Analysis of Mass Transfer Coefficient of CO₂ absorbed by Twocomponent Amine Mixture in a Packed Bed Column



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Chulalongkorn University

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ชนกรกาญจน์ ลิ้มเลิศเจริญวนิช : การวิเคราะห์ค่าสัมประสิทธิ์การถ่ายเทมวลของก๊าซการ์บอนไดออกไซด์ที่ถูกดูด ซึมด้วยสารประกอบเอมีน 2 องก์ประกอบในกอลัมน์แบบบรรจุ. (Analysis of Mass Transfer Coefficient of CO₂ absorbed by Two-component Amine Mixture in a Packed Bed Column) อ.ที่ปรึกษาหลัก : ศ. ดร.ชวัชชัย ชรินพาณิชกุล, อ.ที่ปรึกษาร่วม : รศ. ดร. เกรียงไกร มณีอินทร์

ในปัจจุบันอุตสาหกรรมโรงไฟฟ้าถ่านหินได้เข้ามามีบทบาทในการผลิตพลังงานทั่วโลกซึ่งส่งผลก่อให้เกิดภาวะ เรือนกระจกและภาวะโลกร้อน โดยปริมาณก้าซการ์บอนไดออกไซด์ที่เกิดจากการเผาไหม้ของถ่านหินมีปริมาณมากเป็นอันดับ หนึ่งของโลก อย่างไรก็ตามการกำจัดก้าชการ์บอนไดออกไซด์ที่เกิดมามากนั้นมักจะถูกกำจัดด้วยวิธีการดูคซึมทางเกมี เช่น มอ นอเอทานอลามีน แต่อย่างไรก็ตามสารดังกล่าวก็ยังมีข้อเสียอาทิ ก่าความจุวัฏจักรต่ำ และการกัดกร่อน ดังนั้นวิทยานิพนธ์ฉบับนี้ จึงได้ศึกษาปัจจัยต่าง ๆ ที่มีผลต่อการถ่ายเทโอนมวลของสารใหม่ 2 องก์ประกอบเพื่อทดแทนข้อด้อยของมอนอเอทานอลามีน เพื่อเพิ่มประสิทธิภาพการถ่ายเทโอนมวล และเพิ่มประสิทธิภาพในการดักจับก๊าซการ์บอนไดออกไซด์ ได้แก่ 2-เมทิลอะมิโนเอ ทานอล และใดเมทิลอะมิโนเอทานอล โดยศึกษาอิทธิพลความเข้มข้นอัตราส่วนโดยมวลตั้งแต่ร้อยละ 30:0 จนถึง 0:30 โดย น้ำหนัก อิทธิพลอัตราการไหลของสารดูคซึมที่ 5.3 10.6 และ 15.9 ฉูกบาศก์เมตรต่อตารางเมตรต่อชั่วโมง อิทธิพล ปริมาณกร์บอนไดออกไซด์ไนวัฏจักรก๊าซที่ร้อยละ 5 10 และ 15 โดยปริมาตร อิทธิพลปริมาณการ์บอนไดออกไซด์ อ่ารังเมตรต่อชั่วโมง อิทธิพล ปริมาณกร์บอนไดออกไซด์ไนวัฏจักรก๊าซที่ร้อยละ 5 10 และ 15 โดยปริมาตร อิทธิพลปริมาณกร์บอนไดออกไซด์จาเข้า ในสารดูคซึม 0.0 0.1 และ 0.2 โมลต่อโมล พบว่า การเพิ่มปริมาตรของ 2-เมทิลอะมิโนเอทานอลในสารผสมช่วยเพิ่ม อัตราการถ่ายเทโอนมวลและเพิ่มก่าการดูคซึมของกร์บอนไดออกไซด์ ในทางกลับกันการเพิ่มปริมาตรของไดเมติลอะมิโนเอทา นอลในสารผสมส่งผลให้เกิดการถ่ายเทโอนมวลที่ช้าที่สุด ปัจจัยที่มีผลต่อการถ่ายเทโอนมวลมากที่สุดคืออิทธิพลของอัตราการ ไหล จะช่วยเพิ่มการถ่าทีกบาบิจนอไปข้างหน้าและช่วยอดเวลาในการดูคซึมที่น้อยลง แต่อย่างไรก็ตามการใช้สารเกมิ 2 องก์ประกอบสามารถแก้ไขข้อเสียของสารเดี่ยวได้เป็นอย่างดี และแสดงให้เห็นถึงว่าสารชนิดใหม่มีความเป็นไปได้ว่าจะเป็นสาร ดูคซึมที่จะมีประโยชน์ต่อไปในอนาคต



สาขาวิชา รี ปีการศึกษา 2

วิศวกรรมเคมี 2563

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6070199421 : MAJOR CHEMICAL ENGINEERING KEYWOR CO2 ABSORPTION / PACKED COLUMN / VOLUMETRIC D: OVERALL MASS TRANSFER COEFFICIENT / MONOETHANOLAMINE / 2-(METHYLAMINO)ETHANOL / DIMETHYLAMINOETHANOL

Thanakornkan Limlertchareonwanit : Analysis of Mass Transfer Coefficient of CO_2 absorbed by Two-component Amine Mixture in a Packed Bed Column. Advisor: Prof. Dr. TAWATCHAI CHARINPANITKUL, D.Eng. Co-advisor: Assoc. Prof. Dr. Kreangkrai Maneeintr, Ph.D.

Nowadays, coal fired plant has an important role in generating energy all over the world. It affects to greenhouse gases effect (GHGs) and global warming. Carbon dioxide (CO_2) is a product of coal combustion that is the amount of number one in the world. However, most of the CO₂ usually remove from post-combustion process by chemical absorption which is Monoethanolamine (MEA). Anyway, MEA has a disadvantage such as low CO₂ loading and corrosion. Therefore, this study needs to investigate the effect of the mass transfer for a new solvents, 2-(Methylamino)ethanol (2-MAE) and Dimethylaminoethanol (DMAE), compensate for the drawbacks of MEA to increase in mass transfer rate and performance of CO₂ absorption. Effect of amine concentration by varying weight ratio from 30:0 to 0:30 wt%, liquid flow rate 5.3,10.6 and 15.9 m³/m²•h, CO₂ content in gas phase 5,10 and 15 %v/v, CO₂ initial loading 0.0, 0.1 and 0.2 mol/mol were investigated. From the results, increasing the ratio of 2-MAE in mixed solution increases the highest mass transfer rate and CO₂ absorption performance. On the other hand, increasing the ratio of DMAE decreases the mass transfer rate. The most influencing factor for mass transfer is the flow rate of solution that improves the forward rate of reaction and reduced time for dissolved CO₂. However, two-component of amine solution can improve the drawback of a single-component very well. It can be seen that a new solvent will be useful in the future.

Chulalongkorn University

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Co-advisor's Signature

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Thanakornkan Limlertchareonwanit

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CHAPTER I

INTRODUCTION

1.1 Background and motivation

Currently, climate change is one of the main problems of the world and affects all life, due to an increase in temperature at 1.5° C every year [1]. The problem of climate change is caused by more Greenhouse Gases (GHGs) in the atmosphere which the main current GHGs emission is mostly generated by human activities and industrial activities. Figure 1.1 shows the components of GHGs. The component of GHGs is 81% of carbon dioxide (CO₂), 10% of methane (CH₄), 6% of nitrous oxide (NO₂) and 3% of fluorinated gases [2]. CO₂ is the highest ratio component of GHGs and tends to increase every year. Therefore, CO₂ must be removed to the least ratio.

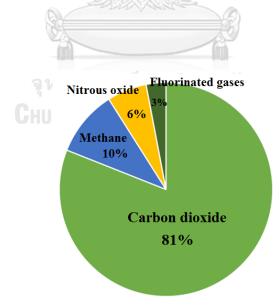


Figure 1.1 The component of greenhouse gases emissions in 2018

GHGs are an element covering of the earth atmosphere and keep the surface temperature warm enough for life balance. It could be absorbed the heat in the atmosphere at day and released the heat at night. If without the GHGs cover the surface, the earth surface temperature would be at -21° C [3]. However, an increase in the GHGs in the atmosphere is resulting in global warming, especially CO₂ causing a life imbalance on the earth due to overheating in the atmosphere. The amount of CO₂ is produced by burning fuel (coal, biomass, natural gas), industry, vehicles and buildings [4]. In addition, there is the advantages of CO₂ such as the main reactant of production a chemical (methane, methanol, urea), dry ice, soft drink and CO₂ cylinder for the experiment. On the other hand, CO₂ is the main component of GHGs issue adversely affects the environment. Therefore, there are many researchers trying to capture excess CO₂ from industrial to storage and to use to the other industries.

1.2 CO₂ emission sources

Figure 1.2 shows the main sources of CO_2 . These sources find from electricity and transportation are the same value at 34% and followed by 15% of total CO_2 emission from industry, 10% of total CO_2 emission from commercial & residential and 6% of total CO_2 emission from other sources [2]. Similarly, the production of electricity from the power generation sector impacts to the environment, whereas power generation is very important in generating electricity for living use, whether using in home, industry, hospital and other places. Therefore, the process needs to control the release of CO_2 to save environmental and prevent global warming.

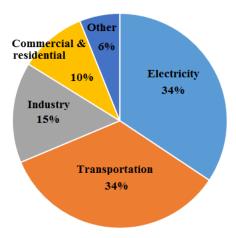


Figure 1.2 CO₂ emission by economic sectors in 2018

1.3 Types of combustion process

Power generation sector is the main source to release the CO_2 into the environment. Therefore, CO_2 must be captured from this sector to reduce environmental problems and transport for storage. There are three main processes that power generation uses to generate electricity from fossil fuel and captures the carbon dioxide: post-combustion process, pre-combustion process and oxy-fuel combustion.

จุฬาลงกรณมหาวทยาลัย

1.3.1 Post-combustion

Post-combustion is the capture of CO_2 from the downstream after fuel combustion: Pulverized Coal Combustion (PCC) and Natural Gas Combined Cycle (NGCC) usually use this technology. The main fuels in this process have combustion with air and fuel, and the latest product of this process is CO_2 and steam. Steam is separated and applied to the conventional process heaters and industrial utility boilers, and CO_2 is captured in the last process. The commonly used technology can be captured CO_2 by chemical absorption with an amine solution. The concentration of CO_2 from this process is 12-15 % v/v from coal and 4-8 % v/v from natural gas [5].

1.3.2 Pre-combustion

Pre-combustion process is the process of converting fuels to CO and H₂ by gasification (by coal and air). CO is converted to CO₂ by water-gas shift and the other product of this process is H₂. H₂ from all processes (gasification and water-gas shift) used to rotate the turbine to generate electricity and CO₂ is separated into the storage. The concentration of CO₂ in this process is 25-40 % v/v and total pressure in the range is 2-5 MPa [5]. Power generation sector: Integrated Gasification Combined Cycle (IGCC) usually uses this technology.

1.3.3 Oxy-fuel combustion

Oxy-fuel combustion process is similar to post-combustion process whereas different air inlet is fed by oxygen (O₂) for combustion. Steam obtained from the process use to rotate the turbine to generate electricity. The concentration of CO_2 is more than 80 %v/v and CO_2 capture technology usually uses cryogenic [5].



1.4 Carbon dioxide capture technologies

This section describes the CO_2 capture process that is commonly used in the industries. There are many ways to capture the CO_2 which is emitted from fossil fuel power generation. These are as follows absorption, adsorption, cryogenic and membrane. Post-combustion process is generated by burning fossil fuels with air and becoming to flue gas. Flue gases consist of NOx, SOx, CO, H₂O and CO₂. The concentration of CO_2 in the system is 12-15% and N₂ is 85-88% from coal. The factors to select the technology to carbon dioxide capture depends on many factors

such as partial pressure of carbon dioxide, acid gases, purity of carbon dioxide and cost [5].

1.4.1 Chemical and Physical absorption

Absorption process is a high efficiency of CO_2 removal [6]. In term of Chemical absorption, Monoethanolamine (MEA) is the most widely used as an absorbent in commercial because there are many advantages such as capability to capture carbon dioxide at low partial pressure, high carbon dioxide capture efficiency and high mass transfer rate, whereas, there is high regenerated energy (as much as 80% of the total energy consumption) and corrosion [5]. However, there are new chemical absorbents such as 2-Methylaminoethanol (2-MAE), Dimethylaminoethanol (DMAE), 3-Amino-1-Propanol (3A1P) and 1-Dimethylamino-2-Propanol (1DMA2P) [7] that was studied the CO₂ absorption in the laboratory for developing the drawback of MEA. In this process, CO₂ is dissolved into a solvent, amine molecules would react with CO₂ molecules and become bicarbonate and carbamate. The operating condition with absorption is at 40°C (1 atm) and desorption is at 80-120°C (1 atm) [8]. The solvent can be regenerated by heat reduction and CO₂ is separated out of the solvent. Therefore, many industries usually have absorption and desorption column in this system. In terms of physical absorption, this process is suitable for using high pressure to absorb CO_2 and combine with CO_2 without any reactions and usually use an organic solvent such as methanol [5].

1.4.2 Adsorption

Adsorption process is the reaction between gases and surface of solid adsorbent. The main criteria for adsorbent selection are temperature, partial pressure, large specific surface area, pore size, high selectivity and high regeneration [5] such as activated carbon, zeolites, calcium oxides, hydrotalcites and lithium zirconate are adsorbing agents. For this process, carbon dioxide is fed to the surface of solid adsorbent in the packed column, but solid adsorbent can adsorb only carbon dioxide and other gases will pass to outside. After solid adsorbent is fully loaded with CO₂, it is regenerated to remove carbon dioxide by pressure swing adsorption (PSA) and temperature swing adsorption (TSA) [5]. Thus, this process is suitable for a small industrial scale.

1.4.3 Cryogenics

Cryogenic technology is widely used in commercial for purified a high concentration of CO_2 at 90-95%. The process is gas separation by using a very low temperature and high pressure. CO_2 is converted to solid, which is cooled at a temperature at -100°C to -135°C and compressed to high pressure at 100-200 atm to separate from other gases [5]. However, a disadvantage of this process uses more energy for refrigeration. Therefore, pre-combustion and oxy-fuel combustion are suitable for this technology with a high CO_2 concentration.

1.4.4 Membrane

Membrane is made of composite polymer with a thin selective layer and is allowed only CO_2 to pass. Gas separation membrane of a gas depends on the pressure from one side to the other side as the driving force and relies on the differences in physical or chemical interactions between gas and a membrane. Gas absorption membrane is microporous solid membranes that used as contact between gas and liquid. CO₂ diffuses through the membrane and is removed by the liquid absorbent [5].

