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An experimental study on CO_2 capture to identify additives to improve the sorption process

Trabajo de integración curricular presentado como requisito para la obtención del título de Ingeniero en Polímeros

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Dedication

"To that little girl who one day dreamed of changing her story. May this work be a testimony of the persistence and desire to achieve goals beyond what was imagined. To that girl, and to all the dreamers who seek to change their destiny, with gratitude and dedication."

Verónica Patricia Calva Salazar

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Resumen

El aumento de las concentraciones de CO_2 en la atmósfera debido a actividades humanas ha llevado a un calentamiento global preocupante. La absorción de CO_2 con aminas ofrece una solución prometedora al capturar el CO_2 emitido por diversas fuentes industriales antes de que llegue a la atmósfera. Por ello, una adecuada selección de aminas permite el desarrollo en la tecnología. Este trabajo se centra en relizar un estudio de sorción con aminas, incluyendo: Metildietanolamina (MDEA), Dietilentriamina (DETA), Trietanolamina (TEA), y Monoetanolamina (MEA), en una solución al 40%, bajo condiciones de alta presión (500 psig) y a una temperatura de 30°C, tanto en sistemas con agitación como sin agitación, ya que la agitación puede tener influencia en la transferencia de masa en sistemas líquidos, así como la difusión del soluto. El estudio incluye, análisis termodinámicos para evaluar la eficiencia de cada una de las aminas, centrándose en determinar la capacidad de carga de CO_2; y análisis cinéticos que permitieron calcular la velocidad de reacción y el tiempo necesario para que el sistema absorba un porcentaje específico de CO_2. De acuerdo a esto, DETA y MDEA presentan los mejores resultados termodinámicos, mientras que MEA y TEA exhiben una mayor velocidad de reacción. Además, se lleva acabo un análisis económico que posibilita evaluar la viabilidad y rentabilidad de implementar las aminas seleccionadas, este análisis reveló que la MDEA tiene el costo más bajo por inversión para absorber una tonelada de amina, siendo 2 a 4.5 veces menos costosa que las otras aminas. Por último, se realizó un estudio de corrosividad con la intención de confirmar la influencia del tipo de aminas en el efecto corrosivo. Siendo MEA, una amina primaria, la más corrosiva, y TEA, una amina terciaria, la menos corrosiva. En conjunto con todos los estudios realizados, se sugiere que MDEA es la amina más favorable para la absorción de CO_2.

Palabras Clave: Captura de CO_2, aminas, absorción, alta presión, reactor.

Abstract

The increase in CO_2 concentrations in the atmosphere due to human activities has led to a concerning global warming. The absorption of CO_2 with amines offers a promising solution by capturing the CO_2 emitted by various industrial sources before it reaches the atmosphere. Therefore, a proper selection of amines allows for technological development. This work focuses on conducting a sorption study with amines, including Metildiethanolamine (MDEA), Diethylenetriamine (DETA), Triethanolamine (TEA), and Monoethanolamine (MEA), in a 40% solution, under high-pressure conditions (500 psig) and at a temperature of 30°C, both in agitated and non-agitated systems, as agitation can influence mass transfer in liquid systems, as well as solute diffusion.

The study includes thermodynamic analyses to evaluate the efficiency of each amine, focusing on determining the CO_2 loading capacity, and kinetic analyses that allowed for the calculation of reaction rate and the time required for the system to absorb a specific percentage of CO_2. According to this, DETA and MDEA show the best thermodynamic results, while MEA and TEA exhibit higher reaction rates.

Furthermore, an economic analysis is conducted to assess the viability and profitability of implementing the selected amines. This analysis revealed that MDEA has the lowest cost per investment to absorb one ton of amine, being 2 to 4.5 times less expensive than the other amines. Lastly, a corrosivity study was carried out with the intention of confirming the influence of the type of amines on the corrosive effect. MEA, as a primary amine, was found to be the most corrosive, while TEA, as a tertiary amine, was the least corrosive.

In combination with all the studies conducted, it is suggested that MDEA is the most favorable amine for CO_2 absorption.

Keywords: Capture of CO_2, amines, absorption, high pressure, reactor.

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Abbreviations

CO_2	Carbon dioxide
BEP	Barrels of oil equivalent
CCS	CO_2 capture and storage
PCC	Post-combustion carbon capture
WGS	Water gas shif
Z	Compressibility factor
P	Pressure
V	Volume
n	Gas mole
R	Universal ideal gas constant
T	Temperature
t	Time
n_{t0}^{gas}	Initial moles of gas
n_{tf}^{gas}	Moles of gas in time (t)
M_i	Initial mass
M_t	Mass at time t

Chapter 1

Introduction

Today, many developing countries face a common challenge: environmental degradation caused by the emission of carbon dioxide CO_2 into the atmosphere [1]. As Sekoai and Yoro (2016) [2] claimed, the increase in industrial activity has led to increased carbon emissions due to the growth of industrialization and urbanization in most developing countries, such as the United States of America, Brazil, European Union, Australia, and Japan. Consequently, a significant increase in the global concentration of greenhouse gases of anthropogenic origin, such as CO_2, has been observed, contributing to global warming and climate change. The latter has generated adverse effects, such as decreased agricultural production worldwide due to lack of precipitation, seasonal changes, and increased temperatures. Many regions of the world are experiencing droughts that make them unsuitable for commercial agriculture due to climate change. However, the immediate effects of climate change go beyond agricultural production, impacting food security, rising sea levels, severe storms affecting coastal areas, health problems, migration, and increasing economic damage [3].

The current level of pollution of human origin and the uncontrolled emission of greenhouse gases into the atmosphere could further aggravate global warming. Therefore, there would be more consequences of the increase in environmental temperature.

Ecuador is no exception to this challenge. According to the Ministry of Energy and Mines (MEM, 2022), ”between 2012 and 2022 energy consumption per inhabitant in the country increased by 4.9%, going from 5.30 barrels of oil equivalent (BEP/inhabitant. at 5.56 BEP/inhabitant"[4]. A similar pattern of increased energy consumption seen in Ecuador was also observed globally. In 2023, global energy demand grew by 2.2%, exceeding its historical average. The BRICS nations drove much of this rise, with a 5.1% increase, representing 42% of the world's energy usage. Notably, energy consumption in China surged by 6.6%, which is twice its average growth from 2010 to 2019, while India saw a 5.1% rise, slightly above its typical rate. In Brazil, energy use grew by 3.3%, significantly faster than its previous decade's average of 0.9% per year [5, 6]. This has led to greater demand and energy total production, which, in the case of Ecuador, comes mainly from fossil sources, covering 86.4% of total production. The consumption of fossil fuels is closely related to CO_2 emissions. The transportation, industrial, and residential sectors present a high demand for fossil sources, and therefore, they occupy the top places in CO_2 emissions, covering 69.9% [4].

It is important to clarify that, although in Ecuador a significant percentage of energy comes from fossil fuels, the country's demand for electricity is mostly covered by hydroelectric resources. In addition, a large part of the energy production from fossil fuels is destined for export, which contributes to the global emissions problem, although not directly to domestic electricity consumption.

In this context, addressing the CO_2 reduction emissions into the atmosphere is essential. Various strategies can be implemented to achieve this, such as controlling energy consumption, promoting renewable sources, and taking advantage of CO_2 capture and storage (CCS) technologies [7]. These technologies focus on separating the CO_2 emitted by industry and other energy sources, compressing it, and obtaining a concentrated stream that can be transported and injected into a suitable geological deposit [8, 9]. The potential of these technologies to reduce CO_2 emissions in various economic sectors is considerable.

According to Koornneef et al. (2012) [10] different methods exist for capturing CO_2, including oxy-combustion, pre-combustion, and post-combustion approaches. Oxy-combustion involves burning fuel with pure or enriched oxygen instead of air, simplifying CO_2 separation. Pre-combustion capture entails converting fuel into carbon monoxide and hydrogen via gasification, followed by CO_2 separation. Conversely, post-combustion capture utilizes chemical solvents like amines, which react with CO_2 to separate it from exhaust gases. The concentrated CO_2 is then released for reuse with the absorbent available and can react again. Regarding industrial application and research, these methods are often ranked as follows: post-combustion > pre-combustion > oxyfuel combustion [11]. Also, Liang et al. (2015) [12] confirm that post-combustion carbon capture (PCC) is the only industrial CO_2 capture technology fully demonstrated at a commercial scale.

Based on the above, this thesis aims to investigate the processes of carbon dioxide (CO_2) capture through the post-combustion method, which involves using amines to absorb CO_2 loads. The studies will be carried out under uniform conditions for all selected amines, including a temperature of 30 °C and a pressure of 500 psig. The volume of the reactors will vary depending on the equipment to be used, being 30 ml for the reactor without stirring and 250 ml for the stirred reactor. Additionally, thermodynamic and kinetic analyses will be performed to provide information on the most efficient solvents for gas capture in future research.

1.1 Problem Statement

Human activities, such as industrial operations, transportation, and electricity generation, contribute to the continuous increase in CO_2 emissions, the primary greenhouse gas. Notably, the transportation and electricity sectors depend on fossil fuels, which is why they emerge as the main contributors to this increase in greenhouse gases [11].

In Ecuador, the economy is dependent on the export of crude oil, this is the source of primary energy consumption in the world according to the Statistical Review of World Energy [13], Therefore the exploitation of this resource and other raw materials produces high levels of environmental degradation in the form of CO_2 emissions [14].

Therefore, capturing and storing CO_2 becomes imperative to counteract the escalating emissions. However, finding the technology, or the compounds that exhibit great capacity or selectivity to these gases, seems to be a challenge in advancing research and development in post-CO_2 capture technologies.

Current advancements in capture processes center around amine purification and thermal regeneration [15]. Although this method has achieved a high level of maturity and widespread application, particularly for its adaptability to existing industrial plants, its efficacy is constrained by the considerable energy consumption during the solution regeneration process.

