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Sustainability assessment of phase-change solvents for CO₂ capture

Benefits and disadvantages from a sustainability perspective

Master's thesis in Sustainable Energy Systems

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Department of Space, Earth and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

Carbon Capture and Storage has been suggested as a crucial tool to reduce carbon dioxide emission from industry and power plant using fossil fuel. The benchmark carbon capture process absorb CO₂ contain in flue gases through chemical absorption in a solution of monoethanolamine (MEA). To recover the absorbed CO₂ an expensive and energy consuming regeneration step is needed. Reducing CCS energy requirement is crucial in order to make CCS commercially viable. Multiple studies have been conducted in order to find more efficient solvents. A new amine solvent family called phase change solvent has demonstrated very promising energetic performance. According to research they could reduce the reboiler duty from 3.7 GJ/tCO₂ for MEA process to 2-2.5 GJ/tCO₂. However most of the studies lead on phase change solvent focused on energy requirement only. Another important aspect to take into account is the sustainability of such processes. Indeed, phase-change carbon capture processes can be energetically more beneficial than traditional CCS using MEA however their overall impact on environment and humans should be at least equal or lower. Thus, it is important to assess their sustainability and the influential factors.

The goal of this work was to develop an LCA framework for phase-change CO₂ capture processes. The framework was applied to a reference system modelled on Aspen Plus v8.8 using a solution of N-methylcyclohexylamine (MCA) as solvent. The developed LCA takes into consideration, additionally to the traditional energy and material flow related factors a first level of degradation product and their treatment, aerosols formation and wash water treatment (e.g the formation of ammonia and its treatment by wash water). The three metrics considered are the Cumulative Energy Demand (CED), the Global Warming Potential (GWP) and the aggregated environmental score ReCiPe.

Six scenarios were considered in order to assess the impact of degradation products, aerosols formation and threshold emission of non-conventional amine. The results presented in this thesis show a total heating requirement similar to the one in literature of 2.6 GJ/tCO₂ but with a different distribution, spending considerably less energy in the stripper reboiler and accordingly more energy in the preheating of the rich CO₂ stream that is fed to the stripper. This result needs to be further investigated by more accurate thermodynamic equilibrium properties estimation. The Life Cycle Impact Assessment demonstrates that MCA emission threshold has more impact on LCA metrics total value than degradation scenarios and that the most influential parameter is the amount of aerosol form in the absorber. The large proportion of loss due to MCA volatility and aerosol, which are directly linked to the volatility, explain that solvent make-up appears as a big contributor for each metrics and scenarios.

Keywords: carbon capture, phase-change solvent, sustainability assessment, LCA.

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Abbreviations

AMP	2-Amino-2-methyl-1-propanol
BDA	1,4-butanediamine
CCS	Carbon capture and storage
CCU	Carbon capture and utilisation
CED	Cumulative Energy Demand
CO	Carbon monoxide
CO ₂	Carbon dioxide
DEEA	2-(Diethylamino)-ethanol
DETA	Diethylenetriamine
DEA	Diethanolamine
DGA	Diglycolamine
DMCA	N,N-dimethylcyclohexylamine
DS	Degree scenario
EOR	Enhanced Oil Recovery
GHG	Greenhouse gases
GWP	Global warming potential
H ₂	Hydrogen
IEA	International Energy Agency
LCA	Life Cycle Assessment
LCIA	Life Cycle Impact Assessment
LCST	Lower Critical Separation Temperature
LLE	Liquid-liquid equilibrium
LLPS	Liquid-Liquid Phase Separation
MAPA	3-(Methylamino)-propylamine
MCA	N-methylcyclohexylamine
MEA	Monoethanolamine
MMEA	N-methylethanolamine
MW	Molecular weight
N ₂	Nitrogen
O ₂	Oxygen
PCC	Post combustion carbon capture
TETA	Triethylenetetramine

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1 Introduction

Global warming is one of the most concerning societal challenges of the 21st century. The global temperature of the atmosphere has been increasing since the industrial revolution and even more rapidly since the second half of the 20th century. The rise in temperature started to provoke a rise in ocean level, glacier retreat and climate abnormalities. Thus, today it appears necessary to mitigate global warming. In 2015, the United Nation Climate Change Conference was held in Paris. The attending countries reached the agreement to keep the increase of Earth temperature under 2°C relatively to the pre-industrial levels. In order to meet this target major changes in technologies and policies have to be implemented[1].

Since the industrial revolution the use of fossil fuels for energy production and other purposes has increased dramatically. It is well known today that the burning of fossil fuels releases various gases that take a major play in global warming. These gases are commonly called greenhouse gases. They consist of nitrous oxide (N₂O), methane (CH₄), fluorinated gases (F-gases) and carbon dioxide (CO₂). CO₂ is the main greenhouse gas released in the atmosphere. In 2010, it represented 76% of GHG emissions [2], around 60% of CO₂ emissions come from energy production and 7% from the rest of the industrial sector. [3].

The International Energy Agency set CO₂ emission limits to prevent the rise of the global temperature for more than 2°C. According to this scenario, CO₂ emissions related to energy production and industrial processes have to be reduced by 60% compared to 2012. Development of renewable technologies, improvement of energy efficiency and fuel switching will contribute to the 2DS. However the IEA states that in 2050, 43% of primary energy will still be supplied by fossil fuels[4]. The only technology that can be used to reduce those emissions coming from the burning of the fossil fuels is carbon capture and storage (CCS). In the 2DS, CCS accounts for 12% of the needed reduction in CO₂ emissions [5].

CCS is an established technology that has been implemented more than 40 years ago. There are currently 21 large scales and over 80 pilot and demonstration CCS facilities worldwide[6],[7]. Different capture technologies exist, but the most mature one is a post- combustion chemical absorption of CO₂ from flue gases. The CO₂ is absorbed in a column by a solvent that is generally a 30wt% water solution of monoethanolamine (MEA). The solvent is then regenerated in a stripping column to be reused in the process and almost pure CO₂ is usually compressed, ready to be transported to a storing station. The solvent regeneration is the most energy consuming and thus expensive part of the process. The recovery of the MEA consumes about 3.7 GJ/tonne CO₂ captured [8]. In case when CCS is used to reduce emissions from power plants, the energy consumed by the CCS can lead to an energy penalty between 14-28% of the total energy produced depending of the type of power plants [9]. Today, numerous studies are carried out in order to find ways to reduce the energy consumption of the solvent regeneration.

When developing and choosing a new process not only the energetic aspect has to be considered. Indeed, a very energetically efficient process can have many other drawbacks such as the toxicity of the products used or the need for extensive effluent treatment. Thus, several aspects towards a holistic sustainability assessment need to be investigated. Around 30 studies on sustainability assessment of MEA – based processes can be found in literature. Most of the papers evaluate the life cycle environmental impacts of CCS technologies implemented at different types of power plants. There are also studies made on comparison of power plants with or without CCS or different type of CCS technologies[10].

As a part of an EU Horizon 2020 project, the Division of Energy Technology of Chalmers is investigating a family of new solvents that can be used in absorption based carbon capture. Those solvents are called phase-change solvents. They have the particular feature to form a vapour-liquid-liquid (VLL) equilibrium at certain process conditions. This behaviour enables the development of new absorber/desorber configurations that are less energy consuming than usual post combustion carbon capture processes utilizing MEA. In addition to the reduced energy penalty and thus cost, these new solvents appear to be promising in terms of sustainability. Project partners have identified some new phase-change alternatives that have beneficial absorption/desorption properties and exhibit good liquid-liquid phase separation. While sustainability assessment of the production stage of such solvents has been performed, the analysis at the process level still needs to be executed [11].

The purpose of this thesis is to develop and apply a framework to assess the sustainability of carbon capture processes that use phase-change solvents for CO₂ capture. The framework should be applicable to different process configurations and variety of solvents.

2 Background: Carbon capture and storage

Carbon capture and storage or sequestration is the operation of removing the CO₂ present in gaseous effluents and its storage in secured reservoirs. CCS is very interesting to implement in fossil fuel based power plants or in industries where flue gases contain large amounts of CO₂. In a classical fossil fuel based power plant the CO₂ concentration is on average 12% [12]. This concentration can vary from 3 to 30% over all types of industries and power plants [13]. CCS can be divided in three main stages: carbon capture, transport and storage. For each of these steps different technologies and methods can be used.

2.1 Carbon capture processes

Various separation technologies can be used for CO₂ capture. They are either based on chemical or physical processes. The mains technologies used today are classified in three categories: Post-combustion, Pre-combustion and Oxy-fuel combustion. It must still be noted that other technologies such as chemical looping or mineralisation are also being carefully investigated. Chemical looping can be considered as a subcase of oxy-fuel combustion and mineralisation has the advantage of being a form of storage.

2.1.1 Post-combustion

The term 'post-combustion' is employed when the CO₂ is removed from the fumes after the combustion step. The fuel is burnt with air in a combustion chamber to produce energy. The flue gases are cleaned to remove impurities and the CO₂ is then retrieved most commonly through chemical absorption by an amine solvent such as MEA. Post combustion capture (PCC) process scheme can be found in figure 2.1.1. PCC using MEA has been used for over 40 years worldwide.

The main advantages of post-combustion processes are the high purity degree of CO₂ recovered, above 99.99% purity can be reach and the possibility to retrofit it easily to an existing plant [14]. Nonetheless the investment of this kind of process is still high and there is a non-negligible energy penalty.

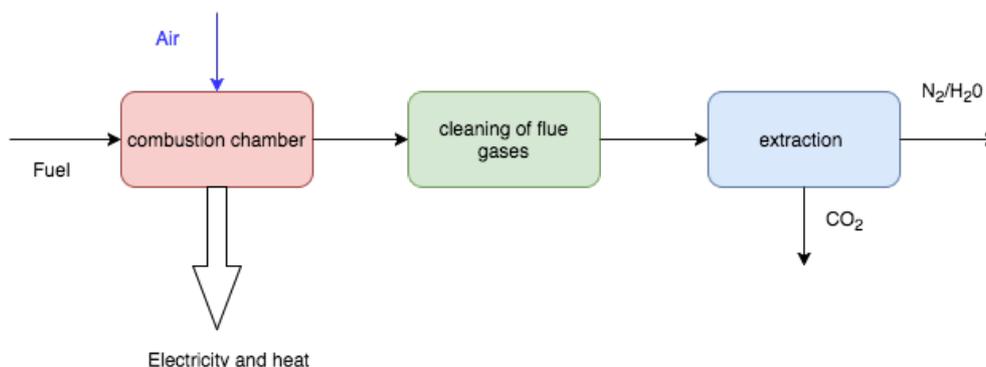


Figure 2.1.1: Post-combustion carbon capture process scheme

2.1.2 Pre-combustion

The principle of pre-combustion carbon capture is to remove the CO_2 from the fuel before the combustion step. If coal or biomass is used as fuel, it goes to a gasifier to be transformed to synthesis gas mainly composed of CO and H_2 . Water gas shift step is then performed in order to only have CO_2 and H_2 . There is no gasification step if natural gas is used as fuel. The gas is directly sent to a steam-reforming unit.

After this stage, CO_2 and H_2 are separated. Since N_2 is not present, a considerably lower amount of gas is treated and CO_2 is in higher concentrations, which makes the separation easier. Moreover pressure swing adsorption can be efficiently used to separate most of the H_2 , which requires less energy. Finally, H_2 is sent to a combustion chamber. This way only water is released in the atmosphere during the combustion step. Even though pressure swing absorption is a good separation technology, the separation step is usually performed by chemical absorption using MEA as in post-combustion processes. One of the main advantages of pre-combustion is that the CO_2 can be separated with high purity and at elevated pressure which reduce the energy consumption compared to a post-combustion process [13]. The air separation situated upstream to the gasification produces relatively pure N_2 that can be sold or used in other parts of the plant.

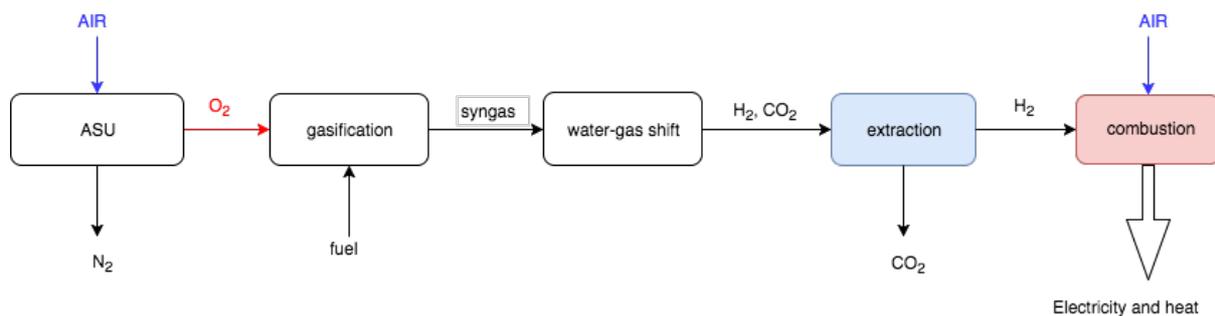


Figure 2.1.2: Pre-combustion carbon capture process scheme for the use of coal

Pre-combustion process is mostly used in Integrated Gasification Combined Cycle (IGCC) that uses coal as fuel or in Natural Gas Combined Cycle (NGCC). High complexity and investment cost of those plants are major obstacles to utilize the technology. Therefore, there are a limited number of industrial scale plants worldwide [14].

2.1.3 Oxy-fuel combustion

In oxy-fuel combustion fuel is burnt in almost pure oxygen instead of air. In usual combustion air is used as an oxidant and thus large amount of N_2 is present in the flue gases. Using only O_2 for combustion allows having flue gases mainly composed of CO_2 and water, separation of which require less energy than CO_2/N_2 separation. The O_2 is first separated from the other air components in an Air separation Unit (ASU), generally by cryogenic distillation. The oxygen is then used in the combustion chamber to burn

the fuel. The flue gases cleaned from impurities continue to a condenser where water is separated from the CO₂.

Oxy-fuel combustion occurs at lower temperatures and thus, protects combustion chamber constituting materials [13]. The N₂ produced by pre-combustion by the ASU can be used for other aims. As mentioned previously oxy-fuel combustion decreases the energy demand for CO₂ separation and all technically required components are commercially available today. On the other hand, the air separation requires a lot of energy which may consume up to 15% of a power plant's total electricity output [9].

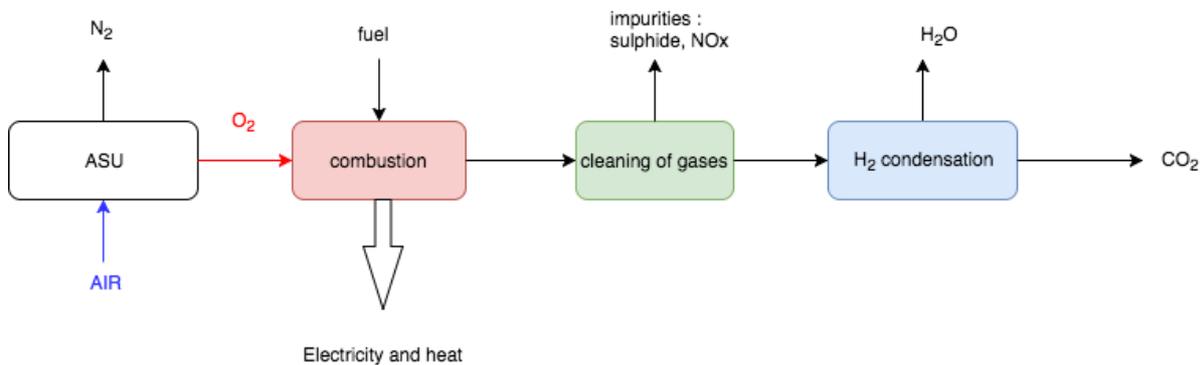


Figure 2.1.3: Oxy-fuel combustion carbon capture process scheme

2.2 Transport and storage

2.2.1 Transport

Various ways are possible to transport CO₂ from the capture plant to storage sites or to other plants for a further use. On-shore pipelines have been used for more than 30 years in the US for enhanced oil recovery. This CO₂ pipeline network is spread over many states all the way to Canada for more than 6000km. Transportation of CO₂ via pipelines is a well developed and economically interesting technology, especially for large quantities of CO₂. On-shore pipelines are the most commercially used mode of transport of CO₂ [13]. In case long distance needs to be covered and if the storage reservoir is located in the sea, shipping appears to be an efficient manner to transport CO₂ since it is less expensive than building under-sea pipeline. CO₂ can also be moved by the railway or road transport when smaller quantities need to be transported and it is expensive to build a pipeline.