From the previous works, there are 3 researchers; Luemunkong [9], Photien [10] and Vaewhongs [11] from the Center of Excellence in Particle Technology and Material Processing (CEPT) in Chulalongkorn University. Luemunkong and Photien studied effect of CO_2 solubility with partial pressure in monoethanolamine (MEA), 2methylaminoethanol (2-MAE) and dimethylaminoethanol (DMAE) with singlecomponent and two-component amine solution for capturing CO₂, respectively. Vaewhongs (2017) studied the overall mass transfer coefficient (K_Ga_v) in the packed absorption column with a single-component amine solution. Also, the two-component amine solution is interesting for this work because the previous works reported the performance of the ability of solute and capture of CO₂. The results showed the advantages and disadvantages of amine solution. For example, MEA can be a faster reaction with CO₂ whereas a lower CO₂ loading than DMAE. Thus, two-component amine solution is an alternative to another way to improve the disadvantages of a single-component amine solution for these problems. Moreover, 2-MAE and DMAE is a new solvent which is not studied in mass transfer coefficient. Therefore, a new solvent is studied in this work.

In this study, the chemical absorption with a good absorption to remove CO_2 such as MEA, 2-MAE will be investigated in the viewpoint of basic knowledge in gas-liquid mass transfer of CO_2 . A significance of volumetric overall mass transfer coefficient (K_{Gav}) is a factor to design the height of an effective absorption column. In general, random packed column can be operated in the ambient temperature and

pressure in the atmosphere, with an advantage of much surface area for contacting between gas phase and liquid phase. Packed absorption method is suitable for a low CO_2 concentration and large-scale plant, which is widely used natural and coal power plant. Thus, this method is chosen to study with a two-component amine solution.

Therefore, this thesis would be dedicated to fundamental investigation to remove CO_2 using a random packed column with a focus on determining the volumetric overall mass transfer coefficient (K_Ga_v). MEA, 2-MAE and DMAE were selected as the liquid absorbents in the column to compare the absorption of a single-component and two-component for determining the K_Ga_v which would be referable for designing a height of a packed column to use in the future.

1.5 Objective

To analyze volumetric gas-phase mass transfer coefficient of CO₂ which is experimentally absorbed in a packed bed column using two-component amine mixture.

1.6 Scope

The scope of work of research is to investigate the mass transfer coefficient in two-component amine. The parameters of this work are type of alkanolamine, amine concentration, liquid flow rate, CO_2 content in gas phase and CO_2 initial loading in amine solution. This section discusses the parameters of the experiment at various conditions.

Table 1 Scope of experiment

Variable	Range
	MEA:2-MAE
Type of alkanolamine	MEA:DMAE
	2-MAE:DMAE
Amine concentration, wt%	30:0, 20:10, 15:15, 10:20, 0:30
Liquid flow rate, $m^3/(m^2 \cdot h)$	5.3, 10.6, 12.9
CO_2 content in gas phase, %v/v	5, 10, 15
CO ₂ initial loading in amine solution,	0.0, 0.1, 0.2
mol/mol	

1. Types of mixed solution; three different types of alkanolamine are combined together for comparing the CO_2 absorption between primary into secondary, primary into tertiary, and secondary into tertiary amine.

2. Amine concentration; it is fixed to a maximum of 30 wt% because the concentration is currently used for commercial. If the concentration is used at higher concentration, the corrosion will affect in the system. The mixed amine solutions are determined at a different ratio to determine effect of amine concentration within mixed solution.

3. Liquid flow rate is compared effect of the different liquid flow rate in the column.

4. CO₂ content in gas phase of mixed amine solution at 5, 10, 15 % v/v(CO₂ concentration in the post-combustion process is 15 % v/v from coal and 5 % v/v from natural gas). 5. CO_2 initial loading in amine solution; it is fixed with 0.0, 0.1 and 0.2 mol/mol. 0.0 mol/mol is a fresh solution for using in the experiment. Meanwhile, 0.1 and 0.2 mol/mol are the CO_2 concentrations in amine solution after regenerating the solution. Thus, to study and compare the different CO_2 initial loading in solution.

The thesis consists of 5 chapters with the key focus on overall mass transfer coefficient in a two-component amine solution system. Chapter 1 describes the general overall introduction to CO₂ capture of the thesis work while Chapter 2 describes the mass transfer in the gas into the liquid by a thin boundary layer on the liquid and provides a literature review of the study. Chapter 3 shows the experimental section. Chapter 4 discusses the mass transfer results between a single-component, MEA, 2-MAE and DMAE, and two-component amine, MEA:2-MAE, MEA:DMAE and 2-MAE:DMAE. Finally, chapter 5 provides a summary of the conclusion and recommendations for future work.

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CHAPTER II

THREOY AND LITERATURE REVIEWS

2.1 Chemical absorption process

2.1.1 Process description

According to Figure 2.1, the process flow diagram of chemical absorption process is presented. Flue gas is fed at the bottom and amine solution is fed into the top of the absorber column. Gas and liquid contact and react with each other. CO_2 is dissolved into the amine solution and the absorption process starts in this part. Absorption process is an exothermic reaction and the temperature occurs at 40°C. Amine solution that absorbs CO_2 is called rich amine. Then, other gases flow out of the absorber column. Rich amine flows through a heat exchanger for increasing the temperature and flow into the top of the stripping column. In the stripping column, there is a reboiler for heating this column to regenerate the solution. The temperature from reboiler in the column is $120^{\circ}C$ [8]. Rich amine flows down from the top of the stripper column. Meanwhile, CO_2 bond is heated and destroyed, rich amine is becoming to lean amine. CO_2 flows out of the stripper column and condensation in storage [12]. Finally, lean amine is fed into the top of the absorber column for using the absorption process [13].

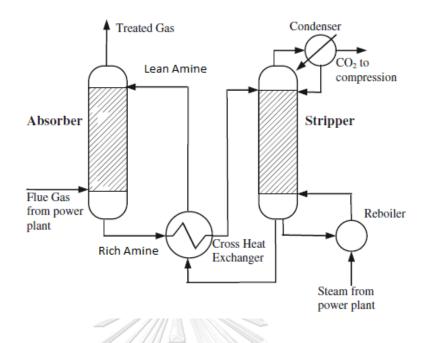


Figure 2.1 Chemical absorption process

2.2 Solvents for CO₂ absorption

Amine solution is commonly used to capture CO_2 in power plant. There is amino group and hydroxyl group in the structure of amine. In term of amino group, this is an alkalinity and can react with CO_2 . In term of hydroxyl group, that is helpful in water solubility. There are 3 different types of amine; primary amine, secondary amine and tertiary amine, which the different types of amine are the number atom of hydrogen with atom bonding of nitrogen. However, tertiary amine represents with no atom of hydrogen bonding with the atom of nitrogen. The amine solution is shown in Table 2.

Alkanolamine	Structures	Туре	Mw (g/mol)
Monoethanolamine (MEA)	H ₂ N OH	primary	61.08
2-methylaminoethanol (2-MAE)	H₃C ^{-N} ∕ОН	secondary	75.11
Dimethylaminoethanol (DMAE)	CH₃ H₃C ^{-N} OH	tertiary	89.14

The mechanism between CO₂ and amines can be described below [14];

- Dissociation of water $H_2O \leftrightarrow H^+ + OH^-$ (2.1)
- Hydrolysis of CO2

$$H_2O + CO_2 \leftrightarrow H^+ + HCO^{3-}$$
(2.2)

• Dissociation of bicarbonate ion

$$HCO^{3-} \leftrightarrow H^+ + CO_3^{2-} \tag{2.3}$$

• Protonation of amine

$$RNH_2 + H + \leftrightarrow RNH^{3+}$$
(2.4)

• Carbamate formation

$$\text{RNH}_2 + \text{CO}_2 \leftrightarrow \text{RNHCOO}^- + \text{H}^+$$
 (2.5)

Reaction (2.1) to (2.5) shows the reaction between amine molecule and CO_2 molecule. Primary and secondary amine can be formed all reaction. The reaction of amine and CO_2 can be changed to be carbamate. Main reaction of primary and secondary amine is shown in (2.6) and (2.7).

• Primary amine (1st) :

$$2RNH_2 + CO_2 \leftrightarrow R_1NCOO^- + RNH^{3+}$$
(2.6)

• Secondary amine (2nd) :

$$2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^- + R_1R_2NH^{+2}$$
(2.7)

The reaction of tertiary amine is shown in (2.1) to (2.4). Tertiary amine cannot directly react with CO_2 because no hydrogen atom to form carbamate. Thus, main reaction of tertiary amine is shown in (2.8).

• Tertiary amine (3rd) :

$$R_1R_2R_3N + CO_2 + H_2O \leftrightarrow R_1R_2R_3NH^+ + HCO^{3-}$$
(2.8)

2.2.1 Amine solutions on a KORN UNIVERSITY

1) Monoethanolamine (MEA) is the primary amine and widely used to the commercial for capturing CO_2 in power plant. There are two hydrogen atoms in nitrogen atom. The advantages of MEA are high mass transfer rate, fast kinetic rate and low molecular weight. And the disadvantages of MEA are low CO_2 loading, high heat of regeneration and corrosion [15]. MEA can be regenerated the solvent at temperature 80-120°C. However, the corrosion is the problem in system. The commercial need to save the equipment and limit the concentration at 5 M or 30 wt%. 2) 2-methylaminoethanol (2-MAE) is the secondary amine. This solution was developed by Haider et al. [16]. There are one hydrogen atom and one methyl group in nitrogen atom. Hydrogen is replaced by methyl group. This result affects to a decrease the dipole-dipole interaction. The result of 2-MAE reported a great CO_2 loading and low heat of regeneration than MEA.

3) Dimethylaminoethanol (DMAE) is the tertiary amine. There are two methyl group with nitrogen atom. All hydrogens are replaced by methyl groups. DMAE cannot directly react with CO₂. However, CO₂ loading of DMAE is higher than MAE [9] and interesting to use with the absorption column.

2.2.2 Mixed amine solution

Mixed amine solution is interesting and a new way to CO_2 absorption. Shen et al. [17] and Photien et al. [10] studied the CO_2 solubility with the mixing ratio. The results showed that an increase in the ratio of secondary and tertiary amine in primary amine affects an increase in CO_2 loading significantly, reflecting the performance of CO_2 solubility with mixed amine.

2.3 Mass transfer principles

Mass transfer coefficient is an important for designing the packed column. At each point of the column, mass transfer occurs between gas and liquid phases. A liquid is soaked onto the packing with a thin film and the gases are contacted and dissolved into the liquid phase. The mass transfer ends when it is reached in equilibrium. Figure 2.2 shows the concept of "Two Film Theory".

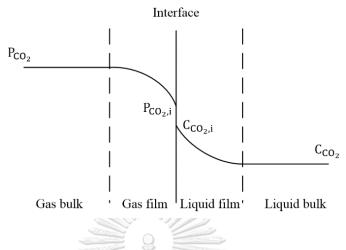


Figure 2.2 Two film theory concept

Two film theory is suggested by Whitman [18], [19], [20]. This film is a thin film between the gas-liquid interface and mass transfer occurs in this area. CO_2 concentration in bulk gas is defined in term of partial pressure (p_{CO_2}) and bulk liquid is defined in term of concentration (c_{CO_2}). Mass transfer depends on the concentration difference or driving force in the system. At steady state, CO_2 transfers to the gasliquid interface and equals its transfer rate through liquid film side. It can write the molar flux as proportionality to concentration difference in Equation (2.9) and (2.10)

$$N_A = k_G(P - P_i) = k_L(C_i - C)$$

• Molar flux from gas-phase to interface

$$N_{CO_2} = k_G (p_{CO_2g} - p_{CO_2j})$$
(2.9)

• Molar flux from liquid-phase to interface

$$N_{CO_2} = k_L (c_{CO_{2,i}} - c_{CO_{2,L}})$$
(2.10)

Henry's law is the two equilibrated interfacial concentration between $p_{CO_{2,i}}$ and $c_{CO_{2,i}}$ on the gas and liquid sides, can be written in Equation (2.11)

$$P_{CO_2} = HC_{CO_{2,i}}$$
(2.11)

From Equation (2.9) and (2.10), mass transfer coefficient is difficult to determine because no equipment can measure the interfacial concentration ($p_{CO_{2,i}}$ and $c_{CO_{2,i}}$). Thus, it is convenient to define the overall mass transfer coefficient in gas phase (K_G) and liquid phase (K_L) which uses Henry's law, and can be shown in Equation (2.12)

$$N_{CO_2} = K_G(p_{CO_{2,g}} - p_{CO_2}^*) = K_L(c_{CO_2}^* - c_{CO_{2,L}})$$
(2.12)

where, $p_{CO_2}^* =$ gas-side concentration that would be in equilibrium with

liquid-phase concentration

 $c_{CO_2}^*$ = liquid-side concentration that would be in equilibrium with

gas-phase concentration

From Equation (2.9) and (2.12) in gas-side

 $k_{G}(p_{CO_{2,g}} - p_{CO_{2,i}}) = K_{G}(p_{CO_{2,g}} - p_{CO_{2}}^{*})$

$$\frac{1}{K_{G}} = \frac{1}{k_{G}} \frac{(p_{CO_{2,g}} - p_{CO_{2}})}{(p_{CO_{2,g}} - p_{CO_{2,i}})}$$

$$\frac{1}{K_{G}} = \frac{1}{k_{G}} \frac{\left(p_{CO_{2,g}} - p_{CO_{2}}^{*}\right) + \left(p_{CO_{2,g}} - p_{CO_{2,i}}\right)}{p_{CO_{2,g}} - p_{CO_{2,i}}}$$

$$\frac{1}{K_{G}} = \frac{1}{k_{G}} + \frac{1}{k_{G}} \frac{(p_{CO_{2,g}} - p_{CO_{2}}^{*})}{(p_{CO_{2,g}} - p_{CO_{2,i}})}$$
(2.13)

From Equation (2.13), Equation (2.14) becomes

$$\frac{1}{K_{G}} = \frac{1}{k_{G}} + \frac{1}{k_{L}} \frac{(p_{CO_{2,i}} - p_{CO_{2}}^{*})}{(p_{CO_{g}} - p_{CO_{2,i}})}$$
(2.14)

Two forms of total resistance, the overall mass transfer coefficient can be calculated by deriving Equation (2.14) with Henry's law as Equation (2.15) and (2.16)

$$\frac{1}{K_{\rm G}} = \frac{1}{k_{\rm G}} + \frac{H}{k_{\rm L}}$$
(2.15)

$$\frac{1}{K_{\rm L}} = \frac{1}{k_{\rm L}} + \frac{1}{k_{\rm G} {\rm H}}$$
(2.16)

