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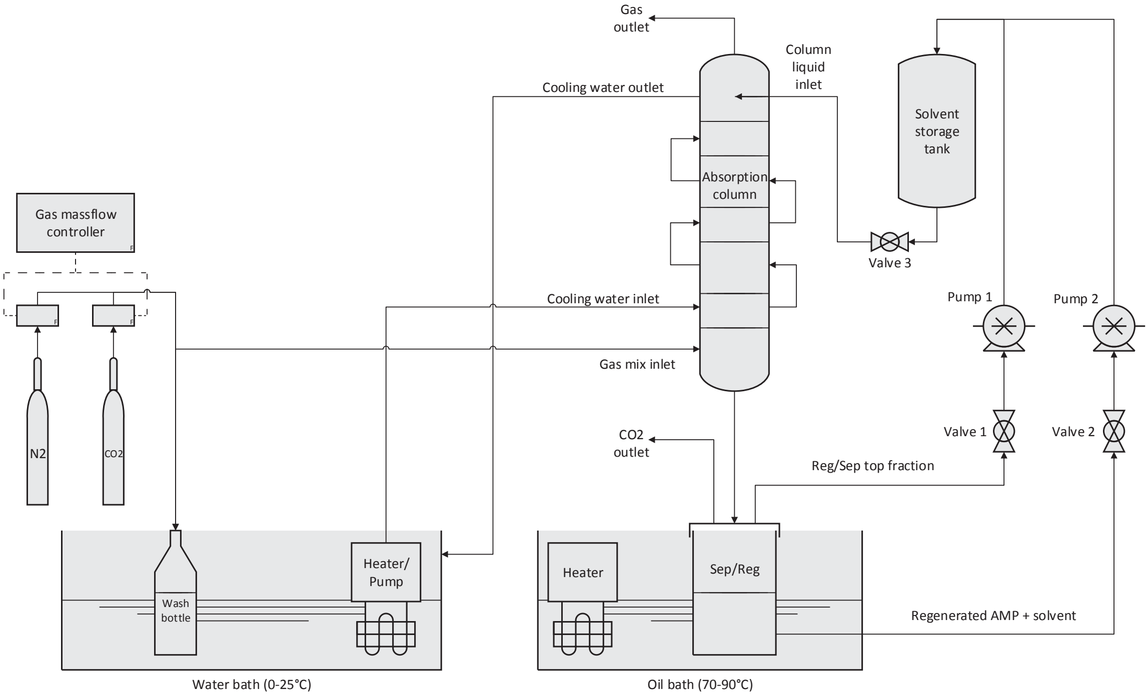

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New technique for energy efficient CO_2-separation through absorption with a sterically hindered amine

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Preface

This report is the result of a Master's thesis project that was carried out during the spring of 2016 at the Chemical Centre in Lund. This report is the final piece in my degree as a chemical engineer. This degree project is also part of a larger research project at the division of chemical engineering at LTH.

I have many people I would like to thank for helping me through my education and now finally my degree project.

First of all I would like to thank my supervisor Helena Svensson for her commitment and for always letting me trying out my ideas, how crazy they might seem. You were always very positive when I had my doubts.

I would also like to thank my Co-supervisor Meher Sanku for the few but very important discussions when Helena was busy.

Apart from my supervisors, I would like to thank Hanna Karlsson for guiding me into the world of lab equipment and for never hesitating to help me when I needed something or had some questions.

I would also like to thank Laura Folkers at CAS for taking your time and helping me with the microscope and the crystal pictures.

Thanks also to my roommates Elias, Philip and Sandra for all the laughs and talks we had whilst working with our separate projects.

I want to give a special thank you to Csaba Humenyik at Humi-Glas, for the help with making the absorption column.

Lastly I would like to thank my friends and family for all of the support throughout my life and education. Without you I would not have been here today.

Abstract

The degree project described in this report also acts as a deliverable for a research project. The research project focuses on a new technique for the upgrading of biogas. This new technology uses a sterically hindered amine to absorb carbon dioxide from the biogas to raise its energy value. The amine used for this method is 2-amino-2-methyl-1-propanol or AMP. When absorbing carbon dioxide with this amine and with an organic solvent, the chemically formed complex forms precipitate. The precipitate can then be separated from the solvent to enable regeneration of the precipitate only and not all of the solvent as the methods used today. This will lower the heating demand. This separation and regeneration is what separates this method from the commercially available. The steric hindrance of the AMP weakens the bond with the carbon dioxide. This weaker bond is what makes it a promising candidate, since there is a possibility that the AMP carbamate can be regenerated using low grade heat at 70-90°C, which makes it possible to use warm water instead of steam.

The deliverable for the research project is to give a proof-of-concept. To do this, an experimental setup has been built.

The setup was run with live conditions with a 25 % CO_2 gas inlet, to mimic raw biogas. The solvent consisted of 10 Vol% AMP and the rest 1-Methyl-2-Pyrrolidinone or NMP at a liquid flow of 20.2 l/hr. CO_2 was absorbed and regeneration was possible at temperatures at and below 90°C. These results proved the concept.

More work is needed with the setup for future tests. The setup should be adapted with gauges for temperature measurements as well as flowmeters for the gas outlets. The rubber tubing needs to be replaced with more resistant tubing. Another separation unit needs to be found for better separation. More optimization of the conditions needs to be done for the setup to be run fully continuous.

Sammanfattning

Examensarbetet som beskrivs i denna rapport fungerar som ett delresultat i ett forskningsprojekt. Forskningsprojektet fokuserar på en ny teknik för uppgradering av biogas. Denna nya teknik använder sig av en steriskt hindrad amin för att absorbera koldioxid från biogas för att på så sätt höja energivärdet. Aminen som används i denna metod är 2-amino-2-metyl-1-propanol eller AMP. När koldioxiden absorberas av denna amin, i ett organiskt lösningsmedel, bildas ett komplex som fälls ut i lösningsmedlet. Fällningen kan därefter separeras från lösningsmedlet och sedan regenereras med hjälp av lågvärdig värme vid 70-90°C. Detta ger möjlighet att använda varmvatten istället för ånga. Denna separation och regenerering är vad som skiljer den här metoden från dem kommersiellt tillgängliga. Det är också dessa egenskaper som gör den till en lovande kandidat. Delmålet för forskningsprojektet är att ge ett så kallat proof-of-concept, vilket innebär det ska bevisas utifall metoden är möjlig. För att göra detta, har en experimentell uppställning byggts.

Uppställningen kördes med riktiga förhållanden med ett inflöde av gas innehållande 25 vol.% koldioxid och resterande kvävgas, för att efterlikna rå biogas. Lösningen bestod av 10 vol.% AMP och resten 1-metyl-2-pyrrolidinon eller NMP vid ett vätskeflöde på 20,2 l/timme. Koldioxiden absorberades och regenerering var möjlig vid temperaturer under 90°C.

Mer arbete krävs med optimering av flöden, temperaturer och koncentrationer för framtida tester. Uppställningen behöver anpassas för vidare mätningar. Temperaturmätare ska installeras, samt flödesmätare för mätning av utgående gas. Gummislangarna behöver ersättas med slang mer resistent mot lösningsmedlet. En annan separationsenhet måste hittas för bättre separation av fällningen. Vidare optimering av parametrarna behöver utföras innan uppställningen kan köras helt kontinuerligt.

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Nomenclature

Abbreviations

MDEA	Methyl diethanolamine
PZ	Piperazine
AMP	2-amino-2-methyl-1-propanol
MEA	Monoethanolamine
NMP	1-methyl-2-pyrrolidinone
TEGDME	Triethylene glycol dimethyl ether
TSA	Temperature Swing Adsorption
PSA	Pressure Swing Adsorption
VSA	Vacuum Swing Adsorption
Sep/Reg	Separator/Regenerator

Symbols

P	Pressure	Pa
K_H	Henry's Constant	$\mathrm{Pa\ m^3\ mol^{-1}}$
C	Concentration	$\mathrm{mol\ l^{-1}}$
N	Mass transfer coefficient	$\mathrm{mol\ m^{-2}\ s^{-1}}$
D_{AB}	Mass Diffusivity	$\mathrm{m^2\ s^{-1}}$
δ	Film thickness	m
K	Overall Heat transfer coefficient	$\mathrm{W\ m^{-2}\ s^{-1}}$
E	Enhancement factor	-
V	Volume	$\mathrm{m^3}$
a_g	Geometric area	$\mathrm{m^2\ m^{-3}}$
A_{column}	Cross-sectional area of column	$\mathrm{m^2}$

Q	Volumetric flow	$m^3\ s^{-1}$
b	Stoichiometric coefficient	-
SR	Stoichiometric ratio	-
h	Column height	m
R	Gas constant	$J\ K^{-1}\ mol^{-1}$
G_G	Molar Gas rate	$mol\ s^{-1}$
v	Velocity	$m\ s^{-1}$
g	Gravitational constant	$m\ s^{-2}$
d_p	Particle diameter	m
ρ	Density	$kg\ m^{-3}$
μ	Dynamic viscosity	Pa s
c_p	Specific heat capacity	$J\ kg^{-1}\ K^{-1}$
ΔT	Temperature difference	K or °C
ΔT_L	Logarithmic mean temperature	K or °C
b_i	Material thickness	m
w	Mass flow	$kg\ s^{-1}$
λ	Thermal conductivity	$W\ m^{-1}\ K^{-1}$

Subscripts

A	Component A
B	Component B
L	Liquid
G	Gas
i	Index
$_0$	Starting value/Normal condition

1 Introduction

1.1 Background

The global warming and the release of greenhouse gases has been a frequent subject for the last decades. Researchers are trying to find different ways of replacing fossil fuels as the source of energy. The development is ongoing in fields as wind power, solar power and bio based fuel. Researchers believe that fossil fuels will remain our main source of energy and fuel for at least the coming two decades. It is therefore important to limit the effect these fuels have on the environment, before they can be fully replaced.

Replacing fossil fuels with bio-based fuels is one way of reducing the carbon dioxide, CO_2, introduced to the atmosphere when using fossil fuels such as natural gas, coal and oil. The CO_2 emitted from bio based material is considered natural, since it is a part of the neutral CO_2-cycle, meaning that no net CO_2 is released to the atmosphere. However the replacement of fossil fuels with bio-based requires upgrades of current equipment and investment for new equipment. This is not cheap and the demand for cheaper and more effective production of biofuels is great.

The area investigated in this report is upgrading of biogas. The produced biogas consists mainly of methane and CO_2. The CO_2 is inert in the combustion process and it therefore lowers the heating value of the biofuel. There are strict demands when it comes to the energy value for fuels supplied to natural gas networks and for vehicles. To be able to use the biogas as a fuel, it is necessary to upgrade it, meaning that the CO_2 needs to be removed to raise the energy value of the fuel.

One of the most common ways of upgrading biogas today is by absorbing CO_2 in a solution containing some sort of amine, often methyl diethanolamine, MDEA or piperazine, PZ, usually dissolved in water. CO_2 reacts with the amine and removed from the gas, generating upgraded biogas. The CO_2 can later be separated from the amine solution in a stripper column, where the solution is heated, causing the CO_2 to desorb. This process is rather energy demanding, since the solution needs to be heated to about 120°C for the CO_2 to desorb and the solvent to be regenerated.

A popular contestant to replace the current process is the use of the sterically hindered version of MEA, called 2-amino-2-methyl-1-propanol, also called AMP. The steric hindrance is a subject for controversy, since the carbamate formed is not stable. It is believed that the steric hindrance will slow down the initial reaction between the AMP and the CO_2. However with the steric hindrance and the weak bond, it is believed that low energy, low grade heat can be used for this step.

Another benefit with AMP is the fact that if dissolved in an organic solvent it will form a precipitate together with CO_2. The precipitate is possible to separate from the solvent using standard solid/liquid separation methods. When separated the energy requirements for desorption process is even lower, since the separated solvent no longer needs to be heated. Heating the precipitate using low grade heat will push the equilibrium to the left, making the CO_2 desorb. The amine will then return to its original liquid state, making it possible to recycle in the process.

1.2 Aim and scope

This report is a study of this process and the purpose of the project is to develop and build a continuous experimental setup of a novel CO_2-separation method using a sterically hindered amine to absorb the CO_2. This technique has promising advantages compared to the commercially available methods, such as the forming of precipitate and the possibility of regeneration at a lower temperature. It is of interest to see if the regeneration could be performed using low grade heat at approximately 70-90°C. This would make it possible to use warm water instead of steam. This will be investigated further within this degree work by designing and building an experimental setup. The experimental setup will be used to provide proof-of-concept for the method. If the results are promising, this technology could make a breakthrough within biogas upgrading, making biogas more of a competitor against fossil fuels. If the regeneration is possible using low grade heat, which is often available as excess heat at chemical plants, this will reduce the costs for upgrading biogas.

1.3 Outline of the report

The first part in this report is a literature study on different carbon dioxide separation methods used today. The most common are listed below:

- Adsorption
- Membranes
- Gas hydrate crystallization
- Cryogenic separation
- Absorption (Physical/Chemical)

Then the report goes in depth into the new method, which is described in sections regarding kinetics, crystallization and finally regeneration.

Then different separation methods for the precipitate are investigated. Different unit operations for sedimentation, filtration and centrifugation are discussed to find a suitable separation method. A hydrocyclone or several hydrocyclones seems to be the most promising method.

After the separation chapter, the report turns its focus towards the different unit operations necessary for the experimental setup and more precisely the theory and designing of these.

Then the building process of the experimental setup is described. The difficulties and solutions are presented here.

The final part is a discussion part where the proof-of-concept experiments are discussed.

The report also has appendix, where some extra information that did not make it into the report is shown.

2 Literature study

2.1 CO_2 separation methods

There are many different ways of separating carbon dioxide from a gaseous stream. This literature study will be a study and a summary of the most common methods. These are adsorption, membranes, cryogenic separation, gas hydrate crystallization and absorption. Lastly the literature study will turn its focus towards the method that is the main focus in this report, which is the absorption with a sterically hindered amine. The kinetics, forming of precipitate, solubility parameters, regeneration and experimental setup will be discussed and summarized for this novel absorption method. Figure 1 below is an overview of the different carbon capture methods used today [1].

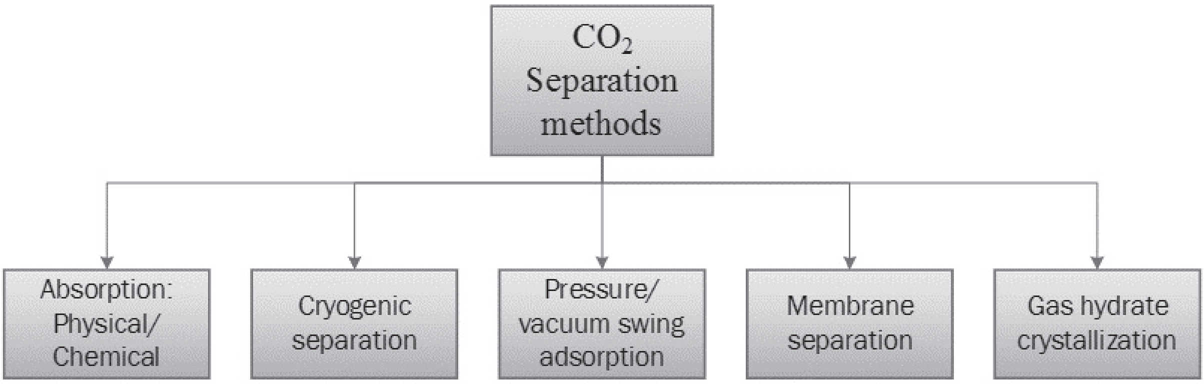

Figure 1. CO_2-separation methods.

2.1.1 Adsorption

Adsorption can be used to separate CO_2 from gas streams, either with temperature swing adsorption (TSA) or with Vacuum or Pressure swing adsorption (VSA/PSA). In all these methods the flue gas passes through a packed bed column. The packing consists of a surface active adsorbent, which adsorbs the CO_2, which is illustrated in Figure 2 below. Then, depending on which method is used, the packing is regenerated by swinging the temperature or the pressure. For the PSA, the gas enters with high pressure until the concentration of the flue gas reaches equilibrium with the active surface of the adsorbent. The pressure is then reduced to detach the CO_2 again. In TSA the method is similar, but the packing or the adsorbent is regenerated by raising the temperature, which releases the CO_2 [1].

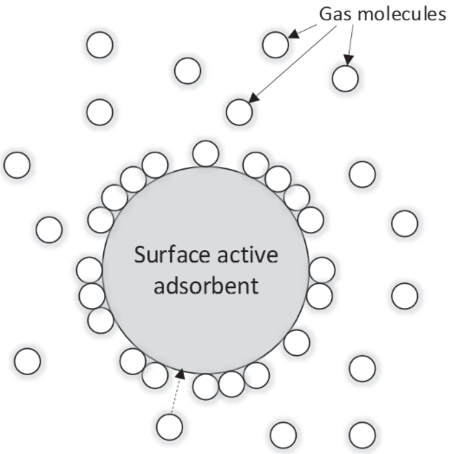

Figure 2. Gas molecules attaching/adsorbing to the surface active adsorbent.

The benefit solid adsorbents have over liquid absorbents is the fact that there is no need for extra liquid, in form of solvent. This is beneficial in the regeneration step, where the solvent is usually heated, and hence requires large amounts of thermal energy. Another advantage with this method is the high operating temperature. The fact that solid adsorption can be performed at high temperatures, means that there is no need for extra cooling if the method is used for flue gas cleaning for instance. This reduces the overall cost since there is no need for extra cooling utilities and equipment [1].

There are generally two types of adsorbents; an equilibrium adsorbent, adsorbing more CO_2 than CH_4, or a kinetic adsorbent, where the CO_2 is adsorbed faster than the CH_4 due to the different diffusion rates. Common materials used today are activated carbon, different zeolites, titanosilicates or silica gels [2].