2.2.2 Storage

After the capture, CO₂ has to be stored in secured reservoirs so that it will not be released into the atmosphere. Storage places have to be carefully chosen. CO₂ needs to be sequestered for prolonged period of time in order to meet the environmental goal defined by the Paris agreement. Different types of storage with various capacities exist worldwide. However their level of development and operation are not equal; geological

storage is already used, its functioning and environmental impact are relatively well known while oceanic storage is still at a development stage [15].

2.2.2.1 Geological storage

Geological storage is based on injecting of previously captured CO₂ to rock cavities located deeply under the ground. Such storage places must be carefully selected taking into account a set of technical, environmental, geological, economical, societal and safety factors. Additionally permeability of the rocks and the capacity of the reservoirs should be considered. CO₂ is stored in a supercritical phase, this way its density is close to liquid and the gas occupies less volume. In order to have pressure and temperature conditions that lead to supercritical CO₂, the minimum depth of sequestration must be around 800m [16].

There are three main options of geological storages: depleted oil and gas reservoir, deep saline aquifers and unexploited coal seams.

Depleted oil and gas fields have one obvious advantage: they previously contained hydrocarbons for thousands of years and their permeability is proven. Moreover, the oil industry has intensively studied those geological formations. Another advantage is possibility to perform Enhanced Oil Recovery (EOR). Most of the time deposits still contain large quantities of hydrocarbons that can be recovered by injection of CO₂. This kind of EOR has been implemented in the US for more than 40 years ago [13].

Deep saline aquifers are geological formations containing highly salted water known as brine. These formations are located between 1000 and 3000m under the Earth surface. They are a lot more common than oil and gas reservoirs and have a much greater storage volume. The main downside is the lack of geological knowledge of those structures [13].

The third main option for geological storage is unexploited coal seams. Coal has a natural affinity for absorbing CO₂ in its pores and can absorb twice as much CO₂ as methane, which is naturally find trapped in coal beds. CO₂ can be used to recover methane from the coal bed to be used as energy source. This process is called Enhance Coal-bed Methane Recovery (ECMR). Such method allows to store CO₂ 300 and 800m under the ground [16].

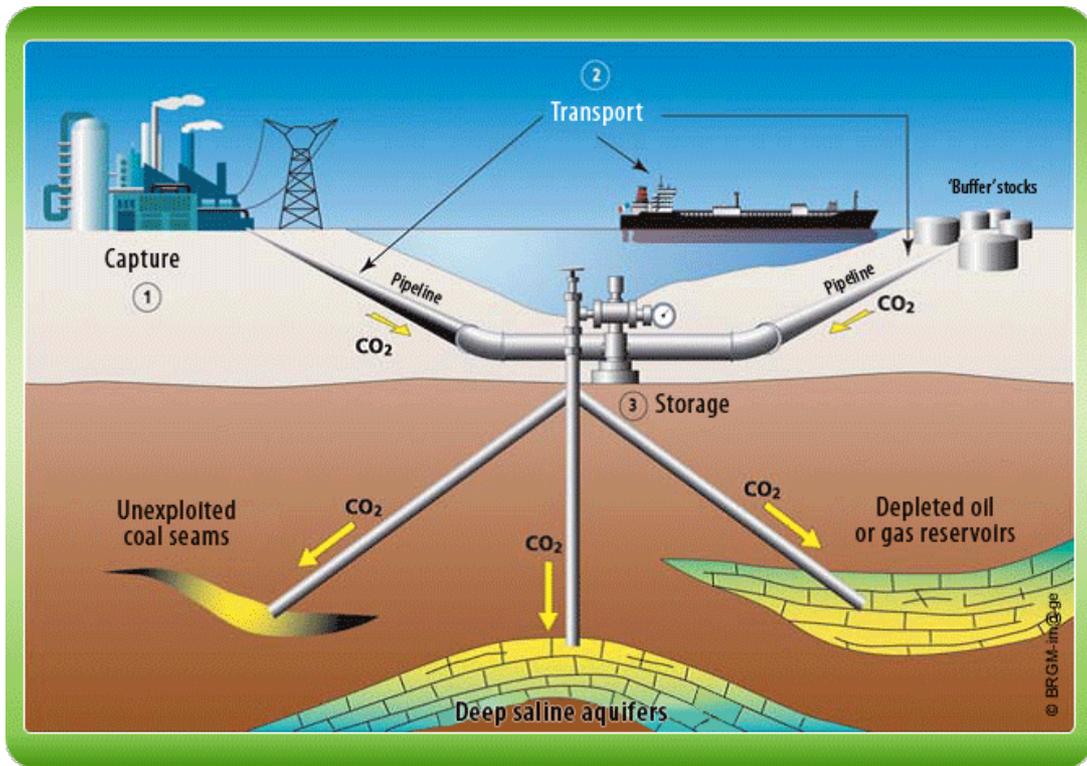


Figure 2.2.1: Three main geological storage options (doc IFP Énergies Nouvelles)

2.2.2.2 Oceanic storage

Oceans could be the other place to store CO₂. They are the largest potential sinks for anthropogenic CO₂. They already contain around 40,000 GtC compared to 2200 GtC captured by terrestrial biosphere and only 750 GtC present in the atmosphere. It is estimated that over a period of 1000 years 80% of current CO₂ emissions will be transferred into the oceans [9]. Ocean storage would accelerate the capture of CO₂ by the oceans. Different methods have been researched. CO₂ can be injected deep under the sea level at around 3km. At that depth CO₂ is denser than water and thus forms CO₂ underwater lake. CO₂ can also be diffused above those depths where it would dissolve into the surrounding waters. Ocean storage is being investigated with regards to feasibility and its potential impact on oceanic fauna and flora.

3 Theory

3.1 Post-combustion

Post-combustion carbon capture is one of the most commonly used processes today due to its ability to be retrofitted into existing plants. MEA is the state-of-the-art solvent used for this process. However, as said previously, there is high energy consumption during its regeneration, which makes researchers look after new alternative solvents. Various performance factors must be taken into consideration when selecting a new solvent: reduced overall energy consumption, high reactivity and capacity with respect to CO₂, low degradation and corrosion. Its impact on environment such as fauna and flora life but also human safety and health must be considered [17].

3.1.1 MEA process

Amine solvents like MEA has been used for several decades to remove acid gases CO₂, SO₂ or H₂S from gaseous mixtures. R.R.Bottoms patented this process in 1930 and the process has not changed a lot since then [18]. The idea of using MEA for capturing CO₂ from flue gases for Enhanced Oil Recovery came in the 1970s. Today, most of the CO₂ retrieved by carbon capture is still used for EOR [19]. The currently operating industrial CO₂ capture plants are based on two main technologies developed during the 1970s and 1980s: the Kerr–McGee/ABB Lummus Crest and Fluor Daniel/ Dow Chemical processes. The first one uses an aqueous MEA solution with 15-20wt% concentration of amine and the second 30wt% amine solution. The Fluor Daniel process has been used in more than 20 plants worldwide [20].

The usual set up of post combustion process using MEA is shown in figure 3.1.1. The process is composed of two main steps: the absorption of CO₂ from the flue gases and the regeneration of the solvent. The flue gases enter an absorption column where they get in contact with an aqueous solution of MEA that absorbs the CO₂. The CO₂ rich solvent is retrieved at the bottom of the absorption column and sent to the regeneration section. The absorption step is enhanced at low temperature and high pressure while the regeneration is favoured at high temperature and low pressure. That is the reason why the rich solvent is heated before entering the regeneration column. The regeneration takes place in a stripper, where the solution is further heated by steam to temperatures between 120-140°C. CO₂ desorbs under the influence of heat and is recovered in gaseous form at the top of the stripper. CO₂ is then compressed and ready to be transported.

This process has several weaknesses. The desorption step is energy consuming, it is responsible for half of the overall process costs. For regular post combustion process the regeneration energy demand is approximately 3,7 GJ/tCO₂ captured. Another weakness is low loading capacity of the MEA. The loading capacity is defined as follows [21]:

$$CO_2 \text{ loading} = \frac{\text{Mole of all } CO_2 \text{ carrying species}}{\text{Mole of all amine carrying species}}$$

CO₂ loading for MEA is around 0.4 for a solution of 30%wt MEA [20]. MEA also undergoes thermal and oxidative degradation [22] that lead to production of unwanted and potentially dangerous substances. The last main problem of using MEA is corrosion [23].

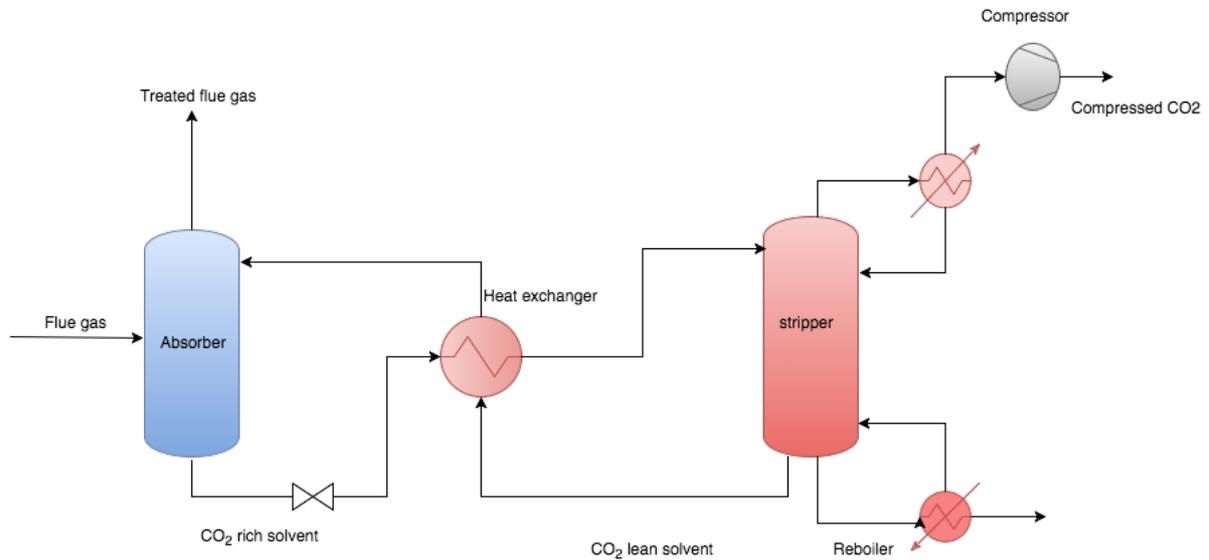


Figure 3.1.1: Usual set up of MEA carbon capture process

3.1.2 Phase-changing solvent processes

For over 10 years now, new, more efficient solvents have been investigated. In the past few years, researchers have highlighted the potential of phase-change solvents. Most of phase-change solvents studied until now are amine solutions. Those solvents undergo a liquid-liquid phase separation upon CO₂ loading. One liquid phase is mainly composed of amines rich in CO₂ and the other mainly aqueous lean in CO₂. Thus, the two phases can be separated and only the CO₂-rich liquid is sent to the stripper. Compared to traditional MEA process the amount of flow going to the stripper is decreased. Moreover, solvent desorption is often easier due to faster desorption kinetic, stripper works at lower temperature and CO₂ loading is bigger. These characteristics result in lower energy consumption for regeneration and a better efficiency regarding the production of CO₂.

Numerous studies have been carried on the absorption and desorption characteristics of new phase-change solvents. Some have been tested in pilot plants with the main objective to decrease the energy requirement of the regeneration step. The main investigated systems and their results are gathered in table 3.1.1. Their set-up is shown in figure 3.1.2 and 3.1.3.

Table 3.1.1: Solvent and results of phase change pilot plants

System	Regeneration requirement
DMX solvents [24]	2,1GJ/tCO ₂
DEEA (5M)/MAPA(2M) [25]	2,4GJ/tCO ₂

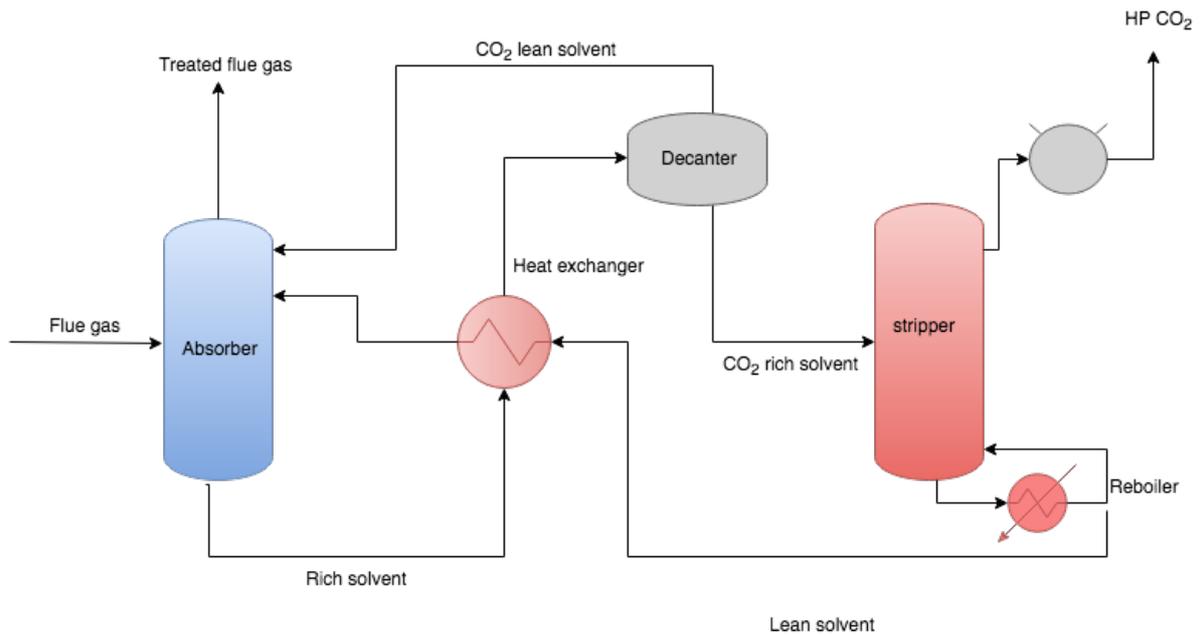


Figure 3.1.2: DMX process set-up

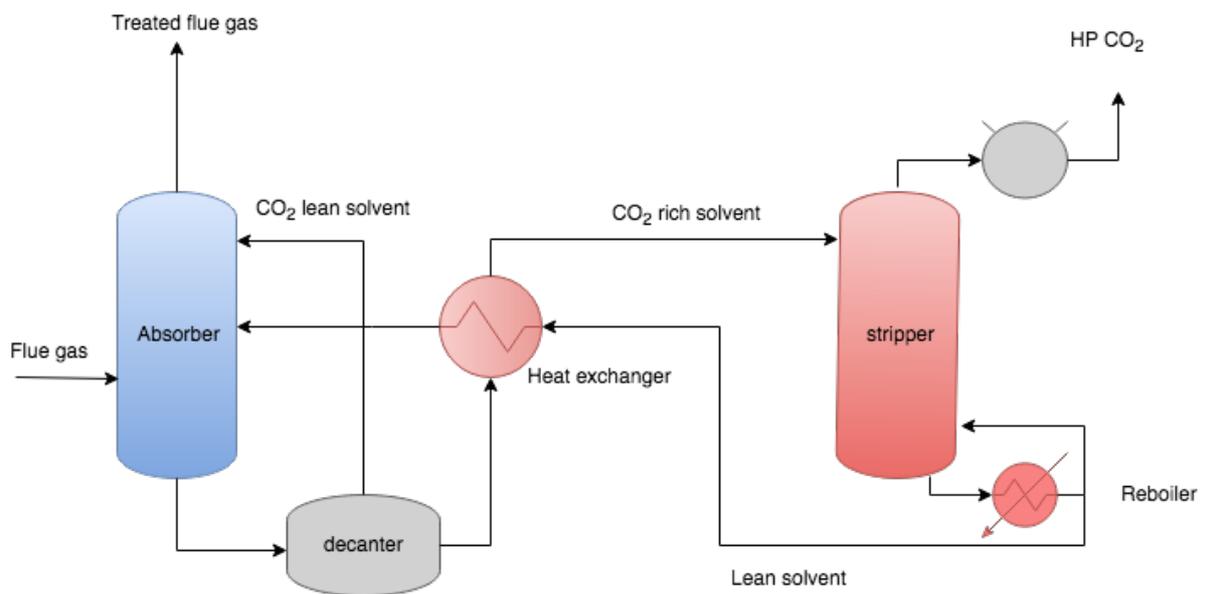


Figure 3.1.3: DEEA/MAPA set-up

3.2 Phase separation temperatures: LCST/LLPS

When choosing a new phase change solvent two temperatures must be looked at: the Lower Critical Separation Temperature (LCST) and the Liquid-Liquid Separation Temperature (LLST). The latter determines if the amine can be used alone in water solution as well as the position of the decanter.