Enhancement factor (I) is defined as the ratio of liquid mass transfer coefficient with chemical reaction and without chemical reaction which defined that the absorption rate increases due to the reaction or not. If I = 1, chemical reaction will not affect the absorption, whereas I > 1 chemical reaction affects the absorption. It can be written in Equation (2.17) and (2.18)

$$\frac{1}{K_{G}} = \frac{1}{k_{G}} + \frac{H}{lk_{L}}$$

$$\frac{1}{K_{L}} = \frac{1}{lk_{L}} + \frac{1}{k_{G}H}$$
(2.17)
(2.18)
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2.4 Mass transfer coefficient in packed column

2.4.1 Determination of overall mass transfer coefficient

Overall mass transfer coefficient in packed column is based on unit volume of the absorber. Thus, Equation (2.12) is multiplied both sides by a_v which is specific area of contactor. In term of partial pressure, it takes with total pressure which is P=py. Overall mass transfer coefficient based on unit volume is shown in Equation (2.19)

$$N_{CO2}a_v = K_G a_v P(y_{CO_{2,g}} - y^*_{CO_{2,i}})$$
(2.19)

 $N_{CO2}a_v$ could not be directly calculated to determine K_Ga_v . Thus, $N_{CO2}a_v$ is changed by using mass balance in part of the elemental section. In steady state, mass balance must be equal inlet and outlet. It could be written as Equation (2.20) and (2.21)

$$G_{CO_2}|_{z+\Delta z} - G_{CO_2}|_z = N_{CO_2}a_v dz$$
 (2.20)

$$G_{CO_2}|_z = G_I\left(\frac{y_{CO_2,g}}{y_{N_2,g}}\right)|_z = G_I\left(\frac{y_{CO_2,g}}{1-y_{CO_2,g}}\right)_z$$
 (2.21)

Substitute Equation (2.21) into Equation (2.20) would provide

$$N_{CO_{2}}a_{v}dz = G_{I}\left(\frac{y_{CO_{2},g}}{1 - y_{CO_{2},g}}\right)_{z+\Delta z} - G_{I}\left(\frac{y_{CO_{2},g}}{1 - y_{CO_{2},g}}\right)_{z}$$

$$N_{CO_{2}}a_{v} = G_{I}\frac{d\left(\frac{y_{CO_{2},g}}{1 - y_{CO_{2},g}}\right)}{dz}$$
(2.22)

Equation (2.22) could be written in a term of $Y = \frac{y_{CO2,g}}{1-y_{CO2,g}}$

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$$N_{\text{CO}_2} \mathbf{a}_{\text{v}} = \mathbf{G}_{\text{I}} \frac{\mathrm{dY}}{\mathrm{dz}}$$
(2.23)

Substitute Equation (2.23) into Equation (2.19) and move the other side to calculate the K_{Ga_V}

$$G_{I} \frac{dY}{dz} = K_{G} a_{v} P(y_{CO_{2,g}} - y_{CO_{2,i}}^{*})$$
$$K_{G} a_{v} = \left(\frac{G_{I}}{P(y_{CO_{2,g}} - y_{CO_{2}}^{*})}\right) \left(\frac{dY}{dz}\right)$$
(2.24)

where, K_{Gav} = Overall volumetric mass transfer coefficient in gas phase

GI = Inert gas flow rate

P = Total pressure

 $y_{CO_2,g}$ = Mole fraction of CO₂ in bulk gas

 $y_{CO_2}^*$ = Mole fraction of CO₂ that equilibrium with $c_{CO_2,i}$

 $\frac{dY}{dz}$ = Concentration gradient with CO₂ molar ratio

2.5 Literature reviews

In In this work, 2-MAE and DMAE are chosen to study the performance of overall mass transfer in packed column because these solvents are higher solubility than MEA. The important factor for choosing the chemical to absorb CO_2 is cyclic capacity. Cyclic capacity is the difference equilibrium solubility of CO_2 loading in absorption and desorption [7] that compare the capacity of CO_2 loading.

Haider et al. [16] studied and compared the solubility between primary amine (MEA) and secondary amine (2-MAE) at 2 M. The results showed that 2-MAE is a higher CO₂ loading than MEA. 2-MAE is higher CO₂ loading in every partial pressure because of 2-MAE is unstable carbamate formation and is hydrolyzed with water. Meanwhile, Luemunkong et al [9] studied the solubility of MEA and MDEA (methyldiethanolamine) at 3 M. MDEA is a higher ability in CO₂ absorption than MEA. CO₂ solubility is sensitive to change CO₂ partial pressure and indicates good performance. Photien et al. [10] studied and compared the solubility of mixed amine solution. An increase in the ratio of secondary and tertiary amine is an increase in cyclic capacity. Thus, secondary and tertiary amine affect the CO₂ loading higher than

primary amine significantly. This work is consistent with previous works with a term of amine solution and results.

Perinu et al. [21] studied CO₂ solubility with blended amine solution between 3-(Methylamino)propylamine or MAPA, which is secondary amine, and tertiary amine (DEEA, EDEA, t-BDEA, BDEA and TEA) at 1:3 ratio. After absorption of CO₂, following this trend: MAPA-DEEA > MAPA-EDEA > MAPA-t-BDEA > MAPA-BDEA > MAPA-TEA. It can be explained that the difference in structure and number of -OH and the number of carbons in the alkyl chain of the tertiary amine was reacted with CO₂.

Hairu et al. [22] studied the overall mass transfer coefficient (K_Ga_v) for CO₂ absorption performance of MEA. The experiments were conducted in packed absorption column with Sulzer metal gauze packing. They reported that K_{Ga_v} was in crease with increasing MEA flow rate and MEA concentration whereas gas flow rate was not affected.

Vaewhongs et al. [11] studied the overall mass transfer coefficient (K_{Gav}) within CHULALONGKORN UNIVERSITY packed absorption column with the Raschig rings. MEA, 2-MAE and DMAE are chosen to study in this work. 2-MAE is the highest K_{Gav}, follow with MEA and DMAE, respectively. The results showed that, 2-MAE provided a better performance of mass transfer than MEA and DMAE.

Le et al. [23] studied the mass transfer performance for CO_2 absorption with tertiary amine, 1-dimetylamino-2-propanaol (1DMA2P) and compared with MDEA. The experiments were investigated in a packed column with random DX packing. As a result, 1DMA2P provided greater K_{Gav} than MDEA. Both of 1DMA2P and MDEA,

amine concentration and amine flow rate increase leading to K_{Ga_v} increase, while K_{Ga_v} was decrease with CO₂ loading increase. Likewise, gas flow rate slightly affected the K_{Ga_v} .

Naami et al. [24] evaluated the blended MDEA-MEA solutions. This work studied the absorption of CO₂ with blended solutions in a packed column with the DX structure. The concentration of MDEA-MEA solutions is 27/3, 25/5 and 23/7 wt% and the feed gas concentration of CO₂ balance with 15%. The researchers have studied a different kinds of effect; effect of MDEA-MEA blended ratio on mass transfer performance, effect of CO₂ loading on mass transfer performance and effect of liquid flow rate on mass transfer performance. The concentration ratio with MEA at 23/7 wt% and 5 m³/m²·h is the highest K_{Gav}. An increase in concentration with MEA can increase K_{Gav} in this system and more amine molecules to contact with CO₂ molecules. In the case of CO₂ loading, an increase in CO₂ loading decreases K_{Gav}. This cause can be explained that an increase of CO₂ loading is a decrease the free amine molecule for contacting with CO₂ molecules.

Conway et al. [25] studied the CO₂ absorption and mass transfer in incorporating primary (MEA), tertiary (DMAE, DEEA) and sterically hindered amine (2-amino-2methyl-1-propanol or AMP). Effect of primary and tertiary/sterically hindered amine concentration, amine component ratios, and CO₂ loading on CO₂ mass transfer in each of the amine solutions had been investigated. MEA/DMAE being a stronger K_{Gav} than MEA/DEEA and MEA/AMP. Similarly, mass transfer was similarly to the CO₂ loading exceeding 0.2 mol/mol. K_{Gav} is lower in all blended solutions when compared with MEA solution at similarly concentrations because of the terms of the physical properties such as viscosity, results in lower CO_2 diffusion and CO_2 mass transfer. In term of CO_2 absorption, the largest CO_2 absorption is MEA/AMP. The significantly better absorption can be performed in the proton accepting role. However, the blended amine solution was higher than the MEA solution at similar total amine concentrations.

Gao et al. [26] studied the blended DEEA-MEA solutions with the ratio at 27/3, 25/5 and 23/7 wt% and used the DX structure for packing in the column. The researchers had studied a kind of different effect: effects of blended MDEA–MEA ratio, effect of lean CO₂ loading and effect of liquid flow rate. A decrease in lean CO₂ loading can increase K_{Gav} in this system and have more free amine molecules to absorb CO₂ molecules. An increase in the flow rate of liquid effects an increase K_{Gav} because in this system it has more amine molecules to contact with CO₂ molecules in gas-liquid interface. Liao et al. [27] studied the same blended. The resulted can be explained that an increase amine solution in this system effect to an increase K_{Gav} .

Therefore, these are the results of similar experiments. Primary amine has more effect than tertiary amine to absorb CO_2 in the system. As the results, an increase in the ratio of MEA could be increased K_{Ga_v} in the system more than an increase in the ratio of tertiary amine (MDEA and DEEA). Mixed amine is another way to improve a disadvantage of only one amine solution. Thus, Mixed amine between secondary and tertiary within primary amine is studied in this work.

CHAPTER III

EXPERIMENT

This chapter studies the detail of the experiment on CO₂ absorption in a random packed column and scope of experiment. Also, the equipment used in this work was illustrated.

3.1 Chemicals

Monoethanolamine (MEA) with purity of 99.9% was purchased from DOW Chemical. 2-(Methylamino)ethanol (2-MAE) and Dimethylaminoethanol (DMAE) with the same purity of 99.9% was purchased from Merck. Hydrochloric acid (HCl) with purity of 99% was purchased from RCI Labscan Limited. De-ionized water from Purelab Classic was used to prepare an amine solution. Methyl Orange solution 0.1% concentration was from Fisher Scientific. For the gas phase, N₂ and CO₂ with the same purity 99.5% were purchased from Linde (THAILAND).

3.2 Experimental method

3.2.1 Equipment

In this study, Raschig rings are used on the packing in the column to study the mass transfer coefficient. Raschig rings usually use in a tower in a variety of chemical processes and mass transfer applications [28]. The characteristics of the packing was shown in Table 3 and a photograph of packing was shown in Figure 3.1 and 3.2. The

advantages of this packing are cheap, low pressure drop, free volume more than ceramic, resistance to temperature and physical force and resistance to amine and alcohol, but the weight is heavier compared to ceramic [29], [30].

Description	Data
Size (DxLxT), mm 5x5x0.3	
Pieces, m ³	5,000,000
Density, kg/m ³	1,000
Surface, m ² /m ³	1,000
Free volume, %	87

Table 3 Characteristics of the packing

Figure 3.1 The drawing of packing in top view



Figure 3.2 The photograph of Raschig ring

The packed column was made from borosilicate glass (silica and boron trioxide are the main glass-forming constituents) because it is resistant to thermal stress better than other common glass [31]. The drawing of packed column was shown in Figure 3.3.

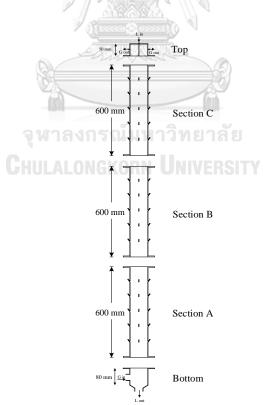


Figure 3.3 The drawing of packed column

3.2.2 Methodology

In the first step, the previous works [10, 11] related to CO₂ capture and storage (CCS) are thoroughly examined to gain basic understanding to capture the CO₂ and the calculation of the mass transfer coefficient. Then, CO₂ absorption applying with single-component amine solutions in the designated equipment was conducted and analyzed to find the best amine solution. Later, CO₂ absorption with a two-component amine solution was conducted and compared with a single-component amine solution for finding the best condition. Finally, all experimental results were discussed and concluded for writing a final thesis.

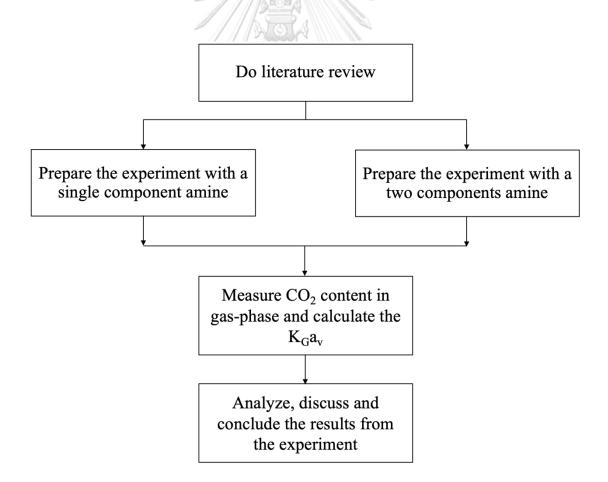
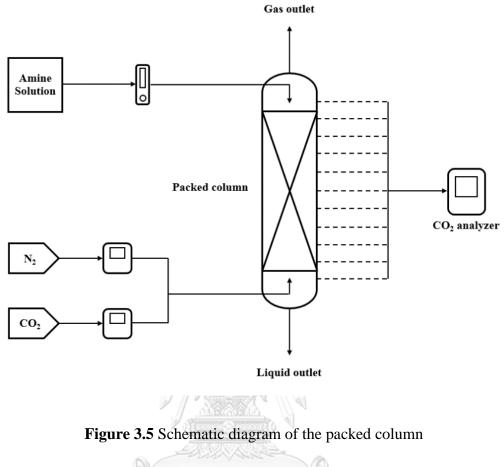


Figure 3.4 Flowchart of methodology

3.2.3 Packed column operation

According to Figure 3.5, N₂ and CO₂ were separately fed into mass flow meter from Aalborg and mixed within a mixing three-way pipe before fed into the column. By the way, the total volume of gas was entered, where the feed volume of N₂ and CO₂ were determined by the CO₂ concentration. Concentration of CO₂ was measured with the IR analyzer (IEQ Chek, Bacharach) within a reliable measurement range of 0-20 %v/v. After that, mixed gases were fed into the bottom of the column. Each amine solution was prepared with de-ionized water to get the specified concentration. It was pumped by a peristaltic pump (BT600-2J, Longer) and flow rate was controlled with PTFE rotameter (Cole-Palmer). The solution was fed at the top of the column. The scope of this study was shown in Table 1.

In this column, there were 11 sampling points along the height of the column. At each point, there were pressure gauges (Imari), temperature probes (Type K, KTT320, Kimo) and CO₂ sampling point to measure the concentration of CO₂ in gas phase. The column was filled with Raschig rings for increasing contact area between liquid and gas phases. Mixed gases and amine solution contacted each other within the column. When the steady state was reached, mixed gases were flown into IR analyzer to analyze the amount of CO₂ in the system at each sampling point along the column. After amine solution had already reacted with CO₂, it was flown to the bottom of the column and analyzed the CO₂ loading in amine solution. Treated gas had already reacted with amine solution, it was flown into the outside.





CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, effects of operating variables, including alkanolamine types, amine concentration, CO₂ content in gas phase and CO₂ initial loading on the mass transfer coefficient were reported and discussed. Mass transfer coefficients for the single-component amine (MEA, 2-MAE, DMAE) and the two-component amine (MEA:2-MAE, 2-MAE; DMAE) were compared.

The CO₂ absorption in single-component and two-component amine solutions were investigated by Photien [10]. A study on overall volumetric mass transfer coefficient (K_{Gav}) in single-component amine solution was conducted by Vaewhongs [11], in which 2-MAE was reported as a superior amine in term of good CO₂ absorption and excellent mass transfer rate. In this study, we studied mass transfer coefficient of a new amine, and compared our results of some mixed amines. Besides, we explored ability in CO₂ capturing when multi-component amine system was utilized.

4.1 Calibration of the packed column

MEA, 2-MAE and DMAE were used as representatives for the alkanolamines. We first calibrated the absorption column by studying types of alkanolamine (Figure 4.1). The liquid flow rate of 10.6 $m^3/(m^2 \cdot h)$, amine concentration of 3 kmol/m³, CO₂ content in gas phase of 15 %v/v and CO₂ initial

loading of 0.2 mol/mol were maintained. It was found that the 2-MAE provided the highest value for CO_2 absorption, as compared to the MEA and DMAE, respectively. The column filled with 2-MAE was able to capture all CO_2 in only a distant of 0.7 meter, while good amount of CO_2 was presence through entire column for MEA and DMAE absorbent. This can be attributed to the fact that 2-MAE is a secondary amine with a high mass transfer rate, while MEA and DMAE is a primary and tertiary amine, respectively. Therefore, the choice of two types of alkanolamine is effect to the greatest of CO_2 absorption. Yet, cost of the substance can be one importance key for utilization of the amines, in which, in our case, the price of 2-MEA is far more expensive than that of the MEA and DMAE.

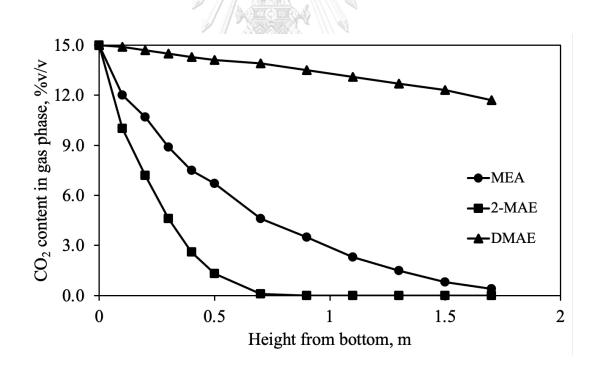
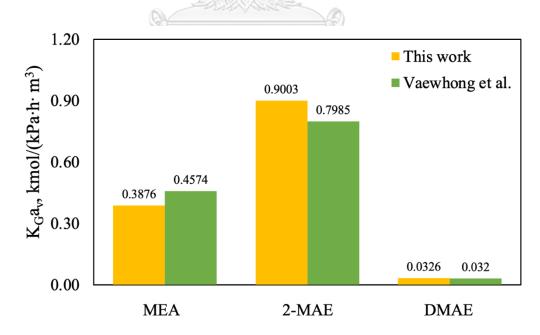
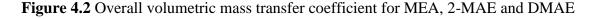


Figure 4.1 CO₂ concentration in gas phase from different height of the column when MEA (\bullet), 2-MAE (\blacksquare) and DMAE (Δ) were tested as an absorbent.

The K_{Gav} values were determined to be 0.9003 kmol/kPa·h·m³ for 2-MAE, and 0.3876 and 0.0326 kmol/kPa·h·m³, for MEA and DMAE, respectively. The MEA and DMAE were only 43.06% and 3.62% effective when compared with the 2-MAE. Our results were compared to those of the Vaewhong et al [11]. Errors K_{Gav} values were found to be 15.26%, 11.30% and 1.84% for the MEA, 2-MAE and DMAE, respectively. We believe that the error can result from atmospheric conditions, operators and experimental procedures [22]. Based on chemical structure, MEA contains primary amine and needs to rely on acid-base reaction between CO₂ and amine for the CO₂ capture. The reaction can be fast and robust but can be limited by nature of the mass diffusion. The 2-MAE uses secondary amine for the acid-base reaction with CO₂, while it can also interact with CO₂, allowing CO₂ to react with water. The DMAE is a tertiary amine with no N-H group. It can only attract CO₂ and catalyze the hydration reaction, which lead to slow CO₂ capture.





of alkanolamine types

From mechanism of reaction of amine with CO₂ as showed in section 2.2.

• Primary amine (1st) :

$$2RNH_2 + CO_2 \leftrightarrow R_1 NCOO^- + RNH^{3+}$$
(2.6)

• Secondary amine (2nd) :

$$2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^- + R_1R_2NH^{+2}$$
(2.7)

• Tertiary amine (3rd) :

$$R_1R_2R_3N + CO_2 + H_2O \leftrightarrow R_1R_2R_3NH^+ + HCO^{3-}$$
(2.8)

The hydrogen atoms of MEA and 2-MAE were directly reacted with CO₂ to form in carbamate formula. However, carbamate form of 2-MAE was an unstable (because of a methyl group in amino group) form which was hydrolyzed with water and formed in bicarbonate and amino group. Amino group of 2-MAE was reacted with CO₂ again. Thus, the reason K_{Gav} of 2-MAE was highest and followed by MEA. In term of DMAE, as mentioned, there is no hydrogen atom in amino group of DMAE. Water was reacted with CO₂ directly and Haritos [32] mentioned that rate of reaction of CO₂ with water was slow. Thus, DMAE showed a lowest K_{Gav}.

4.2 Effect of weight ratio of two-component amine

Two of the three amines were blended at various ratio to observe their combined effects to the CO₂ absorption. The same operating conditions of 10.6 m3/(m2·h) liquid flow rate, 15 %v/v CO₂ content in gas phase, and 0.0 mol/mol CO₂ initial loading were also applied. For the MEA:2-MAE (Figure 4.3), the blended

absorbent handled all CO₂ within the distant of 0.9 meter of the column height for all MEA:2-MAE weight ratio of 30:0, 20:10, 15:15, 10:20 and 0:30. It appeared that changes in weight ratio hardly affect CO₂ absorption ability of the solution, and that a portion of 2-MAE was needed for the CO₂ absorption. For the MEA:DMAE (Figure 4.4), the blended solution poorly captured CO_2 at the MEA:DMAE weight ratio of 0:30 (pure DMAE). The DMAE contained only tertiary amine, relying only on base catalyze hydration for the CO₂ capture, and was reported to offer low kinetic rate mass transfer rate [32]. The other MEA:DMAE weight ratio, including 20:10, 15:15, 10:20 and 0:30 exhibited fair absorption ability. The CO₂ was all removed within 1.3 meter distant from bottom of the column. For the 2-MEA:DMAE (Figure 4.5), the blended solution showed slightly lower ability as compared to that of the MEA:2-MEA. The 0:30 ration of 2-MEA:DMAE (pure DMAE) also demonstrated poor result in CO₂ capture, while the 2-MEA enhanced CO₂ capture ability at any weight ratio we studied. It is worth noting that MEA is a commercial solution for CO₂ capture. Naami [21] reported no more than 30 wt% or 5 kmol/m³ of MEA should be used to avoid equipment corrosion as the CO_2 is the only acid gas component. In fact, only 3 kmol/m³ of MEA is usually advised for industrial uses.

Weight ratio of the blended solution affect the solution's ability to capture CO₂. The bar charts (Figure 4.6) reveal K_{Gav} values for the blended solution. We observed that presence of primary amine (MEA) and secondary amine (2-MAE) increases the K_{Gav}. In general, increasing the availability of amine molecules causes an increase K_{Gav}. The absorption process is controlled by the liquid side and increases the mass transfer in the gas side due to the resistance in the liquid side. In addition, an increase in the concentration of amine solution leads to an increase in viscosity [33].

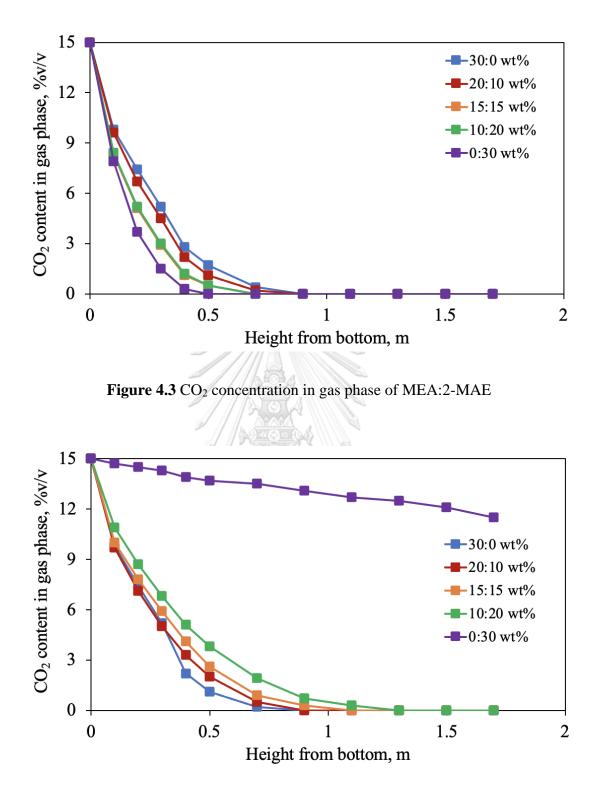


Figure 4.4 CO₂ concentration in gas phase of MEA:DMAE

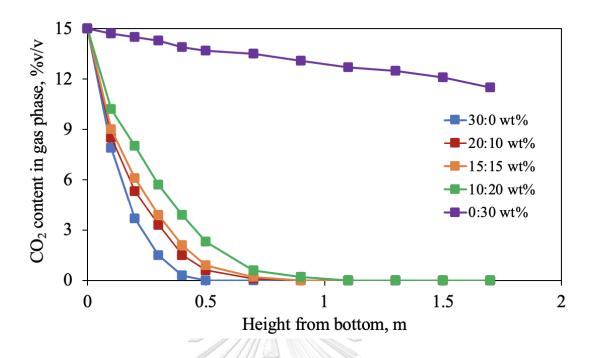


Figure 4.5 CO₂ concentration in gas phase of 2-MAE:DMAE

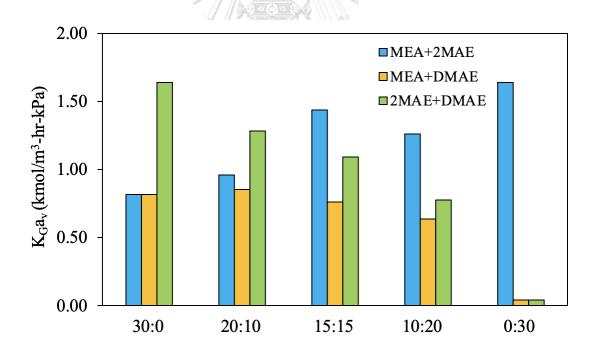


Figure 4.6 Overall volumetric mass transfer coefficient for MEA:2-MAE,

MEA:DMAE and 2-MAE:DMAE

Liao et al [27] reported that an increase in amine concentration led to an increase amount of amine molecules diffusing into the gas-liquid interface. Reaction zone moved closer to the interface where there was a high concentration in amine solution. However, K_{Gav} decreased due to a large concentration led to solution viscosity, which was offset the advantage of active amine molecules.

4.3 Effect of liquid flow rate with two-component amine

The same operating parameters of 15 %v/v CO₂ content in gas phase and 0.0 mol/mol CO₂ initial loading were applied to observe the effects from liquid flow rate on CO₂ absorption ability. An increase in liquid flow rate led to a decrease in gasphase content of the CO₂, as resulted from the expansion of the wet packing surfaces, leading to higher CO₂ absorption [24]. An increase in 2-MAE ratio enhanced CO₂ absorption in MEA:2-MAE and 2-MEA:DMAE blended. The flow rate was found to slightly affect the CO₂ absorption ability in that the ability increased as the flow rate increased. In the case of more MEA in the MEA:2-MAE (30:0 and 20:10), stronger effects from the flow rate were observed, which agreed well with our analysis. The MEA is the primary amine that relies its CO₂ capture on acid-base reaction-fast and robust. The absorption ability was backfired by limited mass diffusion in the absorption column. The MEA system, then, was more sensitive to flow rate increase, as compared to 2-MAE and DMAE [10, 11].