2.1.2 Membranes

Membranes are commonly used in different separation applications. For gas separation the membrane allows for one or several components to pass through the membrane while retaining others, as illustrated in Figure 3. For this method to be useful in this application, it is important for the membrane to have the following properties: high permeability, high selectivity and high physical and chemical resistance. If the membrane in turn is also cost effective, the membrane is suitable for this CO_2 removal [1].

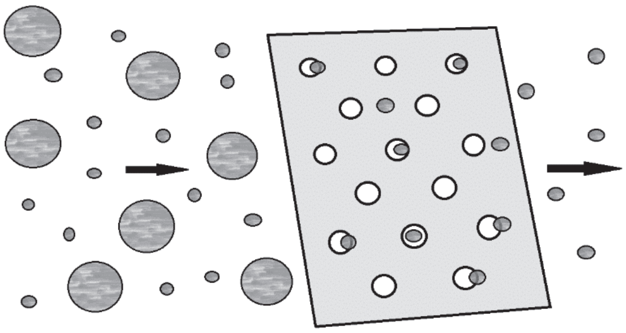

Figure 3. Gas molecules passing through membrane.

There are many different membranes on the market, including porous inorganic membranes, polymeric membranes, ceramic membranes, palladium membranes and zeolite micro-porous silica.

A downside with membranes as a separator is the low degree of separation. To achieve the effective separation needed for biogas upgrading, multiple stages of membranes can be used as well as recycling of some streams. This will however make the utility more complex and hence less cost effective [1].

2.1.3 Gas hydrate crystallization

Another way of separating CO_2 is by implementing gas hydrate crystallization. This method uses crystalline structures which has the possibility to physically capture small gas molecules into the gaps of the crystalline structure. These gaps are often referred to as polyhedral cages, which consists of hydrogen-bonded water molecules, as illustrated in Figure 4. The molecule that is supposed to be captured will find its way into the cage and in there the van der Waals forces that act upon the molecule will be great enough to trap it in the cage [1].

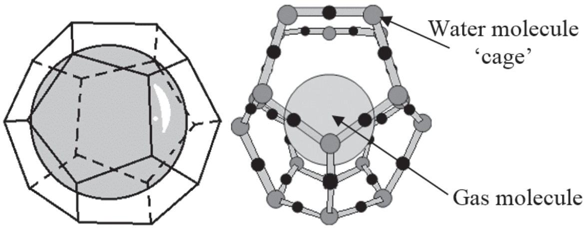

Figure 4. Polyhedral water-cage enclosing gas molecule.

These crystalline structures can enclose and capture small gaseous molecules such as light hydrocarbons, CO_2 and H_2S. This makes it appropriate for flue gas cleaning and carbon capture and storage, CCS. However for biogas upgrading this might not be the best solution, since the purpose with biogas upgrading is to separate CO_2 from CH_4. If both molecules can be trapped by the crystalline structure, this will not be suitable for this kind of separation [1].

2.1.4 Cryogenic separation

Cryogenic separation is a way of separating gases by using the difference in condensation temperature. It is basically distillation but with a reversal of the temperature. A basic flowsheet of cryogenic separation can be seen in Figure 5. A gas is cooled until a component condenses and therefore becomes possible to separate. Today this method is used for CO_2 separation where the gas stream has a high CO_2 content. This method works very well with high pressure streams. The downside is that this method is very energy intensive. Firstly it is necessary to remove all of the water from the gas stream before applying this separation method. After the separation of water the gas needs to be cooled well below zero degrees Celsius. This refrigeration demands high amounts of energy [1].

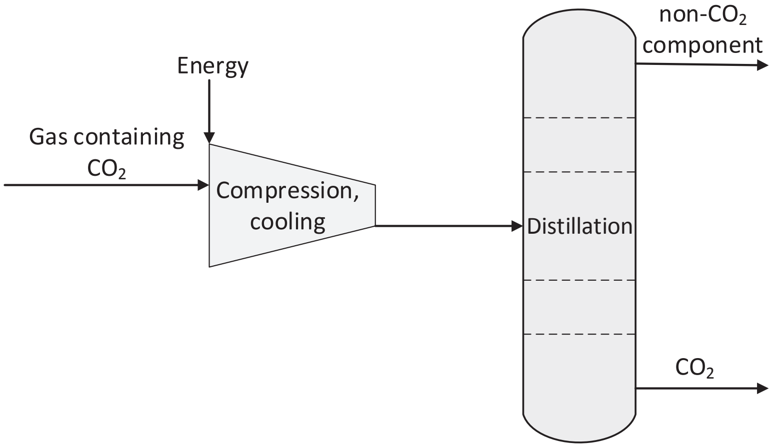

Figure 5. Cryogenic distillation of CO_2.

Since cryogenic separation requires high CO_2 content it would be possible to combine this method with membrane separation. This would lower the energy requirement since the amount of gas that needs to be cooled has been reduced in the membrane separation in the first step [1].

2.1.5 Absorption

Physical absorption

Physical absorption is a method of separation that uses the mass transfer of gas molecules into a liquid. Henry's law states that the amount of absorbed gas is proportional to the partial pressure of the gas.

$$P_A = K_H \cdot C_A \qquad (1)$$

To maximize the mass transfer it is important to create a large area or interface between the gas and the liquid. To achieve this area it is common to use the scrubbing technique, which is a method where the gas enters a packed column from the bottom and the liquid solvent enters from the top. The liquid is finely distributed using a spray nozzle to maximize the mass transfer area within the column. The gas is later separated from the solvent using a stripper column where the temperature is raised and the pressure lowered to push the equilibrium to the point where the CO_2 leaves the solvent [1].

The big disadvantage of this method is its low loading capacity. The loading capacity is determined by the partial pressure of the specific gas. When upgrading biogas the CO_2 content is relatively high, at around 50 %, which means that the driving force for this process will also be high [1].

Scrubber technologies today involve both water scrubbing and organic solvent scrubbing. For both types of solvents the separation of CO_2 and CH_4 depends on the higher solubility of CO_2 compared to the CH_4. The benefit with the organic solvent scrubbing is that the solubility of CO_2 is much higher in the organic solvents. This allows for more compact systems where less solvent needs to be circulated [2].

Chemical absorption

In chemical absorption the gas is not only absorbed into the solvent, it also reacts with a reagent. This reaction allows for the loading capacity to be higher than that of the physical absorption, since the absorption no longer only depends on the equilibrium of Henry's law [1].

Scrubbing gas streams using organic solvents was first used about 60 years ago for the oil and chemical industry to remove H_2S and CO_2. Since then it has been further optimized and a lot of research has been carried out to improve this technology. Now it is the most common flue gas cleaning method for CO_2 capture and removal [1].

Many different amines can be used to absorb carbon dioxide e.g. monoethanolamine (MEA), methyldiethanolamine (MDEA) and piperazine (PZ). These can be seen in the Figure 6 below. Most of the amines used commercially are either primary or secondary amines. Some systems use combinations of the amines to enhance the CO_2 absorption [1].

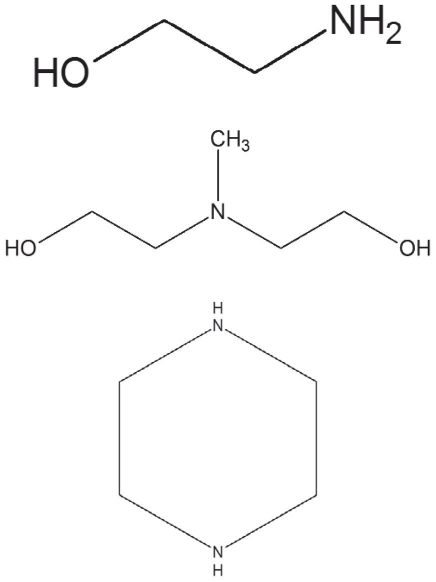

Figure 6. Structural formulas of MEA, MDEA and PZ.

The most common method for upgrading biogas today, using chemical absorption, is by absorption with a MDEA-PZ mixture. MDEA has a low vapor pressure, which makes it suitable for this kind of operation. It can be used in high concentrations without any major losses because of evaporation. MDEA is also highly resistant to degradation and is non-corrosive. However MDEA has a low reaction rate with CO_2. It is therefore often activated by mixing it with PZ, which acts as a promoter. MDEA mixed with PZ is called activated MDEA or aMDEA. aMDEA has a higher absorption capacity than that of regular MDEA [2, 3].

A basic flowsheet of a chemical absorption-stripper setup can be seen in Figure 7 below. Before entering the column, the raw biogas is cleaned from contaminants such as water and hydrogen sulfide. The raw biogas is then introduced to the packed absorption column, where it is contacted by the absorbent. Purified gas or bio methane leaves the column at the top and the rich solvent exits at the bottom. The solvent is pre-heated by a counter current heat exchanger by the regenerated solvent from the bottom of the stripper, before entering the stripper column. The stripper column is equipped with a reboiler where heat is supplied in order to reverse the reactions and release the CO_2. The regenerated solvent exits at the bottom and is cooled by the rich solvent from the absorption column. It is then cooled further to favor the absorption [2, 3].

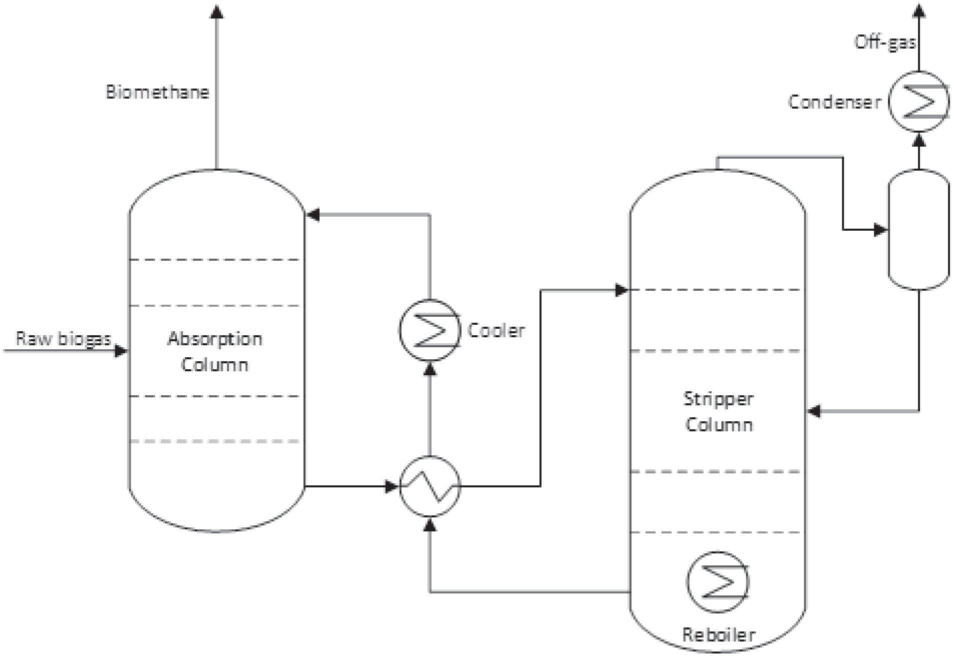

Figure 7. Process flow diagram of standard Absorption-Stripper design.

2.1.6 Absorption with AMP

Sterically hindered amines is a class of amines that has sparked an interest recently. The steric hindrance can be defined as an amine for which a primary amino group is attached to a tertiary carbon atom or a secondary amino group is attached to a secondary or tertiary carbon atom. This can be seen in Figure 8 below, where the structural formula of AMP is illustrated [4].

The reason for why this is of interest is the effect the steric hindrance has on the bond between the amine and CO_2. This hindrance reduces the stability of the carbamate which leads to the forming of a bicarbonate instead, which increases the loading capacity. However it is of interest to keep the carbamate for the lowered binding energy. This can be achieved by replacing water with an organic solvent. The reduction in binding energy could be beneficial when upgrading biogas to better be able to compete with fossil fuels, since low grade heat could be used instead of live steam. This could potentially lower the cost for producing biogas with high energy value.

2-amino-2-methyl-1-propanol, AMP, is the α-dimethylated derivative of MEA and it is an appropriate candidate for these kind of processes [5].

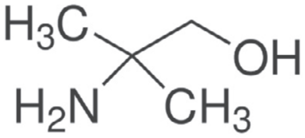

Figure 8. Structural formula of AMP

Kinetics

To get a better understanding of absorption, it is important to know how the reaction mechanism and the kinetic model looks like in order to fully understand the entire passage of events. It all starts with mass transfer. The mass transfer of component A, which in this case is CO_2 can be divided into the following steps:

- Transportation of gas component A from gas bulk to the gas-liquid interface.
- Dissolution of A into the liquid solvent at the interface.
- Transportation of A from the interface into the liquid bulk.

This series of events can be modelled using the basic film theory model as can be seen in Figure 9 [6].

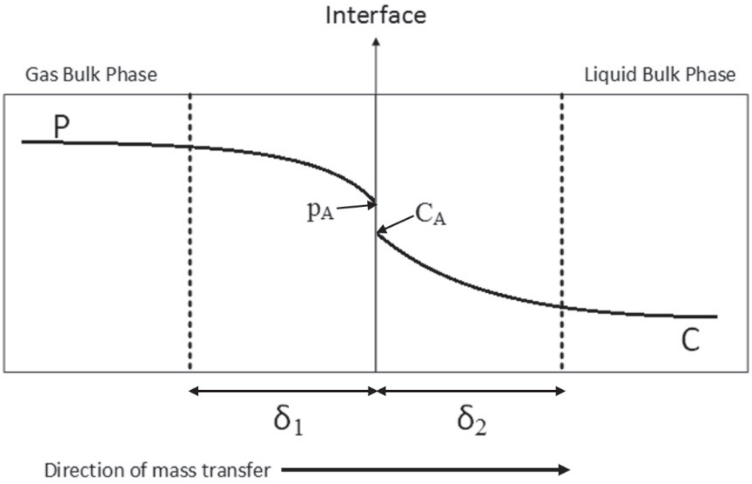

Figure 9. Two-film theory for mass transfer.

In this theory the first step can be modelled with the following equation:

$$N_A = \frac{D_{AG}}{\delta_1} \cdot (P_{AG} - P_{Ai}) \tag{2}$$

Fick's first law is used to determine the mass transfer in the film. It is described as a factor between the diffusion rate and the driving force. The driving force is the pressure difference between the two phases. The δ_1 refers to the thickness of the film between the gas bulk phase and the interface [6].

This model assumes equilibrium at the interface. This equilibrium between gas and liquid can be described using Henry's law:

$$P_A = K_H \cdot C_A \tag{3}$$

Henry's law is valid for gases at low concentrations. For gas cleaning processes this is generally the case. For biogas upgrading the partial pressure of CO_2 is generally higher than for flue gas cleaning. At this range Henry's law is switched to Raoult's law. Raoult's law states that '*the vapor pressure of a solution of a non-volatile solute is equal to the vapor pressure of the pure* *solvent at that temperature multiplied by its mole fraction'*. The third event which is the transfer of component A in the liquid film can be modelled similar to the transport in the gaseous film:

$$N_A = \frac{D_{AL}}{\delta_2} \cdot (C_{Ai} - C_{AL}) \tag{4}$$

By eliminating the concentration at the interface, which is difficult to measure, the model above can be described by the following expression:

$$N_A = K_{AG} \cdot (P_{AG} - P_{AL}) \tag{5}$$

Where the overall mass transfer coefficient can be described using the following expression:

$$\frac{1}{K_{AG}} = \frac{1}{k_{AG}} + \frac{H_A}{k_{AL}^0} \tag{6}$$

However the simplified model above is only valid for physical absorption. To account for chemical absorption some modifications needs to be made [6].

The following equation describes the mass transfer rate within the liquid film where a reaction might occur:

$$N_A = E \cdot k_{AL} \cdot (C_{Ai} - C_{AL}) \tag{7}$$

where: $k_{AL} = \frac{D_{AL}}{\delta_L}$

The newly introduced factor E is often referred to as the enhancement factor. It is a number between unity and infinity and it corresponds to the number of times higher the mass transfer becomes because of the reaction. Simplified, this can easily be explained as when the reaction occurs within the liquid film, this lowers the concentration of component A in the film thus increasing the driving force. The enhancement factor is defined as the ratio between the rate of absorption of a gas into the reactive solvent and the rate of the physical process at identical process conditions. Equation 8 describes this ratio [7, 8].

$$E = \frac{N_A}{N_A^0} \tag{8}$$

To decide what the enhancement factor will be for this system it requires some understanding of the reactions that takes place. The following reaction mechanism, where $R - NH_2$, represent the amine, describes the full reaction in the absorber:

$$CO_2(g) \leftrightarrow CO_2(sol) \tag{9}$$

$$CO_2(sol) + R - NH_2(sol) \leftrightarrow R - NH - COOH(sol) \tag{10}$$

$$R - NH - COOH(sol) + R - NH_2(sol) \leftrightarrow R - NH_3^+ \, R - NH - COO^-(sol) \tag{11}$$

$$R - NH_3^+ \, R - NH - COO^-(sol) \leftrightarrow R - NH_3^+ \, R - NH - COO^-(s) \tag{12}$$

As can be seen in the reactions above, the carbon dioxide is first absorbed into the solvent as can be seen in reaction 9, which was previously described using the film model theory. Then it reacts with the amine to form a zwitterion in reaction 10. This zwitterion bonds with another amine to form a carbamate in reaction 11. In an inorganic solvent this carbamate is insoluble and will form precipitate in the solution as can be seen in reaction 12 [5].

Forming of precipitate

The factor that separates this method from the one currently in commercial use is the forming of a precipitate. To be able to build an experimental setup it is crucial to understand this phenomenon.