Consequently, the primary focus of this thesis project is to identify and assess the efficacy of amine-based additives aimed at ensuring the sorption process, ultimately improving the capture of CO_2. This involved conducting a detailed experimental analysis to evaluate the impact of these additives thoroughly.

1.2 Objetives

1.2.1 General Objective

Study the capture of CO_2 with different additives seeking to improve the sorption process.

1.2.2 Specific objetives

- Select a variety of amines to perform experiments, considering their properties and applicability.
- Perform experiments with various concentrations and combinations of additives.
- Analyze and compare results to identify the additives with the best thermodynamic and kinetic results.
- Carry out an economic analysis to determine the most profitable amine.

Chapter 2

Theoretical Background

2.1 CO_2 Capture

It is inevitable to avoid carbon dioxide emissions. Still, a large part of them can be reduced with carbon capture and storage (CCS) methods and technologies because it is a process that involves the selective retention of CO_2 from industrial and fossil fuel sources before it is released into the atmosphere, which in turn makes it an essential element in the fight against climate change [16, 17]. Carbon capture and storage methods and technologies can be divided into 3 categories: pre-combustion, post-combustion, and oxy-combustion, each presenting its advantages and disadvantages over the others [17, 18].

- The pre-combustion technique is a separation of CO_2 that takes place before fuel combustion. It aims to minimize energy losses and investment costs related to the generation of hydrogen fuel gas. Those are achieved by integrating the reforming WGS (water gas shift) reactions with removing CO_2 in a single process step. This approach alters the reaction equilibrium to obtain a gaseous product with a higher hydrogen content [19].

- Post-combustion techniques entail capturing CO_2 from exhaust gases after combustion. These can be achieved with chemical absorption, physical adsorption, membrane separation, or a chemical circuit [20]. The distinguishing advantage of post-combustion lies in its demonstrated industrial efficiency, setting it apart from the other two categories [12].

- Oxy-combustion technique involves the combustion of fuel using pure oxygen, leading to increased temperatures, reduced fuel consumption, and higher concentrations of CO_2. This method holds significant potential, especially considering its potential integration with other systems [21]. Allowing significantly smaller flue gas conditioning devices downstream of the furnace is a notable advantage of this technology compared to other carbon capture methods. Still, its disadvantage is that it is a costly process associated with producing high-purity O_2 by cryogenic distillation [22].

Also, carbon dioxide can be separated through diverse methods or procedures, which can be categorized into absorption processes, gas–solid reaction processes, adsorption processes, cryogenic processes, membrane processes, and natural inclusion, as shown in Figure 2.1.

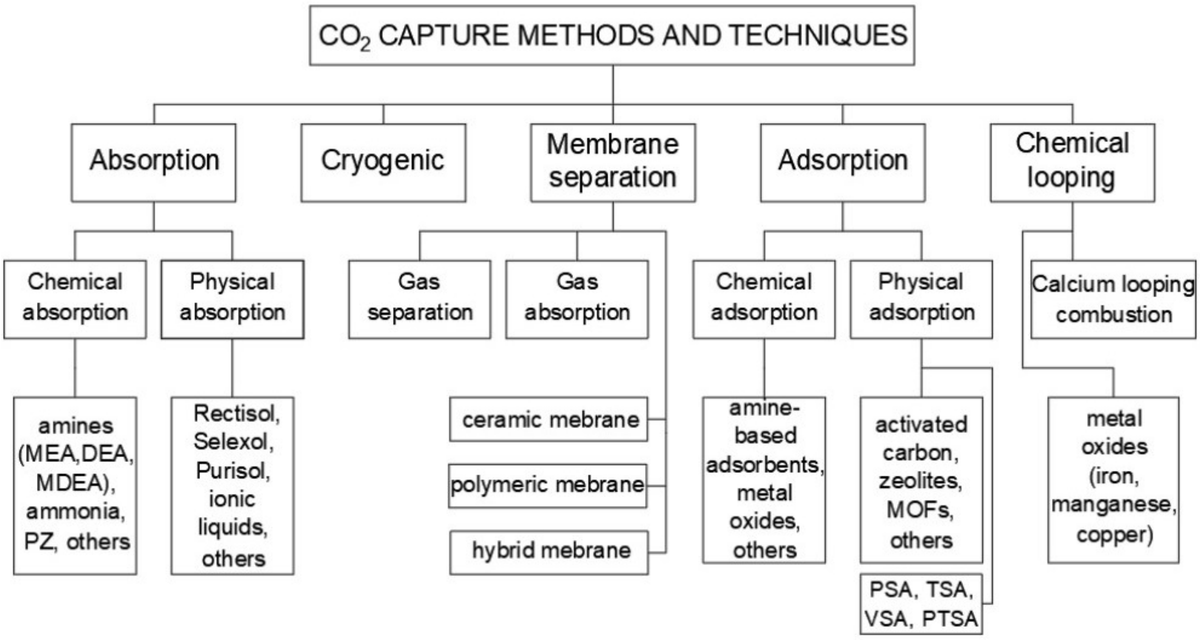


Figure 2.1: Techniques and methodologies for capturing CO_2 [17]

2.1.1 Absorption process

Absorption is a process that aims to selectively remove a component from the gas phase through an absorbent, which could be liquid or solid. There are two main types of absorption: chemical absorption (chemisorption) and physical absorption (physisorption) [18].

Chemical absorption

This approach extracts carbon dioxide from exhaust gases by interacting with chemical solvents, forming intermediate products through the reaction. These solvents encompass amines, amino acid salts, carbonates, ionic liquids, and ammonia [23]. This method is particularly suitable for post-combustion CO_2 capture. It stands out due to its well-established technology, widely applied in diverse industrial settings, such as removing acid gases from natural gas and extracting CO_2 from reformer gases [24].

Common solvents utilized in this process include alkanolamines like monoethanolamine (MEA), diethanolamine (DEA), or methyl diethanolamine (MDEA) in aqueous solutions [18]. These solvents contribute to high process efficiency and yield substantial carbon dioxide purity.

Physical absorption

The physical absorption technique employs a chemically inert solvent that physically absorbs CO_2 through weak interactions like van der Waals forces. This approach yields optimal results under low temperatures and high pressures of the separated gas [17]. Therefore, its frequent application is in pre-combustion capture, particularly for CO_2 capture from coal gasification. Noteworthy processes within this method involve using solvents such as selexol, rectisol, and purisol. [18].

As part of the research, other methods and techniques for CO_2 capture are detailed in Appendix A, which includes descriptions of each technique, comparative analyses, and relevant data to facilitate a complete understanding of the options available.

2.2 Absorption with amines

Amines are considered ideal for capturing CO_2 due to their exceptional reactivity, substantial absorption capacity, thermal stability at elevated temperatures, and high selectivity for CO_2. However, this promising approach has drawbacks, including increased corrosion rates in equipment, substantial energy demands for regeneration, elevated volatility, constrained CO_2 loading capacity, and degradation of the amines [25].

2.2.1 Amines clasification

Chemical compounds containing the amino functional group ($-NH_2$) can be classified in various ways, depending on the criteria used. Below is a general classification of amines:

Based on the number of hydrogen atoms in nitrogen

According to the Nakao et al. (2019) [26] amines can be classified depending on the number of radicals (organic compounds with carbon chains or cycles) directly attached to the central nitrogen atom, as shown in Figure 2.2, primary and secondary amines have nitrogen atoms covalently bonded to two hydrogen atoms and one hydrogen atom, respectively. In contrast, tertiary amines lack hydrogen atoms directly bound to the nitrogen.

- Primary amines have only one radical attached, it displays a rapid reaction rate with CO_2, but their regeneration demands a substantial amount of energy.
- Secondary amines have two radicals attached, and the absorption of CO_2 by secondary amines may lead to the formation of nitrosamines, which are highly toxic substances that pose health risks and contribute to environmental burdens.
- Tertiary amines have three radicals attached, which possess a greater capacity for CO_2 absorption, albeit hindered by a slower reaction rate.

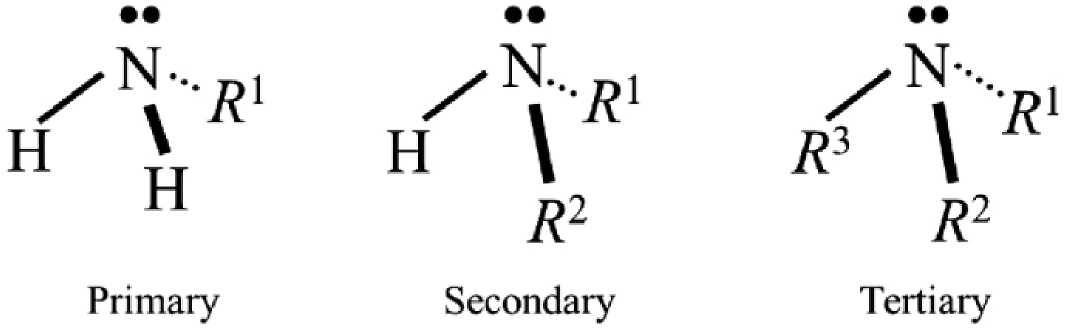


Figure 2.2: Amines classification [26]

Amines are commonly employed as chemical solvents in natural gas processing. Amines are anticipated to be applied in aqueous solutions, typically ranging from approximately 10 to 65 wt% [27]. Nevertheless, it is crucial to note that the concentration of amines may vary in different processes based on the desired capture efficiency, operational configurations of the industrial plant, or the characteristics of the gas stream used, considering corrosion issues.

It is commonly stated that the reactivity towards CO_2 follows the descending order: primary (–NH2) > secondary (>NH) > tertiary (>N–) [26, 28]. This shows the influence of the various structures of amines and their impact on their CO_2 capture activities.

Based on the nature of group R

- Aliphatic amines are organic compounds, indicating a carbon-based nature, with at least one nitrogen atom bonded to a saturated carbon-hydrogen backbone [29].
- Aromatic amines are substances where the amino group is directly bonded to an aromatic ring. The aromatic ring is characterized by a conjugated cyclic structure featuring alternating single and double bonds [29].

By Wang et al. (2020) [30] and Perron et al. (2009) [31], the differences between the properties of aromatic amines and aliphatic amines are given by their pKa values. The pKa enabling aliphatic amines to engage with a broader range of weak acids, such as carbonic acid. Various aliphatic amines, including primary, secondary, and tertiary amines, have emerged as responsive materials to CO_2.

The type of amines significantly impacts the reaction with carbon dioxide. To understand how these interactions occur, it is recommended to consult the Appendix B.

2.3 Additives in capture processes:

Additives play a crucial role in improving the efficiency of capture processes, particularly in the context of carbon capture and storage systems. These systems must operate at extreme efficiency to ensure they capture as much carbon as possible while using significantly less carbon than they are capturing. Additives can enhance the performance and efficiency of various components in these systems, such as filters, heat exchangers, condensers, and gas separation membranes [32, 33].

In previous works [27], we found compounds containing amines are predominantly used in carbon dioxide capture, constituting 74% of the total compounds. The study proposes that the additives are divided into groups. The first group comprises alkanolamines, widely used as promoters in industrial applications due to their properties that improve solubility, particularly notable in Monoethanolamine (MEA), Diethanolamine (DEA), and Methyldiethanolamine (MDEA). Then, amines and heterocyclic amino acids are mainly recognized for their kinetic promotion capabilities and improved water interaction mechanisms, respectively. Third, ionic liquids, which share strong electronic interactions with CO_2, offer remarkable stability but face challenges in synthesis and cost. Of the last groups is the family of amines, classified into monoamines, diamines, triamines, and tetramines. These additives together represent 83% of the total additives. The remaining compounds, such as organic salts, alcohols, surfactants, and corrosion inhibitors, although in smaller proportions, address specific technical aspects of capture, including foaming and corrosion mitigation, rather than directly improving the process capture itself.

Despite being a mature technology, using amines in CO_2 capture requires further research to enhance absorption. This involves exploring novel amines, refining operational parameters, devising regeneration techniques, and tackling issues such as corrosion and related expenses. By making progress in these investigations, it is anticipated that there will be substantial improvements in the efficiency and financial feasibility of CO_2 capture using amines, thereby aiding in the fight against climate change and curbing greenhouse gas emissions.

Chapter 3

Methodology

In the present work, the process has been divided into 4 stages that consist of:

- Amine selection: It is crucial to determine which compounds will most effectively capture CO_2. Several factors will be considered to choose the most suitable amines for the capture process.

- Thermodynamic and kinetic study: to know how amines behave regarding absorption efficiency, reaction speed, and regeneration capacity.

- Corrosion study: allows us to evaluate the impact of CO_2 absorption and how its reaction with different amines can influence the materials used in industrial processes.

- Economic study: agrees to evaluate the financial viability and profitability of the investment costs to process one ton of CO_2.

To determine, optimize, and develop more efficient, economical, and environmentally sustainable CO_2 capture processes, thus contributing to climate change mitigation and reducing greenhouse gas emissions. A schematic representation of the methodology developed in this study is shown in Figure 3.1.

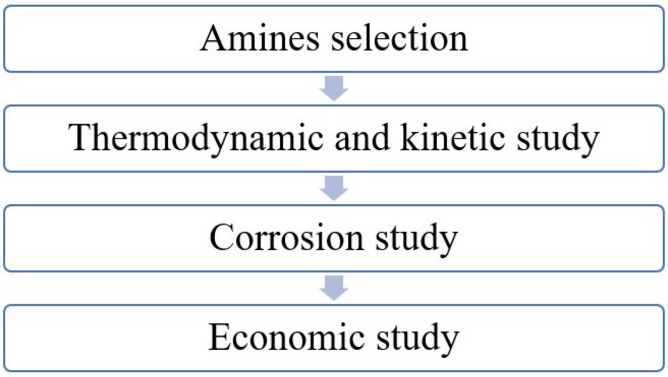


Figure 3.1: Schematic diagram of the methodology

3.1 Amines selection

To begin the selection of appropriate amines for the study, we first considered the list of amines available in the university laboratories. Then, it was proposed to evaluate each one based on criteria such as price, corrosion, capture selectivity, and applied studies. Table 3.1 illustrates the basis for each criterion to establish the values.

Table 3.1: Definition of criteria

Price	**Corrosivity**	**Applied studies**	**Capture selectivity**
The value per liter or kilogram of product.	Depending on the type of amine, primary amines tend to show greater corrosive effect compared to secondary and tertiary amines.	Based on the availability of absorption studies that have been performed.	Depending on the type of amine, tertiary amines tend to show greater selectivity towards CO2 compared to primary and secondary amines.

However, for a proper selection, we aimed to identify the amines that presented the best conditions through three possible scenarios. For each scenario, the percentage assigned to each criterion was varied. This distribution of percentages is detailed in the Table 3.2. Therefore, the reference values being: (1) low, (2) medium, or (3) high. If it is 1, the total percentage assigned to that criterion will be considered; if it is 2, only half; and if it is 3, only 25 percent.

Table 3.2: Percentage distribution for the scenarios

Scenarios	**Price**	**Corrosivity**	**Applied studies**	**Capture selectivity**
Scenario A	30%	25%	15%	30%
Scenario B	40%	15%	10%	35%
Scenario C	15%	35%	10%	40%

3.2 Thermodynamic and kinetic study

After defining the amines, experiments were conducted using the following laboratory equipment :

- **Non-stirred reactor**

  The equipment used is a Parr HPS Series 4790 Pressure Vessel Systems reactor (see Figure 3.2), designed for batch operations. It does not allow continuous entry or exit of chemical species. Manufactured from a C-276 alloy, this reactor is ideal for handling corrosive substances, withstanding extreme pressure conditions of up to 20,685 KPa and temperatures of up to 500 K in acidic environments. It comprises two main parts: a moving head and a cylinder with a capacity of 100 ml, making it an optimal option for studies with small volumes. Standard head accessories include a pressure gauge, rupture disc, and thermocouple to monitor internal vessel pressure and temperature. In addition, it has three valves that enable gas release, liquid sampling, and gas injection into the liquid phase to guarantee homogeneous contact between the solution and the gas. The head part is attached to the cylinder by a split ring which has screws for a complete seal. This safety feature helps minimize risks associated with hazardous materials or reactions by limiting exposure of reagents or products to the outside environment [34].

Figure 3.2: Series 4790 pressure vessel systems

- **Jacketed stirred reactor**

  The stirred reactor used is a Parr model 5100 batch reactor (see Figure. 3.3), designed with a 660 ml capacity vessel, a table stand, and a glass/metal lined wall. This reactor is specially designed to carry out reactions that require stirring, with a stirring speed range of 0 to 1700 rpm. It can operate at relatively high pressures, up to 1000 psi, and temperatures up to 500K, thanks to its stainless steel construction, making it corrosion-resistant in challenging environments. Like non-stirred reactors, this reactor has valves in the head for gas inlet and outlet, liquid sampling, and an internal thermocouple for precise temperature control. To ensure a tight seal, the reactor has an O-ring and a split ring closure that secures the head and vessel [35].

Figure 3.3: Series 5100 reactors

The following two pieces of equipment are auxiliary equipment to the reactors:

- **Controller**

  The reactors are equipped with Parr 4838 controllers, which use a PID system. This has two-way digital communication capabilities in each module. This allows users to record real-time readings on a PC and transmit various parameters, such as set points, agitator speeds, and alarm thresholds, from the PC to the controller and vice versa. [36].

Figure 3.4: Temperature controller Parr 4848 - Non-stirred reactor

Figure 3.5: Temperature controller Parr 4848 - Stirred reactor

- **Refrigerated circulator**

  The circulating bath from PolyScience depicted in Figure 3.6 is designed to provide precise temperature control in a simple way, its temperature range is from 233.15K to 473.15K. It has a capacity of 15 liters and a stainless steel tank [37].

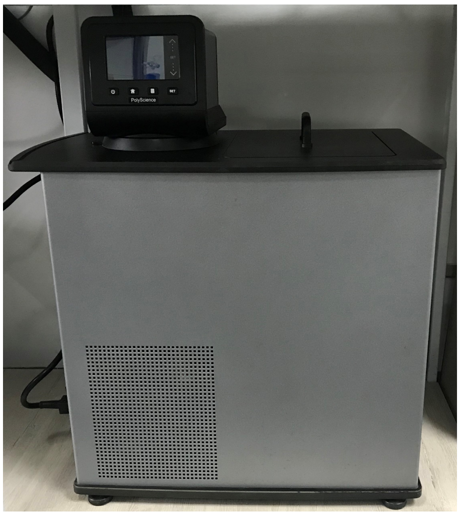


Figure 3.6: PolyScience Circulating Bath

All these studies are recorded using the SpecView data acquisition and control software, which enables the connection between the instrumentation and a computer. SpecView monitors, displays and stores the received information, which are the process parameters, in addition, it allows operating a graphical user interface to visualize the process, execute a strategy controller logic engine for process automation, display the performance of the machine, review the operating parameters of the process and reproduce its conditions, among other functionalities [38].

3.2.1 Experimental setup

The experiments were conducted in two different experimental systems to account for the potential influence of stirring on mass diffusion. Stirring can impact the rate at which mass is transferred within the system, potentially affecting the results obtained. Therefore, by evaluating the performance of the top-performing amines in the unstirred reactor within a stirred reactor, we can also ensure a comprehensive analysis of their effectiveness under different operating conditions. For the experimental setup, 30 mL of solution is loaded into the reactor. Then, the equipment is entirely closed, and the connections are made between the gas inlet and the sensor that sends signals to the controller. Subsequently, the temperature is set at 30 °C, and once reached, the reactor is pressurized to 500 psig. The experiment runs for 20 hours for data recording and for the reaction to reach equilibrium. In the case of the stirred reactor, the only difference is that a larger volume is used (250 ml), and stirring is activated. Initially, several CO_2 solubility tests in water were carried out to validate the experimental setup of the high-pressure system. The objective of these tests was to measure the equilibrium pressure reached by the system at these pressures and verify its accuracy with the data available in the literature. After confirming the configuration was correct, tests were started with 40% solutions of the amines solutions.

3.2.2 Data Processing

In this phase of the study, we worked with the data recorded in the Specview software. These provided time, pressure, temperature, and agitation data. The last one is in the case of the stirred reactor. Furthermore, employing the Peng-Robinson equation of state [39], the compressibility factor (Z) was determined, enabling the computation of the gas moles (n) within the system using the ideal gas equation adjusted for real gases.

$$PV = nZRT \tag{3.1}$$

On the other hand, the absorbed CO_2 is also determined, representing the amount of gas that disappears from the gas phase compared to the initial amount and is introduced into the liquid phase. This calculation takes the difference between the amount of CO_2 initially present in the gas phase and the amount of CO_2 absorbed during the process.

This using the following formula:

$$CO_2 \ removed = n_{t0}^{gas} - n_{tf}^{gas} \tag{3.2}$$

With this, the resulting value is obtained, the amount of total absorbed CO_2, which in turn, divided by mole of solution, allows us to determine the CO_2 load.

$$CO_2 \ loading = \frac{CO_2 \ removed}{n_{amine}} \tag{3.3}$$

Consequently, with these values, graphs are made as a function of time, allowing thermodynamic and kinetic analyses to be carried out. The thermodynamic analysis involves assessing the quantity of moles removed, which also provides insights into the loading capacity per mole of amine. This step is crucial as it helps understand the efficiency of each amine in capturing CO_2 over time, informing on their respective absorption capabilities.

Additionally, as a component of the kinetic study, the time taken for each amine to absorb specific percentages (10%, 25%, 50%, and 90%) of the CO_2 it ultimately absorbed was evaluated at equilibrium. This analysis is essential as it elucidates the absorption kinetics of each amine, shedding light on their respective rates of CO_2 uptake and saturation points.

3.3 Corrosivity study

This part of the study is considered to corroborate the corrosion tendency that amines present according to research and, in the same way, verify that the “corrosivity” criterion has been correctly evaluated to carry out the selection of amines. The study of corrosion was proposed to analyze weight variation. First, the amine solutions that have already absorbed CO_2 will be used. Then, a fragment of steel, approximately 1 inch in size, will be weighed. Finally, it will be submerged in the solution for 4 months. After this time has elapsed, each steel fragment will be exposed to sanding for 3 min, and the mass will be measured again.

To determine corrosion, we will use the following equation:

$$\text{Corrosion Rate (g/year)} = \frac{(M_i - M_t)}{t} * 12 \tag{3.4}$$

Where M_i is the initial mass of the metal fragment, while M_t is the mass at time t, where the time units are evaluated in months.

3.4 Economic study

The economic study considers only the investment cost for the raw material, in this case, the amine, because this constitutes a significant part of the expenses associated with the CO_2 absorption process. With this study, we seek to determine the investment cost per ton of CO_2 absorbed so that the financial viability of the CO_2 absorption process can be evaluated and strategic decisions can be made about its implementation. For this, the load capacity obtained and the price will be considered.

Chapter 4

Results and Discussion

4.1 Selecting Amines

The criteria that are proposed to make the selection are: price, corrosiveness, applied studies, and selectivity. Under these criteria, if the assigned value is 1, the total percentage that each criterion will have is awarded. For values assigned as 2, half that percentage will be assigned, and for those with value 3, only 25% will be assigned according to the percentage established. To begin with the analysis, given that the products used in the university laboratories are from Sigma-Aldrich, the prices of the amines that are reflected in Table 4.1 are referenced by this company [40].

Table 4.1: Amines available at Yachay Tech

Amines	**Price**
Diethylenetriamine	84,30 $/L
Monoethanolamine	95,63 $/L
Ethylenediamine	70,48 $/L
Hexamethylenetetramine	94,03 $/L
Methyldiethanolamine	47,65 $/L
Tetramethyl ethylenediamine	237,45 $/L
Triethanolamine	161,90 $/L
Triethylamine	137,08 $/L
2-Chloroethylamine hydrochloride	81,29 $/L
4-aminophenol	208,85 $/L

In order to assign the values, both for the corrosion criterion and capture selectivity, we focused on classifying the amines according to their primary, secondary or tertiary character, given that, according to the research consulted, an order of decreasing corrosivity was established: primary amines > secondary amines > tertiary amines [41, 42]. In contrast, it was observed that tertiary amines tend to show greater selectivity towards CO_2 compared to primary and secondary amines, attributed to the presence of three less reactive hydrogen atoms that facilitate the formation of stronger chemical bonds with CO_2.

Table 4.2 shows the classification according to its type. Therefore, the values according to the scale previously described are illustrated in Table 4.3.

Table 4.2: Amines classification

Pimary amines	**Secondary amines**	**Tertiary amines**
Monoethanolamine	Diethylenetriamine	Hexamethylenetetramine
Ethylenediamine		Methyldiethanolamine
4-aminophenol		Triethanolamine
2-Chloroethylamine hydrochloride		Triethylamine
		Tetramethyl ethylenediamine

Table 4.3: Weighting of each criterion for amines

Amines	**Price**	**Corrosivity**	**Applied studies**	**Capture selectivity**
Diethylenetriamine	2	2	3	2
Monoethanolamine	3	1	3	3
Ethylenediamine	2	1	3	3
Hexamethylenetetramine	2	3	1	1
Methyldiethanolamine	1	3	3	1
Tetramethyl ethylenediamine	3	3	2	1
Triethanolamine	2	3	3	1
Triethylamine	2	3	1	1
2-Chloroethylamine hydrochloride	3	1	1	3
4-aminophenol	2	1	1	3

Primary or secondary amines typically exhibit a lower capacity to absorb CO_2, usually about half a mole of CO_2 per mole of amine, due to their tendency to form relatively stable carbamate compounds. Consequently, the carbamate decomposes upon heating, releasing CO_2 and rejuvenating the amine. The stability of the carbamate formed during absorption requires a considerable amount of thermal energy to break the bonds and regenerate the absorbent. In contrast, tertiary amines yield an unstable carbamate, leading to the formation of bicarbonate ions. This property grants tertiary amines a higher absorption capacity, enabling the absorption of one mole of CO_2 per mole of amine. At the same time, it also requires less thermal energy than primary or secondary amines [43, 44].

As a final part of the selection, it was established that amines that met at least 70% of the established criteria would be considered for the study. The amines that reach this threshold are shown in Figure 4.1. The results indicate that Methyldiethanolamine outperforms the others in all the scenarios evaluated, followed closely by Diethylenetriamine. Finally, Triethanolamine showed an outstanding performance, reaching the established percentage in two of the three scenarios analyzed, both in scenario A and C. In addition to these three amines, which stand out as the most promising, Monoethanolamine was included as a reference solvent in this type of analysis.

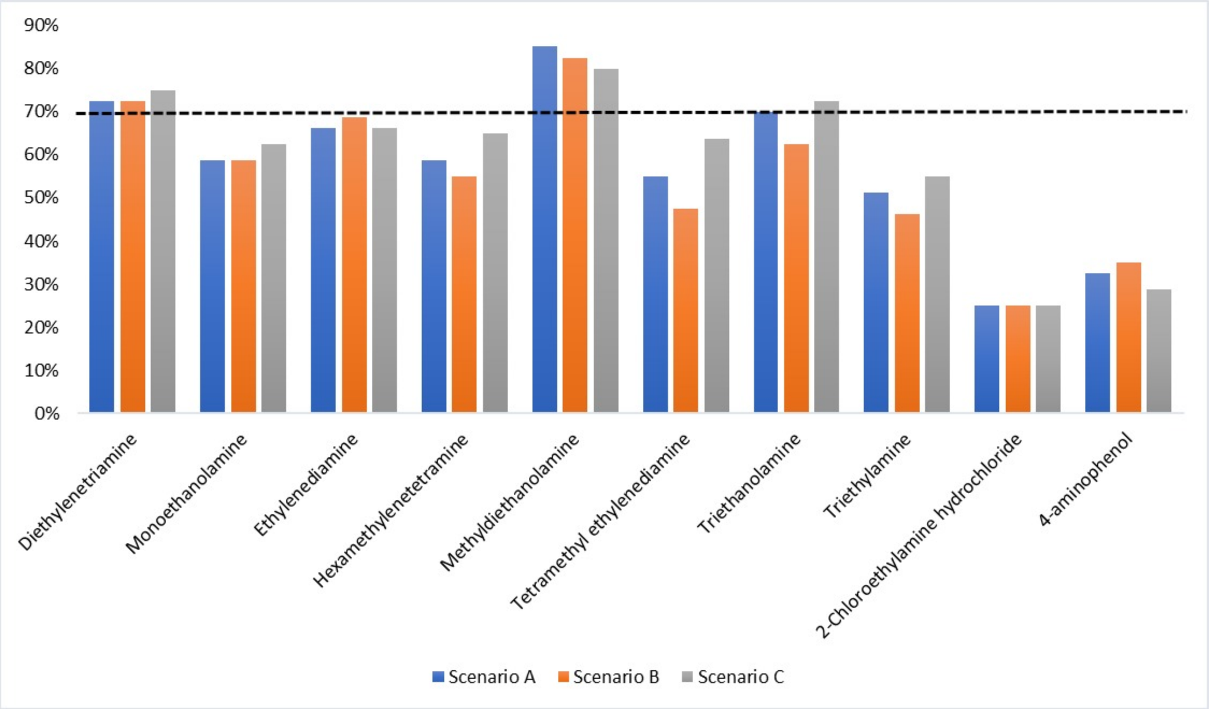
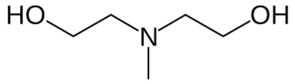
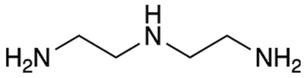
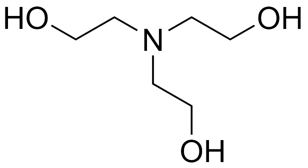
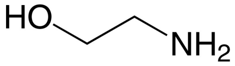