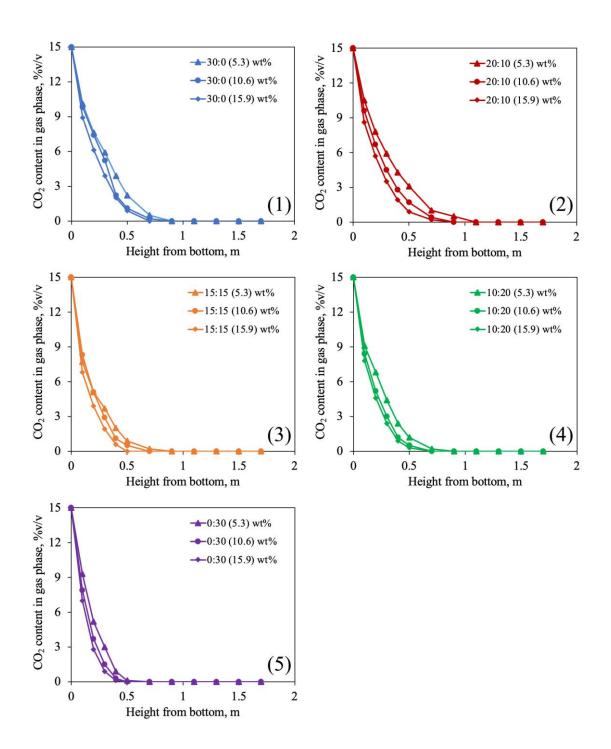


Figure 4.7 CO₂ concentration in the gas phase of MEA:2-MAE on effect of liquid flow rate. (1) weight ratio is 30:0 wt%, (2) weight ratio is 20:10 wt%, (3) weight ratio is 15:15 wt%, (4) weight ratio is 10:20 wt% and (5) weight ratio is 0:30 wt%

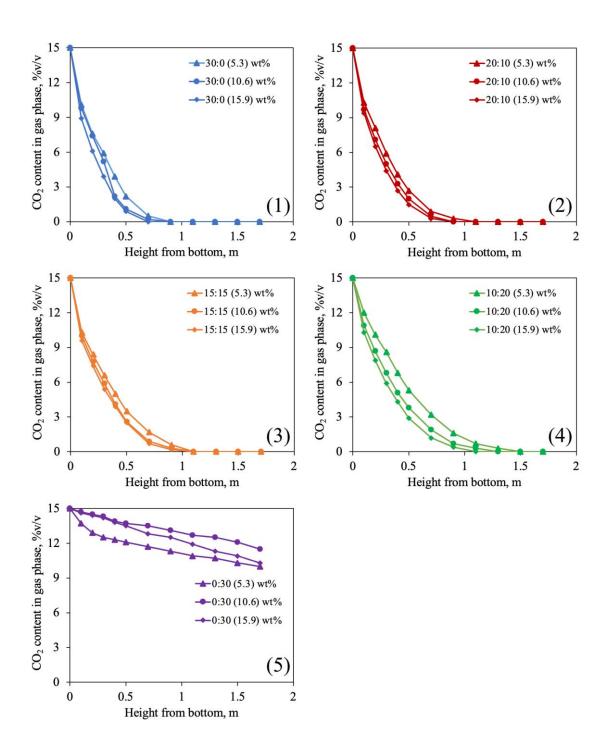


Figure 4.8 CO₂ concentration in the gas phase of MEA:DMAE on effect of liquid flow rate. (1) weight ratio is 30:0 wt%, (2) weight ratio is 20:10 wt%, (3) weight ratio is 15:15 wt%, (4) weight ratio is 10:20 wt% and (5) weight ratio is 0:30 wt%

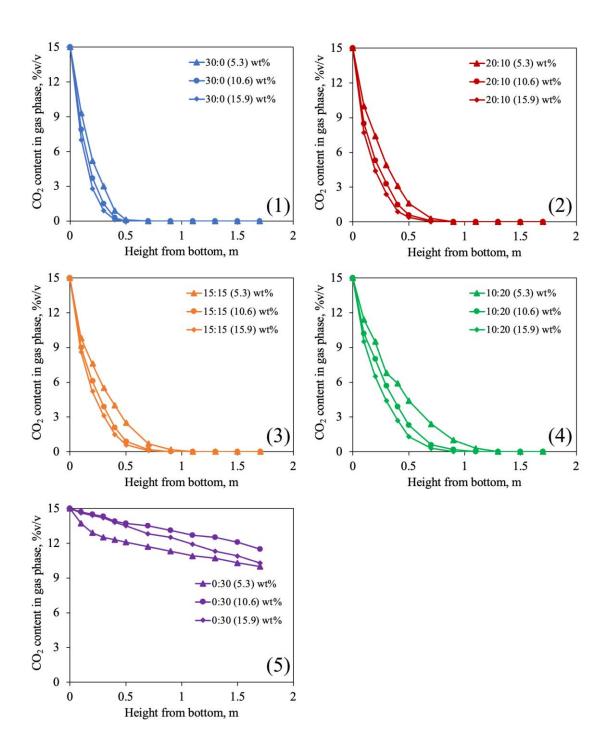


Figure 4.9 CO₂ concentration in the gas phase of 2-MAE:DMAE on effect of liquid flow rate. (1) weight ratio is 30:0 wt%, (2) weight ratio is 20:10 wt%, (3) weight ratio is 15:15 wt%, (4) weight ratio is 10:20 wt% and (5) weight ratio is 0:30 wt%

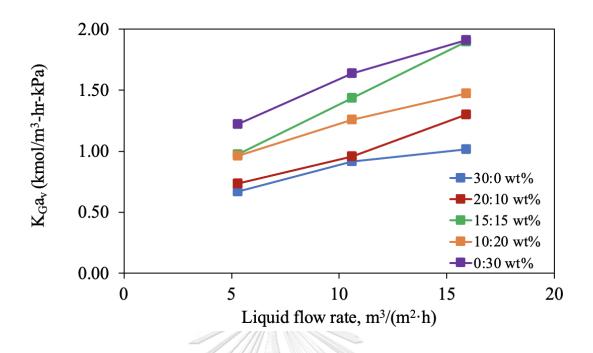


Figure 4.10 Overall volumetric mass transfer coefficient on effect of liquid flow rate

of MEA:2-MAE for 5.3, 10.6 and 15.9 $m^{3}/(m^{2} \cdot h)$

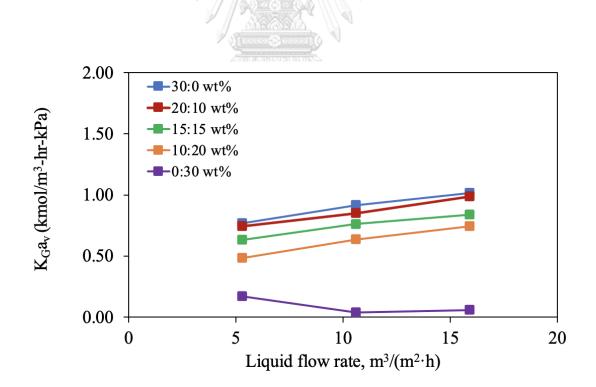


Figure 4.11 Overall volumetric mass transfer coefficient on effect of liquid flow rate of MEA:DMAE for 5.3, 10.6 and 15.9 $m^3/(m^2 \cdot h)$

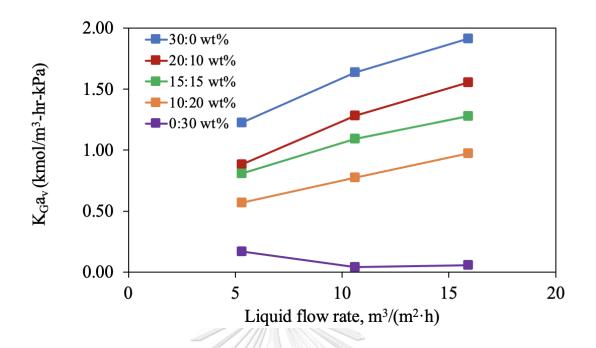


Figure 4.12 Overall volumetric mass transfer coefficient on effect of liquid flow rate of 2-MAE:DMAE for 5.3, 10.6 and 15.9 $m^3/(m^2 \cdot h)$

Effects of liquid flow rate to the K_{Gav} value was studied. The MEA:2-MAE blend offered higher K_{Gav} value, as compared to MEA:DMAE and 2-MAE:DMAE, at the same operating conditions. An increase in liquid flow rate led to an increase in the K_{Gav}. The liquid flow rate has a strong impact on mass transfer rate and CO₂ absorption performance since more amine molecules were made available for CO₂ capture. In addition, an increase in the flow rate yielded more effective area for mass transfer, resulted in more mass transfer coefficient in liquid side (k_L). The k_L value in our case was directly proportional to the K_{Gav} value [34]. Photien et al [10] reported that DMAE has a larger cyclic capacity for CO₂ absorption although its mass transfer was lower than MEA and 2-MAE. The DMAE was tested to provide such CO₂ absorption ability since in the case of pure DMAE the K_{Gav} value even reduced as the

flow rate increased. This could be the nature of the tertiary amine since the base catalyze hydration path occurred to be relatively slow as compared to the acid-base reaction. Besides, the lower the flow rate means the more the retention time in the absorption column. CO₂ absorption in the MEA-based solution showed more sensitivity to flow rate increase, which can be attributed to the enhanced mass diffusion phenomenon. Hairu et al [22] reported that an increase in liquid flow rate led to high turbulence and low contact time between CO₂ and amine molecules. In general, K_{Gav} would not decline with flow rate in 8.7 m³/(m²·h), K_{Gav} showed the highest. However, an increase in liquid flow rate above 8.7 m³/(m²·h) led to a decrease in K_{Gav} . The explanation was a smaller wetted surface area in the packing within a column. However, an increase in liquid flow rate was unsuitable for the system. There are costs and corrosion because an increase in liquid flow rate led to more energy consumption and more erosion in the metal surface.

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4.4 Effect of CO₂ content in gas phase with two-component amine

Effect of CO₂ content in gas phase was studied varying from 5 to 15 %v/v, simulating CO₂ content in natural gas power plant or coal-fired power plant [5]. In case of MEA:2-MAE, at 5-15 %v/v, CO₂ was removed in every condition. It could explain that MEA:2-MAE was a good absorption performance. For MEA:DMAE and 2-MAE:DMAE, at 5-15 %v/v, CO₂ was removed in every condition, except 0:30 wt% that there was still CO₂ remaining in the process. Changing of concentration in CO₂ concentration greatly affected the CO₂ absorption performance.

Figure 4.16, 4.17, 4.18 showed that 5 %v/v was the highest K_{Gav}. Change in CO_2 content in gas phase led to change the partial pressure to dissolved in liquid phase. An increase in driving force resulted in K_{Gav} decrease. In general, an increase in CO_2 partial pressure in gas phase led to K_{Gav} increase. However, this study presented when CO₂ partial pressure increase led to K_{Gav} decrease. According to Yaser et al [35], they reported that (1) an increase in CO₂ partial pressure led to an increase in K_Ga_v, whereas, a decrease K_Ga_v could occurred from more active free amine molecules, and (2) an increase in CO_2 partial pressure led to an increase in K_{Gav} from intensifying the gas flow turbulence in the column. Anindo et al [36] studied K_{Gav} with MEA-AMP blended solution in effect of CO₂ partial pressure. They reported that an increase in CO₂ partial pressure led to a decrease K_{Gav}. As a Two Film Theory, K_{Gav} represented in mass transfer rate per unit driving force. Thus, a decrease K_{Gav} is due to an increase in driving force as deMontigny [37] mentioned. Amine molecules diffusion in liquid phase is restricted that compared with CO₂ from gas phase to gas-liquid phase. The phenomenon is mainly attributed which is controlled mass transfer by the resistance in liquid phase. In packed column, CO2 partial pressure was high at the bottom and low at the top of column. Thus, K_{Gav} showed a small at the bottom and a large at the top which as CO₂ partial pressure increased. Based on mass transfer, an increase in CO₂ content led to nearly equivalent amount of CO₂ solubility in liquid phase. It could conclude that amine solution (such as MEA has a higher reaction kinetic constants) showed a high CO₂ absorption performance in a lower CO₂ partial pressure than higher partial pressure. Thus, liquid phase resistance affected the mass transfer performance [19]. This result corresponds with them.

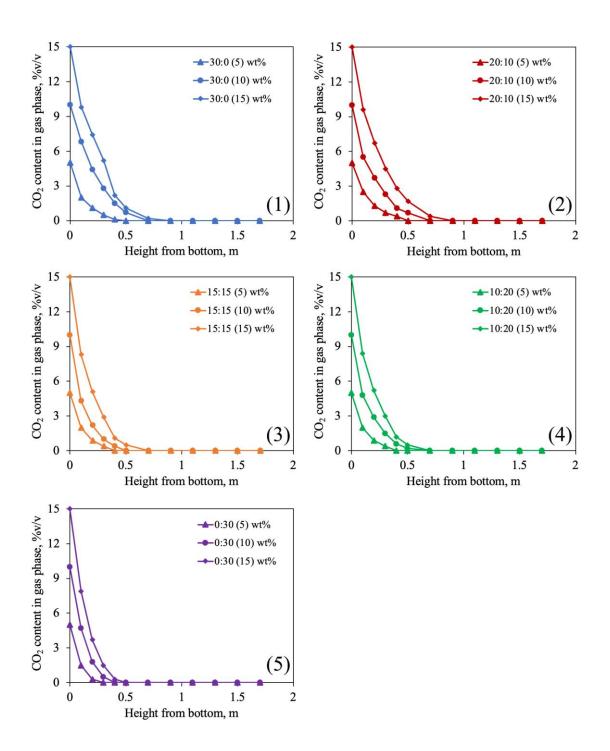


Figure 4.13 CO₂ concentration in gas phase of MEA:2-MAE on effect of CO₂ content in gas phase. (1) weight ratio is 30:0 wt%, (2) weight ratio is 20:10 wt%, (3) weight ratio is 15:15 wt%, (4) weight ratio is 10:20 wt% and (5) weight ratio is 0:30 wt%

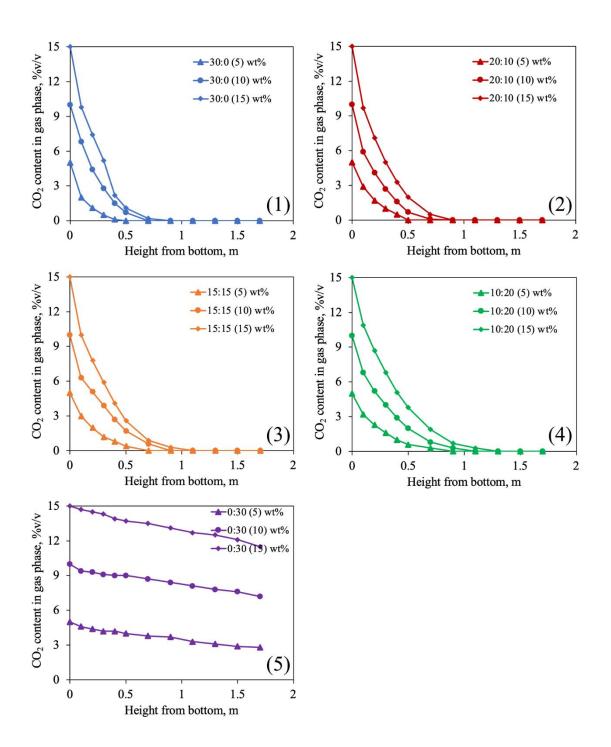


Figure 4.14 CO₂ concentration in gas phase of MEA:DMAE on effect of CO₂ content in gas phase. (1) weight ratio is 30:0 wt%, (2) weight ratio is 20:10 wt%, (3) weight ratio is 15:15 wt%, (4) weight ratio is 10:20 wt% and (5) weight ratio is 0:30 wt%