In an aqueous solution AMP forms a bicarbonate. If an organic solvent such as N-methyl-2-pyrrolidone (NMP) or triethylene glycol dimethyl ether (TEGDME) is used, the AMP and CO_2 will instead form an unstable carbamate, as can be seen in reaction 12 above. The low stability of this formed carbamate is a consequence of the steric hindrance. However this is beneficial when it comes to the regeneration because it allows for regeneration/reversal of equilibrium at a lower temperature. This regeneration can hopefully be achieved at a temperature of 70-90°C, where excess low grade heat is often available. Where it is not available, there will still be an economic gain, since the low grade heat is less expensive [9].

If the different concentrations are carefully chosen, it could be possible to create a system where the carbamate will form precipitate, which can be separate from the solvent. This separation of precipitate from the rest of the solvent will allow for less energy to be used, since it is no longer necessary to heat all of the solvent.

Regeneration

The regeneration can be regarded as the most important stage for energy efficiency as it is a very energy intensive stage in the process. Changes within the regeneration will have great impact on the overall energy efficiency.

Today the entire solvent is heated in the stripper column as described previously in the section about MDEA/PZ absorption. By implementing the AMP technology and by separating the formed precipitate from the organic solvent, a smaller amount of regeneration energy might be needed. Note that extra energy might need to be supplied in the separation unit of choice. There will therefore be a trade-off between the degree of separation and the allowed amount of required regeneration energy [10].

Regeneration of the AMP carbamate requires reversal of the absorption and chemical reaction, therefore the solvent/precipitate needs to be heated. Reducing the pressure will also favor desorption. Due to the steric hinder of the AMP carbamate desorption could be possible at lower temperatures. If it is possible at between 70-90°C, large energy savings could be done, since low grade heat often at these temperatures is available. This would also yield economic savings since there might not be any need for live steam to be supplied to the process [9].

2.2 Separation of AMP carbamate and solvent

It is very common within the chemical industry that a wanted solid is suspended in a liquid media. Suspending a solid in a liquid makes transport easier since it can be pumped and it is also easier to heat and cool.

However at some point of the process it is important to separate the solid product from the transport media. There are many different ways of doing this. The main methods are:

- Sedimentation
- Filtration
- Centrifugal separation

Figure 10 below is a summary of the most common separation processes and when they are applicable.

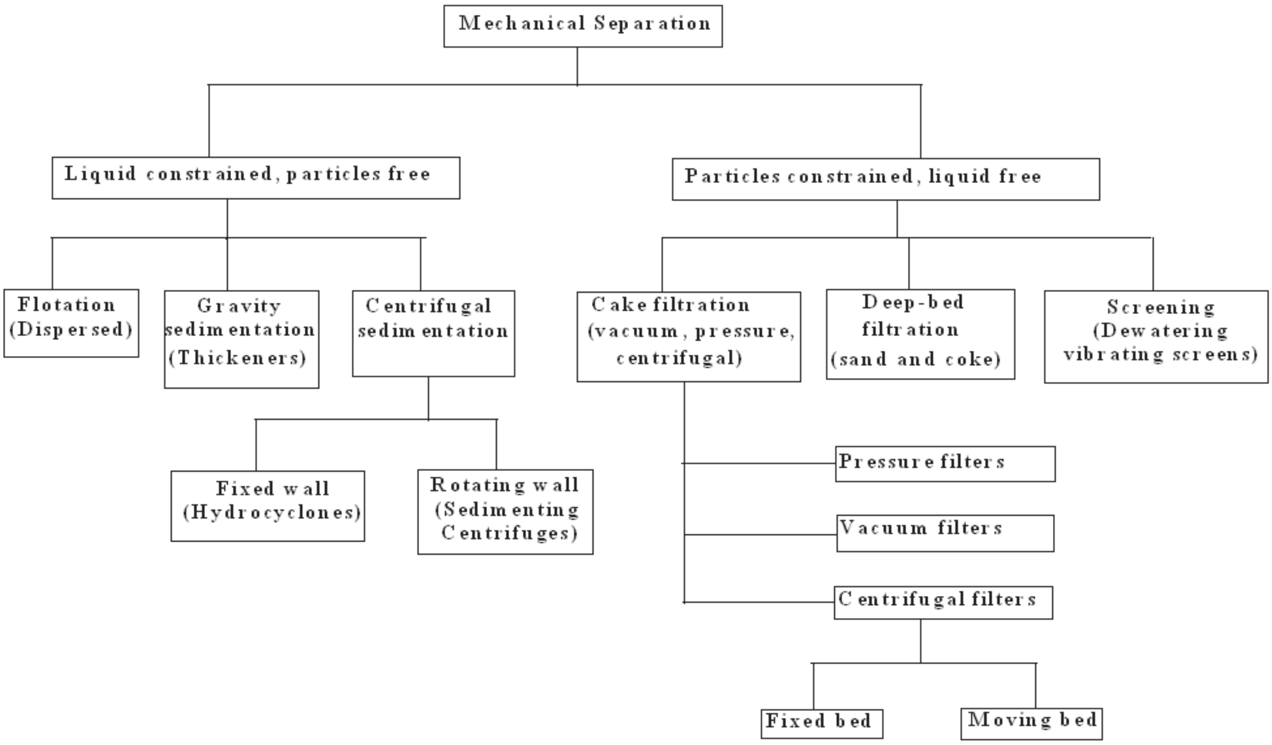

Figure 10. Summary of different solid-liquid separation methods.

This chapter will summarize the different options when it comes to liquid-solid separation. The summary will go through different unit operations, with focus on continuous separation units. There are many batch and semi batch operations, however since this report focuses on continuous processing they will be excluded here.

2.2.1 Sedimentation

Sedimentation is a method of separation that uses the difference in density of the solid and liquid. This difference allows for the solid to settle by gravity through the liquid. A sediment of a highly concentrated sludge will form and can be separated from the transport media [11].

Thickeners and clarifiers

The thickener is an industrial separation unit that uses sedimentation. A thickener generally consist of a large cylindrical vessel equipped with a slowly rotating rake at the bottom. The feed is introduced at the center of the cylinder and well below the surface at an intermediate height to prevent that the slurry exits the tank without separation. The heavy particles settle to the bottom where the rake forces the concentrated liquid to the outlet. The clear liquid at the top exits the tank via an overflow. A clarifier operates in the same manner [12, 13].

The main difference between thickeners and clarifiers is the wanted product. For a thickener the wanted product is the thick, highly concentrated slurry. For a clarifier the wanted product is the clear liquid [12, 13].

Advantages with thickeners and clarifiers:

- Effective solid-liquid separation.
- Can be used for a variety of liquid-solid separations.

Disadvantages with thickeners and clarifiers:

- Ineffective at small scale.
- Large investment cost.
- Large physical footprint.

2.2.2 Filtration

Filtration is a method that uses the size of the particles as the mean of separation. The slurry is often pumped over a porous filter, which allows for the liquid to pass through but not the solid. The solid is then removed from the filter. How the removal is carried out depends on which method of filtration is used [11].

Rotary drum filter

A drum filter consists of a hollow rotating drum, which is submerged into the slurry. A vacuum pump creates a suction that forces the liquid in to the center of the drum. The solid particles end up on the surface of the drum since they cannot permeate. The solids create a cake which follows the drums rotation. The cake is then washed to remove excess solvent. After the cake has been washed, it is removed by a knife. A simple description of the drum filter can be seen in Figure 11 below [11, 14, 15].

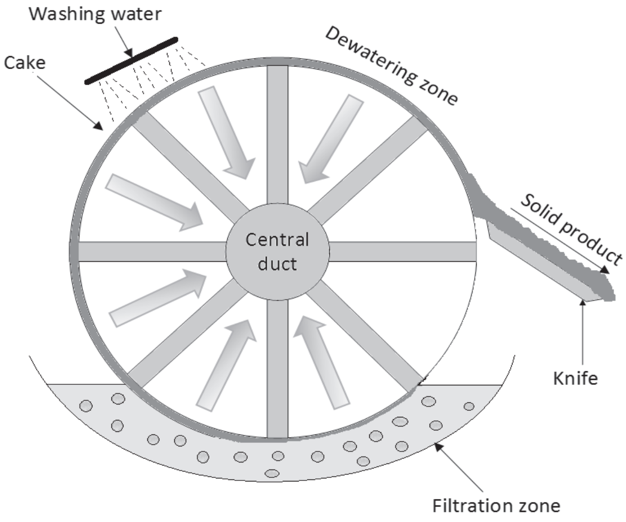

Figure 11. Rotary drum filter.

Belt filter

A belt filter is another method that is very similar to the drum filter previously described. Instead of using a drum, the belt filter uses a filter cloth that rotates using rollers. The cake is distributed onto the rotating cloth. A suction box is positioned under the cloth, creating a vacuum, which sucks the filtrate through the filter cloth, leaving the cake on the cloth. The cake follows the rotation and similar to the rotary drum, the cake is often washed in a washing zone and later dried with a steam box, before being scraped off of the cloth. The filter cloth is then washed to remove any fouling and to secure efficient filtration. Figure 12 below shows a picture of a simplified belt filter [11, 14, 15].

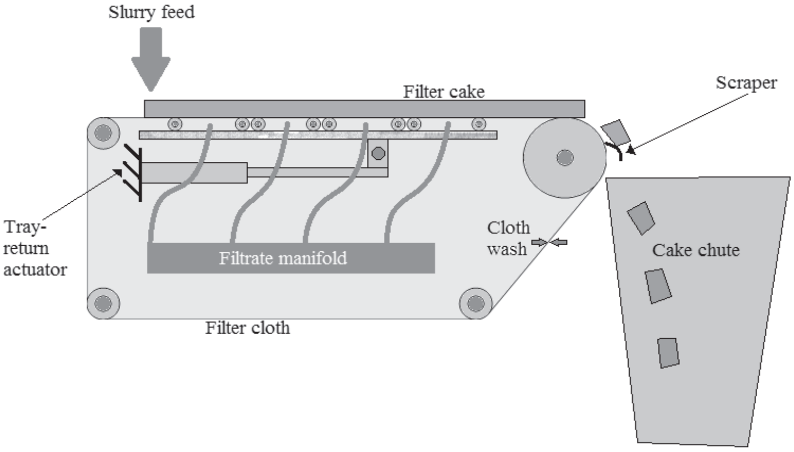

Figure 12. Belt filter.

Advantages with rotary drum and belt filters:

- Flexibility in choice of cake thickness, washing time and drying time.
- Effective on handling heavy, dense solids.
- Allows thorough flooding of cake with wash.

Disadvantages with rotary drum and belt filters:

- Large investment.
- Large footprint.
- Difficult to enclose for hazardous applications.

Wet screening

Screening is another filtration/separation method that uses the size difference for separation. Screening basically means that there is a screen with small holes or apertures, through which the liquid in this case can pass and not the particles of interest [16].

In principle a low feed and a long screening time is necessary for efficient separation. However from an economic standpoint it is necessary with a high feed and low throughput time. There is an apparent trade-off between the efficiency and the economic viewpoint [16].

With a high feed rate a layer of slurry will form on top of the screen. For efficient separation to occur, the liquid at the top of the slurry layer will have to travel through the layer, down to the screen, in order to have the possibility for permeation [16].

Another factor affecting the separation is the shape of the particles. The particles are seldom completely spherical. When an irregular particle meets the aperture, its permeation depends on which permutation it has compared to the aperture. The angle of approach is also important. The most efficient way is if the particle approaches the screen perpendicular, since it then can "see" more of the hole. However this is only an issue when separating differently sized particles and not only one liquid from one kind of particle [16].

To solve the issues above and make the screening more efficient overall, many screening apparatuses has been equipped with vibrators. This vibration throws the particles away from the screen, allowing for movement within the slurry layer. This vibration can be used to transport the slurry forward or to prolong the residence time [16].

It should be noted that screening mainly targets feed streams with a variety of particles, where the mission is to selectively separate the different sized particles. For this application, where there is one type of particle that should be removed from a solvent, it might not be the best alternative [16].

Advantages with screening:

- Continuous operation.
- High capacity.
- Low maintenance cost.

Disadvantages with screening:

- Blinding/clogging reduces efficiency.
- Low effectivity on moist, sticky or irregularly shaped particles.

2.2.3 Centrifugal separation

Centrifugal separation is a method that uses the inertia of the particles as they are subjected to a centrifugal force to separate the solid from the fluid. Centrifuges can be divided into two main classes [13, 17]:

- Sedimentation centrifuges: Separation depends on difference in density between the solid and the liquid.
- Filtration centrifuges: Uses filtration together with centrifugal force to separate the liquid and the solid.

The choice of method depends completely on the properties of the feed and the product requirements. Table 1 below summarizes the different properties of the two main types of centrifuges [13].

Table 1. Comparison between sedimentation and filtration centrifuges.

Factor	Sedimentation	Filtration
Solid size, fine		x
Solid size, >150 µm	x	
Compressible cake	x	
Open cake		x
Dry cake required		x
High filtrate clarity	x	
Crystal breakage problems		x

A general rule of thumb is that sedimentation centrifuges are used if the wanted product is a clear liquid. Filtration centrifuges are to be used if the wanted product is a pure, dry solid [13].

These two classes of centrifuges can be divided further depending on the method of discharge.

Sedimentation centrifuges - Decanter centrifuge

The decanter centrifuge is a continuous version of the scroll discharge centrifuge. The decanter consists of a conveyer screw inside of a rotating bowl. The feed enters through a concentric tube and is fed to the bowl somewhere in the middle. The shape of the housing together with the centrifugal force, forces the liquid to one side of the bowl, where it is discharged. The solids on the other hand are transported by a helical screw to the other side where it is discharged. This can be seen in Figure 13 below [13, 17]:

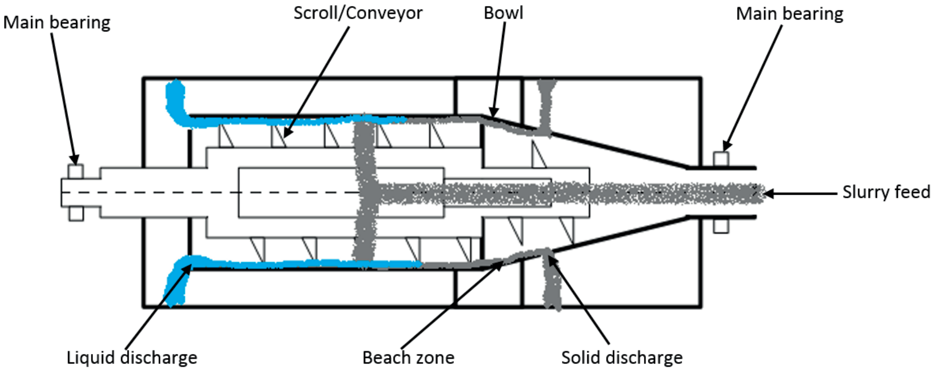

Figure 13. Decanter centrifuge.

Filtration centrifuges - Pusher centrifuge

The pusher centrifuge uses the filtration method. The centrifuge, as can be seen in Figure 14, consists of a rotating bowl. The feed is introduced via a funnel to the center of the bowl. The liquid passes the perforated bowl, but the thicker solids will stay and create a cake on the bowl. The cake is pushed forward by a pusher arm. When the pusher arm later retracts, this will allow for new cake to form on the bowl. The pusher arm pushes the new cake forward and this cycle is repeated continuously. The pusher centrifuge can also be equipped with spray nozzles to wash the cake after it has been pushed forward, to remove leftover solvent. This is usually done with water. Note that it is important to keep the temperature of the washing fluid low. If the cake dissolves, this will ruin the separation [11, 13, 17].

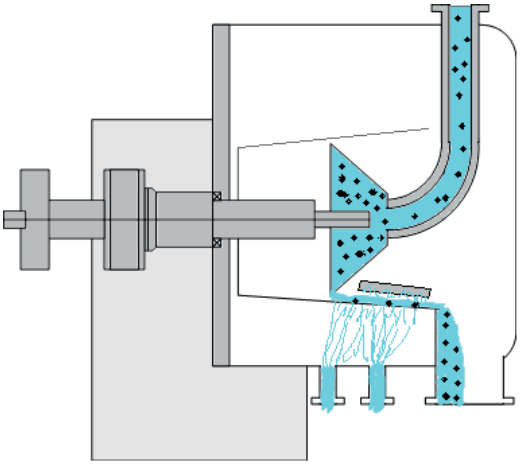

Figure 14. Pusher Centrifuge.

Hydrocyclone

When dividing centrifuges into classes it is also possible to classify them by active or passive centrifugation. The centrifuges above are all active centrifuges, since they have rotating parts to create the centrifugal force necessary for the separation.

The hydrocyclone uses passive centrifugation, as there are no rotating parts in the hydrocyclone. The cyclone consists of a static conical housing, is the difference between the cyclone and other centrifuges. The centrifugal force is created by a pump that launches the fluid into the cyclone. This force together with the conical shape of the housing creates an updraft force, forcing the liquid through a tube, usually called the vortex finder, to the overflow. The solid particles are heavier than the liquid and settles to the bottom of the tube, where there is an outlet. Figure 15 below describes a hydrocyclone with the necessary parts and the path of flow [11, 13, 18].

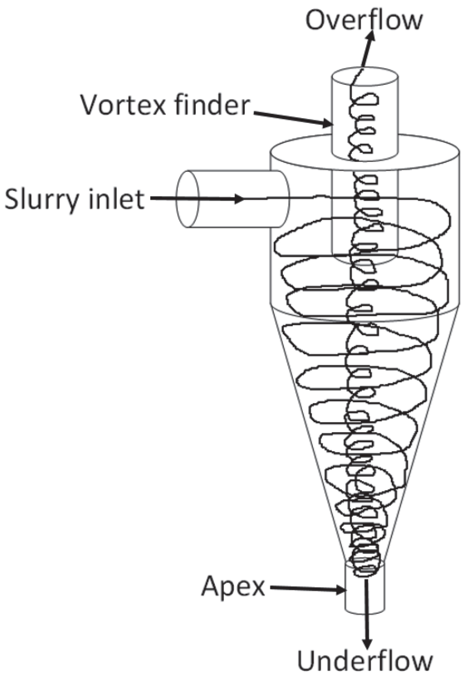

Figure 15. Hydrocyclone.

The list below lists some advantages and disadvantages with the hydrocyclone [18].

Advantages:

- Low capital cost.
- High efficiency for 5-200 µm particles.
- High volume flowrate.
- No moving parts – reduced wear.
- Close to no downtime for maintenance or recovery.
- Versatile operation.
- Small footprint relative to other separation units.
- Operation possible for wide range of temperature and pressure.

Disadvantages:

- Reduced efficiency at less-than-capacity flow.
- Difficult to separate substances of similar densities.
- Can not handle viscous flow.
- Extremely high velocities cause abrasive wear.
- Impossible to create completely dry underflow.
- Clogging of dust in the outlet is common.

3 Method

To be able to provide a proof-of-concept for the investigated absorption system, an experimental setup needs to be built. This section describes the theory behind the designing of the unit operations necessary.

3.1 Experimental setup

Figure 16 below is a simplified overview of the experimental setup that has been built in this project. The thought process behind and specific details of the equipment are described in the following sections for all of the unit operations.

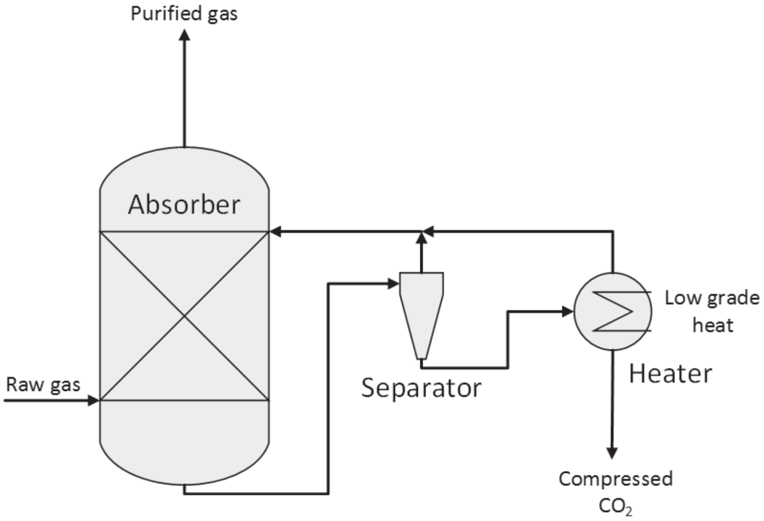

Figure 16. Simplified overview of the experimental setup.

3.1.1 Absorption column

Theory behind designing an absorption column

The purpose of this section is to give a deeper understanding of how the designing of an absorption column is carried out. Before performing the following steps it is important that some assumptions and pre-requisites have been set up [19]:

- The gas has to be specified, where the flow-rate (Q_c) and the concentration of pollutant (C_{Ab}) are known. The assumption that the concentration of pollutant A is low enough to not interfere with the gas-flow after removal.
- The absorption takes place in a counter-current packed column.
- The reaction that occurs is irreversible and of second order. The reaction only occurs within the liquid.
- The calculations are based on the two-film theory.

The first step is to decide which packing to use. When this is decided the geometric area, which is specific for the packing, is known.

The second step is to decide the liquid velocity. The liquid velocity is important since it is in direct correlation with the degree of wetting. The degree of wetting is in turn connected to the specific mass transfer area, where the absorption will take place. A superficial liquid velocity of 0.002 m/s gives a wetting efficiency of about 80 %. Note that this velocity is based on experiments using water as the liquid. For other solvents, the velocity will differ [19].

The true mass transfer area for the packing can then be calculated by multiplying the wetting efficiency and the geometric area.

After these steps there is a standard route to calculate the rest of the parameters necessary for the column design. However these steps were not possible to follow in this project. The only known value before the column was designed was the pump and thereby the liquid flowrate. The liquid flowrate could be used to calculate the cross-sectional area of the column using the following equation:

$$Q_L = V_{0L} \cdot A_{column} \tag{13}$$

To determine the gas velocity, several aspects needs to be taken into account. Firstly it is important to grasp a term called flooding. Flooding is a phenomenon that occur when the gas velocity is too high, causing the liquid to change direction and following the gas upwards in the column. The conditions at which this occur is of course depending on factors like the pressure in the column and what liquid is used.

With an aqueous system at atmospheric pressure, the gas velocity at flooding can be calculated using the following equation:

$$(V_{OG})_F = \left(\frac{5}{\sqrt{a_g}}\right) \cdot \ln\left(\frac{2}{3 \cdot V_{0L} \cdot \sqrt{a_g}}\right) \tag{14}$$

A general rule of thumb is that 60% of the velocity above is used in a full size column.

The next step will be to focus on the reaction mechanism. The simplest case would be an irreversible, one-reaction system. The reaction formula for this case looks like this:

$$A + bB \rightarrow P \tag{15}$$

Where A is the pollutant, B is the absorbent and b is the stoichiometric coefficient for the reaction of A and B. This is however not the case for all reactions and changes needs to be done for different systems.

To later be able to choose a feed rate of absorber solution to the system, the stoichiometric ratio, SR can be used.

$$SR = \frac{Q_{L0} \cdot C_{B0}}{Q_G \cdot C_{Ab} \cdot b} \tag{16}$$

When the stoichiometric ratio has been defined, the liquid flow rate, Q_{L0} can be calculated with the following expression:

$$Q_{L0} = SR \cdot Q_G \cdot b \cdot \left(\frac{C_{Ab}}{C_{B0}}\right) \tag{17}$$

The liquid flow rate of amine can be altered significantly depending on the concentration in the liquid absorbent.

The finals step in the design will be to decide how high the column needs to be. The following integral estimates the packing height:

$$h = \frac{G_G}{P \cdot a} \int_{p_{At}}^{P_{Ab}} \frac{dP_{Ag}}{N_A} \tag{18}$$

where:

$$G_G = V_{0G} \cdot \left(\frac{P}{R \cdot T} \right) \text{ and } P_{AG} = C_{AG} \cdot R \cdot T$$

The mass transfer rate has already been defined in the mass transfer section above to:

$$N_A = K_{AG} \cdot (P_{AG} - P_{AL}) \tag{19}$$

Where the mass transfer coefficient according to the two-film theory will be:

$$K_{AG} = \left(\frac{1}{k_{AG}} + \frac{H_A}{E \cdot k_{AL}^0} \right)^{-1} \tag{20}$$

Note also that for this method the kinetics and mass transfer coefficients are not yet specified. It is impossible to determine an exact height for the column without several assumptions. The height of the designed column is discussed more in a later section.

When the column has been designed, it is very important to see if all of the parameters are reasonable. There are several parameters above that can be altered to change the design in some ways. Note that the calculated height is only the packing height. The column itself should be made higher so that there is room for other equipment such as e.g. gas and liquid distributors. It is also common to add more height and column width as a safety [19].

Packing

An important factor for efficient absorption is the mass transfer area. In gas-liquid absorption the mass transfer area is the interface between the gas and the liquid within the column. If a gas is introduced to a column filled with solvent and no packing, the mass transfer area will be limited to the surface area of the gas bubbles that will travel through the solvent [20].

Another important factor is the residence time. If the gas would simply travel through the solvent from bottom to top, the time for the solvent to absorb the gas would be short.

If a packing is introduced to the column, this will help increase both the mass transfer area and the residence time. A packing will create many different paths within the column, so that the solvent and the gas can no longer travel straight through. The gas and solvent will have to serpentine in these tiny pathways. This will force the gas and liquid to “meet” more, hence increasing the overall mass transfer area. The same applies for the residence time. Forcing the liquid and gas to take these small paths will extend the distance from top to bottom and vice versa in the column. This will therefore also increase the residence time [20].

There are hundreds of different packings for different applications. It is common to divide packing into two main groups:

- Random packing
- Structured packing

The name random packing might be misinterpreted. The packing itself is not random. It is merely how the column is loaded with this kind of packing that is random. The packing is dumped into the column, creating a unique, randomly packed section. The shapes and sizes of the packing itself is known. This can be seen in Figure 17 [20].

Figure 17. Random packing in column.

The random packing however comes in many different shapes and sizes. A few of the different shapes are listed below [20]:

- Raschig rings
- Berl saddles
- Intalox saddles
- Super intalox saddles
- Pall rings
- Flexirings
- Raschig super rings
- Tellerettes
- Hacketts

Note that the packing listed above can come in different materials and sizes. Common packing materials are metal, ceramic, plastic and glass [20].

The structured packing consists of arranged sections that are stacked in the column. These can be designed specifically after application and column cross-sectional area. Different manufacturers have different patterns in their packing.

As mentioned above, the packing generates tiny pathways that forces the gas and liquid to take a different, longer route through the column. Making the packing smaller and more tightly packed will create more and smaller pathways, hence increasing the mass transfer area and the residence time. The downside with this is the pressure drop that will occur in the column. This pressure drop will disfavor the absorption, since the absorption is favored by higher partial pressure of the desired component. It is very important to consider this when choosing the column packing [20].

A general rule of thumb is that the size of the random packing should not exceed 1/8th of the column diameter [21].

3.1.2 Cyclone or sedimentation

After the precipitate is formed, it needs to be separated from most of the solvent for this technique to be as energy efficient as possible. In the separation section above, several different separation methods are listed and evaluated to see which would be suitable in a full scale plant. In this section the separation will occur at a lab scale, which is a bit different. All of the methods listed above are not possible to use and even if they were, some are not available at this scale.

Crystal size

To be able to choose a suitable separation method, some information about the crystals needs to be gathered. It is for example important to have information about the size of the crystals that are formed.

However the size of the crystal depends on the conditions at which the crystals form. It is therefore very difficult to perform exact measurements without the final setup. The following measurements are made on crystals formed in earlier experiments, from a different research project, in a calorimeter. The results are only used to estimate the size of the particles.

To perform the measurements, samples of crystals formed in TEGDME and NMP were examined with a microscope. The pictures taken can be seen in appendix 1. The results are summarized in Table 2 below. Note also that the measurements from this experiments were done using a hand tool on a computer. They are by no means exact and they are only used to get an idea of the crystal size.

Table 2. Approximate crystal size when formed in different solvents.

AMP Carbamate formed in	**TEGDME**	**NMP**	**TEGDME - Recrystallized**
Approximate Width (μm)	12	6.5	12
Approximate Length (μm)	14	9.3	8.8

When examining the crystals it was difficult to distinguish single crystals. The crystals seemed to lump together. One possible reason to this could be that the crystals reacted to the humidity in the air. Pictures of the lumped together crystals can also be seen in appendix 1.

Sedimentation experiment

To be able to find a suitable separation method for the lab scale setup some experimental data was also needed to be gathered. If the crystals are able to settle fast enough, sedimentation could be possible to accomplish. Therefore an experiment was planned and carried out to decide how fast the crystals settle in the solvent. The risk assessment and full method description for this experiment is attached in appendix 2.

The basic experiment followed the following plan:

- Fill test jar with solvent (TEGDME or NMP)
- Add specified amount of AMP carbamate
- Seal test jar with plastic lid
- Shake test jar
- Set down test jar
- Measure the time it takes for the crystals to settle

The purpose of this experiment was to evaluate the sedimentation of AMP carbamate in the different solvents to find a separation method for the experimental setup. If the crystals settle at a rapid pace, it would be possible to use sedimentation for the separation.

Four samples were prepared and their content is listed in Table 3 below. The crystals used were all from the same experiment, where they had formed in TEGDME. It is crystals from the same sample as the ones formed in TEGDME in the crystal size segment above.

Table 3. Sample content prepared for sedimentation experiments

Sample	TEGDME (ml)	NMP (ml)	AMP carbamate (g)
1	10	0	1.83
2	10	0	0.61
3	0	10	1.88
4	0	10	0.64

The amount of AMP carbamate added to the samples corresponds to 15 and 5 % AMP in the solvent, where all of the AMP has reacted to carbamate. The scale used for the measurement of AMP Carbamate was a Mettler AE260 DeltaRange with a readability of 0.001g. Ten tests were conducted on each sample. The sample was shaken for five seconds and then set down. The timer was started manually at the same time. When there was a visible line between the liquid and solid phase, the timer was stopped and the time recorded. The results from the tests can be seen in Table 4.

Table 4. Settling time results from sedimentation experiments

Test	**TEGDME 5 % AMP Settling time (s)**	**NMP 15 % AMP Settling time (s)**	**NMP 5 % AMP Settling time (s)**
1	31	125	20
2	31	119	17
3	28	116	25
4	25	135	26
5	25	126	22
6	28	-	25
7	24	-	30
8	25	-	26
9	25	-	26
10	30	-	25
Avg	27	124	24
Std	2.7	7.3	3.7

The average values and standard deviation can be seen in the bottom of Table 4. It should be noted that the results from these experiments are used to get an idea of the settling velocity and settling time. The deviation of the results is probably a result of human error.

The results for 15 % AMP in TEGDME were discarded since the solution was too turbid to distinguish a clear interface between the solid and liquid. Note that there are only five values for the 15 % AMP in NMP. The reason for this is that the tests were very time consuming and the realization that 15 % AMP equivalence was too much for sedimentation had already been made.

As can be seen in table 4 above, the sedimentation in NMP is slightly quicker. This is consistent with Stokes law, where the terminal velocity of a particle is driven by the density difference of the particle and the liquid surrounding the particle as well as the dynamic viscosity of the liquid.

$$v_t = \frac{g \cdot d_p^2 \cdot (\rho_p - \rho_l)}{18\mu_l} \tag{21}$$

The density of NMP is 1028 kg/m^3, which is slightly higher than for TEGDME at 986 kg/m^3. However at 20-25°C at which the experiments were conducted, the dynamic viscosity μ_l is about 0.00165 kg/m•s for NMP and around 0.00218 kg/m•s for TEGDME. This means that if the particle density is higher than about 1042 kg/m^3, which it is for this type of solid crystals, the terminal velocity will be higher in NMP. This is in line with the results from the experiments [22].

Decision on separation method

The results from the crystal measurements and the sedimentation experiments show that both sedimentation and centrifugation can be used. However after contact with hydrocyclone suppliers the liquid flow generated by the decided pump is too low for a hydrocyclone to be used. For the proof-of-concept setup, sedimentation will instead be used as the mean of separation.

3.1.3 Regenerator

The regeneration of amine is a crucial step in this process to withhold the efficiency and competitiveness of the investigated absorption system. The absorbed CO_2 needs to be desorbed for the amine to be useful again. Desorption requires that the equilibrium of the amine-CO_2 reaction is pushed to the left. This can be done by supplying heat to the slurry containing precipitate of AMP carbamate. This will let the CO_2 leave the slurry, creating a gas phase of CO_2 and a liquid phase containing some solvent and regenerated amine [5].

Theory behind designing a regenerator

Supplying heat to a media can be done in several ways. The two most common ways in industry today is either to heat with electrical energy or to exchange heat between medias of different temperatures.

The most basic heat exchanging can be described as a flux, Q, between media A and media B. This flux can be described as the amount gained or lost energy in a media. This is depicted as a factor of the mass flow, the specific heat and the temperature change. The flux can also be described with a heat transfer coefficient, a heat transfer area and the logarithmic temperature difference [22].

$$Q = w_A \cdot c_{pA} \cdot \Delta T_A = w_B \cdot c_{pB} \cdot \Delta T_B = K \cdot A \cdot \overline{\Delta T_L} \tag{22}$$

Where the logarithmic temperature difference is expressed as following:

$$\overline{\Delta T_L} = \frac{\Delta T_1 - \Delta \mathrm{T}_2}{\ln \frac{\Delta T_1}{\Delta T_2}} \tag{23}$$

The heat transfer coefficient is a combination of the two heat transfer coefficients between the fluids and the material separating the fluids together with the heat conduction in the separating material [22].

$$\frac{1}{K_h} = \frac{1}{h_1} + \frac{b_i}{\lambda_i} + \frac{1}{h_2} \tag{24}$$

This equation is valid for plane walled heat transfer with one material separating the two medias. The equation above can be adjusted depending on the geometry of the interface and the amount of materials layered in between the heat exchanging medias. The two heat transfer coefficients for the different medias needs to be estimated using dimensionless numbers. Depending on the geometry and direction of the flow, the Nusselt number can be described with a correlation between the Prandtl and Reynolds numbers [22].

4 Results & discussion

With the theory above a first draft of a possible absorption column was sketched. Since the mass transfer coefficients and the absorption rates are yet to be known, the idea was to create a column with variable height. Another criteria was the temperature of the solvent. The absorption is exothermic and therefore favored by a low temperature. To keep a low temperature throughout the column, the column can be cooled. The different segments were therefore designed with a jacket for cooling water. The design proposal can be seen in Figure 18 below.

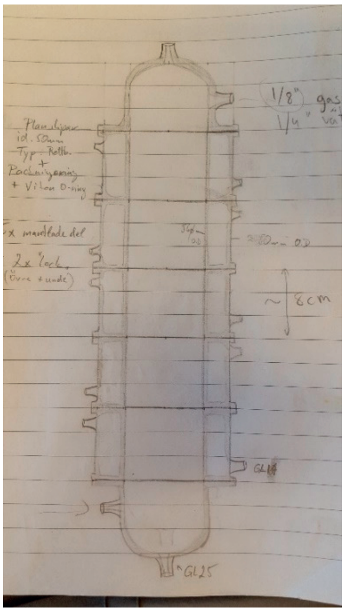

Figure 18. Design proposal of the absorption column.

The blueprint was taken to a glassblower specialized in making lab glassware. Special clamps were found for the connection between the different column segments. These clamps can be seen in Figure 19 below.

Figure 19. Plastic clamp for connecting the column segments.

The clamp is made out of Polypropylene plastic. The two parts are sealed with a Teflon gasket to make the design gas tight.

For the gas and liquid inlets and outlets flexible and leak proof connections were needed. The common screw-type connection was therefore discarded and a glass-metal connection was used instead. This connection can be seen in Figure 20.

Figure 20. Glass-metal connector for gas and liquid inlets and outlets.

The metal part of the connector above is flexible, making the installation of the column with the peripherals easier. The metal tube is compatible with the Swagelok connectors.

For the cooling water there was no need for this extra safety measure, since only water at room temperature will be circulated. For this, standard plastic GL14 connectors with screw cap were chosen. The connector for the cooling water can be seen in Figure 21 below.

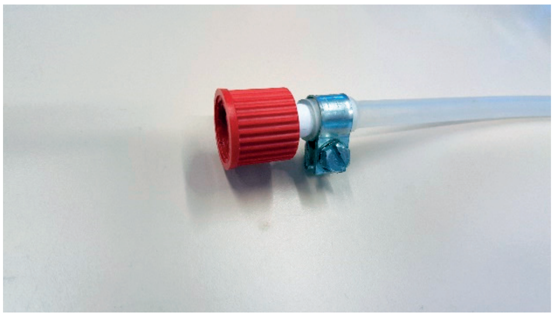

Figure 21. GL14 connector for cooling water system.

With all of the different pieces decided, the column was manufactured. It was delivered in parts as can be seen in Figure 22 and later assembled and mounted inside the fume hood as can be seen in Figure 23.

Figure 22. Parts for the absorption column, including jacketed glass segments, Teflon gaskets, plastic clamps and GL14 plastic connectors.

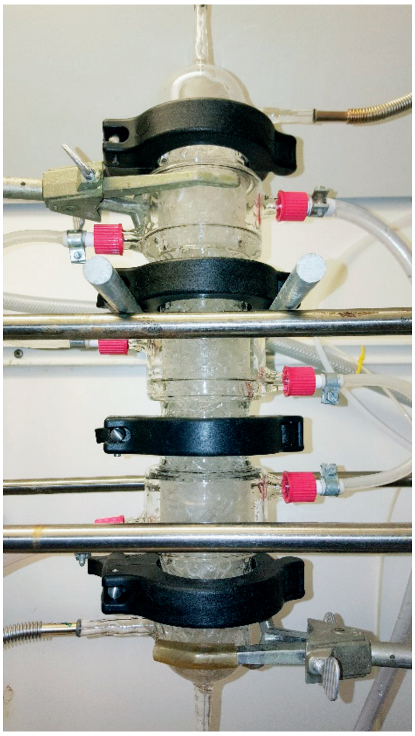

Figure 23. Absorption column assembled and mounted inside the fume hood.

The column in Figure 23 above consists of three of the five jacketed segments together with the top and bottom pieces with the glass-metal connectors. The cooling water has been installed and the column has been filled with 8mm glass Raschig rings.

Since there were no commercial hydrocyclones available at this small scale it was decided that sedimentation was the alternative to us for separation of the solids from the liquid.

The regenerator is basically a heater or a heat exchanger. The biggest issue with this is that the crystals needs to remain in the heater long enough for the reaction to be reversed. A design for a possible regenerator was sketched out and can be seen in Figure 24 below:

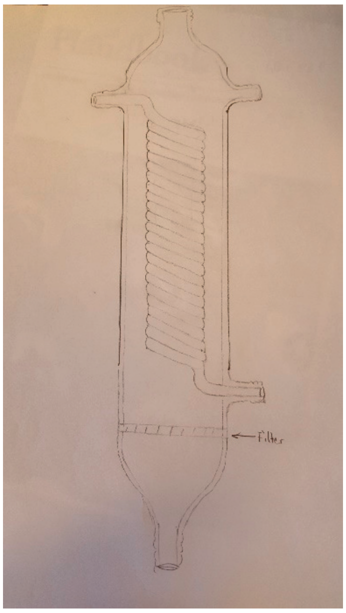

Figure 24. Design proposal of regenerator with heating coil and filter.

The filter in Figure 24 above was implemented to prolong the residence time of the crystals and to let the solvent pass through simultaneously.

Whilst searching for equipment for the separation and regeneration in the different glass storages a piece of equipment was found with possibilities for simultaneous sedimentation/separation as well as regeneration. A sketch of the equipment can be seen in Figure 25 and in Figure 26 the real equipment can be seen in the installation. The equipment consists of a flask with an implemented filter, two inlets at the top and one outlet at the bottom. When combined with the top of a washing bottle in one of the inlets, two outlets are created. One outlet within the glass tube that is submerged just under the surface of the liquid in the flask and one outlet situated at the top of the washing bottle head. In theory with this equipment it is possible to introduce the slurry from the bottom of the absorption column into the inlet at the top, left hand side of the flask. The slurry will then start to sediment as it reaches the surface in the flask. By pumping the liquid out of the submerged glass pipe, the clear liquid can be separated. The flask itself is submerged in an oil or water bath with elevated temperature. However, the entire flask is not submerged. The liquid level at the outside should be carefully chosen so that two theoretical zones are created within the flask. One sedimentation zone and one regeneration zone. When the slurry is heated at the bottom of the flask just above the filter, the reaction will be reversed and the CO_2 will leave the solvent. The CO_2 will then rise to the top of the flask to exit from the outlet in the washing bottle head. The rest of the solvent will be pumped through the filter and out of the bottom of the flask.

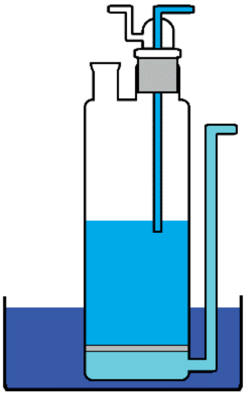

Figure 25. Equipment for simultaneous separation and regeneration.

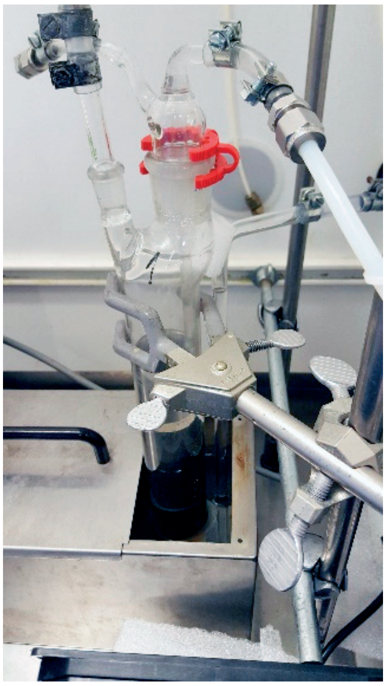

Figure 26. Separator and regenerator installed in the setup.

In Figure 26 above the regenerator/separator can be seen installed in the setup and submerged in the oil bath.

With the column and the Sep/Reg-equipment finished, the liquid system could be installed. Figure 27 below is an early picture of the system with an installed pump and tank for the solvent.

Figure 27. Early picture of the setup with pump and tank.

The setup above used one pump to pump the liquid from both of the regenerator outlets. Two valves where installed for control of the two flows. The regenerator is situated directly under the column and also lowered into the oil bath.

When test running this setup with water, multiple problems occurred. The main issue was the difficulty of controlling the liquid level in the regenerator. This level is very important for the separation to work. A decision was made to install a second pump so that one pump, pumps from the top of the regenerator and the other from the bottom. This solution immediately solved the level control difficulty. The installation can be seen in Figure 28.

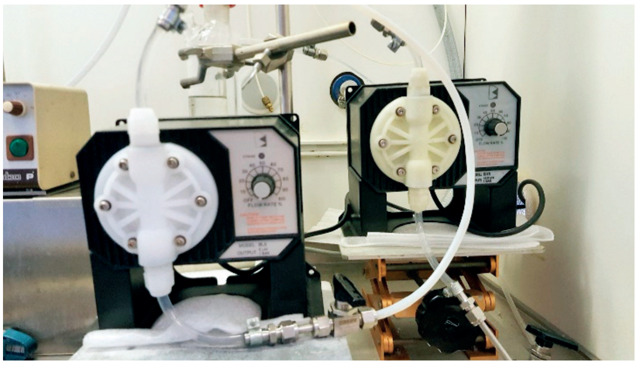

Figure 28. Two pump system for better level and flow control.

When the liquid system was up and running and had been tested with water for longer and longer periods of time to find and fix leaks, it was time to start implementing the gas system. When running the system with gas more problems occurred. The first and most apparent issue was that the gas did not travel to the top of the column, but instead took the fast route down to the regenerator and out through the CO_2 outlet. The pillar of water in the absorption column created a pressure that made the route through the Sep/Reg unit more favorable for the gas. To fix this issue a liquid trap was installed. A flexible metal tubing was placed between the column outlet and the regenerator inlet. This design can be seen in Figure 29 below:

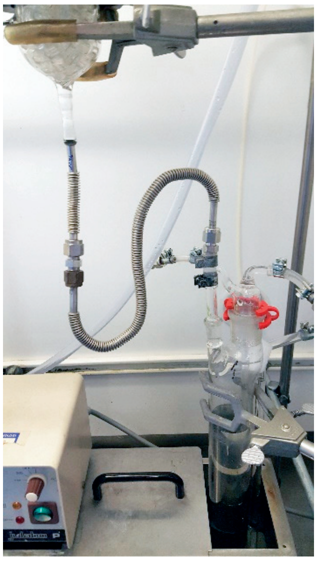

Figure 29. Water trap under column to prevent gas leakage.

This solution solved the issue with the gas leaving the column through the Sep/Reg unit. It also made the design more flexible and easy to handle and made it possible to fit the oil bath within the rack to make the design tighter.

However when the gas finally took the route it was supposed to, another issue occurred. As can be seen in the Figure 30 below, water was entrained in the gas and left the absorption column through the gas outlet. This was a major issue because when the system is operated with the organic solvent, this could be hazardous.

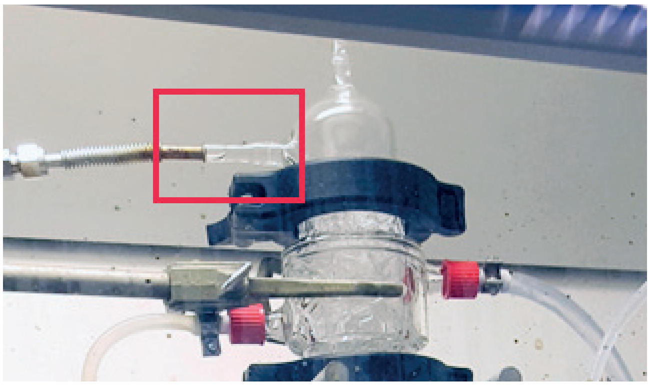

Figure 30. Water following the gas out the gas outlet.

By switching the gas outlet with the liquid inlet, a free space could be created above the liquid and the packing. This would make it close to impossible for the gas to drag liquid through the outlet and would most likely only occur with gas velocities high enough for flooding conditions. However this fix created another problem that needed to be addressed. The liquid now entered the column at the side instead of the column instead of at the top. This created an issue where the water did not fill the entire column, but instead flowed down one side of the column.

This issue was fixed with a piece of rubber tubing, with a hole and a stop. Creating a rubber tubing with the appropriate length and adding a stop to it, could let the liquid enter at the center of the column. Drilling a hole in the bottom of the rubber tubing generated the new inlet in the column. This rubber tube was pushed into the liquid inlet. The solution can be seen in Figure 31.

Figure 31. Rubber tube with stop to introduce the liquid at the center of the column.

The packing was stacked all the way up to the tube to assure that the liquid would spread evenly over the cross sectional area of the column.

Up until this point the gas used had only been nitrogen gas and it had been connected directly to the gas inlet at the bottom of the column. Now it was time to create a gas system with the possibility of mixing nitrogen and carbon dioxide at the wanted partial pressures and also the wanted flow. For this, so called Mass Flow Controllers, MFCs, were used. The MFCs can be seen in Figure 32 below, where they are installed in the setup.

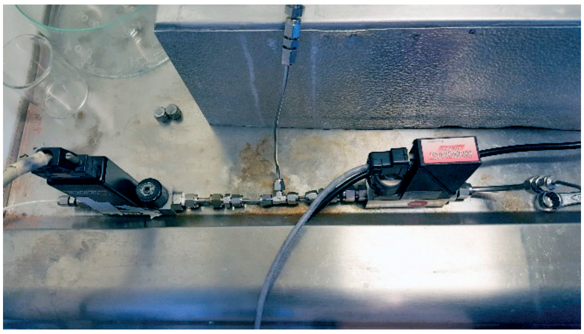

Figure 32. Mass flow controllers for N_2 and CO_2.

The MFCs were plugged into a control instrument to be able to control the flow. This was all calibrated using the software FlowDDE and FlowView from Bronkhorst via a computer. The calibration curves can be seen in appendix 3. After the calibration it is possible to control the gas flowrates using the knobs on the instrument, which can be seen in Figure 33.

Figure 33. Instrument to control the mass flowrate of the two gases.

After the two MFCs, the gas is mixed as can be seen in Figure 32 above. Then the gas should be saturated with the used solvent before entering the column. This is done by letting the gas pass through a washing bottle, filled with solvent before entering the column. The washing bottle is submerged in the same water bath as is used to cool the column, to ensure that the gas enters at the wanted temperature. This installation can be seen in Figure 34 below:

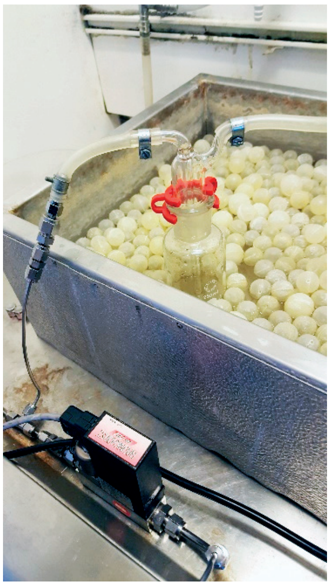

Figure 34. Washing bottle used to saturate and temperate the gas.

With the MFCs calibrated and installed, the gas system was finished. For the proof-of-concept, the entire system was completed for testing. An overview of the entire system can be seen in Figure 35 below:

Figure 35. Overview of finished the setup.

The setup can also be seen in a process flow diagram in appendix 4.

4.1 Experiments

The risk assessment and full method description for the experiments below can be seen in appendix 5.

4.1.1 Experiment 1

The initial testing with real conditions were done with 10 vol% of AMP in NMP. The inlet gas flow was set to 6 liters per minute with a CO_2 flow of 1.5 liters per minute and 4.5 liters per minute N_2. The testing was started by first circulating solvent in the system for about 30 minutes to make sure that the level and flow control could be regulated in a satisfactory manner. The testing was started with the Sep/Reg placed above the heated water bath so that the temperature of the system would stay at room temperature. Then the nitrogen gas was introduced for approximately five minutes to ensure safe operations with the gas flow. Thereafter the CO_2 flow was started and the Sep/Reg was lowered into the heated water bath at 90 degrees centigrade. The setup was run with the conditions above for about fifteen minutes. No forming of precipitate showed in the absorption column could be seen.

To speed up the process, the Sep/Reg was placed above the water bath again. The hope was to saturate the system for the precipitate to form, as the solubility of the AMP carbamate in NMP is rather high. This can be seen in the Figure 36 below. The red squares is the solubility for AMP carbamate in NMP.

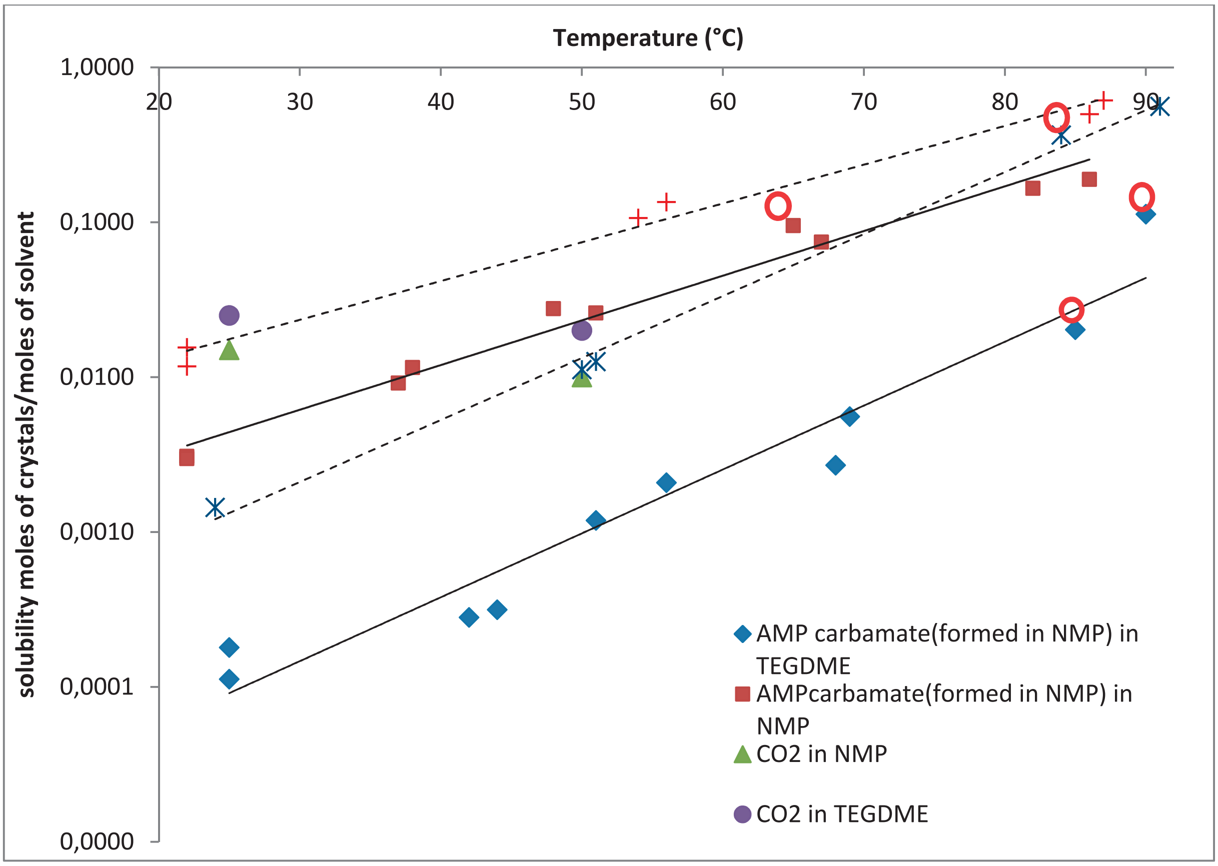

Figure 36. Solubility data for AMP carbamate in different solvents.

In Figure 36 above shows results from previous experiments within this research project.

After about ten minutes it was apparent that precipitate was forming in the absorption and the solvent was getting more and more turbid. The Sep/Reg was then lowered into the oil bath again to start the regeneration. At 90 degrees C the AMP carbamate released its CO_2 within the regenerator. However it was apparent regeneration did not occur at a fast enough rate, since crystals accumulated at the bottom of the Sep/Reg. The CO_2 inlet flow was therefore shut down to see if the system could be regenerated and at which temperatures it was possible to do so. At 90°C the CO_2 left the solvent, at what seemed to be a rapid pace. Bubbles could clearly be seen to be formed and gas was leaving the regenerator. The slurry in the Reg/Sep was getting clear again as a result of the regeneration. The temperature of the water bath and Sep/Reg unit was thereafter planned to be lowered further to see if it was possible to regenerate the system at a lower temperature. However, at this time the formation of a small crack in the tube at the pressure side of one of the pumps was noticed. This caused a small leak of solvent to occur where a small amount of solvent leaked out into the fume hood. The pump was turned off together with all of the equipment immediately and the first experiment was thereby terminated.

The fume hood was cleaned up, in accordance to instructions in the risk assessment. However, the system was still full of slurry. The hope was that the secondary pump could circulate the solvent and that the regeneration experiments could be continued. Therefore the secondary pump was started but the slurry was not able to circulate within the setup. As the primary pump could no longer be used this made it impossible to generate pressure high enough to move the slurry through the experimental setup.

To make further testing of the behavior of the slurry in the absorption column, the former cooling circuit of the column was used as a heater instead. The water in the former cooling bath was set to 85°C to regenerate the slurry in the column. It was clear that the slurry within the column got clearer at the points where heating occurred. The system was thereafter shut down completely and the focus thereafter would be to fix the leak and regenerate the entire solvent volume within the system before evacuating the liquid.

4.1.2 Set-back

The next day it was apparent what had caused the issue the day before as the heated solvent had dissolved the short segments of rubber tubing. All of the pieces of rubber tubing where very soft and seemingly fragile. The first crack that was noticed in the rubber tubing to the primary pump had propagated further and this had also occurred with the tubing to the second pump.

4.1.3 Experiment 2

One positive thing came out of this partially failed experiment. The washing bottle that was supposed to be filled with solvent was accidentally filled with both NMP (solvent) and AMP (amine). When the gas entered the washing bottle, the washing bottle acted as an absorption column and the solution within it absorbed the CO_2 in the incoming gas. This was most likely the reason for the delayed absorption in the previous experiment. AMP carbamate was formed and the solution became saturated and precipitate formed. As an effort to empty the column that was filled with hardened slurry, the cooling bath was used as a heater to regenerate the slurry within the column. When the water bath reached temperatures of 85 degrees at the heater, bubbles formed in the washing bottle. Regeneration occurred in the washing bottle and it happened at temperatures well below 85 degrees since the washing bottle was situated about 30 cm from the heater. Although the regeneration did not occur where it was planned to in this bonus experiment, it was possible to observe that low grade heat could be used for regeneration of the amine solvent for this application.

5 Conclusions

A working experimental setup was designed and built for the proof-of-concept. It was possible to run the setup continuously to perform experiments. The minor setback regarding the rubber tubing is not a real issue. Material problems like these occur all the time and the fix is simple; find another material that works with the solvent and rebuild the setup using this new material.

The main conclusion from the experiments is that regeneration with low grade heat below or at 90°C is possible. This was a very successful result, proving the concept of regeneration with low grade heat.

It was also proved that absorption was possible at the conditions in the first experiment, with the experimental setup. The packed column seemed to work as it was designed to, since precipitate was formed and also “transported” to the Reg/Sep. The issue with this transport occurred only after the crack in the tube, when it was impossible to generate pressure high enough for the thick slurry to circulate through the setup.

A pilot or full scale plant will need to have tubes and equipment more redundant to the chemical exposure. This would most likely not be an issue since full scale plants almost always are built with steel piping. Steel piping with chemical resistance is also common in the industry.

The poor separation caused AMP carbamate to accumulate within the setup, creating a thick slurry. If sedimentation is used, a larger container needs to be used for the precipitate to have enough time to settle. However it would be more beneficial to use a hydrocyclone for the separation, which has already been mentioned above in the method section. What is important is that the AMP carbamate should not accumulate in the system. The separation needs to be efficient enough to reduce the risk of accumulation. For the setup to be run continuously the absorption and desorption should occur at equal rates.

More optimization of the system needs to be performed before a fully continuous setup can be built. However the results from the experiments are promising for future operations. The experiments might have been failures in a sense, but the concept was definitely proven, since low grade heat is possible for regeneration of the amine.

6 Future work

The first thing on the checklist would be to find new rubber tubing, resistant to the chemical wear and the setup will be re-built with the new tubing. Since Teflon tubing is resistant to the solvent, it will be investigated further to see if it would be possible to connect them to the current pumps. If there are no good options for new rubber tubing and/or if the Teflon tubing is not compatible with the pumps, different pumps will be used instead. The best option would be if the new pumps would be compatible with Swagelok.

With the new and improved setup, new experiments can be conducted. Temperature gauges will be installed for improved overview of the regeneration. Flowmeters would be installed in both the gas outlets to be able to measure the two gas streams. The outlet gas streams could also be connected to a gas chromatograph or a mass spectrometer to perform precise measurements on the exiting gas.

The new experiments will focus on collecting data on the regeneration and more specifically at which temperatures it will be possible to run the setup continuously.

Since the separation unit didn't operate fast enough another solution should be found and implemented.

7 References

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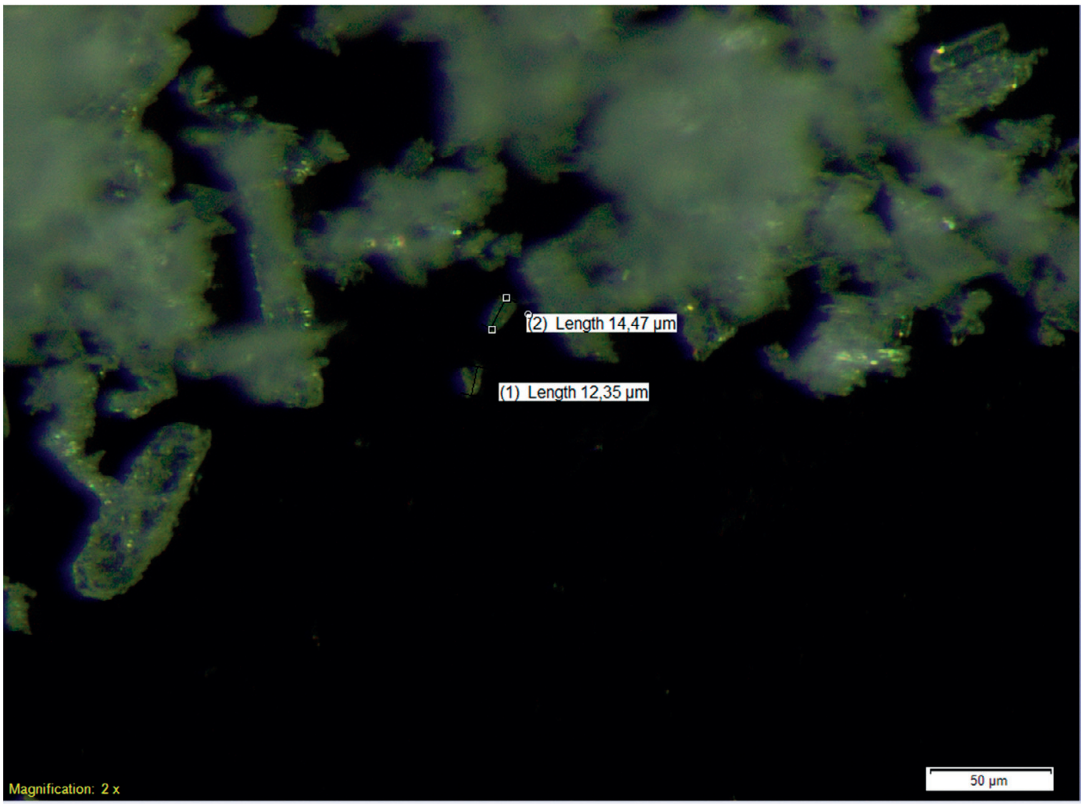
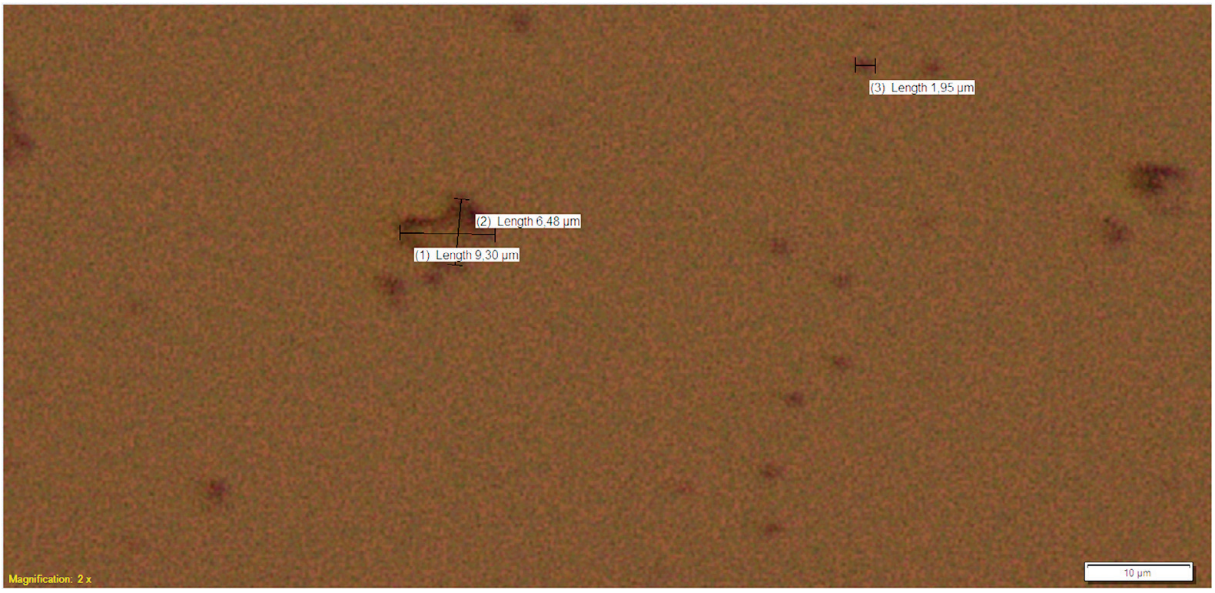
Appendix 1 - Microscope pictures

Appendix 1 consists pictures taken with a microscope on crystals formed in different solvents.

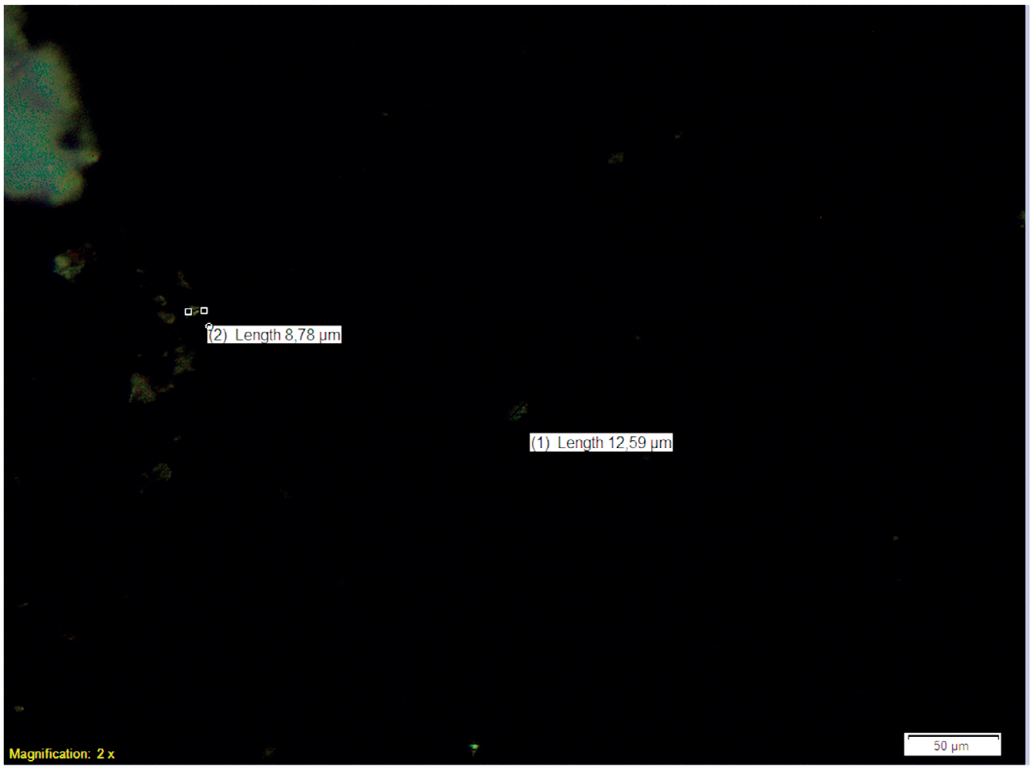
Picture of AMP-carbamate formed in TEGDME:



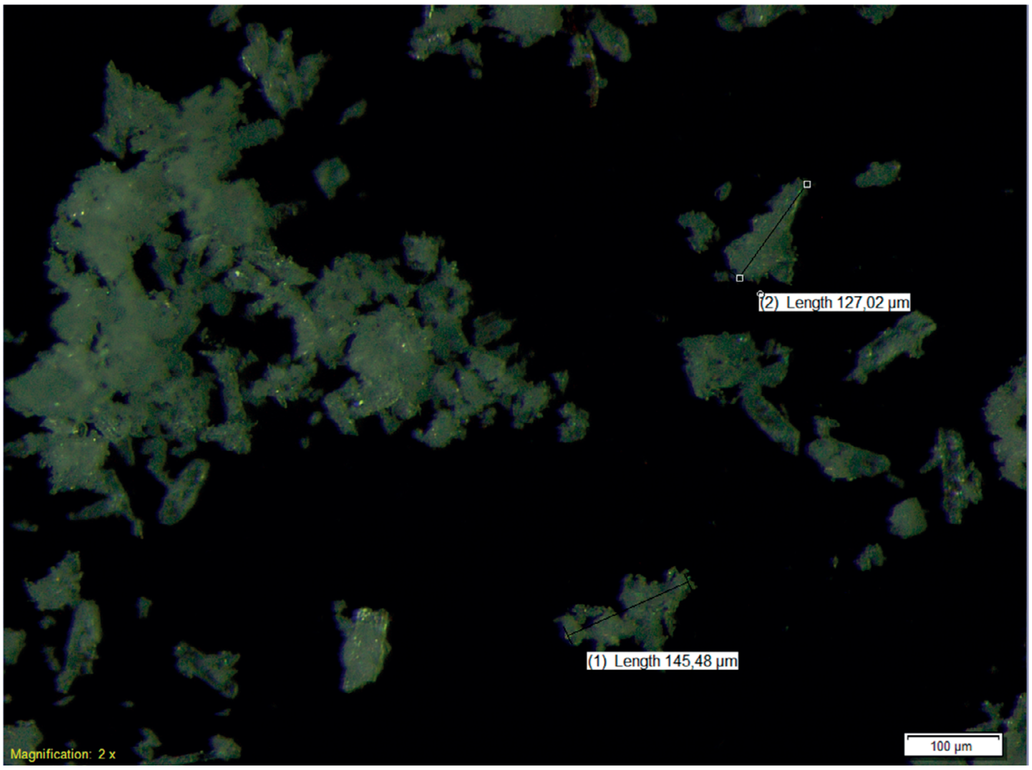
Picture of AMP-carbamate formed in NMP:



