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Screening of Aqueous Solvent Systems for Post-Combustion CO2 Capture by Chemical Absorption

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Declaration of Compliance

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU)

Trondheim, June 2016

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Acknowledgment

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Abstract

The atmospheric CO_2 concentration we see today has likely not been seen before. As carbon dioxide is a strong greenhouse gas, this is a big red flag towards global warming. A higher mean temperature on earth would lead to more extreme weather, sea level rise and increased spread of infectious diseases.

The Paris Agreement, under which nearly 200 countries have committed to trying to limit the global temperature rise this century well below 2 degrees Celsius, has reaffirmed the importance of carbon capture and storage to limit carbon emissions. Absorption of carbon dioxide by amine based solvents is one of the most mature technologies in the portfolio of climate change mitigations. However, CO_2 capture is an expensive and energy demanding process, so substantial R&D is directed to reduction of operating costs and other energy saving measures.

It is therefore essential to establish a novel technology for efficient development of new carbon capture absorbents with optimal properties, and new low energy penalty solvents. In this work a rapid screening apparatus for CO_2 absorption has been applied to test absorption characteristics of amines, alkanolamines and amino acid salts.

The first objective of the research described in this thesis has been to understand the effect of ratio and molecular structure to MAPA promoted tertiary alkanolamines. Five tertiary amines, 2-diethylamino-ethanol (DEEA), triethanolamine (TEA), *N*-Butyldiethanolamine (BDEA), 2-(Dibutylamino)ethanol (EDEA) and *N-tert*-Butyldiethanolamine (t-BDEA) are considered in this work. The influence of amine alkanol groups, as well as alkyl chain structure, is investigated by systematically varying the tertiary amine and the total amine concentration. The experiments were conducted using three different 3° amine/MAPA molar ratios, 3:1, 2:1 and 1:1. The total amine concentration was kept constant at 4 mol/L. In addition the single 3° amines are run at 3M and MAPA at 1M.

The second objective was to cross-validate a model for predicting a compounds basicity, and thereby its ability to absorb carbon dioxide. The commercially available compounds selected for cross-validation are 1,2-Diaminocyclohexane (DACH), N-Benzylmethylamine (BMA), N,N-Dimethylbenzylamine (DMBA), Phenethylamine, Creatine and L-Arginine (ARG).

All screening experiments was compared to the benchmark solvent, 30 wt. % monoethanolamine (MEA). 3M and 4M MEA was used for comparison according to total

amine concentration of the blends. The effect as promotor was compared against 3M DEEA+1M MAPA.

Two liquid samples were collected from the screening experiments, one after absorption and one after stripping. The CO_2 and amine content in these samples, was determined by potensiometric titration, in order to verify the vapor/liquid mass blance. The results showed large discrepancies between liquid analysis and screening data of lean loadings, ranging from 11-513 %. Single tertiary amine systems, with low reactivity, gave the largest deviations.

The screening results indicate that the number of amine alkanol groups affect the system adversely, and lower the absorption capacity. The alkyl chain structure have small negative effect on the absorption rate, as increasing alkyl chain decrease the absorption potential. Addition of hydroxyl groups was found to decrease the absorpion capacity. MAPA is working excellent as a promoter and enhance both reaction rate as well as absorption capacity. The absorption capacity increase with increasing amount of MAPA.

The most promising tertiary amine/MAPA system was 2M DEEA+2M MAPA, with an absorption capacity of 3.31 mol CO_2/kg amine and cyclic capacity of 1.92 mol CO_2/kg amine.

The six non-alkanolamines show poor performances overall. They show various issues with foaming, vapor pressure and phase-separating. 30 wt. % BMAs absorption rate is similar to 1M MAPA and 30 wt. % MEA, but exhibit a low absorption capacity (1.24 mol CO_2/kg amine). As a promoter to 3M DEEA, the 3M DEEA+1M BMA system performed worse than 3M DEEA alone, but with a higher absorption rate. The cyclic capacity for 3M DEEA+1M BMA is 0.36 mol CO_2/mol amine. 14 wt. % L-Arginine exhibit a higher absorption rate and absorption capacity than BMA, but a low cyclic capacity (0.22 mol CO_2/kg amine). As a promoter to 3M DEEA, the blend had the same performance as 3M DEEA alone, but with a somewhat higer absorption rate. 3M DEEA + 5 wt. % ARG achieve a rich loading of 2.08 mol CO_2/kg amine and a cyclic capacity of 1.70 mol CO_2/kg amine.

Table of Contents

List of Abbreviations and Acronyms

Abbreviation	Description
AMP	2-Amino-2-Methylpropanol
ARG	*L*-Arginine
BDEA	*N*-Butyldiethanolamine
BMA	*N*-Benzylmethylamine
CCS	Carbon Capture And Storage
CO_2	Carbon Dioxide
DACH	1,2-Diaminocyclohexane
DEA	Diethylenamine
DEEA	2-(Diethylamino)Ethanol
deNOVO	Evolutionary De Novo Design of Absorbents With Optimal CO_2 Capturing Properties
DFT	Density Functional Theory
DMBA	*N*,*N*-Dimethylbenzylamine
DMMMEA	Dimethylmonoethanolamine
EDEA	*N*-Ethyldiethanolamine
EIA	U.S. Energy Information Administration
HSN	Høgskolen i Sør-Norge
IC	Ione Changed
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
KOH	Potassium Hydroxide
LA	Liquid Analysis
LEPS	Low Energy Penalty Systems
MAPA	3-(Methylamino)Propylamine
MEA	Monoethanolamine
MFC	Mass Flow Controller
N_2	Nitrogen
NA	Not Available
OECD	Organisation for Economic Co-operation and Development
PEA	Phenyletylamine

PZ	Piperazine
QSPR	Quantitative Structure–Property Relationships
R&D	Research and Development
t-BDEA	*N*-*Tert*-Butyldiethanolamine
TEA	Triethanolamine
TMBPA	Bis-(3dimethylaminopropyl)amine

List of Symbols

Symbol	Meaning	Unit
α	CO_2 Loading	mol CO_2/kg amine
C_{am}	Amine Concentration	$mol\cdot kg^{-1}$
C_p	Heat capacity	J/(mol·K)
ΔH	Enthalpy	$kJ\cdot mol^{-1}$
M	Molarity	$mol\cdot L^{-1}$
$M_{solution}$	Amount of Solvent	g
n	Flow o	$NL\cdot min^{-1}$
N_{CO_2}	Accumulated Amount Of CO_2	mol CO_2
NL	Volume	Liter
P	Pressure	kPa
Q	Heat	$kJ\cdot mol^{-1}$
Q_{CO_2}	Amount of CO_2 Absorbed	mol $CO_2\cdot s^{-1}$
Q_{cyc}	Cyclic Capacity	mol $CO_2\cdot s^{-1}$
r	Absorption Rate	mol CO_2/(kg amine·s)
s	Time	second
T	Temperature	°C
x	Volume Percentage	%

List of Tables

List of Figures

1 Introduction

1.1 Background

U.S. Energy Information Administration (EIA) stated in May 2016, that the world energy consumption will increase by 48 % during the next three decades (EIA, 2016a). Non-OECD countries, especially China and India, where demand is driven by strong economic prosperity and expanding population, will stand for most of this growth (IEA, 2015).

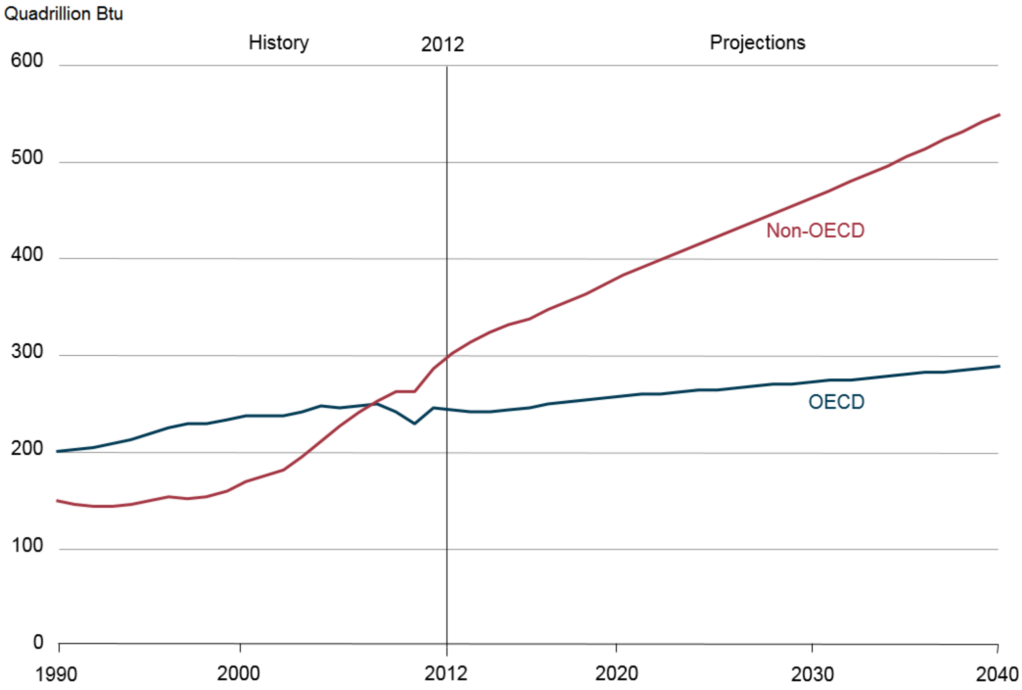
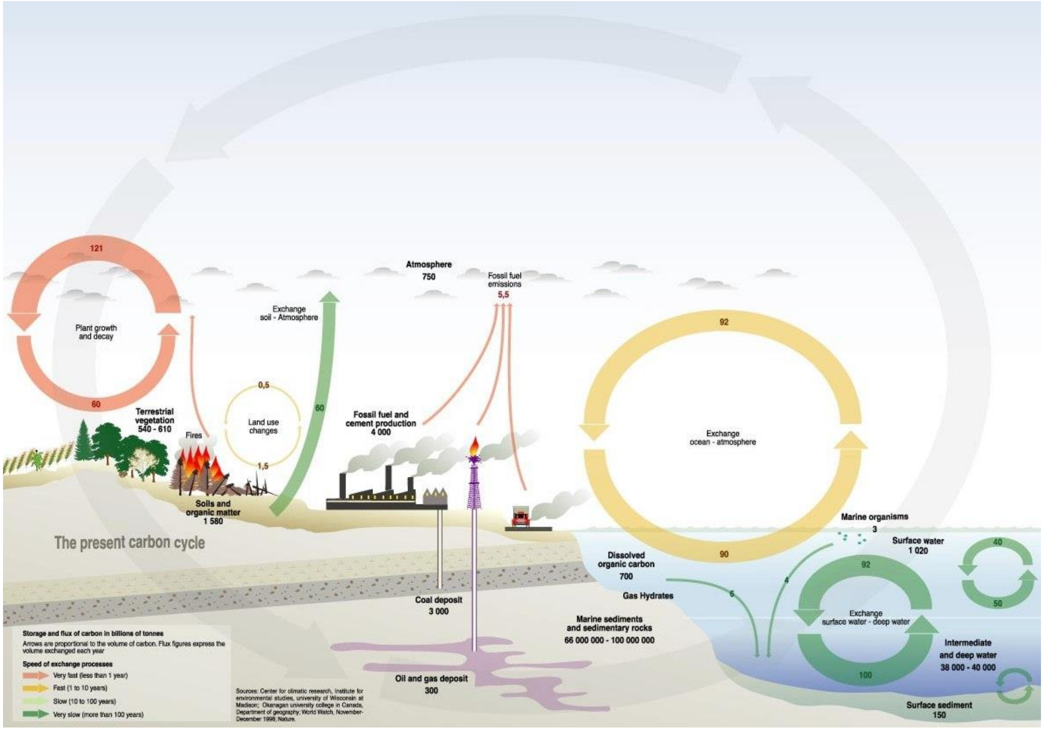


Figure 1.1 World energy consumption per region, 1990-2040

Figure 1.1 show that projected energy demand for Non-OECD countries is a 71 % increase in energy use from 2012 to 2014. In contrast, the more mature energy-consuming and slower-growing OECD economies is projected to have a have an increase in total energy consumption by only 18 % from 2012 to 2040 (EIA, 2016b).

The largest source of energy is petroleum and other liquid fuels, together with coal and natural gas (EIA, 2016b). Economic prosperity and expanding population, will lead to increased carbon dioxide (CO_2) emissions and therefore also rise in the atmospheric CO_2 concentration. Although human CO_2 emissions are small compared to the natural sources, they upset the natural balance of the carbon cycle. Figure 1.2 show the world's present carbon cycle. Fossil fuel combustion, and land-use change, are the largest drivers for CO_2 emitting processes. According to the International Energy Agency, each person emitted 4.5 ton CO_2 in 2012 (IEA, 2016).



Sources: Center for climatic research, Institute for environmental studies, university of Wisconsin at Madison; Okanagan university college in Canada, Department of geography; World Watch, November-December 1998; Nature.

Figure 1.2 Carbon dioxide sources and sinks (GRID-Arendal, 2005a)

Atmospheric CO_2 levels have remained relatively constant until very recently, when the Industrial Revolution started, illustrated by Figure 1.3. The amount of carbon dioxide, has increased by around 38 % since pre-industrial times and is still increasing at an unprecedented rate of on average 0.4 % per year (IPCC, 2014). About 40% of this additional CO_2 is absorbed. The rest remains in the atmosphere, and as a consequence, atmospheric CO_2 is at its highest level in 15 to 20 million years (IPCC, 2007).

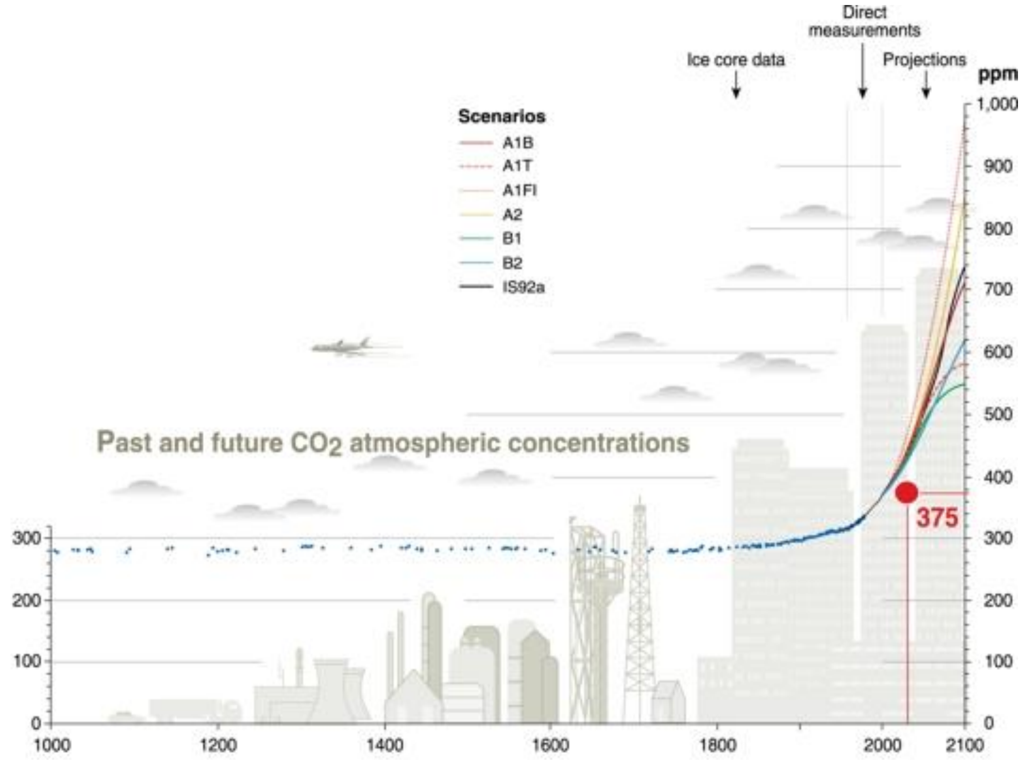


Figure 1.3 Past and future CO_2 atmospheric concentrations (GRID-Arendal, 2005b)

To prevent extensive release of CO_2 into the atmosphere, carbon capture and storage (CSS) is one of the main options for the fossil fuel industry. The technology involves capturing CO_2, compressing it for transportation and then permanently storing it i.e. in depleted oil and gas fields. The largest application for CCS technology are industrial point sources as fossil-fuel power plants, industrial plants (e.g., iron and steel blast furnaces, cement kilns, chemicals processes), hydrogen production facilities and fossil fuel production (Strachan et al., 2015). Since CCS can achieve significant CO_2 emission reductions, it is considered a key option within the portfolio of approaches required to meet CO_2 emission reduction targets (GCCSI, 2014). One of the most mature and well-understood technologies for capturing CO_2 is post combustion CO_2 capture by means of chemical absorbents. The flue gas enters an absorption column, an absorber, where it meets a counter-current stream of solvent. The carbon dioxide's chemical affinity for the solute is exploited, making the CO_2 to preferably dissolve in the sorbent, rather than to linger in the flue gas. The solvent on the other hand has an affection of CO_2, and do not dissolve oxygen, nitrogen or other compounds present in the flue gas stream (Aaron and Tsouris, 2005).

1.2 CO_2 Capture by Temperature Swing Absorption

The most important unit operations for a CO_2 absorption process are the absorber- and desorber-/stripper columns, shown in Figure 1.4. The flue gas is cooled before it enters the bottom of the absorber. The absorber is usually filled with random or structured packing, ensuring a large interfacial contact area and also minimizing the pressure drop throughout the column.

The CO_2 in the flue gas in the counter-current vapor is transferred to the liquid phase by contact throughout the tower. Cleaned gas enters the atmosphere from the top of the absorber, while rich CO_2 solution leaves the absorber from the bottom. CO_2 rich solutions reach the regeneration unit, the desorber/stripper, where the solvent is regenerated by heat. Rich and lean solvents are heat exchanged with each other, as the stripping is performed at higher temperatures than the absorption. And likewise, absorption is performed at lower temperatures, so the temperature of the lean solvent must be reduced. CO_2 released from the solvent during regeneration, leave the top of the stripper for compression and transportation. The CO_2 lean solution is then cooled in order to enter the absorber again for a new absorption cycle (IEAGHG, 2009).

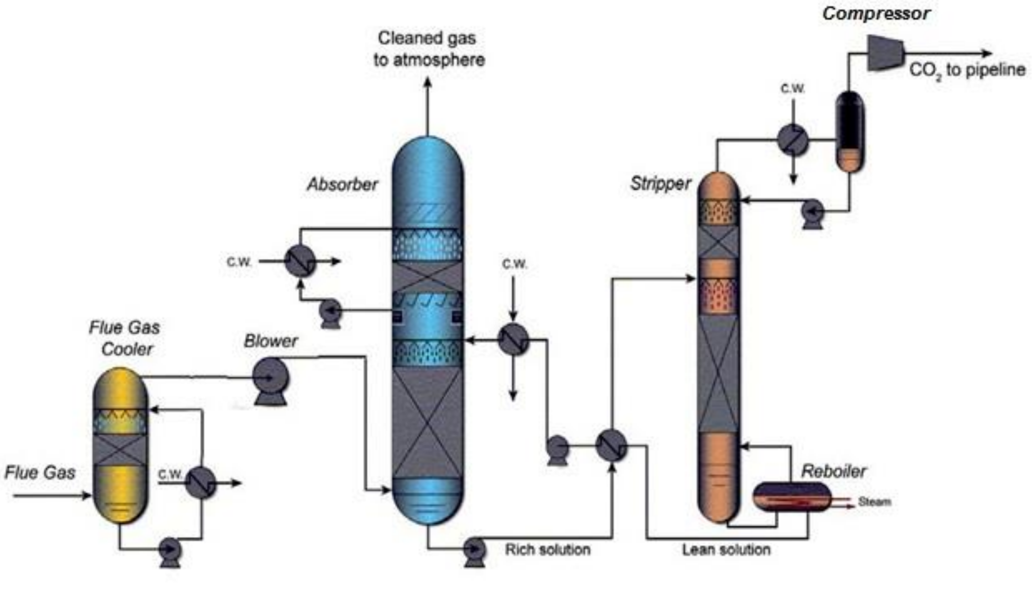


Figure 1.4 Schematic diagram of a typical amine based CO_2 absorption plant (IEAGHG, 2009)

It is mainly the steam required in the reboiler for solvent regeneration and the compressor duty needed to compress CO_2 to transport pressure, that accounts for the energy requirement, and thus the operating cost of the absorption plant (IEAGHG, 2009). Since absorption technology is costly, but may be the most feasible option for large scale CO_2 removal, substantial R&D is directed to reduction of operating costs and energy penalty (Leung et al., 2014).

1.3 Solvent Based CO_2 Absorption

In addition to being the most mature process for CO_2 separation, chemical absorption as a CO_2 capturing technology also serves other advantages, such as high absorption efficiency (>90 %) and that the solvents are regenerable (Leung et al., 2014).

Alkanolamines are among the preferred solvents for CO_2 removal, and are chemical compounds combining amine functionality with a hydroxyl functionality. Some of the amines most commonly used in CO_2 capture are monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA). The alcohol group does not participate in any reaction, but increase the CO_2 solubility in water and by that, giving a higher absorption of CO_2 (Hartono et al., 2016, Raynal et al., 2011). In addition, the alcohol group reduces the solvents vapor pressure, which ensures a more energy efficient stripping. The alcohol group also tune the basicity of the solvent, making it more reactive with acid gases (Raynal et al., 2011).

The most desired absorbents have a high net cyclic capacity, meaning that they have a high absorbtion potential in the absorber and easily remove the captured CO_2 in the stripper. They also require a high reaction rate between amine and CO_2, in addition to a low heat of absorption, a sturdy chemical stability, as the degradation products of amines can be harmful to human health and environment (Knudsen et al., 2009). There is a strong focus on environmental friendly solvents, so ecotoxicity and biodegration must be within accepted levels. Other coveted properties are low vapor pressure, to minimize amine loss and low corrosiveness to the treating unit (Hartono et al., 2016, Nielsen et al., 1995).

In order to achieve a well-functioning solvent, it may be advantageous to blend different classes of amines. A energy modest amine is the basis for the blend, while an amine with high reaction rate is added to promote the parent amine. Typical promoters are 2-amino-2-methyl-1-propanol (AMP), Piperazine (PZ) or MAPA, which all have a fast reaction kinetics with CO_2.

All though alkanolamines are the preferred CO_2 absorbents, other solvent systems are also considered for CO_2 absorption. Aqueous amino acid salts is an interesting alternative to amines for CO_2 removal, they are expected to have high reactivity towards CO_2. In addition to having identical functional group as alkanolamines, amino acid salts have a low environmental impact, a low volatility and a high biodegrability. When neutralized with equimolar amount of base, amino acids react with CO_2 as amines do, by forming a zwitterion (Shen et al., 2016, Li and Rochelle, 2011)

1.4 Scope of Work

The first and predominant part of this work is a part of the ongoing *Low Energy Penalty Solvents* (LEPS)-project run by University College of Southeast Norway (HSN), in cooperation with NTNU and University of Texas, Austin. The aim is to develop CO_2 absorbing solvents giving a lower energy demand in post-combustion CO_2 capture processes involving both absorption and regeneration.

As a segment of that project, this work will give insight to the influence of amine alkanol groups, as well as alkyl chain structure, by systematically varying the tertiary amine and the total amine concentration. Table 1.1 show the whole experiment matrix planned for the performance study, this work targets the framed experiments.

Table 1.1 Experiment matrix LEPS project

Ratio	Compound	mol/L	Compound	mol/L	Compound	mol/L
3	3° amine	3	3° amine	2.25	3° amine	1.5
	MAPA	1	MAPA	0.75	MAPA	0.5
	Total cons.	4	Total cons.	3	Total cons.	2
2	3° amine	2.66666	3° amine	1.99999	3° amine	1.33333
	MAPA	1.33333	MAPA	0.99999	MAPA	0.66666
	Total cons.	4	Total cons.	3	Total cons.	2
1	3° amine	2	3° amine	1.5	3° amine	1
	MAPA	2	MAPA	1.5	MAPA	1
	Total cons.	4	Total cons.	3	Total cons.	2

Due to a high energy demand required to regenerate the rich solvent a blend of two amines combines high absorption rate provided by the primary- and secondary diamine, 3-

methylamino-propylamine (MAPA), and high loading capacity and lower heat of absorption, provided by a tertiary amine. Five tertiary amines, 2-diethylamino-ethanol (DEEA), triethanolamine (TEA), *N*-Butyldiethanolamine (BDEA), 2-(Dibutylamino)ethanol (EDEA) and *N-tert*-Butyldiethanolamine (t-BDEA) are considered in this work. The experiments were conducted using three different 3° amine/MAPA molar ratios, 3:1, 2:1 and 1:1. The total amine concentration was kept constant at 4 mol/L. In addition the single 3° amines are run at 3M and MAPA at 1M. The sum of this workload is later on in this report termed the *1st screening campaign.*

The second part of this work is connected to the ongoing *Evolutionary de novo design of absorbents with optimal CO_2 capturing properties* (DeNOVO)- project. The aim of this project is to establish a novel technology for efficient development of new carbon capture absorbents with optimal properties. The main objective is to increase the efficiency of amine-based capture technology to be applied in the development of the next generation of absorbents, such as new amines, imidazoles and ionic liquids.

A model for predicting compounds basicity, and a model to synthezise new amines, was developed in collaboration with another reasearch group at NTNU. Four imidazole-like compounds, and two amino acid salts, predicted to have a high pK_a, and therefore should be able to absorb CO_2, were suggested from calculations using quantitative structure–property relationships (QSPR) and density functional theory (DFT) (Venkatraman et al., 2016). 1,2-Diaminocyclohexane (DACH), N-Benzylmethylamine (BMA), N,N-Dimethylbenzylamine (DMBA), Phenethylamine, Creatine and L-Arginine (ARG), are the commercially available compounds selected to cross-validate the model. As a part of this cross-validation, this work have conducted screening experiments on the elected compounds in a *2nd screening campaign*. By screening the compounds, one can see if the model is good to predict the elected substances ability to function as CO_2 absorbing solvent and their ability to function as promoter to DEEA. To check the compounds absorption potentials, they were screened as 30 wt. % aqueous solutions. The concentration as promoter was 1M for N-Benzylmethylamine, and 5 wt. % for L-Arginine.

1.5 Outline of the Thesis

The thesis starts with a theoretical overview in Chapter 2. The theoretical framework aims to give the reader an understanding of the reaction mechanisms between amine and CO_2, and why it is of great importance to develop new solvents for CO_2 capture processes. The theoretical framework concentrate on the advantage of amine blends, former work performed on this particular field, along with relevant data found in literature. A consideration of why amino acids are of interest is also given. At last the importance of amines basicity is elaborated, and the dissociation constant is related to absorption rate.

Chapter 3 consists of the Material and Method section. The chapter starts with a description of the screening equipment and the CO_2 and amine analyzers. The section ends with an introduction of the chemicals used in this work, followed by solvent preparation.

Solvent screening experiments were performed using CO_2 absorption and regeneration with selected solvents and the results thereof, together with the results from the liquid analysis, are reported in Chapter 4. First, different absorption capacities from tertiary amines are compared. Then the effect of concentration is presented, followed by the effect of molecule structure. At last, the pK_a values of the tertiary amines are examined to see if there is a trend between pK_a and absorption rate and cyclic capacity. Lastly, the results from the 2nd screening campaign are presented.

Chapter 5 gives a conclusion of the study, while a recommendation for further work is found in Chapter 6.

2 Theoretical Framework

This chapter aims to identify and review available information on CO_2 absorbing solvents. Thermodynamics and energy considerations is included to show why it is important to develop new solvents. In order to limit the data volumes, and to sharpen it towards this work, the target of this rewiev have been on literature data from comparable screening studies of single amines, blended systems and amino acid salts. At the end of the chapter, relevant dissociation constants (pK_a-values) is presented.

2.1 Energy Considerations for a CO2 capture plant

In a capture plant the two main types of energy sinks are electrical energy and heat. Heat is needed in the stripper and in the reboiler, and electrical energy is needed to power liquid circulation pumps and compressors (Svendsen et al., 2011). Figure 2.1 show a typical amine based CO_2 capturing plant, with main energy sinks. The purple circles show the electrical sinks and the red circles represent heat sinks.

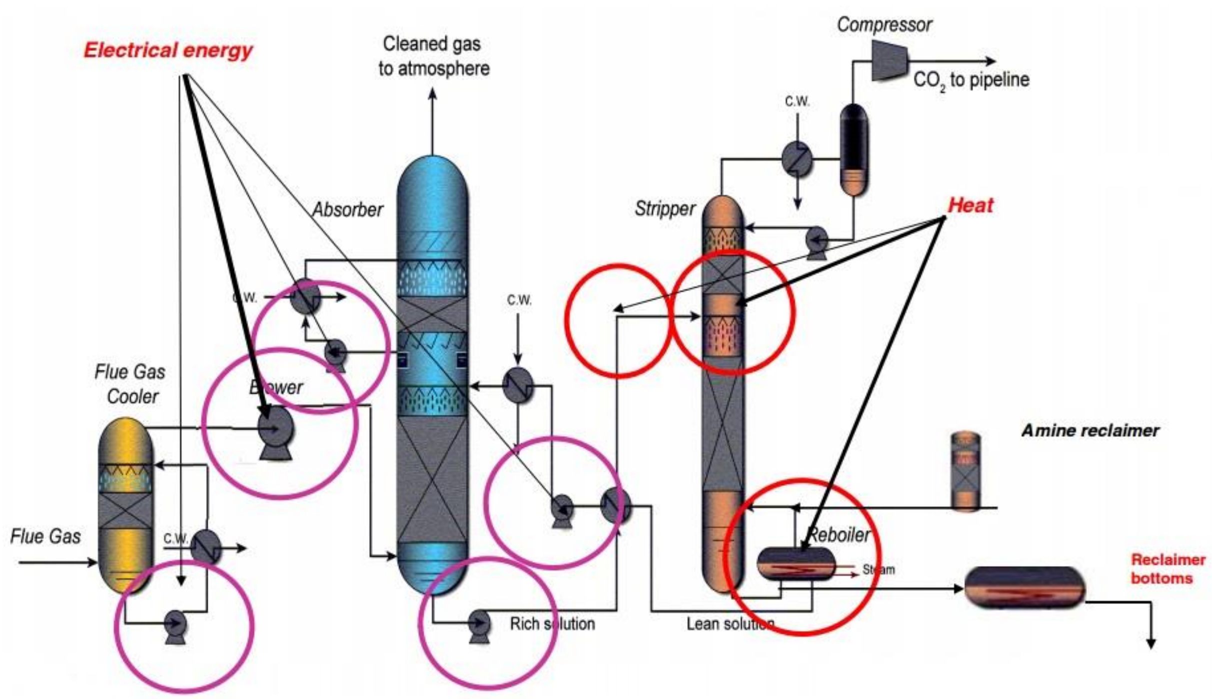


Figure 2.1 Energy sinks in a conventional CO_2 capture process (Svendsen et al., 2011)

The total heat requirement is often referred to as total steam requirement, and is the sum of three different energy sinks. Stripping heat, sensible heat and heat of desorption.