Figure 4.1: Amines evaluation

Table 4.4: Selected amines

Amines	**CAS**	**Molar mass** (g/mol)	**Chemical structures**
N-Methyldiethanolamine (MDEA)	105-59-9	119,16	
Diethylenetriamine (DETA)	111-40-0	103,17	
Triethanolamine (TEA)	102-71-6	149,19	
Monoethanolamine (MEA)	141-43-5	61,08	

Numerous studies mention the usefulness of amines in removing acid gases, and their treatment [43, 45]. It has already been applied in the natural gas recovery industry, which is why the adaptation and modification of the process for its implementation in different industrial environments intended for carbon capture would be advantageous over other techniques, what's more, the development of this method would entail a relatively low investment cost [44]. According to Bonenfant et al. (2003) [46], "the most used alkanolamines in these industrial acid gas treatment methods are monoethanolamine, diethanolamine, triethanolamine, diisopropanolamine (DIPA) and methyldiethanolamine (MDEA)." This indicates that these amines have proven effective in industrial applications similar to carbon capture. Therefore, when selecting these amines for our study, we ensured that we were focused on proven and well-established chemical compounds in the industry, increasing our findings' relevance and applicability.

4.2 Thermodynamic and Kinetic Analysis

At a temperature of 30°C, the influences on the absorption performance of the solvents are being analyzed: MDEA, MEA, DETA and TEA in a volume of 30 ml of 40% solution, Figure 4.2 and Figure 4.3 represent the partial pressure and CO_2 removed versus absorption time, respectively, of the results from the non stirred reactor. In both graphs it can be seen that each solution tends to stabilize at different times because each reactant has a different reaction rate, some faster than others.

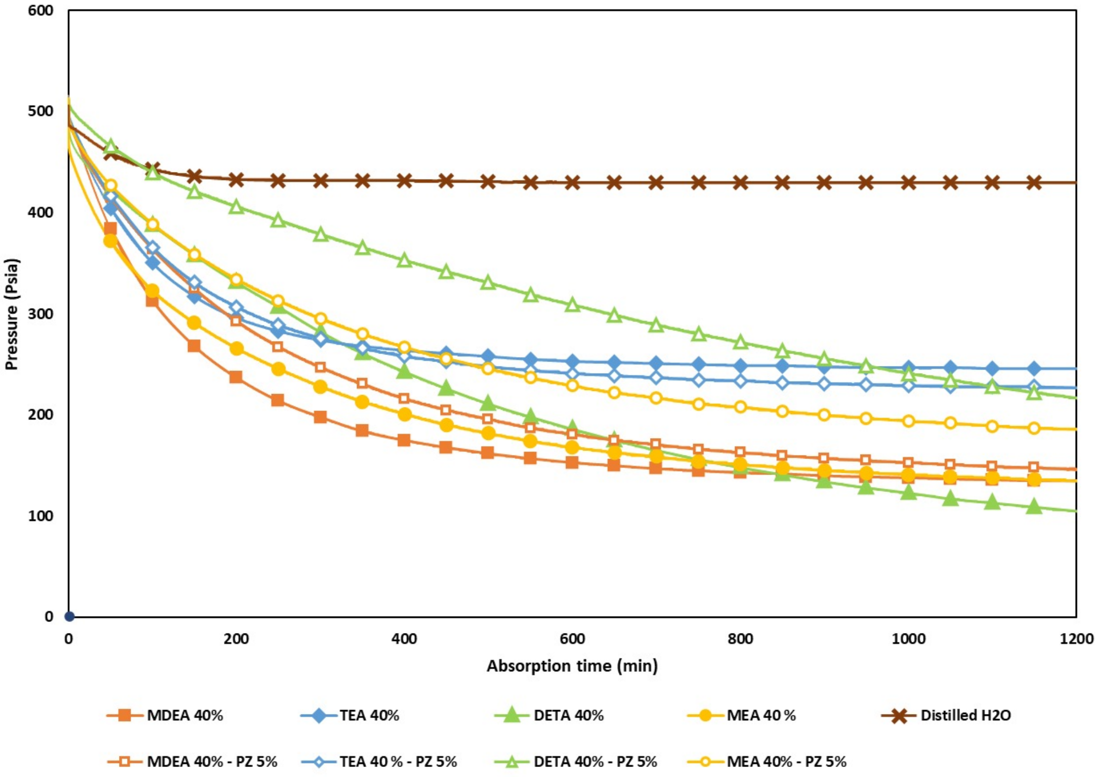


Figure 4.2: The gas phase pressure under 40% solutions in non-stirred reator

Regarding the results obtained, DETA shows a greater removal of CO_2, although it does not reach its equilibrium completely, unlike the other compounds. It is followed by MEA and MDEA, and finally, TEA, which removes three times more moles than water. However, in the same way, the CO_2 loads obtained by each compound are recorded in Table 4.5. This reflects that DETA and MDEA have the highest CO_2 load, with a 0.9 mmol/mmol of amine value. The data obtained contrasts with the reference information available and referenced in the same Table 4.5.

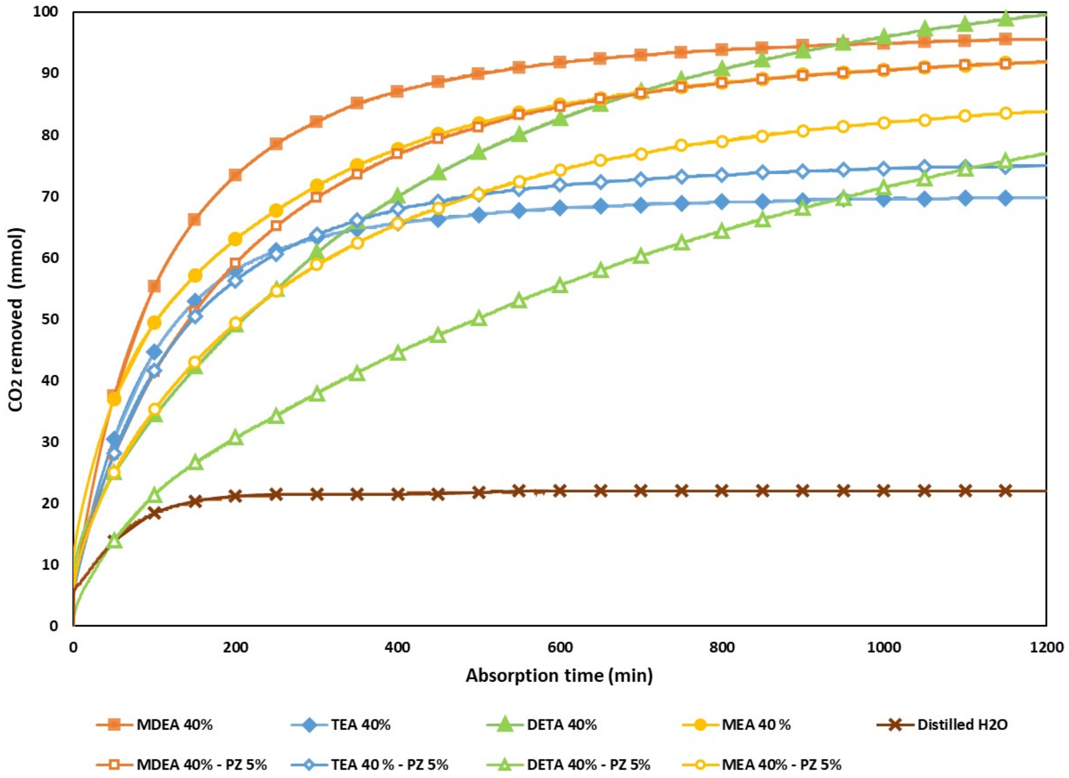


Figure 4.3: CO_2 removed versus time in non-stirred reactor

Table 4.5: Thermodynamic data for non-stirred reactor

Solution	CO_2 removed (mmol)	CO_2 loading (mol CO_2 /mol amine)	Literature range (mol CO_2/mol amine)
MDEA 40%	93.86	0.9	(0.9 - 1) [47]
DETA 40%	102,188	0.92	(0.66 - 1.03) [48]
TEA 40%	69,994	0.77	(0.572– 1.18) [49]
MEA 40%	92,489	0.46	(0.232 - 0.5) [50, 51]
H_2O	22,022	0.01	0.0128 [52]

As the search for references was conducted to corroborate the thermodynamic data, it was found that adding piperazine has a promoting effect on the reaction [53, 54, 55]. Therefore, it was decided to test 5% of piperazine in a mixture with the already defined solutions to be studied. For this reason, the titration curves of these solution mixtures are observed in Figures 4.2 and 4.3. However, upon performing the kinetic study, it becomes evident that solutions containing piperazine do not exhibit this promoting effect, as mentioned in many studies. The kinetic data reflected in the Table 4.6 show how the absorption rate in amine solutions with piperazine decreases compared to solutions of the amine alone. This outcome may be due to insufficient mixing in the unstirred reactor systems, where the lack of agitation could have prevented piperazine from effectively interacting with the amine solutions, thus reducing its anticipated promoting effect.