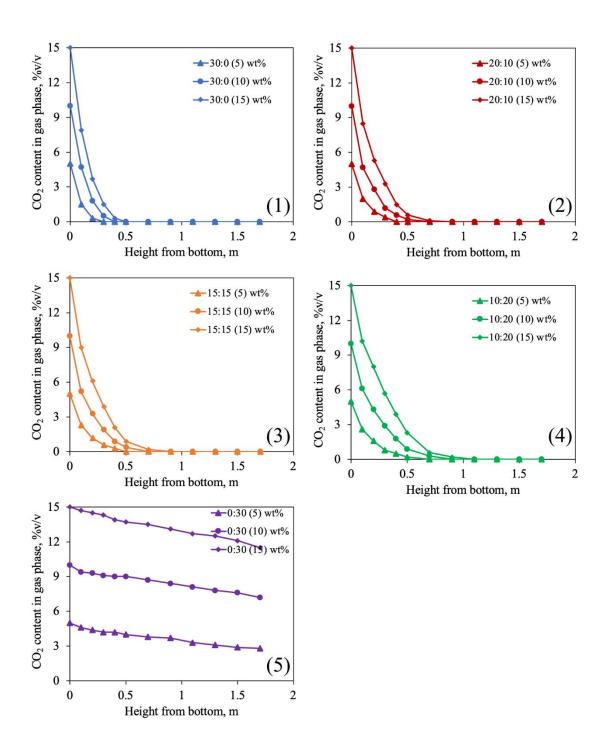


Figure 4.15 CO_2 concentration in gas phase of 2-MAE:DMAE on effect of CO_2 content in gas phase. (1) weight ratio is 30:0 wt%, (2) weight ratio is 20:10 wt%, (3) weight ratio is 15:15 wt%, (4) weight ratio is 10:20 wt% and (5) weight ratio is 0:30 wt%

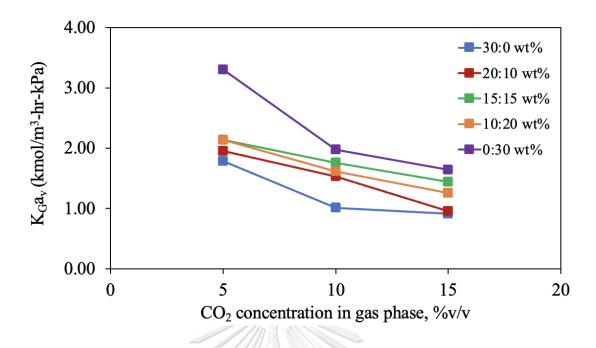


Figure 4.16 Overall volumetric mass transfer coefficient on effect of CO2 content in

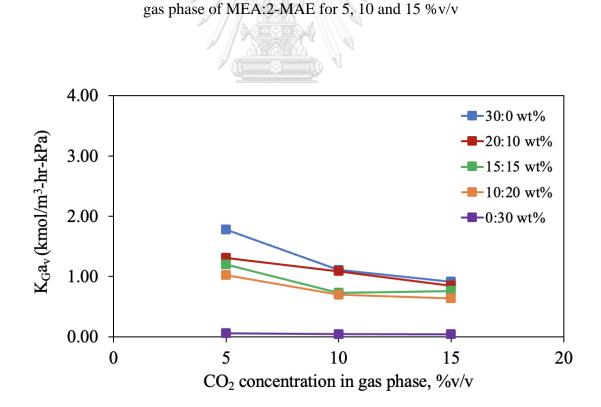


Figure 4.17 Overall volumetric mass transfer coefficient on effect of CO_2 content in gas phase of MEA:DMAE for 5, 10 and 15 %v/v

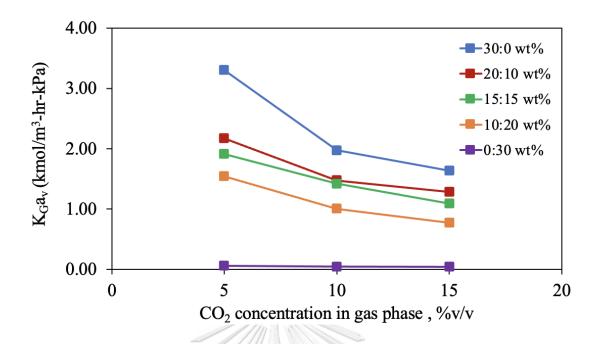


Figure 4.18 Overall volumetric mass transfer coefficient on effect of CO_2 content in gas phase of 2-MAE:DMAE for 5, 10 and 15 %v/v

4.5 Effect of CO₂ initial loading with two-component amine

CO₂ initial loading was the mole of CO₂ per mole of amine solution. CO₂ loading of 0.0 mol/mol was a fresh amine (there is no CO₂ molecule in amine solution), whereas 0.1 and 0.2 mol/mol was a preloaded amine (there are some CO₂ molecules in amine solution). Effect of CO₂ initial loading was shown in Figure 4.19, 4.20 and 4.21. All results were investigated under the same condition, that CO₂ content in gas phase was 15 %v/v, liquid flow rate was 10.6 m³/(m²·h). Under all conditions, MEA:2-MAE could result in the highest CO₂ absorption at 100% and under some conditions, MEA:DMAE and 2-MAE:DMAE exhibited lower performance. This would suggest that DMAE might not be a good solvent for CO₂

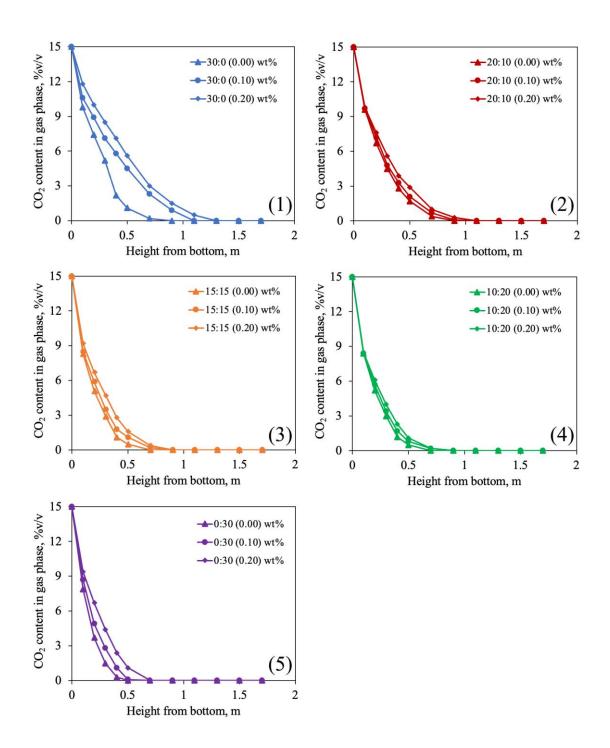


Figure 4.19 CO₂ concentration in gas phase of MEA:2-MAE on effect of CO₂ initial loading. (1) weight ratio is 30:0 wt%, (2) weight ratio is 20:10 wt%, (3) weight ratio is 15:15 wt%, (4) weight ratio is 10:20 wt% and (5) weight ratio is 0:30 wt%

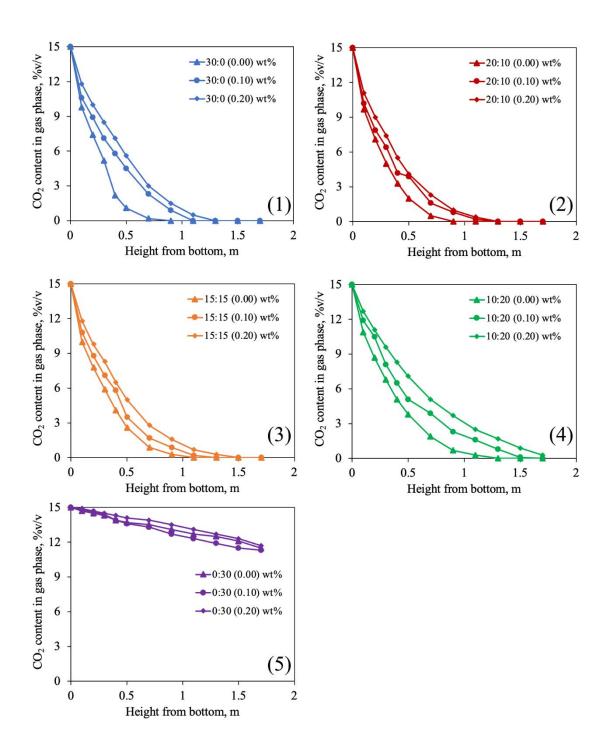


Figure 4.20 CO₂ concentration in gas phase of MEA:DMAE on effect of CO₂ initial loading. (1) weight ratio is 30:0 wt%, (2) weight ratio is 20:10 wt%, (3) weight ratio is 15:15 wt%, (4) weight ratio is 10:20 wt% and (5) weight ratio is 0:30 wt%

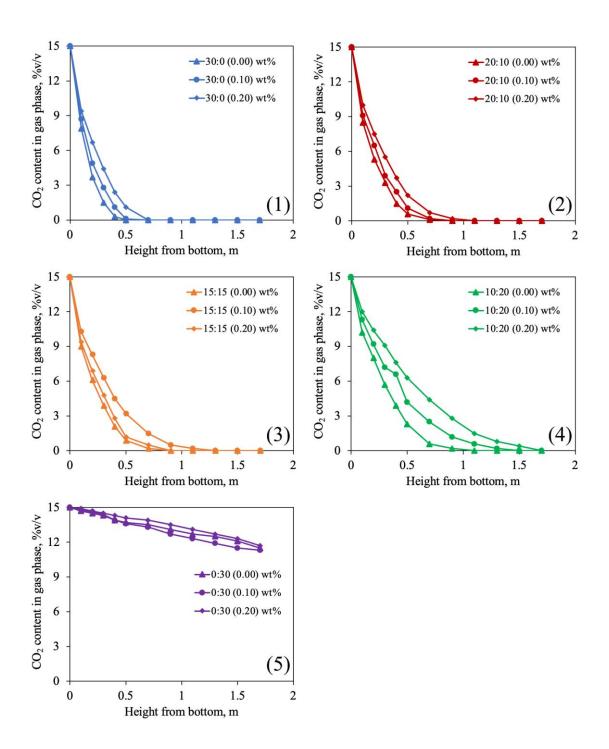
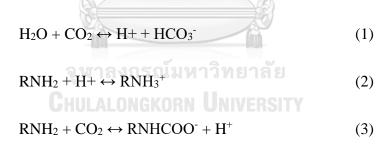


Figure 4.21 CO₂ concentration in gas phase of 2-MAE:DMAE on effect of CO₂ initial loading. (1) weight ratio is 30:0 wt%, (2) weight ratio is 20:10 wt%, (3) weight ratio is 15:15 wt%, (4) weight ratio is 10:20 wt% and (5) weight ratio is 0:30 wt%

capture because it cannot absorb CO_2 while the end of height in the column. According to mass transfer rate, MEA and 2-MAE are primary and secondary amine with a very high mass transfer rate and fast kinetics when compared with DMAE as tertiary amine. An increase in CO_2 initial loading in DMAE that is not much different whereas MEA and 2-MAE is different. Therefore, the unloaded CO_2 into a solution causes more effective for CO_2 capture.

 K_{Ga_v} value at 0.0 mol/mol was the highest, and followed by 0.1 and 0.2 mol/mol. The use of MEA:2-MAE shows the higher K_{Ga_v} than the use of MEA:DMAE and 2-MAE:DMAE. K_{Ga_v} decreased due to the CO₂ initial loading increased, reflecting an amount of free-amine molecules decreased, and causing low K_{Ga_v} of the system. An increase in CO₂ in amine solution led to a decrease of active absorbent, effecting to absorb less CO₂ molecules. According to section 2, it explained by kinetic mechanism,



Primary and secondary (MEA and 2-MAE) could be written in (2) and (3), and tertiary amine (DMAE) could be written in (1). For the reactions, RNH₂ reacts with CO_2 and becomes to RNHCOO⁻ and H⁺, but reaction between H₂O and CO₂ is slow compared to (2) and (3). Secondary amine in the form of carbamate formation is not stable, resulting in a higher mass transfer rate and CO₂ loading. Meanwhile, tertiary amine, carbamate formation cannot produce by (2) and (3) while CO₂ is absorbed by water by (1), affecting a low mass transfer rate, whereas, the stoichiometric ratio of

tertiary amine between amine and CO₂ is 1:1 that provides a higher CO₂ loading than primary and secondary amine. Therefore, at 0.0 mol/mol, give higher rate of reaction due to a higher of RNH₂ to absorb more molecules of CO₂. In case of 0.1 and 0.2 mol/mol, there are some CO₂ molecules in amine molecules, causing to a low RH₂ in the solvent and slow reaction rate than 0.0 mol/mol. The results show that K_{Gav} reduce due to a CO₂ loading increase, resulting in a low K_{Gav}. As CO₂ loading increased, reflecting in the lower amine molecules concentration gave the lower K_{Gav}. The higher CO₂ loading, resulting in had an apparent influence on K_{Gav} and reduced the performance of the column. K_{Gav} decreased because the value changes along the height of the column where the bottom of the column was a high CO₂ loading. Thus, an increase in CO₂ loading reduced free amine molecules and a decrease in driving force, reflecting reduced K_{Gav} [24, 37]. In general, MEA normally archive CO₂ loading in maximum at 0.5 mol/mol. However, regeneration need to consume large amount of energy (80-120°C), and need high cost of CO₂ desorption from a solution.

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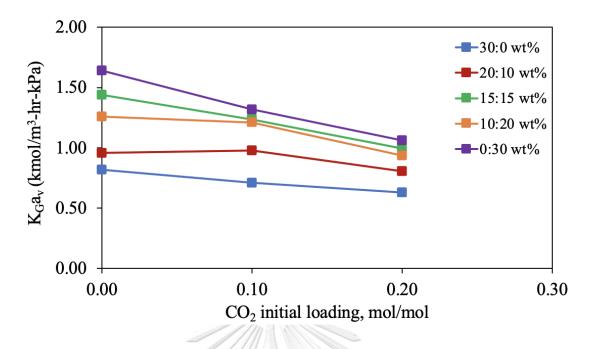


Figure 4.22 Overall volumetric mass transfer coefficient on effect of CO2 initial

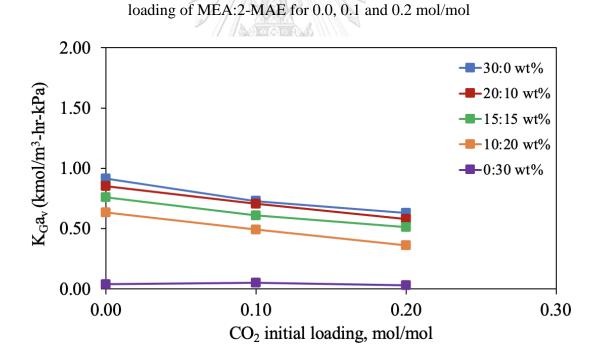


Figure 4.23 Overall volumetric mass transfer coefficient on effect of CO₂ initial loading of MEA:DMAE for 0.0, 0.1 and 0.2 mol/mol

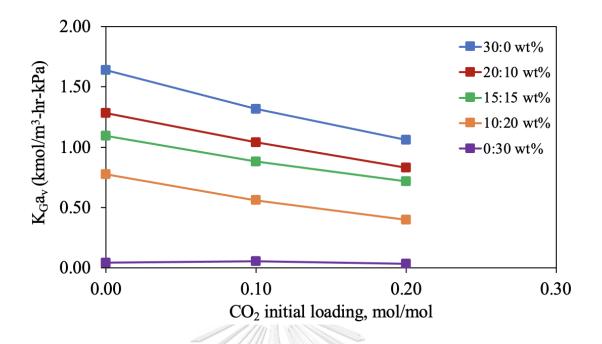


Figure 4.24 Overall volumetric mass transfer coefficient on effect of CO₂ initial loading of 2-MAE:DMAE for 0.0, 0.1 and 0.2 mol/mol

As described above, two-component amine was successful in CO_2 absorption performance and K_{Ga_v} . The results from this study showed that the mass transfer increase as ratio of primary and secondary amine in the mixed solution increase. Moreover, tertiary amine also showed that mass transfer decrease as the ratio of tertiary amine increase in the solution. Thus, it should be noted that an increase in more tertiary amine ratio may be adversely affected for mass transfer rate.