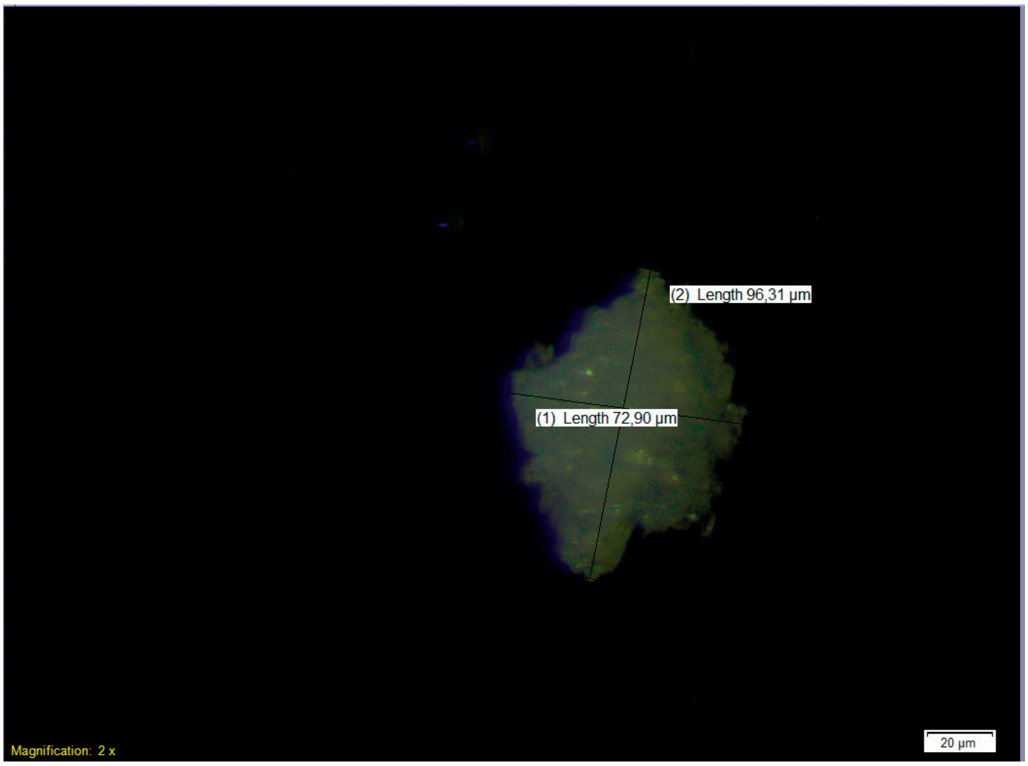
Picture of AMP-carbamate formed in TEGDME and later recrystallized:



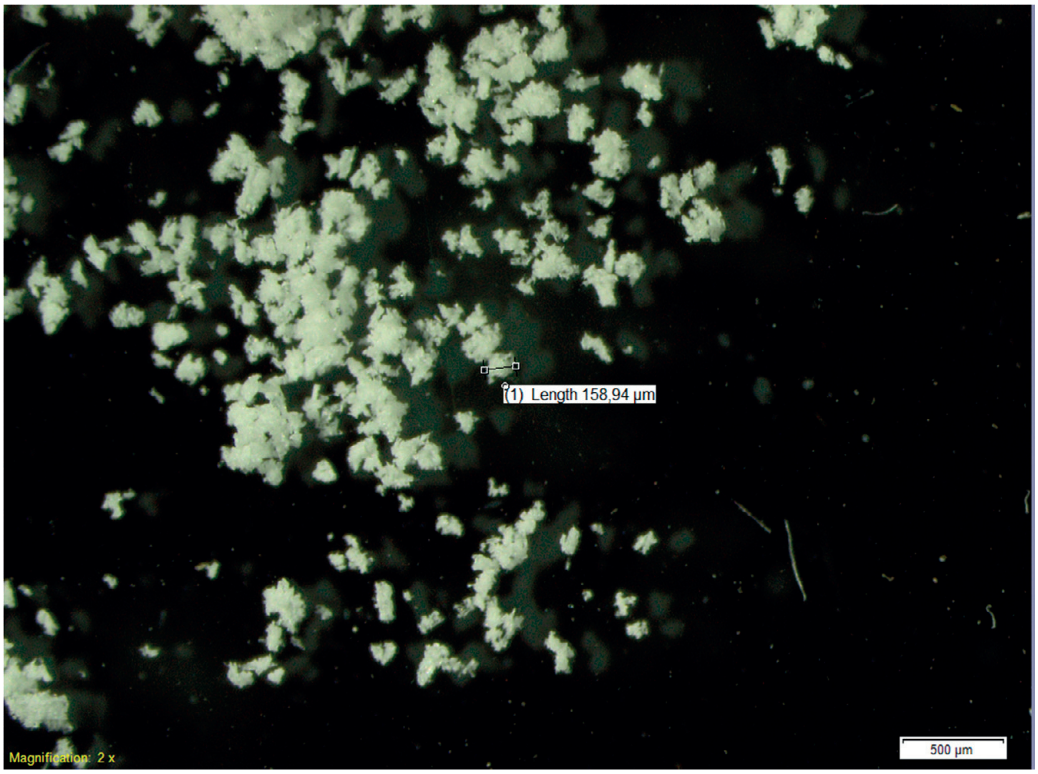
Lumped together crystals formed in TEGDME:



Lumped together crystals formed in NMP:



Lumped together crystals formed in TEGDME (recrystallized):



Appendix 2 - Risk assessment for the sedimentation experiment

Method description

The experiment for which this risk assessment is carried out includes:

Mixing AMP carbamate with TEGDME or NMP solvent and measuring the time it takes for the crystals to settle to the bottom of the beaker/container.

The experiment above will be carried out using mild conditions (Atmospheric pressure, Room temperature)

The laboratory work has been divided into the following operations:

1. Pouring solvent into beaker
2. Adding AMP crystals
3. Rapid mixing
4. Measuring time for crystals to settle
5. Discarding of solution
6. Cleaning equipment
7. Repeat experiment

Risk Assessment[1] of Laboratory Work with Chemicals (AFS 1997:10)[2]

Department/Division: Dept. of Chemical Engineering Room No: +1 O 87-93

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[1] Other regulations (e.g. AFS 2000:4 and AFS 1997:7) also include demands and information on risk assessment.

[2] If the operation is hazardous or very hazardous, the risk assessment is to be documented. This must include a description of the risk-reducing measures. It is also acceptable to refer to other documents. According to the demands in other regulations (see above) all risk assessments are to be documented!

Table 1. THE OPERATION INCLUDES HANDLING OF THE FOLLOWING CHEMICALS, MIXTURES AND SOLUTIONS

Instruction: This list should include products formed during the handling of the single compounds. CAS-number and Safety Data Sheets are to be specified when applicable. Under "Indications of danger" specify classification e.g. Very toxic, Toxic, Extremely corrosive, Corrosive, Extremely flammable, Flammable, Explosive, Oxidizing, Harmful, Moderately harmful, Irritating, Dangerous for the environment, Radioactive. State also if the chemical is Allergenic, Carcinogenic or Toxic to reproduction. If exposure limits exists, write YES and specify details in the appropriate section further down. If not, write NO.

#	Chemical/Mixture/Solution	CAS No.	Safety Data Sheet	Amount	Indications of danger	Exposure Limits
1	1-Methyl-2-Pyrrolidinone (NMP)	872-50-4	attached	ml	Irritating, Toxic to reproduction/unborn child	Yes
2	Triethylene glycol dimethyl ether (TEGDME)	112-49-2	attached	ml	Irritating, Toxic to reproduction/unborn child	N/a
3	AMP Carbamate (crystals)			g	Irritating, Harmful to aquatic life with long lasting effects	N/a

Table 2. IDENTIFICATION OF SEPARATE OPERATIONS/ACTIVITIES THAT MAY INVOLVE RISK OF ACCIDENT OR RISK TO HEALTH

Operations/activities are here listed with using the same numbering as in the Method Description. If there are circumstances or activities worthy of mentioning that cannot be directly linked to the numbering in the Method Description, these circumstances/activities should be named A, B, C etc.

#	Operation/Activity	Risk/problem	Consequence	Probability	Assessed risk	Risk-reducing measure
1	Handling glass equipment	Equipment may break and form sharp shards	Cuts	Medium/Not likely	Not very dangerous	Use of lab coat, gloves, safety goggles. Operating with care.
2	Handling metal equipment	Equipment may be sharp	Cuts	Medium/Not very likely	Not very dangerous	Use of lab coat, gloves, safety goggles. Operating with care.
3	Filling beaker with organic solvent solution	Skin exposure/ inhalation/spillage/splashing	Corrosive, Irritating, Harmful (to aquatic life with long lasting effects), Toxic (to reproduction/unborn child)	Not very likely	Hazardous	Use of lab coat, gloves, safety goggles. Operating under fume hood
4	Mixing solvent with crystals	Skin exposure/ inhalation/spillage/splashing	Corrosive, Irritating, Harmful (to aquatic life with long lasting effects), Toxic (to reproduction/unborn child)	Medium/Not likely	Moderately hazardous	Use of lab coat, gloves, safety goggles. Operating under fume hood
5	Emptying beaker after attempts	Skin exposure/ inhalation/spillage/splashing	Corrosive, Irritating, Harmful (to aquatic life with long lasting effects), Toxic (to reproduction/unborn child)	Medium/Not likely	Moderately hazardous	Use of lab coat, gloves, safety goggles. Operating under fume hood
6	Dishing of equipment	Skin exposure/ inhalation/spillage/splashing	Corrosive, Irritating, Harmful (to aquatic life with long lasting effects), Toxic (to reproduction/unborn child)	Medium/Not likely	Not very dangerous	Use of lab coat, gloves, safety goggles.

REFERENCES/ATTACHMENTS

Attachments: MSDS for: 1-Methyl-2-Pyrrolidinone (NMP), Triethylene glycol dimethyl ether (TEGDME), AMP Carbamate (salt)

Reference: Section about working under fume hood from: General Safety Regulations for Kemicentrum (Online version)

WORKING ALONE

Are rules when working alone observed? Yes

Details are to be specified in table 2 above and/or below in The Department of Chemical Engineering Extension to Lund University Template for Risk Assessment.

POWER FAILURE, WATER CUT OFF AND EVACUATION

Are risks in case of power failure/water cut off or something of the sort and interruption based on evacuation considered Yes

Details are to be specified in table 2 above and/or below in The Department of Chemical Engineering Extension to Lund University Template for Risk Assessment.

THE DEPARTMENT OF CHEMICAL ENGINEERING EXTENSION TO LUND UNIVERSITY TEMPLATE FOR RISK ASSESSMENT

Does the work include activities for which it is prohibited to work alone? **Yes**

Activities for which working alone is prohibited:

Point 3-5 above are activities prohibited to do alone since the risk is moderately hazardous to hazardous

Will substances be handled for which exposure limits exist or is there is a risk that such substances will form? **Yes**

NMP: NGV 50 ppm; 200 mg/m^3

Actions: All work involving NMP should be performed under a fume hood.

Risks and Routines due to power failure, water cut off and evacuation:

Instruction: If the risks and routines are not clearly described in table 2 write the description here.

Power Failure: In case of power failure, all of the electrical equipment will stop, including the fume hood. The fume hood should be remained closed with the beaker containing solvent within.

Water cut off: The experiment is performed without the use of running water.

Evacuation: The beaker will stay in the fume hood with a lid on.

Need for special warning signs etc. **No**

Required	Kind of information	Information on sign/kind of sign
No	Name and phone number to contact person	Anton Johansson 0767744050 Helena Svensson 0768158650
No	Danger symbols	The chemical names will be written on the equipment containing the chemical. No need for extra warning signs.
No	Special instructions to other personnel including cleaners	Do not touch the experimental setup

Comments on need for special warning signs:

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Danger symbols on apparatus and equipment

Need for emergency equipment e.g. alarms etc. **No**

Comments on need for emergency equipment:

There should be no need for emergency equipment if the safety equipment is being used.

Checking of equipment

Visual inspection of the equipment

Comments on need for personal protective gear/equipment

The laboratory worker will use the standard laboratory equipment, including: Lab coat, gloves and safety goggles. The work will also performed under fume hood. The protective gloves used need to satisfy the EN374 standard for handling of the chemicals. The goggles should be equipped with side-shields according to the EN166 standard.

Waste and handling of waste

Kind of waste expected	Plans for handling of waste
Precipitate mixed with solvent and amine	Disposal into solvent waste container

Dealing with accidents and accidental spills

Spillage will be cleaned up using paper towels if the spill is insignificant. If the spill is more than that, vermiculite will be used and later disposed in the Solvent waste container. The contaminated working area will then be cleaned with water.

If an accident occur, the laboratory worker will be taken to the hospital along with this risk assessment.

Other comments or supplemental information:

Protective gear such as gloves and goggles are necessary during the clean-up.

Are other individuals than he/she who made this risk assessment allowed to carry out the activities described? **Yes.**

Helena Svensson

SIGNATURES

Risk assessment carried out **2016-03-11**

Risk assessment valid until (maximum 3 years) **2019-03-11**

Risk assessment carried out under the supervision of the (PhD) students supervisor **Yes**

Risk assessment approved by

Name in print:

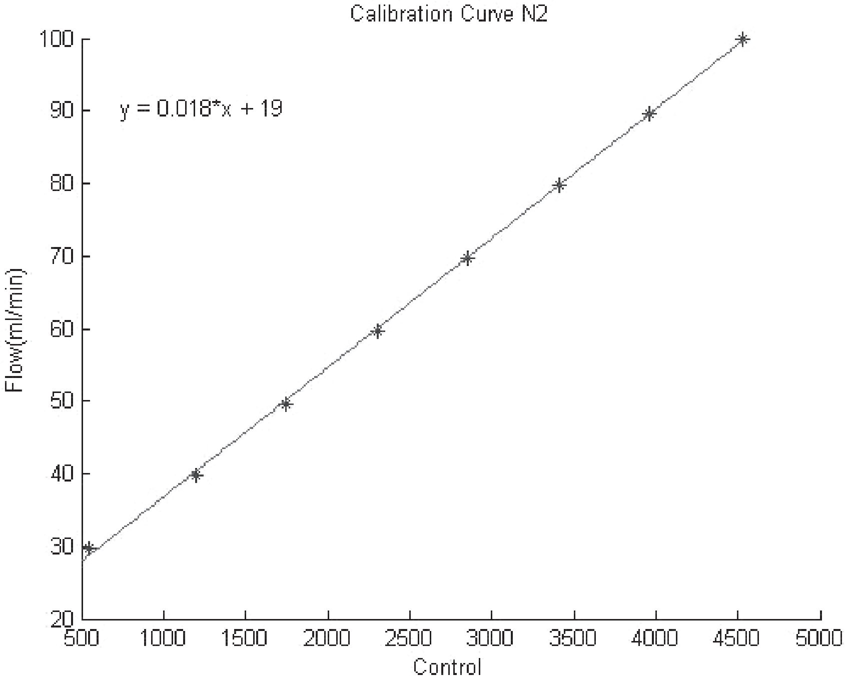
Helena Svensson (Supervisor)

Risk assessment carried out, commented and controlled by

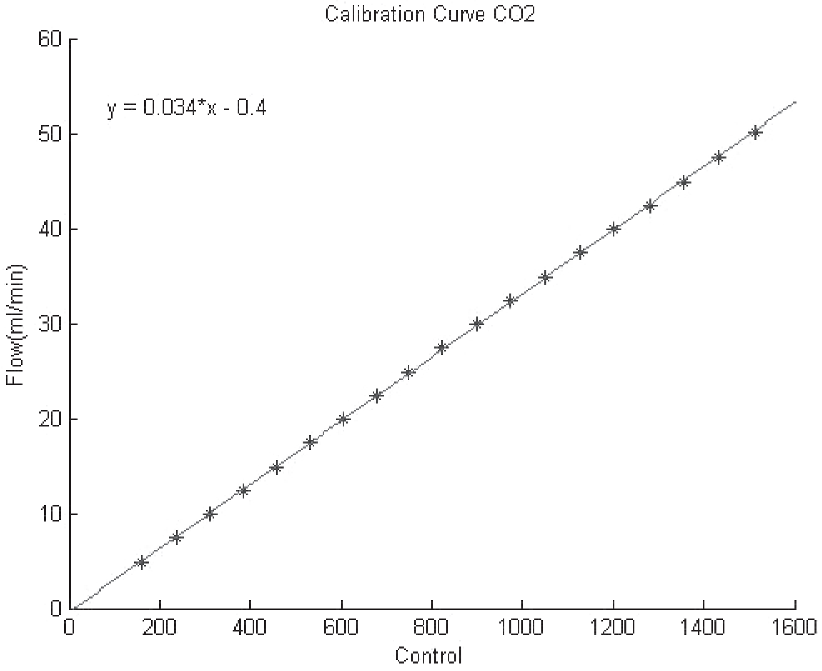
Risk assessment carried out by	Read and commented by	Risk assessment approved by
Name in print: Anton Johansson	Name in print:	Name in print:

