COMPARISON OF EFFICIENCY AND ENERGY CONSUMPTION OF AMINE SOLUTIONS IN DIFFERENT SOLVENTS FOR CO_2 ABSORPTION AND DESORPTION PROCESSES

By

Miss Sasiphan DEENAN

A Thesis Submitted in Partial Fulfillment of the Requirements

for Master of Engineering CHEMICAL ENGINEERING

Department of CHEMICAL ENGINEERING

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Title	Comparison of Efficiency and Energy Consumption of Amine Solutions in Different Solvents for CO_2 Absorption and Desorption Processes
By	Miss Sasiphan DEENAN
Field of Study	CHEMICAL ENGINEERING
Advisor	Assistant Professor Dr. Weerawat Patthaveekongka

Faculty of Engineering and Industrial Technology, Silpakorn University in Partial Fulfillment of the Requirements for the Master of Engineering

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Miss Sasiphan DEENAN : Comparison of Efficiency and Energy Consumption of Amine Solutions in Different Solvents for CO_2 Absorption and Desorption Processes
Thesis advisor : Assistant Professor Dr. Weerawat Patthaveekongka

This study aims to investigate the effects of employing alcohols specifically methanol and ethanol as solvents in amine-based solutions, namely monoethanolamine (MEA) and diethanolamine (DEA), for carbon dioxide (CO_2) absorption processes. Six solution systems, including MEA+H_2O, MEA+MeOH, MEA+EtOH, DEA+H_2O, DEA+MeOH, and DEA+EtOH, were examined to evaluate their physical properties and performance in capturing CO_2 from a simulated flue gas containing 12% CO_2, 5% O_2, and 83% N_2. The performance and energy consumption of each system were further compared with those of the conventional absorption process using water as the primary solvent.

The experimental investigation was carried out under various operating conditions, with the amine solution flow rate ranging from 0.6 to 1.2 L/min, the gas mixture flow rate between 15 and 25 L/min, and the reboiler temperature maintained within 85–100°C. Based on previous literature, the addition of alcohols to amine solutions has been reported to enhance CO_2 absorption efficiency and decrease the energy requirement during solvent regeneration.

The experimental findings revealed that the DEA–ethanol system exhibited the highest CO_2 absorption efficiency of 95.04% and a desorption efficiency of 94.52%, which were superior to those of the conventional MEA–H_2O system (85–90%). Furthermore, the DEA–ethanol solution demonstrated 6–10% higher absorption efficiency than the DEA–methanol system. At a solvent flow rate of 1 L/min, the DEA–ethanol system showed the lowest energy consumption of 24.46 MJ per kilogram of CO_2 separated, representing a reduction of more than 50% compared with the conventional water-based absorption process, which typically requires of

48–50 MJ/kg CO_2.

In conclusion, this study demonstrates the potential of employing alcohols as alternative solvents in amine-based CO_2 capture systems. The use of alcohols not only enhances absorption performance but also substantially reduces energy consumption. These findings provide valuable insights for the advancement and sustainable development of CO_2 capture technologies in the future.

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CHAPTER I INTRODUCTION

Carbon dioxide (CO_2) is a major greenhouse gas that plays a critical role in climate change. The emission of CO_2 from the energy sector, fossil fuel combustion, transportation, and various industrial processes contributes significantly to the greenhouse effect, which is the primary cause of global warming [1] . The continuous rise in global temperature has led to the melting of polar ice caps, rising sea levels, and unpredictable weather patterns, resulting in severe natural disasters such as cyclones, heatwaves, wildfires, and droughts [2]. In addition, CO_2 directly impacts marine ecosystems as it dissolves in seawater and reacts to form carbonic acid (H_2CO_3), causing ocean acidification [3]. This phenomenon adversely affects marine organisms, particularly coral reefs and shell-forming species such as mollusks and zooplankton. Moreover, fluctuations in temperature and rainfall also disrupt agricultural productivity and food security [4].

In general, flue gases from combustion processes contain approximately 10–15% CO_2 [5, 6], which must be properly managed to mitigate environmental impacts. Although CO_2 is a greenhouse gas, it can also be utilized beneficially in several industrial applications, such as synthetic fuel production, the food and beverage industry, enhanced oil recovery (EOR), and the development of construction materials that capture CO_2 [7, 8]. At present, several CO_2 capture technologies have been developed, including physical absorption, membrane separation, and solid adsorption. However, chemical absorption using amine-based solvents such as monoethanolamine (MEA) and diethanolamine (DEA) remains the most widely used method due to its high absorption efficiency and chemical selectivity for CO_2 [9, 10].

Nevertheless, CO_2 absorption using aqueous amine solutions has certain limitations, primarily due to the high energy requirement during solvent regeneration [11]. Since water has a relatively high boiling point, significant thermal energy is needed to

release CO_2 from the amine solution. To address this challenge, researchers have proposed the use of alcohols such as methanol and ethanol as alternative solvents to replace water. Alcohols possess lower boiling points (64.7°C for methanol and 78.37°C for ethanol) compared to water (100°C), leading to a reduction of 20–40% in the thermal energy required for solvent regeneration [12]. Previous studies have shown that the use of DEA in methanol enhances CO_2 absorption efficiency and significantly reduces the energy consumption during the desorption process [13].

Amine-based absorption is one of the most widely applied technologies for CO2 capture in industrial gas treatment processes. The absorption mechanism strongly depends on the chemical structure of the amine and the properties of the solvent, which subsequently influence the energy requirement for solvent regeneration. In general, amines can be classified into primary and secondary amines, each exhibiting distinct CO2 capture pathways[14]:

Primary amines, such as monoethanolamine (MEA), predominantly capture CO2 via carbamate formation, which involves relatively strong chemical bonding and higher reaction enthalpy. In contrast, secondary amines, such as diethanolamine (DEA), mainly absorb CO2 through bicarbonate formation, which generally exhibits weaker chemical interactions between CO2 and the amine[15]. These fundamental differences in absorption mechanisms play a critical role in determining CO2 loading capacity and regeneration energy demand.

In addition to amine structure, solvent properties also significantly affect absorption–desorption behavior. Conventional aqueous amine systems are well known to be energy-intensive due to the high thermal energy required for solvent regeneration [16]. To overcome this limitation, the use of alcohol-based solvents, such as methanol and ethanol, has been proposed as an alternative to water. Methanol and ethanol possess significantly lower boiling points (64.7 °C and 78.37 °C, respectively)

compared to water (100 °C), which is expected to reduce sensible and latent heat requirements during the regeneration process

From a process design and energy efficiency perspective, solvent selection plays a critical role in determining thermophysical properties, including heat capacity, vapor–liquid equilibrium behavior, and mass transfer characteristics. These properties directly influence CO2 absorption performance and regeneration energy demand. Therefore, a systematic comparison of water-, methanol-, and ethanol-based MEA and DEA systems is essential for evaluating their potential to reduce overall energy consumption while maintaining effective CO2 capture. This approach provides a fundamental basis for the development of more energy-efficient and sustainable amine-based CO2 capture processes, which is the main focus of this study[17].

1.1 Objectives of the Research

- To evaluate and compare the performance of carbon dioxide (CO_2) absorption and desorption processes under different operating conditions.
- To investigate the energy consumption involved in the absorption and desorption of CO_2 using amine-based solvents.
- To compare the performance of monoethanolamine (MEA) and diethanolamine (DEA) solutions.
- To assess the effects of different solvents — namely water, methanol, and ethanol — on absorption efficiency and solvent regeneration performance.
- To examine the processes under synthetic flue gas conditions simulating the composition of exhaust gases from a biogas-fueled power plant.
- To utilize the findings of this study as a guideline for the development of more efficient and sustainable carbon dioxide capture technologies.

1.2 Scope of Research

- Utilize a synthetic flue gas composed of 12 Vol% CO_2, 5 Vol% O_2, and 83 Vol% N_2, simulating emissions from biogas-fueled power plants.
- Conduct absorption and desorption experiments using a 1.5-meter pilot-scale amine absorption column with a 10-mm packed bed weighing 14 kg. the boiler, constructed from stainless steel 304, measures 30 cm in diameter and 45 cm in height, and is surrounded by an external oil bath jacket with dimensions of 39 cm in diameter and 30 cm in height.
- Study two types of amines: MEA (monoethanolamine) and DEA (diethanolamine).
- Study three solvents: water, methanol, and ethanol.
- Investigate two amine concentrations: 20 wt% and 30 wt%.
- Examine amine solution flow rates of 0.6, 0.8, 1.0, and 1.2 L/min.
- Test flue gas flow rates of 15, 20, and 25 L/min.
- Vary desorber boiler temperatures between 85–100°C.

1.3 Expectations of Research

- Provide comparative data on CO_2 absorption and desorption efficiency of amine solutions with water, methanol, and ethanol.
- Provide energy consumption data for each solvent-amine system.
- Identify optimal operating conditions for each solvent-amine system.
- Recommend suitable bio-based solvents (methanol and ethanol) for sustainable CO_2 capture.
- Promote greenhouse gas control technologies for biogas-fueled power plants, which currently emit untreated flue gases.

CHAPTER II LITERATURE REVIEWS

This chapter presents a comprehensive review of CO_2 capture technologies, focusing on amine-based absorption processes. Studies on MEA and DEA in aqueous solutions and solutions using methanol and ethanol are discussed, including performance comparisons and energy efficiency improvements for sustainable carbon capture.

Pandey D. et al. (2011) [1] Increasing greenhouse gaseous concentration in the atmosphere is perturbing the environment to cause grievous global warming and associated consequences. Following the rule that only measurable is manageable, mensuration of greenhouse gas intensiveness of different products, bodies, and processes is going on worldwide, expressed as their carbon footprints. The methodologies for carbon footprint calculations are still evolving and it is emerging as an important tool for greenhouse gas management. The concept of carbon footprinting has permeated and is being commercialized in all the areas of life and economy, but there is little coherence in definitions and calculations of carbon footprints among the studies. There are disagreements in the selection of gases, and the order of emissions to be covered in footprint calculations. Standards of greenhouse gas accounting are the common resources used in footprint calculations, although there is no mandatory provision of footprint verification. Carbon footprinting is intended to be a tool to guide the relevant emission cuts and verifications, its standardization at international level are therefore necessary. Present review describes the prevailing carbon footprinting methods and raises the related issues.