The heat of desorption is dependent on the solvent, and is the heat required to reverse the exothermic reaction between absorbent and CO_2 in the absorber. The different amine classes have distinctive heat of absorption. Primary amines have a higher heat of absorption than secondary amines, which in turn have a higher heat of absorption than tertiary amines (Kim and Svendsen, 2011). Since different amines have different heat of absorption, it is important to find an energy friendly absorbent. A low heat of desorption make it possible to perform the stripping at a lower temperature, hence lowering the heat requirement in the stripper.

$$Q_{des} = -\Delta H_{abs_{CO_2}} \tag{1}$$

As CO_2 rich solvent enter the top of the desorber, the CO_2 content is reduced as the solvent flows downwards in the column. Steam is needed to drive CO_2 up and out of the stripper, and the gas leaving the stripper is rich in both CO_2 and steam. This steam needs to be condensed and returned, and the heat loss of this operation is known as stripping heat.

$$Q_{strip} = \frac{P_{H_2O}^{sat}\left(T_{top,des}\right)x_{H_2O,freebasis}}{P_{CO_2}^{*}(T_{top,des}\alpha_{rich})}\Delta H_{H_2O}^{vap} \tag{2}$$

Where $P_{H_2O}^{sat}$is the saturation pressure of water, $T_{top,des}$ is the temperature at the top of the desorber, α is the loading, $x_{H_2O,freebasis}$ is the mole fraction of water steam, $P_{CO_2}^{*}$ is the pressure of pure CO_2, and $\Delta H_{H_2O}^{vap}$ is the energy needed to evaporate the liquid water. The loading, α, is defined as:

$$\alpha = \frac{mol\ CO_2}{mol\ amine} \tag{3}$$

Sensible heat is the heat required to rise the temperature of the rich amine solution to the desired stripping temperature. The rich/lean heat exchanger is not able to bring the rich solvent to desired temperature and the temperature gap is referred to as a sensible heat requirement.

$$Q_{sens} = \frac{\rho C_p \Delta T}{(\alpha_{rich} - \alpha_{lean}) C_{am}} \qquad (4)$$

Where ρ is density, C_p is the heat capacity, ΔT is the rich/lean heat exchange temperature, C_{am} is the amine concentration, and $\alpha_{rich} - \alpha_{lean}$is the cyclic capacity. Most desirable is that the loadings have features so they follow this trend: $\alpha_{rich} > (\alpha_{rich} - \alpha_{lean}) \gg \alpha_{lean}$. In that way the solvents absorb substantial amounts of carbon dioxide, the solvents is easily regenerated and by the means of a high cyclic capacity, the solvent cost is reduced

Sensible heat requirement is soley determined by the process, as long as no desorption takes place in the heat exchanger. But it is important to notice that the need for stripping steam and the heat of desorption are strongly interrelated, and this affects the process (Svendsen et al., 2011).

From the screening results, the main objective is to look at the loadings and the cyclic capacities. From Equation (4) one can see why it is desirable to have as large difference as possible between the rich and lean loadings. A large cyclic capacity reduces the necessity for sensible heat, which in turn reduces the energy demand of the process.

2.2 Reaction Mechanisms

Due to the high recognintion on the topic, one can easily find literature data from modeling work, equilibrium and screening studies. In order to limit the data volumes, and to sharpen it towards this work, the target of this rewiev have been on literature data from comparable screening studies. At the end of the chapter, relevant dissociation constants (pK_a values) is presented.

One of the most promising post-combustion techniques is absorption using amines. Amines are organic derivatives of ammonia. Depending on the number of functional groups attached to the nitrogen atom, amines can be classified into three groups. Primary-, secondary- and tertiary amines, attach respectively one, two or three organic groups connected to the nitrogen (Solomons and Fryhle, 2011). Figure 2.2 illustrates the difference between ammonia and the three different amine classes. R, R’ and R’’ represent organic groups that are attach to the nitrogen atom.

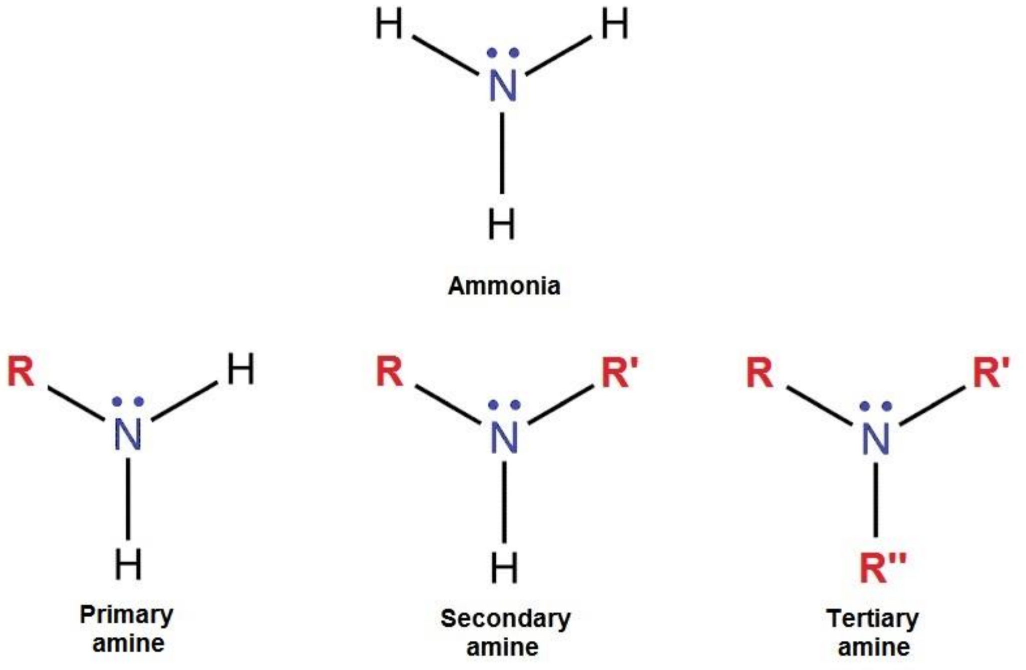


Figure 2.2 Molecular structure of ammonia and primary-, secondary- and tertiary amine

Due to their basicity, and their unshared electron pair, amines can undergo a reversible reaction with acid gases, such as carbon dioxide (Solomons and Fryhle, 2011).

The reactivity with CO_2 depends on the number of functional groups, where primary amines have the highest reactivity, while tertiary amines are the slowest.

First CO_2 is dissolved in water, see Reaction (I):

$$CO_{2\,(g)} \rightarrow CO_{2\,(aq)} \tag{I}$$

And water is ionized as shown in Reaction (II):

$$2\,H_2O \ \leftrightarrow H_3O^+ + OH^- \tag{II}$$

Dissolved CO_2 undergo hydrolysis and ionization. Although no amine molecule appears in Reaction (III), the extent to which this reaction will occure, is governed by the basiticy of the amine (Singh, 2011).

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \tag{III}$$

Reaction (IV) gives the bicarbonate/carbonate protonation:

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \tag{IV}$$

Protonation of amine:

$$RR'NH_2^+ + H_2O \leftrightarrow RR'NH + H_3O^+ \tag{V}$$

Primary- and secondary amines react with CO_2 to form carbamate via two different paths, i.e. a zwitterion mechanism (Danckwerts, 1979) or single-step termolecular mechanism (Crooks and Donnellan, 1989).

$$RR'NCOO^- + H_2O \leftrightarrow RR'NH + HCO_3^- \tag{VI}$$

Reaction (VII)-(VIII) represent the zwitterion formation followed by the removal of proton by a base B (Singh, 2011).

$$CO_2 + RR'NH \leftrightarrow RR'NH^+COO^- \tag{VII}$$

$$RR'NH^+COO^- + B \leftrightarrow RR'NCOO^- + BH^+ \tag{VIII}$$

B represents a base molecule, being water, a hydroxyl ion or an amine functionality. The carbamate formed can undergo hydrolysis, and form bicarbonate by reaction with water (Singh, 2011).

$$RR'NCOO^- + H_2O \leftrightarrow RR'NH + HCO_3^- \tag{IX}$$

Caplow (1968) and Hamborg and Versteeg (2009) reported that there is a strong connection between the carbamate formation equilibrium constant and the basicity (pK_a) of the solvent. It is also reported that an increasing pK_a of the amine leads to increased stability of the carbamate (McCann et al., 2011, Sartori and Savage, 1983).

The stoichiometry between CO_2 and primary or secondary amine is 2:1. The maximum CO_2 loading the amine can achieve is 0.5 mol CO_2 per mol amine. This is valid when carbamate forming is the only reaction in the system (Sartori and Savage, 1983).

Tertiary amines lack the free proton that primary and secondary amines have, and do not react directly with CO_2 according to Reaction (VII), but by promoting the hydrolysis of CO_2 to form bicarbonate and protonated amine. (Blauwhoff et al., 1983, Goel and Johri, 2014, Donaldson and Nguyen, 1980). Reaction (X) display the reaction between a tertiary amine, water and carbon dioxide, giving bicarbonate (Littel et al., 1990). The maximum loading capacity for tertiary amines are restricted to 1.0 mol CO_2 per mole amine.

$$RR'R''NH + CO_2 + H_2O \leftrightarrow HCO_3^- + RR'R''NH^+ \tag{X}$$

It is considered that the equilibrium reaction between free amine and H_2O is instantaneous with respect to mass transfer, since it only involves a proton transfer. (Blauwhoff et al., 1983, Littel et al., 1990).

$$RR'R''NH^+ + H_2O \leftrightarrow + RR'R''NH + H_3O^+ \tag{XI}$$

The heat of absorption for primary and secondary amines are very high compared to tertiary amines. A lower heat of absorption reduce the energy requirement for regeneration of solvent (Hadri et al., 2015). Table 2.1 summarizes the difference between primary, secondary and tertiary amines.

Table 2.1.Differences between primary, secondary and tertiary amines for CO2 absorption

Amine	Maximum loading	Reactivity	Heat of absorption
Primary and secondary	0.5	High	High
Tertiary	1.0	Low	Low

The reaction between primary and secondary alkanolamines and CO_2, that form carbamates occur rapidly. While the hydrolysis reaction between CO_2 and tertiary amine is slower. The reactivity of the primary and secondary amines enables high removal ratios of CO_2 in the absorbers (Singh, 2011, Vaidya and Kenig, 2007).

2.3 Single amines

This section contains a literature review of the amines participating in the 1st screening campaign. A concentration of 30 wt. % is used as standard screening concentration, to easily compare the results with the base-case MEA.

2.3.1 Monoethanolamine (MEA)

30 wt. % monoethanolamine is widely used as a benchmark chemical for amine-based CO_2 capture processes. Substantially amounts of CO_2 loading and cyclic capacity data is therefore available in open literature for this solvent. Table 2.2 show a selection of the accessible screening data. The concentration of most runs in the first screening campaign is kept constant at 4 M, thus concentration 4 M MEA is included in this review.

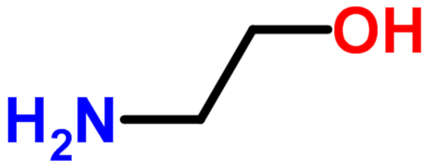


Figure 2.3Molecule structure of monoethanolamine (MEA)

MEA is still considered to be the most favored solvent for low pressure gas cleaning from gas streams containing small fractions of CO_2 and H_2S. MEA have a low molecular weight, 61.08 g·mol^{-1}, and a high alkalinity, which ensure an adequate solution capacity. Although MEA are so preferred, it has several disadvantages. It is highly corrosive at high concentrations (>20 wt. %), and it require substantial amounts of heat for desorption. Due to its high vapor pressure, one can get substantial loss of solvent (Kohl and Nielsen, 1997).

Table 2.2 Screening literature data for monoethanoleamine (MEA)

Amine concentration [wt. %]	Temperature [°C]	CO_2 partial pressure [kPa]	CO_2 loading [mol CO_2/mol amine]	Cyclic capacity [mol CO_2/mol amine]	Reference
30	40	30.4	0.459	0.07	Choi et al. (2014)
30	80	30.4	0.382		Choi et al. (2014)
4[1]	40	15	0.52	0.13	Conway et al. (2015)
30	40	20	0.54	0.17	Chowdhury et al. (2014)
30	120	100	0.37		Chowdhury et al. (2014)
30	40	15	0.58		El Hadri et al. (2016)
30	40	20.3	0.53		Goto et al. (2011)
30	40	9.5	0.525	0.25	Hartono et al. (2016)
30	40	33.8	0.46	0.08	Kim et al. (2014)
30	80	33.8	0.38		Kim et al. (2014)
30	40	13.2	0.56		Puxty et al. (2009)
30	40	15.2	0.49		Puxty et al. (2009)
30	40	15	0.56	0.15	Schäffer et al. (2012)
30	90	15	0.41		Schäffer et al. (2012)
30	30	101.3	0.63		Ye et al. (2015)

[1] *Concentration given in mol/L*

The CO_2 rich loading varies from 0.46-0.53 mol CO_2/mol amine at 40 °C. It is important to note that these screening experiments are performed at different CO_2 partial pressures, and in somewhat different screening equipment. Loadings over 0.5 is not theoretical impossible, the high loadings obtained may be due to uncertainties or influence of water (see Reaction (III)).

Cyclic capacity differs from 0.077 mol CO_2/mol amine to 0.25 mol CO_2/mol amine. Chowdhury et al. (2014) and Schäffer et al. (2012) operate at a higher stripping temperature, at correspondingly 120 °C and 90 °C, than the stripping temperature used in this work (80 °C). Kim et al. (2014) use a semi-batch absorption system explained in Lim et al. (2012), while Conway et al. (2015) use a wetted-wall column contactor setup elucidated by Wei et al. (2014). This work use the same screening apparatus and operate at the same conditions as Hartono et al. (2016).

Choi et al. (2014) and Kim et al. (2014) achieve the same results for both absorption and desorption of 30 wt. % MEA, with a rich loading of 0.46 mol CO_2/mol amine and lean loading of 0.38 mol CO_2/mol amine, although they operate at different CO_2 partial pressures. However, they both use a semi-batch absorption system for screening purpose.

Figure 2.4 clarify the disparity between the different loadings from MEA screenings found in open literature.

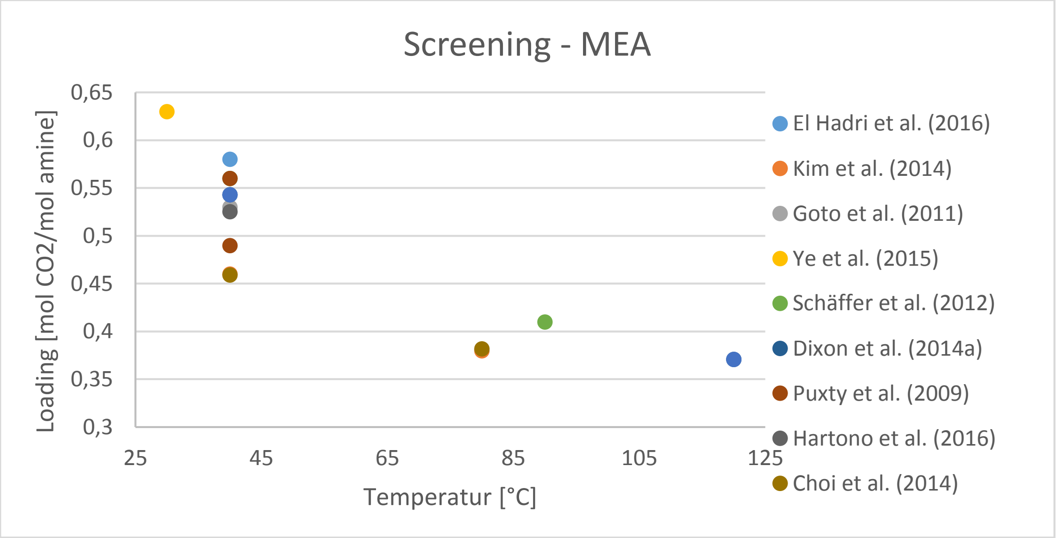


Figure 2.4 Results from screening of 30 wt. % MEA

From vapor/liquid equilibrium, the partial pressure of CO_2 is a function of loading, temperature and mole fraction. This is the reason why it is hard to compare the screening results found in literature. Each temperature and partial pressure corresponds to a certain loading value, as illustrated in Figure 2.5.

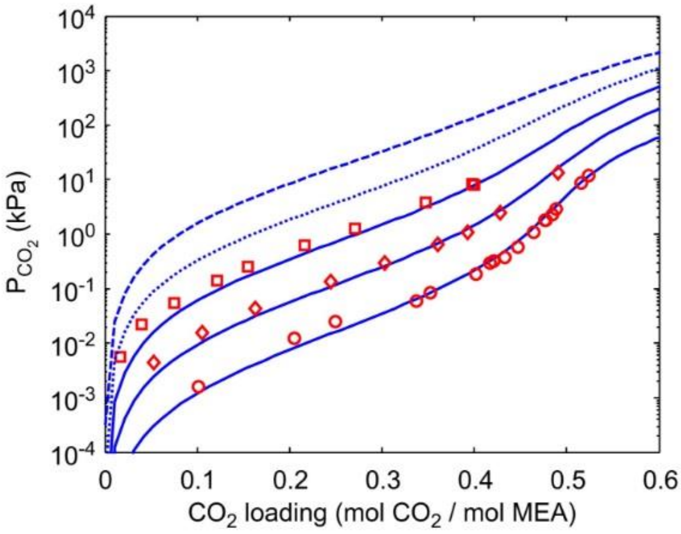


Figure 2.5 CO_2 partial pressure as function of loading for H2O–MEA–CO_2 system. 30 wt., % MEA at 40 °C, 60 °C, 80°C, 100 °C and 120 °C. Points are measurements and lines are model prediction (Aronu et al., 2011a)

In addition to different loading values at different partial pressures, the screening equipment is also different.

2.3.2 N,N-diethylethanolamine (DEEA)

The literature values found for N,N-diethylethanolamine is included in Table 2.3. The concentration 2M is included in the review as one of the experiments in this work contain 2M DEEA (+2M MAPA). It is important to remark that that particular entry is from a equilibrium approach, not a screening experiment.

Table 2.3 Screening literature data for DEEA

Amine concentration [wt. %]	Temperature [°C]	CO_2 partial pressure [kPa]	CO_2 loading [mol CO_2/mol amine]	Cyclic capacity [mol CO_2/mol amine]	Reference
30	40	20	0.83	0.28	Chowdhury et al. (2013)
30	70	20	0.55		Chowdhury et al. (2013)
30	40	15	0.9		El Hadri et al. (2016)
30	40	9.5	0.78	0.36	Hartono et al. (2016)
2[1]	40	15	0.82		Monteiro et al. (2013)[2]
30	40	15.2	0.69		Puxty et al. (2009)

[1] Concentration given in mol/L

[2] Equilibrium data, not screening

Chowdhury et al. (2013) reported the cyclic capacity to be 0.28 mol CO_2/mol amine, while Hartono et al. (2016) found a cyclic capacity of 0.36 mol CO_2/mol amine.

Figure 2.7 show that there is some discrepancies between the results. The absorption capacity of DEEA spans from 0.69 mol CO_2/mol amine to 0.9 mol CO_2/mol amine. Again, this deviations are most likely to originate from different conditions and experimental setup, and the fact that screening is a semi-quantitative measurement.

Figure 2.6 show predicted equilibrium lines for the H_2O-DEEA-CO_2 system. Again, it is easy to see that different pressures and temperatures give different loadings. The only way screening studies can be directly compared, is if both temperature and CO_2 partial pressures are in agreement, and the screening is performed in matching equipment.

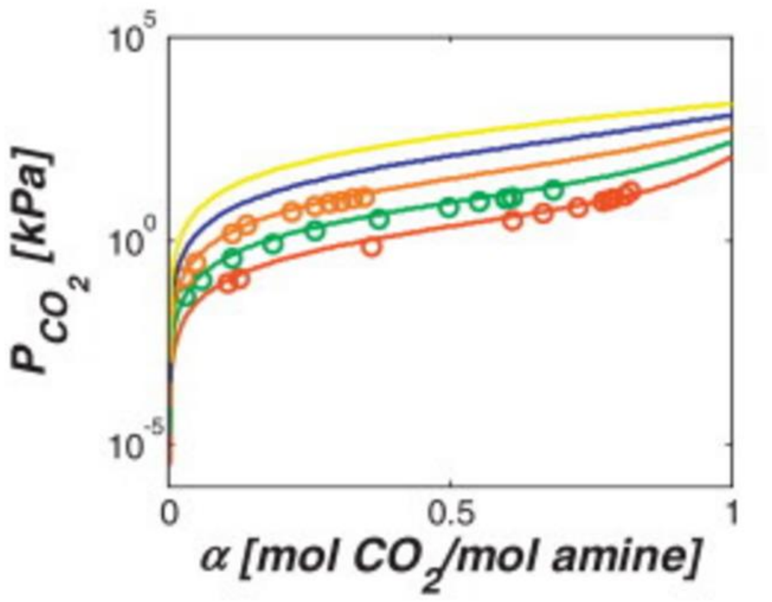


Figure 2.6 CO_2 partial pressure as function of loading for H_2O–DEEA–CO_2 system. 2M DEEA at 40 °C, 60 °C, 80°C, 100 °C and 120 °C. Points are measurements and lines are model prediction (Monteiro et al., 2013)

Figure 2.7 illustrate the challenge of comparing screening experiments, even if they are performed at the same temperature. As long as the partial pressure, temperature and/or the equipment is different, the equilibrium lines show that the experiments must be interpreted individually.

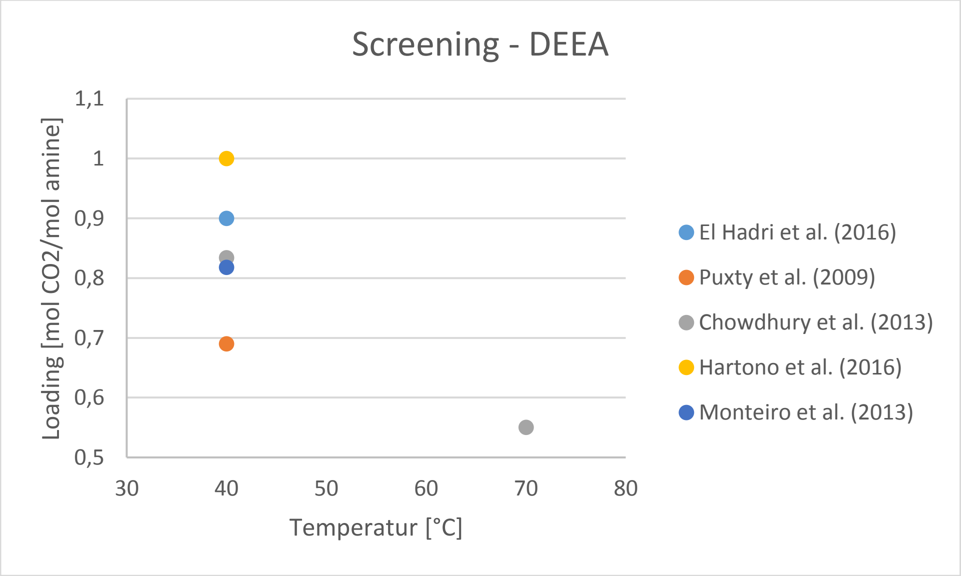


Figure 2.7 Results from screening of 30 wt % DEEA

2.3.3 Triethanolamine (TEA)

It was not found as much literature data on screening of TEA as for DEEA, but the data found is presented in Table 2.4.

Table 2.4 Screening literature data for TEA

Amine concentration [wt. %]	Temperature [°C]	CO_2 partial pressure [kPa]	CO_2 loading [mol CO_2/mol amine]	Reference
30	40	15	0.39	El Hadri et al. (2016)
30	40	13.2	0.24	Puxty et al. (2009)
30	40	20	0.25	Chowdhury et al. (2013)
30	70	20	0.15	Chowdhury et al. (2013)

Both Puxty et al. (2009) and Chowdhury et al. (2013) reported similar results for rich CO_2 loading after screening of 30 wt. % TEA at 40 °C, with correspondingly 0.24 mol CO_2/mol amine and 0.25 mol CO_2/mol amine. El Hadri et al. (2016) obtained a somewhat higher absorption capacity with 0.39 mol CO_2/mol amine. Chowdhury et al. (2013) reported a cyclic capacity of 0.10 mol CO_2/mol amine for their experiment.

2.3.4 N-ethyldiethanolamine (EDEA)

Chowdhury et al. (2013) performed screening experiments on 30 wt. % N-ethyldiethanolamine, and the findings are presented in Table 2.5.

Table 2.5 Screening literature data for EDEA

Amine concentration [wt. %]	Temperature [°C]	CO_2 partial pressure [kPa]	CO_2 loading [mol CO_2/mol amine]	Reference
30	40	20	0.64	Chowdhury et al. (2013)
30	70	20	0.34	Chowdhury et al. (2013)

The cyclic capacity was found to be 0.3 mol CO_2/mol amine.

2.3.5 N-tert-Butyldiethanolamine (t-BDEA)

Table 2.6 show the results Chowdhury et al. (2013) obtained from screening 30 wt. % N-tert-Butyldiethanolamine.

Table 2.6 Screening literature data for t-BDEA

Amine concentration [wt. %]	Temperature [°C]	CO_2 partial pressure [kPa]	CO_2 loading [mol CO_2/mol amine]	Reference
30	40	20	0.39	Chowdhury et al. (2013)
30	70	20	0.24	Chowdhury et al. (2013)

Cyclic capacity was found to be 0.15 mol CO_2/mol amine.

There were no relevant literature data found on t-BDEA being used for CO_2 removal.

2.3.6 Non-alkanolamines

Phenethylamine (PEA), N-Benzylmethylamine (BMA), N,N-Dimethylbenzylamine (DMBA) and 1,2-Diaminocyclohexane are classified as non-alkanolamines in this work.

No relevant literature data was found for the non-alkanolamines investigated in this study.

2.4 Blends of Amines

Due to the advantages and disadvantages of the single amine solvents, blended amines have become an attractive direction in the current research field. The blended amines combines the advantages of primary/secondary amine, which reacts fast with carbon dioxide, and tertiary amines, that have a low heat of absorption. By combining these benefits and thus tailoring the solvent, one can achieve better absorption performance at low partial pressure, as well as high absorption kinetics for reactions with CO_2 (Gervasi et al., 2014, Glasscock et al., 1991, Savage et al., 1984).

Findings from Sakwattanapong et al. (2005) show that blends of tertiary/sterically hindered and primary/secondary alkanolamines improve the thermodynamic efficiency of the solvent. Blended amine systems enhance the absorption capacity compared to single tertiary amines under identical conditions (Barzagli et al., 2010).The blend give a higher equilibrium capacity, which promote bicarbonate formation.

The formation of bicarbonate ions is desirable, since bicarbonate breakdown require the lowest energy input in order to regenerate the solvent. On the other side, carbamate formation has a relatively high heat of formation, so the energetic penalty of the amine regeneration step is greater than for bicarbonate regeneration. Since tertiary amines do not form carbamate in reaction with CO_2 and H_2O, the heat requirement for regeneration is lower than for primary/secondary amines (Zhang et al., 2016).

The effect of solvent degradation stretches from reduction of cyclic capacity, enhanced foaming effects, environmental impacts, corrosion and fouling of equipment (Islam et al., 2011).

2.4.1 MAPA as promoter

3-(methylamino)propylamine (MAPA) is a diamine having a primary and a secondary amine functional group and can theoretically absorb two moles of CO_2 for every mole of amine. Aqueous MAPA, either alone or as a promoter in a blend, has recently received considerable attention due to its high reaction rate and CO_2 solubility (Voice et al., 2013). MAPA is also reported to have a low ecotoxicity and to be biodegradable (Eide-Haugmo et al., 2009).

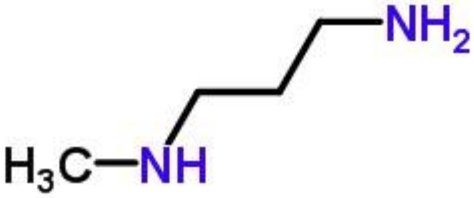


Figure 2.8 Molecule structure of 3-(methylamino)propylamine (MAPA)

Both Kim et al. (2014) and Puxty et al. (2009) have performed screening studies on aquatic MAPA. The results are presented in Table 2.7.

Since MAPA is a diamine it has to amino groups that can react to form mono-/dicarbamate, and reacts according to Reactions (XII) and (XIII) (Ciftja et al., 2013b):

$$R(NH_2)_2 + CO_2 + H_2O \leftrightarrow NH_2RNHCO_2^- + H_3O^+ \tag{XII}$$

$$NH_2RNHCO_2^- + CO_2 + H_2O \leftrightarrow NHCO_2^-RNHCO_2^- + H_3O^+ \tag{XIII}$$

Literature values for MAPA screening is found in Table 2.7.

The reported absorption capacity values are 0.94 mol CO_2/mol amine and 0.78 mol CO_2/mol amine from Kim et al. (2014) and Puxty et al. (2009), respectively. The desorption capacity reported by Puxty et al. (2009), 0.78 mol CO_2/mol amine, is very similar to the absorption capacity found by Kim et al. (2014). Kim et al. (2014) found a cyclic capacity of 0.15 mol CO_2/mol amine for 30 wt. % MAPA.

Table 2.7 Screening literature data for MAPA

Amine concentration [wt. %]	Temperature [°C]	CO_2 partial pressure [kPa]	CO_2 loading [mol CO_2/mol amine]	Reference
30	40	33.8	0.94	Kim et al. (2014)
30	80	33.8	0.79	Kim et al. (2014)
30	40	15.2	0.78	Puxty et al. (2009)

Previous research has indicated that MAPA is an effective promoter to 2-(diethylamino)-ethanol (DEEA) and methyldiethanolamine (MDEA) solutions. As a weak base, it may serve to catalyze proton extractions in the reaction mechanism (Choi et al., 2014, Knuutila et al., 2009, Arshad et al., 2013a). Bruder and Svendsen (2011) tested MAPA as a promoter to Dimethylmonoethanolamine (DMMEA), while Aronu et al. (2011b) used MAPA to promote Bis-(3dimethylaminopropyl)amine (TMBPA). All of the MAPA promoted systems showed outstanding CO_2 carrying capacities, relative to 30 wt. % MEA. Generally, systems with higher MAPA concentration show higher absorption rate and absorption capacity.

Hartono et al. (2013) found that pure MAPA is more volatile than pure DEEA. However, in aqueous solution MAPA was found to be less volatile. A high volatility is associated with great amine loss, hence increasing the cost of the CO_2 capture process. By blending DEEA and MAPA in an aqueous solution, the volatility is lowered, which make the solvent more beneficial for CO_2 capture.

2.4.2 DEEA/MAPA system

The DEEA/MAPA blend is considered to be an interesting system, and a number of publications is recently published on this topic. Some sources are Monteiro et al. (2015a), Monteiro et al. (2015b), Hartono et al. (2013), Arshad et al. (2013b), Arshad et al. (2013c) , Ciftja et al. (2013a) and Pinto et al. (2014a). The work published on this blend ranges from measurements of vapor/liquid equilibrium (VLE), phase change, kinetics, but not much on screening.

A lot of the onging reasearch on DEEA/MAPA is that this blend form two liquid phases upon CO_2 loading at certain concentration. If one can split the two phases and send only the CO_2 rich phase to regenaration, there is potential for reducing the energy consumption. If the CO_2-rich phase show high potential for cyclic capacity, there is possibilities for stripping steam reduction, which again can lead to increased regeneration pressure (Pinto et al., 2014b).

Pinto et al. (2014b) performed screening on a 2M DEEA + 5M MAPA blend, which form a two phase system. The absorption tests showed that the system had vast absorption capacity, and that the CO_2 rich loading mostly consisted of MAPA and water, while the CO_2 poor phase mostly consisted of DEEA.

The DEEA/MAPA ratios in this work are such that the blend is kept in single phase.

2.5 Amino Acid Salts

All though chemical absorption of CO_2 has a broad range of advantages, there is some disadvantages that must be considered. Significant amounts of energy is needed in order to regenerate the absorbent, and challenges with the environmental impacts which amines can cause (Shen et al., 2016).

Aronu et al. (2010) investigated the absorption potential of MAPA promoted amino acid salts; glycine, β-alanine and sarcosine. The promoted amino acid salts were compared with the potassium salt of sarcosine and MEA.The neutralized amino acid solutions attained similar loadings as the base-case 2.5M MEA (0.53 mol CO_2/mol solvent) , and promoted sarcosine and promoted potassium salt of sarcosine achieved higher CO_2 loading than 5M MEA (0.52 mol CO_2/mol solvent). All the systems show a cyclic capacity comparable to MEA, varying from 0.25 mol CO_2/mol solvent to 0.34 mol CO_2/mol solvent.

Muñoz et al. (2009) based their study of new liquid absorbents for CO_2 removal on the compounds chemical and physical properties. L-Arginine was one of the candidates in this study, where the chemicals were tested for two absorption cycles. The aborption capacity for the first cycle were 1.70 mol CO_2 per mol amino acid, and for the second cycle 0.80 mol CO_2 per mol amino acid. It is clear that L-Arginine lose capacity after the first absorption cycle, and it is stated that it remains constant after the second one. Muñoz et al. (2009) concluded that L-Arginine can absorb CO_2 effectively, and with a high absorption capacity.

The addition of 5 wt % L-Arginine was found to be an effective rate promoter to improve the CO_2 capture efficiency of potassium carbonate, with a improved CO_2 uptake by a factor of 2.0-3.0 (Shen et al., 2013, Shen et al., 2016). L-Arginine achieve a higher CO_2 absorption loading than MEA, but suffer from slow reaction kinetics (Yan et al., 2015).

It was not found any literature data of Creatine being used as a CO_2 absorbing agent.

Acid Dissociation Constant (pK_a)

Amines are weak bases which are in equilibrium with their ammonium ion in aqueous solution. Nitrogen is electronegative and therefore more capable of stabilizing a positive charge (Patrick, 2004). The more electronegative the atom, the less basic the compound will be, due to stabilization of the charge by the electronegative atom. Several open publications state that it exsist a correlation bewteen reaction rate and pK_a and report that the reaction rates increase with increased pK_a (da Silva and Svendsen, 2007).

The dissociation of the conjugate base of a primary amine is shown in Equation (XIV). An alkyl group releases electrons, and it stabilizes the alkylaminium ion that results from the acid-base reaction by dispersing its positive charge. It inductively stabilizes the alkylaminium ion to a grater extent than it stabilizes the amine (Solomons and Fryhle, 2011).

$$RNH_3^+ + H_2O \leftrightarrow RNH_2 + H_3O^+ \qquad \text{(XIV)}$$

The basicity of amines increase with increasing methyl substitution: and the order is:

$$RR'NH > RNH_2 > RR'R''N > NH_3 \qquad \text{(XV)}$$

In aqueous solution the aminuim ions formed from secondary and primary amines are stabilized by solvation through hydrogen bonding much more effectively than the aminuum ions formed from tertiary amines are. The tertiary amines only have one hydrogen to use in hydrogen bonding, where primary and secondary have three and two, respectively, possibilities to form hydrogen bonds (Solomons and Fryhle, 2011). In general, one can say that primary and secondary amines are stronger bases than tertiary amines.

Knowing the pK_a value is very helpful for evaluating the proton acceptor ability of the amines, as well as the CO_2 absorption and regeneration processes (Tagiuri et al., 2016). The solvents ability to absorbe CO_2 is amine highly dependent on the alkalinity.

Table 2.8 present the pK_a values for the chemicals used in the 1st screening campaing. The pK_a value decrease with increasing temperature, and this is desirable. When the basicity decrease with temperature, the heat of desorption is decreased, which again reduce the stripping heat (Rayer et al., 2014).

Table 2.8 Measured pK_a for the amines studied in the 1st screening campaign at different temperatures

Compound	T= 25 °C	T = 40 °C	Source
Monoethanolamine	9.45	9.06	(Rayer et al., 2014)
3-(Methylamino)propylamine	10.6		(Puxty et al., 2009)
2-(Diethylamino)ethanol	9.73	9.45	(Rayer et al., 2014)
Triethanolamine	7.73	7.42	(Rayer et al., 2014)
N-Butyldiethanolamine	8.9	8.6	(Rayer et al., 2014)
N-Ethyldiethanolamine	8.8	8.54	(Rayer et al., 2014)
N-tert-Butyldiethanolamine	9.03	8.75	(Rayer et al., 2014)

Figure 2.9 depict the pK_a trends with respect to addition of $-CH_3$ and $-OH$ groups. One can see that the basiticy decrease with increasing -OH functions. The decrease is approximately one pK_a unit per -OH group. The effect of alkyl chain length addition is less clear, but one can see a modest increase from EDEA to t-BDEA.

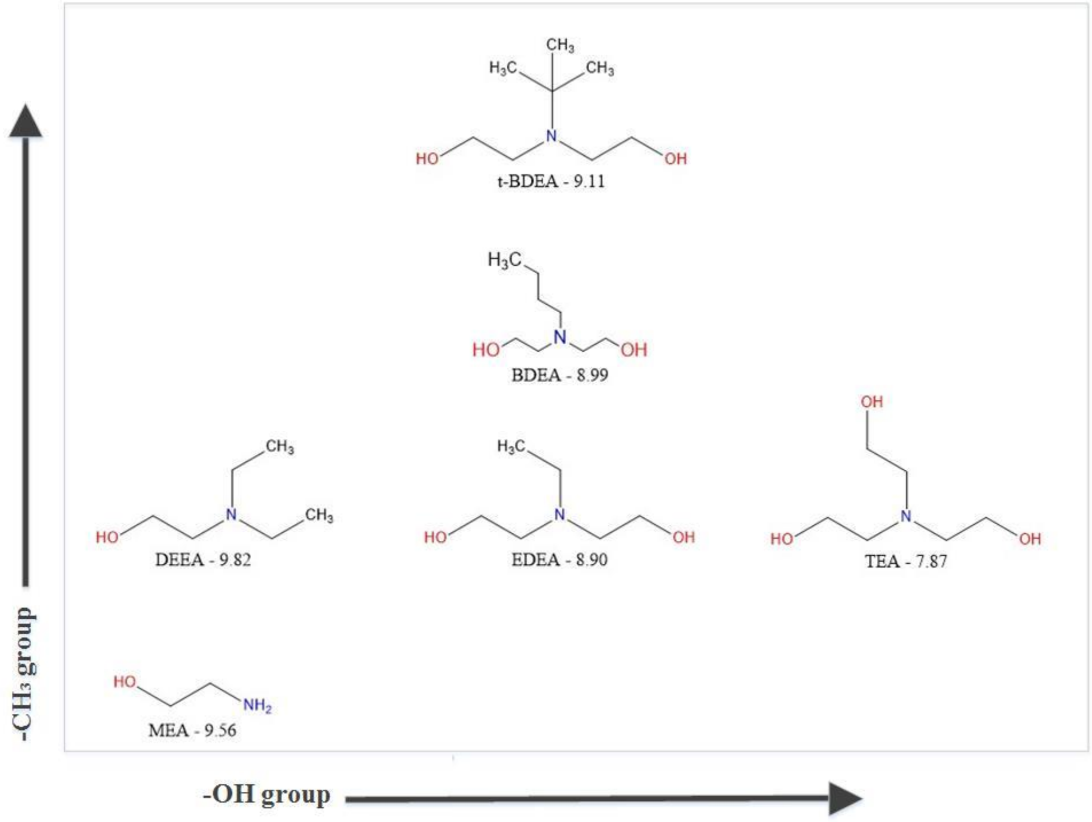


Figure 2.9 Trend in pKa values of the amines with respect to the addition of $-CH_3$ and $-OH$ groups at 20 °C

The dissociation constant for the compounds tested in the 2nd screening campaign are found in Table 2.9. As for the compounds used in the 1st screening campaign, the pK_a value decrease with increasing temperature, which is beneficial for low energy consuming stripping.

Table 2.9 Measured pK_a for the compounds tested in the 2nd campaign of screening experiments

Compound	T= 25 °C	T = 45 °C	Source
1,2-Diaminocyclohexane	9.58	9.27	(Evjen et al., 2016)
N-Benzylmethylamine	9.38	9.10	(Evjen et al., 2016)
N,N-Dimethylbenzylamine	9.02[1]	8.48	(Evjen et al., 2016)
Phenyletylamine	9.93	9.24	(Evjen et al., 2016)
Creatine	12.7[2]		(Politzer and Murray, 1994)
L-Arginine	11.88[3]	11.78[3,4]	(Nagai et al., 2008)
[1] T= 35 °C [2] Temperature unknown [3] pK_a value of the guanidinium group in free arginine [4] T= 40 °C			

The pK_a value for the arginine side chain only decrease slightly with increasing temperature. This may indicate that it is hard to remove the absorbed CO_2 from the solvent, and that regeneration can be challenging.

3 Materials and Methods

This section gives a detailed description of the materials and methods that were used during this work.

3.1 Screening

The screening method is used to acquire first-hand knowledge on the behavior of each solvent system in an absorption process. There is no guarantee that the bubble structure, and therefore the gas–liquid interfacial area was exactly the same during all experiments, therefore it is qualified as a semi-quantitative measurement. However, the superficial gas velocity was the same, so any differences would arise mainly due to variations in interfacial tension, bubble coalescence properties and viscosity (Ma’mun et al., 2007).

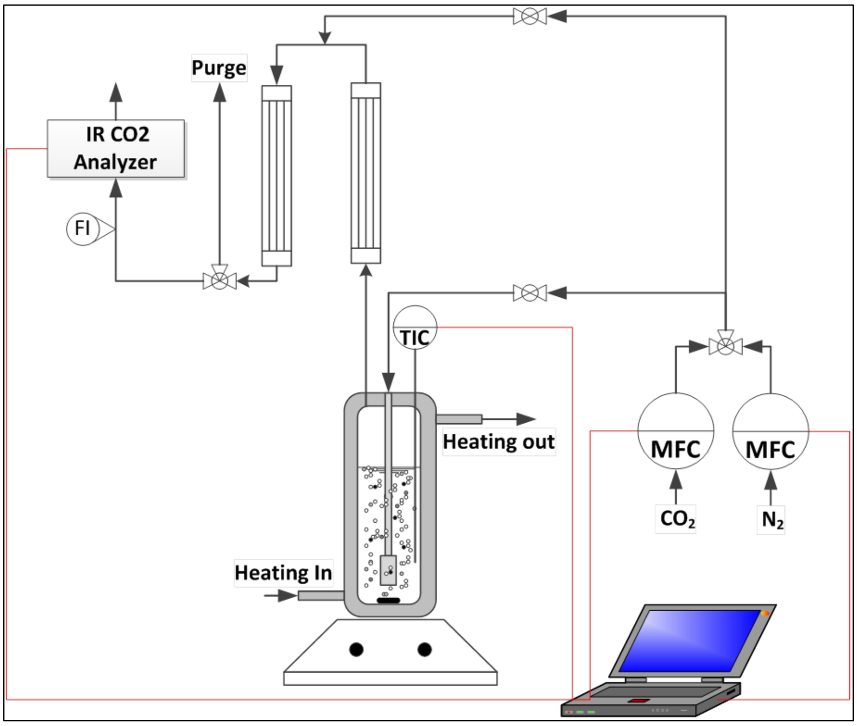


Figure 3.1 Sketch of screening apparatus (Hartono et al., 2016)

The screening apparatus operate under atmospheric conditions up to 80 °C and was applied as described in (Aronu et al., 2011b) and (Hartono et al., 2016). 120 - 125 g amine solution was weighted into a small jacketed reactor. With support from a *Julabo* water bath that is set to 40 degrees for absorption, the temperature is kept constant. The reactor was put on a magnetic stirrer at 450 rpm to ensure good mixing Absorption of CO_2 with solvent took place at 40 °C up to 9.5 kPa CO_2 partial pressure, while stripping of the same solvent occurred at 80 °C down to 1.0 kPa CO_2 concentration in gas phase (Aronu et al., 2011b).

Two *Bronkhors® High-Tech mass flow controllers* (MFC) were used to control the composition of the feed gas, containing 90 % N_2 and 10 % CO_2. The gas mixture is bubbled through the solvent in the reactor. The velocity was set to 1NL/min in order to reduce amine sweep out of reactor. The gas that is not absorbed goes through two condensers before it reaches the *Fisher–Rosemount BINOS® 100 NDIR CO_2 analyzer*. The equipment holds two different channels for adjusting the gas composition. Channel 1 is used up to 10 vol. % CO_2 content in the gas mixture, while channel 2 is used for CO_2 concentrations up to 35 vol. %. The software *LabVIEW* is set to log every minute.

3.1.1 Absorption-Desorption Calculations

LabVIEW logs data such as time [min], mass flow of CO_2 and N_2 gas in to reactor $\left[\frac{Nl}{min}\right]$, temperature [°C], CO_2 out of reactor [vol. %], CO_2 accumulated in solution [Nl] and rate of absorption $\left[\frac{Nl}{min}\right]$ every minute. The amount of CO_2 absorbed by the amine system was calculated with the logged data as a basis, as given in Equation (1).

$$Q_{CO_2}\left[\frac{mol\ CO_2\ in\ solution}{s}\right] = n_{CO_2}^{in} - \frac{x_{CO_2}^{out} \cdot n_{N_2}^{in}}{1 - x_{CO_2}^{out}} \tag{1}$$

$n_{CO_2}^{in}, n_{N_2}^{in}$ and $x_{CO_2}^{out}$ are the amount of CO_2 and N_2 fed into the reactor, and the volume percentage of CO_2 gas leaving the reactor, which was recorded by the MFC and the CO_2 analyzer (Hartono et al., 2016).

The accumulated amount of CO_2 absorbed was then integrated as presented by Equation (2).

$$N_{CO_2}[mol\ CO_2] = \int_0^t Q_{CO_2} \cdot dt \tag{2}$$

Equation (3) calculates the absorption and stripping rates in $\frac{mol\ CO_2}{kg\ solution \cdot s}$.

$$r_{CO_2}\left[\frac{mol\ CO_2\ in\ solution}{kg\ solution \cdot s}\right] = \frac{Q_{CO_2}}{M_{solution}} \tag{3}$$

$M_{solution}$ is the amount of solvent added to the reactor in grams, recorded by *Mettler Toledo MS 603S* balance prior to screening experiment. 5-10 grams sample is withdrawn from the reactor via syringe after absorption is completed. The small amount of sample taken is presumed not to disturb the mass balance during the desorption process.

By dividing total amount of CO_2 absorbed or stripped with the total amount of solvent in the reactor, as seen in Equation (4), we get the loading. α_{rich} is the total amount of CO_2 absorbed by the system, while α_{lean} is the total amount of CO_2 stripped from the system (Aronu et al., 2011b).

$$\alpha\left[\frac{mol\ CO_2}{kg\ solution}\right] = \frac{N_{CO_2}}{M_{solution}} \tag{4}$$

Cyclic capacity is the difference between rich and lean loading, and are calculated by Equation (5).

$$Q_{cyc}\left[\frac{mol\ CO_2}{kg\ solution}\right] = \alpha_{rich} - \alpha_{lean} \tag{5}$$

3.2 CO_2 and Amine Analysis

Samples taken after absorption and desorption of the screening experiments were analyzed for CO_2 and amine content. When knowing these concentrations, the loading was found according to Equation (6).

$$\alpha\left[\frac{mol\ CO_2}{mol\ amine}\right] = \frac{C_{CO_2}}{C_{amine}} \tag{6}$$

Where C_{CO_2} and C_{amine} is the concentration of CO_2 and amine, respectively. To compare with screening results the loading is multiplied with amine concentration [mol·kg^{-1}].

3.2.1 CO_2 Analysis

After terminating the experiment, the absorption and desorption samples were analyzed by the barium chloride method described by (Ma'mun et al., 2007).

25 mL 0.5M $BaCl_2$ and 50 mL 0.1M NaOH dispensed into an Erlenmeyer flask, before the sample was weighted in. The amount of sample was adjusted by the expected CO_2 concentration. Two parallels per sample was prepared, and one additional blank to account for the CO_2 content in the air.

The alkaline environment makes the carbon dioxide precipitate according to Le Châterlier's Principle and Reaction (XVI).

$$Ba^{2+} + CO_2 + 2OH^- = BaCO_3(s) + H_2O \qquad \text{(XVI)}$$

Heat enhances the reaction, so the flasks were set to boil for ~4 minutes. Before filtration with *MF-Millipore 0.45 µm HA membrane filter* the solution is cooled down to ambient temperature. The filtration took place in a standard vacuum filtration setup. After filtration the filter paper was transferred to a 250 mL tall beaker, and the filter cup was rinsed with 50 mL IC-water.

After filtration, 0.1M Hydrochloric acid was dispensed into the beakers to dissolve the filter cake. The beakers were tared on the balance before adding 10 mL 0.1 M HCl to the blank, and 40 mL to each of the samples. The amount of acid added to the beaker was noted in grams.

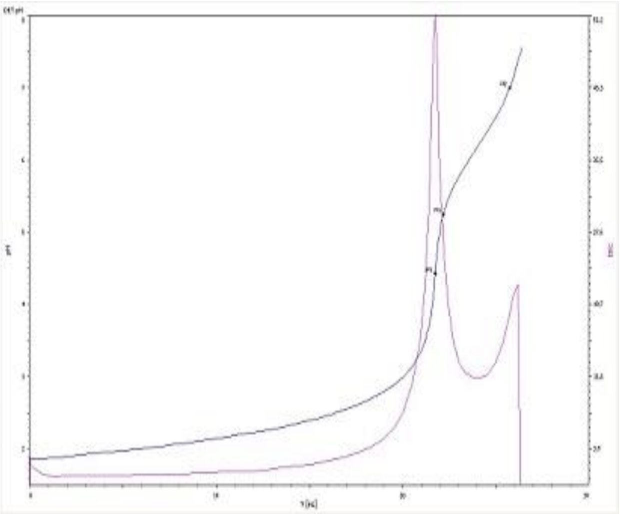
$$BaCO_3(s) + HCl = BaCl_2 + CO_2 + H_2O \qquad \text{(XVII)}$$

Metal carbonate and hydrochloric acid reacted according to Reaction (XVII) to form barium chloride, water and also liberate carbon dioxide into the solution.

To ensure that the precipitate got fully dissolved, the beaker containing a small magnet was placed on a magnetic stirrer. Once the barium carbonate was fully dissolved, the titration was started.

The amount of acid that did not participate in dissolving the solids was titrated with 0.1M NaOH in a neutralization reaction. The equipment used for the potentiometric titration was *Methrom 809 Titrando* together with an *814 USB sample Processor*, and the software *Tiamo 2.3*.

The amount of sodium hydroxide needed to reach pH 5.25 was used to calculate the CO_2 content in the sample.



Left: Figure 3.2 Methrom 809 Titrando and 814 USB sample Processor (Methrom, 2016)

Right: Figure 3.3 Titration curve for determination of CO_2 content in loaded 3M DEEA sample taken after absorption at 40 °C

The concentration of CO_2 is given in $\frac{mol\ CO_2}{kg\ amine\ solution}$, and is found from Equation (7).

$$[CO_2]\left(\frac{mol}{kg}\right) = \frac{HCl(g) - NaOH(mL) - [Blank\ HCl(g) - Blank\ NaOH(mL)]}{20 \times Sample\ (g)} \tag{7}$$

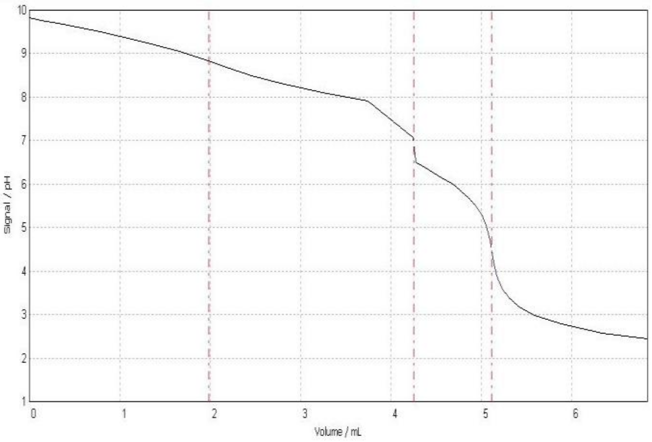
The acceptable deviation between the parallels is 3.0 %.

3.2.2 Amine Analysis

A *Mettler Toledo G20 Compact titrator* with an accompanying *Rondolino TTL* was used to determine the amine concentration of the screening samples by potentiometric titration. *LabX titration* was the software that controlled and set the titration procedure.

0.2 mL sample was weighted into small beakers already containing 50 mL IC-water. The samples were then titrated with 0.1N sulphuric acid until a pH-level of 2.5 is reached.

The reaction is according to Brønsted-Lowry theory of acids and bases, where the base (in this case the functional groups of the amine) acts as a hydrogen ion acceptor (Kauffman, 1988). The stoichiometry is 1:1.



Left: Figure 3.4 Mettler Toledo G20 Compact with Rondolino TTL (Toledo, 2016)

Right: Figure 3.5*Titration curve for determining amine concentration of 3M DEEA after absorption at 40°C*

The first sample of each run is a blank that only contain DI-water.
To ensure trustworthy results, two parallels of each sample are analyzed. Approved discrepancies between parallels are 3.0 %.

$$[Amine]\left(\frac{mol\ amine\ groups}{kg}\right) = \frac{H_2SO_4(ml) \times 0.2(\frac{mol\ H^+}{L})}{Sample\ (g)} \qquad (5)$$

LabX 3.1 titration use Equation 5 to calculate the amine concentration, and give the result in $\frac{mol\ amine\ groups}{kg\ amine\ solution}$.

3.3 Chemicals and Solution Preparation

Commercially available chemicals used in this work are presented in Table 3.1. All of the chemicals were used without further purification.

Aqueous solutions were prepared by dissolving the chemicals into DI-water by gravimetric procedure. The balance used for gravimetric preparation of the solutions was a *Mettler Toledo MS6002 New Classic* with an uncertainty of $\pm 10^{-5}$ kg.

Table 3.1 Chemicals used in this work

Chemical	**Abbreviation**	**Molecular weight [g/mol]**	**CAS**	**Purity [%]**	**Provider**
2-(Diethylamino)ethanol	DEEA	117.19	100-37-8	≥99.5	Sigma Aldrich
N-Butyldiethanolamine	BDEA	161.24	102-79-4	98.60	Sigma Aldrich
N-Ethyldiethanolamine	EDEA	133.19	139-87-7	98	Sigma Aldrich
3-(Methylamino)propylamine	MAPA	88.15	6291-84-5	≥97	Sigma Aldrich
N-tert-Butyldiethanolamine	t-BDEA	161.24	2160-93-2	97	TCI Europe

Triethanolamine	TEA	149.19	102-71-6	≥99.0	Sigma Aldrich
L-Arginine	ARG	174.2	74-79-3	99	Sigma Aldrich
Creatine	CRE	131.14	6020-87-7	≥98	Sigma Aldrich
1,2-Diaminocyclohexane	DACH	114.19	694-83-7	99	Sigma Aldrich
N,*N*-Dimethylbenzylamine	DMBA	135.21	103-83-3	≥99	Sigma Aldrich
N-Benzylmethylamine	BMA	121.18	103-67-3	97	Sigma Aldrich
Potassium hydroxide	KOH	56.11	1310-58-3	85	SdS[1]
Phenyletylamine	PEA	121.18	64-04-0	99	Sigma Aldrich
Polypropylene Glycol	Antifoam	76.10	25322-69-4	NA	NEEC[2]
Carbon Dioxide	CO_2	44.01	124-38-9	99.999	Yara-Praxair
Monoethanolamine	MEA	61.08	141-43-5	≥99	Sigma Aldrich
Nitrogen	N_2	14.01	7727-37-9	99.998	Yara-Praxair

[1] SdS is now known as Carlo Erba Reagents

[2] NEEC = Nalco/Exxon Energy Chemicals L.P.

3.4 Experimental Design

The screening work was divided into two campaigns. The first screening campaign, focused on the effect of molecular structure and molar ratio between the tertiary amine and the promoter in a blended solvent system. The second screening campaign looked at potential new solvents and promoters for CO_2 capture.

3.4.1 Experimental Setup - 1st Campaign

In the first campaign, the molecular structure of the tertiary amine and the molar ratio between the 3° amine/promoter was systematically varied to investigate the effect of absorption and desorption performance.

30 wt. % MEA is used as the base case, while 3M and 4M MEA was used for comparison at equimolar basis. 3M DEEA was screened three times in order to check the reproducibility of the screening apparatus.

Table present the different experiments performed in this campaign. The ratios 3:1, 2:1 and 1:1 have a concentration of 3M tertiary amine/1M MAPA, 2.67M tertiary amine/1.33M MAPA, 2M tertiary amine/2M MAPA, respectively. A total of 24 experiments are evaluated in this part of the study.

Table 3.2 Experiment Matrix – First campaign

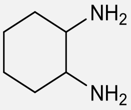
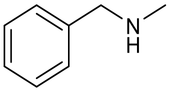
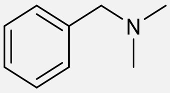
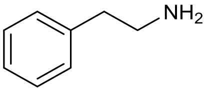
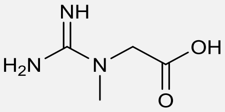
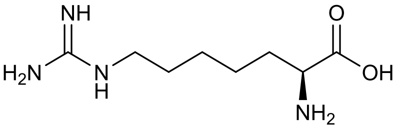
Chemical	Concentration/ratio						
	30 wt. %	1M	3M	4M	3:1	2:2	1:1
MEA	x		x	x			
MAPA		x					
DEEA			x		x	x	x
TEA			x		x	x	x
BDEA			x		x	x	x
EDEA			x		x	x	x
t-BDEA			x		x	x	x

The chemicals selected deviate from each other, either by extending the alkyl chain structure (EDEA → BDEA → t-BDEA) or by adding amine alkanol groups (DEEA → EDEA → TEA). The pK_a values of the single amines were also evaluated against absorption capacity.

3.4.2 Experimental Setup - 2nd Campaign

MAPA is classified as a toxic chemical due to its high volatility and have a very high degradation rate in presence of CO_2. The findings from (Eide-Haugmo et al., 2009) show that the thermal degradation of MAPA in presence of CO_2 is 50 %, this is much higher than the biodegradability. The lack of stability under process conditions creates a desire to find new and promising solvents and promoters. A total of 6 chemicals were outlined as promising for the 2nd screening campaign, as seen in Table 3.3.

Table 3.3 Chemicals elected for second screening campaign

Compound	CAS	Structure
1,2-Diaminocyclohexane	20439-47-8	
N-Benzylmethylamine	103-67-3	
N,N-Dimethylbenzylamine	103-83-3	
Phenyletylamine	64-04-0	
Creatine	57-00-1	
L-Arginine	7200-25-1	

The experiments that were run are found in Table 3.4*3.4*. MEA 30 wt. % was used as reference for the blends, 1M MAPA was as comparison of promoter properties. After single runs, the chemicals were tested if they could act as a promoter to DEEA. The solutions were made in the ratio 3M DEEA + 1M promoter. The new promoter systems were compared against the 3M DEEA + 1M MAPA system screened in the 1st campaign.

Table 3.4 Experiment Matrix – Second campaign

Chemical	Concentration/ratio				
	30 wt. %	1M	14 wt. %	1:3	5 wt. %:3M
MEA	x				
MAPA					
BMA	x			x	
DBMA	x			x	
ARG			x		x

As ARG also have a low solubility in water, a solution of 14 wt. %ARG in water was made. When dissolving ARG in DEEA the solubility decreases drastically. Therefore, a solution containing 5 wt. % ARG and 3M DEEA was prepared and screened.

4 Results and Discussion

The results are discussed in terms of absorption capacities and cyclic capacities. Absorption curves corrected with liquid analyzes are used to explain and evaluate the absorption rates. The liquid analysis is used as a basis for discussing the loadings and cyclic capacities. Lastly cyclic capacity and absorption rate is looked at from a pK_a point of view. It is early emphasized to explain the credibility of screening values seen in light of the liquid analysis.

First out is the discussion of whether screening data is usable or not. And an explanation of why the results are presented as they are, is given. Then, single amine solvents from the first screening campaign are presented, followed by the blended amine solvents. The results from the blended amine solvents is given in two ways, focusing on the ratio between 3° amine and MAPA, or the effect of molecular structure. After that, a discussion on the cyclic capacity and on pK_a of the blends follow. Last out, presentation of the second screening campaign.

4.1 Differences between Screening Values and Liquid Analysis

As discussed in Chapter 2, finding similar screening experimental data are challenging and the obtained data are not directly comparable if the experiment was not conducted at similar temperature, concentration and CO_2 partial pressure. Single tertiary amines pose an additional challenge, because of their slow reaction with CO_2. The CO_2 analyzer drifts a lot, and it is hard to say if the end-point really is where the absorption is stopped. Figure 4.1 show that 3M DEEA is screened three times and 30 wt. % MEA two times. Since the results are similar for the different parallels, we conclude that the reproducibility is sufficient, and that it is no purpose in screening the amines more than once.

However, all though the reproducibility of the screening apparatus is sufficient, there are large discrepancies between screening values and the results given from the liquid analysis. This is discussed further on.

The difference between the two different 30 wt. % MEA runs, depicted in Figure 4.1, is the sinter. One can see that the run with new sinter show a higher absorption rate than the one with the old sinter. The new sinter improves the hydrodynamic gas/liquid contact, and a good gas/liquid enhances the surface contact area, which is important for absorption processes. The rich loading for the experiment conducted with the old sinter was determined to be 2.49 mol

CO_2/kg amine, whereas the experiment performed after sinter change completed at a rich loading of to 2.53 mol CO_2/kg amine. The rich loading difference is expected within 2 %. Beside the 30 wt. % MEA experiment prior to sinter change, the other screening experiments are conducted after the sinter change. Since screening is a semi-quantitative measurement, it is important to keep the layout as similar as possible. All the solvents are therefore screened in the same reactor, with the same magnet and at the same operational conditions. Solely the 30 wt. % MEA screened after sinter change is used in further discussions.

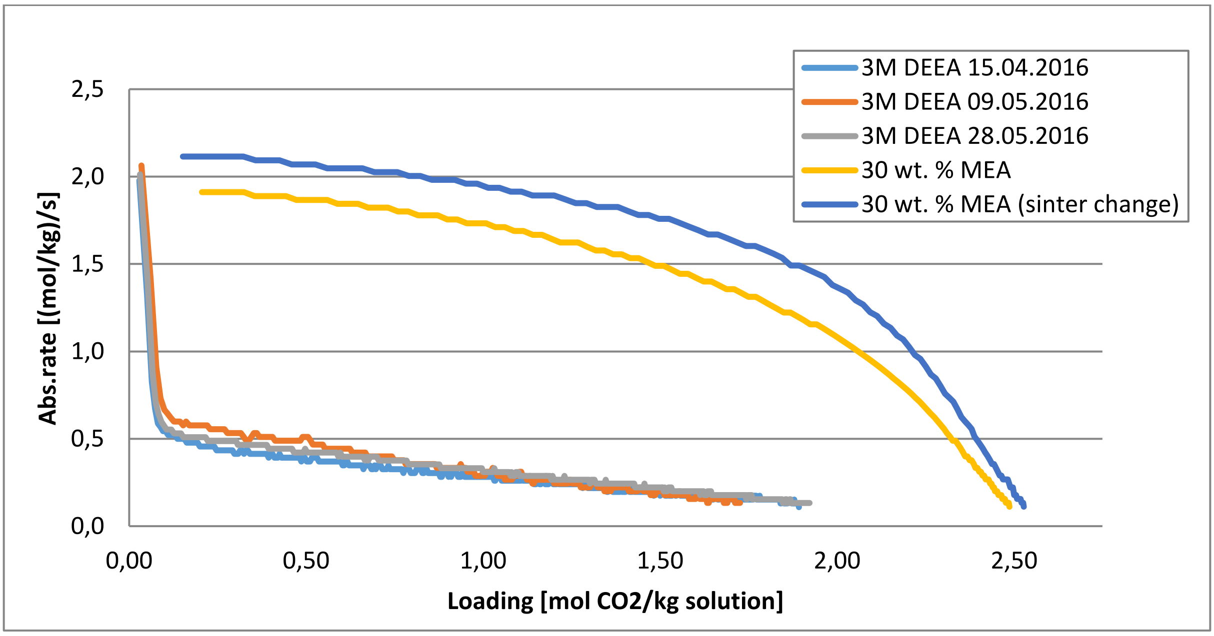


Figure 4.1 Absorption curves from screening of 3M DEEA and 30 wt.% MEA at 40 °C

The rate of the 3M DEEA screening performed 09.05.2016 had a steeper rate drop than the other two 3M DEEA screenings, which caused a shorter duration of the experiment. There was not found a reason why the predictions in this experiment deviated from the two others, other than the plausible reasons discussed later on. One thing that is very interesting is that the deviating screening experiment, display improved coherence between results from liquid analysis and screening. Wort noting is that it is the first 3M DEEA run (15.04.2016) which is used further discussions.

The 30 wt. % screening experiment performed after sinter change was used as the benchmark solvent. In terms of moles, the absorption capacity for 30 wt. % MEA after sinter change was found to be 0.51 mol CO_2/mol amine, while the cyclic capacity was 0.26 mol CO_2/mol amine.

This is in good agreement with the results from Hartono et al. (2016), which used the same equipment under the same conditions. They did not report it any analyze liquid samples taken after absorption and stripping. Therefore it concluded that they only reported their results base on the gas phase calculation (see Equation (1)).

Hartono et al. (2016) also performed screening on 30 wt. % (~2.6 M) DEEA, and got a rich loading of 0.78 mol CO_2/mol amine and a cyclic capacity of 0.36 mol CO_2/mol amine. From the screenings of 3M DEEA in this work, the absorption potentials ranged from 0.56 to 0.63 mol CO_2/mol amine, and the cyclic capacity found from the liquid analysis was determined from 0.51 to 0.57 mol CO_2/mol amine. As for MEA, Hartono et al. (2016) did not perform analyzes on liquid phase after screening DEEA either. The difference may be caused by concentration effect.

Table 4.1 show that there are vast differences between the CO_2 loading from screening, and the results obtained from liquid analysis. Especially the lean loading for 3M DEEA display tremendously deviations, of more than 300 percent. The difference between screening and liquid analysis is less when using amines that react more rapidly (5M MEA), or blends of tertiary amines with MAPA (2.67M BDEA+1.33M MAPA), as seen from the Table 4.1. It was also expected that the lean loading would address larger disagreement than the rich loading, as the error would accumulate from the absorption part of the experiment. One can expect liquid analysis/screening deviation of around 5 % for both absorption and desorption. If better accuracy is needed one should proceed to VLE-experiments. However, as VLE is more time consuming, screening is a good solution for fast characterization and selection of potential solvents.

Table 4.1 Data from the three different 3M DEEA screenings, 30 wt. % MEA and ratio 2 BDEA/MAPA with corresponding results from the liquid analysis. S=screening, LA= liquid analysis and Dev. = deviation

Run	Sample mass [g]	Abs. time [min]	Rich loading [mol/kg]			Lean loading [mol/kg]			Cyclic capacity [mol/kg]		
			S	LA	Dev. [%]	S	LA	Dev. [%]	S	LA	Dev. [%]
3M DEEA (15.04.16)	123	551	2.44	1.89	29	1.03	0.17	513	1.41	1.73	18
3M DEEA (09.05.16)	121	386	1.97	1.73	14	0.68	0.17	304	1.30	1.56	17
3M DEEA (28.05.16)	121	537	2.58	1.92	34	1.18	0.18	567	1.39	1.75	20
30 wt.% MEA	120	124	2.60	2.53	3	1.54	1.25	22	1.06	1.27	17
BDEA/MAPA	120	122	1.84	1.68	18	0.97	0.69	45	0.87	0.99	29

Reasons for discrepancies between screening and liquid analysis may be that the experiment is performed in a small reactor. In larger reactors, the errors would not accumulate to such an extent as in a smaller one. As the absorption takes place at 40 °C and the stripping at 80 °C, there is always some risk associated with evaporation during sampling. After stripping the solvent is cooled down to 40 °C, which reduce the risk of evaporation. Further, if the solvent has a high vapor pressure this could lead to solvent loss, causing deviations in vapor/liquid mass balance.

In addition, there is a possibility for leakage throughout the screening apparatus. This source of error is, however, pretty well under control, since the gas flow is logged every minute. The last, but maybe the most considerable contributor to error between lean loading analyses is due to CO_2 lost during the heating process from 40 °C to 80 °C. Although the data during the heating period also is registered, it is seen in the rotameter that a low gas flow is sent to the CO_2 analyzer. During steady conditions (for both absorption/desorption), 1NL/min of gas was sent to the CO_2 analyzer. This low gas flow affects the reading of the analyzer. As the equilibrium curves showed, the loading is dependent on temperature, and in general heating lower the loading. Thus the solvent release CO_2 which is not perceived by the CO_2 analyzer. Tertiary amines have lower heat of desorption, and therefore release more CO_2 during heating, and this leads to the immense mass balance errors shown in Table 4.1.

Due to the extensive divergence between screening and liquid samples, absorption curves are used to discuss absorption rates. The curves are corrected so that the rich loading corresponds to the loading value obtained from liquid analysis. Liquid analysis is used to present and discuss loadings and cyclic capacities. Since the only the liquid analysis is used for cyclic capacity calculations, the stripping curves are not presented.

The liquid analysis from the first screening campaign is also supported by quantitative NMR-experiments, performed by postdoc Cristina Perinu. The NMR-results show good correlations with the CO_2 analysis, indicating that both results have a good agreement within 10 %.

4.2 Single Amine Solvents

To see the absorption rate and absorption capacities of the tertiary amines, the single amine systems were screened in a concentration of 3 $mol \cdot L^{-1}$.

From Figure 4.2 it is easy to see that the tertiary amines, DEEA, TEA, BDEA, EDEA and t-BDEA, have a low absorption rates, and except for 3M DEEA, they also have low absorption capacities. While MEA is a primary amine and react fast with CO_2.

The figure also illustrate that 1M MAPA have a high absorption rate, but it does not reach as high rich loading as MEA due to concentration difference. 1M MAPAs absorption capacity is found to be 1.12 mol CO_2/kg amine. Because of MAPAs high absorption rate, it is interesting to see its ability to act as a promoter for the tertiary amines.

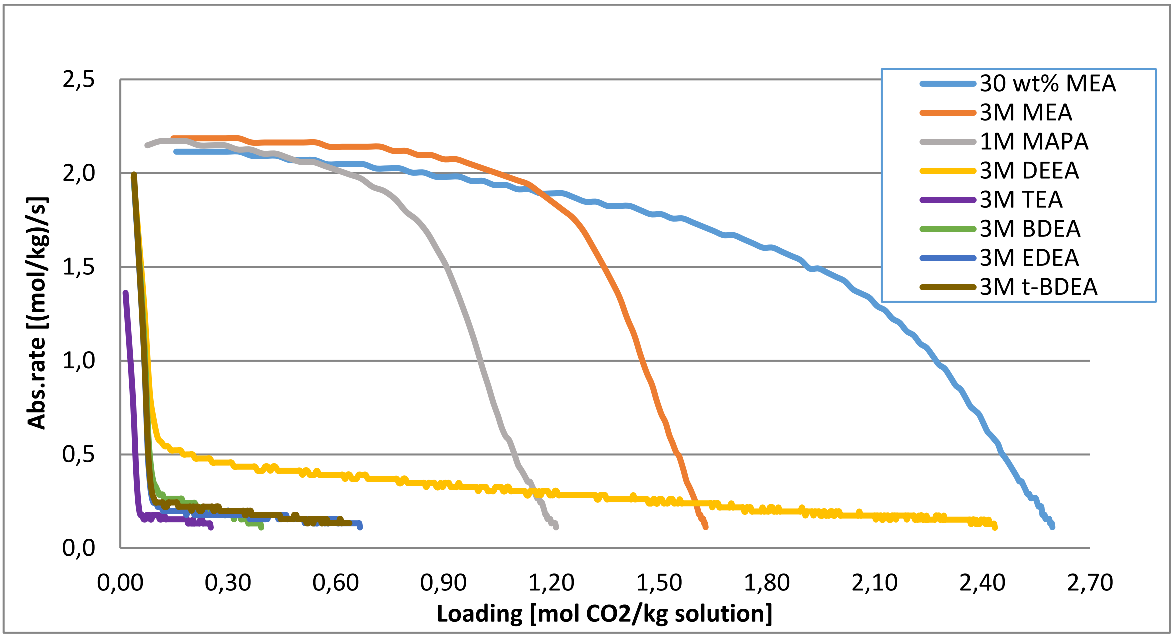


Figure 4.2 Absorption rate of ternary amines plus 30 wt. % and 3M MEA versus loading

The single 3M tertiary amines was evaluated against 3M MEA so that the concentration of amine is comparable, and also against the conventional 30 wt. % MEA. We clearly see that DEEA have a far better absorption capacity than any of the other tertiary amines, at 1.89 mol CO_2/kg amine. The rich loading of 3M DEEA is found to be 18 % higher than 3M MEA (1.60 mol CO_2/kg amine). However, not as high as the loading of the conventional 30 wt. % MEA, which have an absorption capacity of 2.53 mol CO_2/kg amine.

After DEEA, the order of increasing absorption capacity is t-BDEA, EDEA, BDEA and TEA, with absorption capacities of 0.40, 0.35, 0.28 and 0.16 mol CO_2/kg amine, respectively. This is respectively 84 (t-BDEA), 86 (EDEA), 89 (BDEA) and 93 % (TEA) lower than the rich loading of 30 wt. % MEA. The rich loading of t-BDEA and BDEA are similar (0.05 and 0.04 mol CO_2/kg amine, respectively).

From Figure 4.3 one can see the rich and lean loadings and the cyclic capacities, all determined by liquid analysis. All of the tertiary amines exhibit a high cyclic capacity relative to their rich loading. This means that it is easy to regenerate the solvent, which is a typical feature for 3° amines. As a diamine, MAPA have a high rich loading, but is not as easily regenerated as the tertiary amines are.

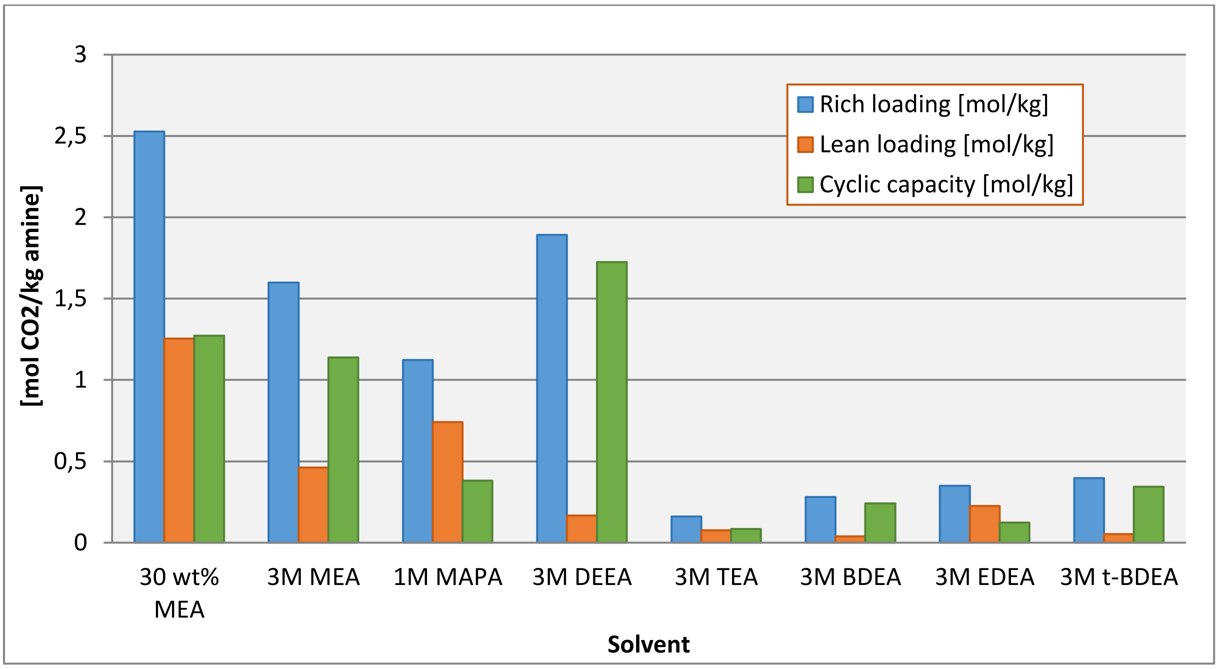


Figure 4.3 Rich and lean loadings and cyclic capacity of tertiary amines plus MEA and MAPA

3M DEEA obtain a cyclic capacity of 1.73 mol CO_2/kg amine, and remove 91 % of the CO_2 captured in the absorption process. This is more than the benchmark solvent, 30 wt. % MEA, which has a 50 % removal degree and a cyclic capacity of 1.27 mol CO_2/kg amine. 3M MEA remove 71 % of the absorbed CO_2, and acheive a lean loading of 1.14 mol CO_2/kg amine. The dissimilarity in removal rate between 3M and 30 wt. % MEA may result from the concentration difference. If more amine is present, and by that a higher amount of CO_2 get absorbed, it will be harder to strip away the CO_2 captured.

MAPA remove only 33 % of the CO_2 captured during the absorption, and have a cyclic capacity of 0.74 mol CO_2/kg amine. 3M TEA, BDEA. EDEA and t-BDEA remove respectively 52, 86, 35 and 87 % of the CO_2 during regeneration. The high removal rates are excpected for tertiary amines, and is why they are interesting to use in blends. High removal rates is beneficial for energy sparse regeneration.

In Figure 4.3 the results from liquid analysis are compared against the screening values. In all the cases, the screening over predicts the loadings, and therefore also the cyclic capacity. Since the relative numbers dealt with are so small, even a small-numbered error will cause a big impact.

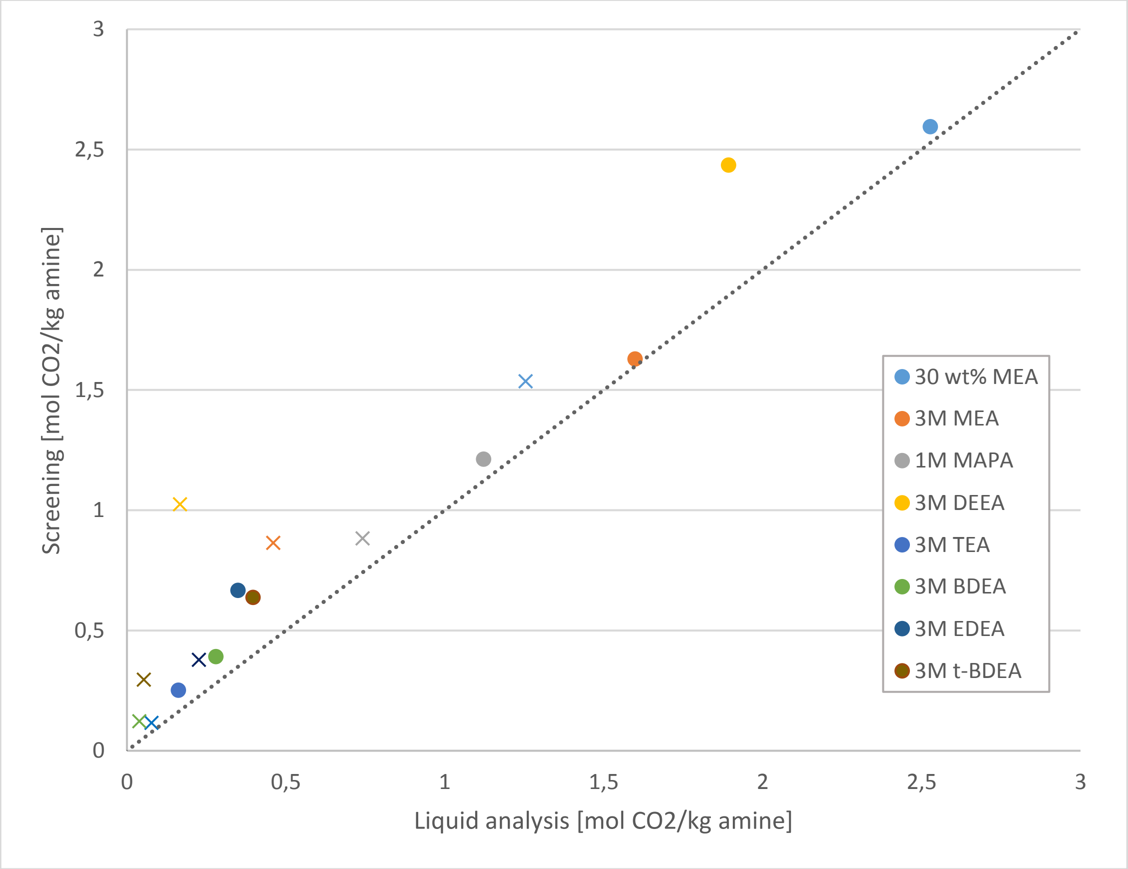


Figure 4.4 Cyclic capacity and loadings from liquid analysis vs. screening values. Circles represent rich loading, and crosses represent lean loading

One can see that the lean loadings (crosses) give larger errors than the rich loadings (circles), due to accumulation of error trough the experiment. One can also see that the faster amines, MEA and MAPA, give a smaller deviation than the slower tertiary amines.

4.3 Blended Amine Solvents

After the single tertiary amines were screened, the blends were run. The results obtained from the blends are interpreted with two different focuses. Equal blends are compared with each other, but with varying concentrations. This approach exposes the effect of the ratio between 3° amine and MAPA.

The different blends are set side by side, all having the same concentrations. By doing this, the molecular structures are compared, and give an insight of which functional groups that could be profitable or inadequate for CO_2 absorption.

Due to foaming of solutions containing EDEA, BDEA and DMBA, 1000 ppm antifoam was added after solution preparation. This high antifoam concentration is not desirable in a conventional chemical absorption process, but regarded as acceptable for screening purposes where only preliminary results are obtained. Antifoam reduces the surface tension of the solvent (Thitakamol and Veawab, 2008).

4.3.1 Equal Ratio Blends - Concentration Varied

MAPA is added to the tertiary amines to enhance the reaction rate. The blends with MAPA are screened with the ratios 3:1, 2:1 and 1:1, with the relation 3° amine/MAPA. The total amine concentration is kept constant at 4M.

There is no doubt that MAPA acts as a promoter to DEEA, according to Figure 4.5. One see a remarkably increase in absorption rate from 3M DEEA to the promoted systems.

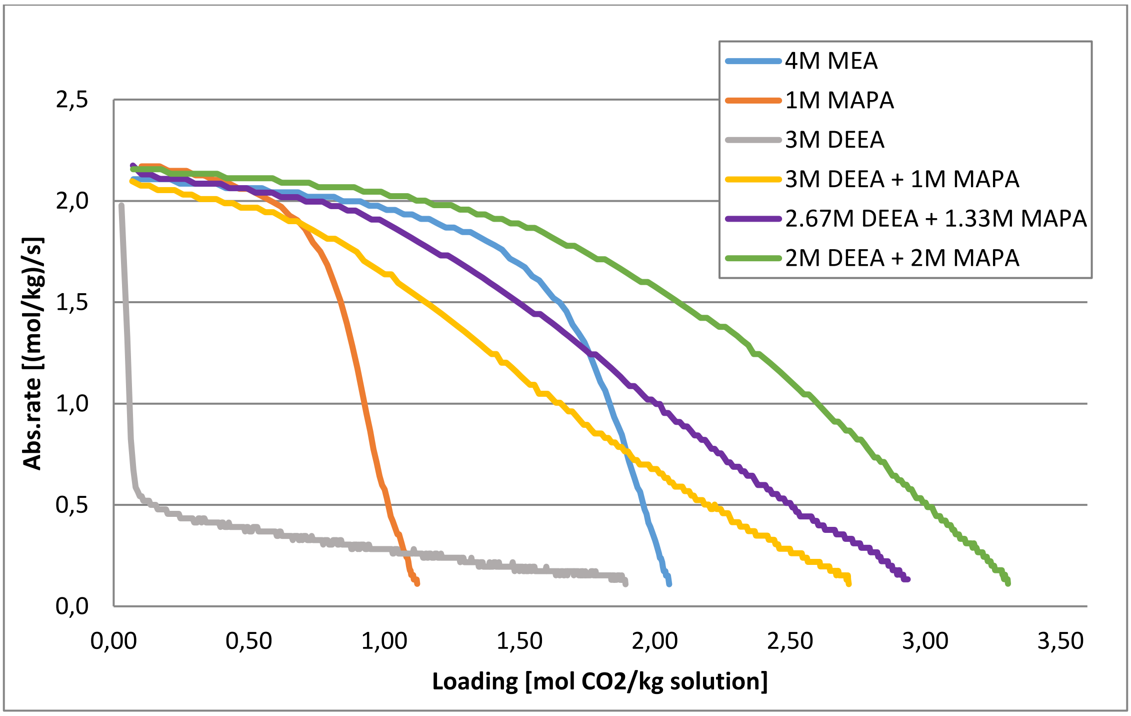


Figure 4.5 Absorption rate plotted against loading for the different DEEA systems

MAPA and MEA have a high absorption rate until the beginning of saturation, when the rate start to drop steeply. In comparison with 4M MEA, the performance of ratio 3:1, 2:1 and 1:1 is 32 %, 43 % and 61 % higher absorption capacities, respectively. The blends of DEEA and MAPA have a much smoother decrease of absorption rate throughout the experiment, and can be seen as a tradeoff by mixing the slow reacting DEEA with the fast reacting MAPA.

4M MEA have an absorption potential of 2.05 mol CO_2/kg amine. Ratio 3:1 gave an absorption capacity of 2.72 mol CO_2/kg amine, ratio 2:1 gave 2.94 mol CO_2/kg amine and 1:1 gave 3.31 mol CO_2/kg amine. Ratios 3:1 and 2:1 have initially a lower absorption rate than 4M MEA, but ends with larger loading, 33 % and 43 % respectively. The ratio 1:1 both show a larger absorption rate than 4M MEA the whole duration of the experiment, and also gave a 61 % higher end loading. MAPA influence the system to absorb more carbon dioxde, and this make sense when one consider MAPAs stoichiometry and reactivity.

Also when added to TEA, MAPA enlarged the reaction rate and loading.
Both ratios 3:1 and 2:1 gave lower loadings than the 4M MEA screenings, with an absorption capacity of 1.22 mol CO_2/kg amine (41 %) and 1.53 mol CO_2/kg amine (25 %), respectively. 3M TEA had the smallest absorption rate of the 3M tertiary amines. This is decisive when adding MAPA to TEA. The more fast-reacting MAPA added to the system, the higher absorption rate the system display. Seen from Figure 4.6, the ratio 1:1 shows similar rate as MEA and MAPA.

Once the blended system starts to saturate, the absorption rate start to flatten, the decrease in rate is less sharp than for MEA and MAPA.

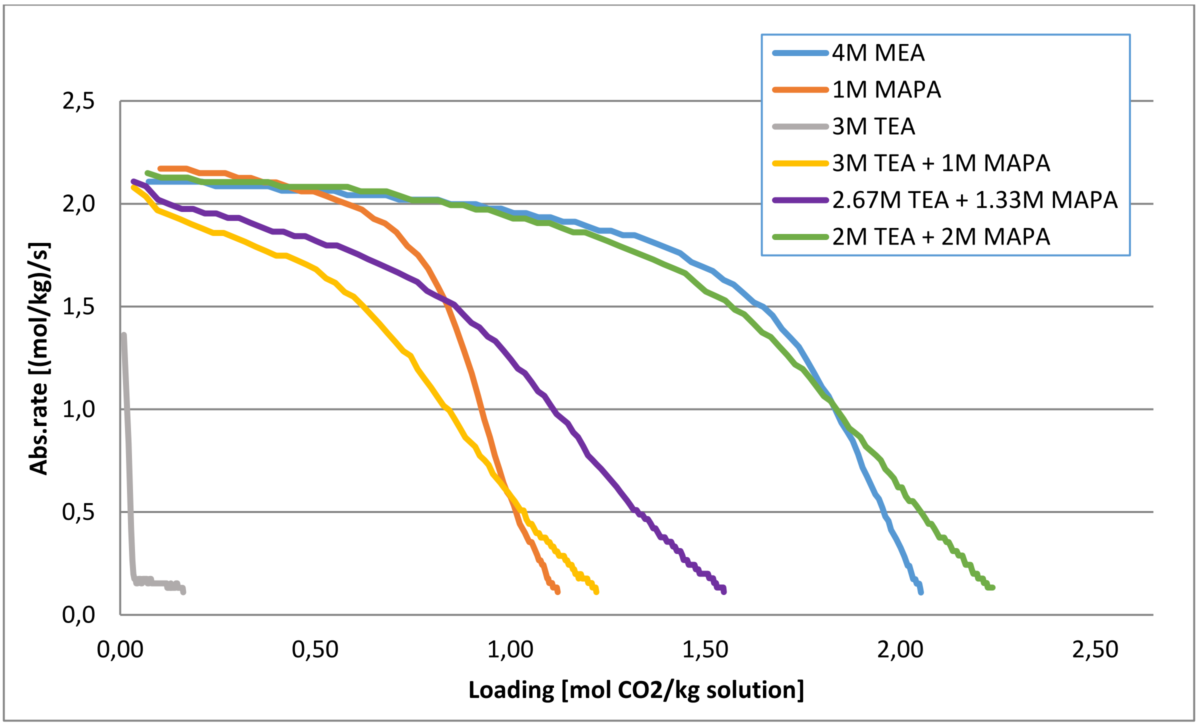


Figure 4.6 Absorption rate plotted against loading for the different TEA systems

Ratio 1, 2M TEA + 2M MAPA, reached a loading a bit higher (9 %) than 4M MEA, with an absorption capacity of 2.23 mol CO_2/kg amine. The absorption rate for ratio 1:1 follow the same absorption rate as 4M MEA initially, but at a loading of around 1.9 mol CO_2/kg amine the absorption rate start to decrease. As for DEEA, the more MAPA added to TEA, the better the blend perform. Figure 4.6 illustrate that there is a bigger leap in end loading from ratio 2:1 to ratio 1:1 (0.71 mol CO_2/kg amine), than from 3:1 to 2:1 (0.31 mol CO_2/kg amine).

Again, it is clear that MAPA reinforce the absorption capacity as well as the absorption rates of the tertiary amine. Figure 4.7 show that 3M BDEA + 1M MAPA have an absorption performance of 1.39 mol CO_2/kg amine, this is 32 % lower than the capacity of 4M MEA. One can see that addition of MAPA to BDEA is a tradeoff between MAPAs reaction rate and BDEAs reaction rate. The rate of the blends are concentration dependent, thus adding extra amounts of MAPA to BDEA enhance the reaction rate additional.

Overall, BDEA demonstrate better performances than TEA. As for TEA, there is a bigger leap in end loading from ratio 2:1 to ratio 1:1, than from 3:1 to 1:1. Increase in loading from ratio 2:1 to ratio 1:1 is 0.73 mol CO_2/kg amine, and from ratio 3:1 to 2:1 the loading increase 0.29 mol CO_2/kg amine.

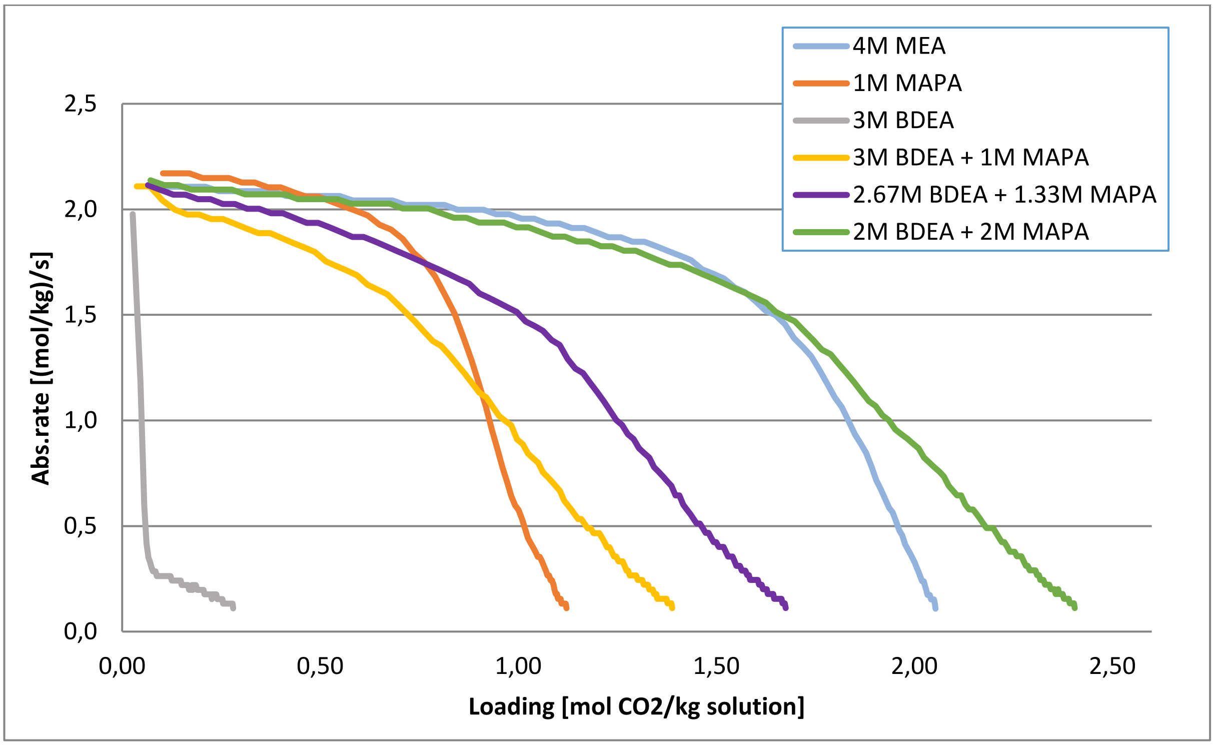


Figure 4.7 Absorption rate plotted against loading for the different BDEA systems

Ratio 2:1 gave an absorption capacity of 1.68 mol CO_2/kg amine. Ratio 1:1, 2M BDEA + 2M MAPA, follow the same absorption rate as 4M MEA, but at a loading at approximately 1.63 mol CO_2/kg amine, 4M MAPAs absorption rate decline faster than the 1:1 BDEA/MAPA blend, giving the blend an end loading of 2.41 mol CO_2/kg amine. This is 17 % higher than the end loading of 4M MEA.

Figure 4.8 display the same trend as the previous 3° amines combined with MAPA. MAPA enhance both the absorption rate and loading. The difference from ratio 3:1 to 2:1 is an increase in loading of 0.33 mol CO_2/kg amine, while the gain from ratio 2:1 to 1:1 is 0.54 mol CO_2/kg amine.

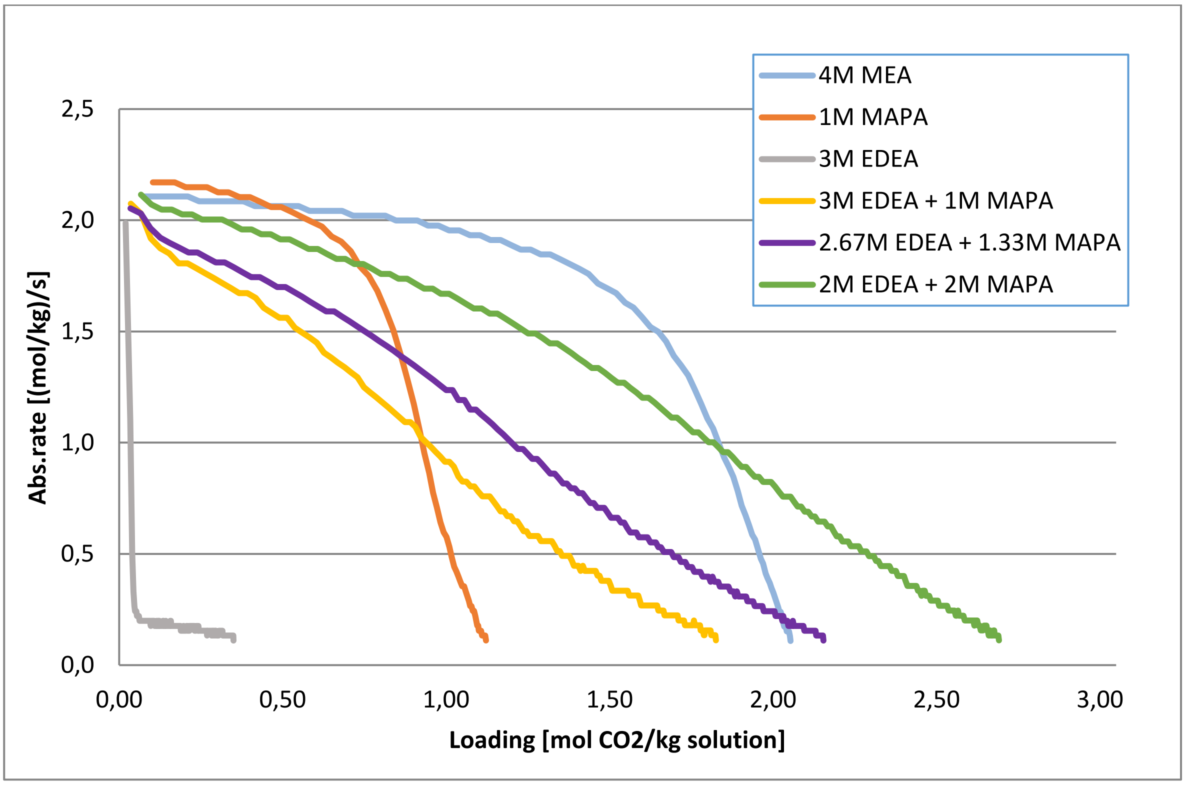


Figure 4.8 Absorption rate plotted against loading for the different EDEA systems

Ratio 2:1 completes with a higher loading than ratio both 3:1 (25 %) and 4M MEA (31 %), and ends with an absorption capacity of 2.15 mol CO_2/kg amine. The highest absorption capacity is given by ratio 1:1 with 2.69 mol CO_2/kg amine. This means than ratio 1:1 gave a 6 % better outcome than the base case, 30 wt. % MEA, mentioned in section 4.2.

2M t-BDEA+2M MAPA exhibit a starting absorption rate similar to 4M MEA and 1M MAPA. Due to t-BDEA, the rate has a smooth decline until the point of rich loading. One do not see the sharp point of where saturation start to occur, but have a descend through the whole absorption process.

Figure 4.9 provide the absorption curves for the different t-BDEA systems. Also here, MAPA gave a significant improvement of the 3° amine’s loading and rate. The ratio from 3:1 to 2:1 gave an improvement of 0.34 mol CO_2/kg amine, and the ratio increase from 2:1 to 1:1 had an increase in loading of 0.71 mol CO_2/kg amine.

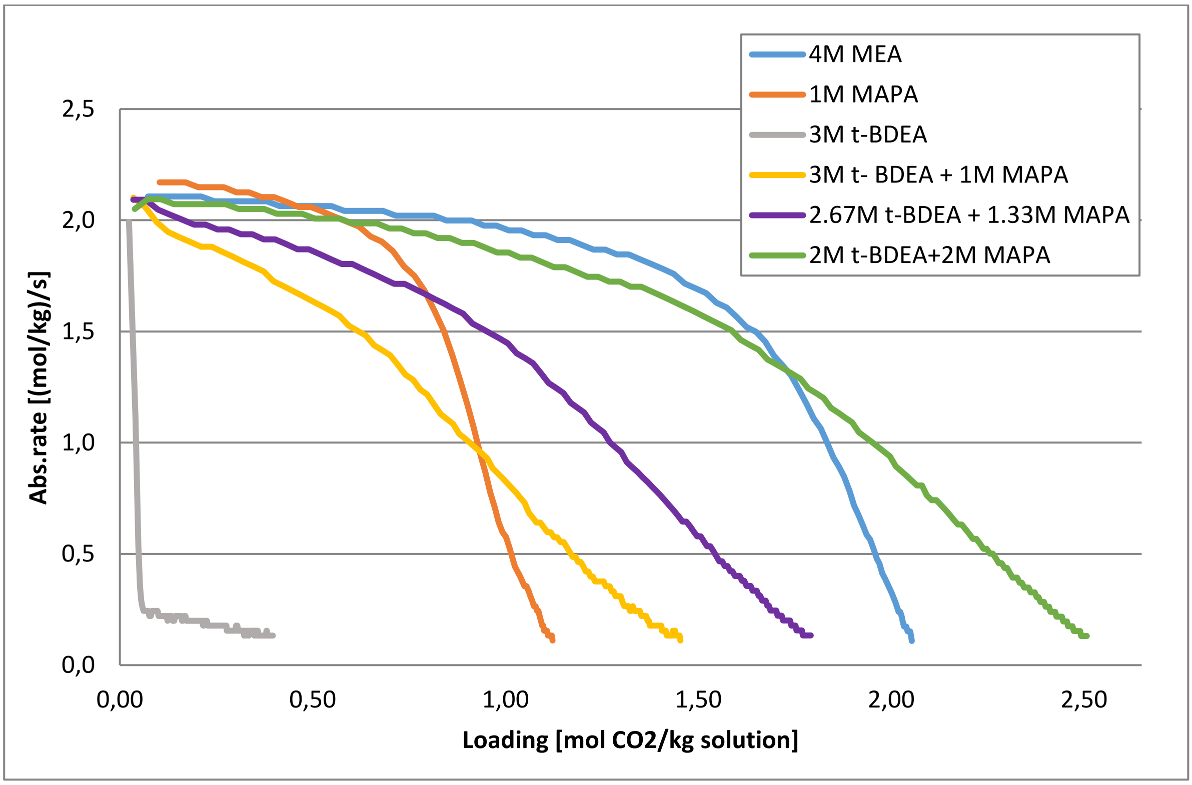


Figure 4.9 Absorption rate plotted against loading for the different t-BDEA systems

Ratio 3:1 give a absorption potential of 1.45 mol CO_2/kg amine, while ratio 2:1 gave a rich loading of 1.79 mol CO_2/kg amine. The ratio 1:1 have an absorption capacity of 2.51 mol CO_2/kg amine. Ratio 3:1 had a absorption performance 66 % lower than 4M MEA, while ratio 2:1 gave a 13 % lower performance relative to 4M MEA. The ratio 1:1 provided an increased absorption capacity of 22 % compared to 4M MEA.

It is interesting that the increase of MAPA added to the tertiary amines from ratio 2:1 to 1:1 gave a higher enhancement in loading and ratio, than the increase from 3:1 to 2:1. This implies that the more MAPA added to the system, the better the outcome of absorption capacity and absorption rate become. The rate window potential is somewhere between the tertiary amines absorption rate and MAPAs absorption rate.

It is consistent that for all the tertiary amines, that it is a clear advantage to increase the concentration of MAPA and lower the concentration of 3° amine in order to reach a high absorption capacity. DEEA and EDEA are the two 3° amines that give the highest absorption capacities this applies to all the ratios. The impact of ratio-change is smaller for DEEA and EDEA amines, than for TEA, BDEA and t-BDEA.

4.3.2 Identical Ratio Blends - Concentration Kept Constant

In order to observe the influence of the molecular structure to the absorption capacities, identical ratio blends with same concentration was compared. The ratios are compared with 30 wt. % MEA, as the blends already have been compared to 4M MEA in section 4.3.1. 1M MAPA and the 3M tertiary amine is plotted for visualization of the rate increase.

Figure 4.10 show that adding 1M MAPA to the 3M tertiary amines enhanced the reaction rate severely for all of the blends. At loadings around 2.5 mol CO_2/kg amine, the blend 3M DEEA+1M MAPA exceed the rate of 30 wt. % MEA, achieving a rich loading 30 % higher than 30 wt. % MEA. The DEEA/MAPA blend is the only blend that exceeds the absorption capacity of 4M MEA and 30 wt. % MEA at this ratio.

The order for the tertiary amine in ratio 3:1 with MAPA, with respect to loading is: DEEA – EDEA –t-BDEA – BDEA – TEA. This is almost the same order as for the tertiary single amine solutions (DEEA, t-BDEA, EDEA, BDEA and TEA), but in mixture with MAPA t-BDEA and EDEA have switched places. All of the blends reach a higher loading than 1M MAPA.

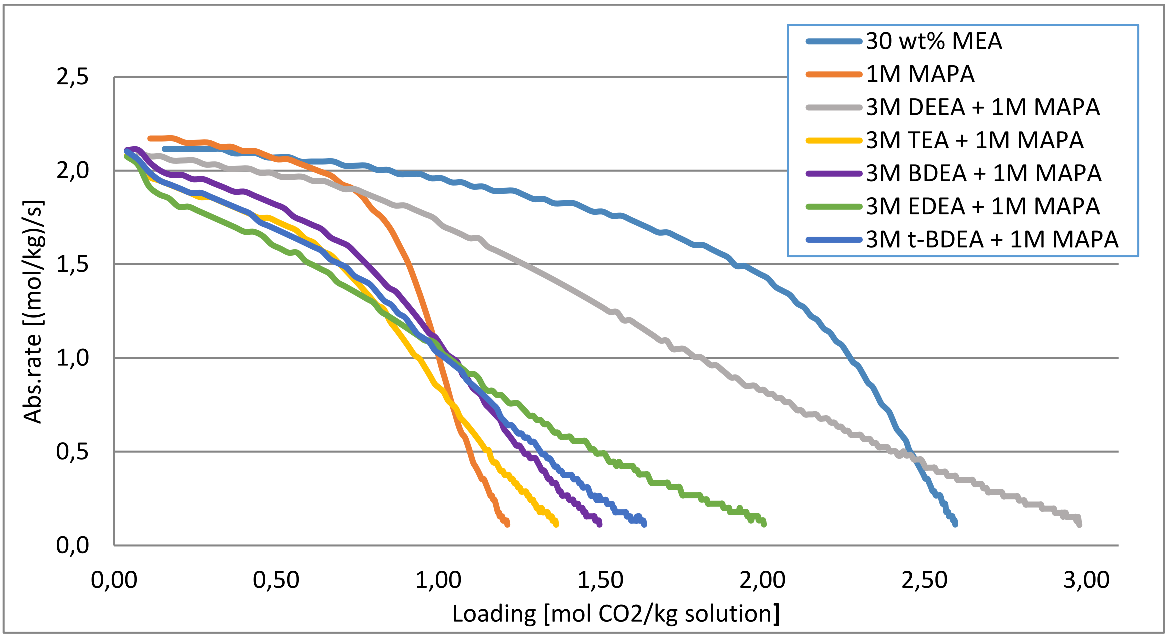


Figure 4.10 Absorption rate against loading for 3° amine/MAPA blends with the ratio 3:1

According to structure at this given ratio, an increase in ethanolamine groups, from DEEA to TEA, decrease the absorption capacity. Change in one ethanolamine group, from DEEA to EDEA constitute a 49 % reduction of absorption potential, and an increase of two ethanolamine groups from DEEA to TEA have a reduction in absorption potential of 55 %. The increase of one ethanolamine group from EDEA to TEA is a decline of 33 %.

If the alkyl chain length is increased, from EDEA to BDEA, the absorption capacity decreases 24 % from 1.83 mol CO_2/kg amine to 1.39 mol CO_2/kg amine. Increased steric hindrance, t-BDEA vs. BDEA, constituted a 5 % increase of absorption capacity.

Figure 4.11 illustrate, that adding MAPA to the tertiary amines in a 2:1 ratio, enhanced the reaction rate even more than it did for ratio 3:1. The amine concentration is 2.67M, and MAPA have a concentration of 1.33M.

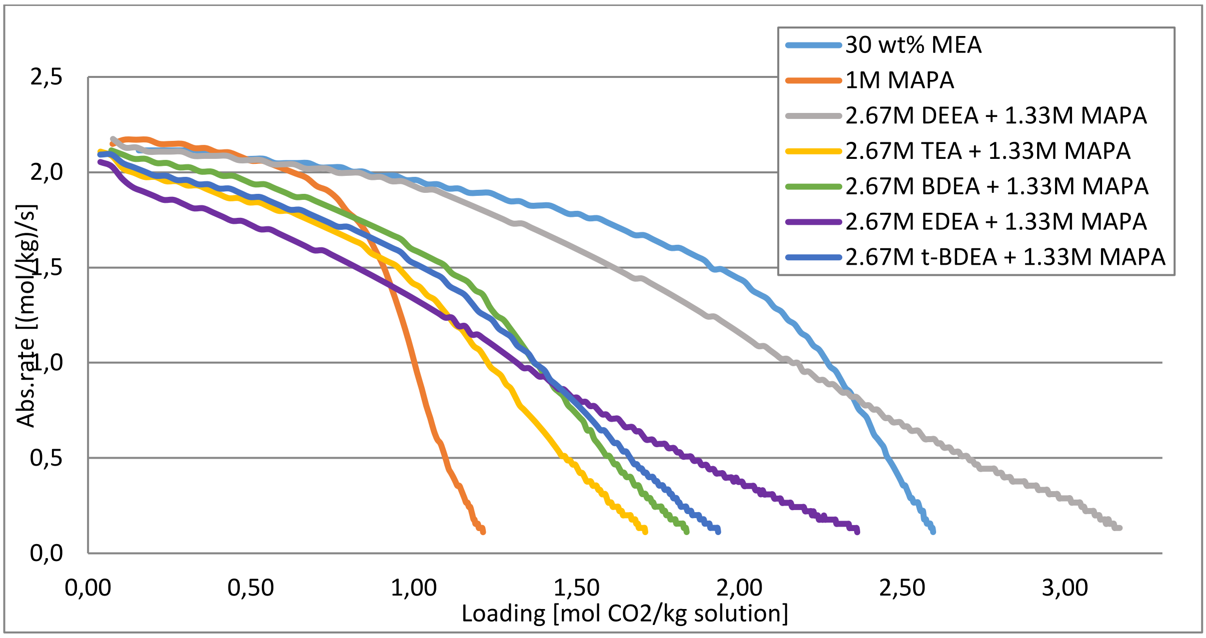


Figure 4.11 Absorption curves of 3° amine/MAPA blends with the ratio 2:1

All of the blends reach a higher loading than 1M MAPA. Ratio 2:1 DEEA perform 16 % better than 30 wt. % MEA. The order for the tertiary amine in ratio 2:1 with MAPA, with respect to loading is: DEEA – EDEA –t-BDEA – BDEA – TEA. This is the same order as ratio 3:1 had.

An increase in ethanolamine groups, also decrease the absorption capacity for this ratio. When the alkyl chain length is increased, from EDEA to BDEA, the absorption capacity is decreased. Regarding, steric hindrance, t-BDEA vs. BDEA, t-BDEA had a somewhat better performance than BDEA at this ratio (7 % or 0.12 mol CO_2/kg amine), 1.91 mol CO_2/kg amine and 1.68 mol CO_2/kg amine, respectively.

Figure 4.12 depict the absorption results for all of blends containing of 2M tertiary amine and 2M MAPA. The order is still the same at the two previous ratios with decreasing loading: DEEA - EDEA - t-BDEA - BEDA - TEA.

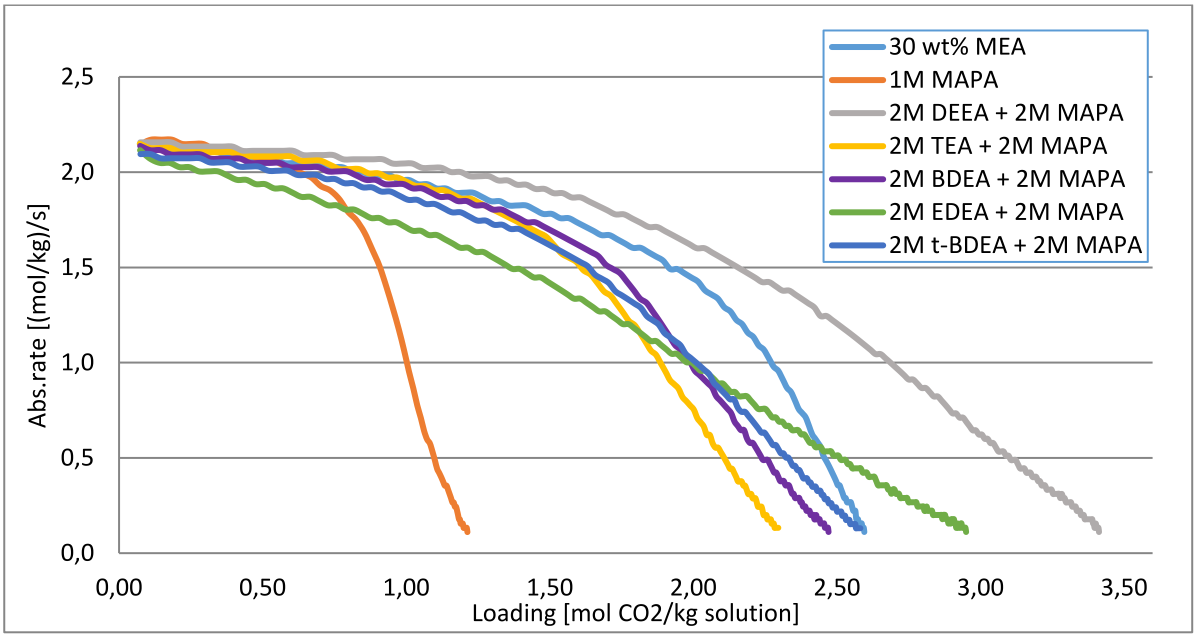


Figure 4.12 Absorption curves of 3° amine/MAPA blends with the ratio 1:1

Both DEEA and EDEA reach an absorption capacity higher than 30 wt. % MEA. DEEA attain a loading of 3.31 mol CO_2/kg amine, which is considered a high rich loading.

The number of ethanolamine groups still restricts the efficiency of MAPA. Fewer ethanolamine groups increase the absorption capacity, 32 % from DEEA to TEA. Likewise, a smaller alkyl chain increases the absorption capacity with 12 % from EDEA to BDEA. Regarding the steric hindrance, at this ratio, t-BDEA surpasses BDEA with a 4 % higher loading.

The overall trend for absorption capacity regarding ratios are: 3:1 < 2:1 < 1:1. MAPA increase the absorption rate, and the rate is dependent on concentration. The rate window spans from the rate of the single tertiary amine to the rate of aqueous MAPA. MAPA is more reactive than tertiary amines, and as a diamine MAPA also has a higher absorption potential. That is why when more MAPA is added to the solutions, the more CO_2 is absorbed by the system.

4.3.3 Cyclic Capacities

The cyclic capacity is the difference between the rich and lean loading, and say something about the amount of solvent needed to be circulated. A high cyclic capacity indicates that less amine needs to be circulated in the process, and this is favorable when it comes to energy consumption due to less sensible heat.

When looking at the cyclic capacity of 3M DEEA+1M MAPA (2.06 mol CO_2/kg amine), one can see that the cyclic capacity is the sum of the cyclic capacities of 3M DEEA (1.73 mol CO_2/kg amine) and 1M MAPA (0.38 mol CO_2/kg amine). For the other systems, TEA, BDEA, EDEA and t-BDEA, this same tendency do not occur. The blend gives a better performance than the sum of 3M tertiary amine and 1M MAPA screenings. For instance, the system 3M EDEA + 1M MAPA give 2.5 times higher capacity than the sum of the screenings by themselves. This is a confirmation that MAPA promote those systems very well, and may also explain why the ratio leap from 2:1 to 1:1 gave a bigger enhancement than from ratio 3:1 to 1:1.

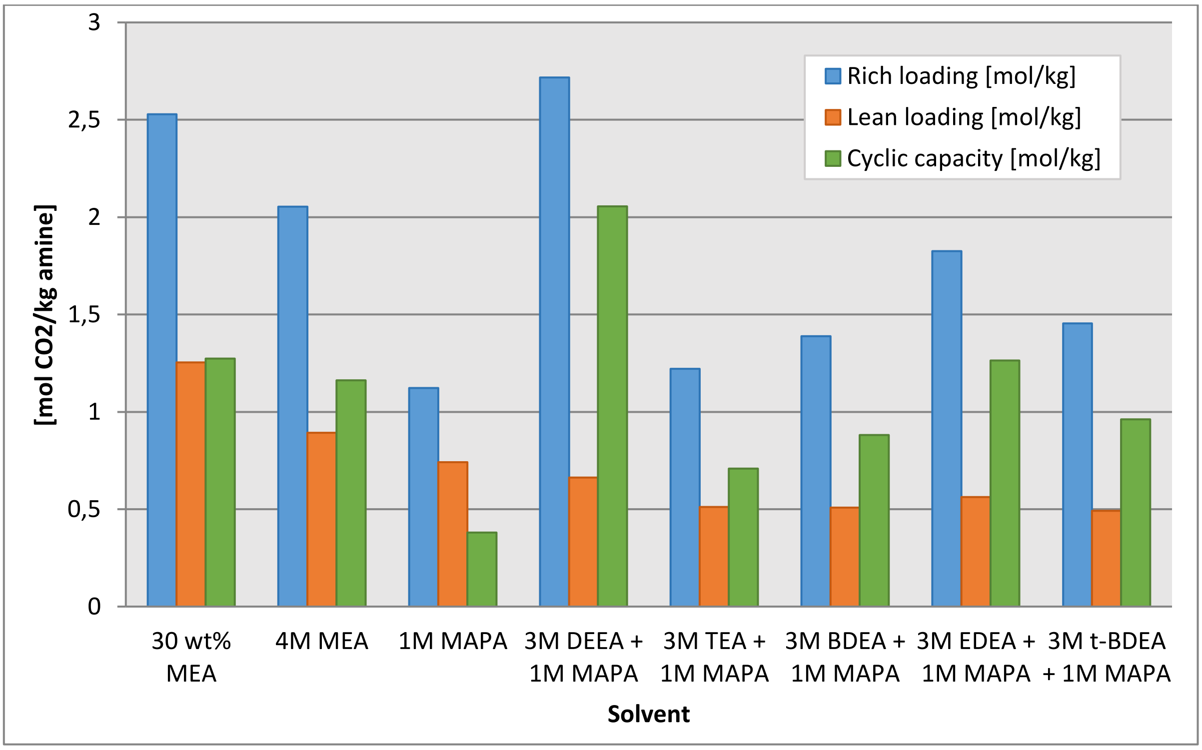


Figure 4.13 Rich and lean loadings and cyclic capacity of ratio 3:1 tertiary amine/MAPA blends plus 4M MEA and 1M MAPA

3M DEEA+1M MAPA remove 71 % CO_2 during regeneration, while 3M TEA+1M MAPA removed 58 % CO_2. 3M DEEA+1M MAPA have a 25 % higher rich loading than 30 wt. % MEA, and a 35 % higher rich loading. The high concentration of tertiary amine relative to MAPA is decisive for the high cyclic capacity. 3M EDEA+1M MAPA and 30 wt. % MEA have the same cyclic capacity, but 30 wt. % MEA have a 28 % higher absorption capacity.

When changing the ratio to 2:1 between tertiary amine and MAPA, the cyclic capacity increase for all the systems. Figure 4.14 show that this is connected to the increased absorption capacity. The lean loadings have also increased, and show that the increased concentration of MAPA effect the heat of desorption.

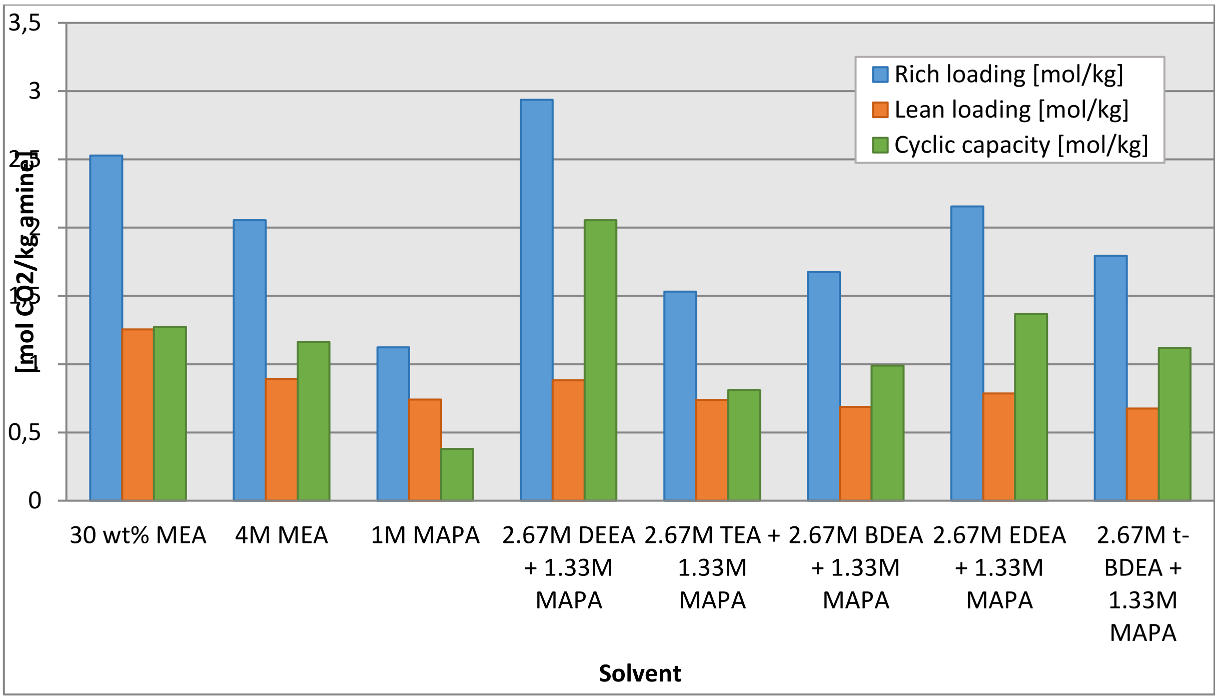


Figure 4.14 Rich and lean loadings and cyclic capacity of ratio 2:1 tertiary amine/MAPA blends plus 4M MEA and 1M MAPA

2.67M DEEA+1.33M MAPA and 2.67M EDEA+1.33M MAPA have cyclic capacities, 77 % and 17% larger than 4M MEA, respectively. At this ratio the blends of TEA, BDEA and t-BDEA with MAPA still give lower absorption capacity and cyclic capacity than 4M MEA.

From Figure 4.15, it is seen that the rich loadings for the ratio 1:1 solvents, is higher compared to 4M MEA. 2M DEEA+2M MAPA and 2M EDEA +2M MAPA achieve a rich loading higher than 30 wt. % MEA, as well.