Appendix 3 - Calibration curves for gas MFCs

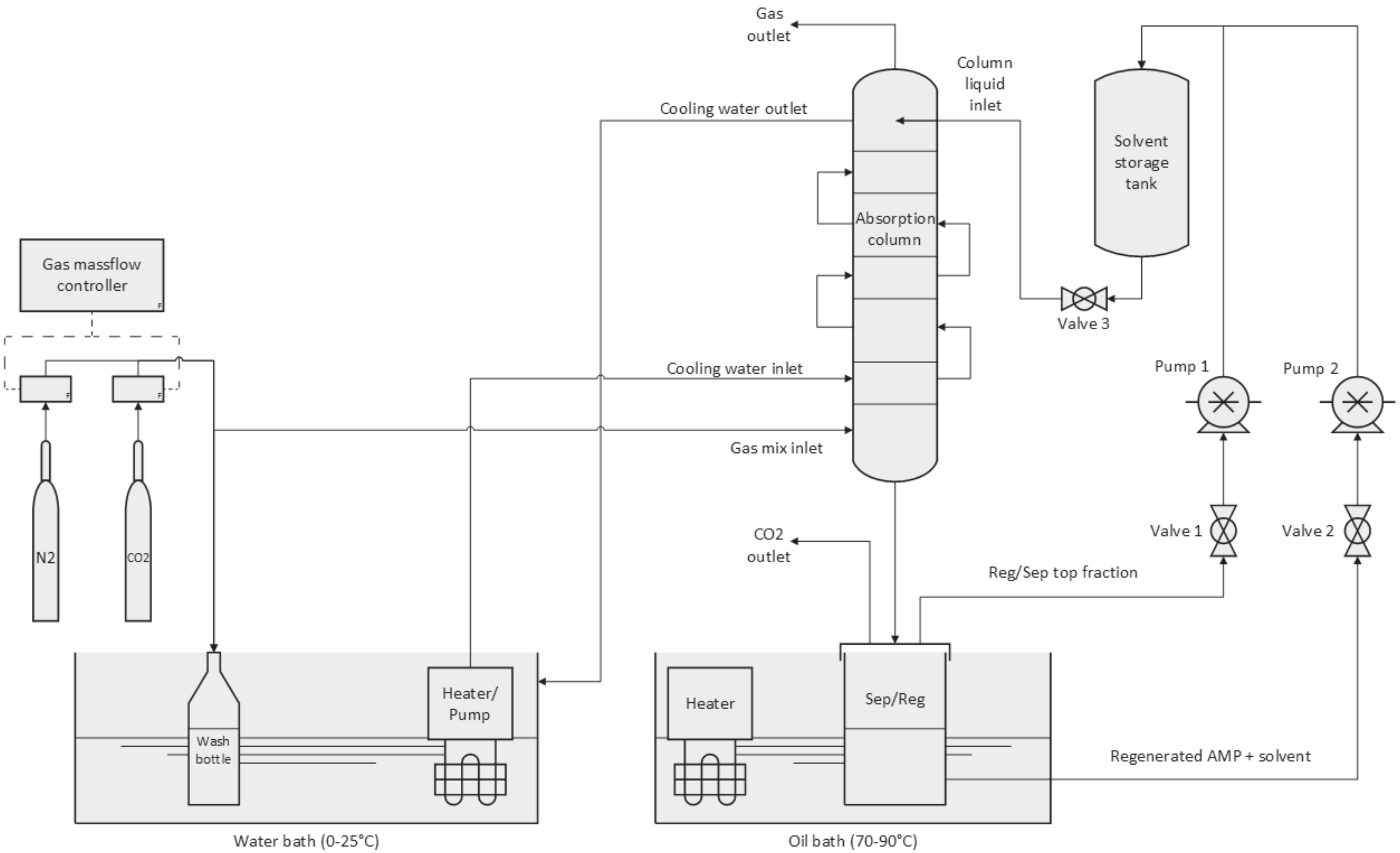
Calibration curve for N_2 inlet stream:



Calibration curve for CO_2 inlet stream:



Appendix 4 – Overview of the experimental setup



Appendix 5 - Risk assessment for the absorption

Risk assessment for the absorption:

Method description – Continuous absorption of CO_2, separation of AMP carbamate and regeneration of AMP.

The experiment for which this risk assessment is carried out includes:

- The continuous absorption of CO_2 with an amine, 2-amino-2-methyl-1-propanol (AMP), in an inorganic solvent, 1-Methyl-2-Pyrrolidinone (NMP) or Triethylene glycol dimethyl ether (TEGDME).
- The separation of the formed precipitate using a sedimentation vessel.
- The regeneration of the amine, by applying low value heat (~85°C).

The experiment above will be carried out using mild conditions (Pressure 1-3 bar, Temperature 20-90°C)

A schematic view of the process can be seen in Figure 37 below and a photo taken of the setup in Figure 38.

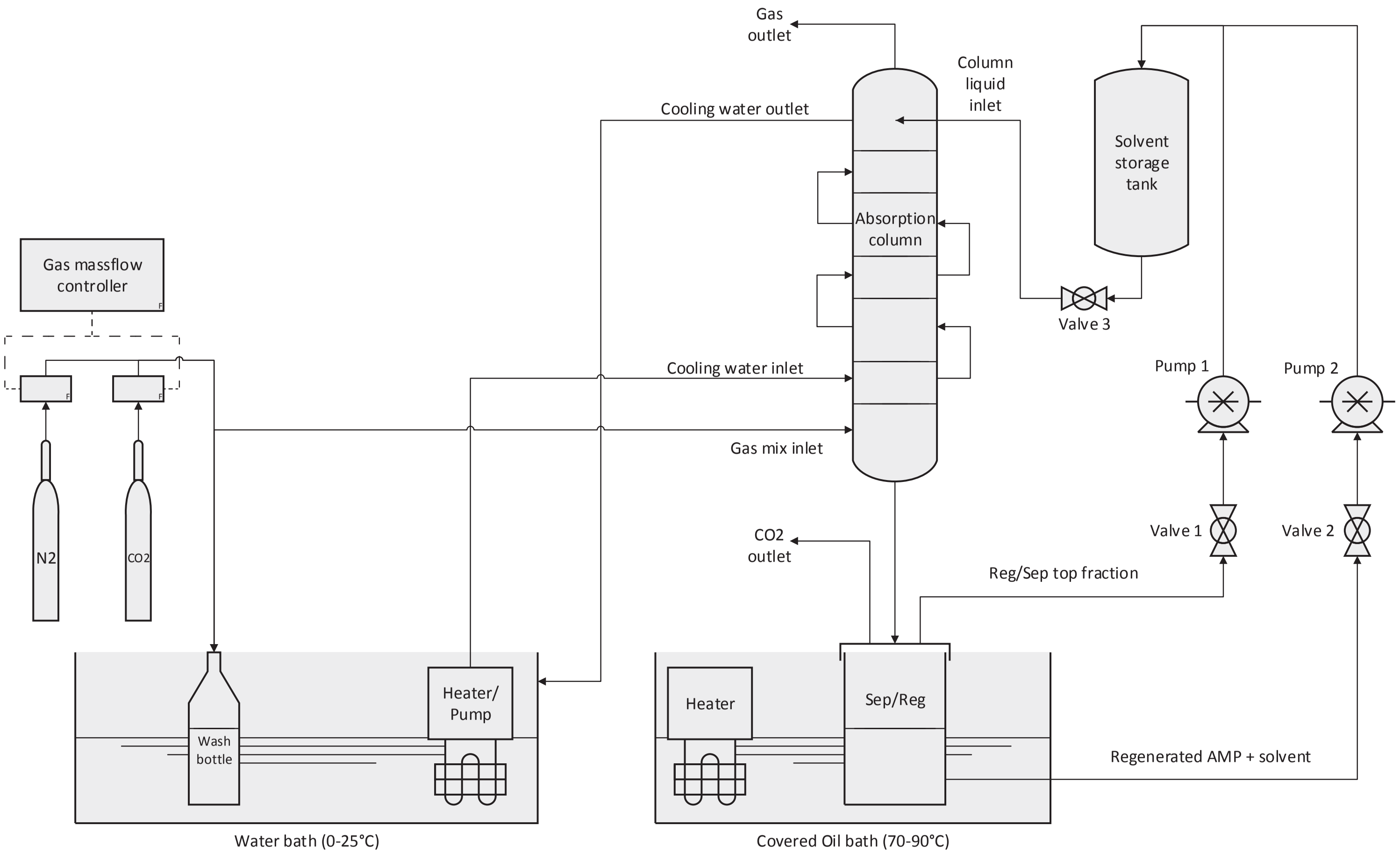


Figure 37. Schematic view of the absorption setup.

Figure 38. Absorption setup installed within the fume hood.

The laboratory work has been divided into the following operations:

1. Mixing the amine-organic solvent solution
2. Pouring the solvent solution into the gas washing bottle, which can be seen in Figure 37 above.
3. Filling the regenerator (Sep/Reg in Figure 37) flask with solution.
4. Starting the pumps, to pump the solvent into the tank, emptying the regenerator. Then repeat step 3 and 4 until correct volume is in the system.
5. Setting pumps (1 and 2) and valves (1-3) to correct settings for even flow and stable level in the regenerator.
6. Starting the water and oil bath, setting the temperatures to the wanted settings.
7. Waiting for water and oil bath to reach wanted temperature.
8. Opening the gas cylinders
9. Setting the gas flowrate (for both CO_2 and N_2)
10. Waiting for steady state
11. If regeneration is successful, the temperature in the oil bath will be lowered.
12. If not, the experiment will be terminated in the following order:
    a. Gas cylinders will be closed
    b. Pumps (1 and 2) and valves (1-3) will be closed
    c. Oil bath will be turned off
    d. Water bath will be turned off
    e. Electrical equipment will be turned off and the fume hood closed.

Emptying and washing of the system:

13. Column liquid inlet tube, located at the top of the column, will be disconnected and lead to a large beaker.
14. Pump 2 will be started and valve 2 and 3 will be opened.
15. The pump will run until system is seemingly drained, then turned off.
16. Column liquid inlet tube will be reconnected to the top of the column.
17. Regenerator will be filled with water and the regenerator bottoms pump (2) started.
18. The water will be pumped in the system for approximately 5 minutes.
19. Repeat 1-6 until system is free from solvent.
20. Solvent and AMP carbamate will be disposed in a solvent waste container.

Risk Assessment[3] of Laboratory Work with Chemicals (AFS 1997:10)[4]

Department/Division: Dept. of Chemical Engineering

Room No: +1 O 87-93

Table 1. THE OPERATION INCLUDES HANDLING OF THE FOLLOWING CHEMICALS, MIXTURES AND SOLUTIONS

Instruction: This list should include products formed during the handling of the single compounds. CAS-number and Safety Data Sheets are to be specified when applicable. Under "Indications of danger" specify classification e.g. Very toxic, Toxic, Extremely corrosive, Corrosive, Extremely flammable, Flammable, Explosive, Oxidizing, Harmful, Moderately harmful, Irritating, Dangerous for the environment, Radioactive. State also if the chemical is Allergenic, Carcinogenic or toxic to reproduction. If exposure limits exists, write YES and specify details in the appropriate section further down. If not, write NO.

#	Chemical/Mixture/Solution	CAS No.	Safety Data Sheet	Amount	Indications of danger	Exposure Limits
1	Carbon dioxide (g)	124-38-9	attached	L	Gas under pressure	Yes
2	Nitrogen (g)	7727-37-9	attached	L	Gas under pressure	No
3	2-amino-2-methyl-1-propanol (AMP)	124-68-5	attached	L	Irritating, Harmful to aquatic life with long lasting effects	No

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[3] Other regulations (e.g. AFS 2000:4 and AFS 1997:7) also include demands and information on risk assessment.

[4] If the operation is hazardous or very hazardous, the risk assessment is to be documented. This must include a description of the risk-reducing measures. It is also acceptable to refer to other documents. According to the demands in other regulations (see above) all risk assessments are to be documented!

4	1-Methyl-2-Pyrrolidinone (NMP)	872-50-4	attached	L	Irritating, Toxic to reproduction/unborn child	Yes
5	Triethylene glycol dimethyl ether (TEGDME)	112-49-2	attached	L	Irritating, Toxic to reproduction/unborn child	N/a
6	AMP Carbamate (salt)			g	Irritating, Harmful to aquatic life with long lasting effects	N/a

Table 2. IDENTIFICATION OF SEPARATE OPERATIONS/ACTIVITIES THAT MAY INVOLVE RISK OF ACCIDENT OR RISK TO HEALTH

Operations/activities are here listed with using the same numbering as in the Method Description. If there are circumstances or activities worthy of mentioning that cannot be directly linked to the numbering in the Method Description, these circumstances/activities should be named A, B, C etc.

#	Operation/Activity	Risk/problem	Consequence	Probability	Assessed risk	Risk-reducing measure
A	Handling glass equipment	Equipment may break and form sharp shards	Cuts	Not very likely	Hazardous	Use of lab coat, gloves, safety goggles. Operating with care.
B	Handling electrical equipment	Shock from electrical equipment	Electrical shock	Unlikely	Moderately Hazardous	Ensure that the electrical equipment is in good condition and is plugged in properly.

1	Preparing AMP/solvent mixture	Skin exposure/inhalation/spillage/splashing	Corrosive, Irritating, Harmful (to aquatic life with long lasting effects), Toxic (to reproduction/unborn child) - Serious	Not very likely	Hazardous	Use of lab coat, gloves, safety goggles. Operating with care and under fume hood.
2	Filling liquid into Regenerator with amine/organic solvent solution	Skin exposure/ inhalation/spillage/splashing	Corrosive, Irritating, Harmful (to aquatic life with long lasting effects), Toxic (to reproduction/unborn child) - Serious	Not very likely	Hazardous	Use of lab coat, gloves, safety goggles. Operating under fume hood
13-15	Emptying system from solvent and AMP carbamate	Skin exposure/ inhalation/spillage/splashing	Corrosive, Irritating, Harmful (to aquatic life with long lasting effects), Toxic (to reproduction/unborn child) - Serious	Not very likely	Hazardous	Use of lab coat, gloves, safety goggles. Operating under fume hood
20	Disposing waste into waste container	Skin exposure/ inhalation/spillage/splashing	Corrosive, Irritating, Harmful (to aquatic life with long lasting effects), Toxic (to reproduction/unborn child) - Serious	Possible	Hazardous	Use of lab coat, gloves, safety goggles. Operating under fume hood

REFERENCES/ATTACHMENTS

Attachments: MSDS for Carbon dioxide (gas), Nitrogen (gas), 2-amino-2-methyl-1-propanol (AMP), 1-Methyl-2-Pyrrolidinone (NMP), Triethylene glycol dimethyl ether (TEGDME), AMP Carbamate (salt)

Reference: Section about working under fume hood from: General Safety Regulations for Kemicentrum (Online version)

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WORKING ALONE

Are rules when working alone observed? **Yes**

Details are to be specified in table 2 above and/or below in The Department of Chemical Engineering Extension to Lund University Template for Risk Assessment.

POWER FAILURE, WATER CUT OFF AND EVACUATION

Are risks in case of power failure/water cut off or something of the sort and interruption based on evacuation considered Yes

Details are to be specified in table 2 above and/or below in The Department of Chemical Engineering Extension to Lund University Template for Risk Assessment.

THE DEPARTMENT OF CHEMICAL ENGINEERING EXTENSION TO LUND UNIVERSITY TEMPLATE FOR RISK ASSESSMENT

Does the work include activities for which it is prohibited to work alone? **Yes**

Activities for which working alone is prohibited:

All activities are prohibited to do alone since the risk is moderately hazardous to hazardous

Will substances be handled for which exposure limits exist or is there a risk that such substances will form? **Yes**

CO_2: NGV 5000 ppm

Actions: All gas tubes are leak tested regularly according to standard procedures (for new installations and every six months thereafter)

NMP: NGV 50 ppm; 200 mg/m^3

Actions: All work involving NMP should be performed under a fume hood.

Risks and Routines due to power failure, water cut off and evacuation:

Instruction: If the risks and routines are not clearly described in table 2 write the description here.

Power Failure: In case of power failure, all of the electrical equipment will stop, including the fume hood. To ensure that no risks occur when the power comes back, the gas flask outlets should be closed. The electrical equipment should be connected to interlocked sockets, to ensure that no risks occur when the power comes back.

Water cut off: In case of water cut off, the experiments will be terminated according to the list above. Water will be kept in a bottle in the lab for emergency washing.

Evacuation: The fume hood will be kept closed and the gas cylinders will be closed. The door to the lab should be closed. All equipment containing solvent should remain in the fume hood.

Need for special warning signs etc. **No**

Required	Kind of information	Information on sign/kind of sign
Yes	Name and phone number to contact person	Anton Johansson 0767744050 Helena Svensson 0768158650
Yes	Danger symbols	Gas tubes (gas under pressure), Harmful; Harmful to aquatic life with long lasting effect. Toxic; Toxic to reproduction/unborn child, Irritating, Corrosive
No	Special instructions to other personnel including cleaners	Do not touch the experimental setup

Comments on need for special warning signs:

Danger symbols on apparatus and equipment. The door to the lab will be equipped with a gas under pressure warning sign.

Need for emergency equipment e.g. alarms etc. **No**

Comments on need for emergency equipment:

There is no need for emergency equipment if the safety equipment is used and the safety regulations followed.

Checking of equipment

The system will be examined prior to the experiments for leaks (both gas and liquid)

The electrical equipment will also be examined so that no sparks can occur.

Comments on need for personal protective gear/equipment

The laboratory worker will use the standard laboratory equipment, including: Lab coat, gloves and safety goggles. The work will also performed under fume hood. The lab goggles need to be equipped with side-shields according to standard EN166. The gloves needs to be approved according to standard EN374.

Waste and handling of waste

Kind of waste expected	Plans for handling of waste
Used solvent and amine solution	Disposal into solvent waste container
Precipitate mixed with solvent and amine	Disposal into solvent waste container

Dealing with accidents and accidental spills

Spillage will be cleaned up using paper towels if the spill is insignificant. If the spill is larger, vermiculite will be used and later disposed in the Solvent waste container. The contaminated working area will then be cleaned with water.

If an accident occur, the laboratory worker will be taken to the hospital along with this risk assessment.

Other comments or supplemental information:

Protective gear such as gloves, goggles and lab coat are necessary during the clean-up.

Are other individuals than he/she who made this risk assessment allowed to carry out the activities described? Yes.

Helena Svensson, Meher Sanku

SIGNATURES

Risk assessment carried out: 2016-05-16

Risk assessment valid until (maximum 3 years): 2016-05-23

Risk assessment carried out under the supervision of the (Degree Project) students supervisor **Yes**

Risk assessment approved by

Name in print:

Helena Svensson (Supervisor)

Risk assessment carried out, commented and controlled by

Risk assessment carried out by	Read and commented by	Risk assessment approved by
Name in print: Anton Johansson	Name in print:	Name in print:

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