Yang F. et al. (2012) [2] Densities of the binary and ternary systems formed by mixtures of bis(2-hydroxyethyl)amine (DEA) + water, DEA + methanol (MeOH), DEA + ethanol (EtOH) and DEA + MeOH + water, DEA + EtOH + water were measured at atmospheric pressure for the whole composition range at temperatures from 278.15

K to 353.15 K using an Anton Paar digital vibrating U-tube densimeter (model DMA 5000M). The excess molar volumes have been calculated from the experimental densities in this work and correlated using the Redlich–Kister equation. A set of parameters for the Redlich–Kister equation has been determined to represent the density of the liquid mixture.

Harbou I. et al. (2013) [4] Adding ethanol to an aqueous amine solution offers several advantages for post-combustion CO_2 capture. The equilibrium isotherms at higher temperatures shift towards lower loadings, leading to an easier desorption. At constant temperature in the desorber bottom, the desorber pressure is increased, leading to energy savings in the CO_2 compression. Alternatively, at constant desorber pressure, the temperature in the desorber bottom is decreased, leading to a smaller efficiency drop of the power plant. Furthermore, the absorption rate of CO_2 is enhanced by adding ethanol. In the present work, the potential of using ethanol as a co-solvent for a 0.3 g/g aqueous monoethanolamine (MEA) solution is assessed based on simulations with an equilibrium stage model. A major drawback is the volatility of ethanol. The recovery of ethanol can be achieved using a water scrubber and subsequent stripping. The recovered ethanol vapor is sent directly to the desorber for heat integration. The process with ethanol recovery results in an increased complexity of the capture plant, difficulties in controlling the water balance and higher investment costs and offers, if any, only a moderate energetic advantage. The process concept could, however, be used for other co-solvents with similar properties as ethanol but lower vapor pressures.

Kim Y. et al. (2014) [5] Some alkanolamine–alcohol mixtures separate into a CO_2 rich phase and a CO_2 lean phase after the absorption of CO_2, which makes possible a new approach to CO_2 capture. In this study, CO_2 absorbent solutions with various concentrations of monoethanolamine (MEA) and diethanolamine (DEA) were

prepared by mixing them with alcohol. The CO_2 absorption capacities of the alkanolamine–alcohol mixtures were investigated by using a semi-batch reactor at 313 K. The species distributions of the absorbents were identified in order to determine the CO_2 absorption mechanism of these solutions. Although the CO_2 absorption capacities of the phase transitional absorbents are lower than that of aqueous solutions, we conclude from our experimental results that the phase transitional solutions have the economic advantages, and in particular lower regeneration energies, because only the CO_2-rich phase needs to be transported to the stripper.

In the case of the non-aqueous MEA solutions, the amine concentration was found to have no effect on the CO_2 loading. However, in the case of non-aqueous DEA solutions, the CO_2 loading is high at high amine concentrations. It was found that the solvents (alcohols) are present in the upper phase, and that amine and amine carbamate are present in the lower phase after the absorption of CO_2. The phase separation of the CO_2-loaded absorbent occurs spontaneously, so the CO_2-rich phase (the lower phase) can easily be transported to the regeneration process. These characteristics show that alkanolamine–alcohol mixtures are promising absorbents for CO_2 capture

Fu K. et al. (2015) [6] The performance of CO_2 absorption into a hybrid solvent such as monoethanolamine (MEA) in methanol (MeOH) was experimentally investigated in a lab-scale absorber packed with Sulzer DX-type structured packing, and compared with that of aqueous MEA solution. The experiments were performed at various key operating conditions over a MEA concentration range of 2.5–5.0 kmol/m^3,a CO_2 lean loading range of 0–0.373 mol/mol, a liquid flow rate range of 2.92–16.09 m^3/m^2 h, an inert gas ow rate range of 24.37–63.54 kmol/m^2 h, a CO_2 partial pressure range of 6.7–13.8 kPa, and an inlet liquid temperature of 10 °C. The

absorption performance was presented in terms of the overall gas phase mass transfer coefficient (KGav), CO_2 concentration and system temperature pro les along the height of the absorber, and the system temperatures at the bottom and the top of the absorber, Tbot and Ttop, respectively. It was found that the KGav for MEA–MeOH was higher than that of MEA–H_2O. In addition, the experimental results showed that key operating parameters such as MEA concentration, CO_2 loading, liquid ow rate and inert gas ow rate have large effect on the performance of CO_2 absorption into the MEA–MeOH.

Gao J. et al. (2016) [7] The regeneration heat duty (Qreg, MJ/kg CO_2) which consists of solvent heating energy (Qsh, MJ/kg CO_2), solvent vaporization energy (Qvap, MJ/kg CO2), and desorption energy (Qdes, MJ/kg CO_2), is a critical parameter in evaluating the performance of a solvent for post combustion CO_2 capture. In this study, Qreg of CO_2 desorption from rich monoethanolamine (MEA)-methanol solvent was experimentally evaluated in a pilot-plant stripper packed with Sulzer packing BX500, Mellapale packing Y500 and Pall rings 16x3x16. And a comparison of Qreg between MEA-methanol and aqueous MEA solvent was performed to evaluate the potential for MEA-methanol's application in industrial CO_2 capture process. Also effects of several operating parameters of the stripper consists of rich CO_2 loading (0.25–0.52 mol/mol), rich solvent flow rate (21.2–51.4 L/h), rich solvent temperature (40–608°C) and regeneration temperature (68–748C) on the regeneration performance of the stripper were studied. It was found that Qreg of MEA-methanol solvent was lower than aqueous MEA solvent (especially Qdes) and Qreg was sensitive to all the four parameters. Also the results obtained in this work showed that the stripper performance of Sulzer BX500 packing was better than Mellapale Y500 packing and Pall rings 16x16 packing was the worst.

Fu D. et al. (2018) [9] The surface tension (c) and viscosity (g) of monoethanolamine (MEA)-methanol (MeOH) and diethanolamine (DEA)-MeOH aqueous solutions were measured by using the BZY-1 surface tension meter and the NDJ-5S digital rotational viscometer. The temperature ranged from 303.2 K to 323.2 K. The mass fractions of MeOH, MEA and DEA ranged from 0.025 to 0.075, 0.2 to 0.4 and 0.2 to 0.4 respectively. Equations were proposed to model the surface tension and viscosity respectively and both the calculated results agreed well with the experiments. The effects of temperature and mass fraction of MeOH/amines on the surface tension and viscosity were demonstrated on the basis of experiments and calculations.

Abroodi, M. (2019) [11] This study aimed to develop a low-temperature and energy-efficient carbon dioxide (CO_2) capture technology using mixed alcohol–amine–water solvents, instead of conventional aqueous amine systems that require high regeneration temperatures and intensive energy consumption. The experimental results demonstrated that the addition of alcohols, particularly ethanol (EtOH), to amine solutions significantly enhanced both the CO_2 desorption rate and the cyclic CO_2 capture capacity compared to conventional MEA–H_2O, DEA–H_2O, and MDEA–H_2O systems. The sorbent mixture containing 40 wt% EtOH, 20 wt% MEA, and 20 wt% H_2O achieved a 6.8-fold increase in cyclic CO_2 capture capacity and up to a 236-fold improvement in CO_2 desorption rate at 75°C. This performance enables the utilization of low-temperature waste heat from power plants for CO_2 capture, making self-sustained CO_2 capture operations feasible. Spectroscopic analyses using Raman and Fourier Transform Infrared (FTIR) techniques confirmed that ethanol in the EtOH–MEA–H_2O mixture altered the reaction pathway by forming $C_2H_5OCO_2^-$ instead of HCO_3^-, which is more stable and difficult to decompose. Additionally, the new process effectively minimized amine degradation, a common issue in conventional

CO_2 capture technologies. Therefore, this newly developed alcohol–amine–water CO_2 capture system presents a promising approach for reducing energy consumption and environmental impact, offering significant potential for sustainable CO_2 capture applications.

Knuutila H. et al. (2019) [13] In the current work five different solvent blends are experimentally studied and the reboiler duties are calculated using the so-called short-cut method. Tertiary amines, 2-(diethylamino) ethanol (DEEA), 3-(Diethylamino)-1,2-propanediol (DEA-12PD), 2-[2-(Diethylamino) ethoxy] ethanol (DEA-EO), 1-(2-Hydroxyethyl) piperidine (12HE-PP) are blended with 3-(Methylamino)propylamine (MAPA) and ethanolamine (MEA). The first results from simple solvent screening are given and the cyclic capacities are calculated based data at 40 °C and 80 °C. Then, five solvent systems are chosen for vapor–liquid equilibrium characterization. The vapor–liquid equilibrium data are then used to estimate cyclic capacities at more realistic temperatures, between 40 °C and 120 °C and by using a short-cut method proposed in the literature the reboiler duties of the characterized solvents are estimated. Finally, the potential of the studied systems is discussed. Several of the characterized blends showed reboiler duties around 2.5 MJ kg 1 CO_2.

Lai Q. et al. (2019) [14] The conventional regeneration processes for aqueous amine-based sorbents require high regeneration temperature and are very energy intensive. In this work, a low-temperature and energy-saving CO_2 capture technology has been successfully developed by using alcohols-amines-water mixtures as sorbents. The addition of certain amounts of alcohols [especially ethanol (EtOH)] to amines can significantly increase the CO_2 desorption rates and cyclic CO_2 capture capacities in comparison with those of monoethanolamine-water, diethanolamine water, and methyldiethanolamine-water systems. The sorbent containing 40wt% EtOH, 20wt% mono ethanolamine (MEA), and 20wt% H_2O can increase cyclic CO_2

capture capacity by 6.8 times and a maximum improvement of 236 times in CO_2 desorption rate at 75°C, which makes the use of the low-temperature waste heat in power plants for CO_2 capture or self-supported CO_2 capture in power plants possible. To the best of authors' knowledge, this is the first time that Raman and Fourier transform infrared spectroscopy characterizations have been used to confirm that ethanol in EtOH-MEA-H_2O can change the reaction pathway by forming $C_2H_5OCO_2$ – instead of HCO3 –, which is difficult to decompose. In addition, the experimental results confirm that the new technology can significantly avoid amine degradation– a common challenge of the state-of-the-art CO_2 capture technologies. Therefore, the new CO_2 capture technology is promising from the perspectives of energy saving and environmental protection.

Rashidi, H. et al. (2019) [15] This study presents a multi-objective experimental optimization of the CO_2 capture process using hybrid solvents composed of amines and alcohols. The main goal was to enhance CO_2 absorption efficiency while minimizing the energy required for solvent regeneration. Various operating parameters—including gas and liquid flow rates, CO_2 concentration, and temperature—were systematically investigated to identify the optimal conditions. The results showed that the addition of alcohols such as methanol and ethanol to amine-based solvents (MEA and DEA) significantly improved CO_2 absorption performance. Alcohol addition enhanced CO_2 solubility and reduced solvent viscosity, which improved mass transfer and absorption rate. Moreover, hybrid solvents demonstrated lower regeneration energy compared to conventional aqueous amine systems, due to the lower boiling points of alcohols. Through multi-objective optimization, the study determined that the best performance was achieved when using a MEA–ethanol mixture under specific flow rate and temperature conditions, resulting in high CO_2 removal efficiency and reduced energy

consumption. the research concluded that hybrid amine–alcohol solvents offer a promising and energy-efficient alternative for CO_2 capture applications. The findings provide valuable insights into the design of optimized solvent systems for sustainable carbon capture technology.

Guo, H. et al. (2019) This study investigated nonaqueous amine-based absorbents for energy-efficient CO_2 capture, using mixtures of monoethanolamine (MEA) or diethanolamine (DEA) with glycol ethers (2-methoxyethanol, 2ME, and 2-ethoxyethanol, 2EE). The goal was to reduce regeneration energy while maintaining good absorption capacity.

Experimental results showed that 5.0 M MEA–glycol ether mixtures achieved CO_2 absorption capacities comparable to aqueous MEA but with higher desorption efficiency and a cyclic capacity of 1.45 mol kg^{-1}. Spectroscopic analyses (^{13}C NMR and FTIR) confirmed that CO_2 reacts with MEA forming both carbamate and carbamic acid species in nonaqueous solvents.

The energy consumption for solvent regeneration was reduced by ~55% compared to aqueous MEA due to the lower specific heat and vaporization enthalpy of glycol ethers. The study concluded that MEA/2ME and MEA/2EE mixtures are promising nonaqueous alternatives offering high efficiency and substantially lower regeneration energy for CO_2 capture applications.

Aghel, B. et al. (2021) This research explored CO_2 desorption from MEA mixed with alcoholic solvents (methanol, ethanol, propanol, and butanol) in a microreactor system. The effects of temperature (55–95 °C), solvent flow rate (1–5 mL min^{-1}), and solvent concentration (10–50 wt%) on desorption energy and performance were systematically studied.

The results showed that replacing water with alcohols significantly reduced energy consumption (E) during CO_2 desorption—by more than one-third. The lowest

energy requirement was observed for the MEA + methanol mixture (0.41 MJ kg^{-1} CO_2), followed by ethanol (0.48 MJ kg^{-1} CO_2), propanol (0.55 MJ kg^{-1} CO_2), and butanol (1.1 MJ kg^{-1} CO_2). For comparison, the MEA + water system required ~1.39 MJ kg^{-1} CO_2.

Using a microreactor further enhanced mass transfer and reduced energy consumption due to its high surface-to-volume ratio. The study concluded that MEA–alcohol systems, particularly MEA–methanol, provide superior energy efficiency and faster desorption compared with traditional aqueous MEA, making them attractive for compact and low-energy CO_2 capture systems.

Schulze-Hulbe, A. et al. (2023) This paper focused on developing thermodynamic modeling parameters for nonaqueous alkanolamine-based CO_2 capture systems using the structural Statistical Associating Fluid Theory (s-SAFT-**γ** Mie) equation of state. The aim was to accurately predict phase equilibria and thermodynamic properties of amine–alcohol–CO_2 systems to guide solvent design.

The authors established new group interaction parameters for primary amines, secondary alcohols, and CO_2, using pure-component and binary mixture data. The model was validated against experimental vapor–liquid equilibrium (VLE) and density data, showing reliable prediction capability.

Results demonstrated that the s-SAFT-**γ** Mie model effectively represents intermolecular interactions and association behavior in nonaqueous systems, allowing comparison with aqueous amine systems. The study provides a systematic and physically meaningful parameterization method that enables accurate modeling of ternary alkanolamine + alcohol + CO_2 mixtures, supporting the development of next-generation low-energy, nonaqueous carbon capture solvents.

Previous studies have extensively investigated the performance of amine-based CO_2 absorption and desorption processes using various solvents to enhance

efficiency and reduce energy consumption during solvent regeneration. Monoethanolamine (MEA) and diethanolamine (DEA) solutions, when mixed with alcohols such as methanol and ethanol, have shown improved energy performance compared to aqueous solutions due to the lower boiling points of alcohols, which reduce thermal energy requirements during regeneration. The addition of ethanol, in particular, has been found to enhance CO_2 absorption rates and enable phase separation after absorption, allowing the CO_2-rich phase to be directly fed into the stripper, thus minimizing energy losses during solvent transport and regeneration. Moreover, the use of alcohols has been reported to alter the reaction pathway and significantly reduce amine degradation, a common issue in traditional aqueous systems, contributing to the long-term sustainability of CO_2 capture technologies. Nevertheless, the use of alcohol-based solvents introduces additional complexity in system design, water balance control, and capital investment, which must be considered for practical implementation.

CHAPTER III THORY

This chapter is divided into three sections, including the properties of materials used, the fundamental theory of amine absorption, and the reaction mechanisms involved in the removal of carbon dioxide (CO_2) from gas streams. The aim of this chapter is to provide the theoretical background necessary to understand the principles and chemical behavior of the amine-based CO_2 absorption process.

3.1 Properties of Materials

The materials used in the CO_2 absorption process primarily consist of amines and solvents, and their properties significantly affect the process efficiency, energy consumption, and operational stability. Amines are organic compounds derived from ammonia in which one or more hydrogen atoms are replaced by alkyl or alkanol groups, enabling them to react reversibly with acid gases such as CO_2 and H_2S to form carbamate or bicarbonate species. Solvents, on the other hand, serve to dissolve the amine, reduce the solution viscosity, and enhance mass transfer between the gas and liquid phases. The selection of appropriate materials is crucial, as they must provide high solubility, thermal stability, chemical compatibility, and resistance to foaming and corrosion, thereby ensuring optimal CO_2 capture performance and sustainable operation of the absorption system.

3.2 Amines (Monoethanolamine; MEA, Diethanolamine; DEA)

Amines are nitrogen-containing organic compounds that play a key role in the chemical absorption of CO_2 due to their ability to react reversibly with acid gases. The selection of appropriate amines is critical, as their chemical structure directly affects the absorption capacity, reaction rate, energy requirement for regeneration, and overall process efficiency. Primary and secondary amines are commonly used in post-combustion CO_2 capture because they can form carbamate species with CO_2, enabling high CO_2 loading in the solvent. The amine solution's performance depends

on factors such as concentration, temperature, and the specific chemical properties of the chosen amine.

Table 3.1 Properties of amine compounds for CO2 capture.

Chemical name	Formula	CAS Number
Monoethanolamine (MEA)	C_2H_7NO	141-43-5
Diethanolamine (DEA)	$C_4H_{13}NO_2$	111-42-2

3.2.1 Monoethanolamine (MEA)

Monoethanolamine (MEA) is a primary amine with the chemical formula $HOCH_2CH_2NH_2$ and is widely used for CO_2 capture due to its high reactivity with acid gases. The absorption reaction is fast and exothermic, forming carbamate ions according to the reaction:

$$2MEA+CO_2 \rightleftharpoons MEACOO^-+MEAH^+$$

Although MEA provides rapid CO_2 uptake and high absorption efficiency, it requires a relatively high energy input for regeneration, because breaking the carbamate bond demands significant heat. MEA is therefore suitable for applications where fast CO_2 removal is prioritized, especially for gas streams with low to moderate CO_2 concentrations.

3.2.2 Diethanolamine (DEA)

Diethanolamine (DEA) is a secondary amine with the chemical formula $HOCH_2CH_2NHCH_2CH_2OH$. Compared to MEA, DEA has a moderate reaction rate with CO_2, forming carbamate ions as follows:

$$2DEA+CO_2 \rightleftharpoons DEACOO^-+DEAH^+$$

DEA requires less energy for regeneration than MEA because the carbamate formed is less stable, allowing CO_2 to be released more easily. Although the absorption rate is slower, DEA is suitable for gas streams with higher CO_2 concentrations and

applications where energy efficiency is a priority. Its higher thermal stability and lower foaming tendency also make it advantageous for long-term operation.

3.3 Solvents

Solvents play a critical role in the CO_2 absorption process by dissolving amines, facilitating mass transfer, and controlling the physical properties of the solution such as viscosity and density. The choice of solvent affects not only the solubility of CO_2 but also the chemical stability, heat capacity, and overall process efficiency. Water is the most commonly used solvent due to its safety, availability, and high heat capacity, which helps maintain thermal stability during the absorption and regeneration steps. Organic solvents such as methanol and ethanol are sometimes used to modify the solution properties, improve gas solubility, reduce foaming, and enhance flow characteristics in the absorber. Proper solvent selection ensures optimal CO_2 capture performance and sustainable operation of the amine-based absorption system.

Table 3.2 Properties of solvents used in amine-based CO2 capture processes.

Chemical name	Density (g/m^3)	Boiling Point (°C)	Purity (%)	CAS Number
Deionized Water	1.00	100.00		7732-18-5
Methanol	0.79	64.70	99.90	67-56-1
Ethanol	0.79	78.40	95.00	64-17-5

3.3.1 Water (H_2O)

Water is the primary solvent used in amine-based CO_2 capture due to its high polarity, non-toxicity, and abundance. It effectively dissolves amines, allowing them to react with CO_2 efficiently. The high heat capacity of water helps buffer temperature changes during the exothermic absorption reaction, preventing local

overheating and ensuring uniform reaction conditions. Water also stabilizes the chemical species in solution and facilitates the transport of CO_2 from the gas phase to the amine molecules.

3.3.2 Methanol (CH_3OH)

Methanol is sometimes used as a co-solvent in CO_2 absorption systems to modify the physical properties of the solution. It can reduce solution viscosity, enhance gas solubility, and decrease the tendency to form foam. Methanol's lower boiling point compared to water can also facilitate energy-efficient regeneration under certain process conditions. However, its flammability and toxicity limit its large-scale use, and it is typically applied in specialized absorption processes rather than conventional water-amine systems.

3.3.3 Ethanol (C_2H_5OH)

Ethanol is occasionally used as a co-solvent to further adjust the solution properties, including viscosity, density, and gas solubility. Its polar nature allows it to interact with amine molecules, improving CO_2 mass transfer. Ethanol can also reduce corrosive effects on equipment and modify the solution's flow characteristics in the absorber. However, like methanol, its flammability and cost limit widespread use, and it is generally used only when specific process advantages are required.

3.4 Reaction Mechanism

This section describes the fundamental reaction mechanisms governing CO_2 absorption in monoethanolamine (MEA) and diethanolamine (DEA) systems using different solvents. Understanding these mechanisms is essential for interpreting the CO_2 loading behavior and regeneration energy requirements discussed in the Results and Discussion chapter.

