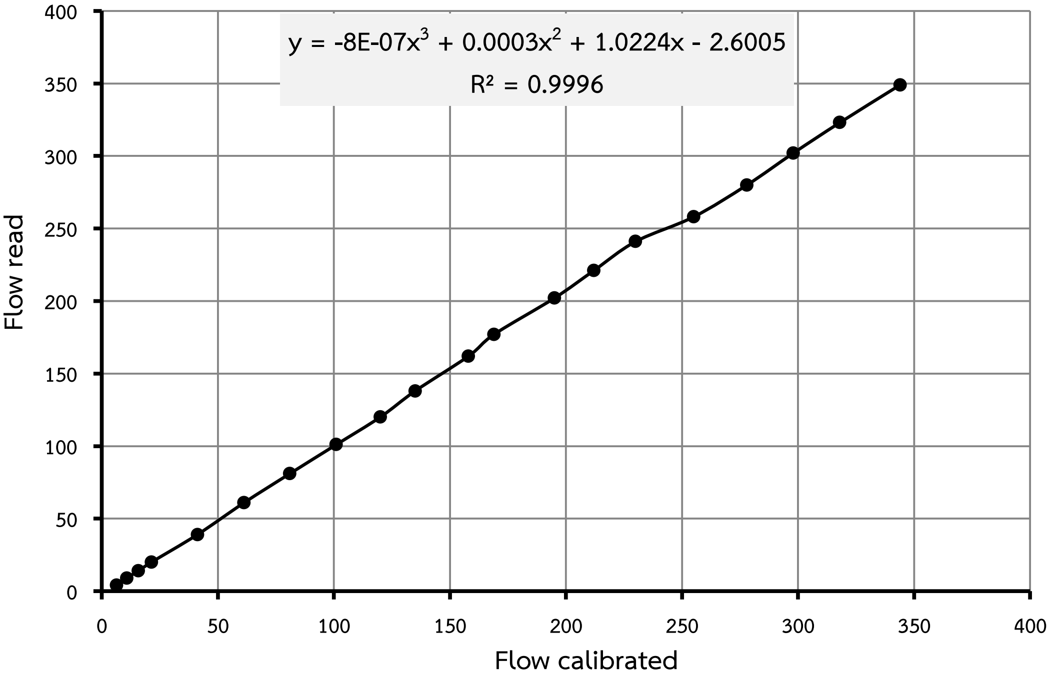


Figure B.2 Calibration curve of CO_2 flowmeter in gas line 1

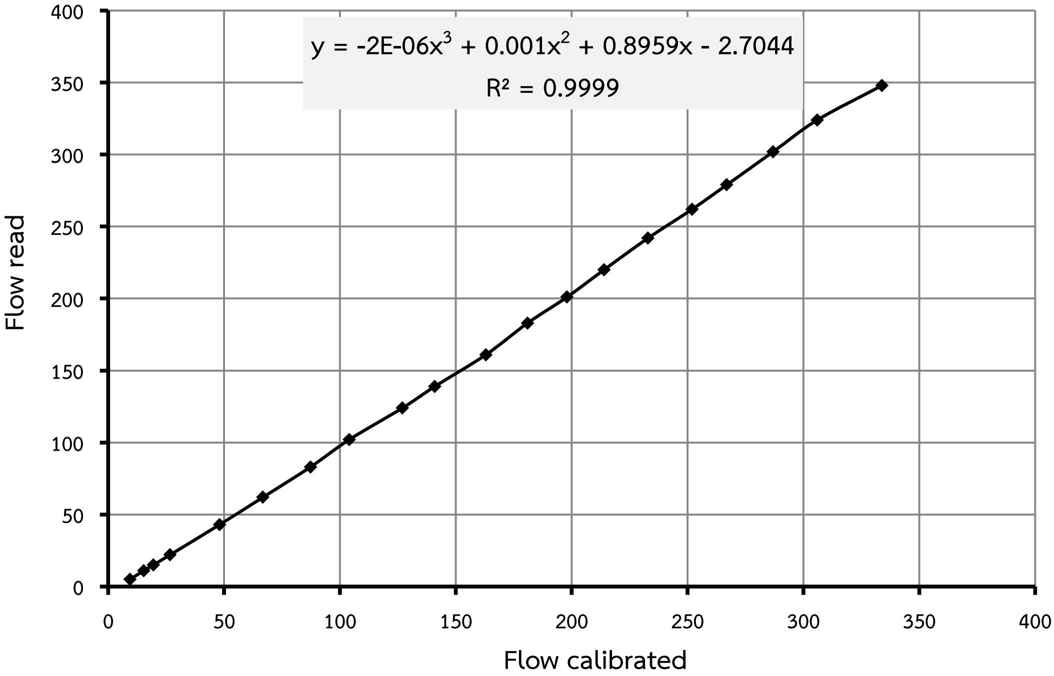


Figure B.3 Calibration curve of N_2 flowmeter in gas line 2

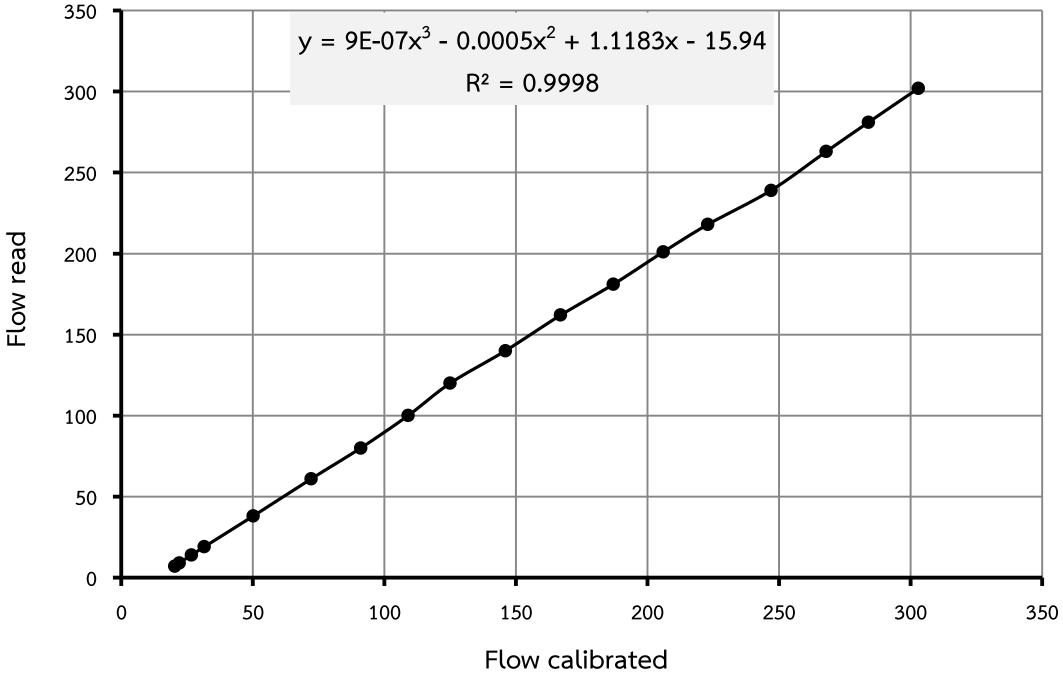


Figure B.4 Calibration curve of CO_2 flowmeter in gas line 2

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

APPENDIX C

EXPERIMENT FORM

The experiment form was created to collect raw data. The volume of HCl that consumed during titration and the volume of emitted CO_2 are recorded. Table C.1 shows this data from.

Table C.1 Experiment data form

V_{DMAE} (ml)	V_{HCl} (ml) (1st time)	V_{HCl} (ml) (2nd time)	$V_{gas\ (per\ tube)}$ (ml)	$V_{gas\ (total)}$ (ml)	V_{CO2} (ml)	Conc of sample (mol/L)	CO_2 loading at 0°C (mol CO_2 /mol sample)	CO_2 loading at 25°C (mol CO_2 /mol sample)	Average
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	
2		12.0		0.0	-12.0	0.00	#DIV/0!	#DIV/0!	#DIV/0!

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

APPENDIX D

LIST OF PUBLICATION

Luemunkong, T., Maneeintr K. and Charinpanitkul T., *Carbon Dioxide Absorption in Aqueous Solution of Dimethylaminoethanol*, Proceedings of International Conference on Business and Industrial Research, 2014: p. 105-108.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

VITA

Mr.Thanaphat Luemunkong was born on 14 May 1990. In 2008, he graduated from high school at Nakhon Nayok Witthayakom, Nakhon Nayok. In 2012, he received bachelor degree at Chemical Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang. And then he received master degree at Chemical Engineering, Faculty of Engineering, Chulalongkorn University in 2014.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY