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Faculteit Industriële Ingenieurswetenschappen
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Masterthesis

Desorption of CO2 from concentrated monoethanolamine solutions

PROMOTOR :
ing. Emine KAYAHAN
Prof. dr. ir. Mumin Enis LEBLEBICI

Jules Feyen
Scriptie ingediend tot het behalen van de graad van master in de industriële wetenschappen: chemie

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Preface

This master's thesis was written to achieve the master's degree in Chemical Engineering Technology. I would like to thank others who helped to build this work.

First of all, I would like to thank my supervisor Prof. Dr. Mumin Enis Leblebici for his input and feedback on my thesis. I would also like to thank my assistant supervisor ir. Emine Kayahan for her support and guidance. The guidance has helped me a lot with the course of the thesis as well as her feedback and insights. I also want to thank ir. Ulderico Di Caprio for his input during the meetings and the help in the lab. Next, I would like to thank Jeroen Lievens for his feedback and seminars. Finally, I would like to thank the doctoral students of the research group CIPT for their assistance during this period.

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Abstract

One way of separating CO_2 from flue gas is the post-combustion process via chemical absorption. However, the regeneration section of this process is very costly and economically not advantageous. By using highly concentrated MEA solutions, the pumping and regeneration costs could be reduced as no water needs to be heated or pumped. The aim of this master thesis is to investigate the behaviour of highly concentrated MEA and to compare it with aqueous MEA solutions.

An absorption process is carried out in which CO_2 is absorbed with both aqueous and pure MEA. The loaded solutions are then prepared and consist of aqueous, pure and pure MEA to which water is added after the absorption process. Samples with a loading of 0.11, 0.18 and 0.3 mol CO_2/mol MEA are used. The loaded samples are then exposed to thermolysis and release CO_2. Eventually the desorption capacities and the lean loadings are compared.

From the experiments, it appears that the desorption capacity and the lean loading are influenced by the temperature, the rich loading and the concentration of MEA. For instance, a concentration of 30 wt.% MEA results in a desorption capacity of 0.040 mol/mol and a concentration of 100 wt.% MEA in a desorption capacity of 0.013 mol/mol. In the ratio of released CO_2 per gram of solution, the yield of CO_2 is highest in the low concentrated MEA solutions. This leads to the conclusion that water is needed in the desorption process. Furthermore, the desorption capacity increases with an increase in rich loading and temperature.

Abstract in het Nederlands

Een manier om CO_2 uit rookgas te scheiden is het naverbranding proces via chemische absorptie. Het regeneratie proces is erg prijselijk en economisch niet voordelig. Door gebruik te maken van hoog geconcentreerde MEA oplossingen zouden de pomp en regeneratie kosten kunnen verminderen omdat hierbij weinig water moet worden opgewarmd of verpompt. Deze masterproef heeft als doel het gedrag van hoog geconcentreerde MEA te onderzoeken en dit te vergelijken met waterige MEA oplossingen.

Er wordt een absorptie proces uitgevoerd waarbij CO_2 wordt geabsorbeerd met zowel waterig als pure MEA. De geladen stalen worden vervolgens bereid en bestaan uit: waterig, pure en pure MEA waaraan na het absorptie proces water wordt toegevoegd. De geladen stalen ondergaan thermolyse in het desorptie proces. Vervolgens worden de desorptiecapaciteiten en de arme ladingen vergeleken.

Uit de experimenten blijkt dat de desorptiecapaciteit en de arme lading worden beïnvloed door de temperatuur, de rijke lading en de concentratie van MEA. Zo resulteert een concentratie van 30 wt.% MEA in een desorptiecapaciteit van 0,040 mol/mol en een concentratie van 100 wt.% MEA in een desorptiecapaciteit van 0,013 mol/mol. In de verhouding van vrijgekomen CO_2 per gram oplossing is de opbrengst van CO_2 het hoogst in de laag geconcentreerde MEA-oplossingen. Dit leidt tot de conclusie dat water een vereiste is in het desorptieproces. Bovendien neemt de desorptiecapaciteit toe met een toename van de rijke belasting en de temperatuur.

1. Introduction

1.1 CONTEXT

A lot of CO_2 is released worldwide. This is largely due to the burning of fossil fuels [1], [2]. One way of capturing the CO_2 is absorption of CO_2. This is applied in both spray columns and packed bed reactors [3]. There are various solvents that have already been researched. The aqueous amines are the most commonly used solvents in CO_2 capture applications. When these amines are diluted with an organic solvents instead of water, they are called hybrid solvents [4].

These solvents absorb CO_2 both by physical and chemical absorption. Physical absorption refers to the solubility of CO_2 in the solvent. On the other hand, chemical absorption means that a molecule of CO_2 reacts with the appropriate functional group and is then absorbed into the structure [4].

The reaction of amines with CO_2 is mainly by the formation of carbamate as the reaction below shows. This is caused by the reaction of an amine and a CO_2 molecule, whereby first a zwitterion is formed and finally this reacts further to form a carbamate. However, this is determined by the type of amine, so primary (MEA), secondary (DEA), tertiary (MDEA) and sterically hindered (AMP) amines have been selected for this experiment. The secondary and primary ones mainly form a carbamate. The tertiary and sterically hindered amines form alkyl carbonate [4], [5]. The absorption reaction is exothermic, which means that heat is required to absorb CO2. As a result, the amine solutions heat up. Desorption requires heat and is therefore endothermic. On heating the loaded solvent, the CO_2 is released .

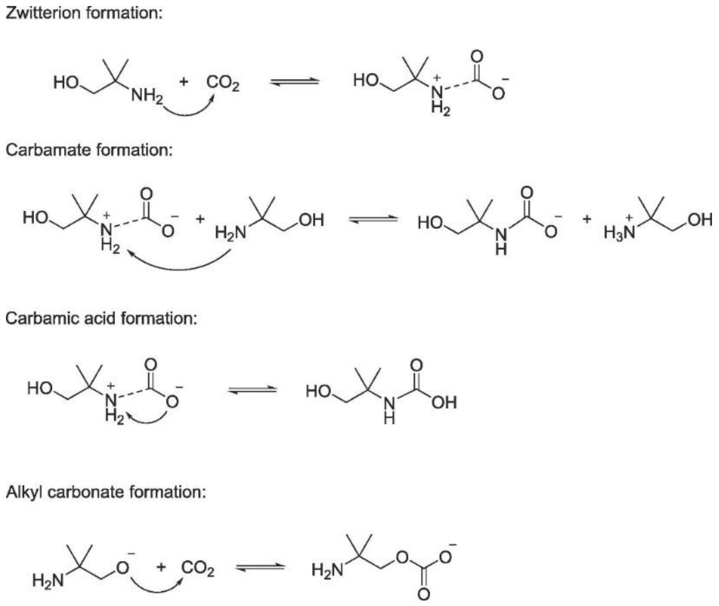


Figure 1: Formation of carbamate [4]

Absorption and desorption processes take place in a cyclic manner in a CO_2 capture plant. CO_2 is absorbed at room temperature and is released from amine solutions at high temperatures. Therefore, in the desorption column, amine solutions are heated up. The released CO_2 is collected at the top of the column [6], [7]. Another important concept is cyclic capacity. Cyclic capacity is the difference of the CO_2 loading in absorption and desorption [8]. It determines how much CO_2 can be absorbed in a CO_2 capture plant.

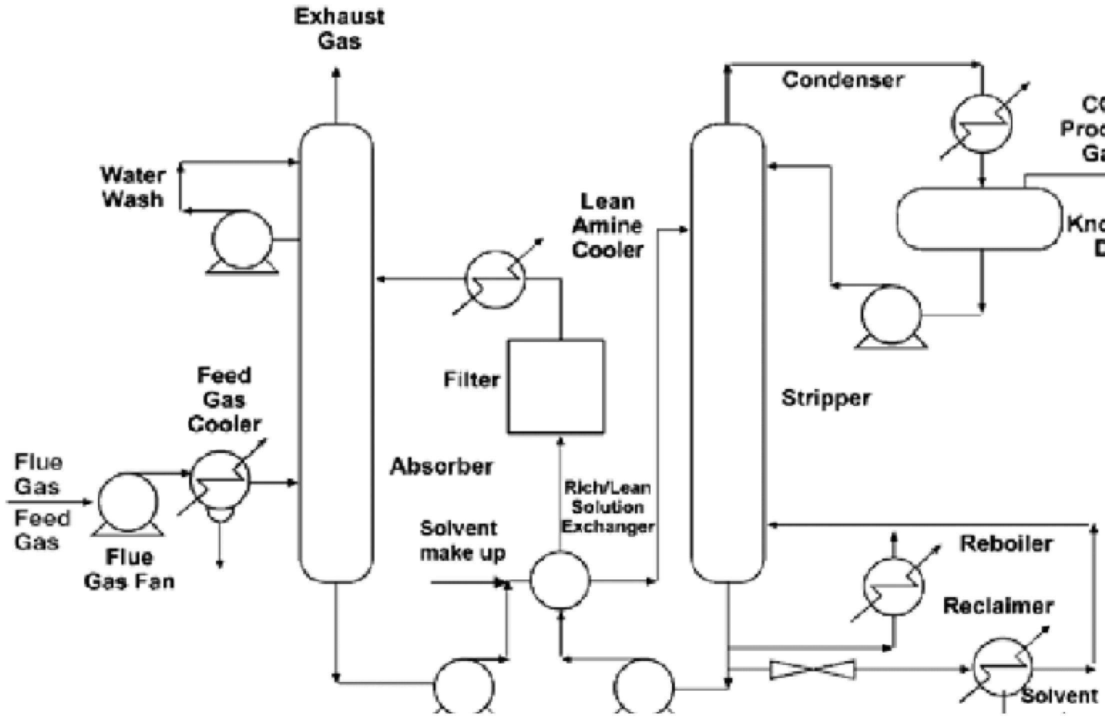


Figure 2: Cyclic absorption and desorption process [6]

Only aqueous amines and hybrid solvents have been tested in the literature so far, some interesting aqueous mixtures of MEA-MDEA and AMP-PZ [9], [10]. This resulted in improvements in several areas such as higher absorption capacity, faster kinetics and a reduction in energy consumption during the stripping of CO_2 [11].

1.2 PROBLEM DEFINITION / RESEARCH QUESTION

The cost of absorbing CO_2 through gas absorption is far too high. This is due to the high energy consumption in the regeneration process. Large amounts of steam are consumed during this process. In industry, absorption by carbon capture and stripping is applied with aqueous amines. The composition is 30% amine (MEA) and 70% water. As a result, some of the energy is consumed to pump water and heat up the water while carrying out this process [12]. Therefore, this work focuses on CO_2 capture into highly concentrated and pure chemical absorbents.

1.3 RESEARCH OBJECTIVES

The aim of this research is to investigate absorption and desorption of MEA at high concentrations that can replace the aqueous amines. The goal is to reduce pumping and regeneration costs. In this research, the cyclic capacity of aqueous and non-aqueous amines is compared to find an alternative for aqueous amines.

2. Literature study

2.4 Carbon capture

Carbon capture has been used for several years to counteract CO_2 emissions [12]. This can be done in various ways such as absorption, physical absorption, membranes and cryogenics separation [6]. The most common techniques being pre-combustion, post-combustion and combustion with a combination of pure oxygen and fuel. Below, I am briefly mentioning all of these techniques.