The absorption pathways are classified according to the amine type (primary and secondary amines) and solvent type (water, methanol, and ethanol), as these factors

significantly influence the reaction pathway and bonding strength between CO_2 and the solvent system, and the overall energy requirement for solvent regeneration.

3.4.1 Primary amine systems (MEA-based solvents)

Monoethanolamine (MEA) is a primary amine that reacts with CO_2 predominantly through carbamate formation. This reaction requires two amine molecules per CO_2 molecule, resulting in relatively strong chemical bonding and a higher heat of absorption compared with bicarbonate-based mechanisms.

(1) MEA–Water system

$$CO_2 + 2HO - CH_2CH_2NH_2 \rightleftharpoons HO - CH_2CH_2NHCOO^- + HO - CH_2CH_2NH_3^+$$

Note: In aqueous systems, CO_2 is chemically absorbed via carbamate formation. The carbamate species formed between MEA and CO_2 is relatively stable, leading to strong CO_2 – amine bonding. As a result, the regeneration process generally requires higher thermal energy to break these bonds during solvent regeneration.

(2) MEA–Methanol system

$$CO_2 + 2HO - CH_2CH_2NH_2 \rightleftharpoons HO - CH_2CH_2NHCOO^- + HO - CH_2CH_2NH_3^+$$

Note: The dominant reaction pathway remains carbamate formation, similar to the aqueous system. However, in non-aqueous solvents such as methanol, the solvent may also participate in reactions with CO_2 as a nucleophile. Under certain conditions, methanol can react with CO_2 to form methyl carbonate species in the presence of the amine:

$$CO_2 + CH_3OH + HO - CH_2CH_2NH_2 \rightleftharpoons CH_3OCOO^- + HO - CH_2CH_2NH_3^+$$

Although carbamate formation is typically the primary pathway, the presence of methanol influences the thermophysical properties of the solvent, including heat capacity and vapor–liquid equilibrium behavior, which affect the heat duty required for solvent regeneration.

(3) MEA–Ethanol system

$$CO_2 + 2HO - CH_2CH_2NH_2 \rightleftharpoons HO - CH_2CH_2NHCOO^- + HO - CH_2CH_2NH_3^+$$

Note: Similar to the methanol-based system, carbamate formation remains the dominant reaction mechanism. However, ethanol may also participate in a parallel reaction pathway forming ethyl carbonate species:

$$CO_2 + C_2H_5OH + HO - CH_2CH_2NH_2 \rightleftharpoons C_2H_5OCOO^- + HO - CH_2CH_2NH_3^+$$

The presence of ethanol modifies solvent properties such as boiling point, vapor pressure, and heat capacity. These thermodynamic differences influence both the absorption equilibrium and the regeneration energy requirement.

3.4.2 Secondary amine systems (DEA-based solvents)

Diethanolamine (DEA) is a secondary amine that forms carbamate species that are less stable than those formed by primary amines. Consequently, CO_2 absorption in DEA systems often proceeds through bicarbonate formation in aqueous environments or through alternative reaction pathways depending on the solvent composition.

(1) DEA–Water system

In aqueous systems, CO_2 absorption by DEA proceeds through a stepwise reaction mechanism involving carbamate formation followed by hydrolysis.

Step 1: Carbamate formation

$$CO_2 + (HO - CH_2CH_2)_2NH \rightleftharpoons (HO - CH_2CH_2)_2NCOO^- + (HO - CH_2CH_2)_2NH_2^+$$

Step 2: Carbamate hydrolysis

$$(HO - CH_2CH_2)_2NCOO^- + H_2O \rightleftharpoons HCO_3^- + (HO - CH_2CH_2)_2NH$$

Overall reaction:

$$CO_2 + H_2O + (HO - CH_2CH_2)_2NH \rightleftharpoons HCO_3^- + (HO - CH_2CH_2)_2NH_2^+$$

Note: The bicarbonate-based mechanism results in weaker CO_2–amine bonding compared with carbamate formation. Consequently, DEA systems typically require lower regeneration energy than MEA systems.

(2) DEA–Methanol system

$$CO_2 + CH_3OH + (HO - CH_2CH_2)_2NH \rightleftharpoons CH_3OCOO^- + (HO - CH_2CH_2)_2NH_2^+$$

Note: In non-aqueous solvents such as methanol, bicarbonate formation is less favorable due to the absence of water. Instead, methanol reacts with CO_2 to form methyl carbonate species, while DEA acts as a proton acceptor. The resulting alkyl carbonate species generally exhibit weaker bonding interactions with CO_2 compared with carbamate species.

(3) DEA–Ethanol system

$$CO_2 + C_2H_5OH + (HO - CH_2CH_2)_2NH \rightleftharpoons C_2H_5OCOO^- + (HO - CH_2CH_2)_2NH_2^+$$

Note: Similarly, ethanol can react with CO_2 to form ethyl carbonate species in the presence of DEA. The formation of these species influences the reaction equilibrium and affects solvent regeneration behavior due to differences in solvent thermodynamic properties.

The differences in absorption mechanisms between MEA- and DEA-based systems, as well as the choice of solvent, significantly influence reaction enthalpy, CO_2 loading capacity, and solvent regeneration energy. Carbamate formation in MEA systems generally results in stronger CO_2 binding and higher heat of absorption. In contrast, bicarbonate or alkyl carbonate formation in DEA systems leads to relatively weaker bonding interactions with CO_2. These mechanistic differences provide the fundamental basis for explaining the variations in regeneration energy observed among the different amine–solvent systems, which are discussed in detail in the Results and Discussion chapter.

3.5 Post-combustion CO_2 Capture

The absorption process is one of the most important techniques for capturing carbon dioxide from post-combustion flue gases, relying on the principles of mass transfer between the gas and liquid phases. Flue gas containing CO_2 is directed into an

absorber column filled with a liquid absorbent. Absorption occurs when the gas phase comes into close contact with the liquid phase, allowing CO_2 molecules to diffuse into the liquid driven by a concentration gradient between the two phases. CO_2 absorption can be classified into two main types: physical absorption and chemical absorption.

3.5.1 Physical Absorption

Physical absorption occurs when CO_2 is dissolved in a liquid due to intermolecular forces, without any chemical reaction. The driving force for absorption is the concentration difference of CO_2 between the gas and liquid phases. This type of absorption is generally favored at high pressures and low temperatures, as solubility increases under such conditions. Physical solvents, such as water or organic solvents, are commonly used when CO_2 concentrations are relatively low, and rapid desorption can be achieved with minimal energy input.

3.5.2 Chemical Absorption

Chemical absorption involves a chemical reaction between CO_2 and the absorbent, such as an amine solution, which allows a higher CO_2 loading and more efficient capture than physical absorption. In this process, CO_2 reacts with primary or secondary amines to form carbamate ions, or with tertiary amines to form bicarbonate ions. The reaction is exothermic, and the absorption efficiency decreases with increasing temperature. Regeneration requires heating to reverse the reaction and release CO_2, allowing the absorbent to be reused in subsequent cycles [18].

3.6 Mass Transfer of Carbon Dioxide (CO_2)

The absorption of carbon dioxide is fundamentally a mass transfer process, in which CO_2 molecules move from the gas phase into the liquid phase through the gas-liquid interface, a critical region for mass transfer. This process is often described using the two-film theory, one of the fundamental models for analyzing diffusion behavior in

absorption systems. According to this theory, thin films exist on both sides of the interface: the gas film and the liquid film. The primary driving force for mass transfer in the gas film is the partial pressure gradient of CO_2, which causes CO_2 molecules to diffuse toward the interface. In the liquid film, the concentration gradient of CO_2 serves as the driving force, allowing molecules to penetrate into the bulk liquid. Within the liquid phase, CO_2 reacts chemically with the absorbent, such as amine solutions, enhancing the overall absorption efficiency. The overall mass transfer rate of CO_2 depends on the driving force provided by the mass transfer potential and the resistances of each film. Reducing resistance in either the gas or liquid film can significantly increase the absorption rate. In amine-based chemical absorption, the mass transfer process occurs simultaneously with chemical reactions near the gas-liquid interface, and the mass flux, representing the amount of CO_2 transferred per unit area per unit time, is influenced by the partial pressure difference in the gas film and the concentration gradient in the liquid film [19].

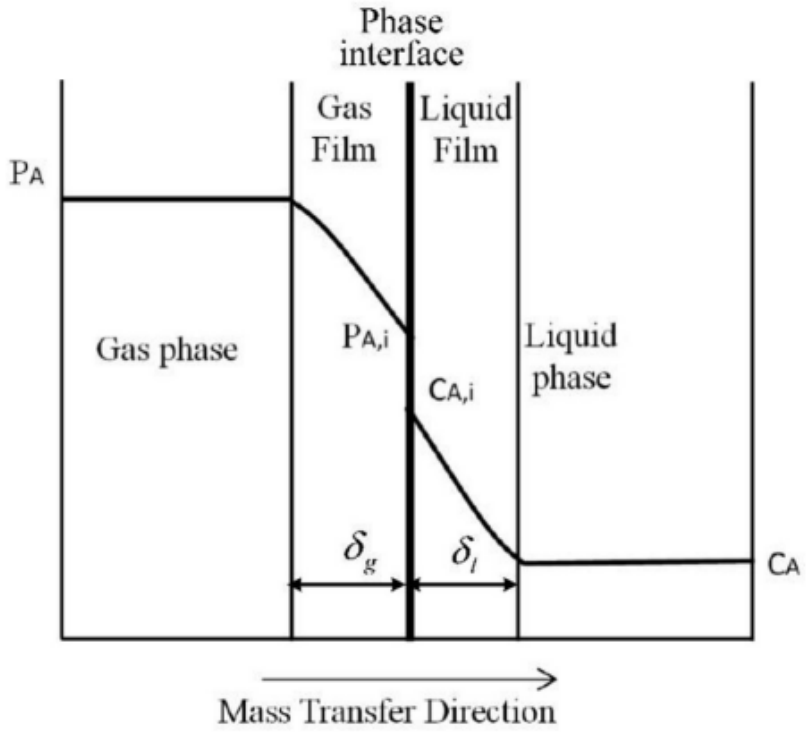

Figure 3.1 Illustration of the two-film model

3.7 Regeneration Heat Duty

Regeneration heat duty is a critical performance indicator in the CO_2 absorption process, as approximately 70–80% of the operational cost of the process is attributed to the thermal energy required to regenerate the absorbent. The heat is used to separate carbon dioxide (CO_2) from the amine solution after the absorption step, allowing the amine to be reused in subsequent cycles. Regeneration heat duty is typically expressed as the amount of thermal energy needed to release one mole of CO_2, in units of MJ/mol CO_2 Generally [20], the total regeneration heat duty ($Q_{(reg)}$) consists of three main components: the heat required for CO_2 desorption ($Q_{(des)}$), the heat required for water vaporization ($Q_{(vep)}$), and the sensible heat required to raise the solution temperature ($Q_{(sen)}$), which can be represented by the equation:

$$Q_{reg}=Q_{des}+Q_{vap}+Q_{sen}$$

3.8 CO_2 Absorption Efficiency (%Absorption)

The calculation of CO_2 absorption efficiency (%Absorption) provides an indication of how effectively the CO_2 capture process operates. It can be expressed as:

$$\%\text{Absorption}=\frac{C_{in}-C_{out}}{C_{in}}\times 100$$

where %Absorption is the percentage of CO_2 absorbed

C_{in} is the concentration of CO_2 before the absorption process

C_{out} is the concentration of CO_2 after the absorption process

A higher %Absorption indicates better performance of the CO_2 capture system.