The LCST is the minimum temperature at which a mixture of water and amine undergoes phase separation. At low and close to ambient temperatures, water and amines are most of the time totally miscible. However, with an increase in temperature two liquid phases are formed. Usually, the absorber works at temperatures around 40°C however most of mixture made of a single amine and water have a LCST lower than 20°C for example : for solution at 30wt% in amine, DPA has a LCST of 2°C and EPD of 15°C [17]. Since the regenerated solvent that goes back to the absorber (lean solvent) is almost exempt of CO₂, Phase separation of the lean solvent in the absorber should be avoided since it will affect the contact of the flue gas with the solvent and inhibit absorption. This behaviour might lead to an oversized absorption column. In order to prevent this phase separation, blend amines can be used, as their LCST is usually higher than single amine solution.

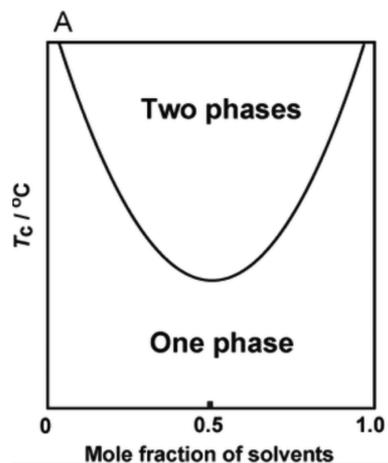


Figure 3.2.1: diagram of usual LCST behaviour

The absorption of CO₂ and production of new species changes the phase behaviour of the systems. The latter can also have LCST behaviour but the corresponding separation temperature is changed due to the presence of CO₂. Phase change PCC processes are based on this property as the system splits into a liquid phase rich in CO₂ and a lean one. The minimum temperature corresponding to this phase separation is called LLPS temperature. Depending on its value, the phase separation unit can be placed just at the absorber outlet, which also means that there would be some phase separation inside the column. If the LLPS temperature is higher than 40°C, the mixture will have to be heated first and so the separation unit is located after the intermediate heat exchanger.

3.3 Solvent degradation

A very important aspect that needs to be taken into account in PCC is solvent degradation. Significant amount of solvent can be lost due to degradation. In MEA process solvent make-up due to degradation accounts for about 10% of the total capture cost. Moreover, degradation products can lead to operational problems such as foaming, fouling or increased rates of corrosion. Substances produced during degradation process are also a source of environmental and safety concerns: some of the molecules are very volatile and have been identified as hazardous. [22]. Thus, degradation products have to be removed or kept at very low concentrations according to occupational health and environmental regulations.

Amine based solvents undergo two main types of degradation: oxidative and thermal. Oxidative degradation occurs in presence of O_2 . It mainly takes place in the absorber column and the intermediate heat exchanger. Metal ions have been found to act as catalysts or inhibitors depending on the type of the ion [26]. Oxidative degradation rate for MEA has been estimated to between 0.29 -0.73 kg of amine per tonne of CO_2 captured [27].

Thermal degradation takes place at high temperatures and usually occurs in the stripper that works between $120^\circ C$ and $150^\circ C$. Thermal degradation is influenced by the concentration of amine and CO_2 loading.

3.4 Life cycle assessment

LCA also known as cradle to grave analysis, is a methodology designed to assess the impacts on human and environment of a product from the raw material production to the disposal or recycling of the product. LCA has been developed in the 1990's and the methodology has been normalised between 1997 and 2000 by the series of ISO standards 14040 to 14043. An LCA study can have two purposes: compare different steps of a product life cycle or compare two competitive products' life cycle. The results help supporting policy choice, running and improving processes or choosing the best possible technology in term of environmental impacts [28].

Around 30 LCA studies of CCS and carbon capture and utilisation (CCU) can be found in literature [10]. They differ by the capture process and the type of power plant considered but also on the way of storing or using the CO_2 . Most of studies assess the environmental impacts of fossil fuel power plant with and without CCS. Post combustion capture (PCC) using MEA is the most studied process. In all LCA studies, system boundaries were coherent and included the extraction and supply of fossil fuel to the power station, power generation, CO_2 capture and compression, transport, injection and storage or use. The only impact considered in all LCA was the Global Warming Potential (GWP), the number of additional impact varied depending on the study. As expected the GWP is lower for plant with CCS in every study, however for other LCA metrics there are wide variations from a study to another.

Thus, so far LCA have mainly been performed on conventional CCS process at industrial or pilot plant scale. The increasing number of studies conducted on phase-changing processes creates the need for new LCA framework adapted to these new systems. Indeed, until today no phase-changing CCS process is operated at industrial scale and very few at pilot plant scale. Moreover a lot of studied solvents are not extensively used in chemical industry. Thus, a number of process parameters such as solvent degradation, emissions or toxicity are not known. The main purpose of this work is to design an LCA framework for phase-change process that takes into account these variables in the form of scenarios. Another goal is to test the framework in a case study of a promising solvent and identify the critical point of the framework uncertainties.

4 Method

This work adapts an existing LCA framework for singlephase solvent based PCC to phase-change PCC. In order to apply the LCA framework some process information has to be known such as the reboiler duty, the consumption of solvent or the volatile emissions. To gather these parameters a process flowsheet was created on Aspen Plus[®] v8.8. The solvent used in the simulation was chosen from a list of promising phase-change solvents identified by partners of the ROLINCAP project [29].

4.1 Solvent selection

Six solvents presenting interesting phase-change properties are presented in the table 4.1 [29].

In order to select a solvent for the process simulation the energy requirement, and phase separation conditions in the absorber and desorption were looked at. It can be seen from the Table 4.1.1 that utilizing solvent blends 1, 2 and 3 results in energy requirement of 2-2.5 GJ per ton of tCO₂ captured. The placement of the intermediate heat exchanger after the decanter indicates that phase separation occurs in the absorber for solvent 3-6. Another beneficial parameter of the solvent is its regeneration temperature. Solvents regenerating at temperatures lower than 100°C are preferable as they enable use of industrial waste heat for the solvent recovery. According to the above-mentioned criteria solvent blend 1 appears to be the most promising solvent.

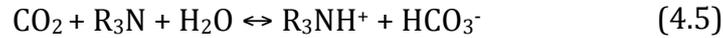
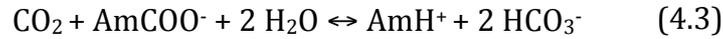
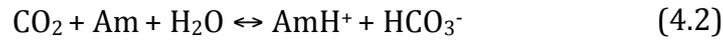
Solvent blend 1 consists of three different amines where DMCA serves as a regenerator promoter, MCA as absorption promoter and AMP as a solubilizer that enables one phase in the absorber. The functionality of each amine is determined by its molecular structure. Primary and secondary amines, like MCA, tend to have better absorption kinetics. The tertiary amines (DMCA) usually demonstrate better regeneration properties. In this work, MCA has been selected as a solvent for the simulation of the process in Aspen due to lack of detailed information with respect to chemical and phase equilibrium of the solvent blend

Table 4.1.1: Solvent identified by the ROLINCAP deliverable 2.1

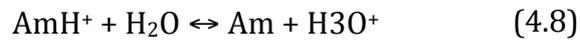
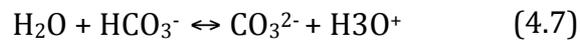
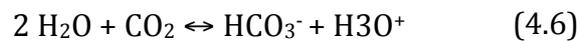
	Solvent mixture	Key performance indicators	Placement of phase separator	Desorption conditions
1	DMCA+MCA+AMP (5.5M, 3:1, 1.5)	Regeneration energy: 2 GJ/tCO ₂	After intermediate HX	60-80°C depending on separation method
2	DMX-1 (blend)	Reboiler duty: 2.5 GJ/tCO ₂	After intermediate HX	Up to 150°C and 5bars
3	DEEA/MAPA (5M, 2M)	2.2-2.4 GJ/tCO ₂	Before intermediate HX	90°C on average or 120°C and P= 6-8 bars
4	BDA/DEEA (2M,4M)	- 46% higher cyclic loading than 5M MEA, - 48% higher cyclic capacity than 5M MEA, - 11% higher cyclic efficiency than 5M MEA.	Before intermediate HX	90°C
5	TETA/DEEA 5mol/kg, 1:4	- 40% higher cyclic loading capacity than MEA, - 15% lower heat of absorption than MEA, - 50% lower sensible heat than MEA, - Stripping heat 30% lower than MEA, - Overall energy requirements 30% lower	Before intermediate HX	80-120°C
6	DETA/Sulfolane/H ₂ O (20wt.%, 40wt.%, 40wt.%,)	- 35% higher cyclic loading than 30wt% MEA	Before intermediate HX	120°C

4.2 Chemistry

The reaction of amines with CO₂ is a complex mechanism that has been extensively studied. Amines can be classified into 3 categories according to the number of substituent of hydrogen atoms: primary for one substituent, secondary for two and tertiary for three. The absorption of CO₂ by primary and secondary amines is assumed to follow three main steps: carbamate formation (4.1), bicarbonate formation (4.2) and carbamate reversion (4.3) [17]. The carbamate formation is the dominant reaction and mainly takes place in a case of amine excess. Bicarbonate formation occurs when there is CO₂ excess. Tertiary amines have a different behaviour and are thought to react with CO₂ according to the reaction (4.6)



It is also possible to present the CO_2 - amines reactions as shown by the equations 4.6 - 4.9 [30].



4.3 Degradation assumption and calculations

The amount of solvent degradation has to be estimated for three main reasons. The degradation can be responsible for a non-negligible part of the solvent loss. So, in order to have an accurate process mass-balance it is necessary to know how much solvent make-up is required due to degradation. The other concerns are that the accumulation of degradation products can cause operating problems and pose a hazard to humans and environment.

As mentioned previously, there are two main types of degradation occurring in PCC: oxidative due to the presence of O_2 in the absorber and thermal due to high temperature in the stripper. In this project a first level of assessment will be done taking into account pseudo-degradation products for both types of degradations. The focus will be on heat stable salts (HSS) and ammonia formation. In real conditions it has been shown that nitrosamines were formed [31],[32]. Nitrosamines are mostly found in the absorber. They are formed because of the presence of NO_x and SO_x in the flue gas. In this work they won't be considered due to lack of quantitative data for their formation from MCA.

4.3.1 Oxidative degradation

According to ROLINCAP deliverable 2.2 [11], the less stable solvents regarding oxidative degradation have the following structural characteristics:

- Amines with only secondary amino group (even cyclic molecules if N is not in the ring)
- Amines with even numbers of carbons between nucleophilic group (especially with only two carbons)

This classification can be found in Appendix 2.

MCA possesses both characteristics, which means that it degrades significantly through oxidative degradation. However its degradation rate is unknown. Zhang [17] showed that it degrades more than MEA for a temperature of 50°C and a gas flow rate made of 98% O₂ and 2% CO₂. In order to estimate MCA degradation rate a solvent that degrades in a similar way and for which oxidative degradation studies have been performed has to be chosen. One solvent that can be classified into both categories mentioned before is N-methylethanolamine: MMEA. Studies have shown that it degrades slightly more than MEA in absorber conditions. It has been decided to approximate MCA degradation rate based on MMEA degradation data. MMEA study conditions are gathered in the Table 4.3.1 and the corresponding results in Appendix 2. Those tables also include Zhang study on MCA oxidative degradation. In all of the studies except for Lepaumier (2011), the same experiment has been performed with MEA in order to compare the performance of the amine of interest.

Table 4.3.1: Results of MMEA and MCA oxidative degradation studies

	Lepaumier et al (2011) [33]	Vevelstad et al (2013) [34]	Liu et al A. (2014) [35]	Zhang B. (2013) [17]
Total amine loss (experiment time)	80% (193h) 81% (311h)	26-32 % (500h)	63 % (263h)	64 % (336 h)
Total MEA loss	6% (200h)	15-19%	78%	21%
Volatile amine loss	≈ 54%	C. -	-	≈ 58%
Amine HSS formation	≈ 27%	0,140 eq/kg solvent	HHS/formate ratio = 5,31 Formate/oxalate ratio = 5,07	≈ 6%
Total percentage of amine loss used further in the calculation	33% HSS 67% volatile compounds	15% HSS 85% volatile compounds	-	-
Ratio Amine / MEA	1,32-2,13		0,81	1,2-3

In order to approximate MCA degradation rate it has been chosen to use the ratio of MMEA% degradation/MEA% degradation for each experiment or MCA% degradation/MEA% degradation for Zhang. This refers to the MMEA to MEA degradation ratio calculated in the same experimental conditions. For Vevelstad and Liu studies this ratio was only calculated with the total loss, which also includes amine volatile losses or volatile degradation product. For Zhang the first value was calculated with the HSS degradation percentage and the second with the total amine loss. It has been proven that when degrading through oxidative degradation amines form ammonia. Studies have also shown that secondary amines are even more likely to produce this product. The calculated ratios can be found in table 4.3.1.

The pilot plant of Nideraußem in Germany identified MEA consumption to be between 0.328 - 0.572 kg_{MEA}/tCO₂ due to volatile degradation product [36]. According to Lepaumier et al. [33] and Vevelstad [34] between 67-85% of MMEA loss during oxidative degradation experiments were due to volatile compounds and thus 33-15%

due to HSS. Those two limit values were assumed for further MCA calculations and sensitivity analysis in the sustainability assessment part.

It is assumed that the volatile losses from the pilot plant occur only due to oxidative degradation, as MEA is not very volatile and thermal degradation forms mainly HSS. Considering the worst-case scenario of the pilot plant: 0.572 kg_{MEA}/tCO₂ loss through volatile oxidative degradation product, HSS would represent between 0.10-0.28 kg_{MEA}/tCO₂ loss. In total it would represent a loss between: 0.672-0.852 kg_{MEA}/tCO₂. For the best-case scenario: 0.32kg_{MEA}/tCO₂ loss through volatile oxidative degradation product, the total loss would be in the range 0.06 - 0.15 kg_{MEA}/tCO₂ captured. Goff et Rochelle showed that theoretically the total amount of MEA losses due to oxidative degradation was between 0.29 – 0.73 kg_{MEA}/tCO₂ captured [37]. The value found with our assumptions and calculations result in a range 0.06-0.85 kg_{MEA}/tCO₂.

Nideraußem pilot plant used a 3M MEA solvent flow rate of 4025 kg/h for 300 kgCO₂captured/h, which gives a total amount of 13,416 kg_{solvent}/tCO₂captured. Thus, between 0.672-0.852 kg_{MEA}/tCO₂ were lost through oxidative degradation for a needed solvent flow of 13,416 kg/tCO₂. The approximated rate for MCA oxidative degradation was calculated as follows:

$$D_{MCA}^{Ox} \left(\frac{kg_{MCA}}{tCO_2} \right) = R_{MCA/MEA}^{Ox} \times D_{MEA,pp}^{Ox} \left(\frac{kg_{MEA}}{tCO_2} \right) \times F_{MCA\ needed, sim} \left(\frac{kg_{MCA}}{tCO_2} \right) \times \frac{1}{F_{MEA\ needed, pp} \left(\frac{kg_{MEA}}{tCO_2} \right)}$$

With:

$D_{MCA}^{Ox} \left(\frac{kg_{MCA}}{tCO_2} \right)$: Oxidative degradation rate of MCA

$D_{MEA,pp}^{Ox} \left(\frac{kg_{MEA}}{tCO_2} \right)$: Oxidative degradation rate of MEA in the pilot plant

$F_{MEA\ needed, pp} \left(\frac{kg_{MEA}}{tCO_2} \right)$: Flow of MEA solvent in the pilot plant per tCO₂

$F_{MCA\ needed, sim} \left(\frac{kg_{MCA}}{tCO_2} \right)$: Flow of MCA solvent in Aspen simulation per tCO₂

$R_{MCA/MEA}^{Ox}$: Oxidative degradation ratio of MCA/MEA

$R_{MCA/MEA}^{Ox}$ range was between 1.2 and 3 according to table 4.3.2. Results from Liu were excluded, as it has been showed in several other studies and at experimental conditions more similar to ours that MMEA degrades more than MEA.

Once the equivalent MCA degradation rate was calculated the composition of the volatile losses had to be decided. The volatile degradation products were not identified in any of the studies used before. However, as mentioned previously ammonia is a known product of amine degradation. Additionally, MCA is more volatile than MEA and MMEA. Thus, it was assumed that the volatile losses are 50% NH₃ and 50% MCA. Moreover, MCA also degrades in HSS. Zhang identified cyclohexanone oxime as the main HSS

formed. For simplification it will be considered that cyclohexanone oxime is the only HSS form during degradation, oxidative as well as thermal. As the degradation chemical reactions are unknown the conservation of mass was used to approximate the formation of degradation product. Thus for 1kg of MEA degraded 1kg of degradation product has to be formed.