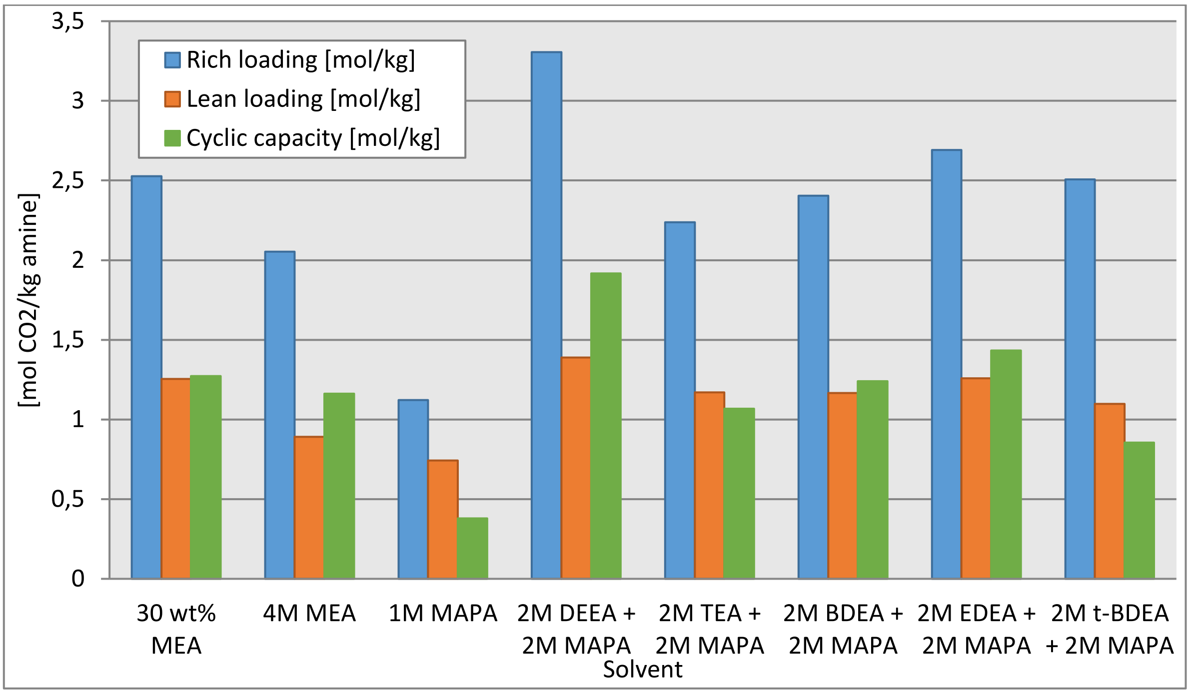


Figure 4.15 Rich and lean loadings and cyclic capacity of ratio 1:1 tertiary amine/MAPA blends plus 4M MEA and 1M MAPA

All solvents, except 2M TEA+2M MAPA express a higher cyclic capacity than 4M MEA. This indicates that the solvent is easily regenerated, and that CO_2 is efficiently released during the stripping process.

Regenerating MAPA is more energy demanding process than regenerating tertiary amines. This is seen by comparing Figure 4.3 for the single tertiary amine solvents and Figure 4.15. Adding MAPA will not only enhance the reaction rate and absorption capacity, but also enhance the lean loadings. Lean loading increase due to the fact that MAPA show a high heat of absorption, since the concentrations are kept constant at 4 M, when more MAPA is added, less tertiary amine is present in the solution. An increased amount of CO_2 captured, make it harder to regenerate the solvent. This is a direct effect of tertiary amines having a lower reaction heat than primary or secondary amines.

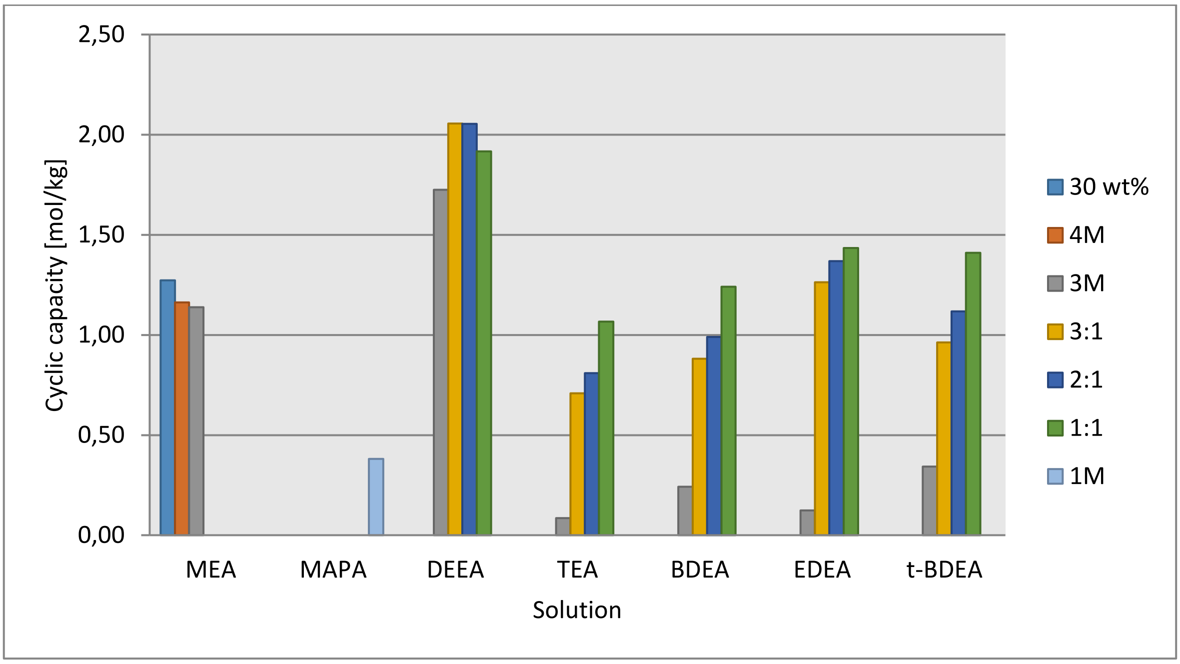


Figure 4.16 Cyclic capacities of the different systems studied in part 1 of this work

The general trend for cyclic capacity equals the trend for absorption capacity; ratio 3:1 < ratio 2:1 < ratio 1:1. This emphasize that the larger the amount of MAPA added to the systems, the better the cyclic capacity get.

Since both rich and lean loading follow the same trend with 3:1 < 2:1 < 1:1, it is natural that the cyclic capacity also follows this trend. Lean loading increase when less of the 3° amine is present.

This is valid for all of the 3° amine/MAPA systems seen here, apart from the DEEA/MAPA system. This can either be caused by measuring errors, or the fact that MAPA provide a larger impact on this system. So when adding more MAPA, it is harder to strip of the CO_2 captured.

As in Figure 4.3, the findings represented in Figure 4.17 show that the screening values are overpredicted relative to the liquid analysis. It is easy to see that the blends perform better than the single tertiary amine systems, but the accumulation of error is still affecting the lean loading.

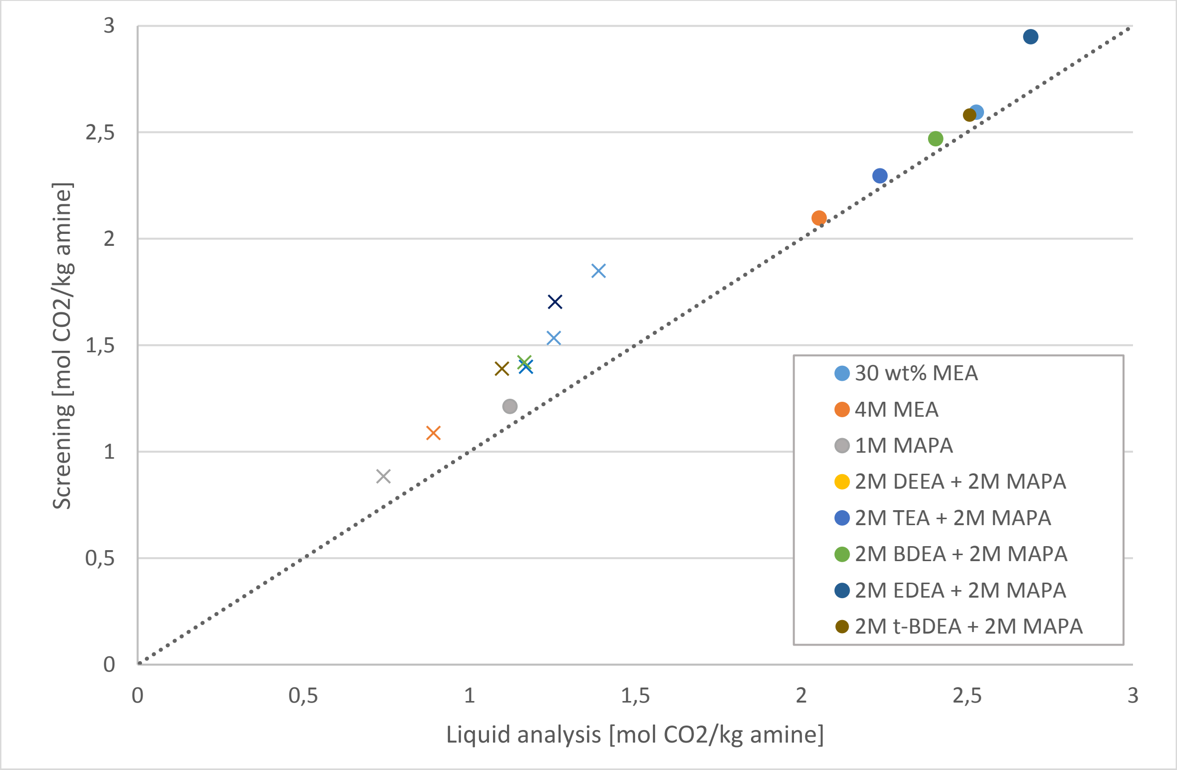


Figure 4.17 Cyclic capacity and loadings from liquid analysis vs. screening values. Circles represent rich loading, and crosses represent lean loading

4.3.4 Acid Dissociation Constant (pK$_a$) Trends

Figure 4.18 illustrate the pK$_a$ values and the molecular structure for the tertiary amines and MEA. DEEA have the highest pK$_a$, followed by MEA, t-BDEA, BDEA, EDEA and TEA.

DEEA showed the highest cyclic capacity, while TEA the worst, this apply to all blends and systems. As Figure 4.18 depict, an increase of hydroxyl functions reduces the pK$_a$ value by approximately one pK$_a$ unit per hydroxyl group.

For the 3M single amine system the trend for cyclic capacity was DEEA, MEA, t-BDEA, EDEA, BDEA and TEA (Figure 4.3). This is fully consistent with the trend for pK$_a$. The cyclic capacity follow the same trend as the pK$_a$ values do. Regarding absorption rate, MEA have the highest rate by far, compared to the tertiary amines. DEEA have the highest rate of the tertiary amines tested, while TEA have the poorest one. BDEA, EDEA and t-BDEA exhibit similar rates, and due to the uncertainty of the screening apparatus it is hard to say which system has the highest rate.

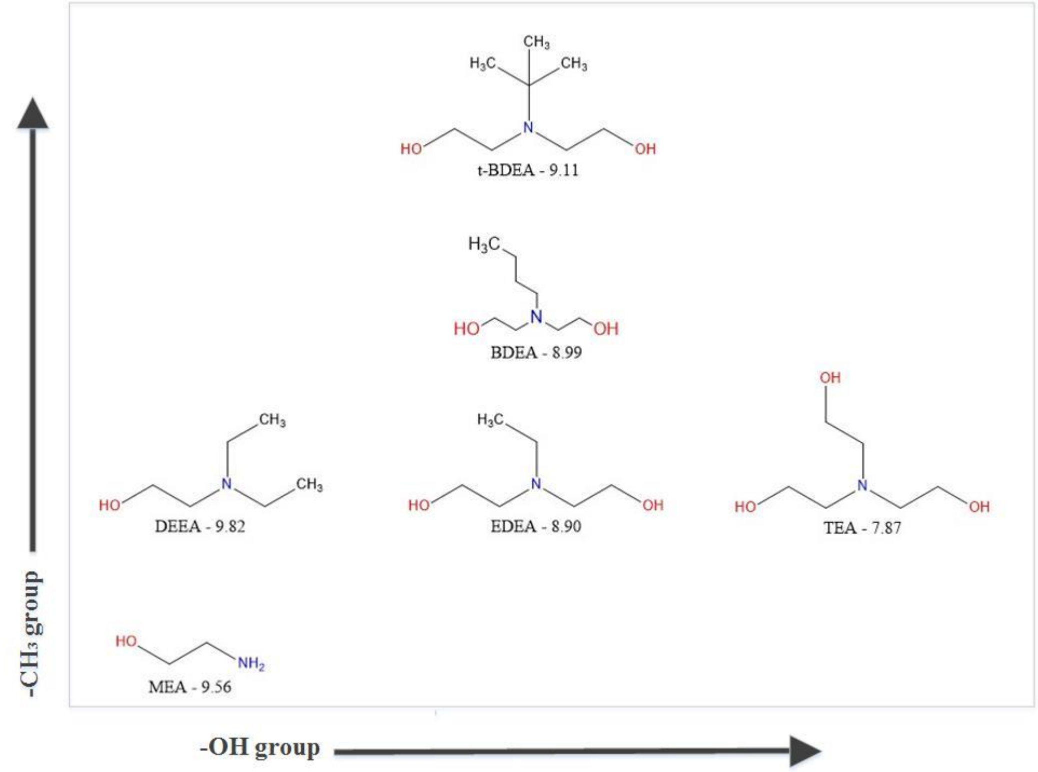


Figure 4.18 Trend in pK$_a$ values at 293.15 K of given amines with respect to addition of -CH$_3$ and -OH groups at 20 ℃

For the blends, the trend for cyclic capacity was DEEA, EDEA, t-BDEA, BDEA and TEA. It is important to notice that the pK$_a$ values found in literature is for single amines, and not for tertiary amine/MAPA blends. However, the pK$_a$ values for EDEA, BDEA and t-BDEA are very similar to one another. The absorption rates for the blends follow the same trend as the cyclic capacity do.

4.4 New Promoters

At the Department of Chemistry, a group is performing QSPR and DFT calculations in order to propose and develop new solvents with improved CO_2 capture capabilities. The models work through *de novo* design principles by using the software to generate structures and then create new structures based on the calculated physical data of the previous “generations”. Calculated properties included pK_a, vapor pressure, toxicity and viscosity. The molecules tested were readily available compounds proposed by these models or similar to the molecules proposed.

The suggested compounds were first tested for their absorption characteristics, and then for their ability to function as a promoter to DEEA. MAPA is classified as a toxic chemical and is very volatile, thus it is of interest to substitute MAPA with novel and more environmental friendly chemicals.

Unfortunately many of the selected chemicals caused a series of problems.

- DACH showed a serious foaming tendency, even after addition of antifoam. The solution turned milky white and became very viscous after around one hour of absorption.
- Phenetylamine made a fine powder that got swept out of the reactor and caused the tubing to clog, and pressure to build up inside the system.
- Creatine has a very low solubility in water,14 $g \cdot L^{-1}$ in water at 20 °C (Song et al., 2016), this concentration was considered too low that it was relevant to run an screening experiment
- DBMA formed two-phases, and since the liquid samples could not be analyzed, the chemical was evaluated not to be explored as a promising promoter.

BMA did not cause any problems, but formed two phases when mixed with water at 30 wt. %. The solvent looked like a white emulsion when stirred. When adding CO_2 during screening, the solution turned blank and shifted to singular phase. The chemical was run at 30 wt. % plus the ratio 1:3 with DEEA (1M BMA + 3M DEEA).

L-Arginine is an amino acid, and had to be neutralized with base prior to CO_2 absorption. The amino acid was neutralized with equimolar amount of KOH-pellets, making ARG to form amino acid salts. It was not possible to make a 30 wt. % ARG solution, because of ARGs low solubility in water. The highest concentration obtained was 14 wt. %, or 0.81M, ARG. The dipole momentum in an aqueous DEEA-H_2O blend is lower than for water alone. Therefore, the charged ARG molecule experience drastically worse solubility in DEEA/water than pure water. It was not possible to make a solution containing 14 wt. % ARG and 3M DEEA, so a concentration of 5 wt. % ARG was used instead.

The potential promoters were first run with a standard screening concentration of 30 wt. %, the results from the absorption are shown in Figure 4.19. 1M MAPA have an absorption capacity of 1.12 mol CO_2/kg amine. The result show that 30 wt. % BMA have a high absorption rate, comparable to the rate of 1M MAPA and 30 wt. % MEA. The initial absorption rate was high, but dropped abruptly when nearing saturation. This is a desired property for CO_2 absorbing chemicals. The absorption capacity of 30 wt. % (~2.48M) BMA was found to be 1.24 mol CO_2/kg amine, or 0.54 mol CO_2/mol amine.

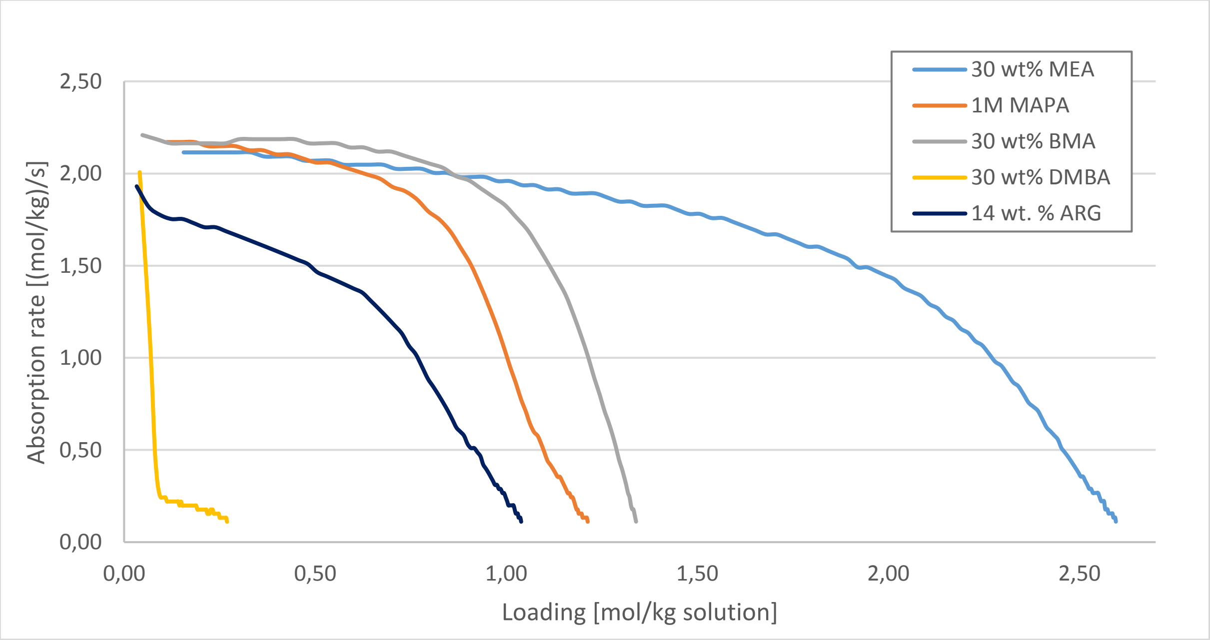


Figure 4.19 Absorption curves after screening novel compounds

14 wt. % ARG demonstrate a lower rate than 30 wt. % BMA, and the rate also decrease more smoothly during the absorption process than it did for BMA. ARG ended with a loading of 1.45 mol CO_2/kg amine after absorption. This high loading made 14 wt. % ARG considered as a promising as promoter. But on the other hand, this loading is above the theoretical maximum if there is only one amine functionality present. A loading of 1.45 mol CO_2/kg

amine equals a loading of 1.28 mol CO_2/mol amine in this case. This high mol/mol loading made ARG considerable as a promising promotor. But on the other hand, this loading is above the theoretical maximum if there is only one amine functionality present.

The ARG molecule contains a primary amino group in addition to a guanidinium group in its side chain. Having different functional groups on the same molecule, make the system quite complex. The guanidinium group can coordinate to CO_2 by itself, and bind up 1 mol CO_2/mole guanidinium, and the primary amino group can bind 0.5 mol CO_2/mole primary amine. For convinence, the guanidinium group is considered as an amine, with a loading capacity of a tertiary amine.

DMBA is a tertiary amine, with both low absorption potential and low absorption rate. In addition, this chemical formed a two-phase system, so it was not possible to evaluate the liquid samples for CO_2 or amine concentration. Since DMBA possesses the same properties as tertiary amines, DMBA cannot act as promoter to another tertiary amine.

A high cyclic capacity is beneficial for CO_2 absorbing systems. As Figure 4.20 depict, 30 wt. % BMA give almost as high cyclic capacity as 1M MAPA. 1M MAPA provide a cyclic capacity of 0.38 mol CO_2/kg amine, while 30 wt. % BMA have a cyclic capacity of 0.35 mol CO_2/kg amine. BMA have a 71 % lower cyclic capacity than MEA, and ARG have a cyclic capacity 83 % lower than MEA.

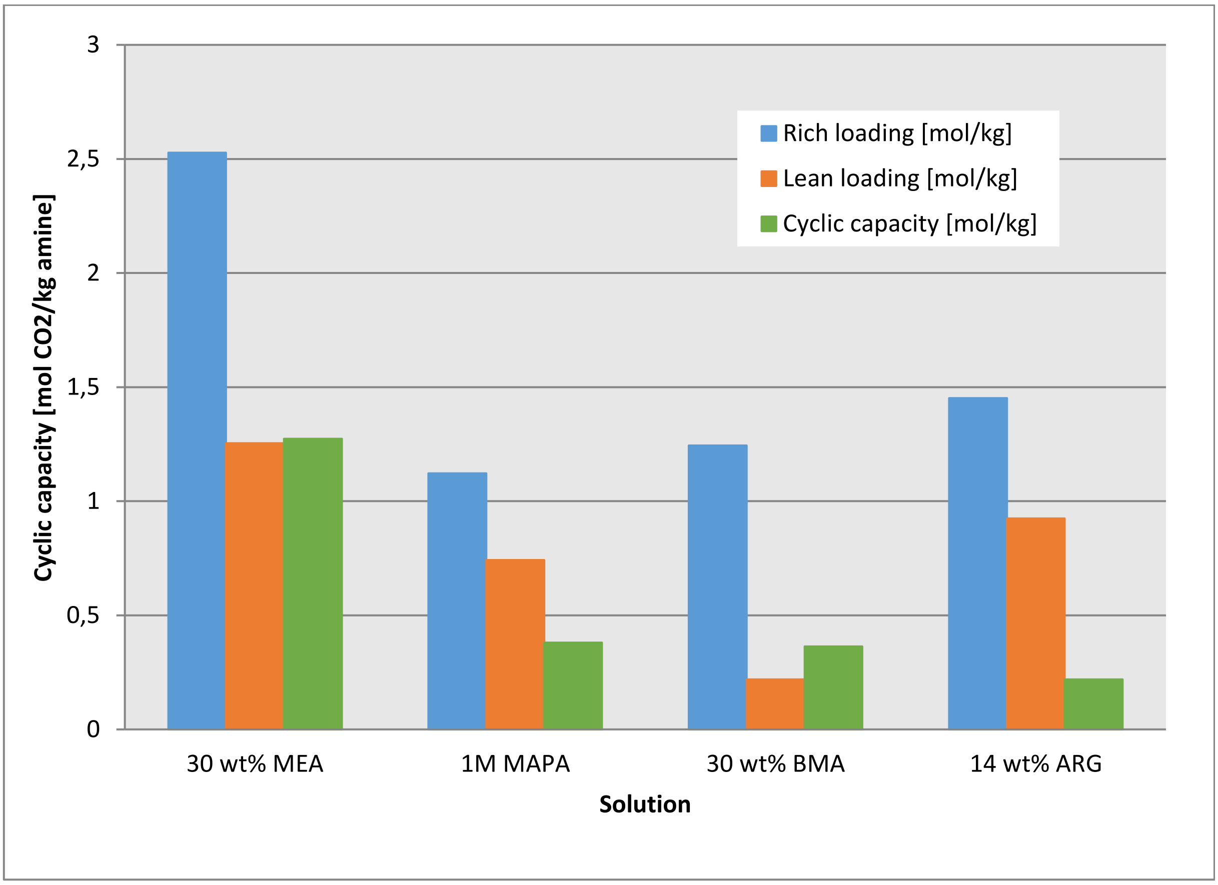


Figure 4.20 Cyclic capacity for 1M MAPA, 30 wt. % BMA and 14 wt. % ARG

14 wt. % ARG show a lower cyclic capacity than both 1M MAPA and 30 wt. % BMA. This indicate that the lean loading is high, and that a lot for carbamate is formed and that it is difficult to strip off the CO_2 captured. Only 36 % of the captured CO_2 that was captured during the absorption process is released during the desorption. Guanidines have a preference to form carbamates, which are bound hard to the amino acid salt and have a high heat of absorption.

The potential promoters were screened together with DEEA, which was considered the most promising 3° amine from screening campaign 1. The blends were compared against 30 wt. % MEA, for conventional purposes, with 3M DEEA in order to see if the tertiary amine had been promoted, and also the 3M DEEA + 1M MAPA blend to study the effect of the promoter. The absorption curves are depicted in Figure 4.21.

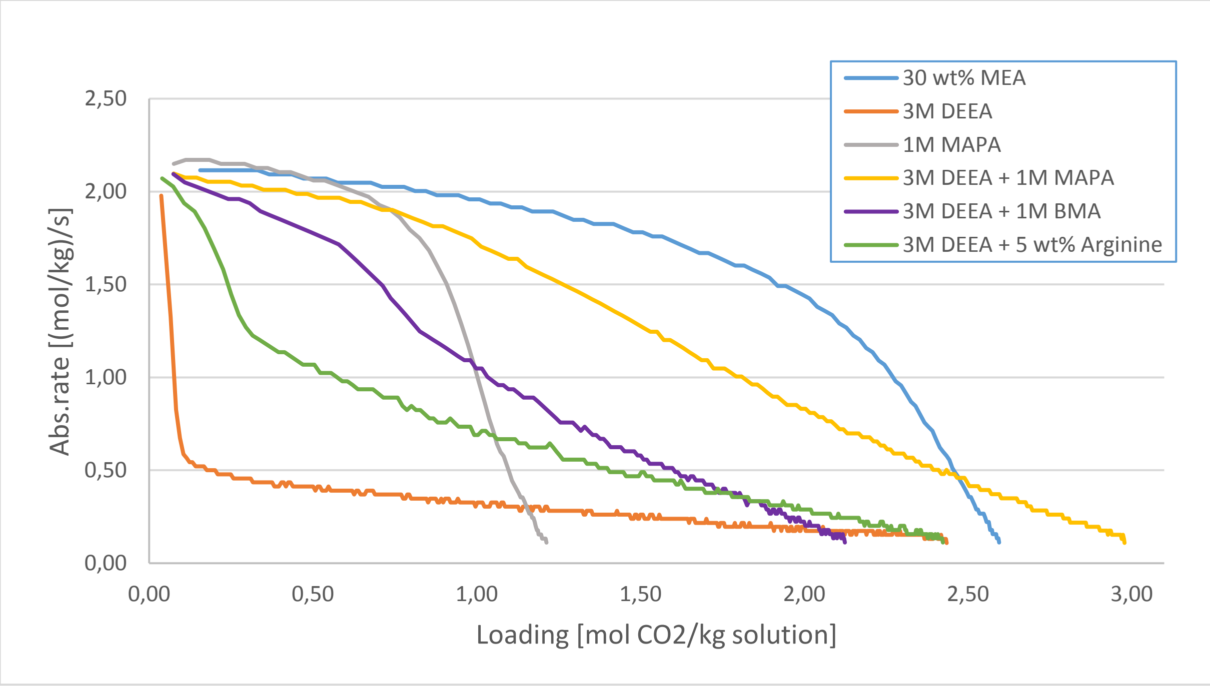


Figure 4.21 Absorption curves of 3M DEEA + 1M promoter-systems compared with 30 wt. % MEA

3M DEEA + 1M MAPA show by far that MAPA is the best promoter of the ones tested, and gain a rich loading of 2.72 mol CO_2/kg amine. This is superior to the benchmark solvent 30 wt. % MEA, which obtain a rich loading of 2.53 mol CO_2/kg amine. Adding 1M BMA to 3M DEEA achieved a loading of 1.90 mol CO_2/kg amine, and ends with almost the same loading as 3M DEEA (1.89 mol CO_2/kg amine). 5 wt. % ARG show a promoting effect on the system, giving a rich loading of 2.09 mol CO_2/kg amine. Both the ARG and MAPA blends with DEEA display a molecular loading 0.72 mol CO_2/mol amine, this is above the molecular loading of the benchmark solvent, which accomplish a loading of 0.53 mol CO_2/mol amine. This is a consequence of the stoichiometry between the amine/amino acid salt and CO_2. Figure 4.22 show that the promoter systems reached a higher cyclic capacity than 30 wt. % MEA, but this most likely due to the fact that they exhibit poorer absorption performances. The DEEA/promoter systems exceed the cyclic capacity given by the systems presented in Figure 4.20. This is most likely caused by the fact that the promoter concentration is significantly reduced, while DEEA is concentration was added in a considerably amount.

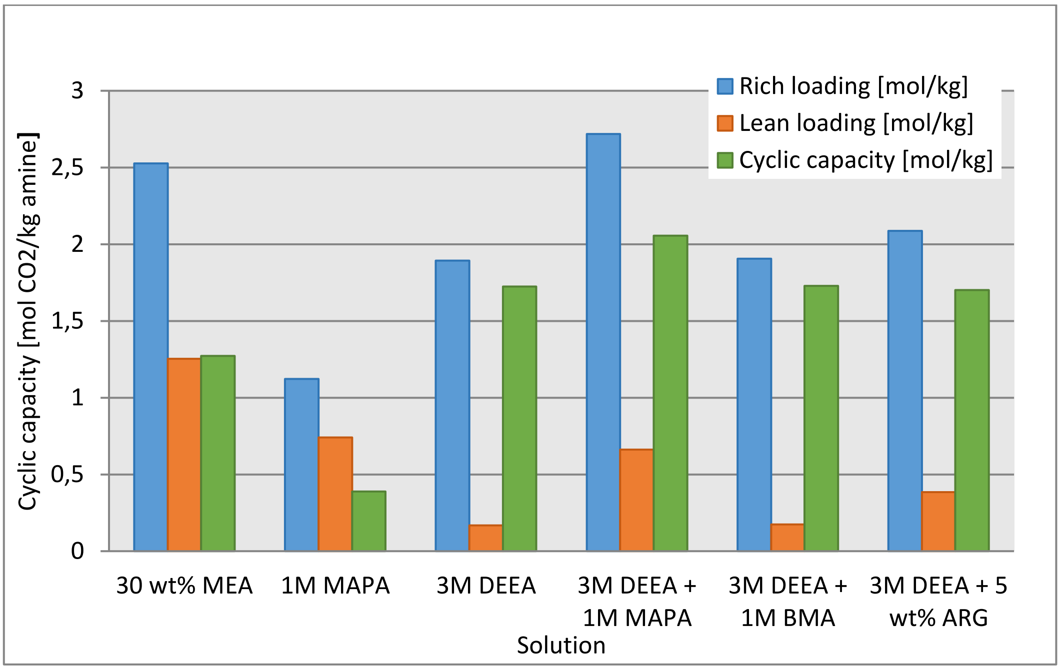


Figure 4.22 Cyclic capacities for DEEA/promoter systems and 30 wt. % MEA

3M DEEA + 1M MAPA are used as a reference, to see how well the proposed promoters perform compared to MAPA. The DEEA/MAPA system reaches a cyclic capacity of 1.59 mol CO_2/kg amine. 3M DEEA have a cyclic capacity of 1.41 mol CO_2/kg amine, while the DEEA/BMA and DEEA/ARG systems have a cyclic capacity of 1.32 mol CO_2/kg amine and 1.48 mol CO_2/kg amine, respectively.

Seen in light of both absorption capacity and cyclic capacity, neither ARG nor BMA is considered to be adequate promoter to DEEA.