3.9 CO_2 Desorption Efficiency (%Desorption)

The calculation of CO_2 desorption efficiency (%Desorption) evaluates the effectiveness of releasing CO_2 from the amine solution, such as MEA, after absorption. It is calculated as:

$$\%\text{Desorption}=\frac{C_{out}}{C_{in}}\times 100$$

where %Desorption represents the percentage of CO_2 released

C_{in} is the concentration of CO_2 absorbed in the solution

C_{out} is the concentration of CO_2 desorbed from the solution

A higher %Desorption indicates that the regeneration process of the absorbent is more effective.

CHAPTER IV EXPERIMENTAL

4.1 Chemicals

Table 4.1 Chemical properties and sources of the solvents and amines used in the study

Chemical Name	formula	grade	Source	CAS Number
MEA (monoethanolamine)	C_2H_7NO	AR Grade	Petronas Chemicals Derivatives Sdn. Bhd.	141-43-5
DEA (diethanolamine)	$C_4H_{13}NO_2$	AR Grade	Petronas Chemicals Derivatives Sdn. Bhd.	111-42-2
Methanol	CH_3OH	AR Grade	Srithana perfect Xo., Ltd.	67-56-1
Ethanol	C_2H_5OH	AR Grade	Trimongkol thurakit company limited	64-17-5
Deionized water	H_2O	AR Grade	TISTR	7732-18-5

4.2 Equipment and Materials

- Synthetic flue gas composition: 12 Vol% CO_2 + 5 Vol% O_2 + 83 Vol% N_2 (supplied by Thai Special Gas Co., Ltd.)
- Gas analyzer: VarioPlus model from MRU
- Gas counter: 100 mL/cycle
- Amine-Based CO_2 Capture Unit: Pilot-scale setup

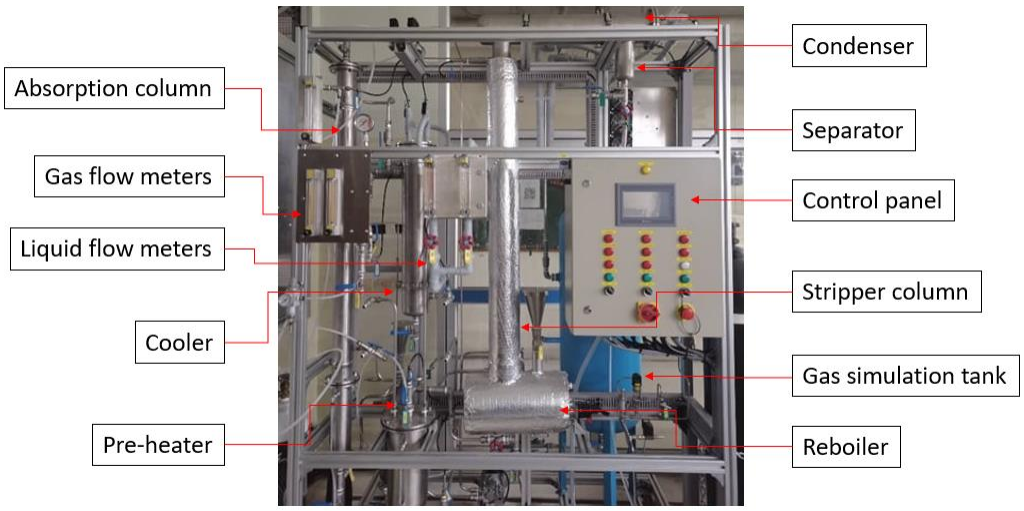

Figure 4.1 Amine-Based CO_2 Capture Unit: Pilot-scale setup

Table 4.2 Specifications of the amine-based CO_2 capture unit: Pilot-scale setup

Component	Size	Materials
Separator 1	3” diameter, 1 meter height	Stainless Steel (SUS304)
Separator 2	3” diameter, 1 meter height	Stainless Steel (SUS304)
Absorber column	4” diameter, 1.5 meter height	Stainless Steel (SUS304)
Flue gas flow meter	Maximum flow rate: 50 L/min	Stainless Steel (SUS304)
Solvent tank	6” diameter, 40 cm height	Stainless Steel (SUS304)
Rich amine pump (WD-50E)	Max pressure: 20 bar, Max temperature: 160°C	Copper/ Stainless Steel
Lean amine pump (WD-50E)	Max pressure: 20 bar, Max temperature: 160°C	Copper/ Stainless Steel
Separator 3	3.5” diameter, 1 meter height	Stainless Steel (SUS304)
Desorber column	3.5” diameter, 1.5 meter height	Stainless Steel (SUS304)
Rich amine flow control	Max flow rate: 1.8 L/min	Stainless Steel/Glass
Lean amine flow control	Max flow rate: 1.8 L/min	Stainless Steel/Glass
Boiler	30 cm diameter, 45 cm height, enclosed in oil jacket (39 cm × 30 cm)	Stainless Steel (SUS304)
Amine solution tank	25-liter capacity	Stainless Steel (SUS304)
Amine solution pump (WD-50E)	Max pressure 20 bar, Max thermal 160 °C	Copper/Stainless Steel

Component	Size	Materials
Gas counter	100 mL per cycle	Acrylic

4.3 Methods

4.3.1 Preparation of Amine–Water Solutions at Various Concentrations

1. Prepare a 20 wt% amine solution in water by weighing 8 kg of amine and 32 kg of deionized water, resulting in a total of 40 liters.
2. Mix the amine and water thoroughly in a high-density polyethylene (HDPE) storage tank and label the solution as 20 wt%.
3. Prepare a 30 wt% amine solution by weighing 12 kg of amine and 28 kg of deionized water for a total of 40 liters.
4. Mix thoroughly in an HDPE tank and label the solution as 30 wt%.

4.3.2 Study of Amine Type and Concentration (MEA vs. DEA)

1. Feed 20 wt% MEA solution from the storage tank into the desorber column.
2. Set the chiller temperature to 25°C.
3. Start the lean amine pump to circulate the solution from the desorber to the absorber, then start the rich amine pump to return the solution from the absorber back to the desorber. Allow the system to stabilize until the liquid levels in both columns remain constant.
4. Set the reboiler temperature to 85°C.
5. Adjust the rich and lean amine flow rates equally to 0.6 L/min.
6. Set the chiller flow rate to 30 L/h for the absorber side and 10 L/h for the condenser on the desorber side.
7. Introduce simulated flue gas at a flow rate of 15 L/min into the absorber, and collect the inlet gas sample using a 50-liter gas bag for analysis with the MRU gas analyzer.

8. Collect outlet gas samples from both the absorber and desorber every 30 minutes using 50-liter gas bags for MRU analysis.
9. Measure the outlet gas flow rates from both columns using a gas counter.
10. Repeat steps 1–9 using 30 wt% MEA solution.
11. Repeat steps 1–10 using DEA instead of MEA.

4.3.3 Comparison of Solvents (Water, Methanol, Ethanol)

1. Select the most effective amine from the previous experiment, prepare a 30 wt% solution using methanol as the solvent (total 40 liters).
2. Pump the amine-methanol solution into the desorber column.
3. Set the chiller to 25°C.
4. Circulate the solution as in section 3.3.2 until stabilized.
5. Set the reboiler temperature to 85°C.
6. Set both lean and rich amine flow rates to 0.6 L/min.
7. Adjust the chiller to 30 L/h for the absorber side and 10 L/h for the desorber condenser.
8. Feed simulated flue gas at 15 L/min to the absorber and collect the inlet gas for analysis.
9. Collect outlet gas samples every 30 minutes for both absorber and desorber sides.
10. Measure outlet gas flow using the gas counter.
11. Repeat steps 1–10, replacing methanol with ethanol.

4.3.4 Effect of Amine Flow Rate

1. Using the most effective amine from earlier experiments, prepare a 30 wt% amine–ethanol solution.
2. Pump the solution into the desorber column.
3. Set the chiller to 25°C.

4. Circulate the amine solution through the system until stabilized.
5. Set the reboiler temperature to 85°C.
6. Vary the amine flow rates (lean and rich) across four levels: 0.6, 0.8, 1.0, and 1.2 L/min.
7. Keep chiller flow rates constant as in previous sections.
8. Introduce flue gas at 15 L/min and analyze the gas composition at both inlet and outlet.
9. Collect samples every 30 minutes and record gas flow rates.
10. Repeat for each specified amine flow rate.

4.3.5 Effect of Simulated Flue Gas Flow Rate

1. Using the selected amine (30 wt% in ethanol), pump the solution into the desorber.
2. Follow the same procedure to stabilize the system.
3. Set the reboiler temperature to 85°C.
4. Maintain the amine flow rate at 0.6 L/min.
5. Vary the simulated flue gas flow rates to 15, 20, and 25 L/min.
6. For each condition, collect and analyze gas samples at 30-minute intervals from both columns.
7. Measure the outlet gas flow rates and compare performance under each gas flow rate condition.

4.3.6 Effect of Reboiler Temperature

1. Prepare the selected amine solution (30 wt% in ethanol) and pump it into the desorber.
2. Stabilize the circulation system as described earlier.
3. Vary the reboiler temperature across the range of 85°C to 100°C in appropriate intervals.

4. Keep all other conditions constant, including amine flow rate (0.6 L/min) and gas flow rate (15 L/min).
5. Collect outlet gas samples every 30 minutes and record the results for each temperature setting.