4.3.2 Thermal degradation

For thermal degradation MCA and MMEA are not in the same stability class identified by ROLINCAP deliverable 2.2. MMEA is in the low stability group as it is a secondary linear amine and MCA in the medium class due to its cyclic structure. The summary of the different stability classes can be found in Appendix 2. However, in this study, MMEA degradation rate is still used to approximate MCA's as no other amine was found to be in the same class as MCA. MMEA thermal degradation rate can be considered as MCA upper limit degradation rate.

Similarly to the case of oxidative degradation, a ratio between MMEA and MEA degradation rate was calculated using various experimental data. The latter can be found in figure 4.3.2. Thermal degradation depends on CO₂ loading; the ones used in experiments do not correspond to the one of the simulation. In order to solve this problem the results of the different experiments were extrapolated for MEA and MMEA for higher loading. According to Eide-Haugmo [38] and Velvestad [34] the loading of the amine considerably affects the thermal degradation rate. 6-9 % increase of degradation per 0.1 molCO₂/mol increase in amine loading has been reported for MEA and 7% for MMEA.

Once the degradation was estimated for the simulation loading, the ratio %MMEA degradation /%MEA degradation for thermal degradation could be calculated. Using the extrapolations presented previously a ratio $R_{MMEA/MEA}^{th}$ in the range 1.48 - 1.61 is obtained for a loading of 0.6. MEA thermal degradation rate at typical industrial conditions has not been reliably quantified. In MEA base case simulation a rate of 0.019 kg_{MEA}/tCO₂ captured was incorporated [39]. This value, also chosen by Badr, is taken for the degradation rate of the Nideraußem pilot plant. MCA thermal degradation rate is thus calculated by the following formula:

$$D_{MCA}^{Th} \left(\frac{kg_{MCA}}{t_{CO_2}} \right) = 0.019 \left(\frac{kg_{MEA}}{t_{CO_2}} \right) \times R_{MMEA/MEA}^{th} \times F_{MCA \text{ needed, sim}} \left(\frac{kg_{MC}}{t_{CO_2}} \right) \times \frac{1}{F_{MMEA \text{ needed, pp}} \left(\frac{kg_{MMEA}}{t_{CO_2}} \right)}$$

With:

$$D_{MCA}^{Th} \left(\frac{kg_{MCA}}{t_{CO_2}} \right): \text{Thermal degradation rate of MCA}$$

$$F_{MMEA \text{ needed, pp}} \left(\frac{kg_{MMEA}}{t_{CO_2}} \right): \text{Flow of MEA solvent in the pilot plant per tCO}_2$$

$$F_{MCA \text{ needed, sim}} \left(\frac{kg_{MCA}}{t_{CO_2}} \right): \text{Flow of MCA solvent in Aspen simulation per tCO}_2$$

$R_{MCA/MEA}^{Th}$: Thermal degradation ratio of MCA/MEA

When taking under consideration the assumptions mentioned before, MCA thermal degradation rate lies within 0.034 – 0.037 kg_{MCA}/tCO₂. The same way as for oxidative degradation the degradation reactions are unknown and the conservation of mass is also used to approximate the quantity of HSS formed.

Table 4.3.2: MEA, MMEA and MCA thermal degradation experiment and calculated degradation ratio amine/MEA.

	D. Zhang (2013) E. [17]	F. Vevelstad et all (2013) G. [34]	H. <i>Ingvild Eide-Haugmo</i> (2011) I. [38]	J. <i>Lepaumier</i> (2009) K. [40]
L. Amine	M. MEA/MCA	N. MEA/MMEA	O. MEA/MMEA	P. MEA/MMEA
Q. Reactor / Time	R. Open / 6 weeks		S. Open / 5 weeks	T. 2 weeks
U. Loading	V. 10ml CO2 saturated amine solution	W. 0,42*2 + 0,44 X. 0,4 (MMEA)	Y. MEA: 0,4/0,5 Z. MMEA: 0,5	AA. CO2 partial pressure: 2MPa
BB. Temperature	CC. 120°C	DD. 135°C	EE. 135°C	FF. 140°C
GG. Amine loss	HH. 6%	II. 89%	JJ. 96%	KK. 89%
LL. MEA loss	MM. 4%	NN. 51/56/50 %	OO. 45% / 56%	PP. 42%
QQ. Ratio Amine/MEA RR. at experimenta	SS. 1,5	TT. 1,74/1,6	UU. 1,71 (for 0,5 loading)	VV. 2,11

l loading				
WW. Other			XX. Almost all deg products = HHS	

4.3.3 Degradation rate summary

For further calculations two degradations scenario are considered, their characteristics are gathered in table 4.3.3

Table 4.3.3: Degradation scenarios characteristics.

	Worst scenario	Best scenario
HSS %	33	15
$R_{MCA/MEA}^{Ox}$	3	1.2
$R_{MCA/MEA}^{Th}$	1.61	1.48
Volatile losses composition	50% NH ₃ / 50% MCA	50% NH ₃ / 50% MCA
Total degradation rate (kgMCA/tCO ₂)	1.716	0.330
Oxidative degradation rate (kgMCA/tCO ₂)	1.679	0.296
Thermal degradation rate (kgMCA/tCO ₂)	0.037	0.034

4.3.4 Aerosols formation

In addition to emissions due to solvent volatility it has been shown that aerosols were formed in the absorber. They can represent a major source of emissions from capture plants and studies have shown that aerosols can increase emissions by 1-2 orders of magnitude if left uncontrolled [41]. In addition to solvent loss, aerosols could be an environmental concern as a source of exposure to amines and more hazardous degradation products such as nitrosamines. Aerosols are formed due to particles and SO₃ in the flue gas which can act as nuclei for mist formation. Recent studies at pilot plant scales show that using a multiple stage washing section can successfully reduce aerosol emissions to acceptable levels [42] while traditional water wash sections are efficient to reduce gaseous solvent emissions but they are inefficient for the management of aerosol [43].

Even though aerosols are not volatile emissions and cannot in real condition be handled as such, for simulation and simplification reasons aerosols will be considered as an increase in volatile loss in this work. In order to take into account that a multiple stage

wash section should be used, it is considered that aerosols could increase the emissions by 2 to 3 orders of magnitude.

4.4 Simulation

The simulation was performed on Aspen Plus v8.8. The purpose of this simulation was to create a reference flow sheet for phase-change processes to further apply the LCA framework. Thus, the optimisation of the flow sheet was not a part of this work; instead, a working base case simulation was the target of this work, considering also published data from pilot plant and/or lab scale experiments.. The detailed modelling methodology is presented in Appendix 1.

4.4.1 Flow-sheet layout

The final process flow sheet can be found in figure 4.4.1. The flue gas enters the absorber at the bottom stage while the lean solvent solution is fed at the top stage. This configuration has been used in various pilot plants [25],[44]. The flue gas compositions and properties are the same as the one in the CAPSOL project [45] and were used by (2016) for the development of her sustainability framework. The flue gas composition and properties comes from the coal-fired Esbjerg power plant operated by Dong energy in Denmark. They are gathered in table 4.4.1.

Table 4.4.1: Flue gas properties.

	Flue gas	
Temperature (°C)	48	
Pressure (kPa)	106	
Flow rate (m ³ /h)	5011	
Composition	CO ₂	11.94 vol%
	H ₂ O	11.25 vol%
	N ₂	71.62 vol%
	O ₂	3.81 vol%

The liquid loaded in CO₂ (rich solvent solution) goes off at the bottom of the absorber; it is pumped up to 2 bars and then heated to the LLPS temperature. As mentioned before MCA LLPS temperature is around 90°C. At this temperature more than 50% of the loaded CO₂ is supposed to be desorbed [17]. However, in our simulation as the kinetic and the thermodynamic properties could not be fitted from experimental values, the loaded solution shows a slightly different behaviour. For that reason, the rich CO₂ liquid is only heated up to 80°C to have phase separation. Moreover in the simulation barely no CO₂ is desorbed at 80°C. During this step a gas phase is formed and needs to be removed. Thus, a flash separation vessel working at 2 bars is placed after the heat exchanger. This gaseous flow still contains a non-negligible amount of MCA and thus has to be washed to reduce MCA concentration at emissions limits. So the flow coming from the top of the

flash is mixed with the gaseous flow at the top of the absorber. The final flow is then sent to a washing section.

The decanter is set to work adiabatically and at 2 bars. As explained in the detailed simulation methodology in Appendix 1, the property model of the decanter is changed from ELECNRTL to UNIF-LL and the chemistry removed. The rich amine flow is sent to the top of the stripper. The column requires a reboiler in order to produce heat to desorb the loaded CO_2 and regenerate the amine solvent. At the top of the stripper a cooler is placed to act as a partial condenser. Once cooled, the rich CO_2 gas goes into an adiabatic flash working at 2 bars. The recovered condensed liquid flow is sent back at the top stage of the stripper while the 98% CO_2 gaseous stream is ready to be compressed and transported.

At the bottom of the stripper a heat exchanger is placed to cool down the regenerated solvent after which a fictive purge is added. The role of this purge is removing the degradation products that would be formed in an actual industrial plant. As a first approximation the split fraction of the purge going to treatment is taken equal to the one found in Badr's works. Then the remaining flow has to mix with the rich water flow coming from the decanter. However, if the two flows were directly mixed, the amount of water would be greater than the flow going into the absorber. The excessive amount of water is due to the water coming from the flue gas as well as the relatively small water loss in the purge and at the top of the absorber. A splitter was added after the decanter in order to solve this problem. Finally, the mixed flow is cooled down and a pure MCA stream make-up is added in order to compensate the losses due to volatility, the purge and the slip after the decanter.

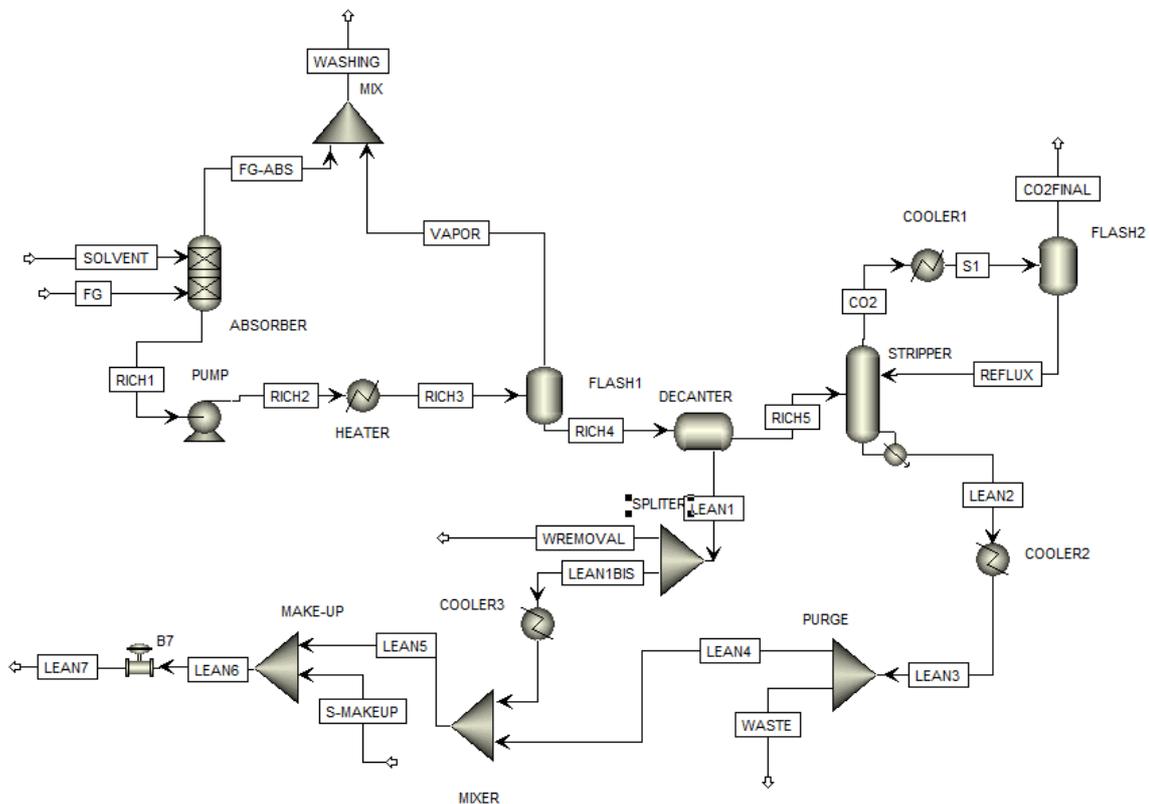


Figure 4.4.1: Final process layout.

4.4.2 Washing section

The flue gas going out of the absorber and the emissions coming from the flash before the decanter still contain concentration of solvent higher than the ones considered as safe for workers. Moreover, according to the degradation assumptions, the flue gas at the top of the absorber contains ammonia. Thus, it appears necessary to wash the flue gas so that MCA and NH_3 concentrations remain under the ones acceptable for worker safety. Threshold Limit Value documented by the American Conference of Governmental Industrial Hygienist in 2014 was used as reference value in this work. TLV values can either be given as TWA: time weighed average or STEL: short-term limit exposure usually in ppm. Generally, TWA is more restrictive than STEL and will be used in this work. As the TLV for MCA was not available, values for other amines were gathered together with those of NH_3 in Table 4.4.2. Based on these values, it is chosen to perform the simulation for two different TLV values for MCA, 5 and 3 ppm.

Table 4.4.2: Amines and Ammonia TLV

	TWA (ppm)
MEA	3
Methylamine	5
Dimethylamine	5
Diethylamine	5
Cyclohexylamine	10
NH_3	25

Two different configurations were evaluated. The objectives were to minimize the amount of wash water needed and if possible recover the maximum solvent lost by volatility. The total flow of solvent at the top of the absorber and the flash previous to the decanter is of 87.8 kg/h, which if not recovered represents a solvent loss of 1%/h of the recycling solvent.

As a first modelling the washing section was simulated on a different Aspen file. Two streams with the composition of the flue gas at the top of the absorber and from the flash previous to the decanter were created. The amount of NH_3 produced by oxidative degradation and MCA emissions due to volatility and aerosols formation were added to the flow coming from the absorber. The first configuration is made of a cooler and a washing unit that is simulated as a flash in which fresh water is added. The two gas flows are mixed, cooled to 25°C and finally sent to the washer. In the second set-up a flash vessel was added between the cooler and the washing section. This way, the part of the flow that condensed in the cooler is separated and only the remaining gas flow is sent to washing. The two layouts are presented in figures 4.4.2 and 4.4.5-3

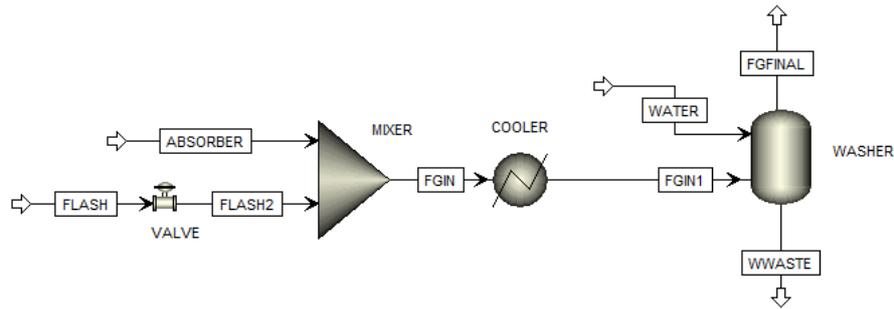


Figure 4.4.2: Washing section, layout 1.

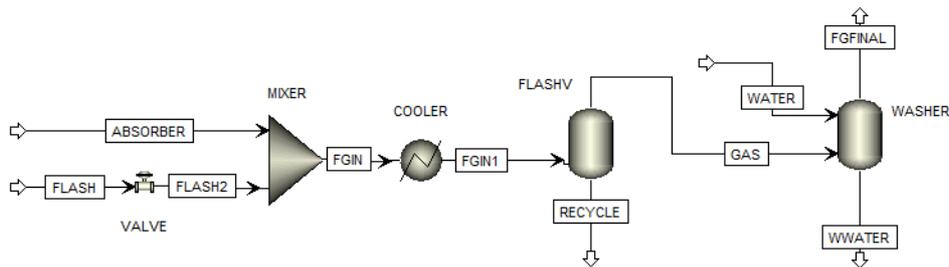


Figure 4.4.3: Washing section, layout 2.