2.4.1 Pre-combustion

Pre-combustion refers to capturing CO_2 before combustions is completed. For example, by partial oxidation of a feedstocks such as coal, syngas or fuel gas is produced. This is a gas mixture consisting of carbon monoxide (CO) and hydrogen gas (H_2). In this process, fuel reacts with O_2 from the air according to a partial oxidation. If steam is used, a simultaneous reaction takes place in which water is converted mainly into H_2, CO and CO_2 [2], [13]. This is shown in reaction number 1 and 2:

$$C_nH_m + \frac{n}{2}o_2 \rightarrow nCO + \left(\frac{m}{2}\right)H_2 \quad (1)$$

$$C_nH_m + nH_2O \rightarrow nCO + \left(\frac{n+m}{2}\right)H_2 \quad (2)$$

The synthesis gas still contains various impurities that must be removed before the CO_2 concentration can be increased. Concentration takes place via a water-gas shift reaction (WGSR) in which CO reacts with steam to form CO_2 and H_2. Then, the separation of CO_2 is possible through physical and chemical absorption processes [2]. What remains is an H_2-rich fuel that is suitable for power generation purposes. This process is shown in figure 3:

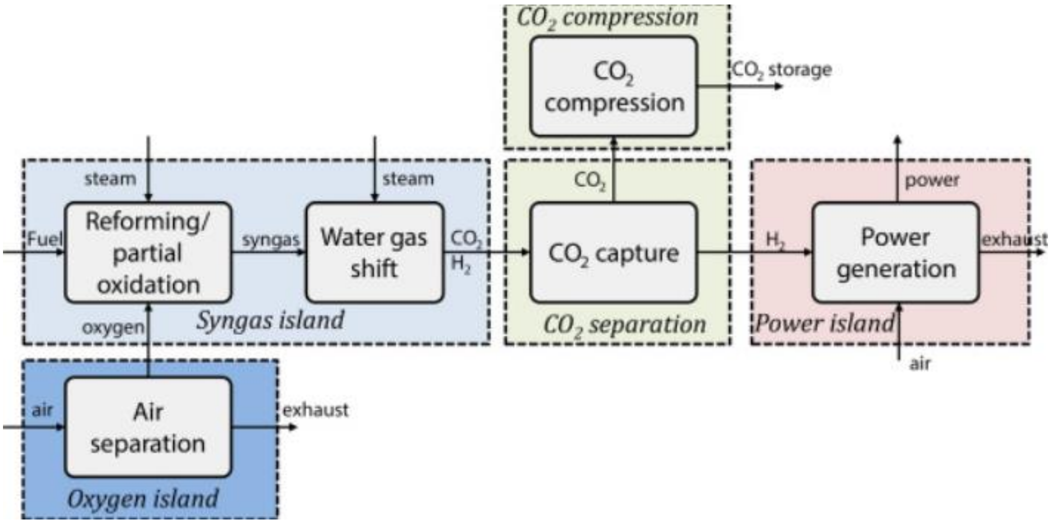


Figure 3: Block diagram pre-combustion [13]

2.4.2 Oxy-fuel combustion

Another technique is oxyfuel combustion. In this technique, instead of air, almost pure oxygen is used in the combustion process [2]. Oxyfuel combustion is used in coal fired power plants and also in gas turbines. The process can be divided into several parts. In the first part the oxygen is separated from the air in an Air Separation Unit (ASU). Then there is a boiler in which the combustion of the fuel takes place. Heat is produced in this unit. Next, the produced gas is exposed to a gas quality control system (GQCS). The last main unit is the CO_2 Processing Unit (CPU) where the final purification is carried out. The purpose of a coal-fired power plant is to separate CO_2 from the flue gas. The CO_2 can finally be separated by dehydration and other purification processes [14]. The block diagram of this process is shown in figure 4.

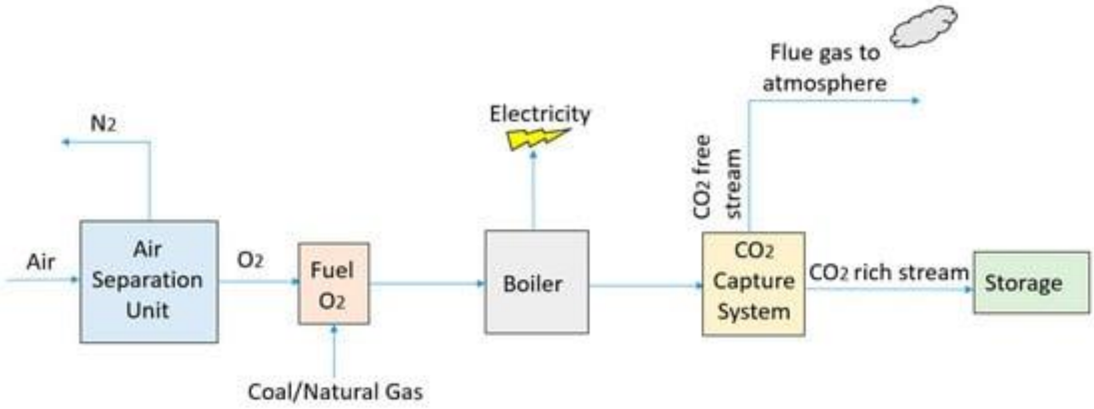


Figure 4: Block diagram oxy-fuel combustion [15]

2.4.3 Post-combustion

Another recognised technique for capturing and separating CO_2 is post-combustion. Post combustion is quite advantageous since the existing combustion processes can still be used without having to modify them or further investigate an alternative [6]. In this process, CO2 in a flue gas is absorbed and consequently desorbed in a cyclic operation. The solvents used to capture CO_2 do so in two different ways. The first type of absorption is the physical absorption where CO_2 dissolves in the solvent and thus refers to solubility. The other type of absorption is the chemical absorption where CO_2 reacts with the solvent [4]. The component in the solvent has a suitable functional group to include the CO_2 molecule in its structure. Amines are often used as chemical absorbents. They react very quickly with CO_2. After absorption of CO_2 into a solvent, CO_2 is released from the solvent in the desorption column. One of the hurdles is that the absorption of CO_2 into amines is often mass transfer limited. Therefore, improvements in the absorption column are still needed. However, this process is still not economically feasible mostly due to the costs associated to the desorption of CO_2 from amine solutions. For example, desorption of CO_2 from the most commonly used amine solution, an aqueous 30 wt.% monoethanolamine (MEA), requires a lot of energy and is therefore very costly, taking up about 75-80% of the total cost [16]. MEA is heated to temperature of 120 °C to 180 °C to desorb CO_2, which requires cooling systems that consequently consume a lot of energy [17]. Since 70 wt.% of the solution that is being heated is water, increasing the MEA concentration can reduce pumping and regeneration costs significantly. In this work, we are interested in using high MEA concentrations.

The process is quite complex with many interrelated parameters. Therefore there are many performance criteria. Below, I am giving the definitions of these performance parameters. The process can be improved by changing several operational parameters, which are further described in section 3.

- Absorption capacity

The absorption capacity or loading is the amount of absorbate (CO_2) taken up by the absorbent (MEA) per mol. This capacity includes both chemical and physical solubility. There are several studies in the literature that attempt to improve the absorption capacity of aqueous amines by using amines that possess multiple functional groups or with mixtures of amines [5].

- Desorption/cyclic capacity

The desorption process is the opposite of absorption. The amount of absorbate that can be released by heating is the desorption capacity. This is also shown per mole of absorbent (MEA).

- Rich loading

This loading is achieved when the solvent leaves the absorber. When the solvent contains the highest load of CO_2, this is called rich loading.

- Lean loading

During the regeneration process, CO_2 is released and the load drops. But not all the CO_2 can be released, because a residual load remains in the absorbent. The amount of resudurable absorbent that is loaded is known as the lean loading.

In this process, a gas mixture that is produced through the combustion of fuel is first purified by denitrification and a desulphurisation step. This is due to the presence of nitrates, nitrites and sulphur compounds that the process becomes more expensive [2]. This is done by releasing CO_2 from the flue gas in an oxidising environment. After the purification step, post-combustion CO_2 can be done via chemical absorption using solvents.

2.4.4 An industrial application of post-combustion carbon capture

Post-combustion is used in industry, an example of which is in Canada's BD3 SaskPower, which captures 1 million tonnes of CO_2 per year [18]. Figure 5 shows an example of an industrially applied post combustion carbon capture. The raw gas enters the inlet where it is separated from liquid and solid particles.

The gas is cooled and enters the absorber. The lean solvent is passed through the column in countercurrent and brought into contact with the gas stream. The solvent reacts with the CO_2 and is now called a rich solvent. This rich solvent is send to a heat exchanger where it absorbs heat from the recycling stream of poor solvent. The purified gas is washed with water and collected at the top of the absorption column.

Then, the heated rich solvent arrives at the top of the stripping column and flows downwards where it is simultaneously exposed to a countercurrent of water vapour. This heats up the rich solution to a higher temperature, which in turn releases CO_2. Due to the steam that is injected at the bottom of the column, the rich solvent loses a large proportion of its absorbed CO_2. The difference in CO_2 concentration between lean and rich amine solution is called cyclic capacity of the solvent. The mixed stream of water vapour and CO_2 passes a condenser where the water vapour condenses and is returned to the column. The hot lean solvent is sent back to the absorption column and releases its heat to the rich solution via a heat exchanger [6], [18].