Table 4.6: Kinetic data for non-stired reactor

Solution	dn/dt (mmol/min)	t_{10} (min)	t_{25} (min)	t_{50} (min)	t_{90} (min)
MDEA 40%	0.54	4.5	24.83	73.5	336.5
DETA 40%	0.23	2.17	53.17	217.5	842.83
TEA 40%	0.37	2.17	20.17	63.5	293.17
MEA 40%	0.55	0.17	17.5	84.5	541.17
MDEA 40% - PZ 5%	0.33	4.5	36.17	123.83	557.5
DETA 40% - PZ 5%	0.18	21.83	89.83	334.83	1043.83
TEA 40% - PZ 5%	0.35	3.5	26.17	83.17	3999.83
MEA 40% - PZ 5%	0.26	3.17	36.5	147.17	691.17
H_2O	0.13	0.08	0.5	31.5	140.5

These results show that the highest reaction rate in the first 100 min in unstirred reactor is for the MEA solution, followed by MDEA, TEA, and DETA. The reaction rate is directly influenced by the formation of carbamates or bicarbonate ions; the former, being more stable, tends to have faster reaction kinetics compared to the formation of bicarbonate [26]. Knowing that primary and secondary amines tend to form carbamates and tertiary amines bicarbonates, the reason for the reaction rate for each one will be explained. This same order is maintained for the mixture solutions with piperazine, although an approximate reduction of 22% for DETA, 8% for TEA, 27% for MEA and 2% for MDEA is observed in the values obtained.

With the amines that gave the best results, both thermodynamic and kinetic, and considering the analysis approach in each part, the experiments were carried out in the stirred reactor, maintaining a temperature of 30 °C and a pressure of 500 psig. At the beginning of the tests, it was initially considered that 6 hours would be sufficient to reach equilibrium. However, as seen in Figures 4.4 and 4.5, this did not occur. Therefore, the time was extended to 20 hours for the other half of the tests.

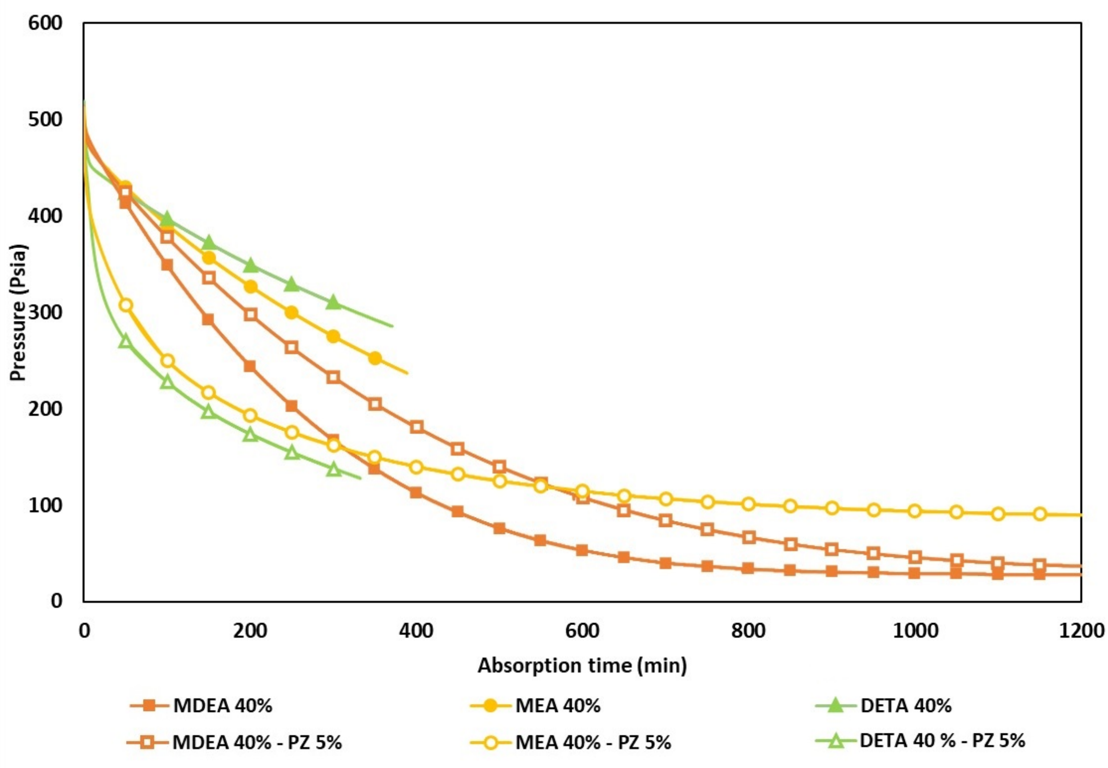


Figure 4.4: The gas phase pressure under 40% solutions in stirred reactor

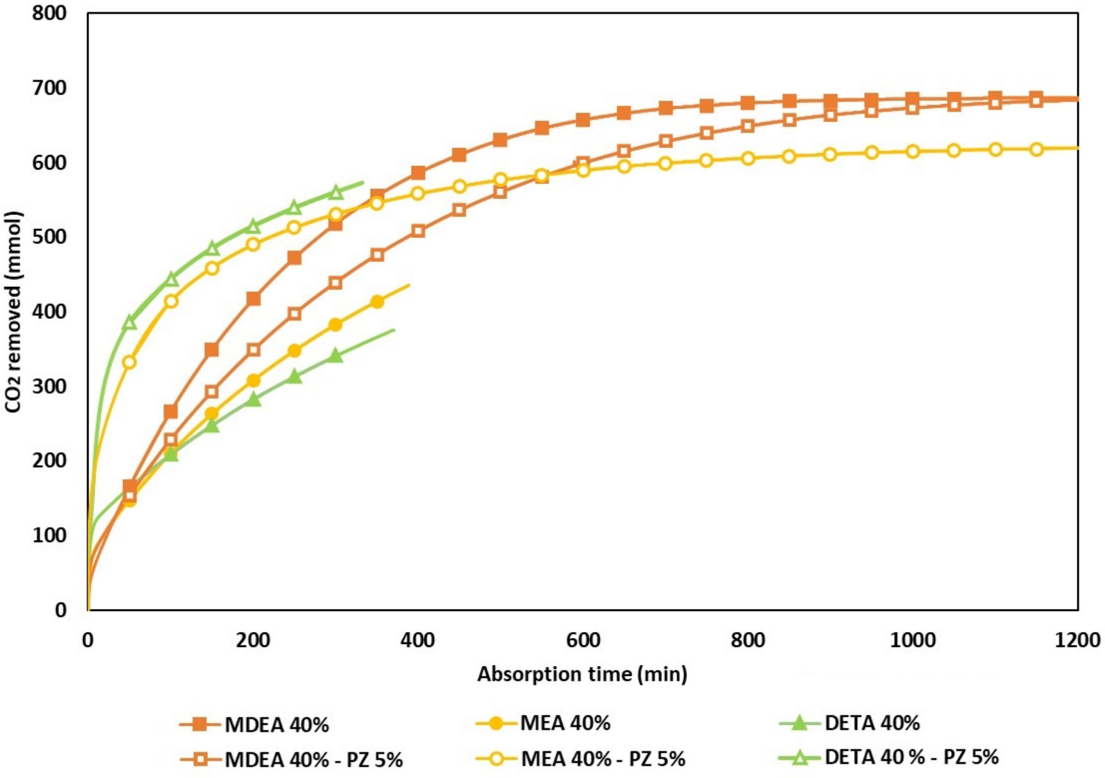


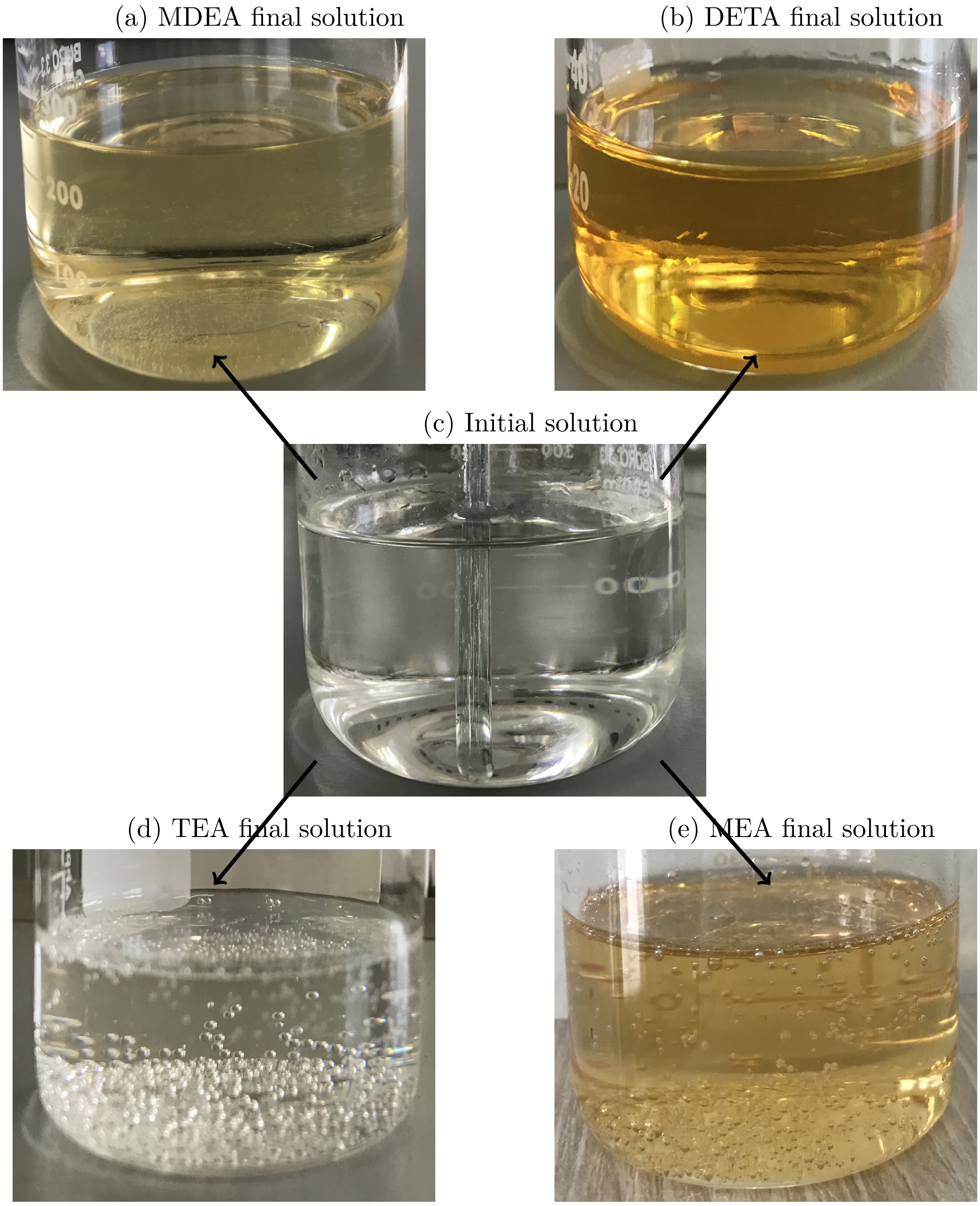
Figure 4.5: CO_2 removed versus time in stirred reactor

Table 4.7 reflects the data obtained from the kinetic study in the stirred reactor, however, the lack of equilibrium in some tests makes it difficult to determine the results and the CO_2 load in each amine. Therefore, there are blank data. On the contrary, in tests where equilibrium was reached, as in the case of 40% MDEA in our study, a loading of 0.79 mol CO_2 /mol amine was obtained. According to the results obtained in the research by Dersk, Hogendoorn, and Versteeg (2010) [56] the results for MDEA under conditions similar to those of our research, which utilizes a batch-type reactor, indicate that the CO2 loading range varies between 0.6 and 0.65. However, it is important to note that the volume used in their study is smaller, which could justify the lower CO2 loading observed. Despite this difference, the CO2 loading recorded in our experiment, which is 0.79 mol of CO2 per mol of amine, is not significantly distant from the results reported by Dersk et. al.

Table 4.7: Kinetic data for stired reactor

Amine Solution	dn/dt (mmol/min)	t_{10} (min)	t_{25} (min)	t_{50} (min)	t_{90} (min)
MDEA 40%	2.33	10.83	52.5	145.83	468.16
DETA 40%	0.97	-	-	-	-
MEA 40%	1.46	-	-	-	-
MDEA 40% - PZ 5%	1.65	4.5	60.83	193.83	658.17
DETA 40% - PZ 5%	1.63	-	-	-	-
MEA 40% - PZ 5%	2.59	0.17	3.83	41.17	410.17

Absorption studies indicate that the reaction rate of CO_2 with MEA and MDEA [57, 58] can be improved by the addition of piperazine. The results demonstrate that piperazine fulfills its role as a promoter in this experimental system, and even the additive amines with piperazine present the best kinetic effects. It is observed in Figure 4.5 that MEA 40% with 5% piperazine has the highest reaction rate, followed by DETA 40% - PZ 5%. It can be interpreted that the promoting effect of piperazine between an agitated system and another without agitation may be due to the distribution and mixing of the reagents. In an agitated system, agitation promotes a more uniform mixing of the piperazine with the amines and CO_2, facilitating its ability to promote the reaction.



(a) MDEA final solution

(b) DETA final solution

(c) Initial solution

(d) TEA final solution

(e) MEA final solution

Figure 4.6: Changes in amine composition during CO_2 absorption.

On the other hand, in all studies, the initial solution was uniformly colorless as seen in Figure 4.6c However, this initial characteristic also allows us to infer the degree of reaction with CO_2. As the color intensifies, it indicates a more significant number of moles of CO_2 that have reacted with the amine. Therefore, it was observed that triethanolamine (TEA) did not present notable changes in color, which coincides with the thermodynamic analyzes that revealed that TEA had the lowest CO_2 loading. Look at the Figure 4.6 to see how to change the colors of each solution.

4.3 Corrosivity studies

The results of the corrosion rate are detailed in the Table 4.8.

Table 4.8: Corrosivity data

Solution/Condition	Initial mass of steel fragment (g)	Final mass of steel fragment (g)	Corrosion rate (g/year)
DETA 40%	4.051	4.035	0.049
TEA 40%	3.929	3.920	0.025
MDEA 40% - PZ 5%	4.173	4.15	0.07
DETA 40% - PZ 5%	4.195	4.184	0.032
MEA 40% - PZ 5%	3.910	3.858	0.172
Ambient air	3.868	3.862	0.025

When comparing DETA, a secondary amine, with TEA, a tertiary amine, in both 40% solutions, it is observed that the corrosion rate of the former is almost double that of the latter, confirming the tendency of secondary amines to corrode more than the tertiary ones. In addition, the results of tests carried out on mixtures of a 40% amine solution with 5% piperazine are presented, considering that MEA is a primary amine, DETA is a secondary amine, and MDEA is a tertiary amine. These results indicate that the primary amine has the highest value, confirming that primary amines corrode more than secondary and tertiary amines. According to the studies of Fleury et al. (2008) [41] and Gunasekaran et al. (2017) [42] it was shown that MEA is the most corrosive of all amines tested.

4.4 Economic Analysis

In this part of the study, the estimated cost that would have to be invested in each of the amines to absorb 1 ton of CO_2 is presented, which is equivalent to 22 752 moles. The respective calculations consider the prices and the CO_2 load detailed in Tables 4.1 and 4.5 respectively, along with the mass and density of each compound. Using the equation (4.1) applied, the volume necessary for the absorption process is estimated, determining the cost associated with carrying out said process.

$$V_{amine} = \frac{n_{amine} * M_{amine}}{\rho_{amine}} \tag{4.1}$$

Table 4.9: Costs associated with the absorption process for each amine

Amines	Molar mass (kg/kmol)	Density (kg/m^3)	Volume (m^3)	Cost (M USD)
MDEA	119.16	1040	2.91	138.6
DETA	103.17	960	2.67	225.23
TEA	149.19	1120	3.90	631.52
MEA	61.08	1010	2.95	282.38

Considering the density, and the study by Klahn et al. (2015) [59] low ion densities result in more considerable average distances between cations and anions. Consequently, the ionic liquid (IL) became less compact, making it easier to insert CO_2. So, it can be mentioned that the higher the density, the lower the CO_2 load there will be; therefore, a greater volume of the amine will be required, which also influences the cost. It is important to consider that the established prices are based on the brand of products the university supplies. However, some reports mention much lower values, such as MDEA at 2.2 \$/kg, MEA at 1.1 \$/kg [60] and TEA at 1.34 \$/kg [61]. If these values are considered, the investment costs would be considerably lower. Therefore, the economic analysis of this table indicates that MDEA emerges as the most profitable option to absorb 1 ton of CO_2, followed by DETA , MEA , and finally TEA , which is positioned as the most expensive alternative. It is important to keep in mind that amines can be regenerated, therefore they can be reused, it is one of the characteristics that makes absorption processes with amines suitable at an industrial level [46, 62].

Chapter 5

Conclusions and Recommendations

The study focuses on selecting optimal amines for CO_2 absorption, considering factors such as price, corrosiveness, available literature, and selectivity. The most suitable being Methyldiethanolamine (MDEA), Diethylenetriamine (DETA), and Triethanolamine (TEA). In addition, Monoethanolamine (MEA) was examined because it is already studied and is defined as a reference amine. The studies carried out in the stirred reactor showed that DETA and MDEA have the best thermodynamic results, obtaining 102,19 and 93,86 mmol removed, respectively, and an absorption capacity of 0.9 mol of CO_2 /mol of amine, while kinetic results placed these two amines as the less favorable according to their values.

On the other hand, thermodynamic data are not presented for the stirred reaction due to lack of evaluation time, so only the reaction speed can be inferred from these, where 40% MEA with 5% piperazine presents the highest speed reaction, followed by the mixture of 40% DETA with 5% piperazine, these amines manage to absorb a high percentage of the total moles in the first 20 minutes, while the rest of the solutions reach this point after approximately 100 minutes, one can assume that diffusion occurs much better due to agitation, which helps piperazine have the promoting effect.

With the thermodynamic data, an economic study is proposed, showing that MDEA is the most promising amine for the absorption of CO_2. It has an absorption cost of a ton of CO_2 of 138.6 M USD followed by DETA, MEA with almost double the price, and TEA with 4.5 times the cost.

Corrosivity studies corroborate that primary amines exhibit higher corrosion rates than secondary and tertiary amines, with MEA being the most corrosive and DETA being the least corrosive. With all these analyses it can be concluded that MDEA is the most favorable amine.

For future work, it is recommended to carry out more detailed studies on the selection of amines in CO_2 capture, considering factors such as impurities and efficiency under industrial conditions. Additionally, it would be beneficial to investigate the entire regeneration cycle before the amine begins to lose effectiveness. Likewise, it is suggested that additional research be carried out on the corrosivity of amines under different environmental conditions and the possibility of mitigating this effect through corrosion inhibitors.

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Appendices

Appendix A

Other methods for CO_2 capture

A.0.1 Cryogenic process

The cryogenic CO_2 capture method employs dynamically operated packed beds, utilizing a steel monolith structure as the packing material. The necessary cold energy is sourced from liquefied natural gas, enabling the simultaneous separation of H_2O and CO_2 from flue gas based on their distinctive dew and sublimation points. This approach, utilizing a cryogenic packed bed, effectively addresses issues related to clogging and pressure drops, distinguishing it from conventional methods that necessitate a chemical absorbent and elevated pressure [63]. In addition to its application in flue gas treatment, cryogenic packed beds exhibit potential in upgrading biogas. CO_2 and H_2S are deposited on the packing bed's surface, while high-purity CH_4 (99.1%) is obtained at the exit without a phase change [64]. However, specific challenges must be addressed despite the evident advantages of the cryogenic process over alternative methods. These include improving thermal insulation to minimize heat loss and the potential rise in operating costs associated with maintaining low temperatures during H_2S removal [65].

A.0.2 Membrane separation

Membrane processes segregate atoms and molecules based on their specific sizes, where larger particles cannot traverse the membrane and are consequently retained [18]. TThe critical parameters governing membrane separation are permeability and selectivity. Yet, achieving high CO_2 recovery and purity simultaneously poses a challenge due to the intricate relationship between membrane separation performance, permeate/feed pressure ratio, and selectivity [66, 67]. Balancing these factors becomes pivotal for optimizing the effectiveness of membrane-based CO_2 separation processes.

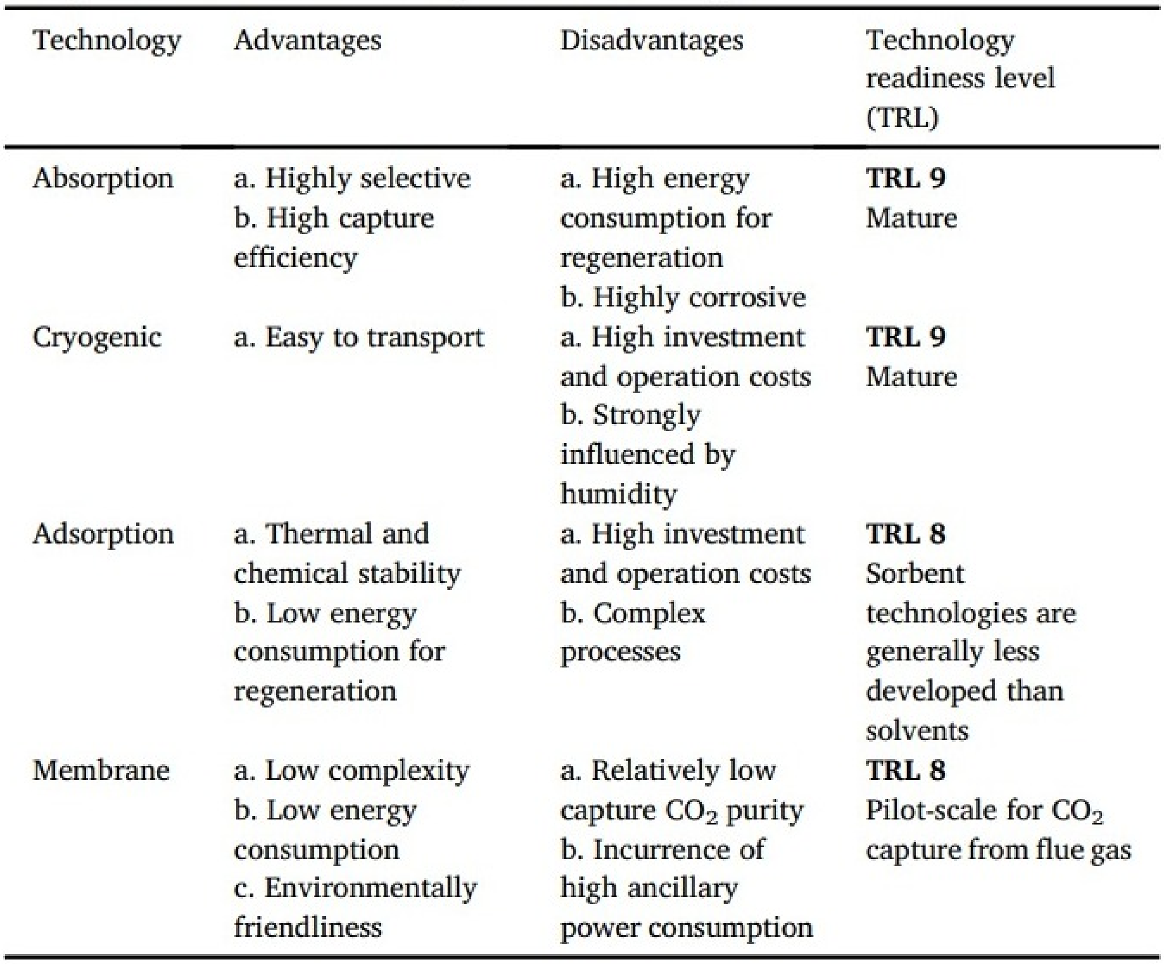
Membrane technology facilitates gas separation by leveraging the varying rates at which gas molecules pass through the membrane under partial pressure differences. This approach eliminates the need for phase change and regeneration operations, contributing to significant energy savings [68]. Membrane systems are characterized by their compact design and small footprints, offering versatility in capturing diverse occasions, in contrast to the space-intensive distillation or absorption columns [69]. Moreover, it requires minimal chemical input compared to conventional separation methods, emphasizing its potential as an efficient and environmentally friendly technology [70].

A.0.3 Adsorption process

Adsorption differs fundamentally from absorption in that, in absorption, the absorbate (fluid) is dissolved within an absorbent, whether solid or liquid. In adsorption, the process occurs on the outer surface, while absorption involves the entire volume of the material. The entities—ions, atoms, or particles—that adhere and form a film on the surface of the substance are termed adsorbate, and the substance to which they attach is referred to as the adsorbent. This distinction lies in the mechanism by which the molecules or particles interact with the material, either on its surface (adsorption) or throughout its volume (absorption) [71, 72].

The adsorption process can be initiated by physical mechanisms involving weak Van der Waals forces (physisorption) or chemically requiring covalent bonds (chemisorption) and can be driven by electrostatic attraction [18]. In capture strategies, chemical absorption, and adsorption systems play an essential role because of the chemical interactions that lead to the formation of molecular structures. Subsequently, recovery of the adsorbed material is achieved by heat treating the system to maintain an appropriate temperature increment [71].

In the field of physical adsorption, various porous materials, such as activated carbon, alumina, metal oxides, and zeolites, play a fundamental role in the absorption of carbon dioxide [17]. Activated carbon materials, known for their unique characteristics such as environmental friendliness, remarkable thermal and chemical stability, exceptional conduction properties (thermal and electrical), and exceptional strength, are typically composed of carbon and additional bonded materials [71]. Meanwhile, metal-organic frameworks (MOFs) exhibit a composition of metal ions or groups of ions connected by organic ligands, forming robust coordination bonds. Notable advantages of MOFs include their ease of design and synthesis, high porosity, and customizable pore properties [17]. Finally, whether synthetically or naturally, zeolites are microporous crystalline silicate framework materials with a uniform pore size (0.5 to 1.2 nm) and a network of connected channels [18].



Technology	Advantages	Disadvantages	Technology readiness level (TRL)
Absorption	a. Highly selective b. High capture efficiency	a. High energy consumption for regeneration b. Highly corrosive	**TRL 9** Mature
Cryogenic	a. Easy to transport	a. High investment and operation costs b. Strongly influenced by humidity	**TRL 9** Mature
Adsorption	a. Thermal and chemical stability b. Low energy consumption for regeneration	a. High investment and operation costs b. Complex processes	**TRL 8** Sorbent technologies are generally less developed than solvents
Membrane	a. Low complexity b. Low energy consumption c. Environmentally friendliness	a. Relatively low capture CO_2 purity b. Incurrence of high ancillary power consumption	**TRL 8** Pilot-scale for CO_2 capture from flue gas

Figure A.1: Comparison among traditional separation technologies [67].

Appendix B

Formations between $\mathrm{CO_2}$ and amines

B.1 Carbamate and bicarbonate formations

Two primary routes that play a role in CO_2 capture using amines in different solvents, adsorbents, or membranes involve the creation of carbamate and bicarbonate anions. When primary and secondary amines interact with CO_2, they produce the carbamate anion and protonated amine [73].

$$R^1R^2NH + CO_2 + B \rightleftarrows R^1R^2NCOO^- + BH^+ \tag{B.1}$$

On the other hand, primary, secondary, and tertiary amines reacting with CO_2 result in the formation of the bicarbonate anion and protonated amine [26].

$$R^1R^2R^3N + CO_2 + H_2O \rightleftarrows HCO_3^- + R^1R^2R^3NH^+ \tag{B.2}$$

An additional potential outcome resulting from the reaction between amines and CO_2 is the formation of carbamic acid.

$$R^1R^2NH + CO_2 \rightleftarrows R^1R^2NCOOH \tag{B.3}$$

However, By McCann et al. (2009) [74] the production of carbamic acid is likely to be minimal, as common materials utilized for CO_2 capture, such as aqueous amine solutions, operate under basic conditions. This basic environment readily accepts protons from carbamic acid, leading to the generation of the more stable carbamate anion. Additionally, as elaborated upon later, the majority of materials used in CO_2 capture processes stabilize ionic products like carbamate and protonated amine due to their inherent polarity. Consequently, charged products, specifically carbamate and proton, tend to exhibit increased stability in most scenarios.

In general, the study conducted by Nakao et al. (2019) [26] indicates that the retraction kinetics of carbamate formation are faster compared to bicarbonate formation. so, understanding the kinetics of these reactions is essential for optimizing processes related to CO_2 capture, particularly when utilizing amines as absorbents. The differences in kinetics between bicarbonate and carbamate formation can impact the overall efficiency and performance of the capture processes.