With the first configuration a washing water flow of around 1600 l/min is needed to achieve a target of 3ppm of MCA in the final flue gas. To lose the minimum solvent the washing water should be sent back to the absorber. However, the ensuing flow of water has a MCA concentration of only 0.9kg/m³, which is really low. It is not possible to recycle this amount of water without diluting the solvent and totally changing its inlet concentration. The second layout gives a water flow around 300 l/min, 5.3 times less than with the previous simulation. Moreover, the condensed stream recovered from the first flash holds 85kg/h of MCA representing 97% of the volatile loss and the water present is approximately equal to the water originally coming from the flue gas. Thus, there is no problem recycling this stream as it is not an addition of extra water.

Considering these results the second configuration was chosen for further simulation and calculations. The washing section was then implemented on the main flow sheet. In real conditions a serie of multiple flashes would be implemented but only one was used in the simulation as an additional simplification. First, only the washing of the volatile losses were considered without adding the degradation products to have a comparative basis. As a simulation improvement the condensed flow was sent back to the absorber. Under these conditions a fresh water flow of 235 l/min was needed. The value is different from the first try because this time the flow sheet includes the chemistry. This configuration was kept and the gaseous stream consisting of the absorber and flash top was duplicated in order to add the volatile degradation products and aerosols produced in the absorber. Thus, it was assumed that the recycle with and without degradation product was the same. The final washing section layout is presented in figure 4.4.4.

thermal reclaimer with a 5% loss of solvent and the assumption of Sexton et al. [47] to keep the HSS concentration at 1.5wt%.

The external mass balance was performed as follow:

The amount of degraded MCA was removed at the bottom of the stripper. Zhang identified the main HSS from oxidative degradation of MCA to be cyclohexanone oxime. All other products detected for oxidative as well as thermal degradation were liquid at process conditions. Thus, as it was assumed that thermal degradation only forms HSS, the calculations were performed with cyclohexanone oxime as the only HSS formed during both degradation processes. All the ammonia is assumed to form in the absorber and leave at its top.

The rest of the mass balance was calculated assuming that the rate of HSS going to the waste treatment plant was the same as the rate of formation. Thus, the same amount has to go to the reclaimer. To do so the mass fraction of the stream entering the reclaimer was adjusted to have the mass fraction of HSS in the rest of the system equal to 1.5wt%. Finally make-up solvent was added to compensate the losses due to volatility, solvent degradation and the 5% loss of the reclaimer.

4.5 Life cycle Assessment

The LCA framework consists of the four well-known distinct phases according to ISO 14040 and 14044: goal and scope definition, inventory analysis, impact assessment and interpretation of results. The previous LCA performed on CCS mentioned before considered all the stage from the extraction and the burning of the fuel in power plant to the storage of carbon dioxide. In this work the system boundaries for the LCA comprise only the CO₂ capture process. The LCA framework is based on the work of the on-going H2020-ROLINCAP project [48].

4.5.1 Scope

The goal and scope of LCA in this framework is to evaluate the cradle-to-gate impact from capturing 1 tonne (t) of CO₂ by phase-change solvent-based capture systems. Contrary to the traditional cradle-to-grave assessment, a cradle-to-gate approach only considers the steps from the extraction of the resource to the factory gate. It does not take into consideration the use of the product and its disposal.

In this case, the functional unit is defined as 1 tonne of 90% captured CO₂ from process gas streams (e.g., post combustion flue gases), with 98% molar purity and at a pressure of 2 bars. The “cradle-to-gate” system boundary is presented in figure 4.5.1. It includes the impacts from solvent, chemical auxiliaries and energy utilities production, the process emissions from the CO₂ capture system, the solvent reclaimer and waste treatment units for processing purge streams from the CO₂ capture process and the water used to wash the volatile gas emissions.

The LCA framework does not include the energy consumption associated with bringing the flue gas to the CO₂ capture process gate. Additionally, it does not take under

consideration the CO₂ compression for storage or utilization purposes. The reason is that these aspects are not solvent or process dependent. The impacts of the plant construction phase, equipment replacement, corrosion and corrosion inhibiting materials are not included either. All the relevant aspects to LCA are presented in table 4.5.1.

Table 4.5.1: Relevant aspect for LCA calculation and their source

Aspects relevant to LCA	Aspects included to the analysis	Calculation method
Make-up of the solvent	1	External material balance combined with scenarios
Reclaimer loss	2	Literature data
Waste water composition	3	Waste treatment models
Reboiler duty	4	Aspen simulation
Energy consumption by pumps	5 a,b	Aspen simulation
Cooling water	6 a,b	Aspen simulation
Loss of the solvent due to degradation	7 a,b	Scenario analysis
Loss of the solvent due to volatility	8	Aspen simulation
Loss of the solvent due to aerosol formation	9	Scenario analysis

Washing water	10	Aspen simulation
Volatile emissions	11	Scenarios analysis

Three LCA metrics are considered in this framework: Cumulative Energy Demand (CED), Global Warming Potential (GWP) and the aggregated indicator ReCiPe (Hierarchist, Approach).

The CED given in MJ-eq is total energy consumed over the whole life cycle in delivering the functional unit [49]. It considers the direct and indirect energy use throughout the life cycle of a product, including the energy consumed during the extraction, manufacturing and disposal of the raw and auxiliary materials. The total CED is composed of the fossil CED e.g, coal, natural gas, oil and the CED of nuclear and renewable energy in the life cycle [50].

GWP, also referred as Carbon Footprint, is a category that reflects climate change impact over a fixed period of time, normally 100 years, in terms of total emissions of greenhouse gases such as CO₂ and other CO₂ equivalents, including methane and nitrous oxide to air across the life cycle of a product used to deliver a functional unit [49]. For CCS, the GWP is also a measure of the process efficiency as CCS is meant to reduce CO₂ release.

ReCiPe is a method for LCIA that aggregates various environmental LCA indicators. The latter are regrouped in two main categories: the midpoints indicators and the end points indicators. Midpoint indicators focus on single environmental problems, such as acidification or ozone depletion. Endpoint indicators show the environmental impact on three higher aggregation levels: effect on human health, biodiversity and resource scarcity. The ReCiPe metric calculates 18 midpoints and 3 endpoints. It converts midpoints to endpoints in order to simplify LCIA interpretation.

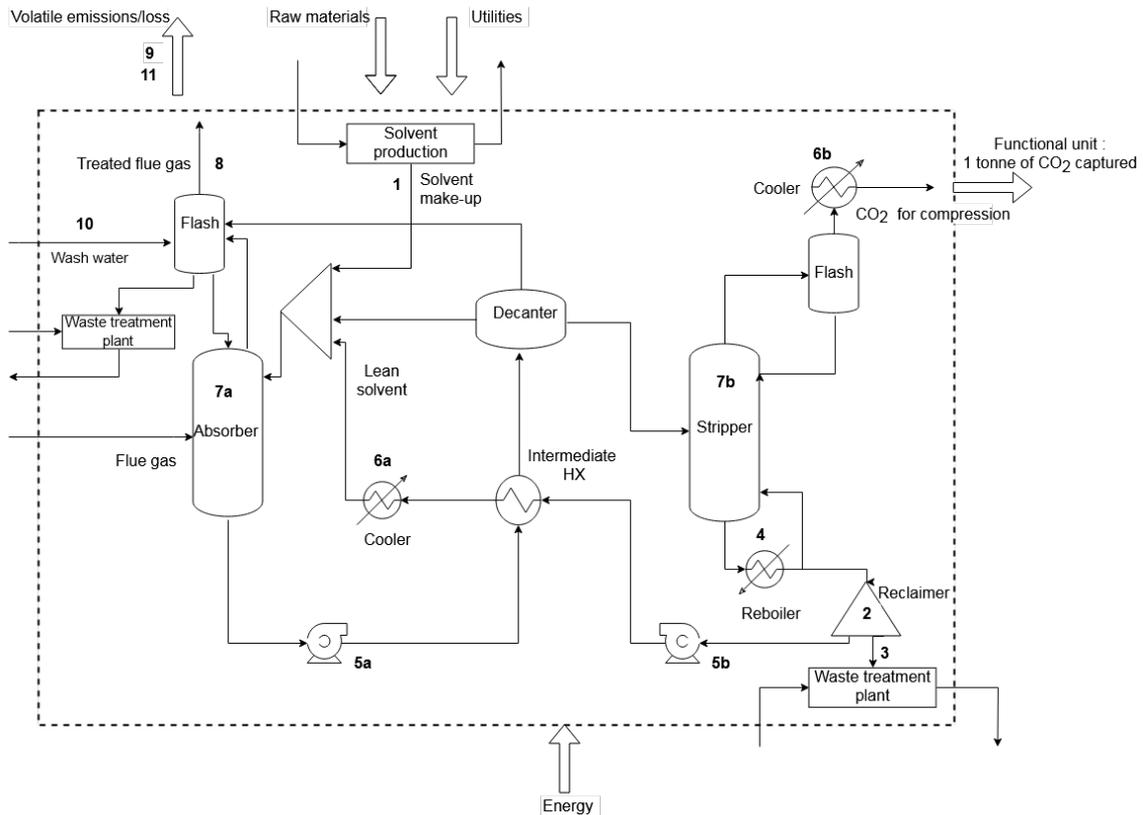


Figure 4.5.1: Simplified process flow sheet and LCA boundaries

4.5.2 Inventory

The inventory gathers all the material and energy flow entering and outgoing of the process needed to perform LCIA. Six main classes can be identified: heating duty, electricity, solvent make-up, washing water, effluent flow and composition, neutralizing agent flow. All those data are either directly retrieved from the Aspen simulation or the external mass balance and combined with literature data, as presented in table 4.5.2.

Table 4.5.2: Inventory data.

Classes	Units	Origin
Heating duty: <ul style="list-style-type: none"> - Reboiler - Reclaimer - Intermediate HX 	MJ/tCO ₂	Simulation Literature data ¹ [47]
Electricity: <ul style="list-style-type: none"> - Pumps - Cooling water (pumping from river) 	MJ/tCO ₂	Simulation Literature model and assumption ² [51]

Solvent make-up	kg/ tCO ₂	Simulation + external mass balance
Washing-water	kg/ tCO ₂	Simulation + external mass balance
Effluent flow and composition	m ³ /tCO ₂	Simulation + external mass balance
Neutralizing agent (reclaimer)	kg/tCO ₂	Literature data ¹ [47]

¹ As mentioned in section 4.4.3 it was chosen to use a thermal reclaimer. This kind of reclaimer necessitates heat and sodium hydroxide (NaOH) in order to neutralize the HSS. The two values taken are the ones found for the MEA reclaiming process: 10.5 kWh/ kgHSS and 1mol NaOH/mol HSS.

² On Aspen the heat exchanger load to cool down the process flow to desired temperature is calculated. Thank to a convertor this duty was traduce in mass flow assuming a temperature delta for the cooling water of 10°C. Cooling water is considered to be river water, thus the only data needed is the energy necessary to pump it from the river. To do so it has been decided to increase the water flow pressure from one to two bars to have an equivalent pumping duty.

Once the process inventories are known, they can be translated into life cycle impact assessment metrics based on background data from databases. Most of the impacts come from the Ecoinvent v3.4 database. For heating demand a CHP plant based on coal was chosen as the flue gas is considered to come from a coal-fired power plant. The values used are the ones for Swedish CHP plants. To be consistent with this choice the Swedish electricity mix value is taken for the calculations. The values for CED, GWP and EI99 for the solvent production are estimated through the FineChem tool. The indicator EI99 is then converted in ReCiPe point thank to the formula given by Dieterich [52].

$$t_{ReCiPe} = 1.2862 \cdot t_{EI99} + 0.0285$$

Washing water and reclaimer wasteare assumed to be treated in typical industrial waste treatment plants and impacts are calculated according to such methodology for the mechanical and biological treatment of wastewater and waste incineration [53],[54].. As the flow coming from the reclaimer is mostly made of MCA, it was decided to use the incineration model while the waste water model is applied to the wash water. The version of the waste treatment model uses some value coming from Ecoinvent v2.2; more over it mainly uses average EU or Swiss related data. Thus, not all Ecoinvent data used for impact calculations come from the same database version and countries. As mentioned before, Ecoinvent v3.4 was chosen for the other metrics values, as they are the most recent ones.

Table 4.5.3: Values of the considered LCA metrics for the different commodities needed.

Impact category	Functional unit	CED (MJ-eq)	GWP (kgCO ₂ -eq)	ReCiPe (Point)
Electricity medium voltage, Sweden ¹	MJ	2.38	0.01	0.0011
Heat, CHP coal,	MJ	0.66	0.019	0.0054

Sweden ¹				
Washing water ¹	kg	0.022	0.016	0.0002
Solvent ²	kg	94.37	3.19	0.36
NaOH ¹	kg	19.82	1.35	0.14

¹ retrieved from Ecoinvent v3.4

² Estimated by the FineChem tool

4.5.3 Scenarios

Various assumptions have been made over the degradation rates, the amine emissions threshold and the formation of aerosols. These parameters can vary widely and have important impacts on LCA. In order to estimate their influence, five LCA scenarios were established. First a base case scenario was designed based on worst-case degradation rate (0.572 kg_{MEA}/tCO₂, 33% HSS, maximum R_{MMEA/MCA}), an amine threshold emission of 3ppm and no aerosol formation. Then for each remaining scenario one parameter was changed: best-case degradation rate (0.32 kg_{MEA}/tCO₂, 15% HSS, minimum R_{MMEA/MCA}), amine threshold emission of 5ppm and aerosol formation increasing 2 or 3 time the volatile losses. The parameters of each scenario can be found in table 4.5.4. The result of the process inventories for each scenario is presented in Appendix 3.

Table 4.5.4: Scenarios parameters

	Degradation	MCA threshold emission	Aerosols
Base case	Worst	3ppm	None
Scenario 1	Worst	5ppm	None
Scenario 2	Best	3ppm	None
Scenario 3	Best	5ppm	None
Scenario 4	Worst	3ppm	× 2
Scenario 5	Worst	3ppm	× 3

5 Results and discussion

5.1 Simulation results

The main simulation results are gathered in table 5.1.1. They are compared to the results of two MEA simulations: one obtained by Badr (2016) for the treatment of the same flue gases with a MEA solution at 3M [27] and one from Gardarsdóttir (2015)[55]. Gardarsdóttir simulation uses a 30wt% MEA solution and the flue gases had the following composition N₂: 76.5%, CO₂: 11.9, O₂: 7.3 and H₂O: 4.3% in molar percentages. In MCA simulation the number of stages of the absorber is lower than the one for MEA. This is consistent with the fact that MCA has been identified to have a fast absorption kinetic [17].

According to Zhang the mixture made of MCA/DMCA/AMP with MCA as the principal component should have regeneration energy around 2.5 GJ/tCO₂. Thus, in a not optimized system using only MCA its energy should be greater. In the simulation the total energy needed is 2.59 GJ/tCO₂, which is close to Zhang result [17]. Nevertheless in Zhang work the regeneration energy only represents the energy used in the stripper. In this simulation the heat contained in the bottom stripper flow is not enough to heat the flow exiting the absorber to 80°C. Thus, in our simulation the total amount of energy needed is close to the literature value but not its distribution in the process. Those results could be explained by different factors.

First the equilibrium constant of the overall reaction may not be accurate, as it does not come from experimental data. Its value is probably lower than the real constant and thus favours desorption more than absorption, which is consistent with the lower desorption energy required. Moreover, studies have shown that at same concentration in amine MCA solution should have a greater rich loading than MEA. This is not the case when we compare our results and MEA simulation results. Jeon et al have a rich loading of 0.46 for a 3M MCA emulsion while the simulation gives a lower loadings of 0.34. The lean loading is however similar 0.08 for Jeon and 0.04 in the simulation [56]. A lower equilibrium constant than expected favouring the desorption rather than absorption would explain a lower reboiler duty, lower loading and thus, the need for more solvent than MEA process for 1 ton of CO₂ captured.

Another source of uncertainty in the energy requirement distribution can be the amount of water in the organic phase leaving the decanter. Indeed, the decanter model was first validated for ELECNRTL model with a solution of water and MCA but not with the system water/MCA/CO₂ as no experimental data were available. Moreover, for simulation convergence reasons, the decanter property model was changed. Thus, it is possible that the decanter does not model the phase separation accurately. The stream going in the stripper could in reality contained more water which would increase the reboiler duty. Additionally, the stripper bottom flow would be bigger and have a greater calorific value since water has a greater calorific value than MCA. It would increase its energy capacity and thus decrease the need for external heat in the cross heat exchanger.

Finally, in the simulation the absorption reaction appears to be endothermic see appendix 4 whereas experiments show that the reaction should be exothermic. This is maybe due to the fact that MCA ions had to be modelled as molecules to have the decanter working properly. This endothermic reaction leads to a temperature lower than it should be at the absorber bottom and thus increases the energy need in the cross heat exchanger.