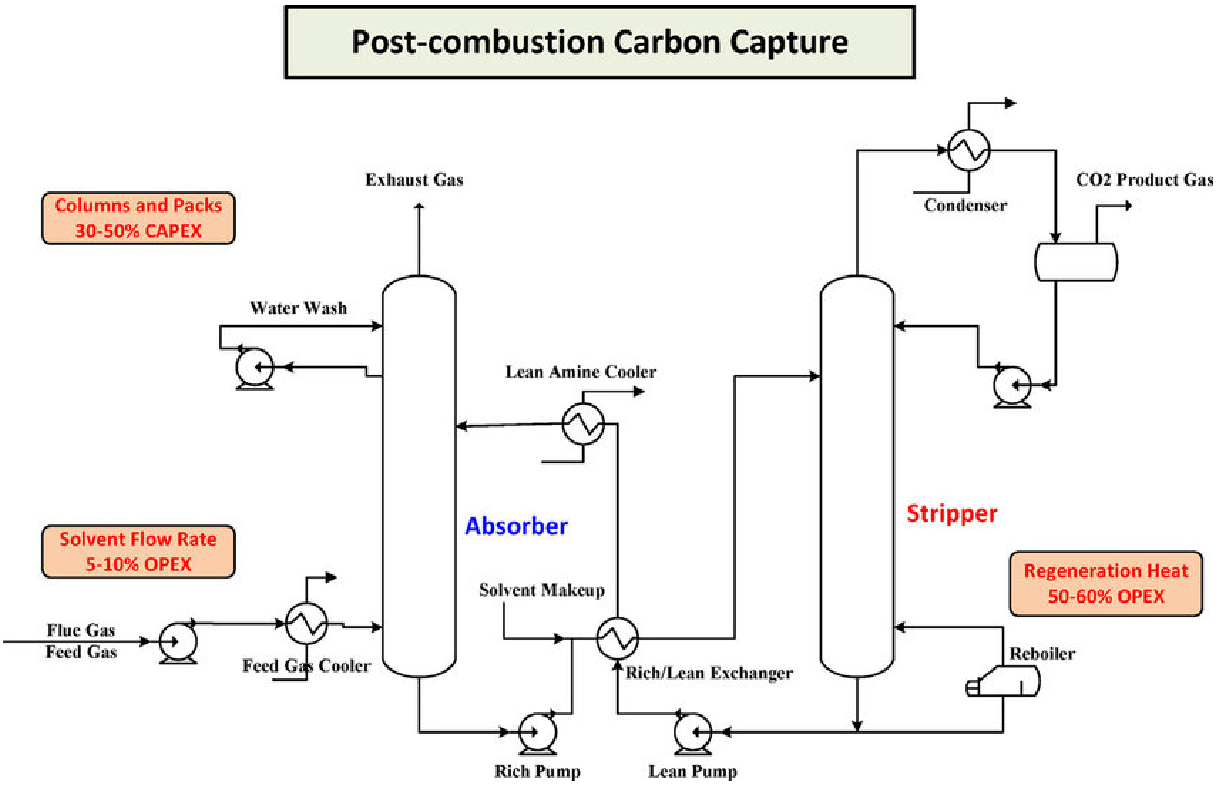


Figure 5: Post-combustion process [13]

2.5 Factors affecting absorption

High absorption is desirable so that most of the CO_2 can be removed from the gas stream. There are several factors that influence the absorption. These factors are described in the following paragraphs.

2.5.1 Column type

The absorption process has different output options namely as a packed column or as a spray column. The reaction of the CO_2 absorption is a fast reaction and therefore mass transfer limited. It is beneficial to increase the surface where absorption can take place so that the overall CO_2 absorption is higher. This results in a higher mass transfer coefficient and thereby a spray column is more suitable for this application [20]. In this process, the solvent passes through a nozzle and is blown into the reactor as fine droplets. As a result, the reaction surface is greatly increased. In the literature, the efficiency of mass transfer of both applications has been tested. This by absorbing CO_2 with aqueous MEA solutions through a packed column and a spray column. The aim is to capture as much and as fast as possible CO_2 from the gas stream. The study shows that the spray column is more efficient than the packed column [21]. Furthermore, several studies have been carried out on spray column, which show that the ratio of CO_2 to MEA has a major influence on the absorption behaviour of the solvent. The more mol MEA, the better the gas stream is absorbed [7]. This makes the use of pure amines interesting because they can be sprayed in a spray column.

2.5.2 Liquid flow rate

This ratio can be influenced by varying the liquid flow rate. The liquid flow rate affects both the rate of absorption and the total mass transfer coefficient. When the flow rate of the liquid is increased, more solvent will pass through the nozzle in the same time period. This will result in an increase in the number of droplets and has the additional advantage of reducing the size of the droplets. The surface area where CO_2 absorption takes place increases, as a result of that the reaction takes place much faster. The higher liquid speed also has the consequence that the boundary layer of the liquid phase decreases, which also reduces the resistance of gas diffusion [20]. However, this effect is not unlimited and can be seen at higher flow rates. This is because the droplets can no longer get smaller and therefore the interface cannot increase any more [7].

2.5.3 MEA concentration

Another parameter that can be varied is the concentration of MEA. This parameter also influences both the mass transfer coefficient and the rate of CO_2 absorption. By increasing the concentration of MEA, the molar ratio of CO_2 to MEA decreases. This has the consequence, as discussed above, that the absorption rate and the size of the reaction surface increase. The reason behind the increase is that the more active MEA molecules are more abundant and diffuse more towards the gas-liquid surface. At the gas-liquid surface the reactive MEA molecules react with the CO_2 in the gas stream. The absorption causes the MEA to become much more viscous and thus less flowing. Because of this phenomenon, there is an increased risk of corrosion problems. The MEA sticks more easily in the installation, which can cause serious damage over time [20].

2.5.4 CO_2 concentration

The effect of CO_2 concentration has an effect on the absorption rate and the mass transfer coefficient. However, this parameter is less suitable to increase, because it has the opposite effect, i.e. when increasing the concentration of CO_2, more CO_2 molecules are present compared to the number of MEA molecules. As a consequence, the speed of CO_2 decreases with increasing CO_2 concentration because the present active molecules MEA are limited. In contrast, increasing the concentration increases the driving force and the mass transfer coefficient in the gas phase, which increases the absorption rate [20].

2.5.5 Gas flow rate

The gas flow rate also has its influence on the absorption. If the flow rate is increased, more gas will flow through the reactor or column while the concentration of CO_2 is kept constant. By increasing the speed of the gas flow, the absorption rate increases but less CO_2 is absorbed against a lower flow rate. As a result, the excess flue gas only comes into limited contact with active MEA molecules. The continuous supply of CO_2 means that every active MEA molecule finds a CO_2 molecule. This is because the CO_2 in the gas-liquid interface is continuously supplied. There is actually a shortage of MEA molecules to be able to purify a large part of the flue gas [20], [22].

2.6 Reaction mechanism MEA

During the reaction of MEA and CO_2, different products can be formed. Studies have been carried out in the literature to discover those products via NMR analyses and pH measurements. From these, it appears that from primary and secondary alkanolamines, the main compounds formed are the carbamates [23]. These are formed via the zwitterion mechanism, which consists of 2 steps. In the first step, a zwitterion is formed after an amine molecule reacts with a molecule of CO_2, this is shown in reaction 3. Then in the second step, the zwitterion is protonated by a base as shown in reaction 4 to form an amine carbamate [4]. They are equilibrium reactions, which means that it can go both ways: via deprotonation, a carbamate is formed, whereas during regeneration, CO_2 is released.

$$AmH + CO_2 \Leftrightarrow AmH^{+}COO^{-} \quad (3)$$

$$AmH^{+}COO^{-} + B \Leftrightarrow AmCOO^{-} + BH^{+} \quad (4)$$

Which direction the reaction goes depends on whether there are adjacent H_2O molecules in the area that can act as base [23]. There is still uncertainty in the literature about the actual reaction but the zwitterion mechanism is the most widely accepted. There are sources that claim that the reaction follows a zwitterion-mediated two-step mechanism [24]. Others think that a one-step reaction mechanism would be more appropriate, but this only concerns the primary alkanolamine. In this kind of mechanism, everything happens in one step whereby the formation of the bond and the transfer of the protons happen simultaneously. The water molecule serves as proton acceptor in this case [25].

Carbamic acid mechanism is a third possible mechanism. This reaction requires 2 molecules of MEA and 1 molecule of CO_2. First MEA reacts with CO_2 to form carbamic acid. Then, another molecule of MEA acts as a catalyst and carbamate is formed [23]. These reactions are shown below.

$$CO_2 + RNH_2 \Leftrightarrow RNHCOOH \quad (5)$$

$$RNHCOOH + RNH_2 \Leftrightarrow RNHCOO^{-} + RNH_3^{+} \quad (6)$$

However, other compounds are formed, namely carbamate, bicarbonates and carbon dioxide, and by means of 1H and 13C nuclear magnetic resonance (NMR) analysis it is possible to obtain a picture of what is present in the solution and in what quantity [26], [27]. Which products are formed depends on the CO_2 loading. This occurs via various reaction types that are shown in figure 6.

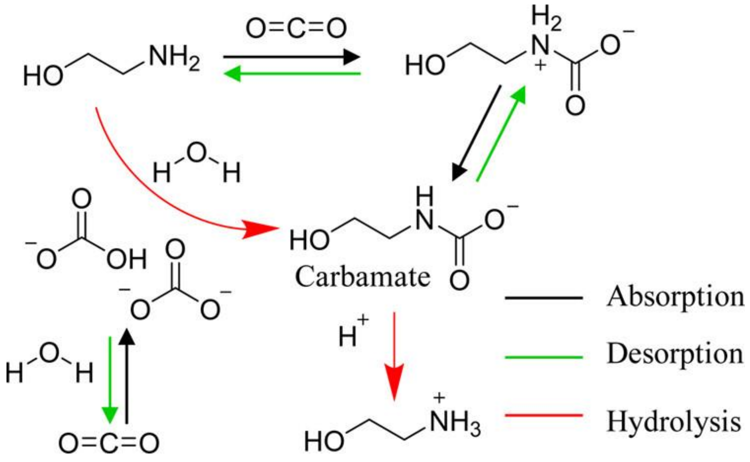


Figure 6: Reaction mechanisms [34]

The reverse process of CO_2 absorption is desorption, whereby the MEA solution is heated. The reaction that takes place depends on the loading of the solvent. If the solvent contains HCO_3^- /CO_3^-, these are first converted to CO_2 (Reaction (8)-(9)). An additional reaction that can take place is the reaction between HCO_3^- and a $MEAH^+$ molecule whereby a carbamate is formed, shown in reaction (10). After this, the carbamate is decomposed by thermolysis whereby the MEA is regenerated and the CO_2 is released (Reaction (11)).

$$CO_3^{2-} + 2\,H^+ \rightarrow CO_2 + H_2O \quad (8)$$

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \quad (9)$$

$$2\,HCO_3^- + RNH_3^+ \rightarrow RNHCOO^- + H_2O + CO_2 \quad (10)$$

$$RNHCOO^- + H^+ \longrightarrow RNH_2 + CO_2 \quad (11)$$

Various dissociation reactions occur in aqueous MEA solutions. These equilibrium reactions influence the pH by the release of H+ or OH- ions. The dissociation of MEAH+ is shown in reaction (12).

$$RNH_3^+ + H_2O \Leftrightarrow RNH_2 + H_3O^+ \quad (12)$$

If the solvent contains HCO_3^- and CO_2 these compounds may also dissociate in water (Reaction (13)-(14)).

$$CO_2 + 2H_2O \Leftrightarrow HCO_3^- + H_3O^+ \quad (13)$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+ \quad (14)$$

The ionization of water is also shown in reaction (15).

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad (15)$$

2.7 NMR analysis and pH

As previously mentioned the formed products can be determined and quantified with the analysis technique NMR. In the literature, research has been done into the formation of these products at which temperature they occur and at which CO_2 loading. Models have also been developed to predict how a certain reaction will behave [27].