4.4 Gas Composition Analysis of the Product

4.4.1 Gas Analyzer

The analysis of the product in our CO_2 capture process was conducted using a Gas Analyzer, which is designed to measure and analyze the gas composition of samples collected from the CO_2 capture process. This instrument is capable of measuring the concentration of various gases, such as carbon dioxide (CO_2), oxygen (O_2), and other gases that may be present in the process or released during the CO_2 capture process. The use of a gas analyzer enables effective control and monitoring of the CO_2 capture process's efficiency. By measuring gas concentrations during the capture process, it allows for the verification of gas absorption and release in the system according to established standards. Gas analysis can be performed in both online (real-time) systems for continuous process monitoring or in offline systems for testing samples collected at specific intervals.

CHAPTER V RESULTS AND DISCUSSIONS

The regeneration energy observed in each solvent system is closely related to the reaction mechanisms governing CO_2 absorption. As described in Section 3.4, MEA-based systems predominantly form carbamate species, whereas DEA-based systems tend to form bicarbonate species in aqueous environments or alkyl carbonate species in alcohol-based solvents. These differences in reaction pathways significantly influence the strength of the chemical bonding between CO_2 and the solvent.

Carbamate formation in MEA systems involves strong chemical bonding between CO_2 and the amine group, resulting in relatively high heat of absorption. Consequently, higher thermal energy is required to break these bonds during the regeneration step. This explains why MEA-based solvents generally exhibit higher regeneration energy compared with DEA-based solvents.

In contrast, DEA systems form less stable carbamate intermediates, which are readily converted to bicarbonate in aqueous solutions. In non-aqueous systems containing methanol or ethanol, CO_2 may react with the alcohol to form alkyl carbonate species. These reaction products generally exhibit weaker bonding interactions with CO_2 compared with carbamate species, thereby reducing the energy required for solvent regeneration.

Furthermore, the choice of solvent also affects the thermophysical properties of the system, including heat capacity, boiling point, and vapor–liquid equilibrium behavior. Alcohol-based solvents such as methanol and ethanol modify these properties, which can further influence the sensible heat and latent heat requirements during the regeneration process.

Therefore, the differences in regeneration energy observed among the MEA–water, MEA–methanol, MEA–ethanol, DEA–water, DEA–methanol, and DEA–ethanol

systems can be explained by the combined effects of reaction mechanisms and solvent thermodynamic properties.

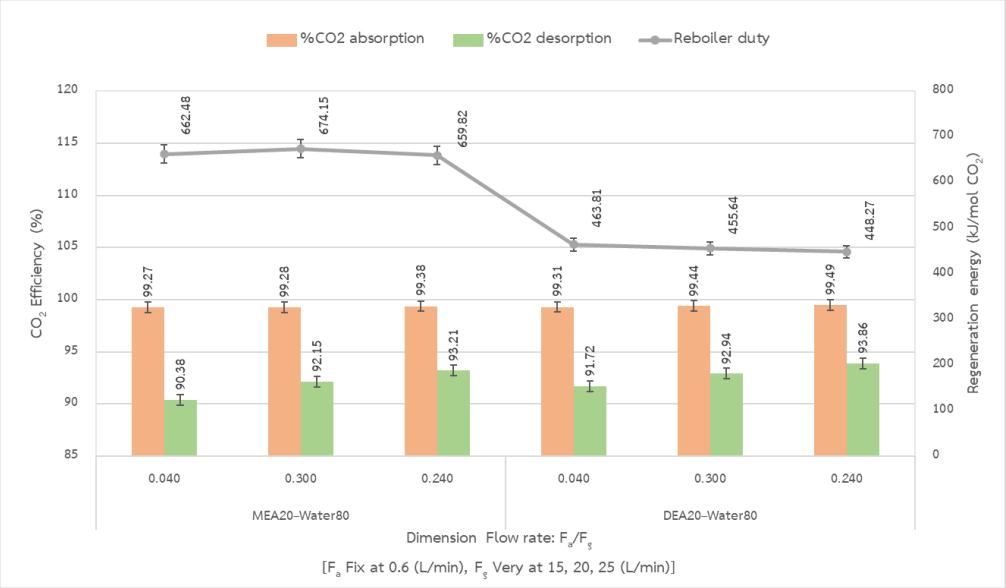

Figure 5.1 Effect of Gas Flow Rate on CO_2 Absorption–Desorption Efficiency and Reboiler Duty for MEA and DEA Solutions (20:80 ratio with Water)

Figure 5.1 illustrates the influence of gas flow rate on CO_2 absorption–desorption efficiency and reboiler duty for MEA and DEA solutions using water as the solvent. As the gas flow rate increases, a clear decrease in absorption efficiency is observed for both amine systems. This trend is primarily attributed to the reduction in gas–liquid contact time, which limits the extent of mass transfer and chemical reaction between CO_2 and the liquid phase. At lower gas flow rates, sufficient residence time allows the absorption reactions to approach equilibrium, resulting in higher CO_2 removal efficiency.

The effect of gas flow rate is more pronounced in MEA systems than in DEA systems. This behavior can be explained by differences in the CO_2 absorption mechanisms of primary and secondary amines. MEA, a primary amine, absorbs CO_2 predominantly through carbamate formation, which involves relatively strong chemical bonding and requires two amine molecules per CO_2 molecule. This reaction pathway is kinetically and thermodynamically sensitive to residence time. As

gas flow rate increases, the limited contact time restricts carbamate formation, leading to a sharper decline in CO_2 loading in MEA systems. In contrast, DEA absorbs CO_2 mainly through bicarbonate formation, which involves weaker chemical interactions and faster equilibrium establishment. As a result, DEA systems exhibit lower sensitivity to changes in gas flow rate.

The impact of gas flow rate on absorption efficiency is directly reflected in the regeneration energy requirement. As CO_2 loading decreases at higher gas flow rates, a larger volume of solvent must be regenerated to release the same amount of CO_2, leading to an increase in reboiler duty per unit of CO_2 desorbed. This effect is particularly significant for MEA systems, where the strong CO_2–amine interactions associated with carbamate species require higher thermal energy for bond cleavage during regeneration. Consequently, operating at excessively high gas flow rates not only reduces absorption performance but also increases the energy penalty during solvent regeneration.

From a process design perspective, the results highlight the importance of optimizing gas flow rate to balance absorption efficiency and energy consumption. While higher gas flow rates may improve throughput, they adversely affect reaction completion and increase regeneration energy demand, especially in carbamate-forming MEA systems. These findings emphasize that hydrodynamic conditions and reaction mechanisms must be considered simultaneously when designing and optimizing amine-based CO_2 absorption–regeneration processes.

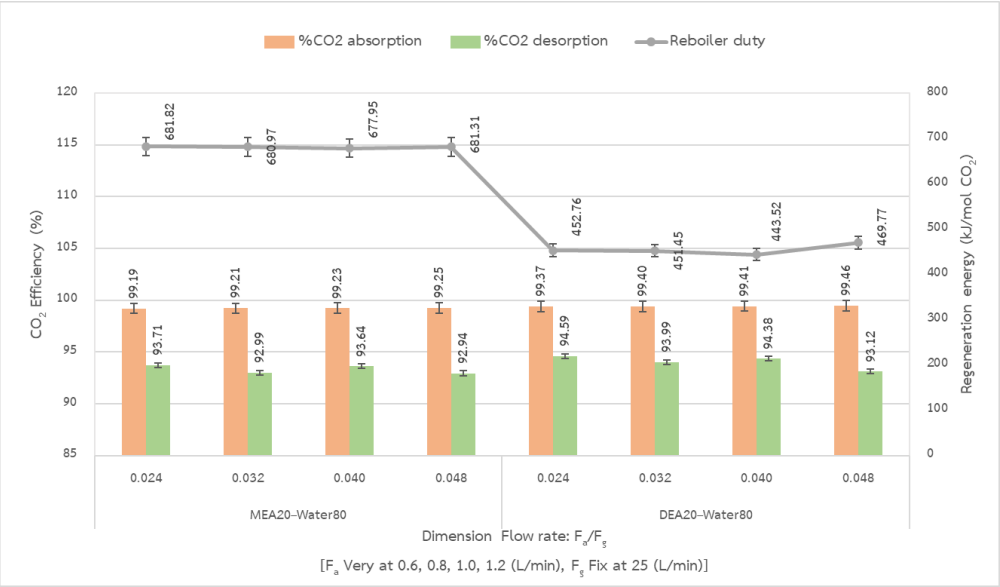

Figure 5.2 Effect of Liquid Flow Rate on CO_2 Absorption–Desorption Efficiency and Reboiler Duty for MEA and DEA Solutions (20:80 ratio with Water)

Figure 5.2 presents the effect of liquid flow rate on CO_2 absorption–desorption efficiency and reboiler duty for aqueous MEA and DEA systems. An increase in liquid flow rate leads to an improvement in CO_2 absorption efficiency for both amines. This behavior is mainly attributed to enhanced wetting of the packing surface and an increased effective gas–liquid interfacial area, which promotes mass transfer and facilitates chemical reactions between CO_2 and the amine solution. At low liquid flow rates, insufficient solvent distribution limits contact efficiency, resulting in lower CO_2 uptake.

Despite the improvement in absorption efficiency, the increase in liquid flow rate also results in a noticeable rise in reboiler duty. This trend is associated with the higher solvent circulation rate, which increases the sensible heat required to raise the solvent temperature during regeneration. In addition, a higher liquid flow rate leads to a greater amount of absorbed CO_2 being transported to the stripper, thereby increasing the total thermal energy required for desorption. The trade-off between absorption performance and regeneration energy becomes more evident at elevated liquid flow rates.

Comparing MEA and DEA systems, MEA exhibits a steeper increase in reboiler duty with increasing liquid flow rate. This is linked to the stronger chemical bonding between CO_2 and MEA through carbamate formation. During regeneration, carbamate decomposition requires significant energy input, and the increased solvent circulation amplifies this energy demand. DEA, which primarily forms bicarbonate species, shows a relatively milder increase in regeneration energy due to weaker CO_2–amine interactions and easier bond cleavage during desorption.

From a process optimization standpoint, the results indicate that while higher liquid flow rates enhance absorption efficiency, they may lead to excessive energy consumption during regeneration. Therefore, an optimal liquid flow rate must be selected to balance mass transfer efficiency and thermal energy requirements. This balance is particularly critical in carbamate-forming MEA systems, where solvent circulation strongly influences overall process energy efficiency.

Figure 5.3 Effect of Amine Concentration on Desorption Temperature in MEA–Water and DEA–Water Systems

Figure 5.3 illustrates the relationship between amine concentration and desorption temperature for MEA–water and DEA–water systems. As the amine concentration increases, a corresponding increase in desorption temperature is observed for both systems. This trend reflects the stronger interaction between CO_2 and the amine at higher concentrations, which stabilizes absorbed CO_2 species and requires higher thermal energy to reverse the absorption reactions during regeneration.