Table 5.1.1: Main MCA and MEA simulation results

	MCA simulation	MEA simulation (Badr)	MEA simulation (Gardarsdóttir)
Absorber			
Stages	7	17	20
Temperature at absorber top (°C)	42.5	63	63
Temperature at absorber bottom (°C)	31	50	41
Bottom absorber flow rate (kg/tCO ₂)	32,270	16,660	19,985
Loading bottom (mol CO ₂ /mol amine)	0.34	0.39	0.54
Intermediate HX			
Inlet temperature of process flow (°C)	31	50	41
Outlet temperature of process flow (°C)	80	108	106
Total duty (GJ/tCO ₂)	6.10	3.94	4.96
Recoverable duty (GJ/tCO ₂) (bottom stripper + decanter flows)	3.76	5.14	5.32
Needed for external heat (GJ/tCO ₂)	2.34	0	0
Decanter			
Lean outlet flow (kg/h)	20,740	-	-
Water mass fraction (%)	99.1		
Outlet temperature (°C)	72	-	-
Stripper			
Number of stages	8	13	20
Temperature at stripper top (°C)	92	110	101
Temperature at stripper bottom (°C)	105	122	121
Inlet flow (kg/t/CO ₂)	10,310	16,660	19,985
Reboiler duty (GJ/tCO ₂)	0.25	4.5	3.66
Lean Loading (mol CO ₂ /mol amine)	0.04	0.15	0.27
Bottom flow (kg/tCO ₂)	9,332	16,020	19,000
Total heating duty needed (GJ/tCO₂)	2.59	4.50	3.66

5.2 LCIA and Interpretation

LCIA has been conducted for the six scenarios described in part 4.5.3 and took into account the CED, GWP and ReCiPe metrics. The relative impact of each commodity and scenarios on LCA scores are shown in charts 5.2-1 to 5.2-3. It can be seen that each commodity has a variable weight for each metric and that the heating proportion does not change as the different scenarios do not affect the heating duty needed in the overall process.

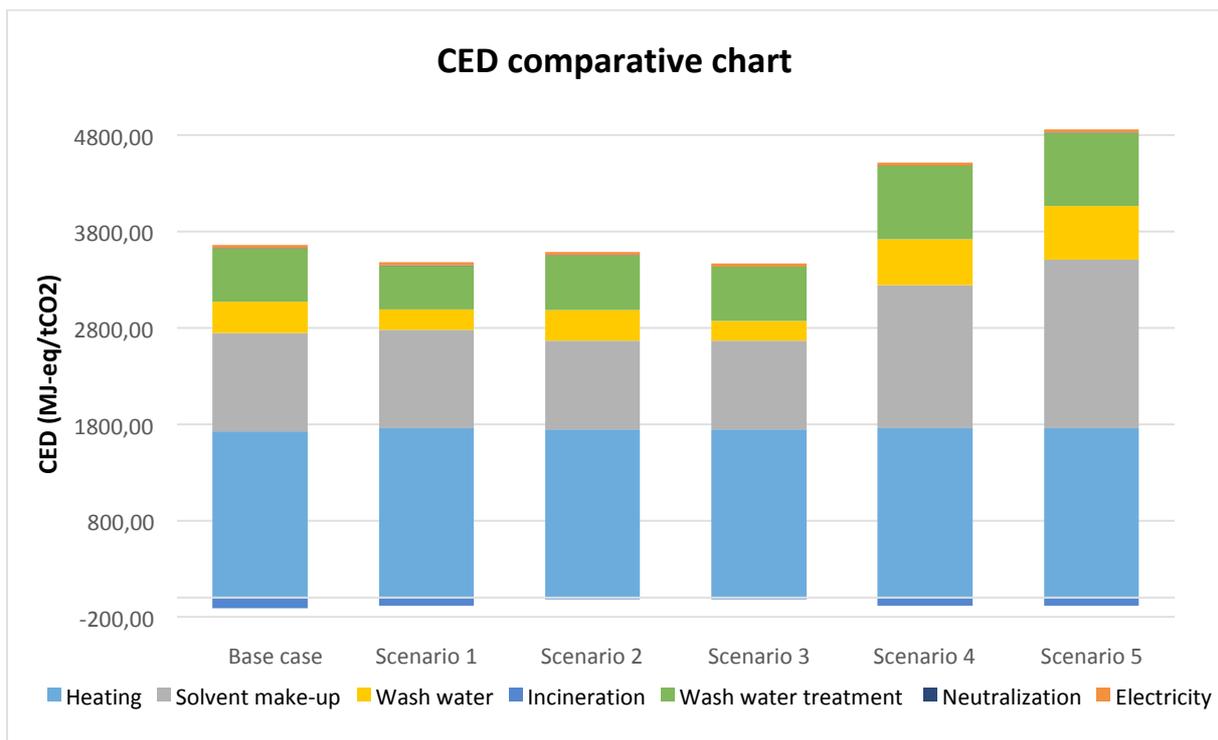


Figure 5.2.1: CED results of LCIA

For CED, heating and solvent make-up contribute most to the total score. The intermediate heat exchanger is the main heat consumer with 2.34GJ/tCO₂, which explains heating as the main CED contributor. Using waste heat in the HX could minimize this value. Indeed waste heat can be used to heat a flow until maximum 100°C while the HX heat the process flow to 80°C. This could be used to reduce total CED. But it has to be kept in mind that the heating requirement distribution of this simulation does not conform to the experimental one. The important contribution of solvent make-up can be explained by the fact that not all the MCA going at the top of the absorber is recovered; it is the main loss of MCA: 0.1-0.2%/h. In comparison, MEA is a much less volatile chemical and its washing by a small amount of water is enough to recover the volatile emission, thus the only losses occur in the purge and in the final CO₂ flow recovered at the top of the stripper.

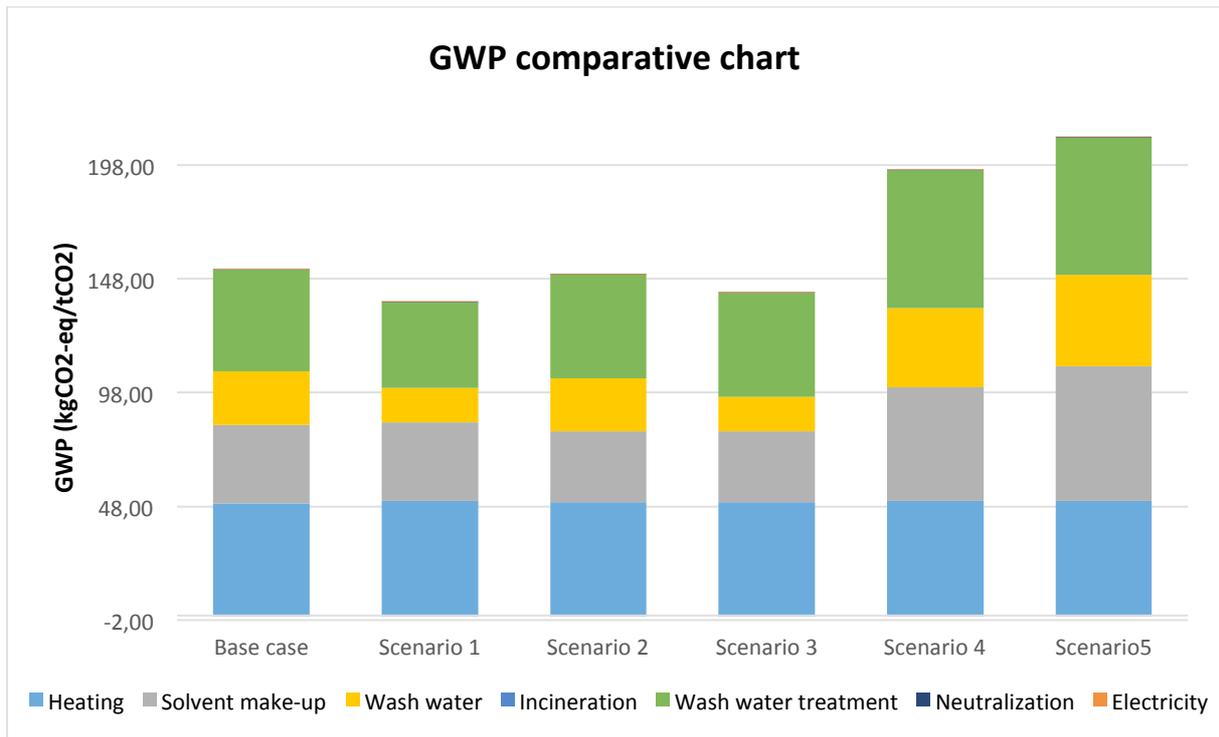


Figure 5.2.2: GWP results of LCIA

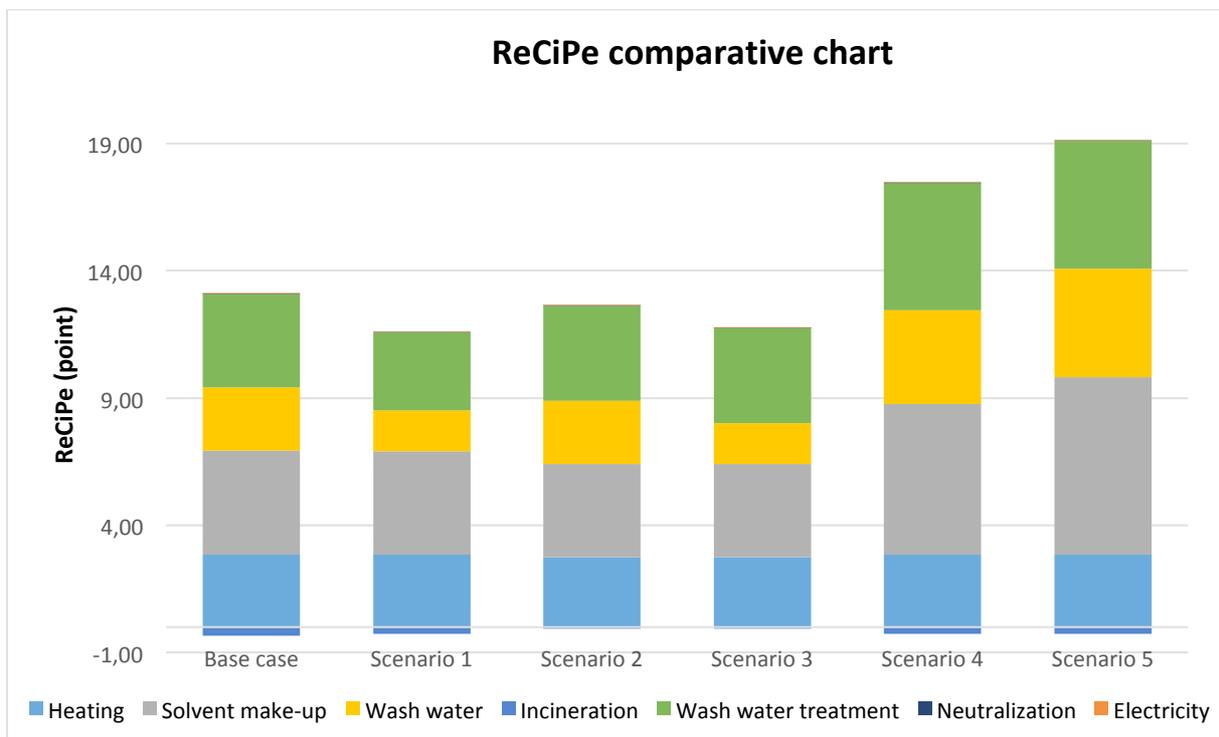


Figure 5.2.3: ReCiPe results of LCIA

Heating contributes the most to GWP score followed closely by wash water treatment and solvent make-up. Heating weight in the total GWP score is consistent with the use of a CHP coal plant as the burning of coal produces a non-negligible amount of CO₂. It could

be reduced for example by using heating coming from a biomass based CHP. The important contribution of wash water treatment can be explained by the need of chemicals such as NaOH or CaO.

Solvent make-up and wash water treatment contributes most and in similar proportion for ReCiPe score. As ReCiPe is a metric aggregating various environmental impacts it appears normal that the process steps using chemical solvents have a larger impact most on ReCiPe score.

For each metrics it can be observed that the most influential parameter is the amount of aerosol formed in the absorber. The high volatility of MCA is the reason for the large amount of aerosol produced. This leads to a less efficient recovery of the solvent by the simple flash simulation and thus a greater need for wash water that has then to be treated. A multi stage washing section may be more efficient in the amount of water used and solvent recovered. It can also be seen that MCA emission threshold has more impact on the metrics total value than degradation scenarios. There is almost no difference for the worst-case and best-case degradation scenario at the same amine emission level. This is due to the very small proportion of solvent loss through degradation compared to the amount lost through volatile emissions.

5.3 Discussion and Outlooks

The simulation and LCA framework involve a number of assumptions and approximations. Thus, it is interesting to compare the results to similar works in order to assess their overall validity. Askmar et Carbol [57] conducted a similar work that also includes the simulation of a phase change capture process and a basic LCA including CED, GWP and ReCiPe. They compare the performances of two different phase change solvents to MEA. Their LCA scope is similar but does not take into account solvent degradation products and volatile emission treatment. Thus LCA only includes heating demand, solvent make-up, electricity and process water. In their study no external heat is needed for the intermediate heat exchanger and the reboiler duty is 1.74GJ/tCO₂. As for LCA the heating demand is what contributes most to each metrics, which is coherent with their LCA scope. Nonetheless their LCIA results, 2.8 GJ-eq/tCO₂ for CED, 0.17 tCO₂-eq/tCO₂ GWP and 16 points for ReCiPe are in the same order of magnitude as in this work.

The purpose of this work was to develop an LCA framework for a reference flow-sheet of phase change CO₂ capture process and later apply the framework to the flow-sheet. The simulation was not the main aspect of the thesis and several improvements could be carried out in order to make the simulation more accurate. More effort should be made to properly represent the ions MCA⁺ and MCACOO⁻ in the decanter equilibrium model. This requires an in-depth study for more accurate thermodynamic properties estimation in Aspen. Moreover, trying different HX-decanter configurations could optimize the flow-sheet configuration itself. In addition, more detailed and precise column and heat exchanger models could be used.

The layout and flow-sheet parameters could be further optimized; however this improvement would be mostly relevant once accurate thermodynamic and reaction

parameters provided. The carbon capture process is ruled by the absorption of CO₂ by the amine. The way to input the corresponding reaction and its parameters in the simulation is one of the settings that have the most impact on simulation results. When represented by equilibrium reactions, coefficients of the equilibrium constant equation with respect to temperature are needed. In this work the equilibrium constant was roughly approximated and is probably underestimated. This results in lower absorption capacity and favors solvent regeneration more than expected. Thus, one of the first things to improve in the simulation is the equilibrium constant value. The best would be establishing experimentally the equilibrium constant temperature dependency.

Another important factor is the thermodynamic equilibrium parameters such for representing the phase-change properties of the MCA/water/CO₂ system (e.g., binary parameters if activity coefficient models are used or group contributions, respectively). No data of MCA/water/CO₂ system were available in the literature, thus it was not possible to fit thermodynamic parameters and they had to be estimated by Aspen. These parameters have major impact on units, which are mainly ruled by phase equilibrium. Thus, phase separation occurring in the decanter (and potentially in the absorber stripper columns) and the volatile emissions are strongly dependent on the accuracy of thermodynamic parameters. For instance, the uncertainty of thermodynamic parameters explains that the phase separation of the loaded mixture already occurs at 80°C instead of 90°C in literature. It also means that the output flows of the decanter in the simulation include some extent of inaccuracies. The same way as for the equilibrium constant the best way to improve the thermodynamic model is to conduct experimental work, in that case VLL equilibrium experiments.

6 Conclusion

The goal of this work was to develop an LCA framework for phase-change CO₂ capture processes. The framework was then applied to a reference system modelled on Aspen using a solution of MCA as solvent. The developed LCA takes into consideration a first level of degradation products and their treatment, aerosols formation and wash water treatment. The results presented in this thesis show a total heating requirement similar to the one in literature of 2.59 GJ/tCO₂ but with a different distribution between process unit operations. In this thesis 90% of the total heating is required by the intermediate heat exchanger while the reboiler consumes only 0.25 GJ/tCO₂, whereas according to literature it should be around 2-2.5 GJ/tCO₂. This difference is due to many uncertainties such as the approximation of the reaction equilibrium constant or other thermodynamic equilibrium parameters. Nonetheless, the overall LCA results are coherent compared to other phase change LCA results.

The LCIA demonstrates that MCA emission threshold has more impact on LCA metrics total value than degradation scenarios and that the most influential parameter is the amount of aerosol formed in the absorber. These results are due to the small quantity of solvent loss through degradation compared to the amount lost through volatile emissions. The large proportion of volatile loss results in solvent make-up being a big contributor for each metric and scenario. Thus, one process improvement is to find a way to reduce the solvent loss through volatile emission.