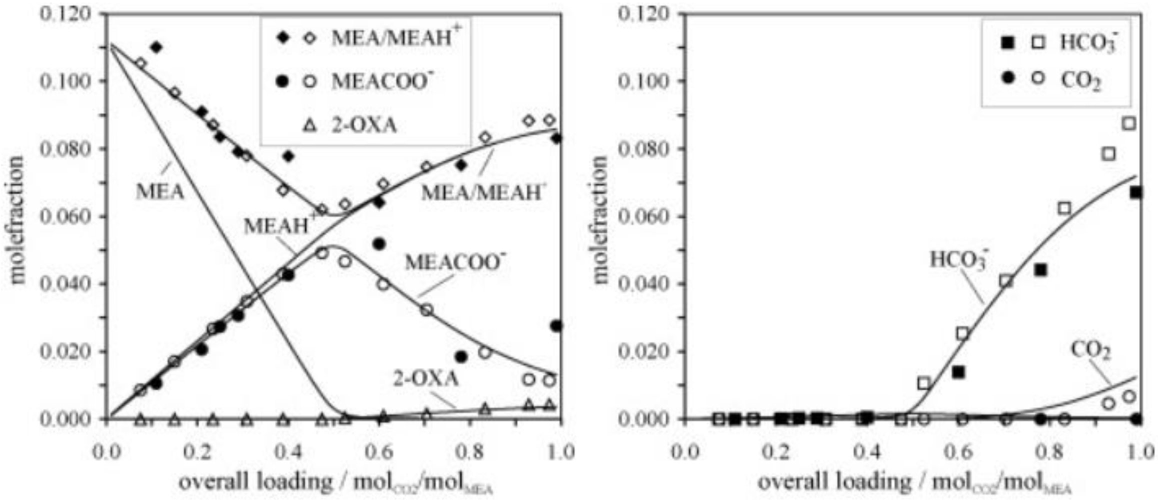


Figure 7: Molefractions of products from MEA-H2O-CO2 mixtures [27]

In the above figures, the carbonic acid species are shown on the right and the amine species on the left. Experimentally, it is not possible to distinguish the protonated and non-protonated amines with NMR. The loading of CO_2 that the solvent carries influences to a large extent which products are formed. The right figure shows that at a rather low loading, almost all CO_2 is removed from the gas stream. This means that all CO_2 is chemically bound in a carbamate. The concentration of carbamate in this area increases linearly with the CO_2 loading. When the loading increases to 0,5 mol CO_2/mol MEA, almost all MEA has reacted with CO_2 or is protonated. With a further increase the number of protonated compounds also increases, but at the cost of formed carbamates. This releases CO_2 which further reacts to form a bicarbonate. This research has further shown that at a loading of 0,7 mol CO_2/mol MEA, molecular CO_2 is also present in the solution. Due to this CO_2 gas as well as the presence of bicarbonate, the pH will rise versus the alkaline solution of amines [27].

The pH meter is used in combination with NMR in which the ion concentration can be determined. These pH measurements are used if common peaks are visible on the NMR spectra. From these, the amount of MEA and protonated MEA or bicarbonate and carbonate can be determined [18], [28].

2.8 Solvent degradation and corrosion

As mentioned in the previous chapters, the flue gas for an afterburning process has to be purified from impurities. These impurities are mainly O_2, NO_x, SO_x and also CO_2 in the stripping section [29]. If these components are not removed before chemical absorption, the solvent will be broken down by degradation. This degradation can occur in different ways in the liquid itself as well as in the gas stream where the degraded molecules are carried along as vapour.

The solvents used contain amines. These compounds are very alkaline and can be a danger to metal parts in the form of corrosion. The literature shows that the weakest points of the installation are the hottest. This in combination with a high CO_2 loading in the solvent gives the highest corrosion rates. Research showed that the entrance and exit of the stripping section were the most vulnerable, as was the underside of the stripper. In this part of the stripper, the corrosion rate rose to 1 mm/year. In the rest of the process parts, the temperature does not rise as high, there is relatively little corrosion here [30].

3. Materials and methods

3.1 Analysis of chemicals

Each experiment was conducted using monoethanolamine (MEA) as the solvent. This was purchased from Sigma-Aldrich and has a purity of 98%. This solvent was used in both the absorption and desorption experiments.

3.2 Absortion section

3.2.1 Sample preparation

There are 2 types of samples, namely the pure sprayed MEA and the aqueous sprayed MEA solutions. For the aqueous sprayed MEA samples the weight percentages 30, 50, 70 and 90 wt.% MEA are chosen. For each of these samples, the parameters were set so that the obtained loading was 0,11-0,12 mol CO_2 per mol MEA. For the samples that were purely sprayed, the loads investigated were 0,107; 0,183 and 0,301 mol CO_2 per mol MEA.

3.2.2 Absorption set-up

Each absorption experiment was carried out in an aerosol reactor (1) with volume 56 ml. This reactor is cooled with cooling water (2) via a cooling jacket. The amines are pumped with a membrane pump (3) and then passed through a pulse damper (4). An ultrasonic nozzle (5) that consists of the Ultrasonic Processor UP200St coupled to the nebulizer sonotrode S26d18S is used to spray the amines. The pressure is controlled with a pressure regulator (6) that keeps the pressure constant at 1 bar. The flow regulators (7) used are the EL-FLOW Prestige MFC and they are protected at 3 bar for N_2 and 5 bar for CO_2. To ensure that no pressure is built up in the system, a safety pressure valve (8) is installed that opens at 0,5 bar. To remove the loaded amines, a gas liquid separator (9) is used. During the experiments, there is a chance that solvent is carried away by the gas flow and is released under the fume cupboard. To prevent this, a silica dryer (10) was placed at the end of the system. Because the presence of O_2 can be dangerous, a concentration meter (11) was installed. There is also a CO_2 concentration meter (12) installed to check the concentration at the exit. If the input and output concentration of CO_2 are the same no leak is present. The setup used is shown in figure 8.

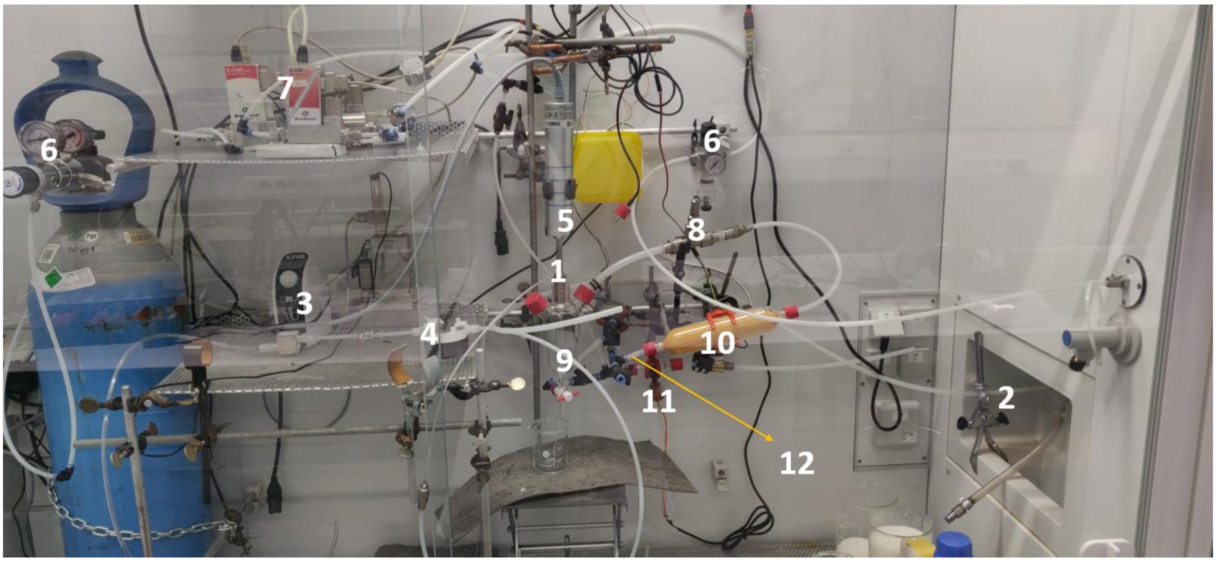


Figure 8: Absorption set-up

3.2.3 Absorption experiment

Before each experiment, the setup is purified by passing a gas mixture of N_2 and CO_2 through it. Experiments can begin when the adjusted supply of CO_2 corresponds to the value at the output. The amines are pumped to the nebuliser at a flow rate that also determines the CO_2 loading. Before they arrive, the ultrasonic nebuliser is switched on. The gas flow is then maintained until the CO_2 level at the outlet stabilises. When the CO_2 level has stabilized, a sample is taken and used in the desorption experiment. A measurement takes 6-10 min. On completion of the experiment the pump is switched off, followed by the nozzle and the gas supply.

3.3 Desorption section

3.3.1 Sample preparation

The samples obtained from the absorption experiment are then prepared for regeneration. In the absorption experiment aqueous MEA solutions have already been sprayed for these samples no further sample preparation is required, this also applies to the pure MEA solutions. Furthermore, samples were prepared by mixing pure MEA with water and the weight percentages are 30, 50, 70 and 90% MEA.

3.3.2 Desorption set-up

The solutions obtained in the absorption section are stripped in the desorption section. The stripping is done in a reactor (1) with a volume of 50 ml. The solution is kept at temperature with a heater (2) and controlled with a thermocouple (3). During an experiment the solution is stirred with a constant stirring rate of 140 rpm. The inert gas used to flush the system is N_2 (11) which acts as a purifier. The N_2 gas stream contains a pressure regulator (4) set at 1,5 bar. A condenser (5) is attached above the reactor which ensures that the gas stream is cooled. The cooling water that flows through the condenser is first cooled to below 10°C with a cooling system (7). This causes the possibly evaporated amines and water to return to their solution. If any amines or water do pass through the condenser, they are collected in the sylica dryer (8). A safety pressure valve (9) is installed to prevent pressure build-up in the installation. The gas is collected in a gas collector (10). The used set-up is shown in figure 9.

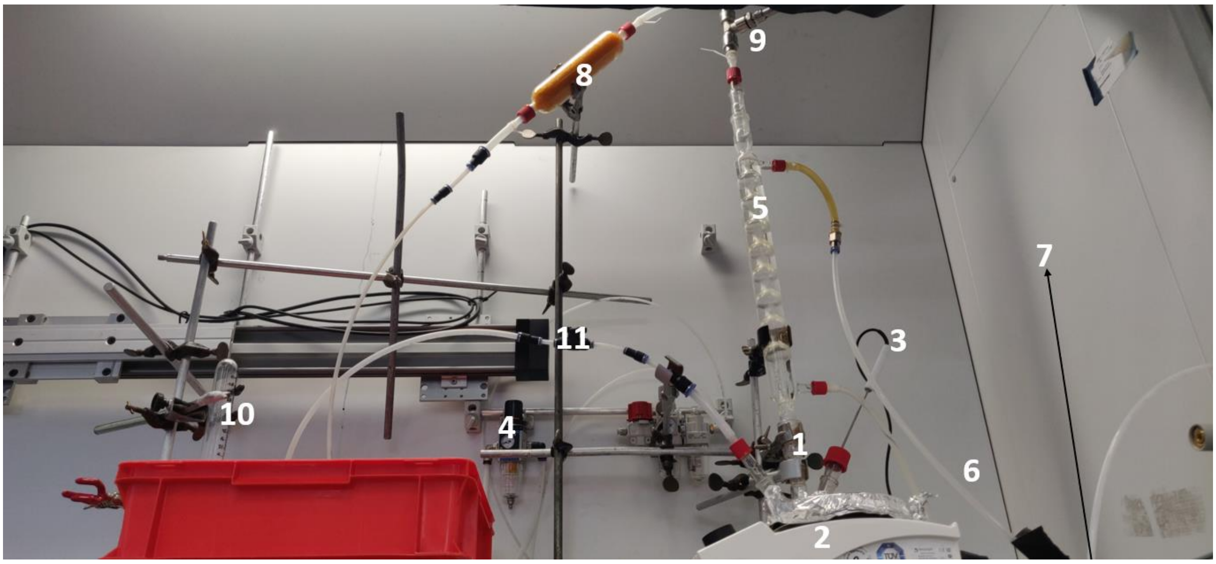


Figure 9: Desorption set-up

3.3.3 Desorption experiment

The reactor is filled with a loaded amine solution of 3 g for an experiment with pure MEA and water added to the desired weight percentage. For an experiment with aqueous sprayed MEA in the absorption set-up the amount used is 5 g. Before the experiments can start, the set-up must be purified with N_2 gas so that O_2 is no longer present. As soon as the setup has been purged, the valve of the N_2 line is closed so that the entire setup is filled with N_2. Then the N_2 flow is turned off. The amines are heated up to a temperature of 80-120°C. CO_2 is released during the heating process and pushes the N_2 molecules further through the set-up. This gas consisting mainly of N_2 is collected in the gas collector. Based on the rich loading and the amount of released gas, the poor loading can be determined. It is also possible to compare the aqueous amines with the pure ones.

3.4 Processing results

The time, temperature and amount of CO_2 released from each measurement were measured. To determine the error on each measurement, a measurement was repeated 6 times. From this, the standard deviation and the 95% confidence interval were determined. This confidence interval is applied to each measurement and shown as error bars in the graphs.

4. Results and discussion

The reaction that takes place during the absorption process requires a base as discussed in section 2.6. Both water and MEA can fulfil this role but it depends on the weight percentage of MEA. If we state that the zwitterion-mediated two-step mechanism takes place, then reaction (3) and (4) are applicable. Here a molecule of CO_2 reacts with a molecule of MEA to form a carbamate, in the second step a base is used. However, pure MEA was sprayed so that only MEA could serve as a base.

When working with pure MEA in the absorption part, a molecule of MEA acts as a base. Therefore the stoichiometric ratio of CO_2 to amine is 1:1. If the water content increases, both one molecule of water and MEA can act as a base. The stoichiometric ratio becomes 1:2 and consequently more base is present which can convert the CO_2 and MEA to carbamates [4]. It is not clear how this change in the stoichiometry affects the desorption process and the cyclic capacity. In this thesis, the effects of water addition before and after the absorption were investigated. In addition to the effects of water addition, the effects of temperature and rich CO_2 load are discussed below.

4.1 Absorption with pure MEA

In the section the samples are made from pure absorbed MEA. The different weight percentages are achieved by adding demineralised water to the loaded pure MEA.

4.1.1 Effect of temperature

To check the effect of temperature on pure MEA, several measurements were carried out, each time with a higher final temperature. The measurements were performed with the same amount of pure MEA and an equal loading. The rich loading of the samples is 0,107 mol CO_2/mol MEA and the desorbed amount is 3 g pure MEA.

Figure 10 a) shows the amount of desorbed mole of CO_2 per mole of MEA on the Y-axis and the temperature on the X-axis. The measurements show a linear behaviour with temperature. The desorption capacity increases with an increasing temperature. The results are as expected but couldn't be compared to literature data because the partial pressure can't be measured with the used set-up.

A final temperature of 80°C has a desorption capacity of 0,01 mol CO_2 per mol MEA. With an increase of 20°C the desorption capacity is 0,015 mol CO_2 per mol MEA. When the temperature rises further to 120°C, the desorption capacity is more than doubled and reaches 0,023 mol CO_2 per mol MEA. The temperature has a direct effect on the CO_2 equilibrium partial pressure and chemical reaction equilibrium constant [31].

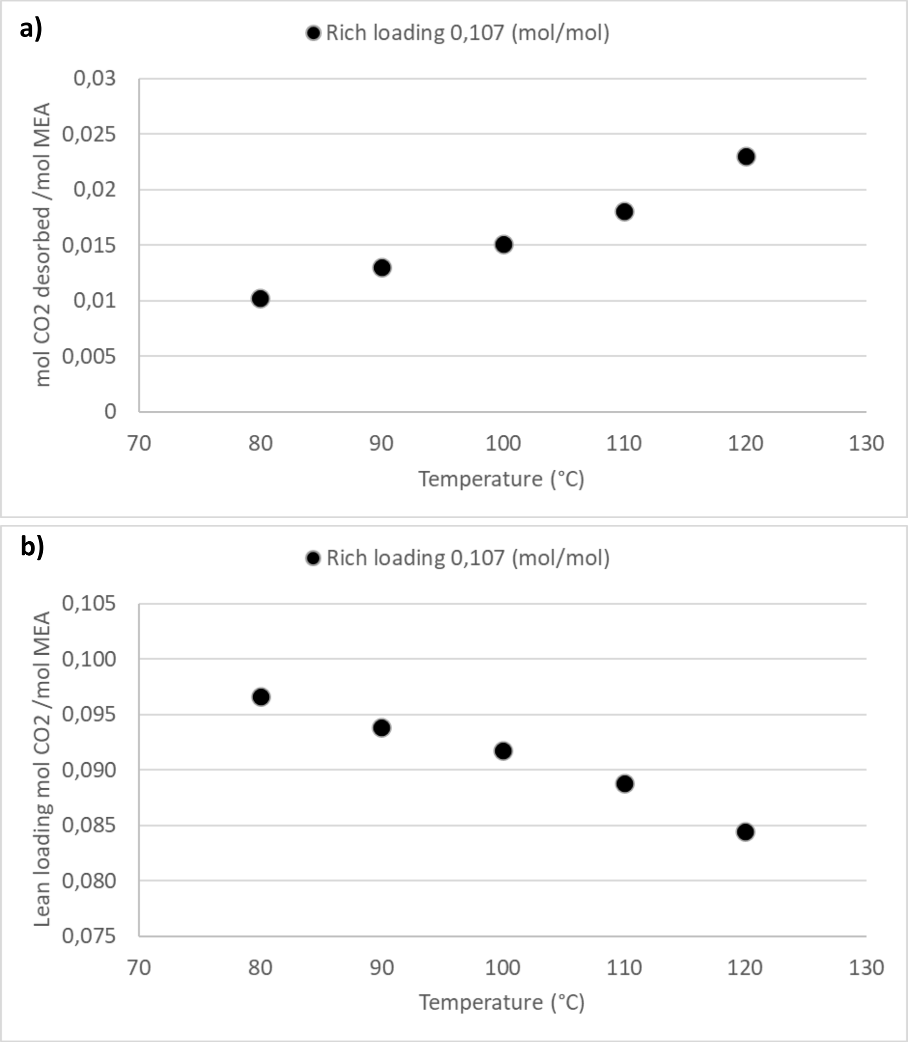


Figure 10: a) Effect of temperature on desorption capacity, b) effect of temperature on lean loading

The temperature also has its influence on the lean loading. As the temperature increases, more carbamates are broken down, releasing CO_2. However, there will always be CO_2 in the solution that cannot be released. This lean loading can be limited by increasing the temperature. Figure 10 b) shows the lean loading on the X-axis. A low lean loading is desirable because less CO_2 remains in the MEA solution. This has a direct influence on the cyclic capacity; if this increases, less MEA solution is required to release the same amount of CO_2. The trend shows that the lean loading decreases with increasing temperature, this is as expected because the reaction of the desorption process is an endothermic reaction and thus requires heat to react.

An advantage of a low lean loading is that the viscosity decreases when CO_2 is released. It is therefore necessary to set the temperature high enough when working with very high loadings of CO_2, because otherwise the pumping costs could increase [32].

The behaviour of the lean loading as a result of the temperature increase for different weight percentages MEA is shown in figure 11 a). As mentioned above, lean loading is an important factor. It determines the efficiency of the process because more can be obtained from the same amount of absorbent. Thus, the lean loading is influenced by several factors which will be discussed below.

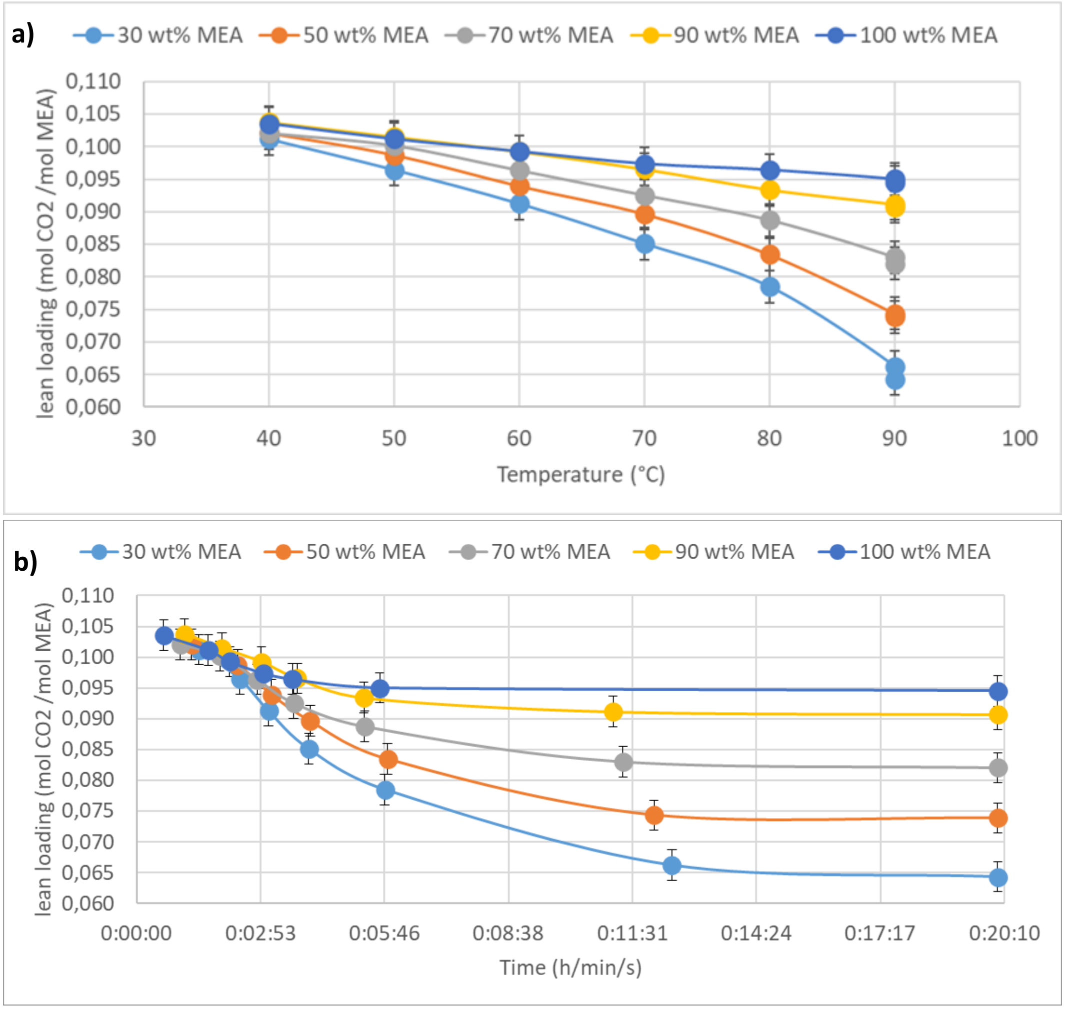


Figure 11: a) Effect of temperature on lean loading, b) effect of time on lean loading

The effect of temperature has already been discussed for pure MEA. Also for solutions where water was added after absorption, the effect of temperature is the same as for pure MEA. But the effect is more pronounced for higher contents of water. For pure MEA, the lean loading is 0,095 mol CO_2 per mol MEA, by increasing the water content to 30 wt.% MEA the lean loading is reduced to 0,065 mol CO_2 per mol MEA. More CO_2 is obtained if more water is present. This could be due to the pH of the solution, when water is added the pH lowers and more H^+ ions are present. Those H^+ ions are then consumed in the thermolysis reaction of carbamate. This affects the thermodynamics of the reaction; the higher water content may shift the equilibrium of the reaction, releasing more CO_2 and thus lowering the lean loading. But the amount of CO_2 released is shown per mole of MEA, it is important to consider that the water that is added must also be pumped and heated, which increases pumping and regeneration costs. The figure 11 b) shows the lean loading on the Y-axis and time on the X-axis. During the measurement, a solution was heated to 90°C and this temperature was maintained until the end of the experiment. The lean loading decreases with time until the final temperature is reached. Keeping the MEA at a temperature of 90°C is useless because no more CO_2 is released. This is as expected because the reaction of MEA and CO_2 to form carbamate are equilibrium reactions. This phenomenon can be observed in every measurement where the lean loading stabilises in time. However, this is a different time for each measurement because the amount of solution varies. The measurement with pure MEA has a weight of 3 g and the sample with 30 wt.% MEA has a weight of 9,30 g but they contain the same amount of CO_2. Consequently, the pure MEA sample needs less time to heat up and stabilises faster in time than the other samples.

4.1.2 Water addition

First, the solutions were prepared by spraying pure MEA and adding water afterwards. Here, the effect of water content is determined by comparing the desorption capacity of different weight percentages. Each measurement contains the same amount of MEA namely 3 g and contain an equal loading of 0,107 mol CO_2 per mol MEA. The final temperature of each measurement is 90°C. The addition of water to pure MEA has not yet been investigated in the literature as well as the desorption of highly concentrated MEA solutions.

In figure 12 the X-axis shows the desorption capacity and this as a function of the weight percentage of MEA. From the trend it can be concluded that more CO_2 is released from the solution at a high water content. The desorption capacity of 90 wt.% is 0,016 mol CO_2 per mol MEA and of the pure sample 0,013 mol CO_2 per mol MEA. The difference between 90 wt.% and 100 wt.% is not very pronounced. By diluting pure MEA to a weight percentage of 70% MEA, the desorption capacity is almost doubled compared to the pure MEA. Accordingly, the desorption capacity for 70 wt% MEA is 0,024 mol CO_2 per mole MEA.

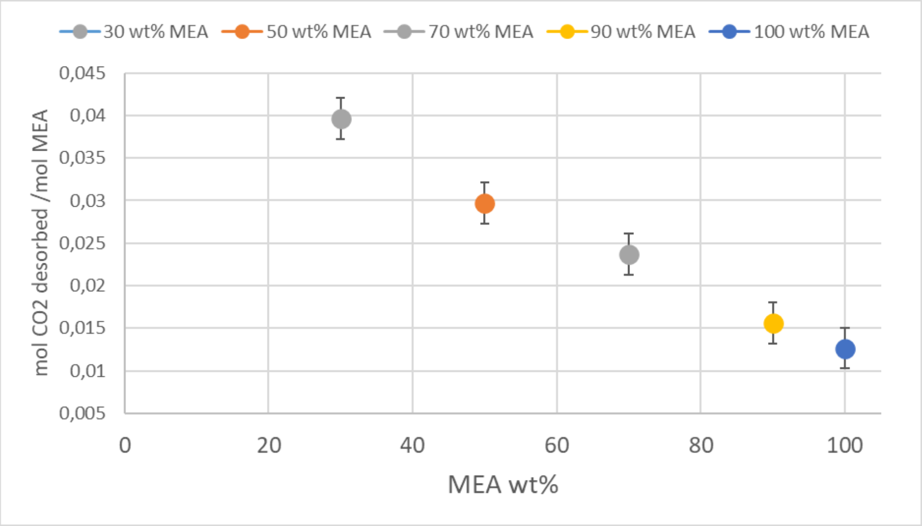


Figure 12: Effect of water addition on pure MEA

The desorption seems to be favoured by the presence of water. The influence of carbamate concentration on the desorption capacity is clarified by the NMR spectrums. In section 4.4 the NMR spectrums of the pure sprayed MEA solutions and its dilution are discussed. The pure sprayed sample has a higher concentration of carbamate than the diluted sample. However, the diluted sample desorbs 0,040 mol CO_2 per mol MEA, which is considerably more than for pure MEA. This shows that a lower concentration of carbamate seems to increases the desorption capacity, releasing more CO_2 and thus reducing lean loading. Another possible explanation for the behaviour of the high concentrated MEA solution is that the desorption reaction that takes place is pH sensitive. The desorption reaction in which a carbamate is broken down to MEA and CO_2 by thermolysis is shown as reaction (11). It follows that H^+ ions are required to release the CO_2. These ions are present in smaller quantities in the higher concentrated MEA solutions than in solutions with a higher water content. This is confirmed in section 4.4 where the pH of different concentrations of MEA is discussed. In aqueous MEA, there are several dissociation reactions that may take place, these are reactions (12)(13)(14)(15). These reactions enhance the concentration of H^+ ions in the solutions. Consequently, more carbamates are able to degrade in aqueous solutions that contain a high water content.

4.1.3 Effect of rich loading

Three loads were tested to check the effect of the rich loading. Each load was taken to a temperature of 90°C and held at that temperature for 20 min. The amount of loaded MEA is 3 g and is equal in each experiment.

It is expected that the highest loading can release the most CO_2. This is shown in figure 13 a) where the desorption capacity is on the Y-axis and the weight percentage of MEA on the X-axis. The blue curve contains the highest load of 0,3 mol CO_2 per mol MEA, the orange curve contains a loading of 0,183 mol CO_2 per mol MEA and the grey curve contains the lowest load of 0,11 mol CO_2 per mol MEA. From the curves it can be concluded that the size of the rich load positively influences the desorption capacity. For example, the desorption capacity of pure MEA increases from 0,013 mol CO_2 per mol MEA to 0,028 mol CO_2 per mol MEA by increasing the rich load from 0,11 to 0,3 mol CO_2 per mol MEA. Also at lower concentrations of MEA the desorption capacity increases with increasing rich load. A higher loading means more carbamates, since there is more CO_2 in the solution. This in combination with a high water content promotes the desorption reaction (11) causing more CO2 to be released.

Figure 13 b) shows the lean loading on the X-axis and the weight percentage of MEA on the X-axis. The obtained curves follow a similar trend and a clear relationship between the rich loading and lean loading is visible. Regardless of the loading, there always remains a part of CO_2 in the MEA solution. For a pure sample with a load of 0,3, the lean loading is equal to 0,273 mol CO_2 per mol MEA. For a pure sample with a load of 0,11 mol CO_2 per MEA, the lean loading is consequently lower because there was initially less CO_2 in the solution, the lean loading being 0,094 mol CO_2 per mol MEA. Not only the rich load affects the lean loading, but also the water content. The lean loading can be limited by working with a higher water content. For example, the lean loading decreases from 0,273 to 0,233 mol CO_2 per mol MEA by increasing the water content to 70 wt.% water.

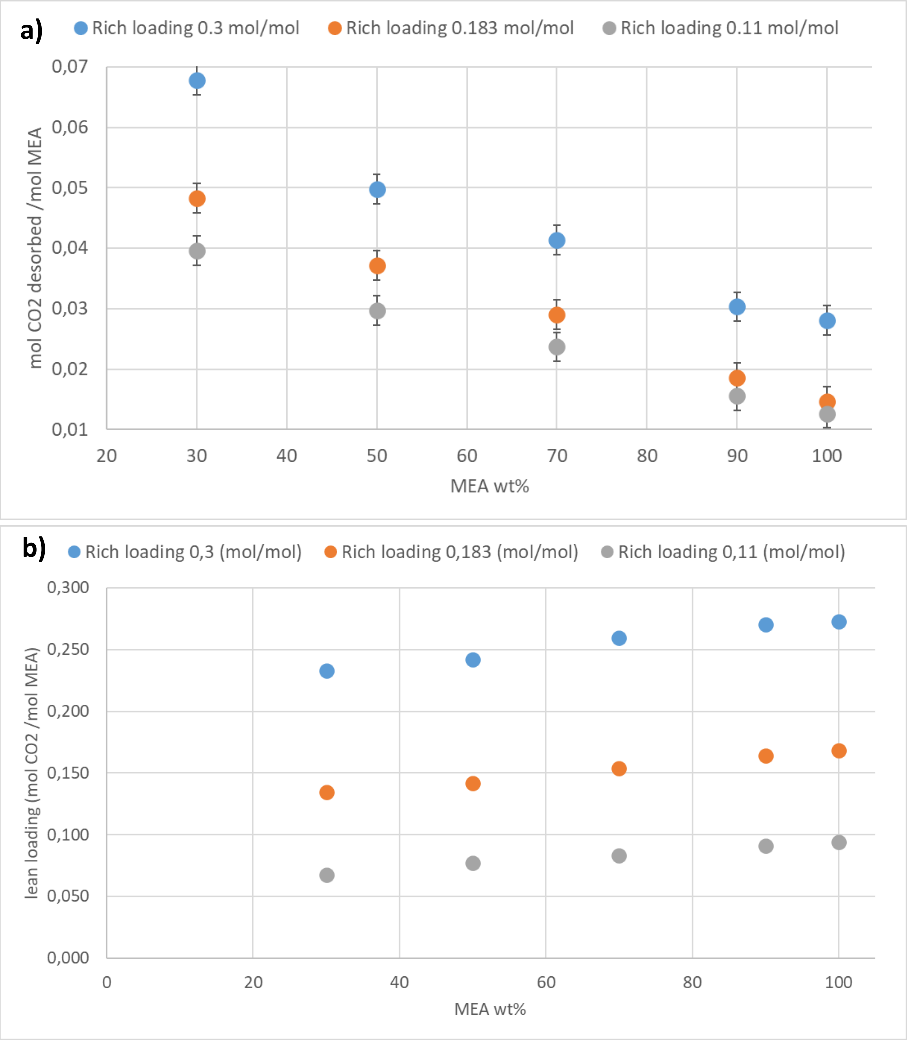


Figure 13: a) Effect of rich loading on the desorption capacity, b) effect of rich loading on the lean loading

Since the desorption capacity is considerably lower with pure MEA, this is less interesting. But when a little water is added, the desorption capacity increases enormously. The sample with wt.% 70 MEA is therefore a suitable composition. This allows working with a high concentration of MEA and thus reduces the amount of water. Thus wt.% 70 MEA (rich load 0,3 mol/mol) has a desorption capacity of 0,0341 mol CO_2 per mol MEA. When this is compared to the high water content sample wt.% 30 MEA with a desorption capacity of 0,0548 mol CO_2 per mol MEA. It can be concluded that the amount of water has a great influence on the desorption capacity. Whether a higher concentrated sample such as wt.% 70 MEA is more economical than the 30 wt.% MEA was not investigated in this study but is interesting to investigate in the future.

4.2 Absorption with aqueous MEA

In this section the samples are sprayed with a mixture of demineralised water and MEA. So there is also CO_2 physically dissolved in the water, but this is included in the chemical absorption and thus in the loading of CO_2 per mole MEA.

4.2.1 Effect of MEA concentration

For these measurements, 5 g of solution was desorbed each time. The loads obtained in the absorption process are around the same values, so the samples can be compared per gram of solution. Because the different samples contain different amounts of MEA, the desorption capacity is given here per gram of solution instead of per mole of MEA.

By increasing the MEA concentration, the desorption capacity per gram of solution decreases. This can be seen in figure 15 where the percentage by weight of MEA is shown on the X axis and the desorption capacity in mmol CO_2 per gram of solution is shown on the Y axis. The samples have approximately the same load and therefore the same amount of CO_2 contained in the solution. The highly concentrated MEA solutions of 90 and 100 wt.% MEA show a desorption of 0,163 and 0,095 mmol CO_2 per gram of solution. When the concentration of MEA drops to 70 wt.%, the amount of released CO_2 doubles to 0,210 mmol CO_2 per gram solution.

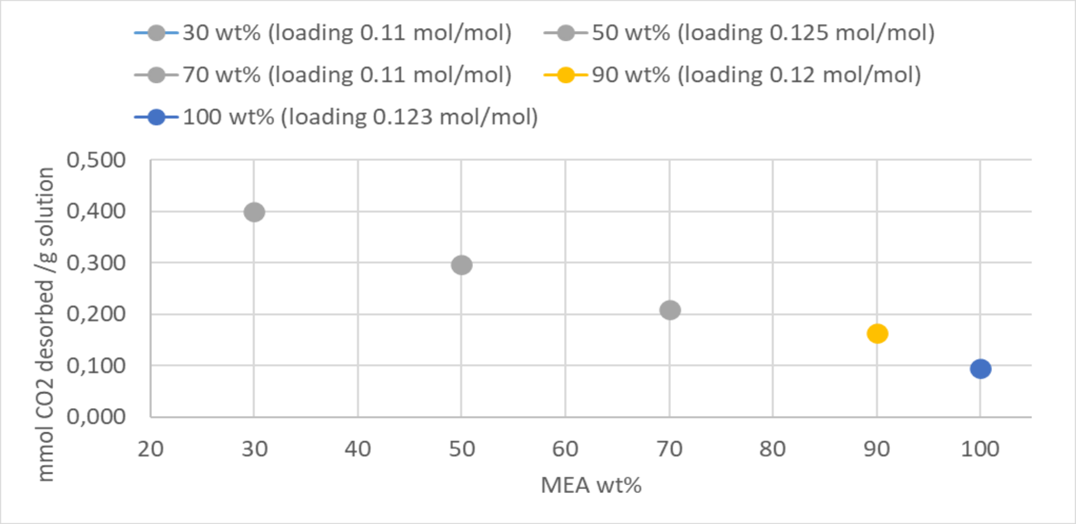


Figure 14: Effect of MEA concentration on aqueous sprayed MEA

The effect of MEA concentration on the amount of CO_2 released per gram of solution is more pronounced at low concentrations. For example, the sample with a weight percentage of 30 wt.% MEA has the highest efficiency per gram of solution. As a result, it is more advantageous to carry out the desorption with a low concentration of MEA. It seems that the desorption process needs water in order to obtain a sufficient CO_2 yield. A possible explanation why samples with a high water content desorb more has already been discussed in section 4.1.2.

4.2.2 Effect of temperature

The effect of temperature on aqueous sprayed MEA is similar to that for pure sprayed MEA. For each sample, 3 g of solution was weighed and then desorbed. The samples contain an equal loading of 0,11 mol CO_2 per mol MEA. The Y-axis shows the amount of desorbed mol CO_2 per mol MEA and the X-axis the temperature.

In figure 16 it can be seen that the desorption capacity increases with increasing temperature. The slope of the pure sample is less steep than the aqueous sprayed solutions. The effect of temperature is therefore less here. The presence of a small amount of water is decisive for the desorption capacity. For example, the desorption capacity of pure MEA is 0,022 mol CO_2 per mol MEA and of 70 wt.% MEA 0,078 mol CO_2 per mol MEA at a temperature of 120°C. As discussed in section 4.1.1, the temperature increase will also reduce the lean loading resulting in a higher desorption capacity.

However, the sample with a weight percentage of 30% MEA desorbs more than its load obtained in the absorption process. A possible explanation is that the cooling system was not strong enough to condense the water within the time that the water vapour partial pressure is larger. Because this sample has a high water content, this is more pronounced than in the other measurements. Water boils at a temperature of 100°C, which means that it quickly passes into the gas phase. And so the CO_2 partial pressure in the reactor is influenced by the partial pressure of water vapour. Another possible explanation is that something went wrong during the desorption process, resulting in a higher rich loading than expected.

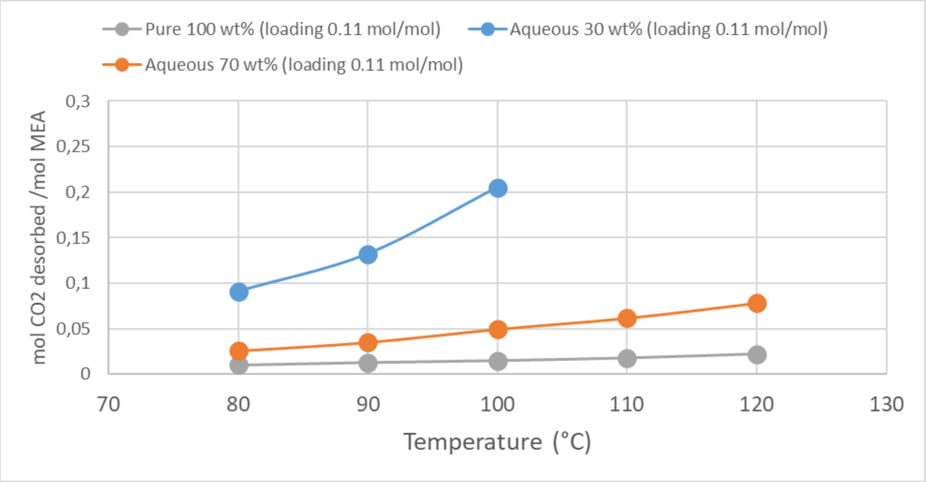


Figure 15: Effect of temperature on pure and aqueous sprayed MEA

It can be concluded that for both aqueous sprayed and pure sprayed with water addition, the thermolysis reaction (11) is enhanced by a higher temperature. And thus the chemical equilibrium shifts to the right, converting more carbamate to MEA and CO_2.

4.3 Comparison between aqueous sprayed MEA solutions and pure MEA with the addition of water

The application to add water only after the absorption is interesting because it allows to work with pure MEA in the absorption process. Below it is discussed whether the use of this application has a difference on the desorption capacity. Figure 17 a) shows desorption capacity on the Y-axis and the weight percentages of MEA on the X-axis. The red points are the aqueous sprayed MEA solutions and the grey points are pure sprayed with water added after absorption. The obtained desorption capacities show a similar behaviour in the range of higher concentrations of MEA. Thus, the desorption capacity of wt.% 70 MEA is equal to 0,022 mol CO_2 per mol MEA for the aqueous sprayed MEA and 0,023 mol CO_2 per mol MEA for the pure sprayed MEA. For rather lower concentrations of MEA, this difference is more pronounced and there may be another factor influencing the measurements.

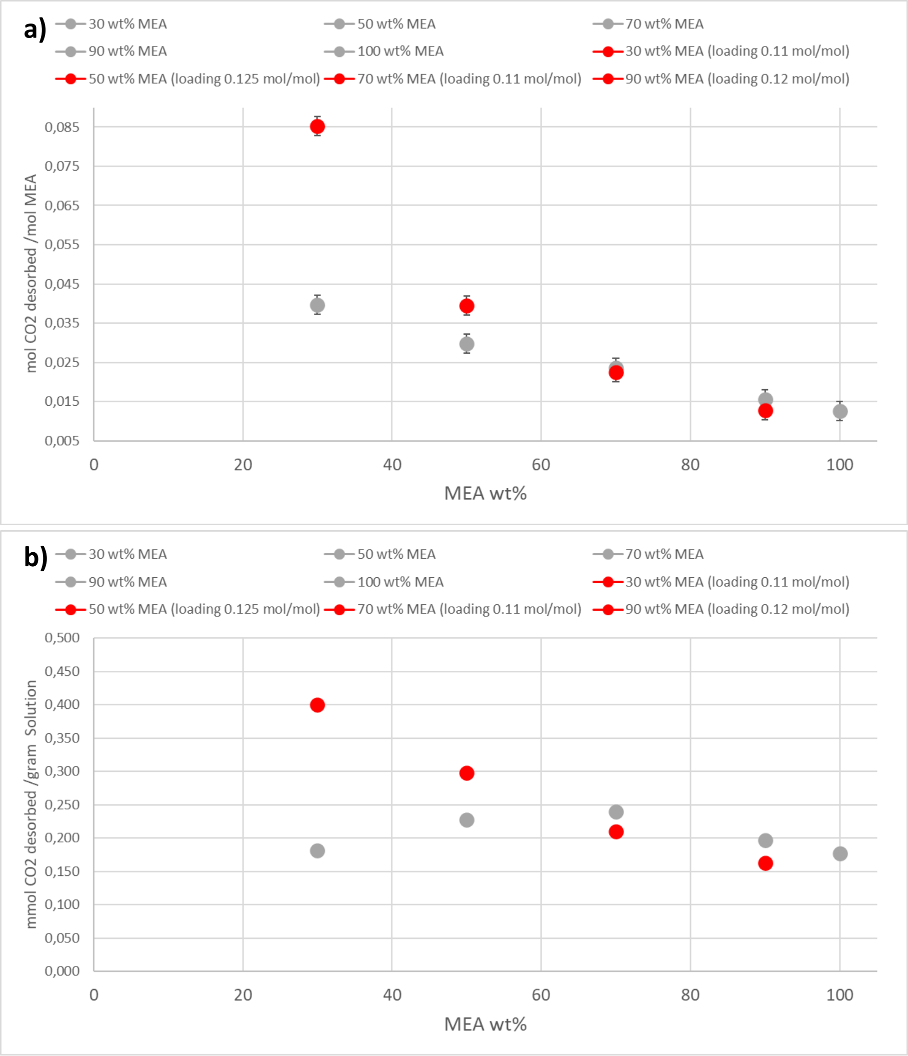


Figure 16: Comparison between aqueous sprayed MEA and pure sprayed MEA with addition of water afterwards, a) desorption capacity, b) desorption per gram solution

It seems that the mass used has an influence on the desorption efficiency per mol MEA. The red dots on the graph contain 5 g of solution. The grey dots all contain the same amount of MEA but the water content differs. Therefore the pure solution has a weight of 3 g and the 30wt.% MEA has a weight of 9,20 g. This explains why the grey trend is more linear as there is the same amount of loaded MEA present and thus the desorption capacity is enhanced by the fraction of water. The red trend is rather exponential, again due to the masses used. Because the amount of loaded MEA used varies from measurement to measurement, the least amount is used at a weight percentage of 30 wt.% MEA. The addition of a large quantity of water lowers the pH, so there are more H^+ ions in the solutions that promote the thermolysis of carbamate.