The increase in desorption temperature is more pronounced for MEA than for DEA. In MEA systems, higher amine concentrations favor carbamate formation, leading to a greater proportion of strongly bound CO_2 species. The decomposition of carbamate requires significant thermal input, thereby elevating the desorption temperature. In contrast, DEA systems primarily form bicarbonate species, which are thermodynamically less stable and can be decomposed at lower temperatures, even at increased amine concentrations.

Additionally, increasing amine concentration affects solvent properties such as viscosity and heat capacity. Higher concentrations generally increase solution viscosity, which can hinder heat and mass transfer during regeneration, further contributing to the requirement for higher desorption temperatures. This effect is again more critical in MEA systems due to their stronger chemical absorption mechanism.

These results highlight the importance of controlling amine concentration to avoid excessive regeneration temperatures that may lead to solvent degradation and increased operational costs. From an energy efficiency perspective, DEA systems offer greater flexibility in operating at higher concentrations with relatively lower regeneration temperatures, which is advantageous for long-term process stability and energy savings.

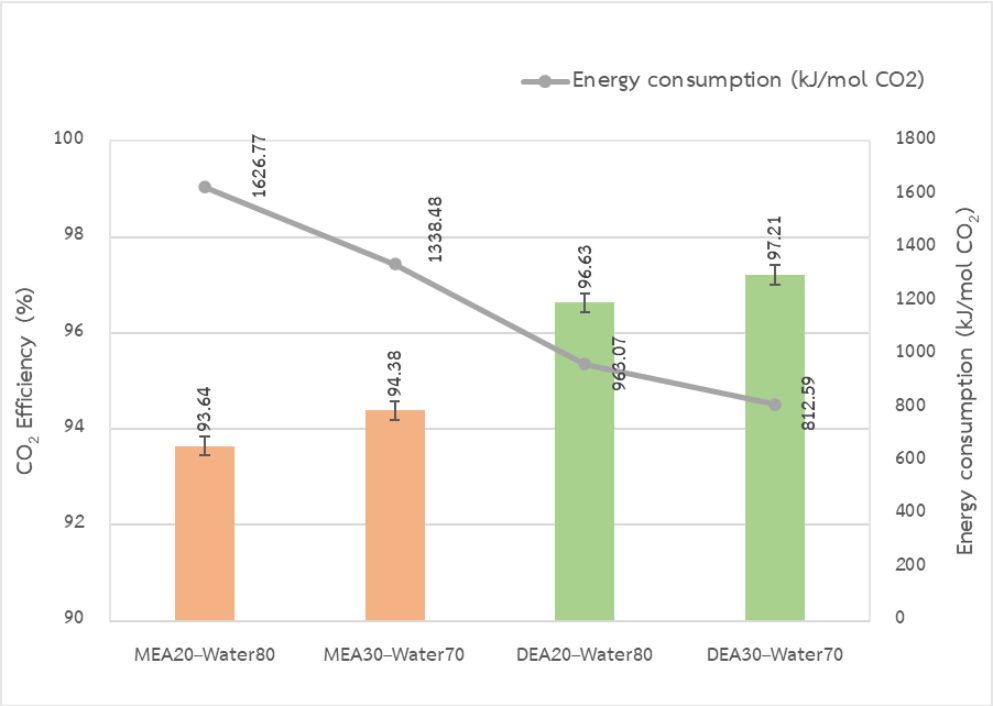

Figure 5.4 Effect of Amine Concentration on Energy Requirement for CO_2 Desorption

Figure 5.4 shows the effect of amine concentration on the energy required for CO_2 desorption. An increase in amine concentration leads to higher regeneration energy demand for both MEA and DEA systems. This behavior is primarily due to the increased amount of chemically bound CO_2 and the higher heat capacity of more concentrated amine solutions, which together raise the thermal energy required during solvent regeneration.

MEA systems exhibit a steeper increase in energy requirement compared to DEA systems. This difference is closely associated with the dominant absorption mechanisms. In MEA solutions, higher concentrations promote carbamate formation, which involves strong chemical bonds that demand substantial energy for dissociation during desorption. Consequently, the regeneration energy increases sharply with concentration. In contrast, DEA systems rely more on bicarbonate formation, which involves weaker interactions and results in a lower incremental energy penalty.

Furthermore, higher amine concentrations increase solvent viscosity, which can negatively affect heat transfer efficiency in the reboiler. Poor heat transfer leads to less efficient energy utilization and further elevates regeneration energy consumption. This effect compounds the already high energy requirement associated with carbamate decomposition in MEA systems.

From a design perspective, these findings suggest that increasing amine concentration to improve absorption capacity must be carefully evaluated against the associated increase in regeneration energy. An optimal concentration range should be selected to maximize CO_2 capture efficiency while minimizing overall energy consumption, particularly in systems dominated by carbamate chemistry.

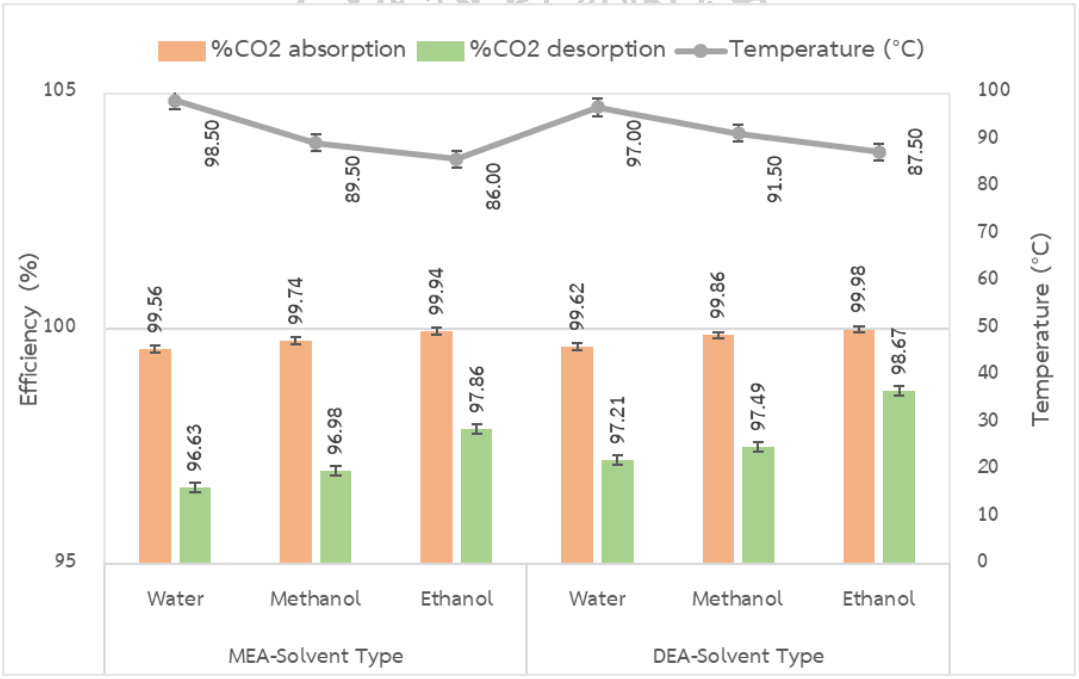

Figure 5.5 Desorption Performance of Amine Systems with Different Solvents

Figure 5.5 compares the desorption performance of amine systems using different solvents, namely water, methanol, and ethanol. The results demonstrate that alcohol-based solvents exhibit improved desorption performance compared to aqueous systems. Specifically, both methanol- and ethanol-based systems require lower thermal input to achieve effective CO_2 release.

The enhanced desorption performance of alcohol-based solvents cannot be attributed solely to their lower boiling points. Methanol and ethanol possess lower dielectric constants than water, which reduces the stabilization of ionic species such as carbamate and bicarbonate. As a result, CO_2–amine interactions become weaker in alcohol-based solvents, facilitating easier desorption. In contrast, water, with its high polarity and dielectric constant, strongly stabilizes ionic absorption products, leading to higher regeneration energy requirements.

In addition, alcohol-based solvents alter the solvation environment around the amine and CO_2 species, shifting the equilibrium toward physically dissolved or weakly bound CO_2. This shift lowers the enthalpy of desorption and reduces the energy penalty associated with breaking chemical bonds during regeneration. The effect is particularly beneficial for MEA systems, where carbamate stability is significantly influenced by solvent polarity.

These findings indicate that solvent selection plays a critical role in controlling desorption behavior. Alcohol-based solvents offer a promising approach to reducing regeneration energy without compromising CO_2 capture performance, thereby improving the overall efficiency of amine-based absorption systems.

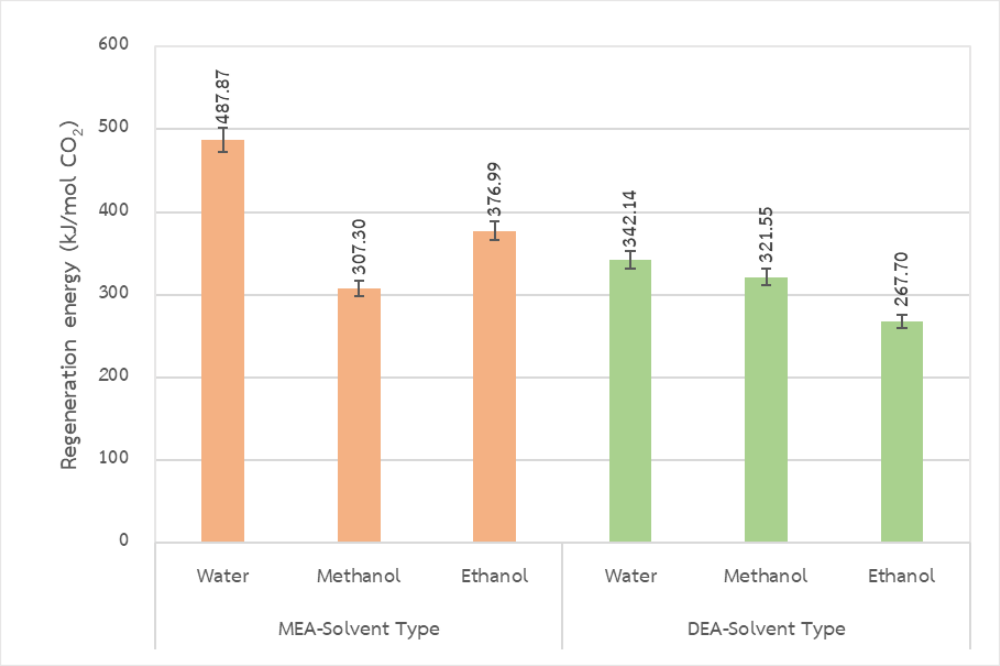

Figure 5.6 Regeneration energy (reboiler duty) for all amine–solvent systems

Figure 5.6 summarizes the regeneration energy requirements for all amine–solvent systems investigated in this study. Among the systems evaluated, aqueous MEA exhibits the highest reboiler duty, while alcohol-based DEA systems show the lowest energy consumption. This trend reflects the combined effects of amine structure and solvent properties on CO_2–amine interaction strength.

MEA systems consistently require higher regeneration energy due to carbamate formation, which involves strong chemical bonding and high reaction enthalpy. The use of methanol or ethanol as solvents reduces this energy requirement by weakening carbamate stability through reduced solvent polarity. DEA systems, which primarily form bicarbonate species, benefit even more from alcohol-based solvents, as the weaker interactions facilitate easier CO_2 release during regeneration.

The comparison between methanol and ethanol shows that methanol-based systems generally require slightly lower regeneration energy, which can be attributed to its lower boiling point and lower heat capacity. However, ethanol-based systems

still demonstrate significant energy savings compared to water, while offering advantages in terms of lower volatility and safer handling.

From an industrial perspective, these results highlight the importance of integrated amine–solvent selection for minimizing regeneration energy. Optimizing both chemical absorption mechanisms and solvent thermophysical properties is essential for designing energy-efficient CO_2 capture processes.

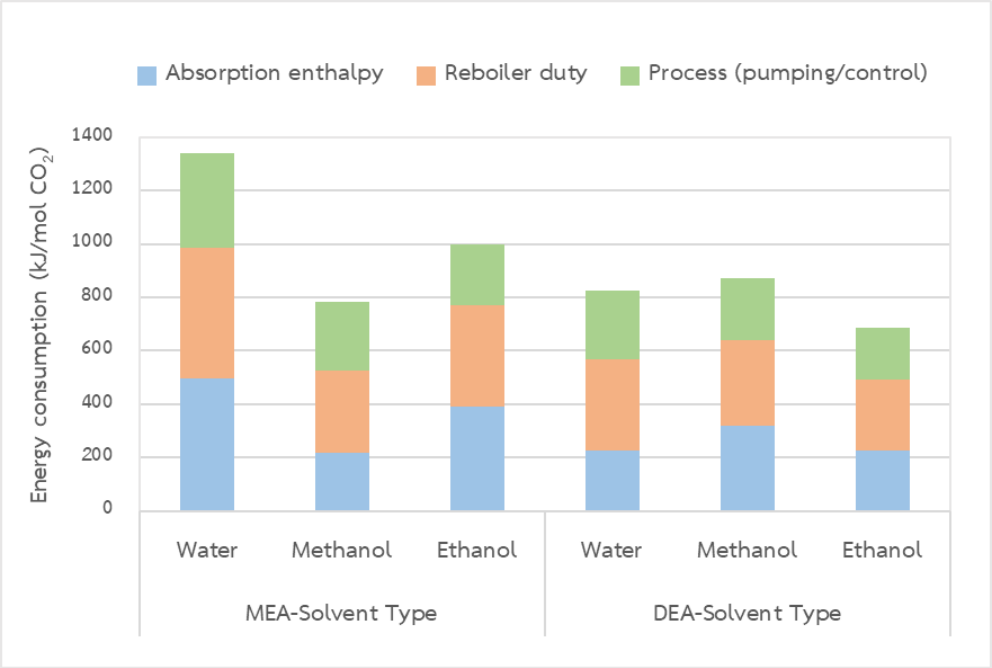

Figure 5.7 Energy consumption by absorption enthalpy, reboiler duty, and process energy

Figure 5.7 illustrates the energy distribution among different components of the CO_2 absorption–desorption process, including absorption enthalpy, reboiler duty, and process energy (pumping/control). The results reveal that the reboiler duty accounts for the largest portion of total energy consumption, approximately 35–45%, followed by absorption enthalpy (30–40%) and process energy (20–25%).

The MEA–Water system exhibited the highest total energy consumption (≈1338 kJ/mol CO_2), while the DEA–EtOH system showed the lowest total energy demand (≈684 kJ/mol CO_2), representing a reduction of more than 48%.

These findings highlight that both amine type and solvent choice significantly influence overall system energy efficiency. Using DEA instead of MEA and replacing high-boiling-point solvents (such as water) with low-boiling organic solvents (such as alcohols) markedly reduces the required heat input. Consequently, CO_2 absorption–desorption can be achieved at lower operating temperatures with improved energy efficiency.

In summary, the experimental results presented in this chapter provide a comprehensive understanding of the effects of operational parameters, solvent type, and amine concentration on CO_2 absorption–desorption efficiency and energy performance. The findings demonstrated that both MEA and DEA aqueous systems achieved consistently high CO_2 absorption efficiencies (>99%) across all tested flow conditions. However, DEA exhibited superior desorption stability and significantly lower regeneration energy requirements compared with MEA.

The optimization of flow parameters revealed that increasing the gas flow rate reduced reboiler duty without compromising absorption performance, while moderate liquid flow rates (1.0 L/min) provided the most favorable balance between CO_2 removal and energy efficiency. Varying the amine concentration further showed that 30 wt% solutions enhanced reaction completeness and reduced regeneration temperature and energy demand.

Table 5.1 Summary of experimental performance metrics for MEA and DEA in each solvent.

Amine type	Solvent type	Temperature (°C)	CO_2 absorption efficiency (%)	CO_2 desorption efficiency (%)	Regeneration (kJ/mol CO_2)	Energy (kJ/mol CO_2)			
						Absorption	Reboiler	Process	Total
MEA	Water	98.00	99.56	96.63	487.87	495.79	487.87	354.82	1338.48
	MeOH	89.50	99.74	96.98	307.30	217.01	307.30	259.78	784.08
	EtOH	86.00	99.94	97.86	376.99	391.25	376.99	228.10	996.34
DEA	Water	97.50	99.62	97.21	342.14	226.51	342.14	256.61	825.26
	MeOH	91.50	99.86	97.49	321.55	318.38	321.55	229.68	869.62
	EtOH	87.50	99.98	98.67	267.10	224.93	267.10	191.66	684.29

When alcohols (methanol and ethanol) were introduced as co-solvents, substantial improvements in desorption temperature and energy savings were achieved. Among all tested systems, the DEA–Ethanol (30:70) solution achieved the lowest reboiler duty (267.70 kJ/mol CO_2), lowest overall energy consumption (≈684 kJ/mol CO_2), and highest desorption efficiency (≈98.7%). These findings confirm that both solvent selection and amine type play crucial roles in minimizing energy consumption in CO_2 capture and regeneration cycles, making DEA–EtOH the most promising system for future process development and scale-up.

CHAPTER VI CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

The reaction mechanisms of CO_2 absorption in MEA- and DEA-based solvent systems vary significantly depending on the type of amine and solvent used. MEA, as a primary amine, predominantly reacts with CO_2 through carbamate formation, resulting in relatively strong chemical bonding and higher heat of absorption. In contrast, DEA, a secondary amine, forms less stable carbamate intermediates that are readily converted to bicarbonate in aqueous systems or alkyl carbonate species in alcohol-based solvents.

In non-aqueous systems containing methanol or ethanol, the alcohol molecules may directly participate in the reaction with CO_2 to form methyl carbonate or ethyl carbonate species. These reaction pathways generally lead to weaker CO_2–solvent interactions compared with carbamate formation.

Therefore, the differences in reaction mechanisms between MEA and DEA systems, as well as the choice of solvent, play a crucial role in determining CO_2loading behavior and the energy required for solvent regeneration. These mechanistic considerations provide a fundamental explanation for the variations in regeneration energy observed among the different amine–solvent systems analyzed in this study.

The key conclusions are summarized as follows:

1. Effect of flow conditions: Both MEA and DEA aqueous systems exhibited excellent CO_2 absorption efficiencies (>99%) under all gas and liquid flow rates. Increasing the gas flow rate reduced the reboiler duty by enhancing heat transfer, while an optimal liquid flow rate of 1.0 L/min provided stable absorption–desorption performance.

2. Effect of amine concentration: Increasing amine concentration from 20 wt% to 30 wt% reduced both desorption temperature and regeneration energy. The DEA solution required a lower regeneration temperature (≈97°C) and energy (≈812.6 kJ/mol CO_2) than MEA, indicating higher energy efficiency due to weaker carbamate bonding.

3. Effect of solvent type: The introduction of alcohol solvents, particularly ethanol, significantly improved energy performance. Alcohol-based systems required lower desorption temperatures (≈86–88°C) and reduced total energy consumption by up to 48% compared with water-based systems.

4. Optimal condition for CO_2 capture: The DEA–Ethanol (30:70) solution was identified as the most energy-efficient solvent system, providing high desorption efficiency (~98.7%) with the lowest reboiler duty (267.7 kJ/mol CO_2) and total energy consumption (~684 kJ/mol CO_2). This system demonstrated a well-balanced combination of chemical reactivity, heat transfer efficiency, and regeneration feasibility.

Overall, this research confirms that solvent modification using alcohols and the selection of an appropriate amine type (DEA) can significantly enhance the energy efficiency of CO_2 absorption–desorption processes. The obtained data contribute to the development of next-generation solvent systems suitable for large-scale CO_2 capture with reduced operational energy demand.

6.2 Recommendations

Based on the experimental findings, the following recommendations are proposed for future research and process development:

1.Process optimization at pilot scale: Further studies should focus on scaling up the DEA–Ethanol system to pilot or semi-industrial levels to evaluate long-term operational stability, solvent degradation behavior, and energy recovery potential.

2.Investigation of mixed-solvent systems: Future work may explore hybrid solvents (e.g., DEA blended with methanol–ethanol mixtures) to identify synergistic effects on absorption kinetics and energy reduction.

3.Modeling and simulation studies: Developing thermodynamic and rate-based models using experimental data would allow prediction of solvent behavior under various temperature, pressure, and flow conditions, aiding in process design and optimization.

4.Environmental and economic assessment: A full life-cycle analysis (LCA) and techno-economic evaluation should be conducted to assess the environmental impact and cost-effectiveness of the optimized DEA–Ethanol system compared with conventional aqueous MEA systems.

5.Integration with renewable energy systems: The combination of low-temperature regeneration solvents with renewable heat sources (e.g., solar-assisted or waste heat recovery systems) should be investigated to further enhance sustainability and reduce carbon footprint.

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