The important factors of contribution to K_{Ga_v} are liquid flow rate and CO_2 partial pressure. As mentioned before, the mass transfer rate was mainly controlled by the resistance of the liquid phase which is directly proportional K_G . Thus, a higher liquid flow rate and lower CO_2 partial pressure were beneficial to enhance K_{Ga_v} .

However, we should consider all factors that are suitable for the system. An increase in liquid flow rate or amine concentration too much affected a decrease in K_{Ga_v} and CO_2 absorption performance. In addition, CO_2 solubility and cyclic capacity, which is defined as the difference of CO_2 solubility of absorption and desorption process, is an important factor for choosing a type of amine because a high cyclic capacity can save a cost for energy consumption (affected to regeneration process) [10]. Meanwhile, mass transfer coefficient should consider with a cyclic capacity that will develop a CO_2 capture in the future.



CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this work, K_{Gav} was studied into a new mixed solution, monoethanolamine (MEA), 2-methylaminoethanol and dimethylaminoethanol (DMAE), 2-MAE and DMAE were added into MEA solution. Comparison mass transfer of CO₂ absorption in mixed amine has been conducted by using a randomly packed column. The operating conditions weight ratio was compared in 5 concentrations; 30:0, 20:10, 15:15, 10:20 and 0:30 wt%, of MEA:2-MAE, MEA:DMAE and 2-MAE:DMAE. Effect of parameters; liquid flow rate, CO₂ content in gas phase and CO₂ initial loading, were studied.

5.1.1 Calibration of the packed column

 CO_2 absorption of single-component amine was compared with those in previous works. With comparison of K_{Gav} to those of Vaewhong [11], an average absolute deviation (%ADD) was 15.26%, 11.30% and 1.84% of MEA, 2-MAE and DMAE, respectively. The results showed that 2-MAE could provide the highest K_{Gav} and followed by MEA and DMAE.

5.1.2 Effect of weight ratio of two-component amine

Investigation on weight ratio of MEA:2-MAE, MEA:DMAE and 2-MAE:DMAE in the range of 30:0, 20:10, 15:15, 10:20 and 0:30 wt% showed that an increase in the ratio of 2-MAE led to an increase in K_{Gav} and CO_2 absorption performance. On the other hand, K_{Gav} decreased due to the ratio of DMAE increased.

Mixed amine solution was a good solvent for CO_2 absorption. It can improve the CO_2 absorption performance and K_{Gav} value than a single amine solution.

5.1.3 Effect of liquid flow rate with two-component amine

Liquid flow rate in the range of 5.3, 10.6 and 15.9 $m^3/(m^2 \cdot h)$ showed that 15.9 $m^3/(m^2 \cdot h)$ could lead to the highest mass transfer rate. MEA:2-MAE exhibited the greatest CO₂ absorption performance when compared with MEA:DMAE and 2-MAE:DMAE. An increase in liquid flow rate led to an increase in free amine molecules and a wet surface of the packing for high CO₂ absorption.

5.1.4 Effect of CO₂ content in gas phase with two-component amine

 CO_2 content in gas phase within the range of 5, 10 and 15 %v/v was studied. K_{Gav} was increased when CO₂ content was decreased. At 5 %v/v showed the highest K_{Gav} and followed by 10 and 15 %v/v. CO₂ absorption process is controlled by the liquid side. Therefore, increasing CO₂ content affects the mass transfer performance.

5.1.5 Effect of CO₂ initial loading with two-component amine

Finally, investigation on effect of CO_2 initial loading in the range of 0.0, 0.1 and 0.2 mol/mol showed that fresh solution (0.0 mol/mol) could certainly provide the highest CO_2 absorption performance and K_{Gav} . An increase in CO_2 initial loading leads to a decrease in CO_2 performance because active amine molecules are decreased. Mass transfer driving force from gas to liquid phase is decreased. The heating to amine solution effect a decrease in CO_2 loading in amine solution.

5.2 Recommendation

The following important conclusions can be developed from the present study: (1) regeneration column is interesting to use a K_{Ga_v} from CO₂ absorption to study CO₂ desorption for designing the column in the next step. (2) we did not characterize of test of amine solution to confirm that amine molecules react directly with CO₂ molecules to form in carbonate and bicarbonate formula. (3) it also included those physical properties test to study the factors affecting mass transfer rate. Thus, this analysis is very interesting.

- Study and design on regeneration column for recycling the amine solution that we've already known a CO_2 absorption and desorption solubility, and mass transfer coefficient of amine solution.

- Analysis of mixed amine solution by using Nuclear Magnetic Resonance Spectroscopy (NMR) is suitable to confirm the reaction of CO₂ with amine molecules.

- Study on physical properties of a mixed amine (such as viscosity) is interesting.

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Appendix A Nomenclature

Symbol	Definition
a _v	Specific area of contactor, m ² /m ³
α	Solution CO ₂ loading, mol _{CO2} /mol _{amine}
α _{eq}	CO ₂ loading of solution in equilibrium with P _{CO2} , mol _{CO2} /mol _{amine}
K _G a _v	Gas-phase volumetric overall mass transfer coefficient, kmol/m ³ -h- kPa
k ⁰ L	Liquid-phase mass transfer coefficient without chemical reaction, kmol-m ³ /m ² -h-kPa-kmol
k _L	Liquid-phase mass transfer coefficient with chemical reaction, kmol- m ³ /m ² -h-kPa-kmol
k _G	Gas-phase mass transfer coefficient, kmol-m ³ /m ² -h-kPa-kmol
K _G	Overall gas-phase mass transfer coefficient, kmol/m ² -h-kPa
K _L	Overall liquid-phase mass transfer coefficient, kmol/m ² -h-kPa
y _{CO2}	Mole fraction of CO ₂ in bulk gas phase, mol/mol
Y _{CO2}	Mole ratio, mol/mol
c _{CO2,i}	Concentration of CO ₂ at gas-liquid interface, kmol/m ³
C _{CO2,1}	Concentration of CO ₂ in bulk liquid phase, kmol/m ³
Н	Henry's constant, , kmol/m ³ -kPa
G _{CO2}	Molar flow rate of CO_2 per cross-sectional area per hour, kmol/m ² -h
GI	Molar flow rate of inert gas per cross-sectional area per hour, kmol/m ² -h

Symbol	Definition
Ι	Enhancement factor
Р	Total pressure of the system, kPa
p _{CO2,g}	Partial pressure of CO ₂ in bulk gas phase, kPa
p _{CO2,i}	Partial pressure of CO ₂ at gas liquid interface, kPa
p [*] _{CO2}	Partial pressure of CO_2 that in equilibrium with $c_{CO2,i}$, kPa
У _{СО2,g}	Mole fraction of CO2 in bulk gas phase
У _{СО2}	Mole fraction of CO_2 that in equilibrium with $c_{CO2,l}$

Primary amine: Monoethanolamine = MEA

Secondary amine: 2-Methylaminoethanol = 2-MAE

Tertiary amine: Dimethylaminoethanol = DMAE

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Appendix B CO₂ loading calculation

Appendix B.1 CO₂ loading calculation

To the calculation of CO_2 loading can be obtained by used CO_2 loading analyzer as shown in Figure B.1. The sample is taken to analysis after the experiment already done. CO_2 loading analyzer can calculate the concentration of amine and CO_2 loading in amine solution by using 1 M Hydrochloric acid (HCl). The sample is taken 2 mL using by volumetric pipette and 2-3 drops of Methyl Orange into the sample flask for measuring the CO_2 loading. After that, HCl is dropped into sample flask until the color of the indicator is changed. Gases push the red color solution in CO_2 loading analyzer and record the amount of gases in the three tubes. The samples are repeated 3 times and calculated as an average of CO_2 loading. The calculation of CO_2 loading could be given by Equation (B.1).

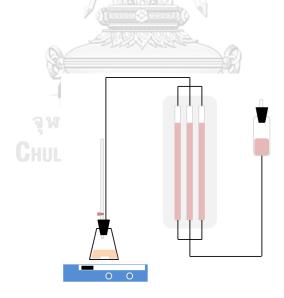


Figure B.1 CO₂ loading analyzer

Equation (B.1) is the equation to calculate CO_2 loading between mole of CO_2 per mole of amine or volume of CO_2 dissolved in amine solution, could be written in this equation

$$CO_2$$
 loading, $\alpha = \frac{\text{mole of } CO_2}{\text{mole of amine}}$ (B.1)

Mole of CO_2 could be explained by Ideal Gas Law as shown in Equation (B.2). Where P is the pressure of the CO_2 at 1 atm, V is the volumetric of CO_2 , n is amount of substance of CO_2 , R is the gas constant at 0.08206 L·atm·K⁻¹·mol⁻¹ and T is the absolute temperature of the CO_2 at 0°C

$$PV = nRT$$

$$mole of CO_{2} = \frac{PV}{RT}$$

$$= \frac{(1 \text{ atm}) V_{CO_{2}}}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) (273 \text{ K})} = \frac{V_{CO_{2}}}{22.4}$$
(B.2)

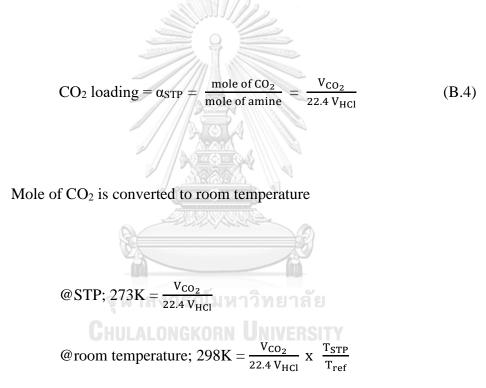
Mole of amine solution could be explained as shown in Equation (B.3). where N_{HCl} is the concentration of HCl at 1 M

mole of amine = mole of HCl

mole of amine =
$$C_{HCl}V_{HCl} = (1 \text{ M}) V_{HCl} = V_{HCl}$$
 (B.3)

Therefore, CO₂ loading at STP could be calculated from Equation (B.4) by

substitute (B.2) and (B.3) into (B.1)



Thus, CO₂ loading equation is shown in Equation (B.5)

$$\alpha = \frac{V_{CO_2}}{22.4 V_{HCl}} \times \frac{T_{STP}}{T_{ref}} = \frac{(3V_{gas} - V_{HCl,excess})}{22.4 V_{HCl}} \times \frac{T_{STP}}{T_{ref}}$$
(B.5)

where,

V_{gas} is the volumetric of CO₂ in tube

V_{HCl,excess} is the volumetric of HCl excess to use in titration

V_{HCl} is the volumetric of HCl to use titration

 T_{STP} is the absolute temperature of the CO2 at 0^{o}C

 T_{ref} is the absolute temperature of the CO₂ at 25°C

Appendix B.2 Example for calculation of CO₂ loading outlet

The experiment represented an amine concentration of 3 kmol/m³, liquid flow rate of 10.6 m³/(m²·h), CO₂ content in gas phase of 15 %v/v and CO₂ inlet of 0.0 mol/mol. From the three tube, it can read the CO₂ of ...mL and take into Equation B.5 in terms of V_{gas}. In terms of V_{HCl}, in Equation (B.3), we already know that C_{amine}=3M, C_{HCl}=1M and V_{amine}=2mL, thus V_{HCl} is showed of 6 mL. The last variable is V_{HCLexcess} as the volumetric of HCl excess to use in titration of 12 mL Therefore, from Equation B.5, we can calculate the CO₂ loading that shows 0.55 mol/mol.

$$\alpha = \frac{(37.2 \text{ mL} - 12 \text{ mL})}{22.4 \text{ (6 mL)}} \text{ x } \frac{273}{298} = 0.172 \text{ mol/mol}$$

Appendix C K_Ga_v calculation

From section 2.4, Equation 2.17 shows the K_{Gav} equation. The experiment represented type of amine is MEA, amine concentration of 3 kmol/m³, liquid flow rate of 10.6 m³/(m²·h), CO₂ content in gas phase of 15 % v/v and CO₂ inlet of 0.0 mol/mol. Figure C.1 shows mole ratio of CO₂ along the height of the column and determine the slope of a line with polynomial function as shows in Figure C.2.

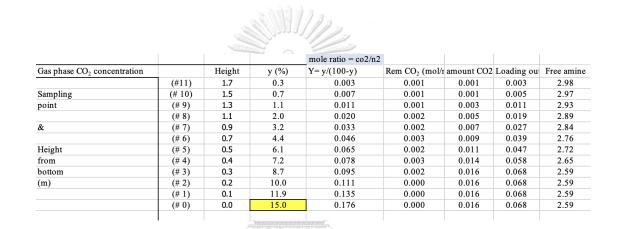
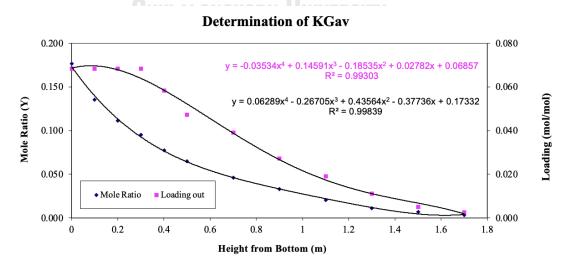
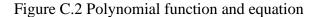


Figure C.1 Mole ratio of CO₂ along the height of column







According to Figure C.2, we know that polynomial function is $y=0.06289x^4$ - $0.26705x^3+0.43564x^2-0.37736x+0.17332$. Thus, we can find the mole ratio of Y which use $Y=ax^4+bx^3+cx^2+dx+e$ (x is height) and determine Y=0.09 by varying the height of the column. K_{Gav} is calculated in along the column (Figure C.3). In this condition, K_{Gav} shows 0.4201 kmol/kPa·h·m³.

	cal from equa			cal from equa	The second second second second							
Height (Z)	Mole ratio Y	Rem CO ₂ (mol/min)	amount CO2	Loading out	у	y*	dY/dZ	GI	Р	KGav	KGav/ Length	Free amine
1.7000	-0.819305	0.125	0.125	-1.829	-4.53419	0	0.024	20.123	101.325	-0.001069	-0.0005	13.97
1.6000	0.003102	0.000	0.125	-1.618	0.00309	0	0.004	20.123	101.325	0.248336	0.1150	12.71
1.50000	0.004557	0.001	0.126	-1.421	0.00454	0	0.024	20.123	101.325	1.051292	0.4867	11.52
1.3000	0.011895	0.002	0.128	-1.064	0.01176	0	0.046	20.123	101.325	0.776523	0.3595	9.38
1.10000	0.021982	0.002	0.129	-0.755	0.02151	0	0.054	20.123	101.325	0.494135	0.2288	7.53
0.90000	0.033147	0.002	0.131	-0.494	0.03208	0	0.059	20.123	101.325	0.363680	0.1684	5.96
0.70000	0.046133	0.003	0.134	-0.280	0.04410	0	0.074	20.123	101.325	0.332099	0.1537	4.68
0.50000	0.064099	0.002	0.136	-0.115	0.06024	0	0.111	20.123	101.325	0.364514	0.1688	3.69
0.40000	0.076597	0.002	0.138	-0.052	0.07115	0	0.141	20.123	101.325	0.393395	0.1674	3.31
0.3147	0.090003	0.000	0.138	-0.009	0.08257	0	0.175	20.123	101.325	0.420117	0.1945	3.06
0.3000	0.092619	0.003	0.142	-0.003	0.08477	0	0.181	20.123	101.325	0.424733	0.1966	3.02
0.2000	0.113238	0.004	0.146	0.033	0.10172	0	0.233	20.123	101.325	0.455184	0.1937	2.80
0.1000	0.139680	0.005	0.151	0.053	0.12256	0	0.298	20.123	101.325	0.482873	0.2236	2.68
0.00000	0.173320	0.000	0.151	0.059	0.14772	0	0.377	20.123	101.325	0.507343	0.2349	2.65

Figure C.3 Determine K_{Ga_v} from height of the column



Appendix D CO₂ outlet loading

Table D.1 CO₂ outlet loading (mol/mol) in effect of alkanolamine types

MEA	2-MAE	DMAE
0.331 ± 0.005	0.336 ± 0.001	0.119 ± 0.001

Table D.2 CO₂ outlet loading (mol/mol) in effect of weight ratio

	MEA:2-MAE	MEA:DMAE	2-MAE:DMAE
30:0	0.126 ± 0.000	0.126 ± 0.000	0.188 ± 0.001
20:10	0.176 ± 0.002	0.145 ± 0.004	0.199 ± 0.002
15:15	0.200 ± 0.010	0.184 ± 0.003	0.219 ± 0.001
10:20	0.190 ± 0.002	0.164 ± 0.001	0.199 ± 0.001
0:30	0.188 ± 0.001	0.092 ± 0.001	0.092 ± 0.001

Table D.3 CO₂ outlet loading (mol/mol) in effect of liquid flow rate

	$5.3 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$10.6 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$15.9 \text{ m}^3/\text{m}^2 \cdot \text{h}$
30:0	0.193 ± 0.001	0.126 ± 0.000	0.120 ± 0.006
20:10	0.191 ± 0.002	0.176 ± 0.002	0.135 ± 0.001
15:15	0.218 ± 0.004	0.200 ± 0.010	0.136 ± 0.001
10:20	0.234 ± 0.001	0.190 ± 0.002	0.148 ± 0.001
0:30	0.236 ± 0.001	0.188 ± 0.001	0.153 ± 0.001

MEA:DMAE _

	$5.3 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$10.6 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$15.9 \text{ m}^3/\text{m}^2 \cdot \text{h}$
30:0	0.193 ± 0.001	0.126 ± 0.000	0.120 ± 0.006
20:10	0.198 ± 0.001	0.145 ± 0.004	0.128 ± 0.002
15:15	0.198 ± 0.004	0.184 ± 0.003	0.134 ± 0.001
10:20	0.256 ± 0.002	0.164 ± 0.001	0.127 ± 0.002
0:30	0.128 ± 0.004	0.092 ± 0.001	0.094 ± 0.006

- 2-MAE:DMAE

2-MAE:DN	лае		
	$5.3 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$10.6 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$15.9 \text{ m}^3/\text{m}^2 \cdot \text{h}^3$
30:0	0.236 ± 0.001	0.188 ± 0.001	0.153 ± 0.002
20:10	0.263 ± 0.002	0.199 ± 0.002	0.152 ± 0.002
15:15	0.253 ± 0.002	0.219 ± 0.001	0.155 ± 0.003
10:20	0.255 ± 0.001	0.199 ± 0.001	0.160 ± 0.001
0:30	0.128 ± 0.004	0.092 ± 0.001	0.094 ± 0.006

Table D.4 CO_2 outlet loading (mol/mol) in effect of CO_2 content in gas phase

	5 %v/v	10 %v/v	15 %v/v
30:0	0.083 ± 0.001	0.126 ± 0.004	0.126 ± 0.000
20:10	0.099 ± 0.003	0.119 ± 0.004	0.176 ± 0.002
15:15	0.110 ± 0.000	0.130 ± 0.001	0.200 ± 0.010
10:20	0.124 ± 0.001	0.101 ± 0.001	0.190 ± 0.002
0:30	0.114 ± 0.002	0.149 ± 0.002	0.188 ± 0.001



	5 %v/v	10 %v/v	15 %v/v
30:0	0.083 ± 0.001	0.126 ± 0.004	0.126 ± 0.000
20:10	0.094 ± 0.001	0.117 ± 0.001	0.145 ± 0.004
15:15	0.145 ± 0.001	0.126 ± 0.001	0.184 ± 0.003
10:20	0.092 ± 0.001	0.123 ± 0.001	0.164 ± 0.001
0:30	0.086 ± 0.003	0.093 ± 0.002	0.092 ± 0.001

- 2-MAE:DMAE

	5 %v/v	10 %v/v	15 %v/v
30:0	0.114 ± 0.002	0.149 ± 0.002	0.188 ± 0.001
20:10	0.112 ± 0.004	0.114 ± 0.001	0.199 ± 0.002
15:15	0.112 ± 0.001	0.145 ± 0.002	0.219 ± 0.001
10:20	0.102 ± 0.003	0.138 ± 0.003	0.199 ± 0.001
0:30	0.086 ± 0.003	0.093 ± 0.002	0.092 ± 0.001

Table D.5 CO₂ outlet loading (mol/mol) in effect of CO₂ initial loading

	0.0 mol/mol	0.1 mol/mol	0.2 mol/mol
30:0	0.126 ± 0.000	0.276 ± 0.001	0.326 ± 0.007
20:10	0.176 ± 0.002	0.210 ± 0.002	0.280 ± 0.002
15:15	0.200 ± 0.010	0.283 ± 0.002	0.343 ± 0.002
10:20	0.190 ± 0.002	0.252 ± 0.001	0.309 ± 0.003
0:30	0.188 ± 0.001	0.274 ± 0.001	0.313 ± 0.001

MEA:DMAE _

	0.0 mol/mol	0.1 mol/mol	0.2 mol/mol
30:0	0.126 ± 0.000	0.276 ± 0.001	0.326 ± 0.007
20:10	0.145 ± 0.004	0.281 ± 0.002	0.324 ± 0.001
15:15	0.184 ± 0.003	0.255 ± 0.001	0.305 ± 0.001
10:20	0.164 ± 0.001	0.270 ± 0.002	0.329 ± 0.004
0:30	0.092 ± 0.001	0.103 ± 0.003	0.282 ± 0.003

- 2-MAE:DN	- 2-MAE:DMAE				
	0.0 mol/mol	0.1 mol/mol	0.2 mol/mol		
30:0	0.188 ± 0.001	0.274 ± 0.001	0.313 ± 0.001		
20:10	0.199 ± 0.002	0.280 ± 0.001	0.325 ± 0.003		
15:15	0.219 ± 0.001	0.291 ± 0.004	0.333 ± 0.006		
10:20	0.199 ± 0.001	0.327 ± 0.002	0.382 ± 0.003		
0:30	0.092 ± 0.001	0.103 ± 0.003	0.282 ± 0.003		

Appendix E K_Ga_v values

Table E.1 K_{Gav} values (kmol/m³·kPa·h) in effect of alkanolamine types

MEA	2-MAE	DMAE
0.3876 ± 0.001	0.9003 ± 0.001	0.0403 ± 0.002

Table E.2 K_{Gav} values (kmol/m³·kPa·h) in effect of weight ratio

	MEA:2-MAE	MEA:DMAE	2-MAE:DMAI
30:0	0.9154 ± 0.000	0.9154 ± 0.000	1.6376 ± 0.002
20:10	0.9573 ± 0.003	0.8511 ± 0.001	1.2827 ± 0.002
15:15	1.4360 ± 0.001	0.7620 ± 0.001	1.0923 ± 0.001
10:20	1.2588 ± 0.002	0.6355 ± 0.003	0.7746 ± 0.001
0:30	1.6376 ± 0.002	0.0403 ± 0.001	0.0403 ± 0.001

Table E.3 K_{Gav} values (kmol/m³·kPa·h) in effect of liquid flow rate

	$5.3 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$10.6 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$15.9 \text{ m}^3/\text{m}^2 \cdot \text{h}$
30:0	0.6704 ± 0.001	0.9154 ± 0.002	1.0145 ± 0.002
20:10	0.7343 ± 0.001	0.9573 ± 0.002	1.3000 ± 0.004
15:15	0.9740 ± 0.003	1.4360 ± 0.002	1.8978 ± 0.001
10:20	0.9625 ± 0.002	1.2588 ± 0.001	1.4722 ± 0.001
0:30	1.2242 ± 0.001	1.6376 ± 0.001	1.9128 ± 0.003

MEA:DMAE _

	$5.3 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$10.6 \text{ m}^{3}/\text{m}^{2} \cdot \text{h}$	$15.9 \text{ m}^3/\text{m}^2 \cdot \text{h}$
30:0	0.6704 ± 0.001	0.9154 ± 0.002	1.0145 ± 0.002
20:10	0.7443 ± 0.001	0.8511 ± 0.001	0.9867 ± 0.003
15:15	0.6317 ± 0.004	0.7620 ± 0.001	0.8395 ± 0.001
10:20	0.4824 ± 0.002	0.6355 ± 0.003	0.7443 ± 0.002
0:30	0.1693 ± 0.001	0.0403 ± 0.001	0.0575 ± 0.003

- 2-MAE:DMAE

- 2-MAE:DN			
	$5.3 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$10.6 \text{ m}^3/\text{m}^2 \cdot \text{h}$	$15.9 \text{ m}^3/\text{m}^2 \cdot \text{h}$
30:0	1.2242 ± 0.001	1.6376 ± 0.001	1.9128 ± 0.003
20:10	0.8819 ± 0.001	1.2827 ± 0.002	1.5542 ± 0.002
15:15	0.8072 ± 0.002	1.0923 ± 0.001	1.2778 ± 0.001
10:20	0.5691 ± 0.002	0.7746 ± 0.001	0.9730 ± 0.001
0:30	0.1693 ± 0.001	0.0403 ± 0.001	0.0575 ± 0.003

Table E.4 K_{Gav} values (kmol/m³·kPa·h) in effect of CO₂ content in gas phase

	5 %v/v	10 %v/v	15 %v/v
30:0	1.7807 ± 0.003	1.0110 ± 0.002	0.9154 ± 0.000
20:10	1.9532 ± 0.001	1.5309 ± 0.001	0.9573 ± 0.003
15:15	2.1390 ± 0.001	1.7566 ± 0.001	1.4360 ± 0.001
10:20	2.1394 ± 0.002	1.6122 ± 0.001	1.2588 ± 0.002
0:30	3.3055 ± 0.000	1.9728 ± 0.001	1.6376 ± 0.002

- MEA:2-MAE

- MEA:DMAE

	5 %v/v	10 %v/v	15 %v/v
30:0	1.7807 ± 0.003	1.0110 ± 0.002	0.9154 ± 0.000
20:10	1.3116 ± 0.001	1.0879 ± 0.002	0.8511 ± 0.001
15:15	1.2019 ± 0.001	0.7286 ± 0.001	0.7620 ± 0.001
10:20	1.0203 ± 0.002	0.6985 ± 0.002	0.6355 ± 0.003
0:30	0.0554 ± 0.002	0.0453 ± 0.001	0.0403 ± 0.001

- 2-MAE:DMAE

	5 %v/v	10 %v/v	15 %v/v
30:0	3.3055 ± 0.000	1.9728 ± 0.001	1.6376 ± 0.002
20:10	2.1715 ± 0.001	1.4749 ± 0.001	1.2827 ± 0.002
15:15	1.9138 ± 0.001	1.4171 ± 0.002	1.0923 ± 0.001
10:20	1.5415 ± 0.001	1.0053 ± 0.003	0.7746 ± 0.001
0:30	0.0554 ± 0.002	0.0453 ± 0.001	0.0403 ± 0.001

Table E.5 K_{Gav} values (kmol/m³·kPa·h) in effect of CO₂ initial loading

	0.0 mol/mol	0.1 mol/mol	0.2 mol/mol
30:0	0.9154 ± 0.000	0.7099 ± 0.001	0.6291 ± 0.002
20:10	0.9573 ± 0.003	0.9750 ± 0.003	0.8055 ± 0.002
15:15	1.4360 ± 0.001	1.2357 ± 0.002	0.9930 ± 0.001
10:20	1.2588 ± 0.002	1.2097 ± 0.001	0.9358 ± 0.001
0:30	1.6376 ± 0.002	1.3162 ± 0.001	1.0595 ± 0.001

MEA:DMAE _

	0.0 mol/mol	0.1 mol/mol	0.2 mol/mol
30:0	0.9154 ± 0.000	0.7099 ± 0.001	0.6291 ± 0.002
20:10	0.8511 ± 0.001	0.7066 ± 0.002	0.5819 ± 0.001
15:15	0.7620 ± 0.001	0.6100 ± 0.002	0.5124 ± 0.001
10:20	0.6355 ± 0.003	0.4933 ± 0.003	0.3613 ± 0.002
0:30	0.0403 ± 0.001	0.0523 ± 0.001	0.0327 ± 0.003

- 2-MAE:DMAE

- 2-MAE:DMAE				
	0.0 mol/mol	0.1 mol/mol	0.2 mol/mol	
30:0	1.6376 ± 0.002	1.3162 ± 0.001	1.0595 ± 0.001	
20:10	1.2827 ± 0.002	1.0384 ± 0.002	0.8289 ± 0.002	
15:15	1.0923 ± 0.001	0.8790 ± 0.002	0.7159 ± 0.001	
10:20	0.7746 ± 0.001	0.5599 ± 0.002	0.3959 ± 0.001	
0:30	0.0403 ± 0.001	0.0523 ± 0.001	0.0327 ± 0.003	

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