One way to do this is to use MCA in a blend. MCA was chosen as a reference solvent for the simulation. However, studies and this simulation have shown that MCA has several drawbacks, when used as a single solvent. The main ones are its high volatility, degradation, phase splitting behaviour in the absorber and theoretical low regeneration efficiency. According to Zhang (2013) a more efficient solvent would be the blend MCA/DMCA/AMP. DMCA and AMP are added to change the solvents properties. The blend is not volatile, stable to degradation, does not undergo phase separation at absorber conditions and has a better regeneration efficiency. Thus, for optimising a flowsheet, the blend should be used in the simulation. However, this may be a cumbersome task, given the fact that even with only MCA as a solvent there are simulation challenges with respect to data availability and required assumptions.

LCA is one of the main tools to assess the sustainability of a process but it does not cover every aspect of sustainability. Moreover, a full LCA study requires numerous process data that are not available at the development stage of a process. The three metrics chosen in this thesis evaluate the energy demand, the greenhouse gases emissions and a global environmental impact. For a full sustainability assessment a more detailed environmental assessment should be carried out, complemented by EHS hazard and risk assessment, techno economic and social impact analysis.

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YY. Appendices

YY.1. Appendix 1: Aspen simulation

YY.1.1. Input of molecules in aspen

Before starting the simulation, all the molecules need to be entered to Aspen. All the basic molecules as CO_2 , H_2O or N_2 as well as MCA exist in Aspen database. The only molecules that had to be introduced were MCA^+ and MCACOO^- ions. They had to be entered manually via *User-Defined* function. Structures of the ions displayed in Figure 4.1.1-1 were drawn and the function *Calculate bonds* used to define their connectivity. Once the structures inputted, the properties of the two ions were estimated by Aspen property estimation tool.

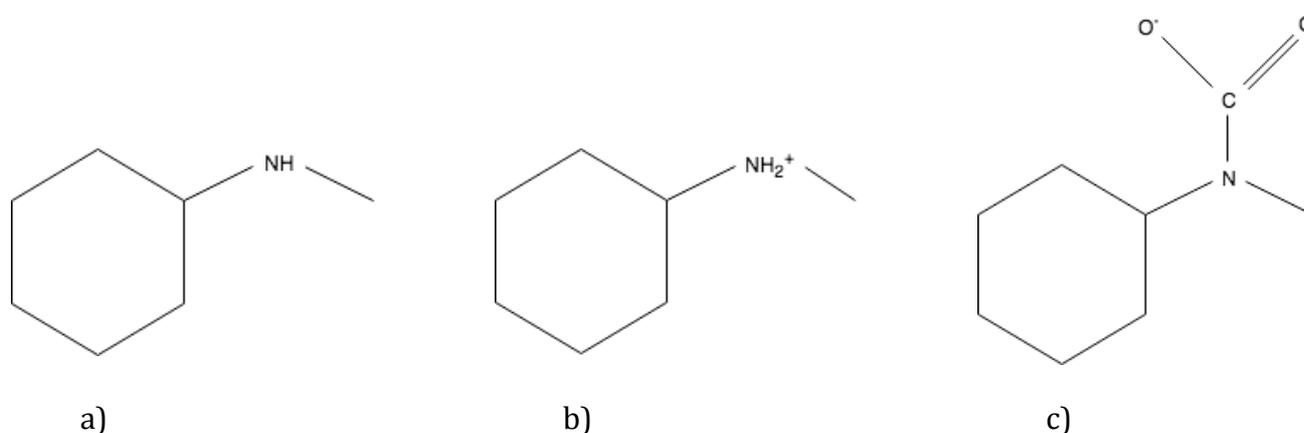


Figure YY.1.1-1: Molecular structure of a) MCA, b) MCA^+ , c) MCACOO^-

YY.1.2. Property check

Aspen does not recognize anions and cations as ions but sees them as molecules when they are entered manually. Therefore, their properties had to be checked and if necessary modified. Molecular weights of MCA^+ and MCACOO^- had to be changed, their calculated and Aspen estimated values can be found in Table A.1.2-1.

Table YY.1.2-1: MCA^+ and MCACOO^-

Compounds	MCA^+	MCACOO^-
Estimated MW	113.2028	157.2128
Calculated MW	114.2108	156.2047

The same way the vapour pressure estimated by Aspen for those two compounds was incorrect since it was calculated for molecules and not ions. Vapour pressure is an important parameter affecting the functionality of the absorber and the stripper in the

model. Aspen uses Antoine extended equation to calculate the vapour pressure (eq 4.1). The coefficients $C_{1,i}$ to $C_{7,i}$ of the equation had to be manually fixed to be equal to value of usual ions such a H_3O^+ present in the database. The values taken for MCA^+ and $MCACOO^-$ are gathered in Table A.1.2-2. In the beginning of the simulation the charge of the ions were entered manually. However, later on due to simulation problems the ions were considered to be regular non-charged molecules.

$$\ln p_i^{*,l} = C_{1,i} + \frac{C_{2,i}}{T + C_{3,i}} + C_{4,i}T + C_{5,i} \ln(T) + C_{6,i}T^{C_{7,i}} \quad \text{for } C_{8,i} < T < C_{9,i} \quad (4.1)$$

Table YY.1.2-2: Extended Antoine coefficient for MCA^+ and $MCACOO^-$

Components	MCA^+	$MCACOO^-$
Temperature units	°C	°C
Property units	bar	bar
1	-1e20	-1e20
2	0	0
3	273.15	273.15
4	0	0
5	0	0
6	0	0
7	0	0

YY.1.3. Equilibrium constant calculations

For practical reasons the equation entered in Aspen was a combination of the equations 4.7, 4.9 and 4.10 resulting in the global equation 4.10.



The calculation of the reaction equilibrium constant, K_{eq} , took place in three steps:

- The estimation of K_{eq} of the reactions 4.8 ($K_{eq}^{4.9}$) and 4.9 ($K_{eq}^{4.10}$)
- The combination of the previously estimated equilibrium constants
- The adjustment of K_{eq} of the reaction 4.10 in order to fit experimental data

The equation 4.6 and its equilibrium constant $K_{eq}^{4.6}$ is standard data existing in Aspen. The Equations 4.8 and 4.19 are not known by Aspen and their equilibrium constants had to be estimated. To do so, a method similar to the one used by Askmar et al [57] was used. The logarithm of the equilibrium constants of available amines in Aspen was plotted as a function of the inversed temperature. The resulting graph is displayed in Figure A.1.3-1. It can be observed that $\ln(K)$ decrease almost linearly with $1/T$. This means that the reverse reaction will be favoured at lower temperatures as well as the formation of protonated and carbamate amine.

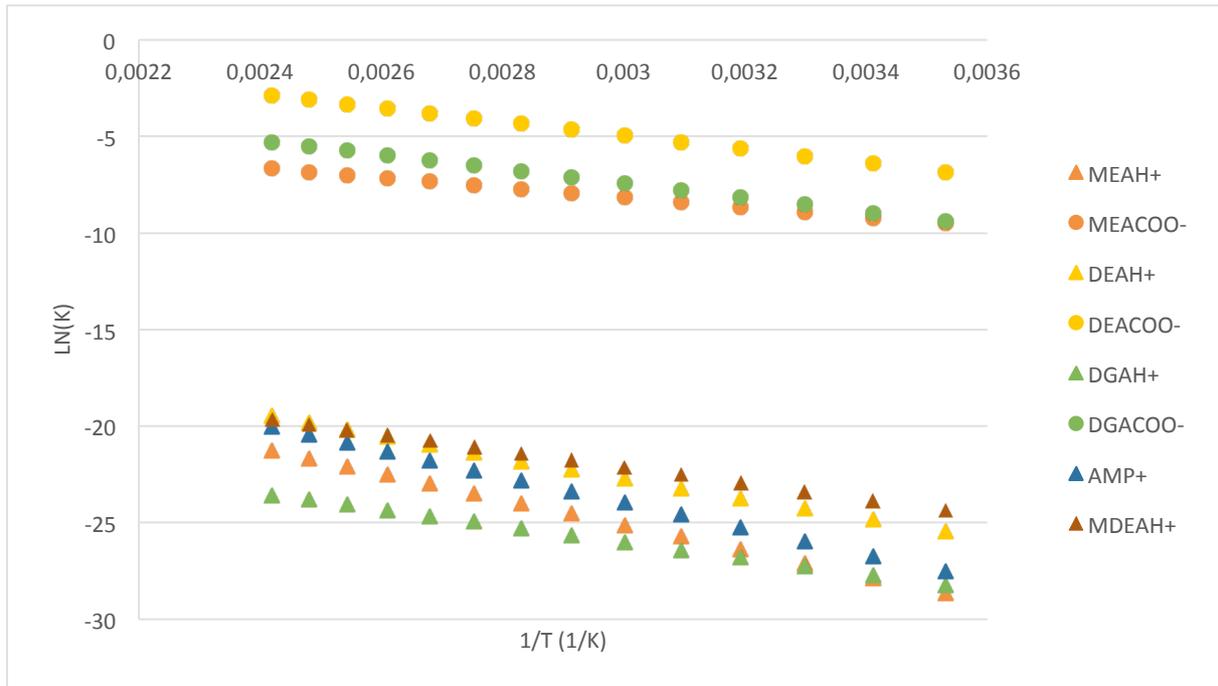
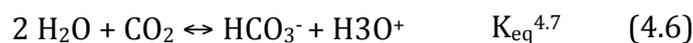


Figure YY.1.3-1: Equilibrium constant temperature dependence

A trend followed by equilibrium constant was used together with concept of Relative Energy Difference (RED) to estimate equilibrium constants of MCA -CO₂ reactions. The RED value describes the ability of a solvent to dilute a solute. In this case RED value can qualitatively indicate the ability of MCA to absorb CO₂. MEA has a high RED number of 4.10, which means that it easily absorbs CO₂. In comparison, MCA has a RED value of 1.84. Thus, MCA is supposed to absorb CO₂ in lower proportion. It's also known that DEA has much lower absorption capacity than MEA. Its RED number was not available but it was assumed to be lower than the one for MCA. Even though MCA has a lower RED than MEA it is considered to have a good capacity of absorption. Thus, it has been decided to calculate a mean of MEA and DEA equilibrium constants $K_{eq}^{4.8}$ and $K_{eq}^{4.9}$ as a first approximation of the coefficients for MCA.

Once the first estimation of $K_{eq}^{4.8}$ and $K_{eq}^{4.9}$ for MCA is done, they were combined with $K_{eq}^{4.7}$ to obtain parameters A-E (A.1) for the global equation 4.10.

The equations taken into account for the equilibrium constant calculation are the following:



In Aspen the equilibrium constant of a reaction takes the following form:

$$\ln(K_{eq}) = A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T + E \cdot \frac{P - P_{ref}}{P_{ref}} \quad A.1$$

For each reaction, the parameters A, B, C, D and E need to be known and inputted either through *Elec Wizard* or manually. Equation 4.7 parameters were already in Aspen database and retrieve with *Elec Wizard*. As mentioned previously, averaging MEA and DEA equilibrium constants was the first approximation for MCA $K_{eq}^{4.8}$ and $K_{eq}^{4.9}$. The A.1 parameters for MEA and DEA were standard values of Aspen and considered to be accurate. Each 10°C between 10°C and 140°C the value of $\ln(K)$ for MEA and DEA was calculated and average. The averaged values were then regressed to obtain an equation of the form of A.1 for MCA.

Equation 4.10 is the result of the combination of 3 others equations 4.6, 4.8 and 4.9. 4.10 can be written as (4.8) + (4.9) - (4.6). For such a combination the global equilibrium constant can be written the following way:

$$K_{eq} = \frac{K_{eq}^{4.9} \cdot K_{eq}^{4.10}}{K_{eq}^{4.7}} \quad (A.2)$$

$$\ln(K_{eq}) = \ln(K_{eq}^{4.9}) + \ln(K_{eq}^{4.10}) - \ln(K_{eq}^{4.7}) \quad (A.3)$$

According to this equation the value of the parameters A-E for the combined equation can be calculated easily by only addition and subtraction. The final results are given in table A.1.

Table YY.1.3-1: Parameters values for $K_{eq}^{4.7}$, $K_{eq}^{4.9}$, $K_{eq}^{4.10}$ and K

Equation	4.6	4.8	4.9	4.10
A	2.161e2	-5.855	2.602	-2.347e2
B	-1.243e4	-6.010e3	-3.051e3	3.031e3
C	-3.548e1	2.139e-3	-7.088e1	3.607e1
D	0	-3.677e-5	1.194e-2	1.190e-2
E	0	0	0	0

YY.1.4. Property method

One of the most important parameters in a process simulation is the choice of the property method. A property method is a collection of methods and models that are used by Aspen to compute thermodynamic and transport properties. The property method has major impacts on modelling accuracy as the calculation of enthalpy and phase equilibrium depends on it. Each property method calculates thermodynamic and transport properties differently and for one system two properties methods can give opposite results. Therefore, the property method used in the simulation must be chosen with a great care. It is also possible to use multiple property methods in different sections of one simulation. Figure A.1.4-1 displays a property method decision tree that can be used to help selecting an appropriate method.

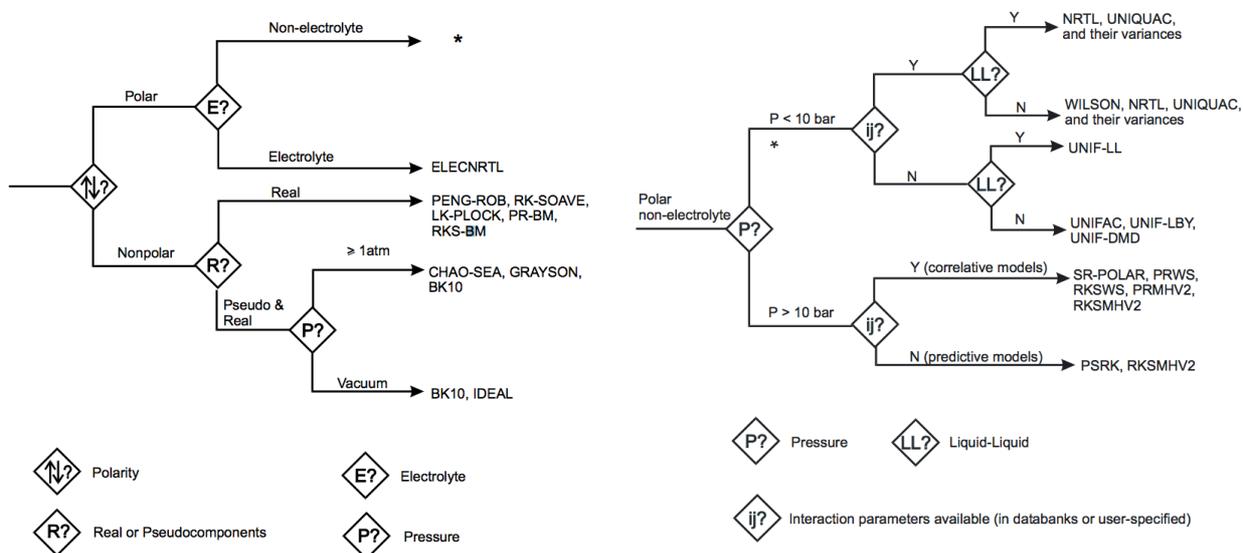


Figure YY.1.4-1: Property method decision tree [58]

In this project the system considered is polar with electrolyte, thus according to the decision tree, ELECNRTL appears to be the most suitable property method. It is a polyvalent electrolyte model, it can handle mixed solvents systems or aqueous solution at both very low and very high concentration [59]. For this model to work properly binary coefficients are needed. Aspen contains over 600 interaction pair parameters between water and ion. If the binary interaction parameters are missing they can be either entered manually or estimated by Aspen [60].

ELECNRTL has been successfully used in the past to model acid gas removal by amine from flue gas or carbon capture using MEA or other alkanolamine. However, it has been noticed that ELECNRTL performed quite poorly with lipophilic amine due to the LCST behaviour of those systems [17]. In this case problem or wrong calculations could occur in the decanter part of the simulation, which is one of the main focus of the study. Thus, other alternative property method has to be selected if any phase equilibrium calculation problem occurs. A property method that works well with LLE when binary parameters are unknown is UNIF-LL. The problem of this method is that it not suitable

for electrolyte solution. In order to bypass this problem the ions MCA^+ and MCACOO^- were defined as molecules. As explained previously some parameters were corrected so that the ions behaviour remained accurate but no charge was assigned to them. That way UNIF-LL can be used later in the simulation.