A higher pK_a value is expected to give a faster absorption rate. In Figure 4.23 absorption rate at lean loading and the cyclic capacity is seen as a function of pK_a.

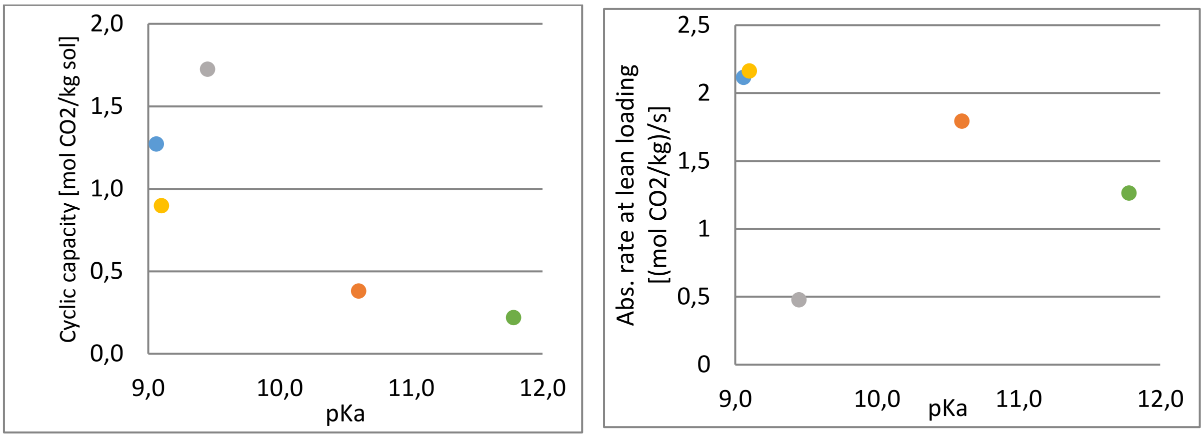


Figure 4.23Absorption rate (left) and cyclic capacity (right) as a function of pK$_a$

Even if DEEA have a high cyclic capacity it have not a high absorption rate. MEA and BMA have approximately the same pK$_a$ value and absorption rate, but MEA seems to have a higher cyclic capacity. MAPA have a high absorption rate, but not a very high cyclic capacity. ARG are the most basic component, and have a mediocre rate compared to the other compounds. ARG exhibit the lowest cyclic capacity. This may be due to its high basicity and ability to bind CO_2 strongly.

5 Conclusion

A total of 31 experiments were performed in a screening apparatus. The experiments were divided into two screening campaigns, with different focuses. The first campaign looked at the effect of molecular structure (addition of –OH groups and/or increase of alkyl chain length) and how the performance of DEEA, TEA, BDEA, EDEA and t-BDEA changed after addition of MAPA as promoter. The second screening campaign sought to cross-validate a model proposes and develop new solvents with improved CO_2 capture capabilities generate. The molecules tested were readily available compounds proposed by these models or similar to the molecules proposed. The absorption rate and cyclic capacity from both the campaigns was compared to basicity.

Absorption of CO_2 with solvent took place at 40 °C up to 9.5 kPa CO_2 partial pressure, while stripping of the same solvent occurred at 80 °C down to 1.0 kPa CO_2 partial pressure. To check the integrity of the screening apparatus and the vapor/liquid mass balance, a sample was taken from the solution after absorption and after desorption.

The findings from the first screening campaign showed that an increase in alcohol groups and/or alkyl chain length reduced the absorption capacity. Steric hindrance did not impose a change in either absorption rate or absorption capacity. MAPA promoted the tertiary amines, by enhancing the absorption rate as well as the absorption capacities. 2M MAPA+2M DEEA expressed the best performance in this work, with an absorption capacity of 3.31 mol CO_2/mol amine and a cyclic capacity of 1.92 mol CO_2/mol amine.

The second screening campaign encountered various problems, such as foaming and low solubility. From a total of 6 proposed compounds only two were fully characterized. L-Arginine was considered the best system of the two remaining compounds, both as single solvent and as promoter to 3M DEEA. As single solvent, it reached a rich loading of 1.45 mol CO_2/mol amine and as promotor a rich loading of 2.09 mol CO_2/mol. Unfortunately, L-arginine bind the CO_2 so strong that it is hard to regenerate.

6 Recommendations for Further Work

For the first screening campaign, one could see a correlation between amine alkanol groups as well as alkyl chain structure and absorption capacity. The most promising tertiary amine was DEEA. DEEA have the highest pK_a, absorption rate and cyclic capacity of the tertiary amines tested. To perform screening experiments on compounds similar to (but more basic than) DEEA would be of interest. Aktuelle compounds could be (MEEA, pK_a 9.74 and reduction of alkyl chain) or Triethylamine (TREA, pK_a 10.67 and no –OH groups). One should be careful to not select compounds with too high pK_a, as they migh be difficult to regenerate.

By examine if it is the pK_a value itself, or if it is the difference of pK_a between tertiary amine and MAPA that enhance the rate and absorption capacity, it might be easier to select more economical and environmentally friendly solvents in the future. The pK_a values in this work was found in literature, and was only for single amines. One could measure the pK_a of the blends and try to find a connection with the absorption rates and cyclic capacity.

The absorption mechanism should also continue to be examined by NMR-experiments to get a bigger understanding of the reaction between amine and carbon dioxide, and the distribution of species.

Make a model of mass transfer in MATLAB to improve screening calculations. A more accurate mass transfer model could improve the inconsistency between gas and liquid phase.

Since the chemicals tested in the second screening campaign exhibit poor cyclic capacity, regeneration of solvent is found to be difficult. One could therefore try to find and perform screening other less basic guanidines. Possible compounds are guanidines with one or several –OH groups, as hydroxyl groups reduce the pK_a value.

7 Literature and References

AARON, D. & TSOURIS, C. 2005. Separation of CO2 from Flue Gas: A Review. *Separation Science and Technology,* 40, 321-348.

ARONU, U. E., GONDAL, S., HESSEN, E. T., HAUG-WARBERG, T., HARTONO, A., HOFF, K. A. & SVENDSEN, H. F. 2011a. Solubility of CO2 in 15, 30, 45 and 60 mass% MEA from 40 to 120 °C and model representation using the extended UNIQUAC framework. *Chemical Engineering Science,* 66, 6393-6406.

ARONU, U. E., HOFF, K. A. & SVENDSEN, H. F. 2011b. CO2 capture solvent selection by combined absorption–desorption analysis. *Chemical Engineering Research and Design,* 89, 1197-1203.

ARONU, U. E., SVENDSEN, H. F. & HOFF, K. A. 2010. Investigation of amine amino acid salts for carbon dioxide absorption. *International Journal of Greenhouse Gas Control,* 4, 771-775.

ARSHAD, M. W., FOSBØL, P., VON SOLMS, N., FJØSNE SVENDSEN, H. & THOMSEN, K. 2013a. Vapor-Liquid Equilibrium of CO2 with Aqueous Solutions of DEEA, MAPA and their Mixture. *2nd Post Combustion Capture Conference.* Bergen, Norway.

ARSHAD, M. W., FOSBØL, P. L., VON SOLMS, N., SVENDSEN, H. F. & THOMSEN, K. 2013b. Heat of Absorption of CO2 in Phase Change Solvents: 2-(Diethylamino)ethanol and 3-(Methylamino)propylamine. *Journal of Chemical & Engineering Data,* 58, 1974-1988.

ARSHAD, M. W., VON SOLMS, N., THOMSEN, K. & SVENDSEN, H. F. 2013c. GHGT-11 Proceedings of the 11th International Conference on Greenhouse Gas Control Technologies, 18-22 November 2012, Kyoto, JapanHeat of Absorption of CO2 in Aqueous Solutions of DEEA, MAPA and their Mixture. *Energy Procedia,* 37, 1532-1542.

BARZAGLI, F., MANI, F. & PERUZZINI, M. 2010. Continuous cycles of CO2 absorption and amine regeneration with aqueous alkanolamines: a comparison of the efficiency between pure and blended DEA, MDEA and AMP solutions by 13C NMR spectroscopy. *Energy & Environmental Science,* 3, 772-779.

BLAUWHOFF, P. M. M., VERSTEEG, G. F. & VAN SWAAIJ, W. P. M. 1983. A study on the reaction between CO2 and alkanolamines in aqueous solutions. *Chemical Engineering Science,* 38, 1411-1429.

BRUDER, P. & SVENDSEN, H. F. Solvent comparison for postcombustion CO2 capture. 1st Post Combustion Capture Conference. Abu Dhabi, Kingdom of Saudi Arabia, 2011.

CAPLOW, M. 1968. Kinetics of carbamate formation and breakdown. *Journal of the American Chemical Society,* 90, 6795-6803.

CHOI, S. Y., NAM, S. C., YOON, Y. I., PARK, K. T. & PARK, S.-J. 2014. Carbon Dioxide Absorption into Aqueous Blends of Methyldiethanolamine (MDEA) and Alkyl Amines Containing Multiple Amino Groups. *Industrial & Engineering Chemistry Research,* 53, 14451-14461.

CHOWDHURY, F. A., YAMADA, H., HIGASHII, T., GOTO, K. & ONODA, M. 2013. CO2 Capture by Tertiary Amine Absorbents: A Performance Comparison Study. *Industrial & Engineering Chemistry Research,* 52, 8323-8331.

CHOWDHURY, F. A., YAMADA, H., MATSUZAKI, Y., GOTO, K., HIGASHII, T. & ONODA, M. 2014. 12th International Conference on Greenhouse Gas Control Technologies, GHGT-12Development of Novel Synthetic Amine Absorbents for CO2 Capture. *Energy Procedia,* 63, 572-579.

CIFTJA, A. F., HARTONO, A. & SVENDSEN, H. F. 2013a. Experimental study on phase change solvents in CO2 capture by NMR spectroscopy. *Chemical Engineering Science,* 102, 378-386.

CIFTJA, A. F., HARTONO, A. & SVENDSEN, H. F. 2013b. GHGT-11 Proceedings of the 11th International Conference on Greenhouse Gas Control Technologies, 18-22 November 2012, Kyoto, JapanCarbamate Formation in Aqueous - diamine - CO2 Systems. *Energy Procedia,* 37, 1605-1612.

CONWAY, W., BRUGGINK, S., BEYAD, Y., LUO, W., MELIÁN-CABRERA, I., PUXTY, G. & FERON, P. 2015. CO2 absorption into aqueous amine blended solutions containing monoethanolamine (MEA), N,N-dimethylethanolamine (DMEA), N,N-diethylethanolamine (DEEA) and 2-amino-2-methyl-1-propanol (AMP) for post-combustion capture processes. *Chemical Engineering Science,* 126, 446-454.

CROOKS, J. E. & DONNELLAN, J. P. 1989. Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution. *Journal of the Chemical Society, Perkin Transactions 2*, 331-333.

DA SILVA, E. F. & SVENDSEN, H. F. 2007. Computational chemistry study of reactions, equilibrium and kinetics of chemical CO2 absorption. *International Journal of Greenhouse Gas Control,* 1, 151-157.

DANCKWERTS, P. V. 1979. The reaction of CO2 with ethanolamines. *Chemical Engineering Science,* 34, 443-446.

DONALDSON, T. L. & NGUYEN, Y. N. 1980. Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes. *Industrial & Engineering Chemistry Fundamentals,* 19, 260-266.

EIA. 2016a. *Developing economies in Asia lead projected growth in world energy use* [Online]. http://www.eia.gov/pressroom/releases/press432.cfm: U.S. Energy Information Administration. [Accessed June 09 2016].

EIA. 2016b. *International Energy Outlook 2016* [Online]. http://www.eia.gov/forecasts/ieo/pdf/0484(2016).pdf: U.S. Energy Information Administration. [Accessed June 09 2016].

EIDE-HAUGMO, I., BRAKSTAD, O. G., HOFF, K. A., SØRHEIM, K. R., DA SILVA, E. F. & SVENDSEN, H. F. 2009. Environmental impact of amines. *Energy Procedia,* 1, 1297-1304.

EL HADRI, N., QUANG, D. V., GOETHEER, E. L. V. & ABU ZAHRA, M. R. M. 2016. Aqueous amine solution characterization for post-combustion CO2 capture process. *Applied Energy*.

EVJEN, S., KROKVIK, I. R. T., FIKSDAHL, A. & KNUUTILA, H. K. 2016. Analysis of the absorption properties and thermal decomposition of non-alkanol amines. Norwegian University of Science and Technology.

GCCSI 2014. The Global Status of CCS: 2014. *In:* INSTITUTE, G. C. (ed.). https://www.globalccsinstitute.com/publications/global-status-ccs-2014.

GERVASI, J., DUBOIS, L. & THOMAS, D. 2014. 12th International Conference on Greenhouse Gas Control Technologies, GHGT-12Screening tests of new hybrid solvents for the post-combustion CO2 capture processby chemical absorption. *Energy Procedia,* 63, 1854-1862.

GLASSCOCK, D. A., CRITCHFIELD, J. E. & ROCHELLE, G. T. 1991. CO2 absorption/desorption in mixtures of methyldiethanolamine with monoethanolamine or diethanolamine. *Chemical Engineering Science,* 46, 2829-2845.

GOEL, M. & JOHRI, V. 2014. Carbon Capture, Storage, and Utilization–An Appraisal of Current Situation in Coal-based Economies. *Carbon Capture, Storage and, Utilization: A possible climate change solution for energy industry*, 31.

GOTO, K., OKABE, H., CHOWDHURY, F. A., SHIMIZU, S., FUJIOKA, Y. & ONODA, M. 2011. Development of novel absorbents for CO2 capture from blast furnace gas. *International Journal of Greenhouse Gas Control,* 5, 1214-1219.

GRID-ARENDAL 2005a. Carbon cycle. http://www.grida.no/publications/vg/climate2: GRID-Arendal.

GRID-ARENDAL 2005b. Past and Future CO2 concentrations. http://www.grida.no/publications/vg/climate2: GRID-Arendal.

HADRI, N. E. L., QUANG, D. V. & ABU-ZAHRA, M. R. M. 2015. Study of Novel Solvent for CO2 Post-combustion Capture. *Energy Procedia,* 75, 2268-2286.

HAMBORG, E. S. & VERSTEEG, G. F. 2009. Dissociation Constants and Thermodynamic Properties of Amines and Alkanolamines from (293 to 353) K. *Journal of Chemical & Engineering Data,* 54, 1318-1328.

HARTONO, A., CIFTJA, A., VEVELSTAD, S. J., KIM, I. & KNUUTILA, H. 2016. Screening of strong bicarbonate forming solvents for CO2 capture. Norwegian University of Science and Technology.

HARTONO, A., SALEEM, F., ARSHAD, M. W., USMAN, M. & SVENDSEN, H. F. 2013. Binary and ternary VLE of the 2-(diethylamino)-ethanol (DEEA)/3-(methylamino)-propylamine (MAPA)/water system. *Chemical Engineering Science,* 101, 401-411.

IEA 2015. Energy Balances of Non-OECD Countries. *In:* AGENCY, I. E. (ed.). Paris, France: International Energy Agency.

IEA 2016. Tracking Clean Energy Progress 2016. http://www.iea.org/topics/ccs/publications/: International Energy Agency.

IEAGHG. 2009. Evaluation of novel post-combustion CO2 capture solvent concepts.

IPCC 2007. Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. *Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.).* Cambridge University.

IPCC 2014. Climate Change 2014: Synthesis Report. . *In:* CORE WRITING TEAM, R. K. P. A. L. A. M. E. (ed.) *Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.* http://www.ipcc.ch/report/ar5/syr/: Intergovernmental panel on climate change.

ISLAM, M., YUSOFF, R., ALI, B., ISLAM, M. & CHAKRABARTI, M. 2011. Degradation studies of amines and alkanolamines during sour gas treatment process. *Int. J. Phys. Sci,* 6, 5877-5890.

KAUFFMAN, G. B. 1988. The Bronsted-Lowry acid base concept. *Journal of Chemical Education,* 65, 28.

KIM, I. & SVENDSEN, H. F. 2011. Comparative study of the heats of absorption of post-combustion CO2 absorbents. *International Journal of Greenhouse Gas Control,* 5, 390-395.

KIM, Y. E., MOON, S. J., YOON, Y. I., JEONG, S. K., PARK, K. T., BAE, S. T. & NAM, S. C. 2014. Heat of absorption and absorption capacity of CO2 in aqueous solutions of amine containing multiple amino groups. *Separation and Purification Technology,* 122, 112-118.

KNUDSEN, S., KARL, M. & RANDALL, S. 2009. Summary Report: Amine Emissions to Air during Carbon Capture, Phase I: CO2 and Amines Screening Study for Effects to the Environment. *Norwegian Institute for Air Research (NILU).*

KNUUTILA, H., SVENDSEN, H. F. & JULIUSSEN, O. Kinetics of carbonate based CO2 capture systems. Energy Procedia, 2009. 1011-1018.

KOHL, A. L. & NIELSEN, R. 1997. *Gas purification*, Gulf Professional Publishing.

LEUNG, D. Y. C., CARAMANNA, G. & MAROTO-VALER, M. M. 2014. An overview of current status of carbon dioxide capture and storage technologies. *Renewable and Sustainable Energy Reviews,* 39, 426-443.

LI, L. & ROCHELLE, G. 2011. Amino acid solvents for CO2 absorption. PCCC1.

LIM, J.-A., KIM, D. H., YOON, Y., JEONG, S. K., PARK, K. T. & NAM, S. C. 2012. Absorption of CO2 into Aqueous Potassium Salt Solutions of l-Alanine and l-Proline. *Energy & Fuels,* 26, 3910-3918.

LITTEL, R. J., VAN SWAAIJ, W. P. M. & VERSTEEG, G. F. 1990. Kinetics of Carbon Dioxide with tertiary Amines in aqueous solution. *AIChE Journal,* 36, 1633-1640.

MA'MUN, S., SVENDSEN, H. F., HOFF, K. A. & JULIUSSEN, O. 2007. Selection of new absorbents for carbon dioxide capture. *Energy Conversion and Management,* 48, 251-258.

MCCANN, N., PHAN, D., FERNANDES, D. & MAEDER, M. 2011. A systematic investigation of carbamate stability constants by 1H NMR. *International Journal of Greenhouse Gas Control,* 5, 396-400.

METHROM 2016. Methrom 809 Titrando and 814 USB sample Processor. http://www.metrohm.com/applications/#methods=85DA50DEAF4544C58A3B6EB5DA25F512.

MONTEIRO, J. G. M. S., KNUUTILA, H., PENDERS-VAN ELK, N. J. M. C., VERSTEEG, G. & SVENDSEN, H. F. 2015a. Kinetics of CO2 absorption by aqueous N,N-diethylethanolamine solutions: Literature review, experimental results and modelling. *Chemical Engineering Science,* 127, 1-12.

MONTEIRO, J. G. M. S., MAJEED, H., KNUUTILA, H. & SVENDSEN, H. F. 2015b. Kinetics of CO2 absorption in aqueous blends of N,N-diethylethanolamine (DEEA) and N-methyl-1,3-propane-diamine (MAPA). *Chemical Engineering Science,* 129, 145-155.

MONTEIRO, J. G. M. S., PINTO, D. D. D., ZAIDY, S. A. H., HARTONO, A. & SVENDSEN, H. F. 2013. VLE data and modelling of aqueous N,N-diethylethanolamine (DEEA) solutions. *International Journal of Greenhouse Gas Control,* 19, 432-440.

MUÑOZ, D. M., PORTUGAL, A. F., LOZANO, A. E., JOSÉ, G. & DE ABAJO, J. 2009. New liquid absorbents for the removal of CO 2 from gas mixtures. *Energy & Environmental Science,* 2, 883-891.

NAGAI, H., KUWABARA, K. & CARTA, G. 2008. Temperature Dependence of the Dissociation Constants of Several Amino Acids. *Journal of Chemical & Engineering Data,* 53, 619-627.

NIELSEN, R., LEWIS, K., MCCULLOUGH, J. G. & HANSEN, D. Controlling corrosion in amine treating plants. Proceedings of the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, 1995.

PATRICK, G. L. 2004. *Instant notes organic chemistry,* London, BIOS.

PINTO, D. D. D., KNUUTILA, H., FYTIANOS, G., HAUGEN, G., MEJDELL, T. & SVENDSEN, H. F. 2014a. CO2 post combustion capture with a phase change solvent. Pilot plant campaign. *International Journal of Greenhouse Gas Control,* 31, 153-164.

PINTO, D. D. D., ZAIDY, S. A. H., HARTONO, A. & SVENDSEN, H. F. 2014b. Evaluation of a phase change solvent for CO2 capture: Absorption and desorption tests. *International Journal of Greenhouse Gas Control,* 28, 318-327.

POLITZER, P. & MURRAY, J. S. 1994. *Quantitative treatments of solute/solvent interactions*, Elsevier Amsterdam.

PUXTY, G., ROWLAND, R., ALLPORT, A., YANG, Q., BOWN, M., BURNS, R., MAEDER, M. & ATTALLA, M. 2009. Carbon Dioxide Postcombustion Capture: A Novel Screening Study of the Carbon Dioxide Absorption Performance of 76 Amines. *Environmental Science & Technology,* 43, 6427-6433.

RAYER, A. V., SUMON, K. Z., JAFFARI, L. & HENNI, A. 2014. Dissociation Constants (pKa) of Tertiary and Cyclic Amines: Structural and Temperature Dependences. *Journal of Chemical & Engineering Data,* 59, 3805-3813.

RAYNAL, L., ALIX, P., BOUILLON, P.-A., GOMEZ, A., DE NAILLY, M. L. F., JACQUIN, M., KITTEL, J., DI LELLA, A., MOUGIN, P. & TRAPY, J. 2011. 10th International Conference on Greenhouse Gas Control TechnologiesThe DMX™ process: An original solution for lowering the cost of post-combustion carbon capture. *Energy Procedia,* 4, 779-786.

SAKWATTANAPONG, R., AROONWILAS, A. & VEAWAB, A. 2005. Behavior of Reboiler Heat Duty for CO2 Capture Plants Using Regenerable Single and Blended Alkanolamines. *Industrial & Engineering Chemistry Research,* 44, 4465-4473.

SARTORI, G. & SAVAGE, D. W. 1983. Sterically hindered amines for carbon dioxide removal from gases. *Industrial & Engineering Chemistry Fundamentals,* 22, 239-249.

SAVAGE, D., SARTORI, G. & ASTARITA, G. 1984. Amines as rate promoters for carbon dioxide hydrolysis. *Faraday Discussions of the Chemical Society,* 77, 17-31.

SCHÄFFER, A., BRECHTEL, K. & SCHEFFKNECHT, G. 2012. Comparative study on differently concentrated aqueous solutions of MEA and TETA for CO2 capture from flue gases. *Fuel,* 101, 148-153.

SHEN, S., FENG, X. & REN, S. 2013. Effect of Arginine on Carbon Dioxide Capture by Potassium Carbonate Solution. *Energy & Fuels,* 27, 6010-6016.

SHEN, S., YANG, Y.-N., BIAN, Y. & ZHAO, Y. 2016. Kinetics of CO2 Absorption into Aqueous Basic Amino Acid Salt: Potassium Salt of Lysine Solution. *Environmental Science & Technology,* 50, 2054-2063.

SINGH, P. 2011. *Amine based solvent for CO2 absorption" From molecular structure to process".* PhD, University of Twente.

SOLOMONS, T. W. G. & FRYHLE, C. B. 2011. *Organic chemistry,* Hoboken, N.J, Wiley.

SONG, L., WEI, L., SI, T., GUO, H. & YANG, C. 2016. Solution thermodynamics of creatine monohydrate in binary (water + ethanol) solvent systems at T = (278.15 to 328.15) K. *The Journal of Chemical Thermodynamics,* 92, 139-145.

STRACHAN, N., FOXON, T. & FUJINO, J. 2015. *Modelling long-term scenarios for low carbon societies*, Routledge.

SVENDSEN, H. F., HESSEN, E. T. & MEJDELL, T. 2011. Carbon dioxide capture by absorption, challenges and possibilities. *Chemical Engineering Journal,* 171, 718-724.

TAGIURI, A., MOHAMEDALI, M. & HENNI, A. 2016. Dissociation Constant (pKa) and Thermodynamic Properties of Some Tertiary and Cyclic Amines from (298 to 333) K. *Journal of Chemical & Engineering Data,* 61, 247-254.

THITAKAMOL, B. & VEAWAB, A. 2008. Foaming Behavior in CO2 Absorption Process Using Aqueous Solutions of Single and Blended Alkanolamines. *Industrial & Engineering Chemistry Research,* 47, 216-225.

TOLEDO, M. 2016. Mettler Toledo G20 Compact titrator with Rondolino TTL. http://us.mt.com/us/en/home/products/Laboratory_Analytics_Browse/Product_Family_Browse_titrators_main/Compact_Titration.html.

VAIDYA, P. D. & KENIG, E. Y. 2007. CO2-Alkanolamine Reaction Kinetics: A Review of Recent Studies. *Chemical Engineering & Technology,* 30, 1467-1474.

VENKATRAMAN, V., GUPTA, M., FOSCATO, M., SVENDSEN, H. F., JENSEN, V. R. & ALSBERG, B. K. 2016. Computer-aided molecular design of imidazole-based absorbents for CO2 capture. *International Journal of Greenhouse Gas Control,* 49, 55-63.

VOICE, A. K., VEVELSTAD, S. J., CHEN, X., NGUYEN, T. & ROCHELLE, G. T. 2013. Aqueous 3-(methylamino)propylamine for CO2 capture. *International Journal of Greenhouse Gas Control,* 15, 70-77.

WEI, C. C., PUXTY, G. & FERON, P. 2014. Amino acid salts for CO2 capture at flue gas temperatures. *Chemical Engineering Science,* 107, 218-226.

YAN, S., HE, Q., ZHAO, S., ZHAI, H., CAO, M. & AI, P. 2015. CO2 removal from biogas by using green amino acid salts: Performance evaluation. *Fuel Processing Technology,* 129, 203-212.

YE, Q., WANG, X. & LU, Y. 2015. Screening and evaluation of novel biphasic solvents for energy-efficient post-combustion CO2 capture. *International Journal of Greenhouse Gas Control,* 39, 205-214.

ZHANG, R., LIANG, Z., LIU, H., RONGWONG, W., LUO, X., IDEM, R. & YANG, Q. 2016. Study of Formation of Bicarbonate Ions in CO2-Loaded Aqueous Single 1DMA2P and MDEA Tertiary Amines and Blended MEA–1DMA2P and MEA–MDEA Amines for Low Heat of Regeneration. *Industrial & Engineering Chemistry Research,* 55, 3710-3717.