It is possible to express the amount of CO_2 released per gram of solution. This is shown in figure 17 b). The Y-axis shows the released CO_2 in mmol per gram of solution and the X-axis shows the weight percentage of MEA. It follows that for a constant weight of MEA but with different weight fractions of water, the sample with a 70 wt.% is the most efficient per gram of solution. It desorbs more CO_2 than the aqueous sprayed MEA solution of 70 wt.%. However, it appears that 30 wt.% MEA sprayed aqueously can release the greatest amount of CO_2 per gram of solution. Thus, the desorption per gram of solution is 0,400 mmol CO_2 and for a pure sample it is 0,177 mmol CO_2 per gram of solution.

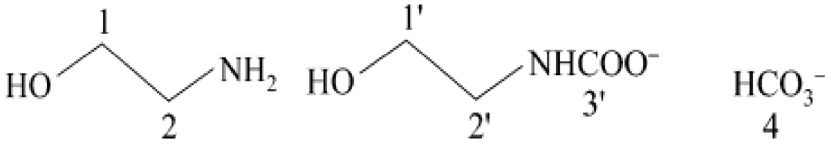
4.4 NMR analysis and pH measurements

The NMR was used to find out what is happening at the molecular level and which bonds are being formed in the absorption process. The NMR spectrum of 3 samples was recorded and the loading, the weight percentage MEA and the integration of the peaks are shown in table 1 below, as well as the average pH.

Tabel 1: Samples NMR

ID	MEA% by weight	mol CO2 absorbed/ mol MEA	AVG pH	Piek 1	Piek 2	Piek 1'	Piek 2'	Piek 3
7	100	0,27	11,03	54,33	52,78	23,99	23,99	23,44
7d	30	0,27	10,78	42,49	41,8	17,11	16,99	17,11
1	30	0,16	10,74	21,32	20,7	5,46	5,44	5,19

The NMR spectrum of one sample is shown in figure 18. Which compound belongs to which peak is indicated by a number. Peak 1 and 2 belong to an MEA molecule that is unloaded. And neighbouring peaks 1', 2' and 3 correspond to a carbamate. Finally, there is a 4th peak but it is only visible at rich loadings of 0,5 mol CO_2 per mol MEA. Since there are no samples with such a high loading, this peak is not visible on the spectrums.



The first sample examined is pure sprayed and has a loading of 0,27 mol CO_2 per mol MEA. The spectrum shows the presence of both MEA and carbamate. A peak belonging to the HCO_3^- is not visible since the loading is lower than 0,5 mol CO_2 per mol MEA. This indicates that the dissociation of CO_2 to HCO_3^- has not taken place, nor has carbamate been converted to HCO_3^-. This is logical since there is no water present to accomplish reversion of carbamate. To find out what the addition of water does to the composition of the sample, the spectrum of sample 7 diluted with water to a weight percentage of 30 wt.% MEA was recorded. Table 1 shows the intensities of the peaks. The intensity of peak 1 and 2 that correspond to MEA decreases by 22% due to the addition of water. Peaks 1', 2' and 3 correspond to the compounds of carbamate decrease by 29%. Why the decrease in carbamate is more pronounced than in MEA molecules is unclear. But a possible cause is that in aqueous solutions of MEA, various compounds dissociate due to the presence of water. For example, CO_2 reacts with water to carbonic acid (H_2CO_3) which then dissociates to hydrogen (H^+), bicarbonate (HCO^{3-}) and carbonate ions (CO_3^{2-}) [33]. The dissociation lowers the pH because more H_3O^+ ions come into solution. Diluting the sample with water decreased the pH from 11.03 to 10.74.

Sample 1 contains a 30 wt.% MEA and is sprayed aqueous. The peaks corresponding to MEA and carbamate are present. However, the intensity of the peaks is difficult to compare with the other samples because the sample has a different load. Sample 1 has a loading of 0,16 mol CO_2 per mol MEA and sample 7d has a loading of 0,27 mol CO_2 per mol MEA. It is therefore expected that sample 7d will show a greater peak intensity for the carbamate compounds than sample 1. It seems that the proportion of carbamate is higher in the pure sprayed samples than the aqueous sprayed samples. A possible explanation is that the water causes additional reactions that reduce the proportion of carbamate through hydrolysis. But since the loading of both samples is different and there is no sign of hydrolysis, no concrete conclusion can be drawn because the loading also has an influence on the products that are formed [26]. Lv et al. discovered that hydrolysis only occurs when the loading was around 0,4 mol CO_2 per mol MEA for high water content of 30 wt.% MEA [34].

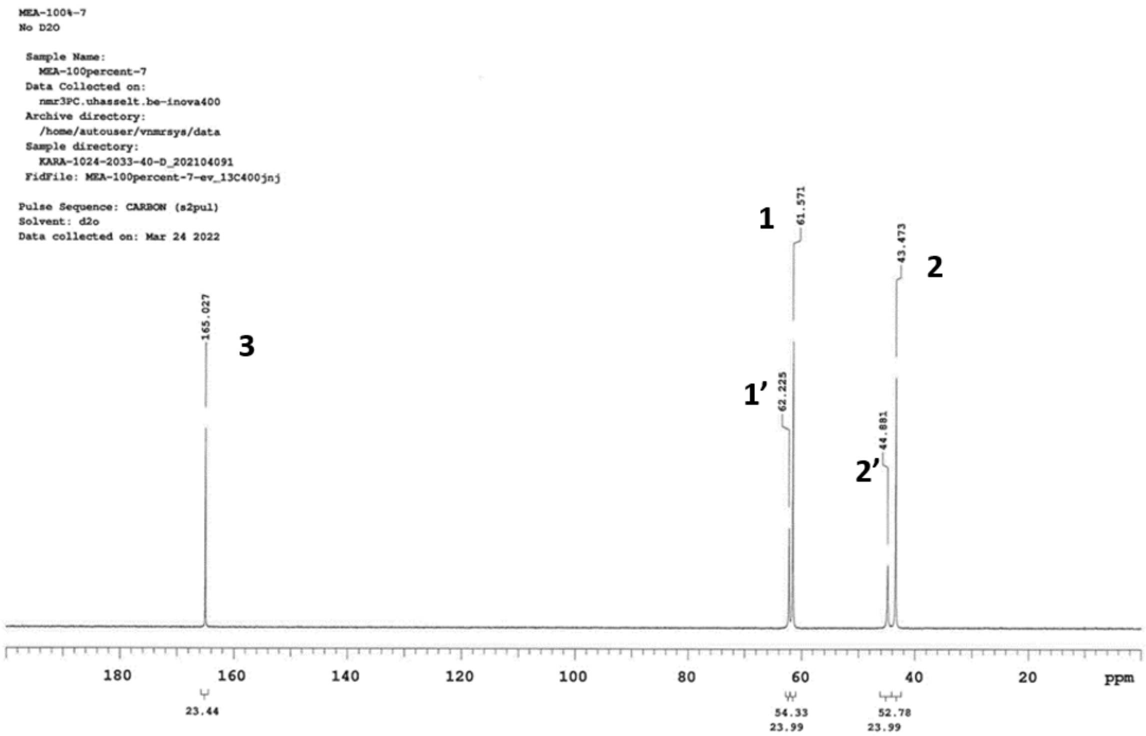


Figure 17: NMR spectrum pure MEA

The pH of different weight percentages was recorded both before and after desorption. The results obtained are shown in table 2. Before the loaded sample goes through the desorption process, it still contains a high load of CO_2. During the desorption process, CO_2 is released and the load of the solution decreases. Since the load also determines the pH, it will be different before and after desorption. The desorption reaction needs protons to release CO_2, therefore H^+ are consumed in the solution and consequently the pH rises. Another aspect that is notable from the obtained pH values is that they decrease at a higher water content. As discussed above, dissociations occur when water is added. More H^+ are released into the solution, causing the pH to drop. When the pH values before and after desorption are compared, it is observed that the pH values decrease with an increasing load of CO_2, this is also confirmed in the literature [22].

Tabel 2: pH values before and after desorption

wt% MEA	pH before desorption	pH after desorption
30	10,19	10,41
50	10,37	10,66
70	10,6	10,78
90	10,78	10,96
100	10,95	11,07

5. Conclusion and future work

In this master thesis, the behaviour of highly concentrated MEA solutions was investigated and compared to aqueous MEA solutions. Different parameters were varied and their influence on the lean loading and desorption capacity determined.

First, the influence of temperature on both pure and aqueous MEA was investigated. An increase in temperature causes an increase in desorption capacity and a decrease in lean loading. The thermolysis of carbamate is positively influenced by temperature. The same applies to the water content, which also has a positive influence on the desorption capacity and the lean loading. The results show that the desorption process needs water to obtain a sufficiently high desorption capacity. For example, the desorption capacity of pure MEA is 0,013 mol CO_2 per mol MEA and that of 30 wt.% MEA is 0,040 mol CO_2 per mol MEA with both a rich loading of 0,11 mol CO_2 per mol. The effect of rich loading on aqueous and pure MEA is also positive. Higher rich loading results in a higher desorption capacity and lean loading. The effect of MEA concentration on the amount of desorbed CO_2 per gram of solution was also investigated. This showed that the aqueous MEA solution of 30 wt.% sprayed aqueously was the most efficient.

A comparison was made between the aqueous and pure sprayed MEA solutions. Since the masses of the samples vary, it is not possible to draw a concrete conclusion in terms of desorption capacity per mole of MEA. However, the yield of CO_2 per gram of solution can be compared. This shows that pure samples with water addition after absorption obtain the highest yield of CO_2 at a weight percentage of 70% MEA. The yield is just under 0,250 mmol CO_2 per gram of solution. The aqueous sprayed solution of 30 wt.% MEA is the most efficient and achieves a yield of 0,400 mmol CO_2 per gram of solution.

NMR and pH analysis was used to find out what was occurring at the molecular level. This shows that the thermolysis of carbamates requires H^+ ions to break down. This is confirmed by the results of the pH measurements which indicate that the pH rises after desorption. The effect of water addition on the pH was also investigated. Adding water to the MEA solutions increases the pH and enhances thermolysis. The NMR analysis shows that the amount of carbamate does not result in an increased desorption capacity. For example, the sample with 30 wt.% of MEA has a lower peak intensity for carbamates than the pure sprayed sample and yet a higher desorption capacity per mole of MEA is achieved. This indicates that a certain amount of water is essential for the conversion of carbamate to CO_2 and MEA.

In future research, it is interesting to work with another solvent that can serve as H^+ donor. These solvents could then be compared on the basis of their yield of CO_2 per gram of solution and lean loading. A more appropriate solvent could reduce the amount of solution and consequently reduce the cost of pumping and heating the solution.

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