YY.1.5. Binary parameters

In order for the phase behaviour to be as accurate as possible when using ELECNRTL property method binary parameters are needed. Aspen database gather a lot of binary parameters for usual components. In this case the binary parameters of MCA and water and MCA and CO_2 were not known. When not presented in Aspen database they can be either estimated by Aspen or regressed using experimental equilibrium data. The latter is best option as it is based on actual physical data. No MCA/ CO_2 phase equilibrium experiments were found in literature so Aspen estimation was used. One experimental set of LLE values were available for the system MCA/water [61]. The Aspen regression tool was used and the final binary parameters can be found in table A.1.5-1.

Table YY.1.5-1: NRTL binary coefficient for the system MCA/ CO_2

Component i	H2O
Component j	MCA
Temperature units	$^{\circ}\text{C}$
Aij	-4.02848
Aji	14.4522
Bij	950.9785
Bji	-4128.7750
Cij	0.6583
Dij	-0.0025
Eij	0
Eji	0
Fij	0.0174
Fji	-0.0039

YY.1.6. VLE study

The base of this work stands on the phase separation property of the solvent. The latter has been demonstrated by experimental work but in order to conduct this project VLE has to be predicted the most accurately possible by Aspen. A first screening tool for VLE behaviour is the Aspen ternary diagram. Ternary diagram for the system water/MCA/ CO_2 was plotted using the property method ELECNRTL and UNIF-LL. When calculating ternary diagram Aspen could not handle any ions. Thus, the diagrams obtained only take into consideration a purely molecular system and ignore reaction and electrolytes. As a consequence, the obtained diagram shown in Figures A.1.6-1 and A.1.6-2 give only an approximation of the system VLE.

Outside of the envelope the system is made of a single liquid phase while the phase splitting behaviour occurs inside of the envelope. Each line gives an system equilibrium and each edge gives the composition of the two resulting phase. From the diagrams it

can be seen that the property method UNIF-LL predicts a better phase splitting behaviour of the system. Thus, from a first screening UNIF-LL appears more able to handle phase separation. A more in depth assessment have to be lead with the use of a decanter.

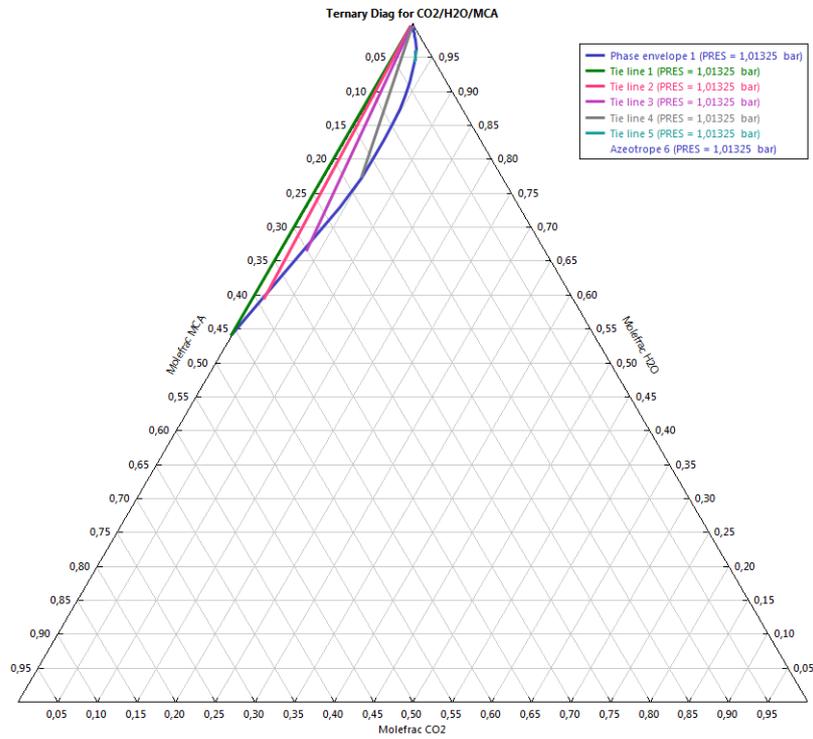


Figure YY.1.6-1: Water/MCA/CO₂ ternary diagram plotted with ELECNRTL

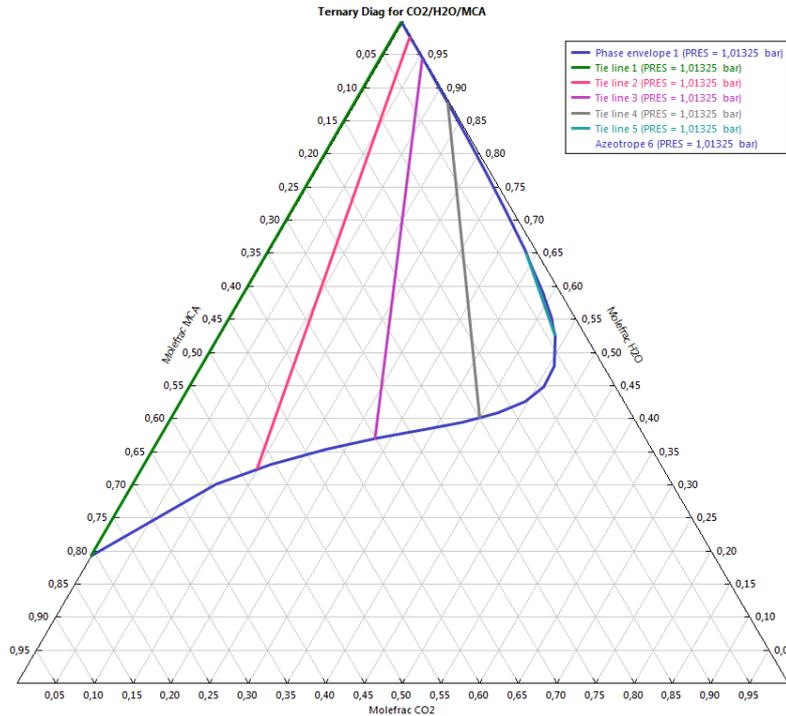


Figure YY.1.6-2: Water/MCA/CO₂ ternary diagram plotted with UNIF-LL

YY.1.7. Decanter study

Ternary diagram provided a first level study of the phase separation modelling but a more detailed and accurate method is needed. To do so the Aspen decanter block can be used. It simulates decanter or other single stage separation without a vapour phase.

A mixer is used to model more simply the absorption column. The composition and stream conditions used are the same than in the actual simulation and can be seen in table A.1.7-1. A flash follows the mixer in order to remove the vapour that the decanter can't handle. Finally, a pump and a heat exchanger are added to achieve 2 bars and 80°C at the entrance of the decanter. The first part of the modelling was run with ELECNRTL property method as it handles better electrolytes. Then, in the decanter both ELECNRTL and UNIF-LL were tried by creating a second flow-sheet section.

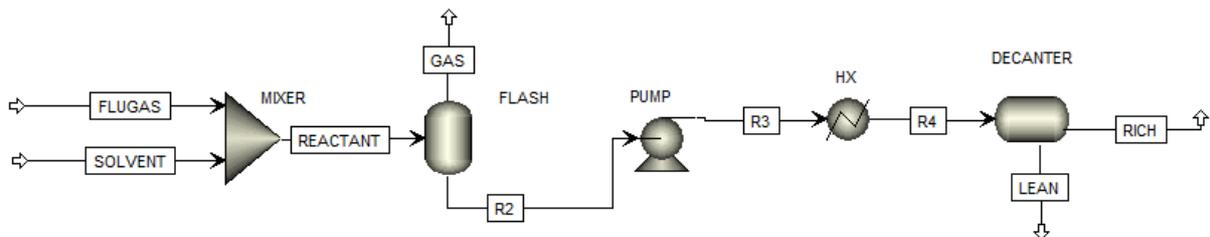


Figure YY.1.7-1: Set-up of the decanter study

Different errors were observed during the decanter study. The first problem was that the decanter could not handle the chemistry written as equations 4.8 and 4.9 described in the section 4.2 because of the defined ions. To solve this problem the chemistry was rewritten as only one equation (4.10) and the defined ions were no longer attributed a charge. They were defined as molecules for which only the Antoine parameters and molecular weight were changed as mentioned in section A.1.1. When changing the reaction equation the decanter worked with UNIF-LL but not ELECNRTL. Moreover the phase compositions obtained with UNIF-LL were very far from what was expected because of the reaction calculations into the decanter. Those results can be found in the table A.1.7-2. To deal with it the flow sheet sections containing the decanter were changed so that no reaction occurs in the decanter.

From the result of the decanter study, it has been chosen to perform the phase separation in a flow-sheet section that has UNIF-LL as property method and no reaction occurring. The rest of the simulation is run with ELECNRTL and the reaction 4.10.

Table YY.1.7-1: Inlet flows, flash and decanter characteristics.

	Flue gas	Solvent
Composition	N ₂ : 0.73 vol% CO ₂ : 0.1194 vol% H ₂ O: 0.1125 vol% O ₂ : 0.0381 vol%	MCA: 3M solution
Flow rate (m ³ /h)	5011	25
Temperature (°C)	48	35
	Flash	Decanter
Pressure (bar)	1.06	2
Duty (MW)	0	0

Table YY.1.7-2: Result for UNIF-LL property model

<i>Rich phase</i>	With chemitry	Without chemistry
Total amine (kmol/h)	74.56	74.58
MCA (kmol/h)	66.95	35.56
MCACOO- (kmol/h)	3.30	19.46
Total amine mol%	71	76.50
<i>Lean phase</i>		
Total amine (kmol/h)	0.37	0.35
MCA (kmol/h)	0.32	0.16
MCACOO- (kmol/h)	0.03	0.13
Total amine mol%	4.16e-2	3.97e-2

YY.1.8. Absorber-Stripper

The absorption column and the stripper were modelled using *RadFrac* columns. *RadFrac* is a rigorous model that can handle all types of vapour-liquid fractionation operations. It is suitable for many operations including absorption and stripping. This model can work with two or three-phase systems which is crucial for the MCA simulation. Indeed, as explained previously due to MCA low LCST two liquid phases are present in the absorber. *RadFrac* column has two main calculation methods: equilibrium and rate-controlled. The equilibrium method assumes that phases are at equilibrium at each stage of the column, which is not always accurate. Contrary the rate-based method takes into account the heat and mass transfer. For accuracy purpose it would be better to use the rate-based calculation method. However the only way for Aspen to calculate a 3 phases system is to use equilibrium. As a consequence the equilibrium method was used in the absorber column and the rate-controlled one in the stripper.

In the stripper, calculation method for the interface between the liquid and the gas was changed in order to correctly model the stripping. The two films theory was first used by Kucka et al [62] to propose an asymmetric discretisation of the liquid film. The asymmetric discretisation allows a good modelling of the fast absorption/desorption of CO₂. It achieves similar results using less equidistant located point while reducing computational load. This model has been tested for CO₂ capture with MEA and present good agreement between experimental and simulated data. In order to discretized the liquid film in Aspen the film resistance method *Discrxn* was used. For the gas side as no reaction occurs the film method was chosen. The same discretisation point as Askmar et al [57] was used and can be found in the table A.1.8-1.

Table YY.1.8-1: Discretisation points for liquid film

Points	Normalised distance from the vapour/liquid interface
1	0.001
2	0.005
3	0.01
4	0.05
5	0.1
6	0.15
7	0.2
8	0.3

In both columns a first guess for the number of stage had to be entered, it was chosen to be 10. This number was changed along the simulation for convergence purpose and was minimized as much as possible. As said before the absorber calculation type was set as equilibrium and the valid phase as Vapor-Liquid-Liquid in the *Configuration* tab of the absorber. Under the *3-Phase* tab the 3 phase calculations were considered over the entire column: from stage one the 10 with MCA as the *Key component* to identified the second liquid phase. So as to have more accurate calculations and the column

dimensions the tab *Packing Rating* was filled. A packing material had to be supply. Mellapak™ 250Y was selected, as it is a benchmark material for flue gas treatment and MEA carbon capture, it usually gives a low pressure drop [63]. A regular height of 0.6m per stage was chosen.

When using the rate-based method for the stripper packing, height per stage and column diameter had to be provided as a first estimation. As for the absorber Mellapak™ 250Y packing and a height of 0.6m per stage was chosen. The diameter was taken to have a ratio diameter/total height of at least 2. Then under the tab *Packing Rating* the option *Design* was selected, the base stage entered as 2 and the base flood as 0.8. This way, Aspen automatically calculates the stripper diameter based on the height per stage and the number of stage.

In order to be able to later compare results to Badr (2016) work and others phase change solvents that will be later assess, two key performance were decided: 90% CO₂ recovery and the 98% purity. To reach those goals two design specifications were set in the Aspen simulation. The first one called *Recovery* varies the stripper reboiler duty in order to have the final mole flow of CO₂ equal 90% of CO₂ mole flow in the flue gas entering the process. The design specification *Purity* changes the outlet temperature of the cooler placed at the top of the stripper so as to reach the 98% purity desired.

YY.2. Appendix 2: Degradation

YY.2.1. Oxidative degradation

Table YY.2.1-1: MMEA and MCA oxidative degradation studies conditions.

Conditions	H.Lepaumier et al (2011)	Vevelstad et al (2013)	Liu et al (2014)	Zhang (2013)
Amine	MMEA	MMEA	MMEA	MCA
T (°C)	55	50-55	70	50
Amine concentration	30 wt%	30 wt%	10M	
Gas composition	Air with 5%CO ₂	Same ?	98 kPa O ₂ 2k Pa CO ₂	2 % CO ₂ 98 % O ₂
Gas flow rate	Sparge	Counter current to liquid flow	100ml/min	100ml/min
Type of reactor	Open batch	Closed batch	Open semi-batch jacked reactor	Glass bubble column
Other	0,4 CO ₂ loading Atmospheric pressure	0,4 CO ₂ loading Atmospheric pressure	1400 rpm 0,4nM Fe ³⁺ 0,2nM Mn ²⁺ 0,1nM Ni ²⁺ 0,05nM Cr ³⁺	0.2 mM Fe ₂₊ /FE ₃₊

YY.2.2. Thermal degradation

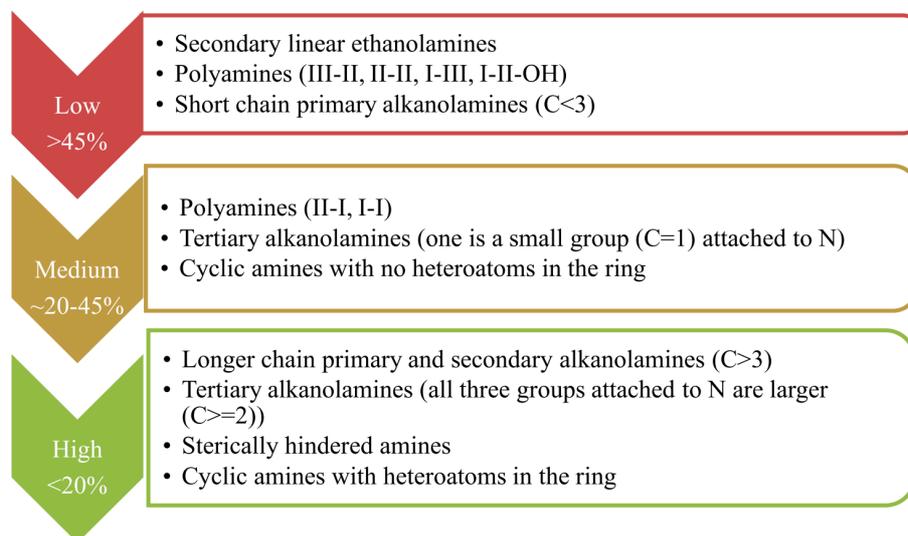


Figure YY.2.2-1: Thermal stability of amines in the stripper based on their structure. Percentage shows the potential degradation rate (based on Eide-Haugmo, 2011: degradation after 5 weeks at 135°C with a loading of 0.5 mol CO₂/mol amine). I – primary amino group, II-secondary, III -tertiary.

YY.3. Appendix 3: Inventory results

Table YY.3-1: Inventory results for each scenario

	Base case	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Reboiler duty (MJ/tCO ₂)	250.4	250.4	250.4	250.4	250.4	250.4
Reclaimer duty (MJ/tCO ₂)	22.3	22.3	4.3	4.3	22.3	22.3
Intermediate HX duty (MJ/tCO ₂)	2392	2392	2392	2392	2392	2392
Pumps duty (MJ/tCO ₂)	5.3	5.3	5.3	5.3	5.3	5.3
Cooling water pumping (MJ/tCO ₂)	8.8	8.8	8.8	8.8	8.9	9.0
Solvent make-up (kg/tCO ₂)	10.8	10.8	9.7	9.7	15.7	18.6
Wash water (kg/tCO ₂)	14620	9440	14618	9438	21720	25072
Neutralizing agent (kg/tCO ₂)	0.21	0.21	0.04	0.04	0.21	0.21

YY.4. Appendix 4: Absorber profile temperature

Figure YY.4-1: Profile temperature in the absorber