8 Appendix I - Solution Preparation

Date	Solution	Actual gram added			Total	
		Amine	MAPA	H2O	Mass	Volume
17.03.2016	3M DEEA + 1M MAPA	70.36	17.73	106.13	194.22	0.20
05.04.2016	2.666 M DEEA + 1.333M MAPA	62.52	23.51	108.43	194.46	0.20
12.04.2016	3M DEEA	70.35	0	125.74	196.09	0.20
19.04.2016	2M DEEA + 2M MAPA	46.88	35.40	112.36	194.64	0.20
02.05.2016	3M DEEA	70.31	0.00	125.85	196.16	0.20
27.05.2016	3M DEEA	70.32	0.00	125.73	196.05	0.20
22.03.2016	3M TEA + 1M MAPA	89.51	17.65	104.14	211.30	0.20
05.04.2016	2.666 M TEA + 1.333M MAPA	79.70	23.59	106.13	209.42	0.20
12.04.2016	3M TEA	89.6	0	122.95	212.55	0.20
15.04.2016	2M TEA + 2M MAPA	59.74	35.39	111.11	206.24	0.20
21.03.2016	3M BDEA + 1M MAPA	96.74	17.69	83.76	198.19	0.20
05.04.2016	2.666 M BDEA + 1.333M MAPA	85.98	23.60	88.13	197.71	0.20
12.04.2016	3M BDEA	96.77	0	103.49	200.26	0.20
18.04.2016	2M BDEA + 2M MAPA	64.52	35.28	96.89	196.69	0.20
22.03.2016	3M EDEA + 1M MAPA	79.96	17.69	106.24	203.89	0.20
11.04.2016	2.666 M EDEA + 1.333M MAPA	71.13	23.67	107.29	202.09	0.20
21.04.2016	3M EDEA	79.93	0	125.68	205.61	0.20
21.04.2016	2M EDEA + 1M MAPA	53.28	35.28	112.78	201.34	0.20
24.03.2016	3M t-BDEA + 1M MAPA	96.80	17.64	86.70	201.14	0.20
11.04.2016	2.666 M t-BDEA + 1.333M MAPA	86.18	23.62	90.35	200.15	0.20

14.04.2016	3M t-BDEA	96.74	0	105.77	202.51	0.20
14.04.2016	2M t-BDEA + 2M MAPA	64.5	35.39	98.8	198.69	0.20
27.05.2016	2M t-BDEA + 2M MAPA	80.64	44.09	124.38	249.11	0.25
17.03.2016	1M MAPA	0	17.81	180.06	197.87	0.20
09.05.2016	30 wt% MEA	60.03	0	139.68	199.71	0.20
16.02.2016	30 wt% MEA	59.93	0	140.08	200.01	0.20
18.05.2016	3M MEA	36.66	0	164.56	201.22	0.20
20.05.2016	4M MEA	61.1	0	190.75	251.85	0.25
17.03.2016	30 wt. % DMBA	59.95	0	140.08	200.03	0.20

		Actual gram added				
Date	Solution	N-Benzylmethylamine	DEEA	H2O	Mass	Volume
09.05.2016	3M DEEA + 1M BMA	24.25	71.30	98.44	193.99	0.20
18.02.2016	30 wt% BMA	36	0	84	120.00	0.20

		Actual gram added					
Date	Solution	L-Arginine	KOH	H2O	DEEA	Total	Volume
06.04.2016	14.15 wt% ARG	60.24	22.83	342.90	0	425.97	0.20
19.05.2016	3M DEEA + 5 wt % ARG	10.87	4.14	115.01	70.52	200.54	0.20

9 Appendix II - Amine/CO$_2$ Analysis

Screening date	Name	Sample			Blank		Total CO2	[Amine]	diff	loading	loading*	Cyclic capacity
		Mass (g)	HCL(g)	NaOH(ml)	HCl(g)	NaOH(ml)	(mol/kg)	(mol/kg)		(mol amine group)	(mol CO2/mol amine)	(mol/mol)
18.03.2016	3M t-BDEA + 1M MAPA absorpsjon	0.512	40.074	25.247	10.431	10.139	1.4194	4.84		**0.29**	**0.37**	0.24
		0.522	40.174	25.182	10.431	10.139	1.4080	4.84	0.8			
							1.4137	4.84	0.0			
18.03.2016	3M t-BDEA + 1M MAPA desorpsjon	1.104	40.145	28.854	10.431	10.139	0.4981	5.12		**0.10**	**0.12**	
		1.047	40.118	29.307	10.431	10.139	0.5023	5.01	-0.8			
							0.5002	5.06	2.1			
22.03.2016	3M BDEA + 1M MAPA absorpsjon	0.540	40.060	25.390	10.431	10.139	1.3313	4.87		**0.28**	**0.34**	0.22
		0.496	40.073	26.417	10.431	10.139	1.3472	4.87	-1.2			
							1.3392	4.87	0.0			
22.03.2016	3M BDEA + 1M MAPA desorpsjon	1.053	40.133	28.976	10.431	10.139	0.5159	5.16		**0.10**	**0.13**	
		1.020	40.094	29.190	10.431	10.139	0.5202	5.14	-0.8			
							0.5181	5.15	0.4			
24.03.2016	3M EDEA + 1M MAPA absorpsjon	0.579	40.041	19.692	10.431	10.139	1.7320	4.72		**0.37**	**0.46**	0.32
		0.549	40.110	20.719	10.431	10.139	1.7394	4.62	-0.4			
							1.7357	4.67	2.3			
24.03.2016	3M EDEA + 1M MAPA desorpsjon	1.098	40.425	27.399	10.386	9.764	0.5648	4.99		**0.11**	**0.14**	
		1.061	40.331	27.559	10.386	9.764	0.5726	4.95	-1.3			
							0.5687	4.97	0.9			
23.03.2016	3M TEA + 1M MAPA absorpsjon	0.553	40.378	26.649	10.386	9.764	1.1851	4.58		**0.26**	**0.32**	0.19
		0.557	40.425	26.688	10.386	9.764	1.1773	4.58	0.7			
							1.1812	4.58	0.1			
23.03.2016	3M TEA + 1M MAPA desorpsjon	1.095	40.383	28.420	10.386	9.764	0.5179	4.75		**0.11**	**0.14**	
		1.089	40.471	28.813	10.386	9.764	0.5067	4.72	2.2			
							0.5123	4.73	0.7			
05.03.2016	30 wt% MEA absorpsjon	0.560	40.465	13.465	10.386	9.764	2.3552	4.55		**0.51**	**0.51**	0.26
		0.558	40.504	14.079	10.386	9.764	2.3121	4.52	1.9			
							2.3336	4.53	0.5			
05.03.2016		1.074	40.484	12.891	10.386	9.764	1.2556	4.93		**0.26**	**0.26**	
		1.073	40.343	12.855	10.386	9.764	1.2519	4.89	0.3			

	30 wt% MEA desorpsjon						1.2538	4.91	0.7			
18.03.2016	3M DEEA + 1M MAPA absorpsjon	0.548	40.547	12.792	10.585	10.044	2.4830	4.72		**0.53**	**0.66**	0.50
		0.544	40.327	13.033	10.585	10.044	2.4589	4.66	1.0			
							2.4710	4.69	1.2			
18.03.2016	3M DEEA + 1M MAPA desorpsjon	0.510	40.440	33.304	10.585	10.044	0.6466	5.11		**0.13**	**0.16**	
		0.478	40.364	33.483	10.585	10.044	0.6632	5.08	-2.5			
							0.6549	5.10	0.5			
18.03.2016	1M MAPA absorpsjon	0.526	40.484	28.462	10.585	10.044	1.0913	1.97		**0.55**	**1.10**	0.37
		0.523	40.488	28.782	10.585	10.044	1.0674	1.96	2.2			
							1.0794	1.96	0.4			
18.03.2016	1M MAPA desorpsjon	0.514	40.337	32.332	10.585	10.044	0.7261	2.02		**0.36**	**0.73**	
		0.512	40.408	32.317	10.585	10.044	0.7373	2.01	-1.5			
							0.7317	2.01	0.1			
06.04.2016	2.67M DEEA + 1.33M MAPA absorption	0.542	40.061	10.751	10.484	10.041	2.6630	5.02		**0.54**	**0.71**	0.50
		0.548	40.041	10.143	10.484	10.041	2.6875	4.97	-0.9			
							2.6753	5.00	0.9			
06.04.2016	2.67M DEEA + 1.33M MAPA desorption	1.018	40.070	21.563	10.484	10.041	0.8872	5.51		**0.16**	**0.21**	
		1.027	40.160	21.411	10.484	10.041	0.8912	5.55	-0.4			
							0.8892	5.53	-0.6			
08.04.2016	2.67M BDEA + 1.33M MAPA absorption	0.547	40.050	21.804	10.268	9.418	1.5901	5.13		**0.31**	**0.41**	0.24
		0.537	40.070	21.971	10.268	9.418	1.6061	5.17	-1.0			
							1.5981	5.15	-0.9			
08.04.2016	2.67M BDEA + 1.33M MAPA desorption	1.021	40.099	25.066	10.268	9.418	0.6946	5.43		**0.13**	**0.17**	
		1.010	40.063	25.195	10.268	9.418	0.6940	5.50	0.1			
							0.6943	5.46	-1.2			
12.04.2016	2.67M t-BDEA + 1.33M MAPA absorption	0.560	40.442	20.733	10.271	9.738	1.7121	5.13		**0.34**	**0.45**	0.28
		0.525	40.373	21.697	10.271	9.738	1.7279	5.11	-0.9			
							1.7200	5.12	0.3			
12.04.2016	2.67M t-BDEA +	1.054	40.380	25.322	10.271	9.738	0.6890	5.46		**0.13**	**0.17**	
		1.018	40.470	26.140	10.271	9.738	0.6777	5.36	1.7			

	1.33M MAPA desorption						0.6833	5.41	1.9			
12.04.2016	2.67M EDEA + 1.33M MAPA absorption	0.555	40.228	17.332	10.434	9.799	2.0055	4.96		**0.41**	**0.54**	0.34
		0.541	40.381	17.811	10.434	9.799	2.0273	4.95	-1.1			
							2.0164	4.95	0.2			
12.04.2016	2.67M EDEA + 1.33M MAPA desorption	1.081	40.371	22.789	10.434	9.799	0.7839	5.26		**0.15**	**0.20**	
		1.049	40.379	23.415	10.434	9.799	0.7783	5.25	0.7			
							0.7811	5.25	0.4			
11.04.2016	2.67M TEA + 1.33M MAPA absorption	0.560	40.392	23.304	10.271	9.738	1.4781	4.85		**0.30**	**0.40**	0.21
		0.558	40.354	23.444	10.271	9.738	1.4675	4.86	0.7			
							1.4728	4.85	-0.3			
11.04.2016	2.67M TEA + 1.33M MAPA desorption	1.101	40.330	23.596	10.271	9.738	0.7357	5.11		**0.14**	**0.19**	
		1.095	40.405	23.686	10.271	9.738	0.7391	5.06	-0.5			
							0.7374	5.09	1.0			
21.04.2016	2M DEEA + 2M MAPA absorption	0.283	41.599	24.306	10.604	10.094	2.9652	5.55		**0.54**	**0.80**	0.47
		0.325	41.666	22.126	10.604	10.094	2.9277	5.46	1.3			
							2.9464	5.51	1.7			
21.04.2016	2M DEEA + 2M MAPA desorption	0.516	41.326	27.016	10.845	10.453	1.3486	5.98		**0.22**	**0.34**	
		0.517	41.763	27.548	10.845	10.453	1.3368	5.95	0.9			
							1.3427	5.97	0.5			
21.04.2016	2M BDEA + 2M MAPA absorption	0.538	41.431	16.890	10.972	10.406	2.2282	5.69		**0.39**	**0.59**	0.30
		0.530	41.486	17.302	10.972	10.406	2.2281	5.61	0.0			
							2.2281	5.65	1.4			
21.04.2016	2M BDEA + 2M MAPA desorption	1.052	41.416	16.784	10.972	10.406	1.1438	6.03		**0.19**	**0.29**	
		1.058	41.535	16.707	10.972	10.406	1.1466	5.97	-0.2			
							1.1452	6.00	1.0			
16.04.2016	2M t-BDEA + 2M MAPA absorption	0.540	41.061	15.184	19.165	8.394	1.3987	5.62		**0.25**	**0.37**	0.21
		0.548	40.930	14.980	19.165	8.394	1.3849	5.68	1.0			
							1.3918	5.65	-1.0			
16.04.2016	2M t-BDEA + 2M MAPA desorption	1.054	41.090	16.839	19.165	8.394	0.6395	6.04		**0.10**	**0.16**	
		1.042	41.105	17.291	19.165	8.394	0.6259	6.01	2.2			
							0.6327	6.03	0.4			

12.04.2016	2M EDEA + 2M MAPA absorption	0.573	41.687	12.796	10.604	10.094	2.4765	5.49		**0.45**	**0.68**	0.36
		0.573	41.756	13.057	10.604	10.094	2.4598	5.44	0.7			
							2.4682	5.47	1.0			
12.04.2016	2M EDEA + 2M MAPA desorption	1.085	41.678	14.709	10.604	10.094	1.2193	5.80		**0.21**	**0.32**	
		1.076	41.786	14.606	10.604	10.094	1.2393	5.85	-1.6			
							1.2293	5.83	-0.8			
19.04.2016	2M TEA + 2M MAPA absorption	0.516	41.451	19.718	10.711	10.189	2.0553	5.43		**0.38**	**0.58**	0.27
		0.515	41.511	19.300	10.711	10.189	2.1057	5.41	-2.4			
							2.0805	5.42	0.4			
19.04.2016	2M TEA + 2M MAPA desorption	1.086	41.320	15.864	10.972	10.406	1.1459	5.72		**0.20**	**0.30**	
		1.090	41.377	15.868	10.972	10.406	1.1442	5.69	0.2			
							1.1451	5.71	0.4			
15.04.2016	3M DEEA absorption	0.538	40.989	20.682	10.320	9.766	1.8358	3.01		**0.62**	**0.62**	0.56
		0.534	41.005	20.619	10.320	9.766	1.8569	2.96	-1.1			
							1.8464	2.99	1.8			
15.04.2016	3M DEEA desorption	1.001	41.014	36.998	10.320	9.766	0.1729	3.21		**0.05**	**0.05**	
		0.999	40.977	36.878	10.320	9.766	0.1774	3.20	-2.5			
							0.1752	3.21	0.5			
22.04.2016	3M EDEA absorption	0.524	41.742	37.582	10.845	10.453	0.3595	2.98		**0.12**	**0.12**	0.04
		0.513	41.762	37.746	10.845	10.453	0.3532	2.97	1.8			
							0.3564	2.97	0.2			
22.04.2016	3M EDEA desorption	1.006	41.736	36.646	10.845	10.453	0.2335	3.01		**0.08**	**0.08**	
		1.033	41.744	36.556	10.845	10.453	0.2321	3.00	0.6			
							0.2328	3.00	0.3			
14.04.2016	3M TEA absorption	0.536	40.975	38.637	10.320	9.766	0.1664	2.90		**0.06**	**0.06**	0.03
		0.536	40.883	38.557	10.320	9.766	0.1653	2.89	0.7			
							0.1659	2.90	0.4			
14.04.2016	3M TEA desorption	1.079	40.984	38.725	10.320	9.766	0.0790	2.91		**0.03**	**0.03**	
		1.077	40.985	38.707	10.320	9.766	0.0800	2.92	-1.3			
							0.0795	2.91	-0.1			
14.04.2016	3M BDEA absorption	1.015	31.256	25.073	11.177	10.844	0.2882	3.11		**0.09**	**0.09**	0.08
		1.023	31.197	24.881	11.177	10.844	0.2924	3.10	-1.5			
							0.2903	3.10	0.2			
14.04.2016	3M BDEA desorption	4.037	15.604	11.907	10.660	10.250	0.0407	3.15		**0.01**	**0.01**	
		4.032	32.245	28.594	10.660	10.250	0.0402	3.12	1.3			
							0.0405	3.14	0.9			
18.04.2016	3M t-BDEA absorption	0.522	41.532	36.741	10.711	10.189	0.4089	3.04		**0.13**	**0.13**	0.12
		0.522	41.473	36.730	10.711	10.189	0.4043	3.03	1.1			

							0.4066	3.04	0.5			
18.04.2016	3M t-BDEA desorption	1.032	41.020	39.441	10.677	10.255	0.0561	3.10		**0.02**	**0.02**	
		1.029	41.066	39.500	10.677	10.255	0.0556	3.08	0.8			
							0.0558	3.09	0.7			
09.05.2016	3M DEEA absorption (2)	0.529	40.550	22.187	11.023	10.310	1.6682	2.96		**0.56**	**0.56**	0.51
		0.530	40.540	22.167	11.023	10.310	1.6660	2.95	0.1			
							1.6671	2.95	0.5			
09.05.2016	3M DEEA desorption (2)	1.468	40.576	34.761	11.023	10.310	0.1738	3.18		**0.05**	**0.05**	
		1.461	40.353	34.556	11.023	10.310	0.1740	3.15	-0.1			
							0.1739	3.16	1.0			
16.02.2016	30 wt% MEA absorption (2)	0.560	45.141	17.792	10.678	9.394	2.3272	4.62		**0.51**	**0.51**	0.24
		0.560	45.050	17.758	10.678	9.394	2.3221	4.56	0.2			
							2.3247	4.59	1.2			
16.02.2016	30 wt% MEA desorption (2)	1.072	45.170	15.570	10.678	9.394	1.3207	4.92		**0.27**	**0.27**	
		1.088	44.962	15.164	10.678	9.394	1.3104	4.80	0.8			
							1.3155	4.86	2.6			
27.05.2016	3M MEA absorption	0.540	45.135	27.701	10.678	9.394	1.4954	2.83		**0.54**	**0.54**	0.38
		0.540	45.141	27.289	10.678	9.394	1.5341	2.82	-2.5			
							1.5147	2.83	0.2			
27.05.2016	3M MEA desorption	0.977	45.100	31.255	10.678	9.394	0.6428	3.12		**0.21**	**0.15**	
		0.975	45.087	31.457	10.678	9.394	0.6331	3.07	1.5			
							0.6380	3.10	1.7			
27.05.2016	4M MEA absorption	0.549	45.123	22.874	10.678	9.394	1.9094	3.73		**0.52**	**0.52**	0.29
		0.554	45.062	22.349	10.678	9.394	1.9340	3.70	-1.3			
							1.9217	3.72	1.0			
27.05.2016	4M MEA desorption	0.983	45.071	26.314	10.678	9.394	0.8888	3.98		**0.22**	**0.22**	
		0.977	45.140	26.591	10.678	9.394	0.8836	3.91	0.6			
							0.8862	3.95	1.7			
28.05.2016	3M DEEA absorption (3)	0.540	40.513	18.937	10.678	9.394	1.8789	3.01		**0.63**	**0.63**	0.57
		0.538	40.574	19.037	10.678	9.394	1.8822	2.98	-0.2			
							1.8806	2.99	0.8			
28.05.2016	3M DEEA desorption (3)	0.996	40.530	36.289	10.791	10.290	0.1878	3.24		**0.06**	**0.06**	
		0.994	40.736	36.500	10.791	10.290	0.1879	3.24	-0.1			
							0.1878	3.24	-0.3			
29.05.2016	2M t-BDEA + 2M MAPA	0.537	40.738	15.444	10.791	10.290	2.3085	5.59		**0.42**	**0.62**	0.35
		0.539	40.716	15.122	10.791	10.290	2.3277	5.55	-0.8			
							2.3181	5.57	0.8			

	absorption (2)											
29.05.2016	2M t-BDEA + 2M MAPA desorption (2)	1.039	40.703	17.633	10.791	10.290	1.0861	5.97		**0.18**	**0.27**	
		1.051	40.735	17.465	10.791	10.290	1.0832	5.94	0.3			
							1.0846	5.95	0.4			

		Sample			**Blank**		**Total CO2**	**[Amine]**		**loading**	**loading***	**Cyclic capacity**
Date	**Name**	**weight (g)**	**HCL (g)**	**NaOH (ml)**	**HCL (g)**	**NaOH (ml)**	**(mol/kg)**	**(mol/kg)**	**diff**	(mol amine group)	(mol CO2/mol amine)	(mol/mol)
18.02.16	30 wt% Benzylmethylamine absorption	0.528	40.198	27.018	10.484	10.041	1.2062	2.40		**0.50**	**0.50**	0.41
		0.523	40.274	27.265	10.484	10.041	1.2013	2.39	0.4			
							1.2037	2.39	0.2			
	30 wt% Benzylmethylamine desorption	1.009	40.197	35.396	10.484	10.041	0.2160	2.48		**0.09**	**0.09**	
		1.016	40.097	35.196	10.484	10.041	0.2194	2.45	-1.6			
							0.2177	2.47	1.1			
07.04.16	14.15 wt% L-Arginin absorpsjon	0.539	38.214	27.361	10.268	9.418	0.9279	0.51		**1.79**	**1.79**	0.65
		0.558	38.615	27.644	10.268	9.418	0.9069	0.51	2.3			
							0.9174	0.51	-0.6			
	14.15 wt% L-Arginin desorpsjon	1.094	39.793	25.465	10.268	9.418	0.6160	0.55		**1.14**	**1.14**	
		1.092	40.040	25.790	10.268	9.418	0.6136	0.53	0.4			
							0.6148	0.54	2.0			
10.05.2016	3M DEEA + 1M BMA absorption	0.531	40.625	20.754	11.023	10.310	1.8040	3.96		**0.46**	**0.46**	0.41
		0.530	40.626	20.740	11.023	10.310	1.8088	3.95	-0.3			
							1.8064	3.95	0.4			
	3M DEEA + 1M BMA desorption	0.977	40.645	36.489	11.023	10.310	0.1762	4.26		**0.04**	**0.04**	
		0.992	40.675	36.419	11.023	10.310	0.1786	4.17	-1.3			
							0.1774	4.22	2.2			
20.05.16	3M DEEA + 5 wt% L-arginine absorption	0.485	41.251	20.016	10.743	9.679	2.0795	3.39		**0.62**	**0.62**	0.51
		0.511	41.349	19.040	10.743	9.679	2.0788	3.32	0.0			
							2.0791	3.35	2.2			
	3M DEEA + 5 wt% L-arginine desorption	1.027	41.487	31.780	10.743	9.679	0.4208	3.65		**0.11**	**0.11**	
		1.033	41.651	32.068	10.743	9.679	0.4123	3.66	2.0			
							0.4166	3.65	-0.3			

10 Appendix III - Risk Assessment

Detaljert Risikorapport

ID	3850	**Status**	**Dato**
Risikoområde	Risikovurdering: Helse, miljø og sikkerhet (HMS)	Opprettet	01.02.2016
Opprettet av	Iris Renate Tøkje Krokvik	Vurdering startet	03.02.2016
Ansvarlig	Iris Renate Tøkje Krokvik	Tiltak besluttet	
		Avsluttet	

EEART, Master student 2016, Iris Renate Tøkje Krokvik

Gyldig i perioden:

2/1/2016 - 2/1/2019

Sted:

Laboratories K4, 3rd and 4th floor

Mål / hensikt

Risk assessment of the laboratory work Iris Renate Tøkje Krokvik will perform related to the master thesis at IKP.

Bakgrunn

Activities to be done in the lab:
- Solution preparation and transportation
- Amine screening
- CO2 and amine analysis
- Thermal degradation
- Waste management

Beskrivelse og avgrensninger

Different amine solutions are made and screened in the screening apparatus, then the CO2 and amine content is analysed. Some of the amines are classified as toxic, and spill of chemical can occur. Thermal degradation is done to see the the thermal degradation effect on the amine solution after screening. The thermal degradation samples is 5 tubes x 7 mL, and the temperature is set to be 135 *C. After experiments are done, the waste must be taken proper care of. Spill of waste can occure, and the waste containers are quite heavy.
After the lab work is done, there should be written a report. Ergonomical issues with office work may happen.

Forutsetninger, antakelser og forenklinger

Existing risk assessments for equipments and activities:
- K4.316 CO2 and amine analysis
- K4-310 - Screening apparatus for non-toxi solutions, MAPA and Imidazole
- EEART, Method, 2015, Solution preparation and transportation (Absorption)

Risk assessments above are valid (see references), and the equipment/activities will be used according to the risk assessment. These activities will not be risk assessed again.

A risk assessment for thermal degradation is done (se attached), but this risk assessment is no longer valid. However, this activities related to this operation is assumed to be of the same caracter as the old risk assessment, and will be used as of it was still valid.

Vedlegg

Risk asssessment Thermal degradation.pdf

Referanser

Norges teknisk-naturvitenskapelige universitet (NTNU)	**Utskriftsdato:**	**Utskrift foretatt av:**	**Side:**
Unntatt offentlighet jf. Offentlighetsloven § 14	29.06.2016	Iris Renate Tøkje Krokvik	1/12

EEART, Method, 2015, Solution preparation and transportation (Absorption)(https://avvik.ntnu.no/Risk/EditRiskAssessment/162)
K4-310 - Screening apparatus for non-toxi solutions, MAPA and Imidazole(https://avvik.ntnu.no/Risk/EditRiskAssessment/177)
K4.316 CO2 and amine analysis(https://avvik.ntnu.no/Risk/EditRiskAssessment/265)
MSDS DEEA (2-Dietylaminoetanol)(https://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=NO&brand=ALDRICH&productNumber=D94003&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D100378%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS MAPA (3-(Methylamino)propylamine)(http://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=NO&brand=SIAL&productNumber=65690&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D6291845%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS EDEA (N-Ethyldiethanolamine)(https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=NO&language=no&productNumber=112062&brand=ALDRICH&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D139877%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS TEA (Triethanolamine)(_https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=NO&language=no&productNumber=90279&brand=SIGMA&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D102716%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS BDEA (N-Butyldiethanolamine)(_https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=NO&language=no&productNumber=471240&brand=ALDRICH&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D102794%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS DBAE (2-(Dibutylamino)ethanol)(_https://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=NO&brand=ALDRICH&productNumber=550035&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D102818%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS t-BDEA (N-tert-Butyldiethanolamine)(_http://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=NO&brand=ALDRICH&productNumber=455709&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3DN-tert-Butyldiethanolamine%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS N-Benzylmethylamine(https://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=NO&brand=ALDRICH&productNumber=B25606&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D103673%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS N,N-Dimethylbenzylamine(https://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=NO&brand=ALDRICH&productNumber=185582&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D103833%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS Phenethylamine(https://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=NO&brand=ALDRICH&productNumber=241008&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D64040%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS Creatine monohydrate(http://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=NO&brand=SIGMA&productNumber=C3630&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3Dcreatine%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
MSDS L-Arginine(https://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=NO&brand=SIAL&productNumber=A5006&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D74793%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)
Thermal analysis equipment(https://avvik.ntnu.no/Risk/EditRiskAssessment/1573)
MSDS 1,2-Diaminocyclohexane (DACH)(https://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=NO&brand=ALDRICH&productNumber=132551&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D694837%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DNO%26focus%3Dproduct)

Oppsummering, resultat og endelig vurdering

I oppsummeringen presenteres en oversikt over farer og uønskede hendelser, samt resultat for det enkelte konsekvensområdet.

Farekilde: **Solution preperation**

Uønsket hendelse: **Spill on humans**

Konsekvensområde: Helse — Risiko før tiltak: 🟢 Risiko etter tiltak: ○

Uønsket hendelse: **Spill on table and/or floor**

Konsekvensområde: Helse — Risiko før tiltak: 🟢 Risiko etter tiltak: ○
Ytre miljø — Risiko før tiltak: 🟢 Risiko etter tiltak: ○

Uønsket hendelse: **Inhalation**

Konsekvensområde: Helse — Risiko før tiltak: 🟢 Risiko etter tiltak: ○

Farekilde: **Running screening apparatus**

Uønsket hendelse: **Risks with running the apparatus**

Skal ikke analyseres.

Farekilde: **Doing CO2 and amine analysis**

Uønsket hendelse: **Risks when doing CO2 and amine analysis**

Skal ikke analyseres.

Farekilde: **Doing thermal degradation**

Uønsket hendelse: **Risks with thermal degradation**

Skal ikke analyseres.

Farekilde: **Waste handling**

Uønsket hendelse: **Spill from waste canister**

Konsekvensområde: Helse — Risiko før tiltak: 🟢 Risiko etter tiltak: ○

Farekilde: **Waste handling**

Uønsket hendelse: **Spill from waste canister**

Ytre miljø — Risiko før tiltak: 🟢 Risiko etter tiltak: ⚪

Uønsket hendelse: **Ergonomic issues**

Konsekvensområde: Helse — Risiko før tiltak: 🟢 Risiko etter tiltak: ⚪

Farekilde: **Ergonomic issues with office work**

Uønsket hendelse: **Belastningsskader**

Konsekvensområde: Helse — Risiko før tiltak: 🟡 Risiko etter tiltak: ⚪

Endelig vurdering

Oversikt involverte enheter og personell

En risikovurdering kan gjelde for en, eller flere enheter i organisasjonen. Denne oversikten presenterer involverte enheter og personell for gjeldende risikovurdering.

Enhet /-er risikovurderingen omfatter

- Institutt for kjemisk prosessteknologi

Deltakere

Hanna Knuutila
Ardi Hartono
Gøril Flatberg
Gunn Torill Wikdahl

Lesere

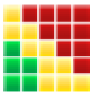
[Ingen registreringer]

Andre involverte/interessenter

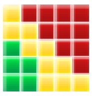
[Ingen registreringer]

Følgende akseptkriterier er besluttet for risikoområdet Risikovurdering: Helse, miljø og sikkerhet (HMS):

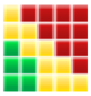
Helse



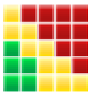
Materielle verdier



Omdømme



Ytre miljø



Oversikt over eksisterende, relevante tiltak som er hensyntatt i risikovurderingen

I tabellen under presenteres eksisterende tiltak som er hensyntatt ved vurdering av sannsynlighet og konsekvens for aktuelle uønskede hendelser.

Farekilde	Uønsket hendelse	Tiltak hensyntatt ved vurdering
Solution preperation	Spill on humans	Personal protective equipment
	Spill on humans	Fume hood/cabinet
	Spill on humans	MSDS
	Spill on table and/or floor	Personal protective equipment
	Spill on table and/or floor	Fume hood/cabinet
	Spill on table and/or floor	MSDS
	Inhalation	Personal protective equipment
	Inhalation	Fume hood/cabinet
	Inhalation	MSDS
Waste handling	Spill from waste canister	Personal protective equipment
	Ergonomic issues	
Ergonomic issues with office work	Belastningsskader	Hånleddstøtte

Eksisterende og relevante tiltak med beskrivelse:

Personal protective equipment
Goggles, labcoat and gloves.

Fume hood/cabinet
All work with chemicals should be conducted in a fume cabinet or under a fume hood.

A lot of the equipment is placed in and operated in fume cabinets

HSE-course prior to accessing the lab
Two HSE-courses is compulsory before granting permission to enter the lab facility

Training from apparatus responsible
Before operating the equipment alone, the apparatus responsible have to give and approve training.

Commercially bought equipment
[Ingen registreringer]

MSDS
[Ingen registreringer]

Hånleddstøtte
[Ingen registreringer]

Risikoanalyse med vurdering av sannsynlighet og konsekvens

I denne delen av rapporten presenteres detaljer dokumentasjon av de farer, uønskede hendelser og årsaker som er vurdert. Innledningsvis oppsummeres farer med tilhørende uønskede hendelser som er tatt med i vurderingen.

Følgende farer og uønskede hendelser er vurdert i denne risikovurderingen:

- **Solution preperation**
  - Spill on humans
  - Spill on table and/or floor
  - Inhalation
- **Waste handling**
  - Spill from waste canister
  - Ergonomic issues
- **Ergonomic issues with office work**
  - Belastningsskader

Oversikt over besluttede risikoreduserende tiltak med beskrivelse:

Solution preperation (farekilde)

Preperation of amine solutions, where some of the amines is classified as toxic.

Solution preperation/Spill on humans (uønsket hendelse)

Samlet sannsynlighet vurdert for hendelsen: Sannsynlig (3)

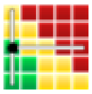
Kommentar til vurdering av sannsynlighet:

Det verste som kan skje er at det kommer løsning inn på øyet. MSDS for den giftige aminen viser ingen akutt forgiftning ved hudkontakt.

Vurdering av risiko for følgende konsekvensområde: Helse

Vurdert sannsynlighet (felles for hendelsen): Sannsynlig (3)

Vurdert konsekvens: Liten (1)



Kommentar til vurdering av konsekvens:

[Ingen registreringer]

Solution preperation/Spill on table and/or floor (uønsket hendelse)

Samlet sannsynlighet vurdert for hendelsen: Sannsynlig (3)

Kommentar til vurdering av sannsynlighet:

Vurderer at det er lite sannsynlig å miste hele kolben med 200 g løsning. Antar mer årvåkenhet ved arbeid med toksiske aminer.

Vurdering av risiko for følgende konsekvensområde: Helse

Vurdert sannsynlighet (felles for hendelsen): Sannsynlig (3)

Vurdert konsekvens: Liten (1)

Kommentar til vurdering av konsekvens:

Ved søl av hele flasken (ren amin) vil man benytte gassmaske.

Solution preperation/Inhalation (uønsket hendelse)

Samlet sannsynlighet vurdert for hendelsen: Lite sannsynlig (2)

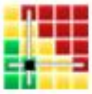
Kommentar til vurdering av sannsynlighet:

Ren MAPA skal ikke brukes veldig ofte.

Vurdering av risiko for følgende konsekvensområde: Helse

Vurdert sannsynlighet (felles for hendelsen): Lite sannsynlig (2)

Vurdert konsekvens: Middels (2)



Kommentar til vurdering av konsekvens:

Ved knus av flaske med ren MAPA blir rommet evakuert.

Waste handling (farekilde)

Waste handling/Spill from waste canister (uønsket hendelse)

Samlet sannsynlighet vurdert for hendelsen: Sannsynlig (3)

Kommentar til vurdering av sannsynlighet:

[Ingen registreringer]

Vurdering av risiko for følgende konsekvensområde: Helse

Vurdert sannsynlighet (felles for hendelsen): Sannsynlig (3)

Vurdert konsekvens: Liten (1)

Kommentar til vurdering av konsekvens:

[Ingen registreringer]

Waste handling/Ergonomic issues (uønsket hendelse)

Samlet sannsynlighet vurdert for hendelsen: Lite sannsynlig (2)

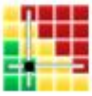
Kommentar til vurdering av sannsynlighet:

[Ingen registreringer]

Vurdering av risiko for følgende konsekvensområde: Helse

Vurdert sannsynlighet (felles for hendelsen): Lite sannsynlig (2)

Vurdert konsekvens: Middels (2)



Kommentar til vurdering av konsekvens:

[Ingen registreringer]

Ergonomic issues with office work (farekilde)

Ergonomic issues with office work/Belastningsskader (uønsket hendelse)

Samlet sannsynlighet vurdert for hendelsen: Sannsynlig (3)

Kommentar til vurdering av sannsynlighet:

[Ingen registreringer]

Vurdering av risiko for følgende konsekvensområde: Helse

Vurdert sannsynlighet (felles for hendelsen): Sannsynlig (3)

Vurdert konsekvens: Middels (2)

Kommentar til vurdering av konsekvens:

[Ingen registreringer]

Oversikt over besluttede risikoreduserende tiltak:

Under presenteres en oversikt over risikoreduserende tiltak som skal bidra til å reduseres sannsynlighet og/eller konsekvens for uønskede hendelser.

Oversikt over besluttede risikoreduserende tiltak med beskrivelse: