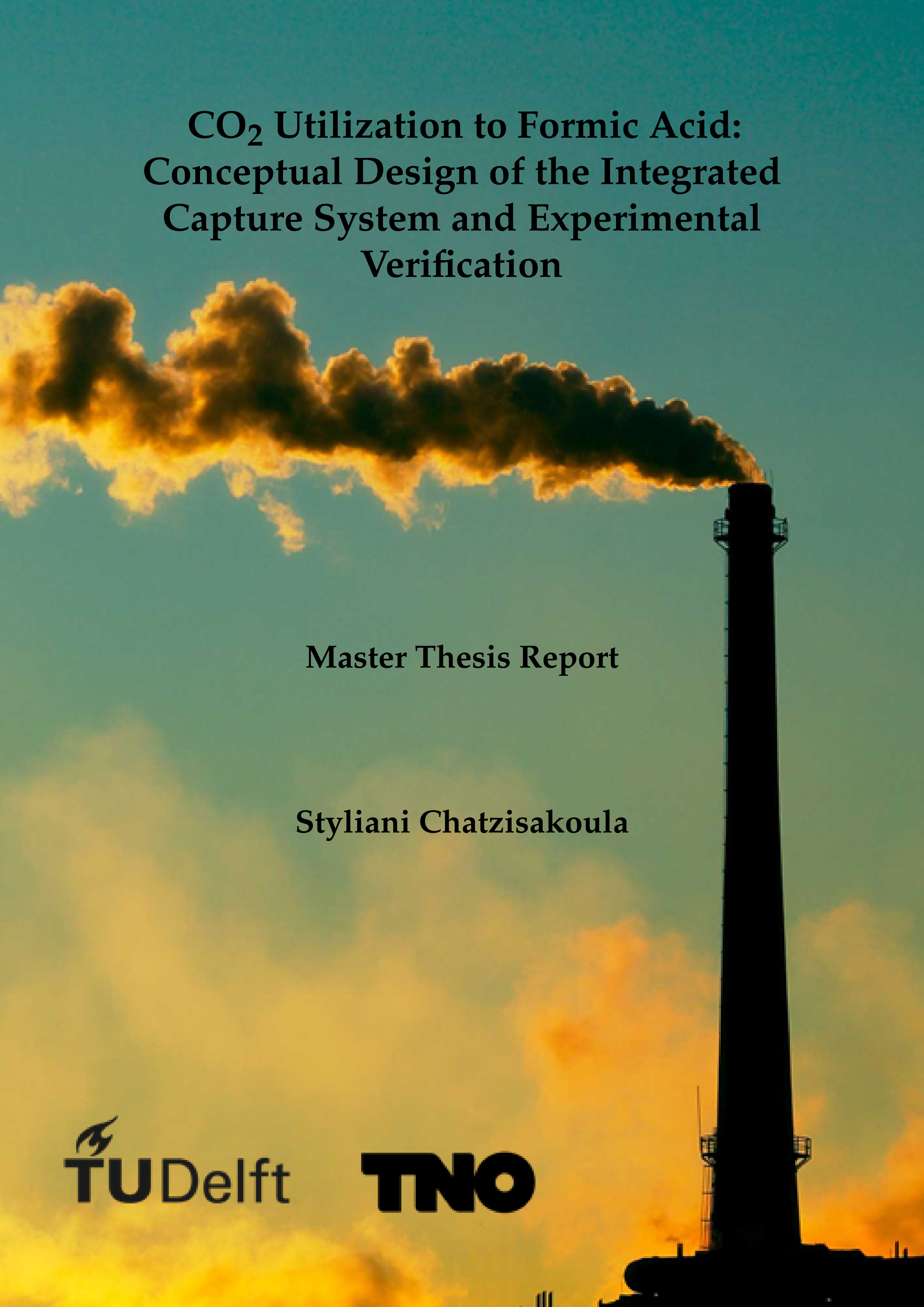


CO_2 Utilization to Formic Acid: Conceptual Design of the Integrated Capture System and Experimental Verification

Master Thesis Report

Styliani Chatzisakoula

TU Delft

TNO

CO_2 Utilization to Formic Acid Conceptual Design of an Integrated Capture System and Experimental Verification

by

Styliani Chatzisakoula

to obtain the degree of Master of Science in Sustainable Energy Technology
at Delft University of Technology,
to be defended publicly on Thursday 26 September, 2019 at 09:30 AM.

Student number:	4736036	
Project duration:	January 1, 2019 – September 26, 2019	
Supervisor:	Prof. Dr. ir. Earl Goetheer	
Thesis committee:	Prof. Dr. ir. Earl Goetheer,	TU Delft, TNO
	Prof. Dr. ir. Wiebren de Jong,	TU Delft
	Prof. Dr. ir. Bendiks Jan Boersma,	TU Delft
	MSc Maartje Feenstra,	TNO

Acknowledgements

This report is been prepared to review my thesis project that took place at TNO in the SPES department, located in Leeghwaterstraat 44 in Delft. During my thesis project I worked on the CO_2 utilization to formic acid and further to formaldehyde, integrated with a CO_2 capture system. For the absorption system, ammonia solution is used to capture a flue gas stream.

This study contains comparison of valuable end-products derived from capturing of CO_2 and been produced through a number of thermochemical step reactions. Formic acid and formaldehyde are the two main products that were selected for further investigation, since research gap was indicated. This study relates to the integrated systems starting from CO_2 capturing until the production of the end-product, including a techno-economic analysis. The process design initiates with the capture of CO_2 in bicarbonate salts in the chemical absorption step. Hydrogenation of the latter results in ammonium formate and lastly distillation at high temperature leads to the formation of formic acid and ammonia. Further hydrogenation of formic acid produces formaldehyde, a valuable end-product with higher and broaden market compared to formic acid.

During my thesis project I worked along with Maartje Feenstra, junior scientist innovator in the SPES department of TNO. I would really like to thank her for her continuous help and advises during all the months of my thesis. She did help me in any difficulty I encountered for any issue I had both in basic chemistry and in process engineering. Her calmness and positive attitude as a person made me believe more in myself during the whole process.

Part of my project also includes experimental proof of concept of several chemical reactions and that was really out of my safe zone in the beginning. To achieve all the results of this work I would really like to thank all the people intensively helped me in the lab, namely Arjen Huizinga, Roberta Veronezi Figueiredo, Ivan Bakker, Daphne Iwaarden-Bakker, Richard van Someren and Nathan Godefroij. They were all personally eagerly helped me out understand every single detail both regarding the background knowledge of the chemical reactions as well as the experimental setup located in the laboratory of the SPES department.

Most of all, I would like to thank my supervisor Earl Goetheer for giving me inspiration throughout all the months of my thesis. He really trusted me his idea and was guiding me with accurate and interesting inputs and feedback on my work. A person dedicated to research and able to solve every limitation and problem we encountered during the process with a smart and creative way. He has been more than inspiration for me those months, both concerning my project as well as my future decisions and plans.

Last but not least, I would like to thank my family and my friends that were patient with me all this time period and fully supporting me to go through this procedure. Without them, I would not be able to accomplish all the things I have done, since they always believe in me and my abilities.

Stella Chatzisakoula
Delft, September 2019

Summary

CO_2 emissions rate is increasing with an alarming pace during the last decades. Carbon capture and storage could be an effective methodology for reducing CO_2 emission on a short term due to its relatively mature status. Moreover, carbon utilisation, as a closing the carbon cycle approach, is gaining significant attention on a scientific level and on a public level. A large amount of technical possible directions for CO_2 utilisation have been identified and examined. However, the majority of these reaction pathways are focused on the use of pure CO_2, leading to a relatively high overall cost for commodity chemicals. It would be beneficial from a cost perspective to integrate the capturing of CO_2 with the utilisation and this is the focus of this thesis.

The research described in this thesis is centred around the novel methodology to capture CO_2 from flue gases using an aqueous ammonia based solution. Instead of a conventional thermal swing process, hydrogen is used to convert the captured CO_2 (in the form of ammonium bicarbonate) towards formate. A distillation process has been developed to basically split the ammonium formate solution in an ammonia solution and a concentrated formic acid solution. This formic acid solution can be used as such or even further converted via hydrogen towards formaldehyde.

It is of importance to note that this pathway has been selected based on in principal known chemical steps but combined in an innovative manner. A theoretical (modelling) approach is combined with an experimental part to achieve proof of principle of all the key steps, leading towards a detailed techno-economic evaluation. A design has been made for a 100 kton of flue gas captured and utilised system. Starting point is the capturing of CO_2 from a 6 v/v % flue gas concentration with a capture efficiency of 90%. Depending on the methodology used this can lead, after hydrogenation and distillation, to a formic acid product with a concentration between 32 - 37 % wt. It can be stated that the above described process could be economically feasible, with payback time of 9.3 years and an interest of 8%. A final production price of formic acid at 400 €/tn making the process attractive compared to the market price of formic acid.

Sensitivity analysis is been conducted towards various parameters that may affect and influence these production costs, such as electricity price, capital cost of the electrolyzer and lifetime of the capture plant. The market for formic acid is relatively small, however, this thesis discusses as well the possibility of converting the formic acid to formaldehyde, which is a very important commodity chemical. A concentrated formaldehyde is produced, comparable to the 37 % wt commercial product. Recommendations are discussed for process options which can in principal lead to significant improvement towards the basic design of the integrated capture and conversion method.

Contents

List of Figures

List of Tables

List of Symbols

C_0	Initial Investment	[€]
C_t	Cash flow at period t	[€]
E	Activation energy	[cal $\cdot mol^{-1}$]
i	Interest	[%]
K_s	Equilibrium constant	[-]
k	Kinetic factor	[-]
L/G	Liquid to gas ratio	[kg liquid $\cdot hr^{-1}$ / kg gas $\cdot hr^{-1}$]
$\dot{m}$	Mass flow rate	[kg $\cdot s^{-1}$]
MR	Molar mass	[g $\cdot mol^{-1}$]
$[M]$	Concentration	[mol $\cdot L^{-1}$]
n	Lifetime	[year]
p	Pressure	[bar]
P^0	Vapor pressure	[bar]
pK_a	Acid dissociation constant	[-]
R	Gas constant	[$J \cdot mol^{-1} \cdot K^{-1}$]
r	Stirring speed	[rpm]
T	Temperature	[ºC]
t	Retention time	[hr]
V	Operating Voltage	[eV]
$\dot{V}$	Volumetric flow rate	[L $\cdot min^{-1}$]
Vol	Volume	[m^3]
w	Weight	[kg]
ΔG	Gibbs Energy	[$kJ \cdot mol^{-1}$]
λ	Wavenumber	[cm^{-1}]

Abbreviations

$APEA$	ASPEN Process Economic Analyzer
CAP	Chilled Ammonia Process
$CAPEX$	Capital Expenditure
$CAPEX_{ann}$	Annualized Capital Expenditure
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
CF	Cash Flow
CWE	Central West Electricity
$DACE$	Dutch Association of Cost Engineers
DMA	Dimethylamine
DOE	Department of Energy
ED	Electrodialysis
FA	Formic Acid
FIC	Fixed Capital Investment
$FOPEX$	Fixed Operating Expenditure
$FTIR$	Fourier transform infrared spectroscopy
GHG	Greenhouse Gases
$HPLC$	High Performance Liquid Chromatography
LC/MS	Liquid Chromatography-Mass Spectrometry
LHV	Lower Heating Value
MEA	Monoethanolamine
NPV	Net Present Value
$NRTL$	Non-random two-liquid model
Octavius	Optimization of CO_2 Capture Technology Allowing Verification and Implementation at Utility Scale
$OPEX$	Operating Expenditure
PCC	Post Combustion Capture
PEM	Proton Exchange Membrane
pH	Potential Hydrogen
$Rotovap$	Rotary Evaporator
SLV	Solid-Liquid Vapor Equilibrium
SMR	Steam Methane Reforming

SPES	Sustainable Process & Energy Systems
TDPC	Total Direct Plant Cost
TEC	Total Equipment Cost
TIC	Total Capital Investment
TIPC	Total Indirect Plant Cost
TMA	Trimethylamine
TNO	Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek
VOPEX	Variable Operating Expenditure

Chemical Formulas

CeO_2	Cerium oxide
CH_4	Methane
CH_3COOH	Methyl formate
CH_3NH_2	Methylamine
$(CH_3)_2NH$	Dimethylamine
$(CH_3)_3N$	Trimethylamine
CH_3OH	Methanol
C_2H_4	Ethylene
$C_4H_6O_6$	Tartaric acid
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate
$C_2O_4H_2$	Oxalic acid
$(CONH_2)_2$	Oxamide
H_2O	Water
H_3O^+	Hydronium ion
$HCHO$	Formaldehyde
$HCOO^-$	Formate
$HCOOH$	Formic acid
$HCOONH_4$	Ammonium formate
$HCONH_2$	Formamide
HCO_3^-	Bicarbonate
N_2	Nitrogen
NH_3	Ammonia
NH_4^+	Ammonium
NH_3COO^-	Carbamate
$(NH_4)_2CO_3$	Ammonium carbonate
$(NH_4)_2C_2O_4$	Ammonium oxalate
NH_2COONH_4	Ammonium carbamate
NH_2COOH	Carbamic acid
NH_4HCO_3	Ammonium bicarbonate
$(NH_4)_2 \cdot 2NH_4HCO_3$	Ammonium sesqui-carbonate

$(NH_4)_2O$	Ammonium oxide
Ni	Nikel
NO_x	Nitrogen oxide
OH^-	Hydroxide
Pd	Palladium
SO_2	Sulphur dioxide
TeO_2	Tellurium dioxide

Chapter 1

Introduction

1.1 Thesis motivation

During the last decades the subject of climate change has been extensively discussed and investigated. Researchers along with industries are on the same track on finding and applying sustainable and renewable solutions to limit the excessive use of fossil fuels. The demanding target of the European Union of significant reduction of greenhouse gas emissions up to 90% by 2050 is limiting more and more the industrial CO_2 emissions. Efficient and direct measurements are considered an urgent necessity. In order to move towards such a direction, the most efficient ways to achieve such a tremendous reduction can be accomplished by various ways: [1]

- Improvement of the energy efficiency of already existing power plants
- Use of carbon free fuels and renewable energy, like biomass, wind and solar energy
- Carbon capture and storage (CCS)
- Carbon capture and utilization (CCU)
- Reduction of energy consumption

It is apparent that CO_2 emissions are increasing in an alarming rate and the concentration of CO_2 in the atmosphere is elevating. This increase is caused mainly by anthropogenic activities during the last decades. These activities include the extensive use of fossil fuels and the high dependence on fuels rich in carbon, making this the main source of carbon dioxide emissions in the atmosphere. Especially during the last couple of decades, the increase of CO_2 concentration in the atmosphere is extreme and in 2019 reaches the level of 409 ppm, as can be seen in Figure 1.1. This concentration is almost 300 times more dilute compared to regular flue gases consisting around 12% of CO_2 by volume. Purification processes are costly, making point sources a more attractive carbon source. [2]

Capturing CO_2 from air has its own challenges in terms of investment, operating and energy cost. A dilute stream of CO_2 emissions when compared to a concentrated one derived from power plants, may result to a whole different perspective of a system design. An increase of the captured CO_2 derived from industries will lead to more efficient decrease of carbon emissions in the atmosphere.

Storage of CO_2 can be implemented on a short term, however, it is not a circular concept. An alternative way to take advantage of these emissions is utilization, with the potential beneficial end use. Capturing CO_2 can be considered a viable short - term goal, and if combined with utilization, it leads to the production of valuable end-products and chemicals. So, capturing is the first required step and conversion of CO_2 to useful products is an attractive route providing a long term solution towards a sustainable future.

This approach of producing alternative valuable end-products is studied in this thesis as a positive impact towards the reduction of the emissions of greenhouses gases. This work aims to investigate of the different alternative routes of CO_2 products in a techno-economic perspective, taking into account the different reaction steps taking place in every end-product. In this work utilization to production of valuable products will be investigated and more precisely to the production of formic acid and formaldehyde.

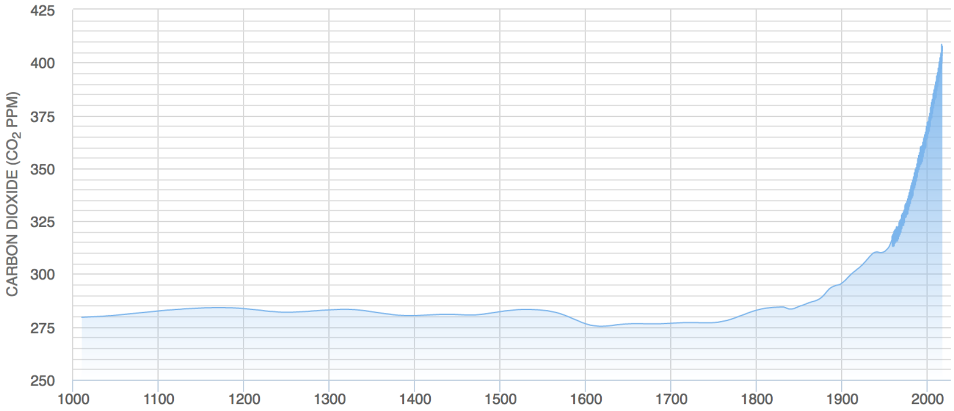


Figure 1.1: CO_2 concentration in the atmosphere throughout the years.[3]

During the last decades due to increasing technological development, the amount of Greenhouse Gases (GHG) emitted in the atmosphere is rapidly increasing. Carbon Capture and Storage (CCS) can be considered a CO_2 effective technology that can be used to make use of these emissions. Capturing CO_2 is considered to be more effective when flue gas is derived from energy intensive industries at point sources. Especially when compared with the diluted CO_2 in air, the process of Direct Air Capture (DAC) is challenging. For such a mature technology, three different approaches are been developed:

- **Post-combustion capture (PCC)**: CO_2 stream is removed after the combustion of fossil fuels. Such a technology is well established, mature and already applied in industrial scale.
- **Pre-combustion capture**: the removal of CO_2 from fossil fuels takes place before the combustion process.
- **Oxy-fuel combustion**: fuel is burnt in pure oxygen instead of air and the resulting product is almost pure CO_2. It is a promising technology, but air separation is still energy intensive.

In this work a post-combustion technology is selected for capturing CO_2 from flue gas. Such a system has many advantages, such as:

- it can be applied to already existing power plants and energy intensive industries. It can also be constructed for new infrastructure achieving high CO_2 conversion and reduction
- applicable in any kind of power plant, from coal, steel and natural gas based industries
- the risk of the investment is lower compared to other technologies, due to its high maturity

1.2 Thesis scope

The focus of this thesis is to investigate on how CO_2 capture and conversion could be integrated. This has a very broad scope therefore an extensively research survey has been done to narrow down the research questions. In this section the research questions that were posed are presented as well as the methodology that was followed during this process.

1.2.1 Research questions

The overall goal of this research project is the research of the alternative routes for CO_2 utilization. Analyzing the different routes, a comparison in mass, thermal and techno-economic perspective would lead to a summarizing evaluation of the different alternatives. The direction to a specific route will be selected for further investigation with the overall conceptual design of the process design, starting from the capture process to the final utilization of CO_2. Simulation of the process and selection and sizing of the necessary equipment are to be determined. All the above can be translated to the following research questions posed over this research and development project and to be fully answered are the following:

- What are the different paths of CO_2 products and which routes are the most attractive?
- Can ammonia CO_2 capture be integrated with CO_2 utilization?
- Is it techno-economically feasible to capture CO_2 with aqueous ammonia and produce concentrated formic acid?

1.2.2 Methodology

The methodology that was followed to fully answer the posed research questions can be divided to a four level approach. This approach includes the following: a literature survey, a process design, experimental proof of concept and techno-economic evaluation.

1.3 Thesis outline

The structure of the report is as follows. In Chapter 2, a general description and mapping of all the different routes and different valuable end-products are presented as well as the main strategy for the decision of the more focused definition of this project. Additionally, all the background knowledge for the participating chemical steps is presented. In Chapter 3 the followed method for the proposed system is explained in detail. Both simulation parameters and conditions of the experiments are shown. Chapter 4 focuses on the results of the simulated integrated systems and on the experimental proof of concept of the reactions.

In Chapter 5 a techno-economic analysis is performed for the evaluation of the examined integrated systems, including a crystallization system or not. Finally, Chapter 6 presents briefly the basic results of the study and in Chapter 7 the report concludes along with some recommendations for the project and an alternative approache that could be useful in the overall integrated system, such as a tertiary amine, trimethylamine.

Chapter 2

Theory - Background knowledge

In this Chapter an overview of the background theory for this specific work is presented. This Chapter contains all the necessary information about the capturing process and the characteristics of ammonia as a capturing solvent. The proposed systems are presented in this Chapter, including all the participating thermochemical steps. The theory and chemical background behind the chemical reaction steps necessary for producing different products are also included. Moreover, an introduction of the crystallization system and its benefits is done.

2.1 CO_2 Utilization - Mapping and Evaluation of products

In this Chapter the wide variety of thermochemical pathways is described. Depending on the market size, demand and research interest, numerous products can be investigated, such as formic acid, methanol, syngas etc. Production of such products can also be done in an electrochemical manner and the future potential of electrochemical conversion depends both on technical and economic aspects. A comparison between electricity cost and market price is illustrated in Figure 2.1 and it can be seen that formic acid and CO gather some additional advantages that will be discussed in the following paragraphs.

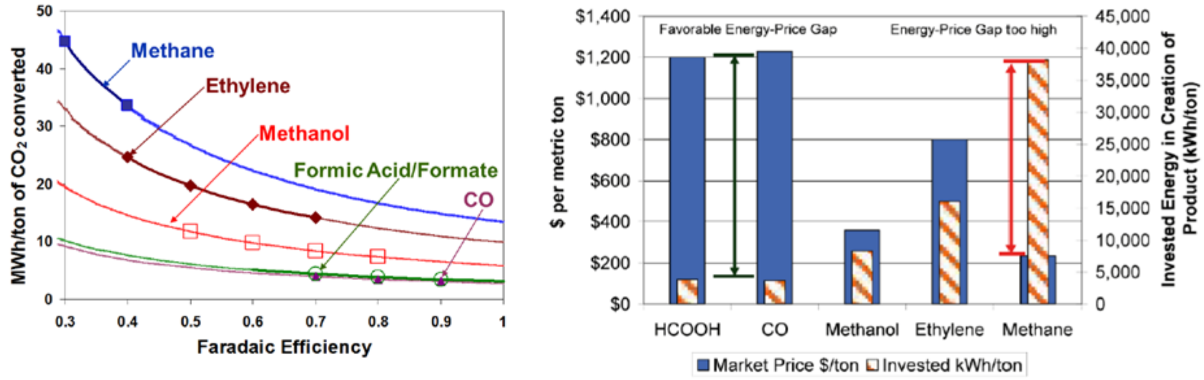


Figure 2.1: Comparison of market price and and energy costs. [4]

CO_2 conversion reactions towards valuable end-products may take place with a change in the oxidation state of the carbon, such as towards carbonates and polycarbonates. There can either be a change in C-O bonds, keeping the +IV oxidation state towards production of urea, as can be seen in Figure 2.2. In addition, reduction of carbon oxidation state may result in the production of products, such as RCOOH, formaldehyde HCOH, methanol CH_3OH and methane CH_4.

It can be seen in Figure 2.2 that CO_2 is in a high oxidation state (+IV), indicating a highly stable compound. The reduction of the oxidation state of carbon has high energy requirements and such processes are energy intensive. Based on the above, valuable products like methane and liquid hydrocarbons need a higher amount of energy, thus alternative routes towards formic acid and formaldehyde are proposed in this project.

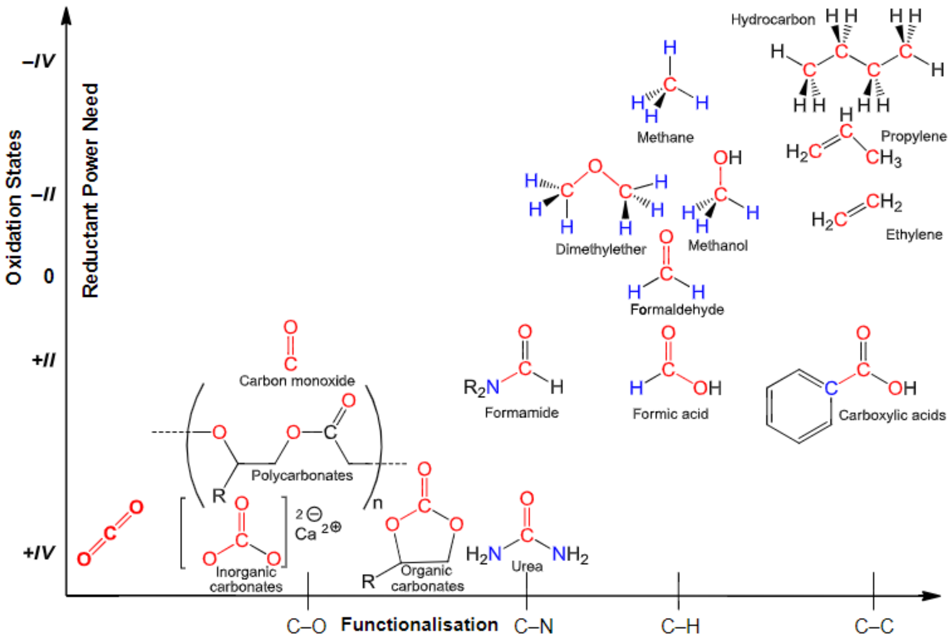


Figure 2.2: Products obtained from CO_2 Utilization with the possibility to modify both the oxidation state and functionalisation. [5]

In Figure 2.3 a potential projection of CO_2 conversion routes is illustrated for short, medium and long term solutions compared to what is being done today. It can be seen that the production of chemicals will account for a large part of CO_2 utilization. [6] So, CCU is an innovative and effective manner to produce valuable products and replace the process design they were produced.

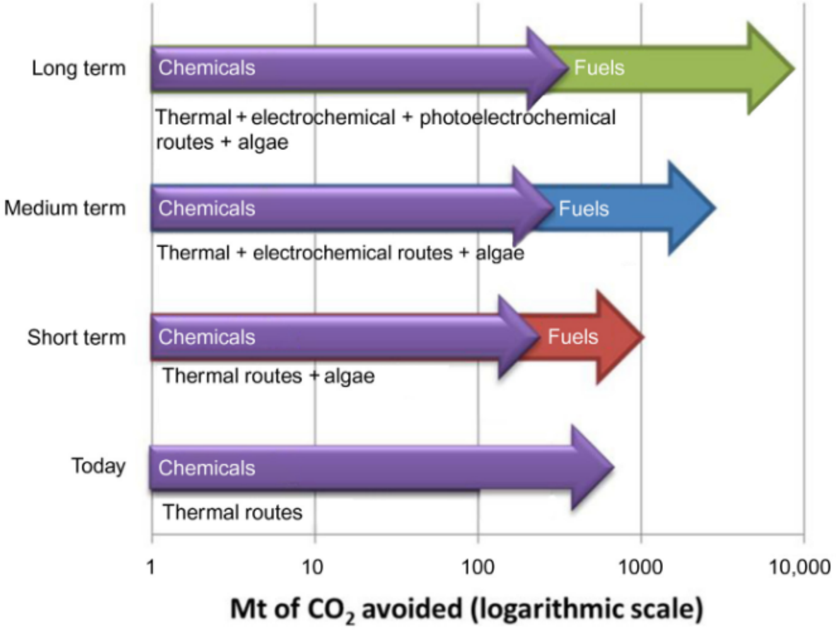


Figure 2.3: CO_2 avoided for different routes.[7]

Different routes of CO_2 utilization are investigated in this project, comparing different technologies and different valuable end-products. In order to have an overview of the opportunities, mapping is a necessary tool to examine each route towards end-products, as can be seen in Figure 2.4. Aqueous ammonia is examined as a capture solvent in this work, producing bicarbonate salts.

Thus, as base chemical for the different CO_2 utilization routes, ammonium bicarbonate NH_4HCO_3 is produced by a CO_2 capture reaction with an aqueous ammonia solution. In this term, an analysis of different options is investigated including ammonium formate $HCOONH_4$, formic acid $HCOOH$, formaldehyde $HCHO$, methanol CH_3OH, methyl formate CH_3COOH, ammonium oxalate $(NH_4)_2C_2O_4$, ammonium carbonate $(NH_4)_2CO_3$, ammonium oxide $(NH_4)_2O$, formamide $HCONH_2$, oxalic acid $C_2O_4H_2$ and oxamide $(CONH_2)_2$.

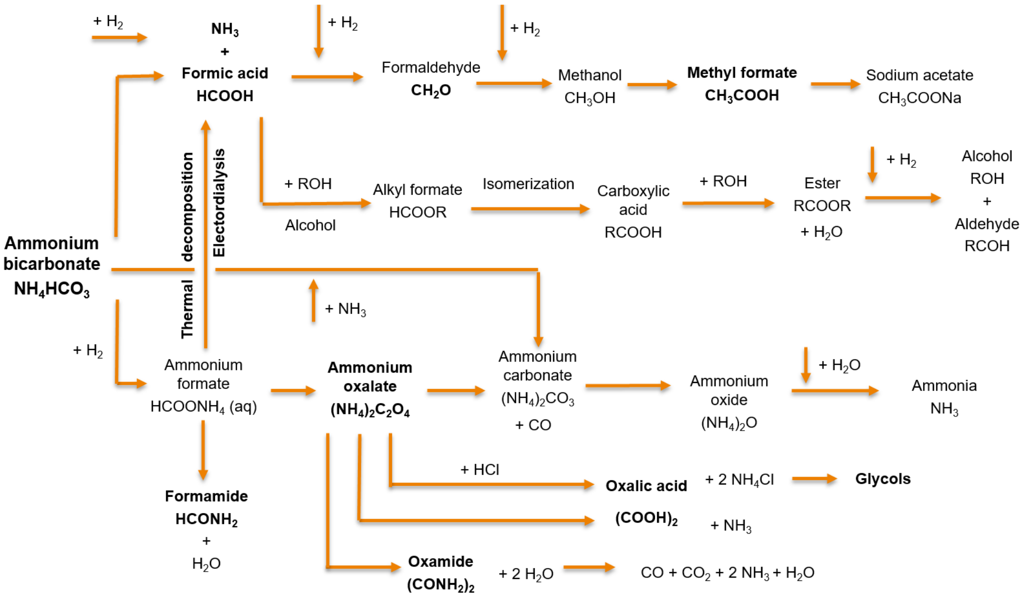


Figure 2.4: Mapping of different routes for valuable end-products.

Energy cost and market prices per kilogram of product are used for the comparison of alternative chemical routes. In Appendix A, market prices and some chemical properties of all the referred products are listed. In the following section a more detailed insight will be presented and after a thorough research on different options and step reactions the overall mapping of different selections can be seen in Figure 2.5.

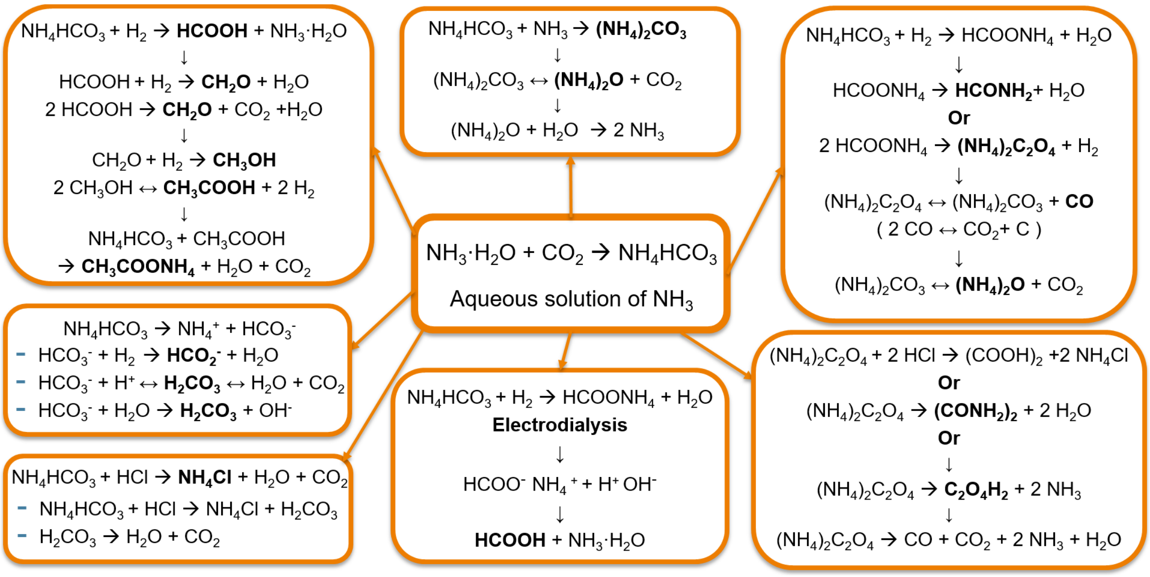


Figure 2.5: Mapping of reaction equations to valuable end-products.

In Figure 2.5 a more detailed mapping of variable products is depicted. Possible chemical reactions can be seen, highlighting the complexity for the selection due to high number of choices. Observing the Figures 2.4 and 2.5 it can be seen that a list of products is included for the further continuation of the research of this project. In this Chapter an overview of all the different end-products will be investigated, as far as properties, market place and field of application are concerned. Each and every product that participates in the step reactions is important to be investigated as for the technology involved for its production and regarding its economic perspective. It is clear that the chemical reaction paths are infinite and the final selection was determined also based on an existing research gap.

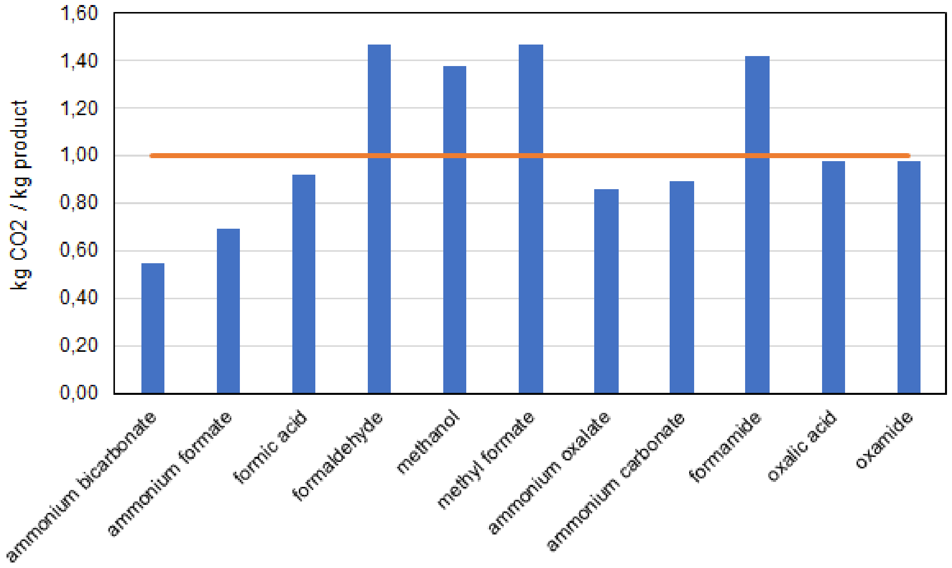


Figure 2.6: Amount of CO_2 required to produce a product, compared to unity.

Mass balances of each investigated step process is calculated. A fair comparison can be done in a base of CO_2 used to produce a certain product, taking into account all the participating reactions. In Figure 2.6 the kg of CO_2 used per kg of each product is illustrated and compared with the unity. It should be noted that ammonium formate, formic acid and ammonium oxalate can be considered as attractive paths for further processing.

2.1.1 Investigation of products - Market and range of applications

In this Chapter a comparison of all possible products is presented, regarding their market range and field of applications.

1. Ammonium formate

Ammonium formate is the ammonium salt of formic acid with chemical formula $HCOONH_4$. It is a white solid salt with a slight odor of ammonia and can be used as a buffer in High Performance Liquid Chromatography (HPLC) as well as with liquid chromatography-mass spectrometry (LC/MS). Additionally, a lot of issues appear with the use of urea solution and in this term there is value in replacing the aforementioned product with an alternative ammonia precursor compound like ammonium formate. Ammonium formate appears to be thermally stable, freeze at lower temperatures, with higher ammonia storage capacity and more selective decomposition.

From a health point of view, inhalation may cause nose and throat irritation and ingestion may cause mouth and stomach irritation. Concerning fire risks, toxic ammonia and formic acid as products of the salt may form in fire. [8]

2. Formic acid

Formic acid is a product widely used as textiles, natural rubber, leather processing, pharmaceutical and food industries. Also as a preservative and antibacterial agent in livestock feed. In addition, it can be used in agriculture and in the production of cosmetics, disinfectants, detergents and medicines. Market demand of formic acid can be characterized as small, around 579 kt in 2013, where 34% associated with animal feed, 32% for leather tanning and 13% of that for textile dyeing, as can be seen in Figure 2.7. [9] Additionally, almost 620 kton accounts for its global production in 2012, and gradually growing and expected to reach 760 kt in 2019 with an annual growth rate of 3.8 %.

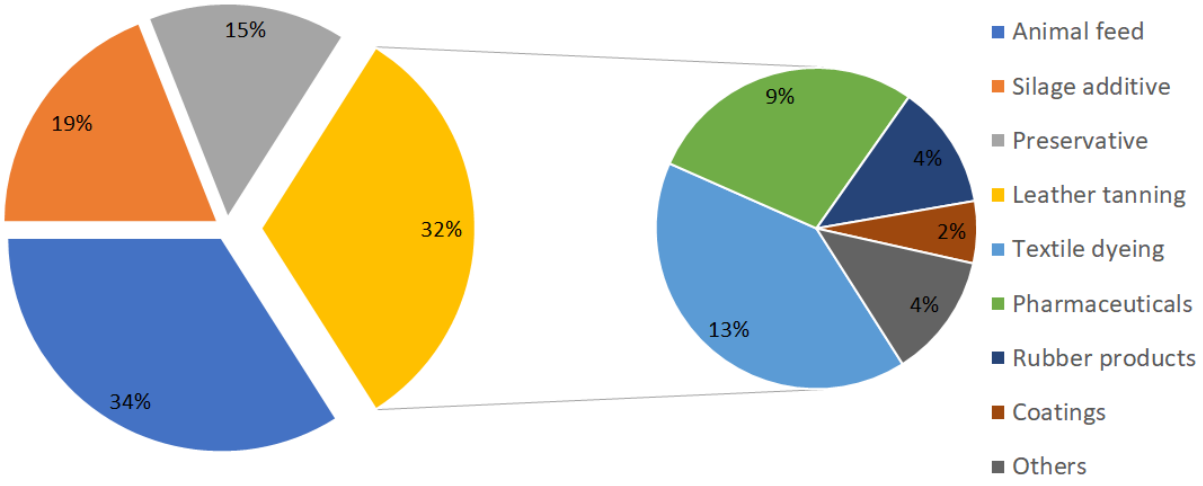
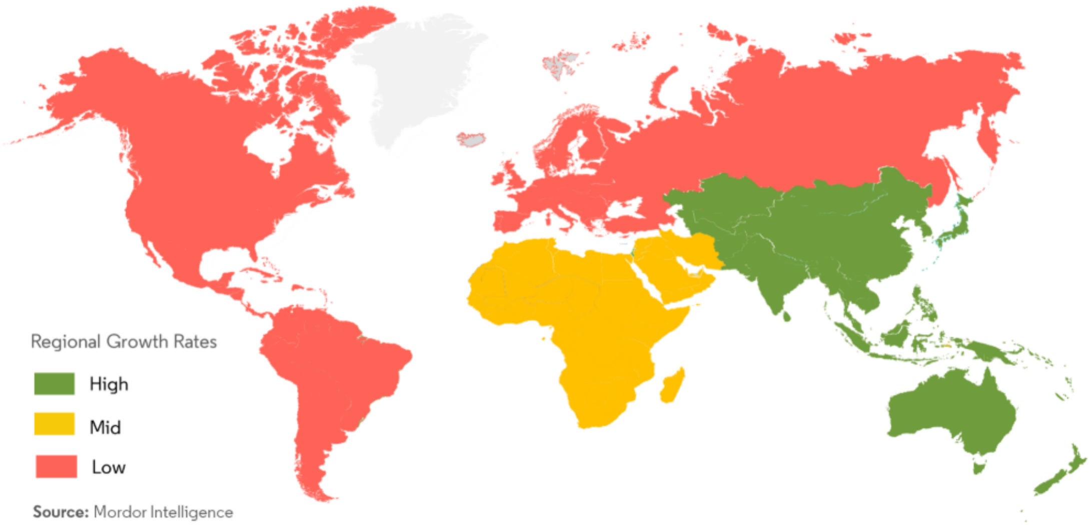


Figure 2.7: Market of formic acid.[10]

In Figure 2.8 the global market of formic acid per region is depicted. The Asia-Pacific area is dominant in the global market distribution with high growth rates. This region is expected to remain dominant, mainly due to animal feed and textile industries in countries like China and India.



Source: Mordor Intelligence

Figure 2.8: Formic Acid market - Growth Rate by Region, 2019-2024.[11]

In general, formic acid can be considered a valuable intermediate product that can be used for the production of other chemical products, whose market is larger and their demand is more attractive for the industry. Such products can be formaldehyde, methanol, carbon monoxide and methyl formate as can be seen in Figure 2.9.

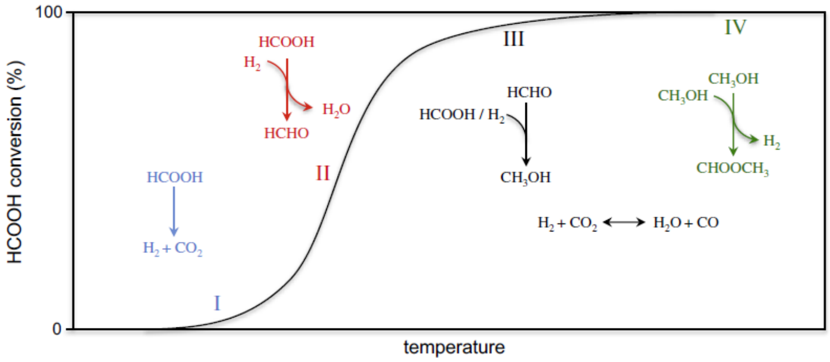


Figure 2.9: HCOOH conversion with respect to temperature. [12]

In the Figure above, an overall overview for reaction pathways to convert HCOOH to valuable products is illustrated, considering thermal decomposition of formic acid. Such a scheme illustrates the different reactions occurring at different ranges of conversion in accordance to reaction temperatures. So, at low formic acid conversion only dehydrogenation takes place towards the production of CO_2 (I). For higher and intermediate conversion rates, the production of formaldehyde takes place simultaneously with the consumption of hydrogen (II).

At full conversion of formic acid and higher temperatures, methanol is produced (III) and selectivity towards formaldehyde decreases. Finally, at a higher temperature and still at high conversion rates, the catalyst surface has no longer formic acid. Thus, other side reactions take place such as the dehydrogenation of methanol towards the production of methyl formate (IV), according to the following equation:

$$2CH_3OH \Longrightarrow CHOOCH_3 + 2H_2 \tag{2.1}$$

Table 2.1: Physical and chemical properties of organic acids compared to formic acid. [13]

Acid	Formula	pKa	g/mol	mol/kg
Formic	HCOOH	3.75	46	21.7
Acetic	CH_3COOH	4.75	60	16.7
Propionic	CH_3CH_2COOH	4.87	74	13.5
Butytric	$CH_3CH_2CH_2COOH$	4.82	88	11.7
Lactic	$CH_3CHOHCOOH$	3.86	90	11.1
Benzoic	C_6H_5OH	4.19	122	8.2
Citric	$CH_2(COOH)COH(COOH)CH_2(COOH)$	3.08	192	5.2

In Table 2.1 a comparison of organic acids with formic acid is presented, considering their pK_a values, their molecular weight and density. Formic acid is the simplest organic acid, since its R-group (R-COOH) is a hydrogen atom. Formic acid has a lot of advantages including the lowest molecular weight and the greatest molecular density. Thus, it can be concluded that it can result in the formation of greater concentration of active ingredient within the same formulation space. [13]

3. Formaldehyde

Formaldehyde can be considered a versatile and vital chemical compound, manufactured on an industrial scale and is been used in a wide range of applications in large scale industrial processes. It is used in the production of industrial resins and in textile industry as finisher to make fabrics crease-resistant. Additionally, formaldehyde resins have high chemical and heat resistances, making them appropriate materials both for automotive and airplane parts. Formaldehyde is also used as an intermediate product for the production of other chemicals, playing an important role on coating and plastics. [14]

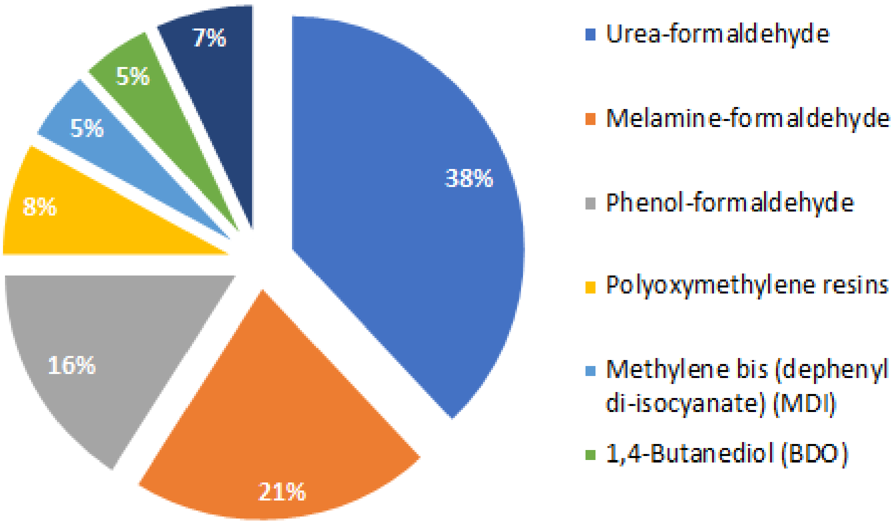


Figure 2.10: Application of formaldehyde in production of chemicals. [15]

Methanal (formaldehyde) is typically used in aqueous solution of 37 % wt, named as formalin. In Figure 2.10 the various uses of methanal for the production of methanal resins can be seen where the major uses correspond to urea, melamine and phenol production. The annual production of formaldehyde worldwide for 2012 was about 41 million tonnes and it is expected to be gradually growing up to 55 million tonnes in 2019. [16]

4. Methanol

Methanol is the simplest alcohol and typically produced by hydrogenation of CO on an industrial scale. Methanol has a wide range of applications and can be used to produce heavy chemicals, fuels for vehicles. Also used as an energy carrier, since it can be much easier to store such a liquid compared to hydrogen and natural gas.

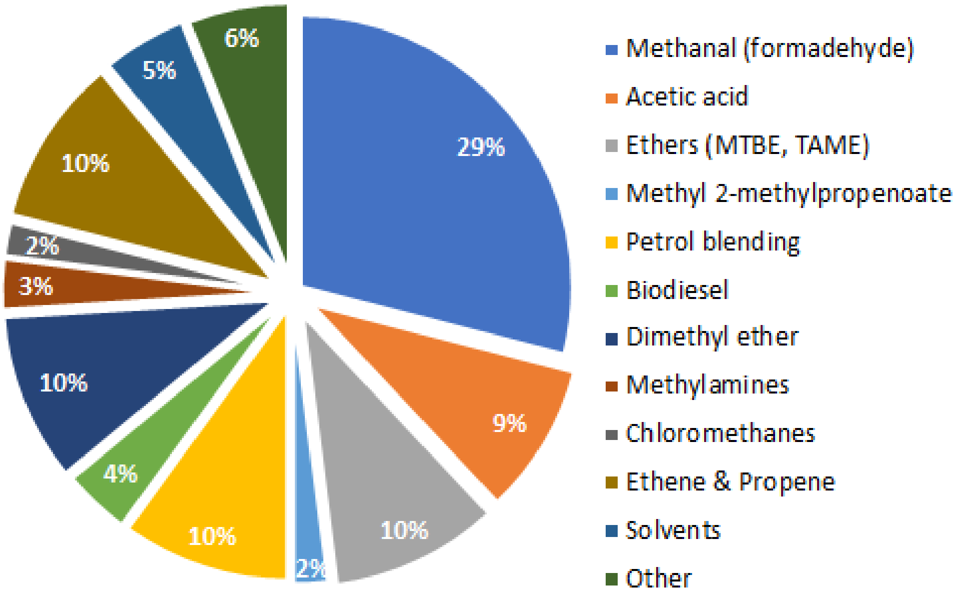


Figure 2.11: Uses of methanol. [17]

In Figure 2.11 all the different uses of methanol are illustrated, where the largest part corresponds to feedstock for the plastic industry. Based on that, methanol is used to make methanal that has application in a variety of plastics as discussed in the above paragraph concerning the uses of formaldehyde.

As for its production, in 2016 it accounts for about 80 million tonnes and expected to grow up to 100 million tonnes in 2020. [18]

5. Methyl formate

Methyl formate is mainly used for the production of formamide, dimethylformamide and formic acid. Such chemicals are vital for the further production of other useful end products. Additionally, methyl formate is used for the manufacture of chemical derivatives, as a blowing agent for foams and as an agricultural fumigant. Methyl formate has zero global warming potential and can also be used as a pesticide. [19]

6. Ammonium oxalate

Ammonium oxalate is the salt of oxalic acid and ammonium, is typically used for the determination of metal concentration and can effectively be used as a buffering reagent. Ammonium oxalate is used in blood testing, for the prevention of coagulation of plasma. Additionally, it is applied for the manufacture of explosive and polishing substances. [20]

7. Ammonium carbonate

Ammonium carbonate is widely known as baker's ammonia and is used as water softener, food processing aid, pH modifier, swimming pool chemical and electrolyte. Also in the manufacture of glass, paper, soaps and detergents. Moreover, ammonium carbonate can be used as an active and emetic ingredient in syrups relieving some of the symptoms of bronchitis and also as an ingredient for smokeless tobacco products. [21]

8. Formamide

Formamide is a chemical compound also known as methanamide, an amide originated from formic acid. Typically used in biochemistry and molecular biology. It is used as a chemical feedstock in large scale applications for manufacturing sulfa drugs, pharmaceuticals, herbicides, pesticides and for the production of hydrocyanic acid. It is also used as a softener for paper and fiber as well as a solvent for ionic compounds, for resins and plasticizers. [22]

9. Oxalic acid

Oxalic acid can be found in a various number of vegetables, such as potatoes, cucumbers and brocolli. However, topical or oral application for humans can be highly toxic because of its corrosive properties. The aforementioned properties turn out to be very useful for waste water applications, thus oxalic acid is widely used in such applications as well as in cleaning products. More particularly oxalic acid can be used as mordant in dyeing processes, in bleaches especially for pulpwood, in baking soda and as a third reagent in silica analysis instruments. [23]

10. Oxamide

The diamide of oxalic acid, or oxamide, can have many applications in the chemistry field both as a finished product and as an intermediate product. It is commonly used in agriculture as a slow-release fertilizer, as an additive for fodder, as a stabilizer and as an intermediate product for several other end-products like diacetyl-oxamide, used in the field of detergents. Oxamide is mainly made from the hydrolysis of cyanogen in an acetic medium, releasing nitrogen slowly and so is used as a slow-release fertilizer. Oxamide is a white crystalline, a non-hygroscopic fertilizer containing about 32% of nitrogen and most of it is insoluble in water at 25°C. [24]

In this project the thermal decomposition of ammonium oxalate is investigated according to the following reaction:

$$(NH_4)_2C_2O_4 \Longrightarrow (CONH_2)_2 + H_2O \tag{2.2}$$

Based on very poor and not recent literature, the aforementioned reaction was tested at 130°C resulting in low temperature thermal decomposition based on the proton transfer mechanism. [25], [26]
During this thesis project numerous experimental trials were conducted without any success on the precipitated desired end product. No recent literature turned out to be helpful, so this specific route was not investigated further.

2.2 Selection of investigated route

In Appendix A an overall listing of the alternative products that can be accomplished are illustrated, along with their properties including their enthalpy of formation, their solubility in water and their price per tonne.

Taking into account all the above information it is clear that the comparison of a specific route is complex and not straight forward, since multiple factors are important for their evaluation. Thus, the decisive parameter for the determination of the examined route is the research gap of such a system. To begin with, the initial step of absorption can be considered as a base for the system. More specifically, the flue gas is inserted in the system along with the ammonia-based solvent towards the production of ammonium bicarbonate. Further to the process, high-pressure hydrogen enters for the hydrogenation of bicarbonate to formate. Thermal decomposition of the latter results to the formation of formic acid and ammonia.

In the following Chapters the aforementioned chemical reaction steps will be translated to reactors and operating blocks. Along with the simulation part, an experimental proof of concept is included, further establishing the system. For the overall evaluation of the integrated system a techno-economic analysis is presented including all capital, operating, utilities and feed costs.

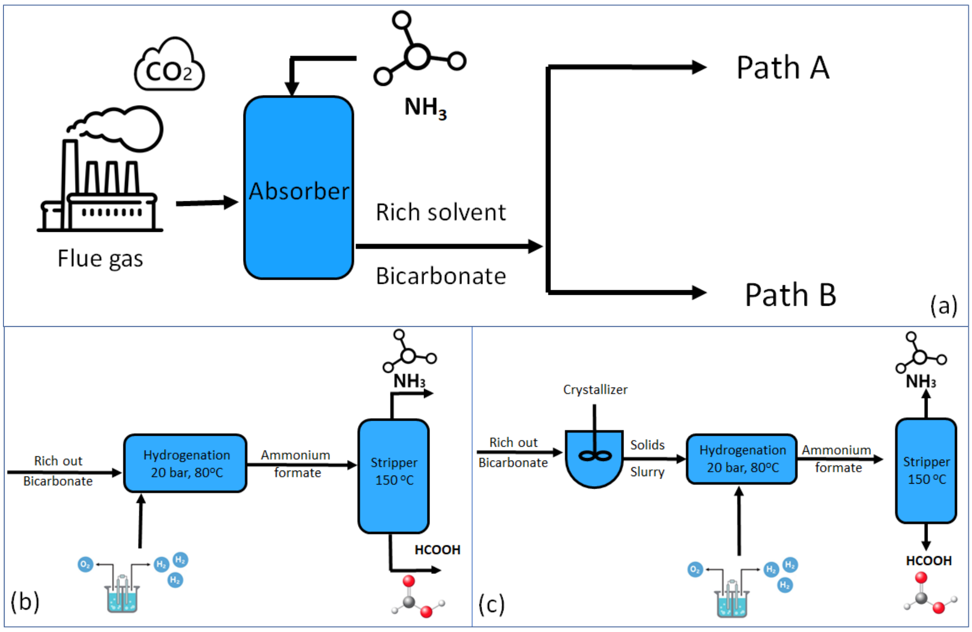


Figure 2.12: Overall scheme of proposed systems.

In Figure 2.12 a representation of the proposed systems is depicted, where (a) is the absorption step, (b) Path A without a crystallizer and (c) the proposed system including a crystallizer.

2.3 Post-combustion CO_2 Capture Methods

CO_2 capture processes are established, thoroughly investigated and applied in energy intensive industries during the last decades. CO_2 can be captured in different steps of an industrial process in a power plant, as discussed in Chapter 1.1. More specifically, before or after combustion of a fuel and by oxy-fuel combustion. In this project post-combustion method is used with generally low driving force depending on the type of industry. There are various categories and technologies currently available in the market and are shortly described.

Membranes

Membranes with high selectivity can be efficiently used for the separation of gases taking advantage of differences in chemical or physical relations and properties of the gases. Typically, membranes are widely used for the separation of CO_2 and natural gas. Membranes gather a lot of advantages, such as the lack of moving parts, no regeneration energy, compared to amines. As for disadvantages, membranes need a higher driving force. [27]

Adsorption

The method of adsorption incorporates a solid area that is used to separate CO_2 from a gas mixture. Widely used adsorbents are polymers, activated carbon and zeolites that are desorbed via regeneration. Adsorption of CO_2 at low pressures is not yet an economically established and mature technology to be used in conventional large scale applications. [28]

Physical Adsorption

Physical absorption is a process where flue gas enters the absorption column in a counter current configuration with the solvent. The rich out exiting, goes through a series of flash operation blocks at various pressures. Due to low driving force, physical absorption cannot be considered as an effective method, but it could be more effectively used in pre-combustion processes where driving force is much higher. [29]

Cryogenic process

In cryogenic processes high partial pressure of CO_2 is required, making this technology suitable for oxyfuel and pre-combustion capture processes. [29] In such a process, a series of steps are used to produce liquefied CO_2, namely compression, cooling, condensation and distillation.

Chemical absorption

Chemical absorption is the technology used in this project, where a flue gas stream enters an absorption column in counter current with a lean solvent solution. The rich solution enters a stripping column where CO_2 is stripped off from the CO_2 based on a thermal swing process. The absorption liquid that could contain amines, such as MEA. The main challenge of this technology is the regeneration of the solvent, which is highly energy intensive. [28] Amines are typically used but also ammonia has been experimentally demonstrated that could be an effective method for removing CO_2 from flue gas. In this project aqueous ammonia is used as a washing solvent .

Packed Absorbers

Packed absorption columns are typically used for CO_2 capturing processes and are suitable for large scale industrial applications. Such columns are based on counter current fashion and typically their packing material is either structured or random packing material. [30]

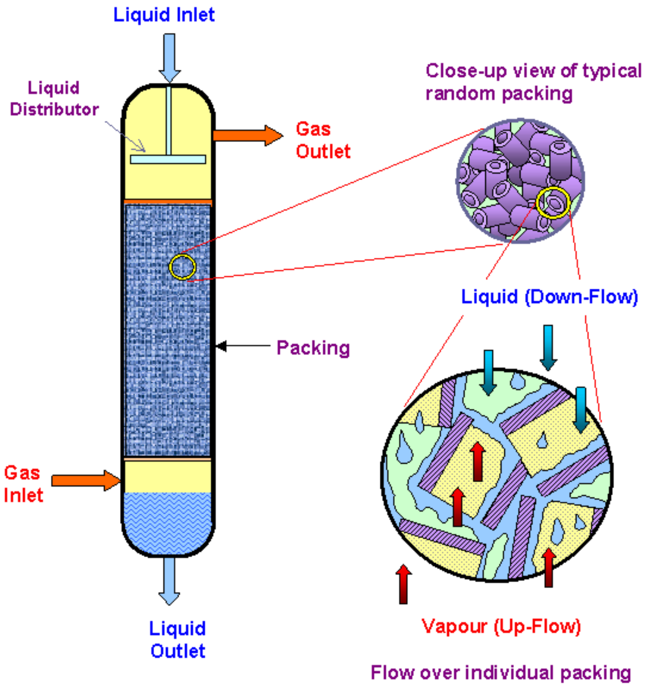


Figure 2.13: Scheme of packed absorber. [31]

In Figure 2.13 a representation of a packed absorption column is depicted, where all the gaseous and liquid inlets and outlets are illustrated. A zoom-in of the packed material is also presented, showing in detail the principle of the absorber with the relative contact of liquid and gas streams.

Membrane contactors

Membrane contactors are considered an innovative absorber configuration that is found to gather advantages and improvements in performance, compared to the conventional packed columns. [32] The main principle of the membrane contactors can be seen in Figure 2.14, where a microporous membrane is used as a non-selective barrier for the flue gas and the solvent.

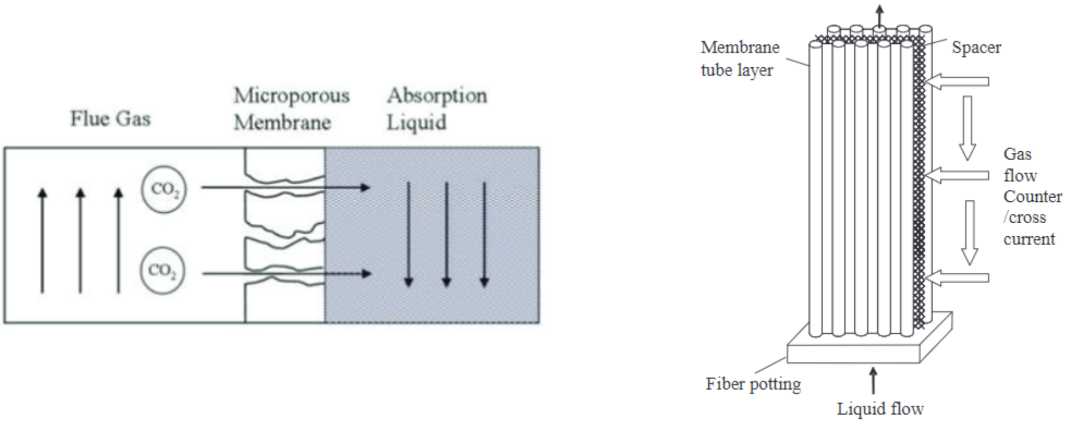


Figure 2.14: Membrane contactor principle.[32]

The main advantages of a membrane contactor are: no sensitivity to motion and higher surface area resulting to reduction of the size of the downstream equipment. Additionally, such a membrane between the gas and the liquid phase can effectively prevent phenomena such as flooding, channeling or foaming. [32] This is one main difference compared to typical packed absorbers, that could result to deterioration of the efficiency of such an operating block.

The overall scheme of the aforementioned types of absorbers is similar and can be considered as a design decision of the project, since the final desired outcome strongly depends on the performance and regeneration of the solvent used in the system. However, membrane contactors are not yet considered as mature technology and may lack mostly in experience in the field.

2.4 Ammonia as a solvent

Many studies and thorough investigation on various parameters have been conducted, especially for the mature technology of capture with amine solvents, but the disadvantages of the amine solvents promote the further research investigation of ammonia solvents. [33] MEA is typically used in capture systems and it is a mature and widely applied amine in existing capture plants.

On the other hand, ammonia as a solvent in a carbon capture process has many advantages when compared to amine based systems. [34] However, ammonia is a volatile compound and such a characteristic can be a disadvantage in conventional capture systems. It will be clear that ammonia as a solvent in this proposed system is wisely chosen and its high volatility turns out to be an advantage for the development of the integrated system that is to be examined in detail in the following Chapters. In Figure 2.15 the phase diagram of the compound is depicted. In such a diagram of temperature and pressure, the areas of phase changes are illustrated along with ammonia's critical point and triple point.

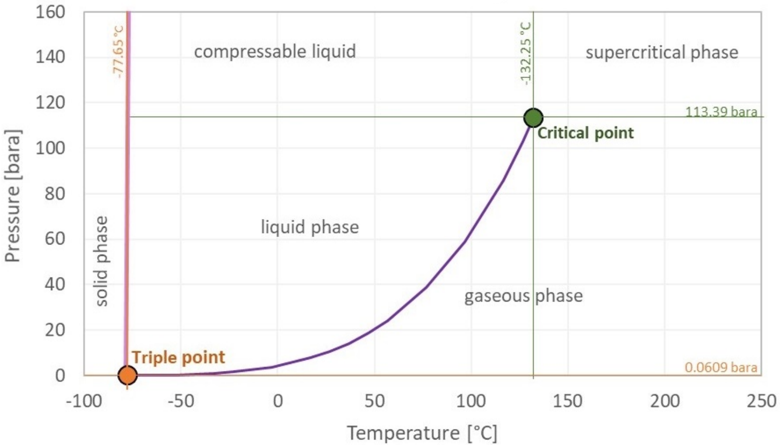


Figure 2.15: Phase diagram of ammonia. [35]

Lately, aqueous ammonia as a solvent in absorption columns drives a lot of attention and a lot of research work is conducted both in an experimental and process modelling point of view. A fair comparison can be conducted with a typically used benchmark solvent, monoethanolamine (MEA), and investigation of the research gap is done when compared to the case of ammonia. As far as ammonia is concerned, it is the simplest type of amine and has some attractive characteristics as lean solvent in the absorption and further utilization process:

- High availability and low cost of ammonia solvent
- High CO_2 capture capacity
- Less corrosive to instrument
- Chemically stable system

It should be noted that the volatility of ammonia is an important parameter that has been taken into consideration for the design of the capture system, despite its negative impact on conventional capture systems. In Figure 2.16 the vapor pressure development is illustrated with respect to ammonia concentration at 20°C. Extrapolating the data, an ammonia solution of 40 %wt results to a vapor pressure of 106.7 kPa and can be characterised as volatile.

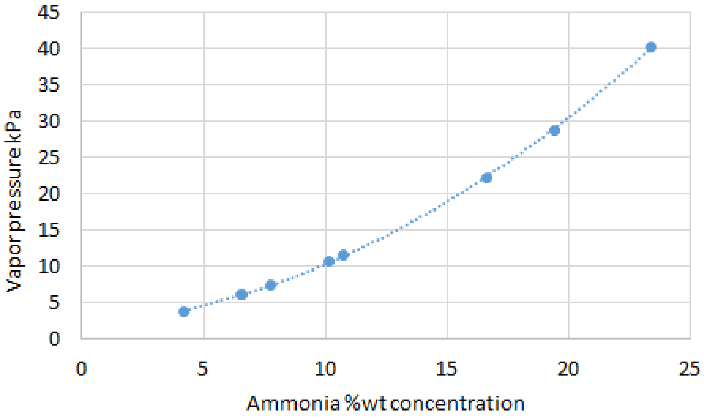


Figure 2.16: Vapor pressure of aqueous ammonia at 20°C.

An innovative aspect of the system is the high weight percentage of the ammonia solvent. A study investigated a concentration of ammonia at 28 wt%, which may imply some challenges due to the high level of ammonia losses. [36] In this project, a higher concentrated ammonia solvent is used, at around 40 wt%.

Ammonium bicarbonate is the main product exiting the absorption column. This product itself can be used as a fertilizer and also used for the production of valuable end-products, such as formic acid. Taking into consideration all the above about NH_3 as a capture solvent, the model that is developed for this work is explained in detail with all the necessary assumptions. In Figure 2.17 the fraction of carbonic acid can be seen at low pH levels. At non-acidic pH values, the CO_2 and water equilibrium may shifts towards the formation of bicarbonate and at even higher pH values to carbonate.

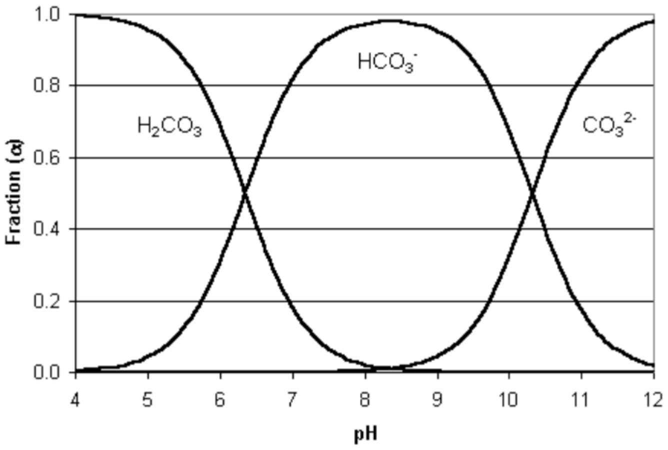


Figure 2.17: Fractions of carbonic acid, bicarbonate and carbonate ions at different pH values.[37]

As far as the solid formation is concerned, CO_2/NH_3 ratio in carbonate is 0.5, while in bicarbonate is 1. From the above it can be concluded that bicarbonate is a much more efficient chemical compound for CO_2 absorption and CO_2 carrier.

The absorption rate of CO_2 is dependent on various parameters, such as ammonia and flue gas concentration, pH value and inlet's temperature. With higher ammonia concentration and lower CO_2 concentration the absorption rate of CO_2 decreases. This can also be seen in Figure 2.17 showing the carbonate dissociation, where the best pH value is illustrated. At pH values 7-9, the main product out of the absorber is bicarbonate, while at higher pH values the carbonate is the main product. At lower pH values 4-6 the production of carbonic acid is dominant. At ammonia mole of 0.5 and pH=9.5, the conditions facilitating the production of bicarbonates as indicated in various studies, as can be seen in Figure 2.18. [38]

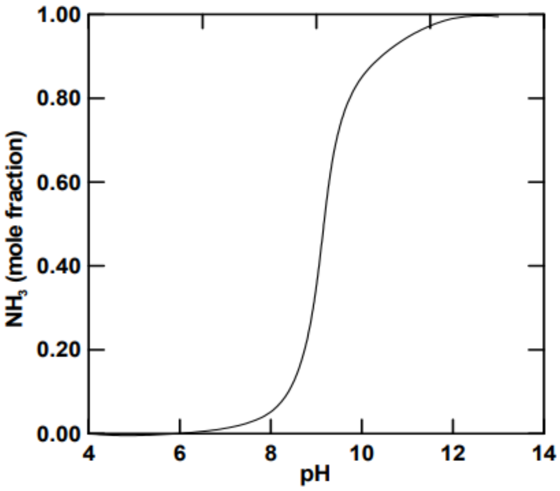


Figure 2.18: pH value as a function of ammonia molar fraction. [38]

2.5 Ammonia losses

Ammonia is a volatile compound indicating a high percentage of loss in the gaseous top outlet of the absorber. There are various methods for the minimization of such losses: [39]

- **Introduction of an aqueous ammonia solvent in lower mass concentration.** This is an effective way to decrease ammonia slip, but it opposes the innovative part of the study which is a more concentrated ammonia solvent for more concentrated ammonium bicarbonate in the outlet bottom of the absorber.
- **Lower operating temperature.** The operating temperature of the absorber is mainly dependent on the temperature of the ammonia solvent, since the flue gas temperature is not affecting the outlet liquid products. A temperature range of 5-40°C is proposed and most preferably of 5-20°C, limiting the ammonia slip in the gaseous outlet. However, a lower temperature leads to the precipitation of ammonium bicarbonate and this should be taken into consideration. A higher L/G ratio (liquid to gas) is promoted around 2, in order to avoid solid formation inside the absorber.
- **Higher absorption pressure.** This method inhibits high energy costs associated with the preprocessing of the feeds. More specifically, higher solvent mass flow is required and higher heat requirements. Additionally, energy needs for the mechanical compression of the flue gas are critical.

The amount of ammonia evaporating out of the absorber is significant and needs to be taken into consideration. Minimization of these losses and maximization of the concentration of ammonium bicarbonate, influences the final purity of formic acid. Literature showed that ammonia slip depends slightly on the ammonia concentration in the range of high solvent concentrations 28-40 %, but it mostly is dependent on the operating temperature.

2.6 Crystallization system

The system of capturing CO_2 uses an absorber with a flue gas and ammonia temperature low temperatures, preventing precipitation issues that would lead to severe maintenance problems and additional costs. The formation of precipitating ammonium bicarbonate is minimized with methods, as presented in the previous paragraphs. Nevertheless, solid formation downstream to the absorber could turn out to be advantageous for the proposed system. The high concentration of ammonia promotes many disadvantages and challenges namely the higher rate of precipitate bicarbonate. For this case a whole different strategy is to be followed, without precipitation inside the absorber, but with crystal formation downstream to it. [40]

A high liquid ammonium bicarbonate is preferred. So, crystallization of the outlet of the absorber is examined. The solid formation results to a more advantageous system: [41], [42]

- Minimization of ammonia slip in the absorber
- A more concentrated desired product and separation from the remaining liquid part. This leads to more concentrated stream of ammonium bicarbonate

The overall scheme of the advanced capturing system is the same including the absorption column, adding the crystallizer after the absorber. From an engineering perspective, handling solids in a packed column is challenging and costly. Thus, the precipitation in the rich solution is limited to a crystallizer downstream of the absorber, as can be seen in Figure 2.19. The main concept of such a system is the reduction in mass flow of the rich out, so the solid part exiting the crystallizer is afterwards separated via a cyclone, a solid separator. [43] The separated slurry enters a dissolution reactor and is regenerating.

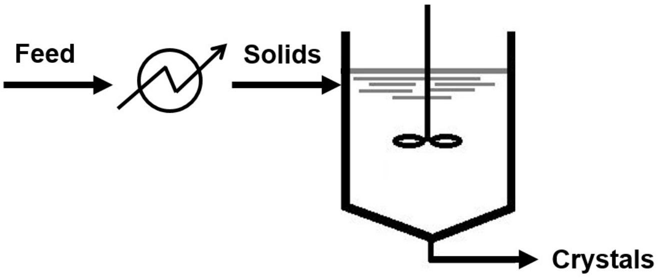


Figure 2.19: Crystallizer overview. [41]

An important parameter is the temperature of the rich out stream, that needs to be cooled down to 5°C for the easier formation of solid ammonium bicarbonate. [44] Crystallization is used as a purification step as well as for recovery of solid materials. [45] In this work, crystallization is used for the handling of solids that are formed within the system. In this way, even higher bicarbonate concentration can be conducted, since there is further separation of the solid compound out of the liquids.

2.7 Ammonium bicarbonate to ammonium formate

Formates can be considered as effective hydrogen storage carriers according to recent studies. One main aspect for hydrogen storage is the volumetric density of the formate which depends mainly on the solubility of the salt in water. Thus, ammonium formate has such an advantage on that term due to its high solubility even at room temperature. Recent study has shown that the produced ammonium formate can be effectively used in a H_2 battery with much higher volumetric energy compared to the diatomic hydrogen. [46]

The transformation of CO_2 to more valuable products is the main goal of this research. Formic acid can be considered quite an attractive option, however direct hydrogenation of CO_2 to formic acid is not thermodynamically favorable. [47] Thus, a base additive as an intermediate reaction step can be used to overcome this boundary and in this work the hydrogenation of ammonium bicarbonate is to be investigated.

$$CO_2(g) + H_2(g) \Longrightarrow HCOOH(l) \qquad \Delta G^o_{298K} = 32.9kJ \cdot mol^{-1} \tag{2.3}$$

The investigation of the reduction of bicarbonate to formate is of great research interest, connecting inorganic and organic chemistry, according to the following equation:

$$HCO_3^- + H_2 \Longrightarrow HCOO^- + H_2O \tag{2.4}$$

Indeed, the use of pressurized hydrogen is an important aspect of the system in order to result to high product yields. A promising study has a 74.7% formate yield with test conditions of 23h at 70°C and 60 atm of hydrogen inlet. [48] Mild conditions of atmospheric hydrogen pressure, can also lead to a 50% conversion. The use of heterogeneous catalysts is advantageous, since it provides ease of handling, separation and recovery in the system. Several studies have investigated the hydrogenation of bicarbonates towards formates with the use of pressurized hydrogen with metal catalysts. [49] The most common and widely used catalysts are Nickel and Palladium.

Hydrogenation of bicarbonate is much easier, while that of carbonates can be limiting towards the reaction rate. [46] Various studies promoted the efficient hydrogenation of bicarbonates towtoards high yield of formates, especially in the case of ammonium. [50] The reaction may shift either to the production of carbonate or bicarbonate depending on the pH value. Thus, decreasing the pH the reaction shifts towards bicarbonates decreasing the yield of carbonates, as was investigated by several studies. [46] In general, the main conditions that determine the final formate yield are the pressure of the initial H_2, temperature and residence time.

In this work, the hydrogenation of ammonium bicarbonate is indeed an important part of the research, since with ammonium bicarbonate as a starting reactant, ammonium formate can be produced. Then further thermal decomposition can result in the production of formic acid and evaporation and separation of ammonia out of the system. In Table 2.2 the basic characteristics and properties of the participating compounds are presented, including solubility levels and boiling points of the chemicals.

Table 2.2: Characteristics of reactant and products of reaction to formic acid.

	NH_4HCO_3	**$HCOONH_4$**	**HCOOH**	**NH_3**
Molar mass [g/mol]	79	63	46	17
Solubility in water [g/L]	119 (0 °C) 216 (20 °C) 248 (25 °C) 366 (40 °C)	102 (0 °C) 143 (20 °C) 202 (40 °C) 516 (80 °C)	1000 miscible	900 (0 °C) 550 (20 °C) 300 (40 °C) 150 (60 °C)
Boiling point [°C]		180	100.8	-33.34
Melting point [°C]	41.9	116	8.4	-77.73

There are a number of parameters that need to be taken into account for the design of such a reactor, some of them are:

- Catalyst
- Hydrogen pressure
- Temperature
- Reaction time

The above are only a number of parameters that were taken into consideration. To begin with, the selection of a catalyst can be an important aspect of the system. In Table 2.3 a brief comparison of homogeneous over heterogeneous catalysts is presented, indicating the advantages of the latter.

Table 2.3: Comparison of catalysts

Homogeneous catalysts	**Heterogeneous catalysts**
Popular and widely known	Easier to separate
Catalyst recovery still challenging	Easily recovered
Lower cost	High conversion and high cost

2.8 Ammonium formate to formic acid and ammonia

Thermal decomposition of ammonium formate results to the formation of formic acid and ammonia based on the chemical reaction:

$$HCOONH_4 \Longrightarrow HCOOH + NH_3 \tag{2.5}$$

Stripping can be accomplished either in a packed, in a trayed column, a spray tower or a bubble column, as can be seen in Figure 2.20. Such configurations are effectively used in industrial scale both as absorption as well as stripping columns. In this work, a trayed stripping column is assumed due to its scalability. In the system of the stripping column, there are widely used stripping agents. The most common are:

- steam
- air
- inert gases
- hydrocarbon gases

At this point, it should be noted that the level of recovery depends highly on the volatility of the organic compound, in this case of ammonia. This is the main advantage of the overall conceptual design of this particular proposed system along with the use of aqueous ammonia as absorption solvent. This property of ammonia is its basic feature, enabling and promoting the further processing and utilization of CO_2 towards the production of a valuable end-product.

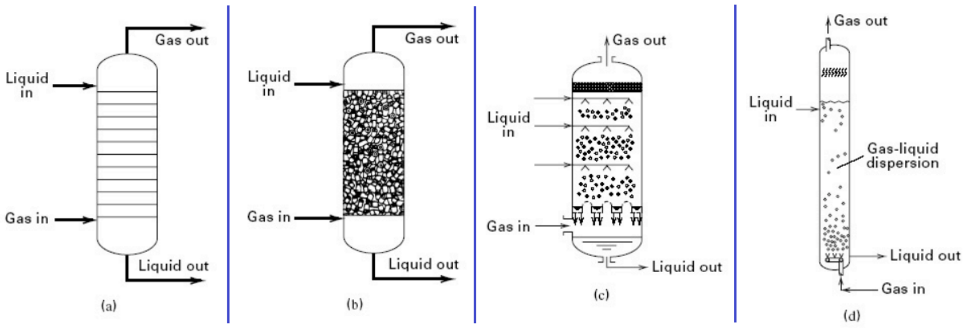


Figure 2.20: Type of industrial absorbers and strippers: (a) trayed tower, (b) packed column, (c) spray tower, (d) bubble column. [51]

The vapor pressure of water and formic acid can be seen in Figure 2.21 for a wide range of temperature values, since thermal decomposition occurs at elevated temperatures, in a range of 120-150°C. Similar volatilities of the referred compounds, leads to a challenging separation. Higher temperature is not promoted for such a reaction, since ammonium formate may produce other products, like CO_2 or CO or worse decarbonization and formation of carbon.

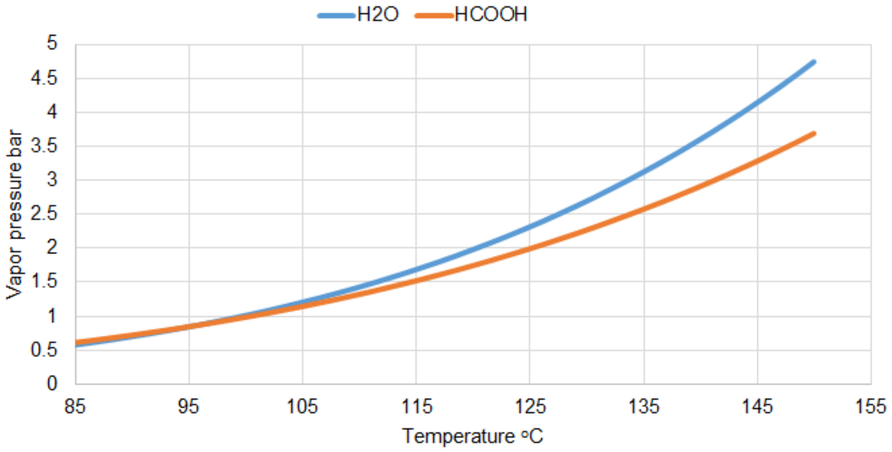


Figure 2.21: Vapor pressure of water and formic acid. [52]

High temperature is required for this reaction so that decomposition occurs, in a temperature range of 120-150°C. As can be seen in Figure 2.21 water and formic acid have similar behavior as far as vapor pressure is concerned. At the examined temperature ranges water appears to be more volatile. For the efficient separation of the compounds the appropriate pressure level should be defined, both for water and formic acid to remain in liquid state and not evaporate out of the top of the stripper. Combinations of pressure and temperature levels are presented in Table 2.4, for the effective separation of aqueous solution of formic acid from ammonia solution. The above conditions should be taken into consideration to prevent evaporation of formic acid along with ammonia in the top outlet of the stripper.

Table 2.4: Operating conditions of the stripper.

Temperature	Pressure	Temperature	Pressure
115 °C	2 bar	135 °C	3.5 bar
120 °C	2.3 bar	140 °C	4 bar
125 °C	2.5 bar	145 °C	4.5 bar
130 °C	3 bar	150 °C	5 bar

As an initial sign for the separation of ammonia from formic acid HCOOH, the measurement of pH can be a fair indication. In Table 2.5 the dissociation constants of formic acid are presented for the general reaction of ionization of formic acid:

$$HCOOH + H_2O \Longrightarrow H_3O^+ + HCOO^- \tag{2.6}$$

Its values are at a range of 2-3.2 and pH value can be determined based on the following equation, taking into account K_a of formic acid.

Table 2.5: Values of dissociation constants and acid strength.

K_a	pK_a	K_b	pK_b
$1.78 \cdot 10^{-4}$	3.75	$5.6 \cdot 10^{-11}$	10.25

$$K = \frac{[H_3O^+] \cdot [HCOO^-]}{[H_2O] \cdot [HCOOH]} \Longrightarrow K_a = K \cdot [H_2O] = \frac{[H_3O^+] \cdot [HCOO^-]}{[HCOOH]} \quad , pH = -log_{10}[H_3O^+] \tag{2.7}$$

2.9 Formic Acid to Formaldehyde

Formaldehyde is industrially produced via the oxidation of methanol at high temperatures of 600°C. [53]

$$CH_3OH + \frac{1}{2}O_2 \Longrightarrow HCHO + H_2O \tag{2.8}$$

Alternatively, a further step in the overall integrated system is the conversion of formic acid to the production of formaldehyde via hydrogenation reaction:

$$HCOOH + H_2 \Longrightarrow HCHO + H_2O \tag{2.9}$$

For this work, formic acid reacts over a metal oxide catalyst. The hydrogenation reaction takes place at mild conditions and is temperature sensitive. Both TeO_2 and CeO_2 as catalysts indicate a high selectivity towards formaldehyde production. Also metal catalysts show high selectivity like Pd catalyst. [54] For a more sustainable approach on the process design, water electrolysis can be used to derive the required hydrogen.

Chapter 3

Method - Simulation and Experiments

In this Chapter, all the reaction steps that take place in the overall system are investigated thoroughly. For each one of them, an experimental proof of concept is included, namely the hydrogenation of ammonium bicarbonate, the separation of ammonium formate to formic acid and ammonia and the hydrogenation of formic acid to formaldehyde.

The capturing process of CO_2 from flue gas with the use of an aqueous ammonia solvent will be examined, at relatively low operating temperatures. In this system, CO_2 is captured in ammonia solution producing ammonium salts, mainly ammonium bicarbonate. As an innovative added value, a higher concentration of ammonia is used of 40 wt%, compared to standard similar systems where aqueous solutions of ammonia of 10-15 wt% are used. [55] In the absorption system, a looping of ammonia solvent is used to minimize ammonia losses from the top of the absorber as outlet gas.

3.1 Modelling of absorber

In this section, modelling of the absorption column is used for the NH_3-CO_2-H_2O in order to calculate with accuracy the solid-liquid-vapor (SLV) equilibrium of the system. In this work, all the participating ionic reactions of the CO_2-NH_3-H_2O system are investigated and analyzed in detail with a focus on the solid formation of ammonium bicarbonate. The formation of such a solid intermediate product in an operating block is of crucial importance, since the solid production may lead to undesired phenomena, such as clogging and high maintenance costs or even worse plant shutdown. [4] In Table 3.1 the inlet conditions of the absorption column are presented.

Table 3.1: Inlet operating conditions.

Flue gas temperature	10 °C	**Flue gas flow rate**	12.5 tn/h
Lean solution temperature	10 °C	**Lean solution flow rate**	25 tn/h
Concentration of CO_2	6 % v/v	**Concentration of NH_3**	40 % wt

For the process modelling, Aspen Plus ® V10.0 is used, to simulate the integrated system of CO_2 capture and Utilization. For the precise simulation of the absorber of the system a rate-based system is simulated, by using ionic reaction as well as precipitating reactions. For the modelling of the capturing process, the definition of the equilibrium constants K_s need to be defined for the different reactions that take place in the absorber depending on the temperature and according to the following formula:

$$lnK_s = A + \frac{B}{T} + C \cdot lnT + D \cdot T \tag{3.1}$$

As far as the kinetic reactions are concerned, data for the pre-exponential factor and the activation energy were used for the determination of the kinetic factor according to the following formula:

$$K_{eq} = k \cdot exp(-E/R \cdot T) \tag{3.2}$$

The most commonly used model for the simulation of a rate-based absorber is the Electrolyte NRTL method for the properties in liquid phase and RK equation for the vapor phase. In Table 3.2 all the involved reactions in the capturing system are presented along with their equilibrium constants.

Table 3.2: Fitting parameters for the equilibrium constant K_s for the reactions involved in the capturing process. [56]

Equilibrium reactions

No.	**Chemical Reaction**	**A**	**B**	**C**	**B**
1	$CO_2 + 2H_2O \Longleftrightarrow H_3O^+ + HCO_3^-$	231.47	-12092.7	-36.78	0
2	$HCO_3^- + H_2O \Longleftrightarrow H_3O^+ + CO_3^{-2}$	216.05	-1243.7	-35.48	0
3	$NH_3 + HCO_3^- \Longleftrightarrow NH_2COO^- + H_2O$	-4.5834	2900	0	0
4	$NH_3 + H_2O \Longleftrightarrow NH_4^+ + OH^-$	-1,2566	-3335,7	1,4971	-0,0370566
5	$2H_2O \Longleftrightarrow H_3O^+ + OH^-$	132,899	-13445,9	-22,4773	0

Kinetic Reactions

No.	**Chemical Reaction**	**k**	**E [cal/mol]**
1	$HCO_3^- \Longrightarrow CO_2 + OH^-$	2.38 e+17	29451
2	$CO_2 + OH^- \Longrightarrow HCO_3^-$	4.32 e+13	13249
3	$NH_3 + CO_2 + H_2O \Longleftrightarrow NH_2COO^- + H_3O^+$	1.35 e+11	11585
4	$NH_2COO^- + H_3O^+ \Longleftrightarrow NH_3 + CO_2 + H_2O$	4.75 e+20	16529

Salt Reactions

No.	**Chemical Reaction**	**A**	**B**	**C**	**B**
1	$NH_4HCO_3 \Longleftrightarrow NH_4^+ + HCO_3^-$	8.06448	-5013.76	0	0

Thus, depending on the temperature of the process, some of the reactions are more favourable compared to some others, resulting to the shifting of the reactions either to the products or reactants. [57] The parameters illustrated in Table 3.2 appear to have good fit with experiment data with R^2>0.99. [58]

In the model described above in Table 3.2 all the participating reactions were taken into account, including the formation of ammonium bicarbonate as the only solid compound. However, some other possible solid formation are ammonium carbonate $(NH_4)_2CO_2 \cdot H_2O$, ammonium carbamate NH_2COONH_4 and ammonium sesqui-carbonate $(NH_4)_2 \cdot 2\,NH_4HCO_3$ according to the following reactions:

$$NH_2COO^- + NH_4^+ \Longrightarrow NH_2COONH_4(s) \tag{3.3}$$

$$2NH_4^+ + CO_3^{2-} + H_2O \Longrightarrow (NH_4)_2CO_3 \cdot H_2O(s) \tag{3.4}$$

$$3NH_4^+ + CO_3^{2-} + HCO_3^- \Longrightarrow (NH_4)_2CO_3 \cdot NH_4HCO_3(s) \tag{3.5}$$

Based on literature, the formation of ammonium bicarbonate is the dominant solid formed in the outlet of the absorber. [59] Thus, for the conduction of simulation results only the formation of ammonium bicarbonate is taken into consideration in this work. Behind that assumption, there is an explanation. [60] Ammonia solvent absorbs CO_2 forming carbamic acid NH_2COOH that instantly looses its proton, forming carbamate NH_2COO^-. During the process of CO_2 capturing, there is change in the pH value and the equilibrium shifts and the carbamate results to the formation of ammonia and bicarbonate.

Simulation of absorption column

In this project aqueous ammonia is used in a temperature range of 2 to 10 °C, the so called Chilled Ammonia Process (CAP). In such levels there is reduced ammonia slip from the absorber, but at the same time this may facilitate precipitation of solid ammonium carbonate salts. Ammonium bicarbonate can precipitate at low temperatures and decomposes at elevated temperatures, which is an advantageous characteristic. [39] Also the ammonia losses coming out of the absorber are significant, thus a recovery system is designed to minimize these losses. [61] For the capturing of CO_2 a typical inlet flow of flue gas is used with 6% v/v of CO_2. The conditions of the absorber are shown in Table 3.3 as well as the resulting outlet of the aforementioned block.

Table 3.3: Conditions of the absorber for CO_2 capture with ammonia.

Calculation type	Rate-based absorber	**Packing type**	Packed MELLAPAK
Flow model	Mixed	**Number of stages**	10
Absorber diameter [m]	1.5	**Packing height [m]**	12

In an initial step, a simple flash was used as an operating block, being a simple representation of the system with no temperature difference throughout the absorber and not including kinetic reactions. A simple flash proposes a complete mixing of the phases and transport properties are assumed as a simple number, like efficiency. Therefore, a RadFrac is used instead as an absorption column. [62], [63] This RadFrac model requires a number of inputs, such as properties of the absorbent, dimensions of the column, packing type and column internals. The proposed system for CO_2 capture with concentrated ammonia includes an absorber represented as a RadFrac column.

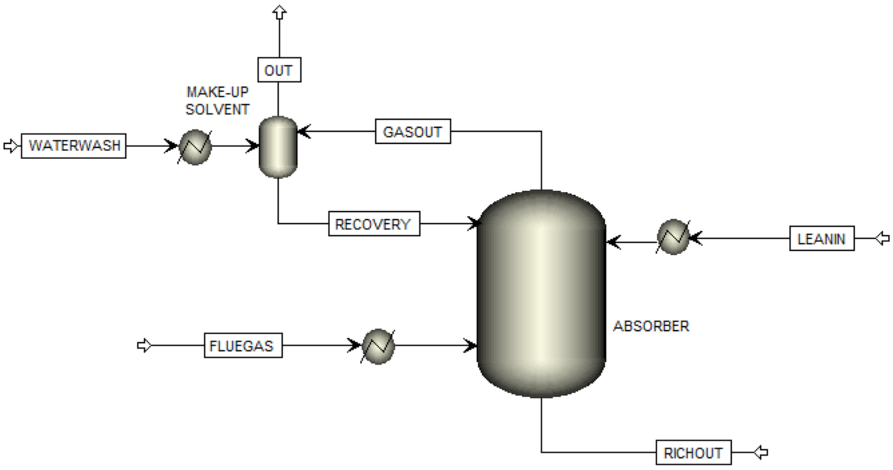


Figure 3.1: Representation of the absorber of the system.

In Figure 3.1 the scheme of the modelled absorber is illustrated, where FLUEGAS and LEANIN are the two inlets of the operating block, as can be seen in Table 4.1 and GASOUT and RICHOUT the respective outlets of the system. In the GASOUT a percentage of NH_3 is exiting the system. WATERWASH is the water wash used to dissolve ammonia and RECOVERY is the amount of aqueous ammonia inserted again back in the system. OUT represents the leftover ammonia that evaporates out of the system.

3.2 Hydrogenation of ammonium bicarbonate

The hydrogenation reaction is simulated in Aspen Plus ® V10.0 using a Plug Flow Reactor, taking into account the amount of catalyst that is necessary in this reaction, as seen in Figure 3.2. This hydrogenation is a slightly exothermic reaction and utilities for its execution is assumed to be minor. The results of the simulated reactor indicate an attractive route, since the amount of the formate $HCOO^-$ formed is higher than the amount of bicarbonate HCO_3^- used.

For the proof of concept, the hydrogenation of ammonium bicarbonate was investigated, where the inlet solution of ammonium bicarbonate is inserted to a pressurized reactor, leading to the formation of the aqueous solution of ammonium formate. Such a hydrogenation reaction is slightly exothermic, according to the following equation:

$$NH_4HCO_3 + H_2 \Longrightarrow HCOONH_4 + H_2O \qquad \Delta G^o_{298K} = 5.9kJ \cdot mol^{-1} \tag{3.6}$$

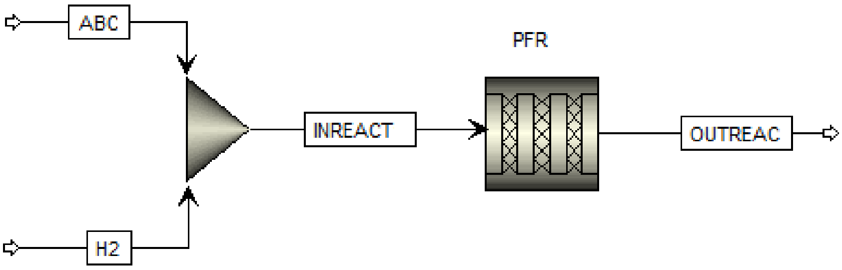


Figure 3.2: Simulation of pressurized reactor.

For the conduction of the experiment a thorough research of such a process was done in the following conditions as depicted in Table 3.4. In Figure 3.3a a small scale of pressurized reactor is depicted and used in lab of TNO, while in Figure 3.3b a larger scale is illustrated and used. In the small scale setup 10 ml of solution are inserted, while in the bigger scale 100 ml of solution can be used.

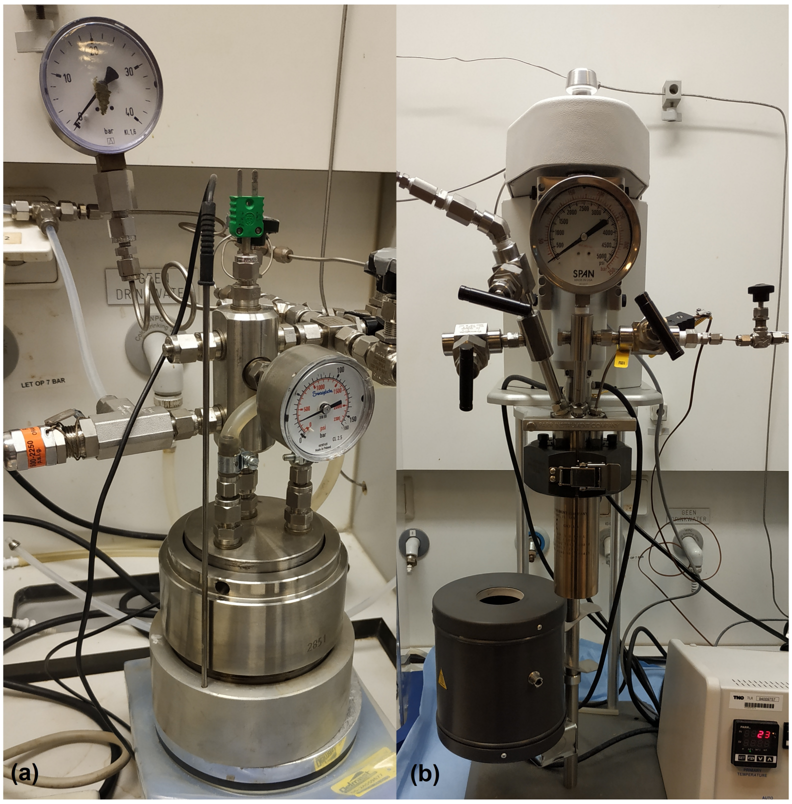


Figure 3.3: Setup for hydrogenation reaction.

After the completion of the experiment the samples are filtered from the Pd/C catalyst. The solutions then are going through measurement methods, both HPLC and FTIR. HPLC measures formate ions HCOO$^-$, while FTIR is an analysis technique that with only a drop of material can identify the organic materials contained in a solution. So, FTIR is a testing process that can within a wide range of wavenumber absorb and/or transmit the material and indicate a peak or a valley respectively in that area within the infrared spectrum. Those results indicating a proof of concept are presented in the following Chapter.

Table 3.4: Conditions of hydrogenation of ammonium bicarbonate.

Hydrogenation Reactor	
Operating temperature [°C]	80
H_2 pressure [bar]	20
Retention time [h]	2
Pd/C Catalyst	5 % wt
Stirring speed [rpm]	250

3.3 Thermal decomposition to formic acid and ammonia

Ammonium formate is a compound that when heated decomposes producing formic acid and ammonia according to the following reaction:

$$HCOONH_4 \Longrightarrow HCOOH + NH_3 \tag{3.7}$$

For the simulation of the separation step, a distillation column is used to model accurately the thermal decomposition of ammonium formate. Such a stripping column is used to imitate the separation process of liquid formic acid in water at the bottom and gaseous ammonia at the top of the column. Stripper columns are considered a known and mature technology, widely used in conventional capture system, for the separation of CO_2.

In this work, the same principle is used, but the main product that evaporates out is ammonia mainly, due to its high volatility. For the simulation of the stripping column Aspen Plus ® V10.0 is used. RadFrac is properly modelling the separation of formic acid from ammonia as can be seen in Figure 3.4.

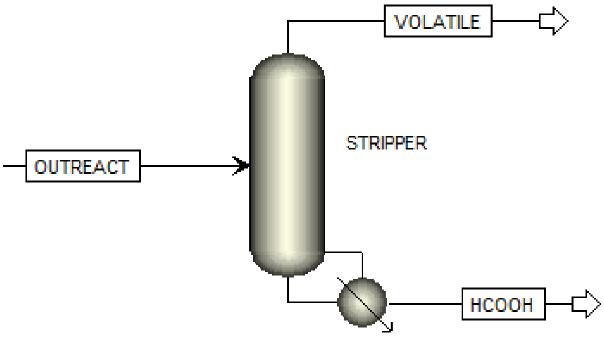


Figure 3.4: Simulation of stripping column.

The inlet of the stripper entering the column at 130°C mainly consists of ammonium formate. At that temperature level, thermal decomposition occurs towards the production of formic acid and ammonia. In Table 3.5 the conditions of the stripping column are presented, indicating the pressure of the condenser and the temperature of the reboiler.

Table 3.5: Operating conditions of stripper.

Stripper column conditions			
Operating temperature [°C]	130	**Condenser pressure**	3 bar
Number of stages	30	**Distillate rate Mass**	1000 kg/hr
Partial Reboiler	Kettle	**Reboiler Duty**	100 kW

For this chemical part, a series of experiments were conducted in a setup of the lab at higher temperatures of 150°C for 45 minutes. In the system, 1.5M of ammonium formate were inserted and after the completion of the experiment samples of the distillate part and the left over part, were analyzed using FTIR (Fourier transform infrared spectroscopy) and HPLC.

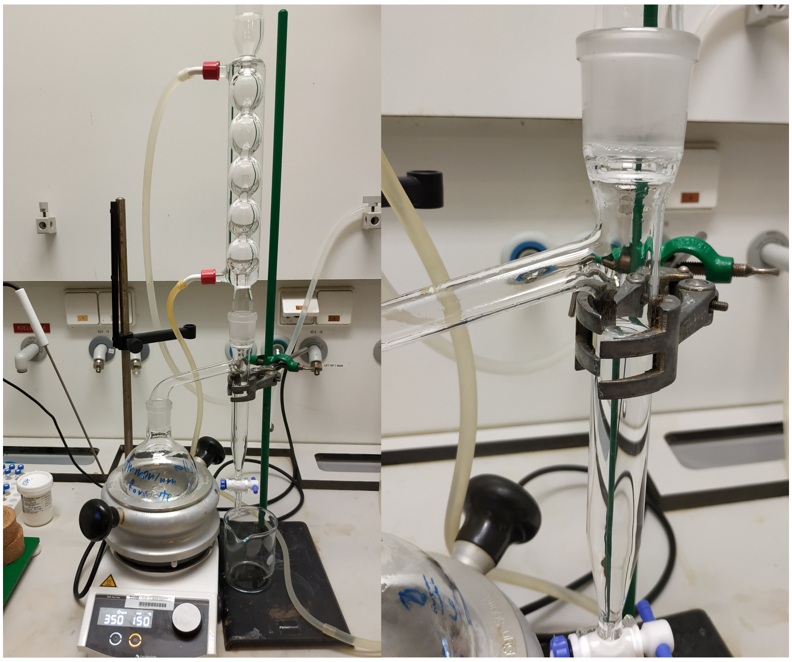


Figure 3.5: Lab distillation column for decomposition of ammonium formate.

In Figure 3.5 the setup for the distillation column is depicted and used in the lab of TNO in the SPES department. The sample is heated up to 150°C and in the right Figure the condensate part is depicted.

3.4 Hydrogenation of Formic Acid to Formaldehyde

Experiments also took place for the chemical conversion of formic acid to formaldehyde with the help of the experienced lab staff of TNO. The examined reaction appears to have high selectivity at the temperature range of 80-120°C. For the experimental proof of concept of the hydrogenation of formic acid to formaldehyde, the conditions displayed in Table 3.6 were used. Two solutions of formic acid were prepared, of 1.5M and 2.5M in watery solution and were both tested in the same conditions.

Table 3.6: Conditions of hydrogenation of formic acid to formaldehyde.

Hydrogenation Reactor II			
Operating temperature [°C]	100	**Retention time [h]**	3
H_2 pressure [bar]	20	**Pd/C Catalyst**	5 % wt

It should be noted that samples of formic acid and the produced ones were analyzed in HPLC in their formate $HCOO^-$ ions, at retention time 17.6 minutes. These samples were also analyzed based on their infrared spectrum, showing differences in their valleys throughout a wide range of wavenumbers.

Chapter 4

Simulation Results and Experimental Proof of Concept

In this Chapter the main results of the thesis are presented, including simulation results and experimental proof of principle. The overall flowsheet of the system includes the capturing process, the crystallization step, the hydrogenation of ammonium bicarbonate and lastly the separation step towards formic acid and ammonia. Description of the integrated systems is also part of this Chapter, for the process design of systems including a crystallizer or not. Lastly, possible heat integration in the system is investigated for a more efficient waste heat recovery.

4.1 Integrated system without crystallization

In Figure 4.1 the overview of the integrated system is illustrated, presenting all the participating reaction steps of the process. To begin with, the absorption column of the system has two inlets, the flue gas entering from the bottom the column and the aqueous solvent of ammonia entering in the top of the absorber. The system has two outlet streams, namely the gaseous outlet coming out of the top of the absorber and the liquid rich solvent exiting the system from the bottom containing mainly ammonium bicarbonate in liquid state.

The gaseous outlet contains high amount of ammonia and that is the reason why there is a recovery system for this lost solvent in gaseous state. Ammonia is dissolved in fresh water and recycled back in the absorber for minimization of the losses. This is an important step of the system, since the operating temperature is that low to also decrease the ammonia slip. Ammonia losses are minimized and the remaining gaseous ammonia is further washed and processed to reach ppm levels for its release to atmosphere at allowed levels.

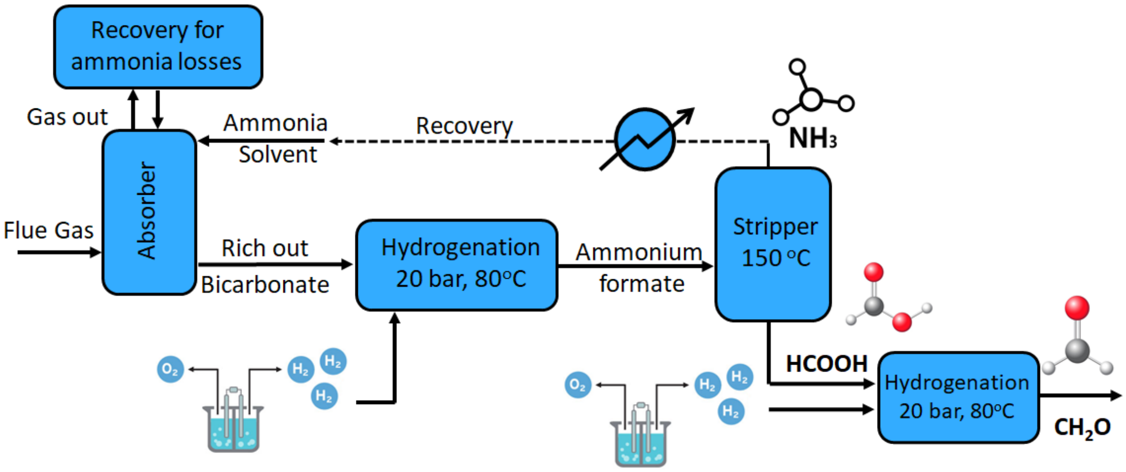


Figure 4.1: Overview of the integrated system.

The main product of the absorption column is ammonium bicarbonate and analysis on its solubility is conducted to reassure there is no solid formation inside the reactor that could damage or deteriorate the operation of the system. High concentration of ammonia solvent leads to high concentration of ammonium bicarbonate which is an initial indication for a final high concentration of formic acid.

Additionally, the hydrogenation of ammonium bicarbonate follows, which is one inlet of the reactor in liquid solution at 80°C. Pressurized hydrogen is the second inlet of the reactor, assumed to be derived from water electrolysis. In this manner, the mechanical compression of gaseous hydrogen is prevented, a way more energy intensive process. As an alternative, pressurized hydrogen could also be derived as a by-product from another part of a power plant.

From the process described in the previous paragraph, production of ammonium formate takes place and is further processed. A stripping column is then used for the thermal decomposition of ammonium formate towards formic acid and ammonia and at the same time is capable of the separation of these two products of the system. The separated ammonia evaporated out of the top of the stripper is inserted back to the system in the absorption column, as a regeneration of the solvent. High formic acid concentration is achieved at 35 % wt in watery solution.

An additional step is added, where hydrogenation of the produced formic acid takes place for the final production of formaldehyde. A pressurized catalytic reactor is used in this additional step. The description of the integrated system constitutes an alternative system for formaldehyde production, in already existing carbon point sources such as power generation plants or waste incinerators.

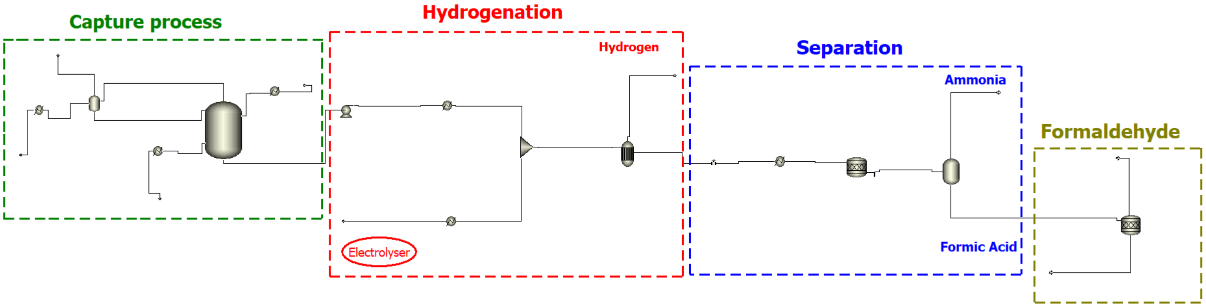


Figure 4.2: Representation of the simulated integrated system.

In Figure 4.2 the simulation of the integrated system is illustrated that was conducted in AspenPlus ® V10.0. The overall process flowsheet can be seen, grouped in the different processes participating in the system, starting from the capturing towards the production of the final end-product.

4.2 Integrated system with crystallization

In this section the description of the overall process design of the integrated system of CO_2 capture to the production of formic acid is investigated, including the crystallization system. A representation of the system can be seen in Figure 4.3, where the initial step of CO_2 chemical absorption, derived from flue gas, is similar to the base case scenario that was explained in detail in Chapter 4.1.

After the production of ammonium bicarbonate at the bottom of the absorber, cooling down to 5°C follows resulting in precipitation of the latter product. This cooling step is added in the proposed design to take advantage of the crystallization of the solid compound. As a result, the solids are well organized into crystals, an effective way for solid handling. The formed slurry enters a crystallizer, forming crystals of ammonium bicarbonate that are separated from the liquid part of the stream.

In this manner, higher concentration of ammonium bicarbonate can be achieved of approximately 47 % wt. The slurry then proceeds to a dissolution step including a heater, that will reassure no slurry and no solid will enter the next reactor of the system. From that point on, the reaction steps remain the same compared to the already examined system. Hydrogenation reaction takes place at mild conditions of 80°C and 20 bar of hydrogen. The last part of separation is simulated with a stripper column operating at 150°C and the required pressure. The ammonia evaporates out and a regeneration system is included for the recovery of ammonia back in the top of the absorber in the first step.

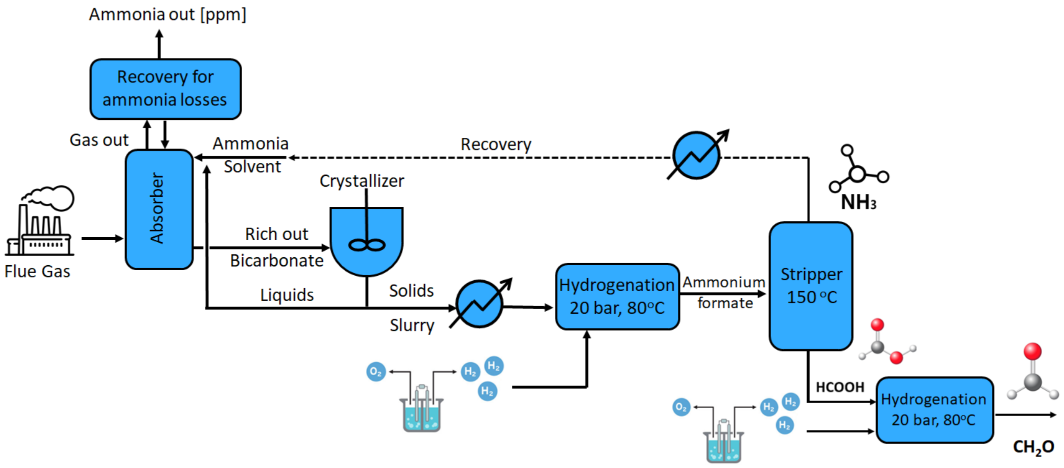


Figure 4.3: Overview of the integrated system, including crystallization.

In Figure 4.3 the integrated system of CO_2 capture and utilization towards the production of formaldehyde is illustrated. Additional pressurized hydrogen derived from an electrolyzer enters the system, where hydrogenation of formic acid results to such a valuable end-product. The production of formaldehyde is an innovative addition to this study, since its market is much bigger compared to that of formic acid. The simulation of the integrated system described in this paragraph is conducted in AspenPlus ® V10.0 and can be seen in Figure 4.4, where all the participating processes are depicted.

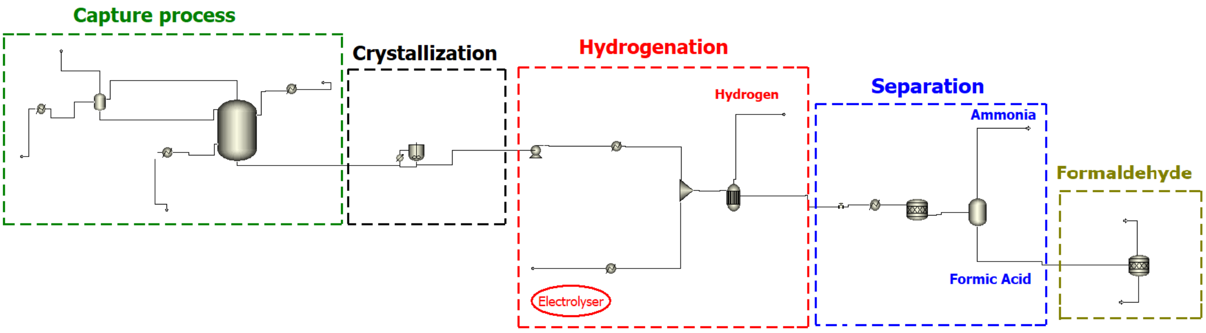


Figure 4.4: Representation of the simulated integrated system with crystallization.

For the simulation of the crystallizer AspenPlus ® V10.0 is used, to simulate the formation of the solid compounds in the system as well as their further processing, including a cyclone for the separation of the solid part and heating system for the regeneration of this part. The stream that is left proceeds further to the next process step that is the hydrogenation reaction.

After simulation of the process, ammonium bicarbonate has increased in mass concentration and reaches the high level of 47 % wt, indicating an attractive process in terms of final product concentration. This additional operating block includes solids handling that can be challenging in an engineering point of view and this should also be taken into account. In the following sections, a techno-economic comparison will be conducted in these two systems that are described and finally will be critically compared, in terms of final formic acid concentration and economic point of view.

4.3 Simulation and experimental results

In this section the results of the simulated model are shown for the absorption column. Additionally, experimental proof of concept is presented regarding the hydrogenation of ammonium bicarbonate and separation of ammonium formate.

4.3.1 Ammonium bicarbonate production

The feed of the system is a flue gas stream 6 v/v % of CO_2, inserting the system and the solvent consists of 40 wt% of aqueous ammonia. In the examined system, ammonium bicarbonate is assumed to be the only solid compound precipitating. Higher concentration of ammonia in the lean solvent of the absorber leads to high ammonia slip. [64] The combination of high ammonia concentration and low lean loading ratio leads to significant increase of the ammonia slip, escaping at the top of the absorber. [65] This is mainly due to its volatility and ammonia tends to evaporate out of the absorber. European regulations, as far as the ammonia emissions rate is concerned, are very strict because they may cause undesired harm and health issues to the operators of the plant as well as severe environmental effects. Such regulations constrain the ammonia emissions to a range of 20-50 ppm. [66]

Ammonia emissions from the top of the absorber are reduced by entering a water wash section, but an additional acid wash follows helping decrease the ammonia out to acceptable levels. The investigation of the acid wash is not part of this study, but the concentration of the ammonia stream entering the acid wash should be relatively low in order to reduce the consumption of acid. Typically, sulfuric acid is used that results to the formation of ammonium sulfate. [67] In Table 4.1 the results of the outlet streams are shown including the recovery system.

Table 4.1: Molar fraction of outlets of the absorber.

	FLUEGAS	LEANIN	RICHOUT	GASOUT	WATERWASH	RECOVERY	OUT
CO_2	0.06	0	2.44e-06	5.17e-06	0	8.18e-12	1.27e-12
NH_3	0	0.27	0.19	0.35	0	0.26	0.02
H_2O	0	0.58	0.45	0.01	1	0.53	0
N_2	0.94	0	0	0.64	0	0.001	0.98
HCO_3^-	0	0	0.07	0	0	0	0
CO_3^{2-}	0	0	0.03	0	0	0	0
NH_2COO^-	0	0	0.01	0	0	0	0
NH_4^+	0	0.15	0.25	0	0	0.2	0
NH_4HCO_3	0	0	no solid	0	0	0	0

Observing the Table 4.1 all the different ionic components are presented in the participating streams of the absorber and the ammonia recovery system. The RICHOUT stream is the outlet of the absorber containing ammonium bicarbonate in liquid state.

The rate-based model that is implemented can predict the performance of the absorber in an effective and reasonable way. Some of the initial conclusions from the model are that the absorber can achieve high CO_2 absorption rates and at the same time high ammonia losses in the gaseous outlet of the system. Thus, an overall investigation on the operating parameters and configurations of the system is necessary to improve these factors, for example a lower solvent temperature can limit the ammonia losses of the system.

Solubility of ammonium bicarbonate

In Figure 4.5a the predicted solubility of ammonium bicarbonate is illustrated as function of liquid to gas ratio (L/G), lean solvent to flue gas inlets. The molar fraction of ammonium bicarbonate is illustrated for different ammonia concentrations, all cases at 10°C operating temperature. For the case of 40% wt, a 2.1 value of L/G is selected to reassure there is no solid formation of bicarbonate. In Figure 4.5b the solubility is depicted as a function of different temperatures with respect to the rich CO_2 loading, calculated based on Equation 4.1. In the region below of every operation curve, ammonium bicarbonate salts remain in liquid state, indicating the area of operation.

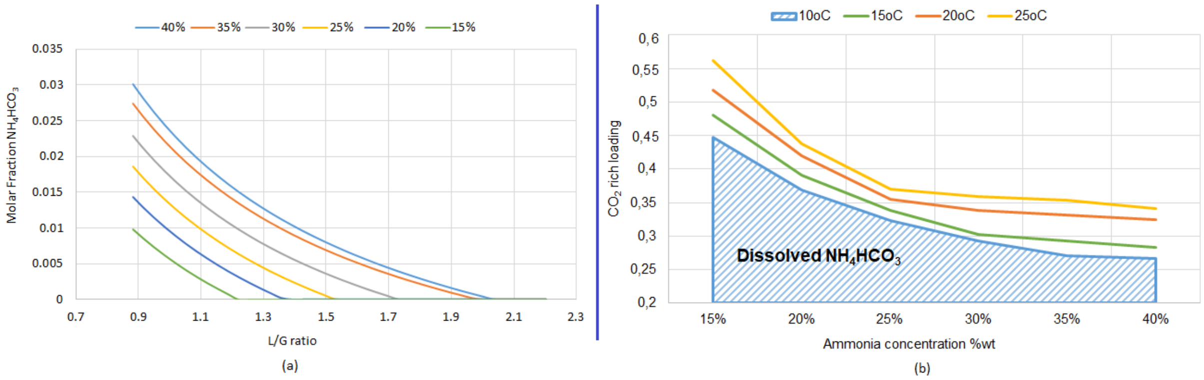


Figure 4.5: Operating area with respect to (a) L/G ratio, (b) ammonia concentration.

CO_2 loading as well as ammonia concentration are both investigated in order to reassure that ammonium bicarbonate exits the bottom in a liquid state and does not precipitate. The ammonia slip and losses are weakly dependent on ammonia concentration but depend mainly on the absorber temperature.

$$rich \quad CO_2 \quad loading = \frac{[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [NH_2COO^-]}{[NH_3] + [NH_4^+] + [NH_2COO^-]} \tag{4.1}$$

In Figure 4.6a the temperature of the solvent is investigated, resulting in a molar fraction profile for the participating components in the absorber. It should be noted that this is the base case scenario that is described in the previous paragraphs. In the plot derived from AspenPlus, it can be seen that at 10°C there is no longer solid formation which is one main goal to prevent undesired problems in the operation of the system, such as clogging and further additional maintenance costs.

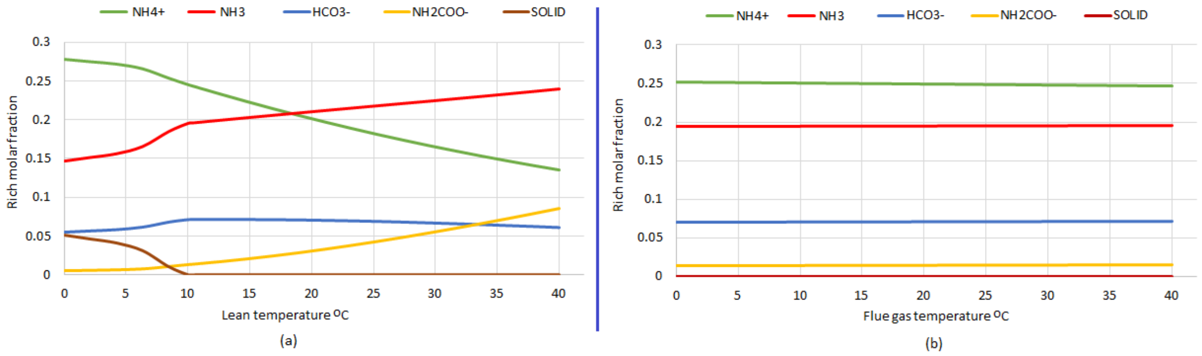


Figure 4.6: Rich out composition with respect to (a) lean and (b) flues gas temperature.

In Figure 4.6b the components profile of the rich out of the absorber can be seen as a function of the flue gas temperature. The effect on the composition of the outlet can be seen and it can be concluded that the flue gas temperature has barely any effect on the rich out composition. As a result, only the temperature of the liquid is affecting the products. [67] [68]

In Figure 4.7a L/G ratio is illustrated with respect to different lean solvent temperatures. These values vary from around 1 to 2 also depending on the concentration of the ammonia solution.

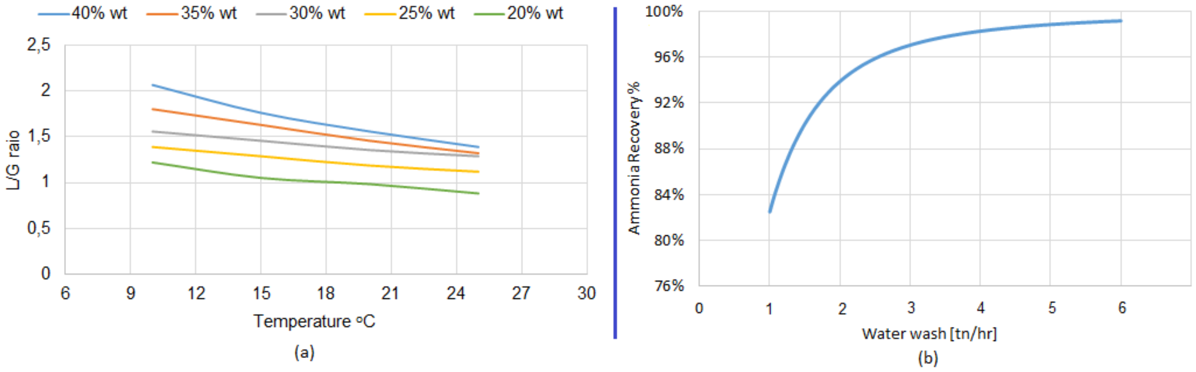


Figure 4.7: L/G ratio for different operating temperatures

In Figure 4.7b ammonia recovery is investigated. Water wash is used in a flash operating block for the recovery of ammonia back in the top of the absorber. It can be seen that the higher the amount of water solution is used, the higher the % of ammonia recovery that is achieved, even up to 99%. This though has an impact on the concentration of ammonium bicarbonate, since it becomes more diluted and should be further optimized as indicated in Chapter 7. From the procedure of the conceptual design of the absorber it should be noted that the outlet bicarbonate concentration is approximately 35 % wt, preparing the ground for the final concentration of formic acid.

4.3.2 Ammonium formate production

For this experiment both a small and a larger scale reactor are used with duplos and results are similar leading to the same desired result. For the evaluation of the outlet solution, a calibration curve is prepared with different concentrations of ammonium formate and all the samples were analyzed in the HPLC setup resulting in the mass yields depicted in Figure 4.8.

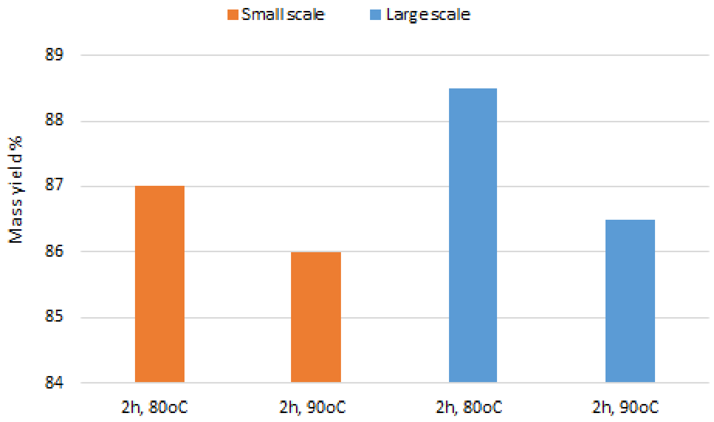


Figure 4.8: Calibration curve of ammonium formate.

The outcome of the aforementioned experiments works as a proof of concept of the reaction, since it leads to a mass yield of 87.5 % of ammonium formate. For the continuation of the experiment, the produced ammonium formate was used and inserted to a lab distillation column for the evaporation of ammonia and production of formic acid.

4.3.3 Formic acid separation

The simulation of the above mentioned stripping column results in the following streams, presented in Table 4.2. In Figure 4.9 the results of the % transmittance of the initial ammonium bicarbonate, the distillate part and the left-over part are presented, after the completion of the experiment. It can be concluded from the results above, it is a proof of concept of the thermal decomposition of ammonium formate. To begin with, ammonium formate is presenting some transmittance valleys at wavelengths of 1600 and 1300 cm^{-1}. [69] As for the formic acid sample, that corresponds to the left-over part, its curve presents some valleys at wavelengths of 1750 and 1200 cm^{-1}. Lastly, the distillate part, derived from the experiment, corresponds to the ammonia produced and its peak on the absorbance curve appears to be at wavelength of 1100 cm^{-1}. The peaks indicated in this curve on wavelengths of 3400 cm^{-1} for formic acid and ammonia and also at 1650 cm^{-1} for the latter, correspond to the concentration of water. [70]

Table 4.2: Stream results of the stripping column/separation step.

Mass fraction %	Formic acid	Ammonia	CO_2	Water
OUTREACT	0.3	0.11	0.02	0.56
HCOOH	0.35	0.002	6.3 e-05	0.64
VOLATILE	0.05	0.52	0.06	0.37

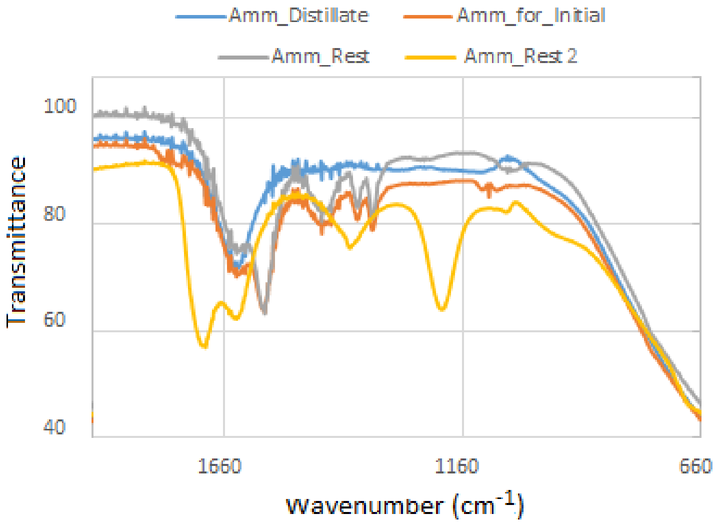


Figure 4.9: FTIR analysis for ammonium formate decomposition.

In Table 4.3 the analysis conducted in HPLC is seen, for both samples that were collected. HPLC can identify formate ions at the retention time of 17.6 minutes, so the area at that peak is calculated for both samples. As expected the area for the alkaline sample is relatively smaller compared to the acidic sample. Normalization on the relative volume is executed and this procedure leads to the calculation of ammonium formate towards formic acid of 57.2%, translated to evaporated ammonia.

Table 4.3: Calibration results and conversion measurement.

M	mL	moles	pH_i	$pH_{distillate}$	pH_{rest}	$Vol_{distillate}$	Vol_{rest}
1.5	200	0.3	7.5	13.1	4.1	70	115
Area rest	**Area distil**	**mg/mL rest**	**mg/mL distil**	**mol/L rest**	**mol/L distil**	**moles**	**Separation %**
3.055e+06	1216.95	84.54	0.035	1.83	0.0021	0.275	**57.2**

From the above, it can be concluded that there is a proof of concept in such a production route, since formic acid is effectively being separated from ammonia.

4.3.4 Formaldehyde production

The samples taken out of the laboratory pressurized reactor were analyzed in HPLC as for their formate ions and in FTIR for their composition. In Table 4.4 the results of the HPLC measurements are presented. The two solutions of formic acid were inserted in the reactor and the remaining area is filled with pressurized hydrogen at 20 bar. Measurements of pH before and after the experiment is done, for an initial indication of the result.

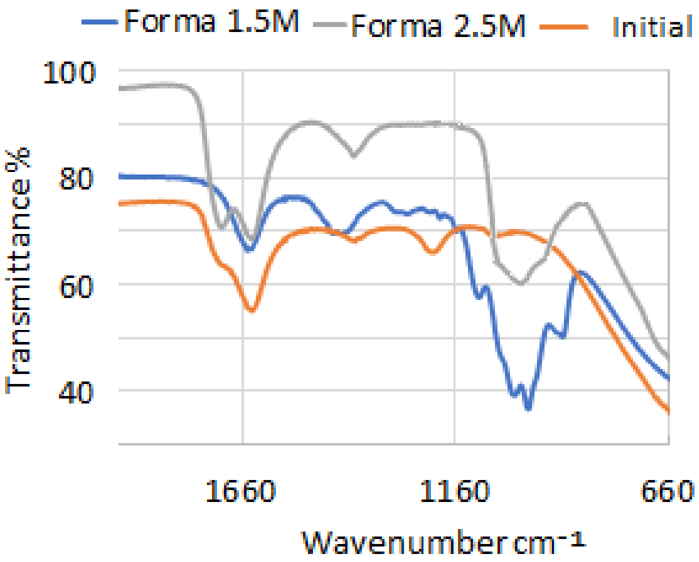


Figure 4.10: FTIR analysis for formaldehyde conversion.

Table 4.4: HPLC measurements for formaldehyde.

# 1	$[FA]_{1.5M}$	$pH_{1.5M}$	$pH_{1.5M\text{ - After}}$	# 2	$[FA]_{2.5M}$	$pH_{2.5M}$	$pH_{2.5M\text{ - After}}$
	1.5	2.7	6.2		2.5	2.8	6.8

In Figure 4.10 the transmittance profile can be seen, indicating the formation of formaldehyde under the described conditions. Observing the infrared spectrum analysis it can be concluded that there is conversion of the examined solutions of formic acid. It can seen that formaldehyde shows a valley of transmittance at around 900 cm^{-1}, indicating the formation of formaldehyde. [70] Additionally, at wavemumber of 1600 cm^{-1}

4.4 Heat Integration

Heat integration in energy systems is an important parameter that needs to be taken into consideration. However, it should be done in a careful manner and in parts of the system that is indeed needed, otherwise it turns out to be an additional CAPEX and utility costs added to the system. Generally, the conditions, regarding temperature and pressure in the system are not that extreme, where the temperature of 130°C appears to be the highest operating temperature. Further investigation of heat integration is highly recommended for further optimization

Chapter 5

Techno-economic analysis

In this Chapter an overall techno-economic analysis is to be conducted including all the CAPEX and OPEX costs taking place in the process system. Such an analysis is vital so as to characterize the feasibility of a system by calculating the annualized cost and cost of formic acid produced. A sensitivity analysis is also conducted to evaluate the associated costs of the system.

5.1 Methodology

For the economic evaluation of the integrated system a complete procedure was followed by a combination of APEA ® V10.0 (ASPEN Process Economic Analyzer) and the Octavius methodology specifically used for capturing systems. [71] Aspen Process Economic Analyzer is a formal databased procedure verified against the Dutch Association of Cost Engineers (DACE) booklet. The scheme of the methodology that is followed can be seen in Figure 5.1 with all the steps towards the economic evaluation of the system.

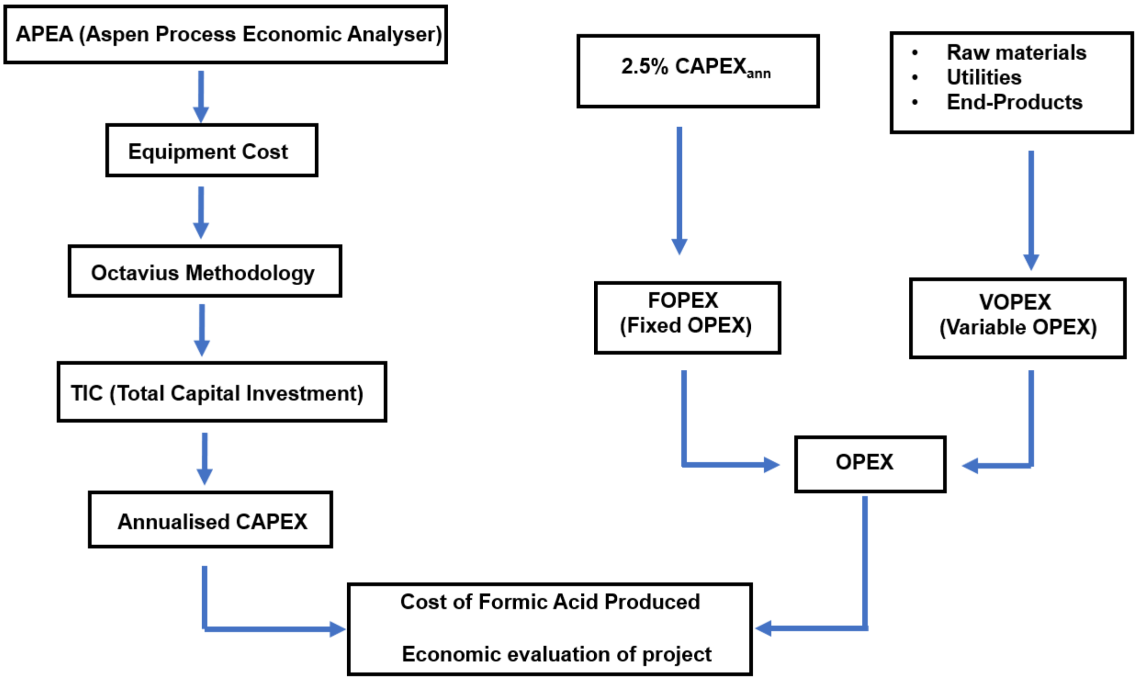


Figure 5.1: Methodology of economic evaluation of the project.

The economic evaluation consists of two main parts of calculation, the CAPEX and OPEX costs resulting to the calculation of the cost of formic acid produced and the overall economic evaluation of the system. A cash flow analysis is also conducted with a certain lifetime of the capture plant. From the above, the predicted payback period is calculated as well as the Net Present Value (NPV).

The capital cost for designing an integrated system includes the conceptual design of the plant, the detailed design, the procurement step, the actual construction and operation of the power plant. [72] In Figure 5.2 the influence of the design decisions is depicted in comparison to the costs associated with all the participating steps for the designing of a power plant. It can be seen that the conceptual design is the heart of a project for the determination of the overall project.

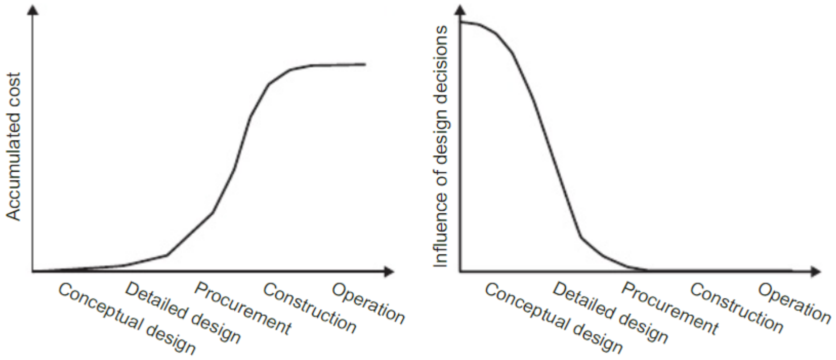


Figure 5.2: Difference between design decisions and actual cost of a system.[73]

The total equipment cost is calculated through the databased APEA and can be seen thoroughly in the following paragraphs. For the total capital investment the Octavius methodology is followed, which is described thoroughly in the following section. It should be noted that the economic evaluation is done for the integrated system without the crystallization system. A comparison is further done with the integrated system including the crystallizer that results in relatively higher concentration of formic acid, lower capital costs and lower operating costs.

5.2 Electrolyzer cost

Hydrogen mechanical compression is an energy intensive process. For such application hydrogen derived from high pressure electrolysis is preferred especially for practical reasons. Water electrolysis has an electricity requirement of 50 kWh to produce 1 kg of hydrogen according to the lower heating value of water. With an electricity cost of 0.06 €/kWh this would lead to the hydrogen cost of 3 €/kg. In Figure 5.3 the x axis represents the natural gas prices of 2016, while the y axis represents the cost of hydrogen derived from SMR (Steam Methane Reforming). It can be seen that the cost price of hydrogen derived from electrolysis is still almost in double levels, even in DOE (Department of Energy) target prices. [74] Worldwide the price of hydrogen derived from SMR is between 1 - 3 €/kg, making the cost of hydrogen through electrolysis attractive and competitive. [75]

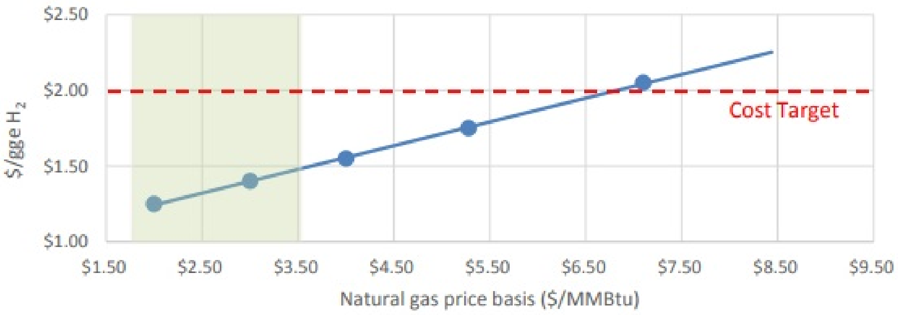


Figure 5.3: H_2 production cost at varying natural gas prices.[76]

However, having pressurized hydrogen as inlet feed in the system would result to an OPEX-based system appear to be an unrealistic approach. Water electrolysis produces hydrogen at elevated pressures and its cost includes the capital cost of the electrolyzer and the required electricity. In this specific work the type of the electrolyzer is not defined, but it could be either a PEM or an alkaline electrolyzer that have the capability of producing hydrogen at elevated pressures.

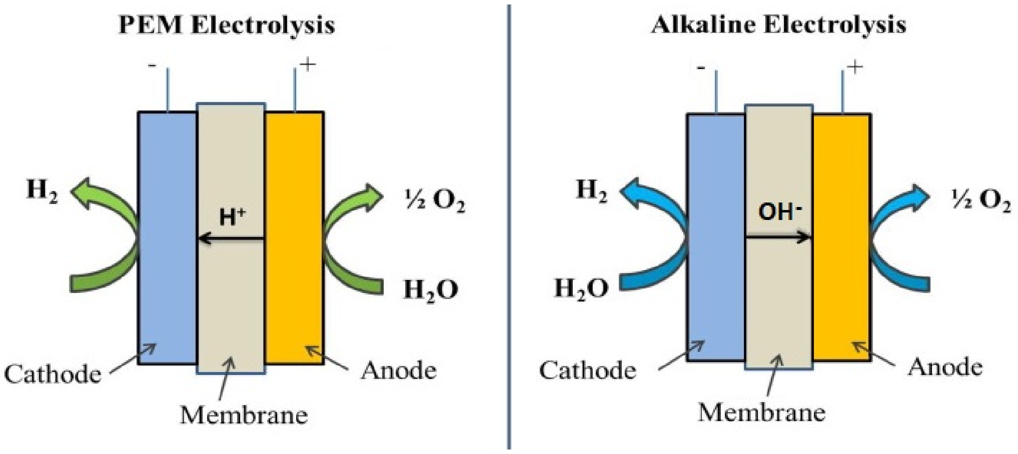


Figure 5.4: Schematic illustration of PEM and Alkaline water electrolysis. [77]

The required pressure of hydrogen for this specific work is 20 bar and the characteristics of the available technologies that can be utilized are presented in Table 5.1. A representation of PEM and alkaline electrolyzers are presented in Figure 5.4.

Table 5.1: Characteristics of electrolyzers.[78]

Type of Electrolyzer	**Capacity [Nm^3/h]**	**Hydrogen Pressure [bar]**	**Type of Ion Transport**	**Hydrogen Purity [%]**	**Efficiency [%]**
PEM	0.26 - 250	8 - 85	H^+	99.999	52 - 56
Alkaline	1 - 760	2 - 30	OH^-	99.3 - 99.999	56 - 67

The total cost and efficiency of the electrolyzer is related to the operating voltage and the relative pressure that is required, as can be seen in Table 5.2.

Table 5.2: Operating voltage with respect to the required pressure.[79]

Pressure [bar]	Operating Voltage [eV]	Gibbs Energy [kJ/mol]
1	1.229	237.1
10	1.273	245.6
30	1.294	249.69
Required: 20	1.28	247.66

The total cost associated with the production of pressurized hydrogen corresponds to the capital investment of the electrolyzer (including the stack), its operating cost and the required electricity. As for the first, this cost is related to the capacity of the electrolyzer linked to the total amount of hydrogen that needs to be produced. Prediction of the aforementioned costs for these two different technologies can be seen in Figure 5.5.

The capital cost of the PEM electrolyzer was almost 2,500 €/kW in 2012, while its reduction is predicted to be much higher compared to alkaline electrolyzers. As for the operating costs they were assumed to be 10% of the total capital investment. [79] The efficiency of the electrolyzer is calculated according to the Lower Heating Value (LHV) of water at 60-65 %.

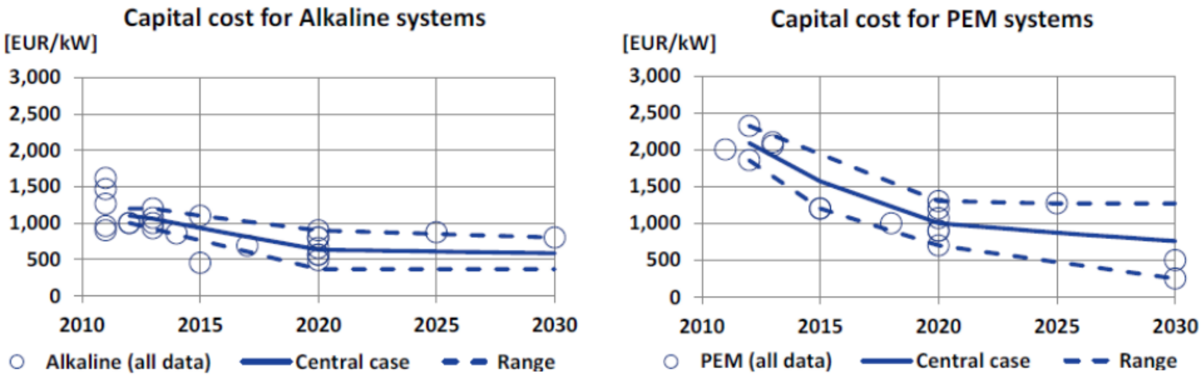


Figure 5.5: Prediction of capital cost of electrolyzer. [79]

For the base case of the techno-economic analysis a capital cost of an alkaline electrolyzer of 18.6 MW capacity is assumed to cost 650 €/kW, with an efficiency of 63.7% according to the LHV of water electrolysis.

5.3 Total Capital Investment TIC

Total Equipment Costs TEC

The Equipment Costs are obtained from mass and energy balances from the simulations ran for the integrated system. In such costs the following operation blocks are included: absorber, solvent make-up, cooler for solvent make-up, cooler for flue gas, cooler for solvent, pump, heater of bicarbonate, electrolyzer, heater of the H_2, pressurized reactor, heater before separation and stripper. In Table 5.3 all the necessary information of the aforementioned blocks are presented.

Table 5.3: Total Equipment Cost of the integrated system.

#	Type of operating block	Cost [k€]
1	Absorber	99
2	Cooler for make-up	45
3	Cooler for flue gas	61
4	Cooler for solvent	47
5	Pump	37
6	Heater for bicarbonate	75
7	Electrolyzer	5.2e+03
8	Heater for H_2	51
9	High Pressure Reactor	200
10	Heater for separation	50
11	Stripper	85
12	Cooler for regeneration	80
	Total Equipment Cost TEC	6e+03

The overall procedure for the calculation of the total equipment costs is found to be 35.8 million €. In the following paragraphs the equations of the Octavius methodology are to be implemented, taking into account all the additional costs, such as engineering, piping etc.

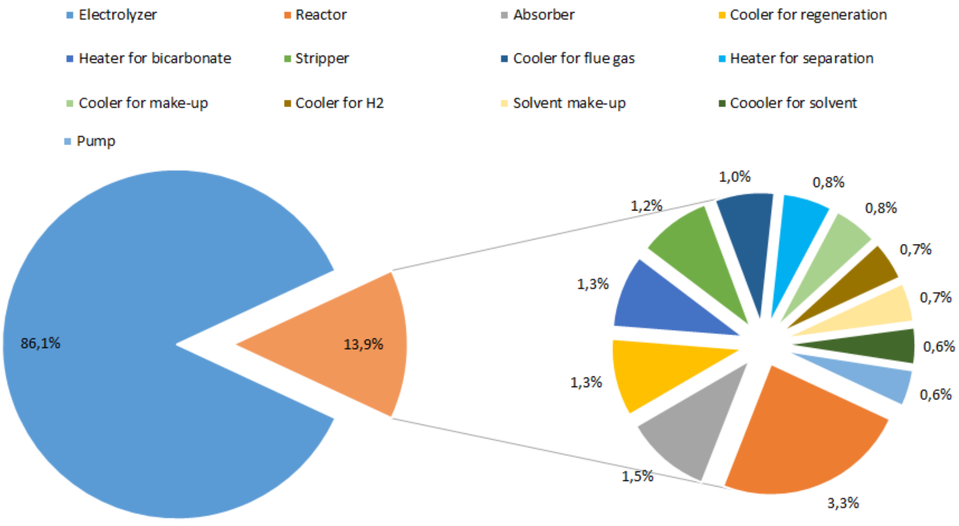


Figure 5.6: Distribution of CAPEX of the integrated system.

In Figure 5.6 the distribution of the total equipment cost is illustrated and can be seen that the dominant equipment costs correspond to the electrolyzer, stripper, reactor and absorber of the system, which amount to over the 75% of the overall costs.

Total Direct Plant Cost TDPC

The TDPC incorporates Instrumentation and Controls, Piping, Electrical Equipment and Materials, Civil works, Erection, Steel structures and painting. Thus, the aforementioned cost is calculated based on the following equation according to the OCTAVIUS methodology: [71]

$$TDPC = 2.01 \cdot TEC = 12.1\,\text{m€} \tag{5.1}$$

Total Indirect Plant Cost TIPC

The TIPC incorporates the Yard improvements, Service facilities, Engineering, Supervision and construction and Buildings. Such cost is calculated based on the equation below:

$$TIPC = 0.14 \cdot TDPC = 1.7\,\text{m€} \tag{5.2}$$

Fixed Capital Investment FIC

The FIC can be calculated as the sum of the TIPC and the TDPC according to the following equation:

$$FIC = TIPC + TDPC = 13.8\,\text{m€} \tag{5.3}$$

Following the described procedure, the total investment cost can be calculated as:

$$TIC = \frac{FIC}{0.8} = 17.2\,\text{m€} \tag{5.4}$$

Annualized cost

In order to calculate the annual capital cost, the total capital investment (TIC) is multiplied by the capital factor taking into account the discount rate i and the number of the years n, as seen in Table 5.4.

$$\text{CAPEX}_{\text{ann}} = \frac{i \cdot (i+1)^n}{(i+1)^n - 1} \cdot TIC = 1.76\,\text{m€} \tag{5.5}$$

Table 5.4: Parameters for the evaluation of the system.

Plant lifetime n	20 years
Interest i	8 %
Maintenance per year	2.5 %
Operating hours per year	8,000

5.4 Operating Expenditure (OPEX)

The operating costs include both the fixed (FOPEX) and the variable (VOPEX) operating costs and their calculation is presented in detail in the following paragraphs.

5.4.1 Fixed Operating Expenditure (FOPEX)

As far as the FOPEX is concerned, such costs in a power plant can be considered to account for 2-3 % of the capital costs according to the following formula:

$$\text{FOPEX} = 2.5\% \cdot CAPEX_{\text{ann}} = 0.26\,\text{m€} \tag{5.6}$$

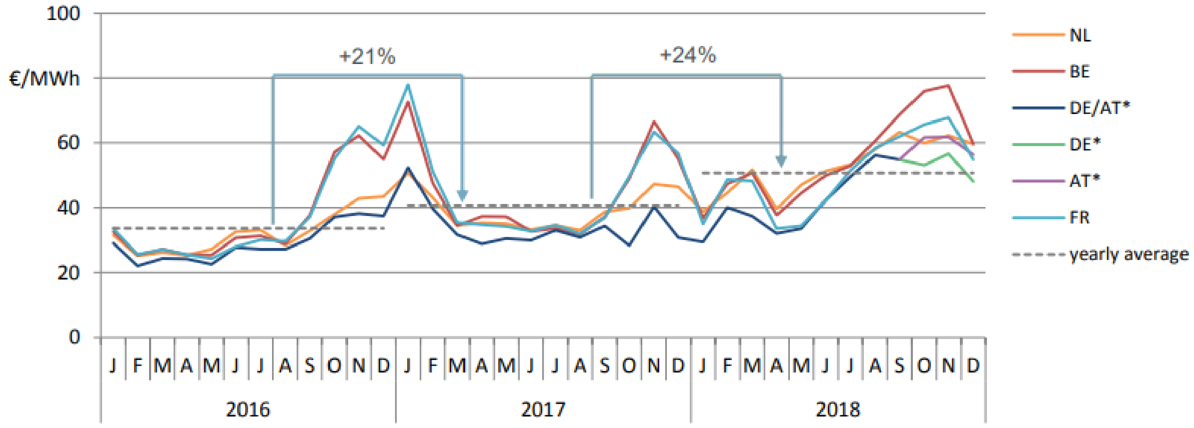
These fixed costs include the maintenance cost that needs to be spent during the operation of the power plant. [80]

5.4.2 Variable Operating Expenditure (VOPEX)

The operating costs include all operating units and their relative utilities as well as the inlet feeds of the system. This is being conducted by converting the utilities in accordance to the requirements of the operating blocks along with the prices. In the following paragraphs all the participating utilities and feed costs will be presented, along with some summarizing tables with the assumptions that were used.

5.4.2.1 Cost of electricity

The cost of electricity is an important parameter that influences directly the economic evaluation of the integrated system. The price of electricity is varying during the year and also depends on the country. For industrial use the price is assumed to be constant throughout the year and as for the latter parameter the variability of price can be seen in Figure 5.7. [81]



* On October 1st, 2018 the German/Austrian bidding zone split into two seperate bidding zones

Figure 5.7: Monthly Average Day-ahead Wholesale Prices in the CWE region. [81]

The cost of electricity appears to have fluctuating values during the last years, even during the last months of 2018. For this work, a price of 0.053 €/kWh is assumed as a representative price, neither optimistic or pessimistic, but appropriate in order to produce realistic outcomes of the investigation.

5.4.2.2 Steam cost

Steam is typically used in chemical and power plants as a heat source for various operating blocks as a hot utility. [73] Depending on the operating temperature and pressure, LP (Low), MP (Medium) or HP (High) Pressure Steam needs to be used. In Table 5.5 all the parameters for the steam are defined.

Table 5.5: Characteristics of LP, MP and HP Steam. [73]

Steam	**LP**	**MP**	**HP**
Pressure [bar]	6	20	40
Saturation Temperature [°C]	159	212	250
Superheat Temperature [°C]	160	300	400
Steam price [€/tn]	13.34	18.11	21.45

All the parameters presented above are necessary to define the type of steam that needs to be used in the system, influencing the cost of the steam utilized. The saturation temperature of the steam is an important parameter defining the type of steam required in the system. For this work, low pressure steam is used, since temperatures within the system are not surpassing the saturation temperature of the steam.

5.4.2.3 Summarizing utilities costs

In this paragraph the summary of all the utilities cost is presented. In Table 5.6 all the participating utilities and inlet feeds prices are displayed. CO_2 inlet price in the system is assumed to be zero, since it is a CO_2 capture system where the flue gas is derived from already existing power plants, emitting all the required amount of CO_2.

Table 5.6: Utilities costs.

	Price	**Unit**	**Reference**
Ammonia	450	€/tn	[9]
Water	0.11	€/tn	[82]
CO_2	For free	-	-
Electricity	0.053	€/kWh	[83]
LP Steam	13.34	€/tn	[84]
Cooling Water	0.017	€/m^3	[82]
Demineralised Cooling Water	0.033	€/m^3	[85]
Demineralised Chilled Water	0.045	€/m^3	[85]

In Table 5.7 all the participating operation blocks using utilities are presented along with their capacity and their final total operating cost. It can be seen that the parameter that influences these costs the most is the electricity required for the electrolyzer.

Table 5.7: Utilities for equipment of the system.

#	**Type of operating block**	**Type of Utility**
1	Cooler for solvent make up	Demineralised chilled water
2	Cooller for ammonia solvent	Demineralised cooling water
3	Cooller for flue gas	Demineralised cooling water
4	Crystallizer	Cooling water
5	Crystallizer	Electricity
6	Pump	Electricity
7	Heater for bicarbonate	LP Steam
8	Electrolyzer	Electricity
9	Heater for H_2	LP Steam
10	Reactor	Cooling water
11	Heater for separation	LP Steam
12	Stripper	MP Steam, Electricity
13	Cooler for regeneration	Demineralised chilled water
	Total Utilities Costs	3.1 million €

The procedure that is explained in detail in the previous paragraphs, results to the production of Figure 5.8 where the distribution of CAPEX-OPEX of approximately is 70-30 % respectively. As far as the OPEX distribution is concerned, it accounts for 40-60 % for Utilities and inlet ammonia respectively.

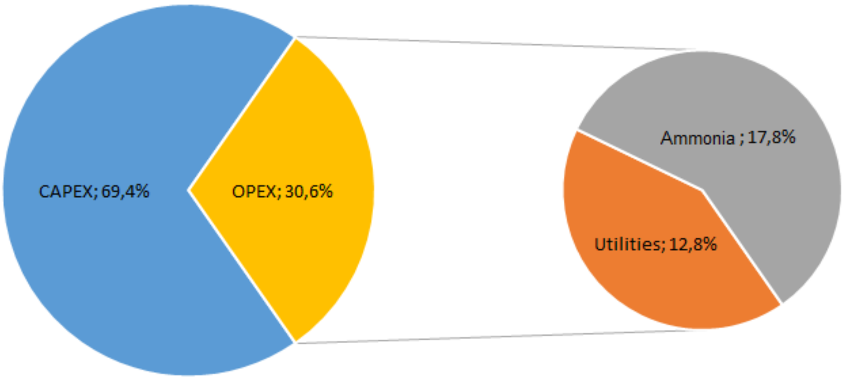


Figure 5.8: CAPEX and OPEX distribution.

5.5 Net Present Value NPV and Cost of Produced Formic Acid

In this Chapter the calculation of the NPV is determined, in order to define and calculate the present value of the future cash flows, according to Equation 5.7: [86]

$$NPV(i,N) = \sum_{t=1}^{N} \frac{C_t}{(1+i)^t} - C_0 \tag{5.7}$$

where C_t is the net cash flow at time period t, i is the discount rate, t the time period, N the total number of periods and C_0 the initial investment at time period 0.

The lifetime of the capture plant is assumed to be 20 years. According to the formula 5.7, all the discounted cash flows are determined and the cumulative depreciated cash flows is illustrated in Figure 5.9. The expected payback time of the CO_2 capture plant is estimated at 9.3 years. In Figure 5.9 the cumulative depreciated cash flows are illustrated throughout the lifetime period of the capture system.

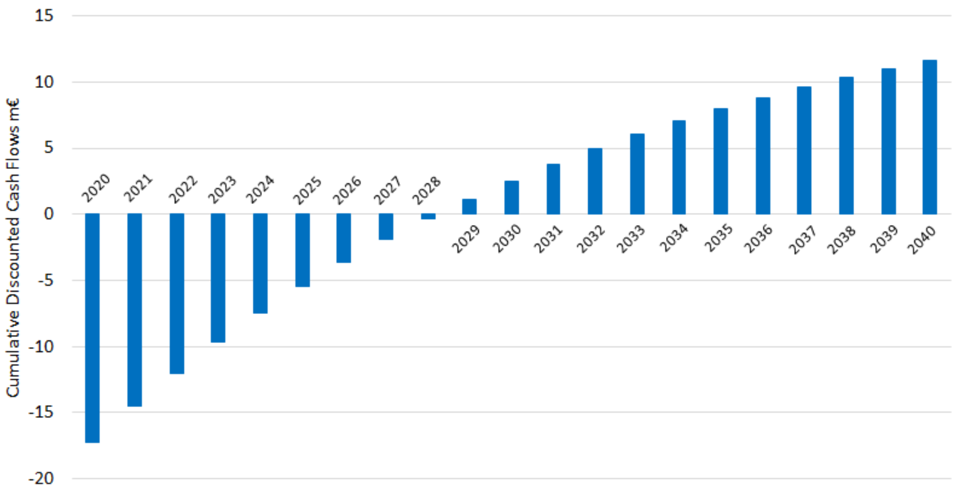


Figure 5.9: Net Present Value of the system throughout its lifetime.

In this paragraph also the cost of the amount of formic acid produced is to be defined taking into account all the aforementioned costs. It can be calculated according to the following equation:

$$\text{Cost of Produced Formic Acid} = \frac{CAPEX_{\text{ann}} + FOPEX + VOPEX}{\text{Produced Formic Acid}} = 400\,€/\text{ tn FA} \tag{5.8}$$

From the results that are described above it can be concluded that the total investment of the examined capture plant is profitable and the production cost of formic acid is attractive when compared to the market price of formic acid, which is 550-650 €/tn.

5.6 Sensitivity Analysis

In this section a sensitivity analysis of the plant is been done regarding some sensitive parameters that affect directly and significantly the outcome of the base case scenario. The effect of these parameters is illustrated din this section, in comparison to the market price of formic acid, highlighting the lower level of production costs.

Capital cost of electrolyzer

The capital cost of the electrolyzer is a fluctuating value, since water electrolysis is becoming more and more mature and demand is getting higher, reducing the cost of the electrolyzer, as discussed in Chapter 5.2.

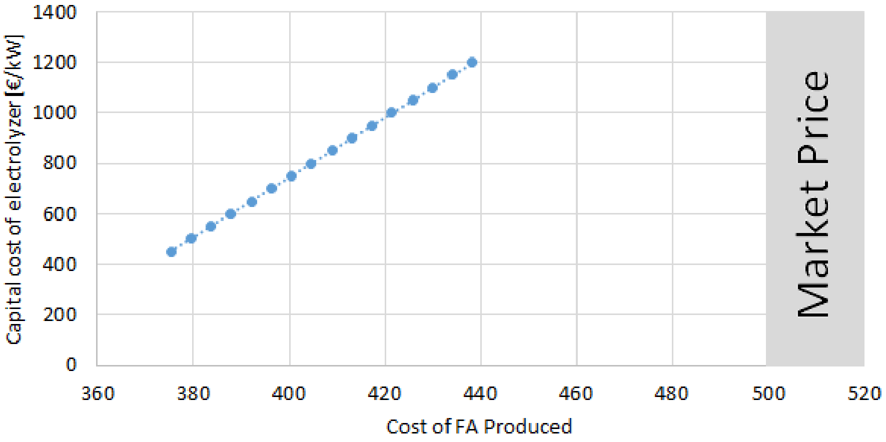


Figure 5.10: Cost of FA with respect to the capital cost of electrolyzer.

With various prices of either PEM or alkaline electrolyzer, the production costs are affected as can be seen in Figure 5.10. The production cost of formic acid varries within the range of 375-440 €/tn, showing some slight effect.

Electricity price analysis

Electricity price can fluctuate a lot and in Figure 5.11 a sensitivity analysis is presented as a function of the production cost of formic acid. At a high cost of electricity of 0.08 €/kWh the cost of formic acid reaches the market price levels.

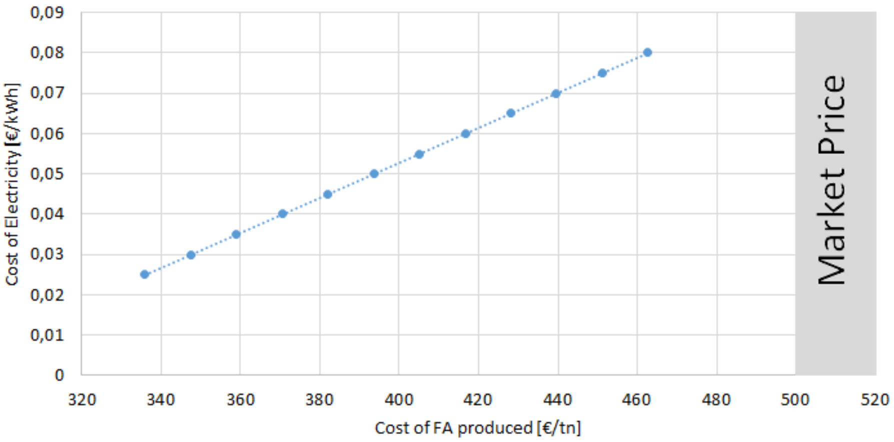


Figure 5.11: Cost of FA with respect to electricity price.

An optimistic value of electricity price results to a significant decrease in the production costs of formic acid. As discussed in Chapter 5.4.2.1 the cost of electricity changes a lot over the years and a price drop is possible.

Lifetime of the capture integrated system

The predicted lifetime of a power plant can affect the annualized capital cost and as a result the cost of formic acid. In Figure 5.12 this correlation is depicted. A very low expected lifetime such as 5 years is no longer realistic for the scale of such an integrated system.

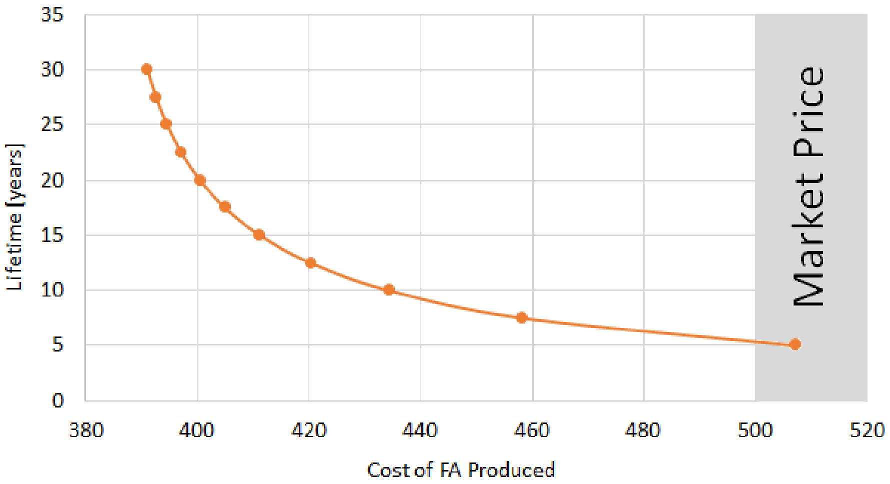


Figure 5.12: Cost of FA with respect to lifetime of the CO_2 capture plant

The lifetime of the base case scenario is 20 years, making the overall scenario attractive and the investigation profitable. A lifetime period of 30 years does not affect the price of formic acid to a great extent.

Payback time prediction

The selection of the value of the discount rate is arbitrary and this is the main reason a sensitivity analysis on various values is valuable.

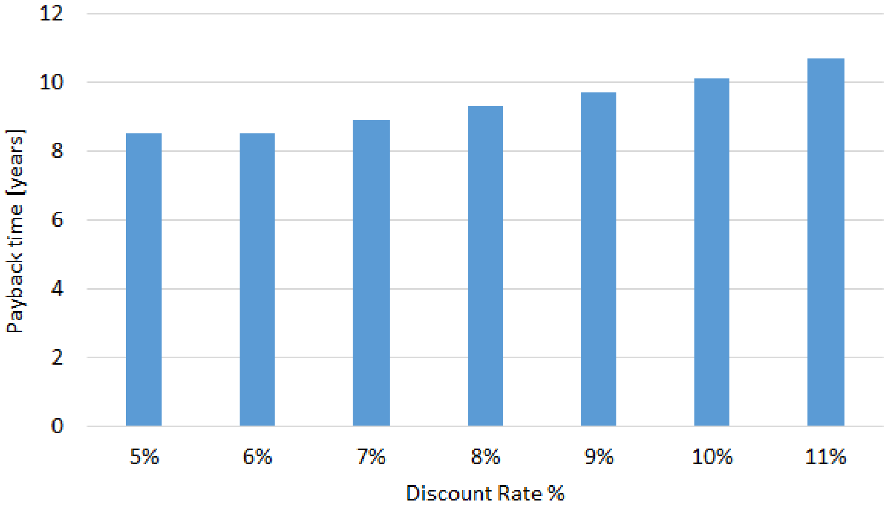


Figure 5.13: Payback time with respect to discount rate

In Figure 5.13 the calculated payback time is depicted for various values of discount rate, starting from an optimistic value of 5% towards a pessimistic one of 11%.

Optimistic and pessimistic scenarios

In this section an overview of an optimistic and a pessimistic scenarios can be seen in Figure 5.14 for the different investigated parameters that affect the final production cost of formic acid. The base case scenario that was explained in detail in the paragraphs above represents the 0.0% in the graph.

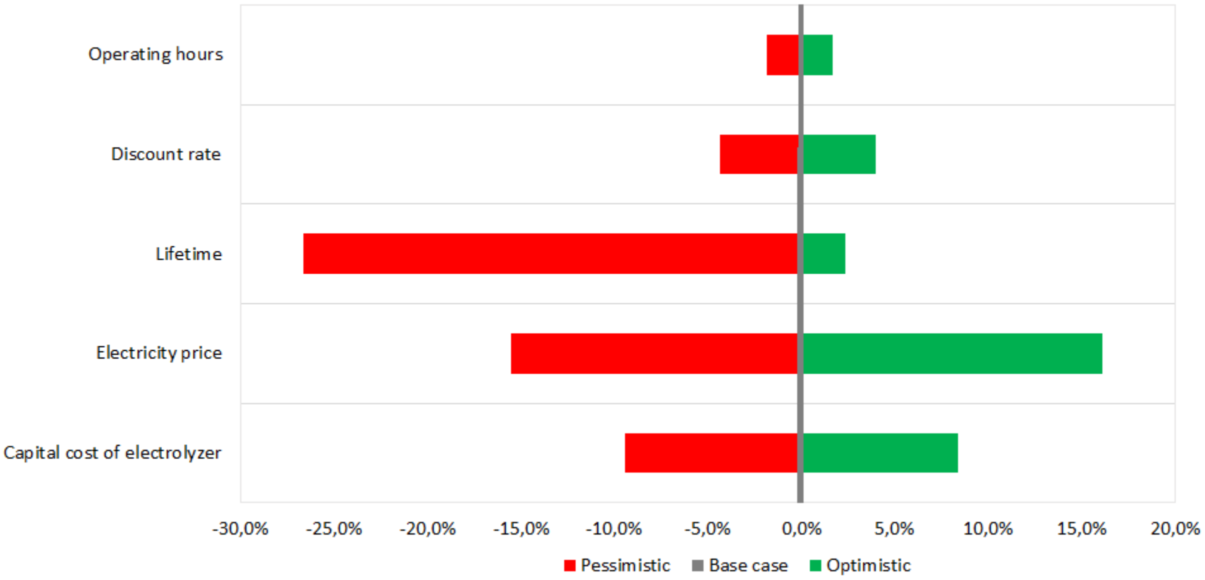


Figure 5.14: Sensitivity analysis on the investigated parameters.

5.7 Comparison of the proposed systems

In this paragraph a comparison of the two integrated systems is depicted in Figure 5.15, indicating the difference in CAPEX and OPEX costs. The system with crystallization appears to have lower capital investment due to the fact that lower amount of inlet is assumed after the separation of the crystals and the liquid products.

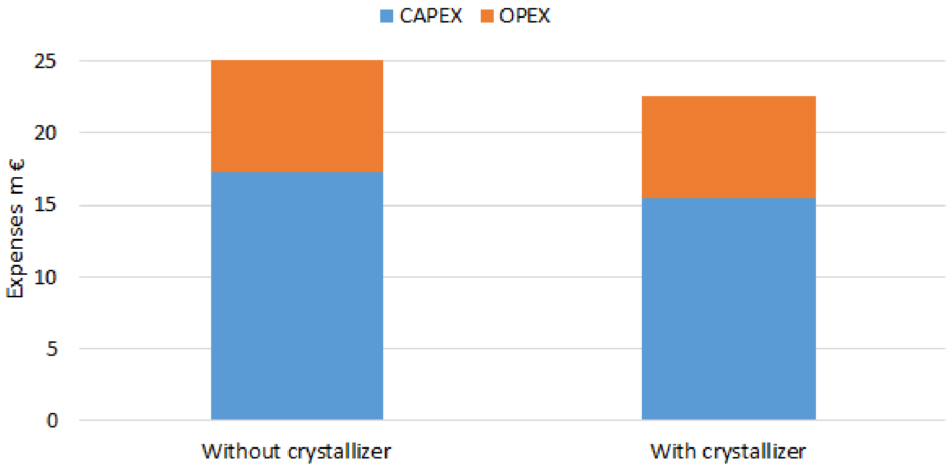


Figure 5.15: Comparison of integrated systems, with and without crystallizer.

To sum up, the system including crystallization appears to have lower operating and capital total costs as well as a higher concentration of formic acid. However, the relative difference of these two integrated system cannot be considered that significant. In that term, the integrated system without a crystallizer is preferable, since it does not include handling of solids that may turn out to be tricky and challenging in practice.

5.8 Cost of formaldehyde produced

In this section, the additional cost for the production of formaldehyde is investigated, including the additional amount of pressurized hydrogen as well as the pressurized reactor. For the incorporation of the formaldehyde production cost, the additional amount of required hydrogen is included. This is the main CAPEX and OPEX of this chemical reaction, the capital cost of electrolyzer and the cost of electricity for the operation of a 18 MW alkaline electrolyzer. From the above, a production cost of formaldehyde of 570 €/tn is calculated at a 35 % concentration. This production cost results to an attractive route, since the market price of formalin is 300-500 €/tn, at similar levels of concentration (37% purity).

Chapter 6

Conclusions

In this work, the conceptual design of a CO_2 capture system is proposed with an aqueous ammonia solvent as well as experimental verification of the thermochemical reaction steps taking place in the proposed system. The CO_2 captured is then utilized thermochemically to the production of formic acid and further on to formaldehyde. The integrated system of the overall project is presented, with and without a crystallization system, along with a techno-economic analysis to evaluate the feasibility of the system. In this Chapter, the main conclusions and contributions of the project are to be described, defined and all the research questions are to be answered thoroughly.

- **What are the different paths of CO_2 products and which routes are the most attractive?**

CO_2 utilization is driving more and more the attention in the energy field and in the worldwide energy transition. The possible routes can be infinite and an initial limitation and definition of the research boundaries is necessary. After thorough literature survey on absorption solvents, ammonia as an indicated solvent can be very advantageous for the proposed system, since it can result to a large variety of end-products. The main limitation applied is the selection of ammonia as solvent of the absorption column that is used to produce ammonium bicarbonate salts in the outlet of the absorber. Ammonium bicarbonate appears to be an attractive intermediate product that can be used for the production of different valuable end-products, such as formic acid, methanol, formamide and oxalic acid.

In an initial step, ammonium formate and ammonium oxalate appear to be more attractive both in terms of mass and energy balance. These products are intermediates and need further processing. In this work, ammonium formate is studied as a carrier of formic acid and ammonia. Thermal decomposition of this product appears to be effective and is the main subject of the work, more specifically the separation towards formic acid and recycling of ammonia. Ammonia as a compound is very volatile, which in conventional capture systems is a drawback, while in this work is the main driving force and necessary aspect of the system. Its volatility makes its separation much easier, making the use of volatile solvents an advantage towards widely used ones.

- **Can ammonia CO_2 capture be integrated with CO_2 utilization?**

CO_2 capture is widely used with commercial solvents, such as MEA, ammonia and NaOH. Such conventional systems consist of an absorber and a stripper, to remove CO_2 gas from industrial flue gases. Chemical absorption is used in large scale power plants and is economically attractive. Ammonia as a solvent has many advantages, such as the cost, high availability, low regeneration energy and is much more volatile compared to MEA. The latter feature in concentional capture systems is limiting, but in the proposed systems of this work, this high volatility is a huge advantage of the idea. A more chilled process at a range of temperatures 5-15°C is required in order to minimize ammonia slip out of the absorber. An innovative added value of the system is the concentrated ammonia solvent of 30-40 %wt, with simultaneous careful process design for the prevention of solid precipitation.

The captured CO_2 can be then processed, via utilization and production of valuable chemicals and fuels. This can be done either electrochemically or chemically to final valuable products. In this work, an alternative case of the conventional capture system is examined. Between the absorber and the stripper of the system there is a set of chemical reactions that are used to produce formic acid in the bottom of the stripper. So, CO_2 utilization is integrated in the capture system, highlighting a research gap that is in the process of been fulfilled.

In this specific system, After the production of ammonium bicarbonate, the liquid product enters a hydrogenation reactor, with pressurized hydrogen derived from water electrolysis, towards the production of ammonium formate. Thermal decomposition proceeds, where ammonia and formic acid are produced. The volatility of ammonia in this system is a major advantage of the system, since it can evaporate out of the top of the stripper and regenerate back in the top of the absorber.

High ammonia concentration in the inlet of the absorber, results in high bicarbonate and further in high formate concentration. These process steps lead to a relatively concentrated stream of formic acid in watery solution. The conceptual design of the aforementioned system results to a formic acid concentration of around 32-37 % wt. An alternative addition to the integrated system is a crystallization system downstream to the absorber, creating crystals of ammonium bicarbonate which are further separated from the liquid part of the stream. In this manner, a more concentrated liquid solution of ammonium bicarbonate enters in the hydrogenation reaction. Following the same reaction steps this lead to a final higher concentration of formic acid close to 47% wt.

- **Is it techno-economically feasible to capture CO_2 with aqueous ammonia and produce concentrated formic acid?**

A techno-economic analysis of the system is conducted. Taking into account, the capital investment of the participating blocks, the inlet feeds as well as the utilities used in the system, it appears that the examined system including is profitable with production cost of formic acid at 400 €/tn, compared to 550-650 €/tn of the market price and a payback time of 9.3 years. A sensitivity analysis is also been conducted for various parameters that affect the outcome of the investigation, such as electricity price, capital cost of electrolyzer, the interest rate, the lifetime of the plant and the operating hours during a year.

An additional value in the system and the final concentration of formic acid is the introduction of a crystallizer system. The slurry that is formed downstream of the absorber is separated from the liquid part of the stream and higher concentration of formic acid is achieved. Due to lower mass flows in this system, CAPEX and OPEX appear to be lower compared to the initial investigated system. However, the incorporation of crystallization and solids handling can be challenging in real life power plants, making the more simpler system much more attractive, realistic and applicable.

The integrated system that is the main subject of this work, appears to have some innovative chemical steps towards the production of formic acid, indicating a research gap. The combination of the examined steps, results to an innovative process of producing formic acid or further formaldehyde. A techno-economic evaluation of the production of formaldehyde is roughly defined, resulting in cost of 550 €/tn at high concentration, comparable to the one that formaldehyde is indeed been sold.

To sum up, the conceptual design of the integrated system of CO_2 capture with aqueous ammonia is a promising and attractive method of CO_2 utilization to the production of formic acid. The experimental proof of concept is an added value to the project, indicating the realisation and feasibility of the study. The production cost of formic acid is found to be much lower compared to the market price of the end product, indicating the research gap of the investigated system.

Chapter 7

Recommendations

7.1 Improvements on the proposed system

Ammonia as a volatile compound results to high ammonia losses out of the absorber. A conceptual design for water wash is studied in this study, however its further optimization is worthwhile. This is the main disadvantage of the system, ammonia slip out of the absorber.

In the proposed systems, an aqueous solution of ammonia is examined. The resulting product of formic acid is also in aqueous solution, resulting to a relatively low purity. Formic acid in a commercial perspective, is sold in high purities, typically at 85 %wt. It should be noted that further separation of formic acid from water is needed, however it is a costly and energy intensive process.

The investigation of alternative organic solvents seems to be an added value to the whole process design and also to the final purity of the product. A water-miscible organic solvent can be used with a mixture of water and for instance methanol. Methanol has a boiling point of 64.7°C, leading to a more effective separation step. At the operating conditions of the stripper discussed in this thesis, methanol along with ammonia will evaporate out of the top of the absorber. In this way, an even more concentrated formic acid solution can be achieved.

7.2 Tertiary amine solvents

In the initial proposed innovative concept, the production of formic acid from CO_2 from flue gas is investigated. This described concept can also be applied using several tertiary amines as a CO_2 capture solvent. As can be seen in Figure 7.1 similar steps as the integrated system of ammonia can be used with tertiary amine solvents. [87]

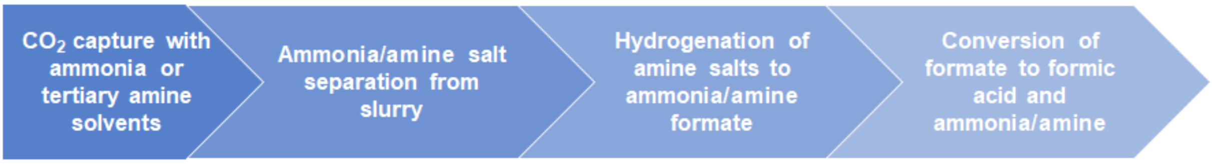


Figure 7.1: Process flow diagram of the innovative system.

The selection of the appropriate solvent in a system is essential, as far as its absorption capacity is concerned. Such an appropriate solvent with a high cyclic capacity may effectively result in significant reduction of the overall dimensions of the amine based plant, since smaller flow rate is circulating in the system.

Table 7.1: Ammonia based solvents. [88]

Component	Boiling point °C	Comment
Ammonia NH_3	-33	Simplest pnictogen hydride
Methylamine CH_3NH_2	-6.6	Simplest primary amine
Dimethylamine $(CH_3)_2NH$	7-9	Secondary amine
Trimethylamine $(CH_3)_3N$	3-7	Tertiary amine

In Table 7.1 the ammonia-based solvents are presented that can be utilized as capturing solutions. Ammonia is the simplest amine solution consisting of three hydrogen molecules, while trimethylamine (TMA) consists of three methyl compounds instead. All ammonia-based solvents described in Table 7.1 gather similar characteristics and advantages, compared to ammonia. They can effectively be used in similar systems as the proposed ones, taking advantage of the volatility of such compounds. [89]

Table 7.2: Vapor pressure of ammonia and trimethylamine. [90], [91]

Gaseous component, 20°C		**40% wt aqueous solution, 20°C**	
NH_3	**TMA**	**NH_3**	**TMA**
1003 kPa	223.8 kPa	106.7 kPa	67 kPa

More particularly TMA is a tertiary amine that is less volatile compared to ammonia, as can be seen in Table 7.2 where its vapor pressure is much lower. TMA is not a widely used capturing solvent and there is barely any established research on its use in conventional CO_2 capture systems. [90] However, its use in a system where the captured CO_2 is further utilized can be designed in an effective manner. Additionally, its boiling point is 3 - 7°C, making its separation step much easier, compared to the ammonia system.

The CO_2 capture system with trimethylamine (TMA) was not intensively studied, mainly due to its high volatility as well as its intense fishy odor. The characteristic of volatility of a compound can be compared in terms of its vapor pressure. In particular, vapor pressure of TMA 40% aqueous solution is 67 kPa. [92]

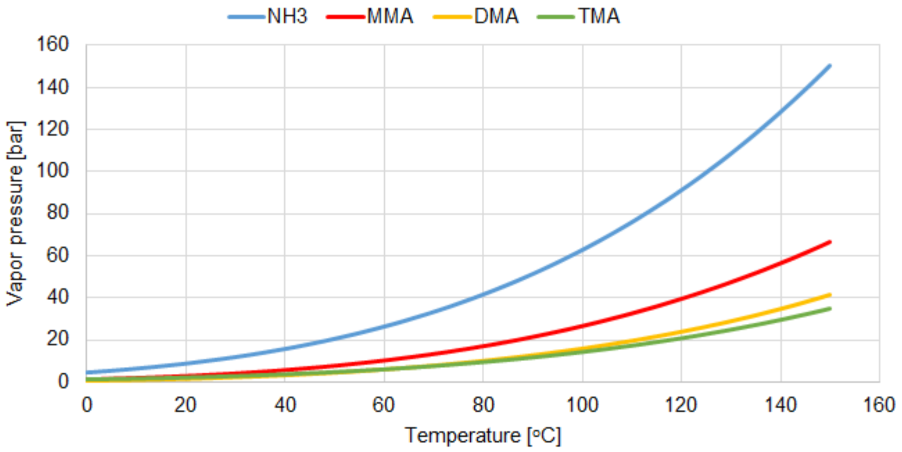


Figure 7.2: Vapor pressure of ammonia, TMA, DMA and MMA.

Similar to the integrated system that was described and investigated in this thesis work, trimethylamimne can be used as an aqueous solvent. In the rich outlet of the absorber the production of the bicarbonate of TMA takes place. Further on, hydrogenation reaction leads to the production of TMA formate. The last step of the process is the production of formic acid as the main product and TMA is evaporated out of the stripper and can be regenerated back to the inlet of the absorber.

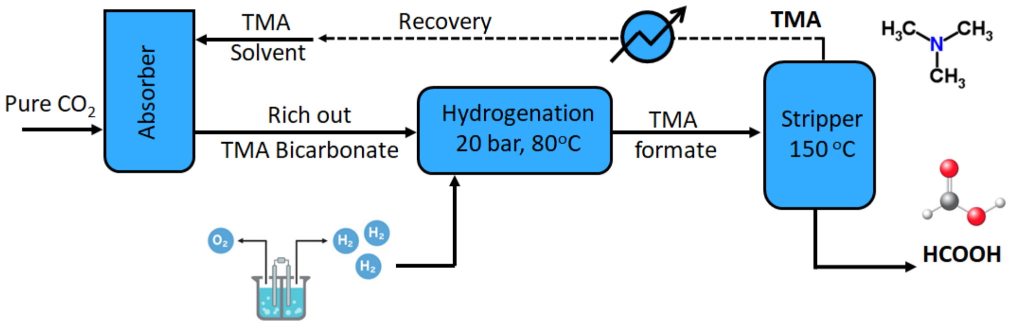


Figure 7.3: Schematic overview of integrated system via aqueous TMA solvent.

Some differences from the already examined system should be noted. First of all, the absorption column is enclosed on top, resulting to the formation of liquid products only at the bottom of the absorber, mainly TMA bicarbonate. TMA is indeed less volatile compared to ammonia, but practical properties of it, such as its fishy smell, promote a closed system. Thus, TMA slip can be maximized in case of a conventional absorber design including a gaseous outlet. Secondly, pure CO_2 inlet stream is used in the absorption column of the capturing step instead of a flue gas derived from power generation point sources. In this way, there are no further contaminants and the system results to the production of TMA bicarbonate in liquid state. Also in this system the formation of solids is avoided so as to prevent the formation of slurry inside the absorber and additional maintenance costs.

Such a system has not been investigated in research level, but due to its higher boiling point it appears to have an easier separation step from formic acid, compared to ammonia. An experimental proof of concept has been conducted, using a laboratory distillation column with the help of the experienced lab staff of TNO. To begin with, TMA formate is prepared carefully with the acid-base reaction of TMA and formic acid diluted in water, based on the reaction:

$$(CH_3)_3N + HCOOH \Longrightarrow (CH_3)_3NHCOOH \tag{7.1}$$

Further to the experiment, the aqueous solution of formate is inserted in the distillation column at operating temperature of 150°C and the experiment ran for over 40 minutes. The conditions and results of the experiment are shown in Table 7.3 and the necessary analysis is being conducted with FTIR and HPLC methods. The difference in the pH is presented, both for the distillate and the remaining part, indicating a very basic and vary acid compound respectively. HPLC measures $HCOO^-$ ions at a certain retention time and it can be seen that the distillate part has no such peak in that time. The area of the remaining part indicates strongly the formate ions.

Table 7.3: Conditions of TMA experiment.

% wt	**mL**	**gr$_{\text{amine}}$**	**gr$_{\text{formic acid}}$**	**pH$_{\text{i}}$**	**pH$_{\text{distillate}}$**	**pH$_{\text{rest}}$**
5	200	22.28	7.88	7.1	12.4	3.9
Vol$_{\text{distillate}}$	**Vol$_{\text{rest}}$**	**Area rest**	**Area distil**	**mg/mL rest**	**mol/L rest**	**Separation %**
50	150	1.848e+06	-	51.14	0.48	**49**

Analyzing the results of the experiment it can be concluded that the thermal decomposition and separation of TMA formate towards TMA and formic acid is effective, giving an added value to the whole integrated system. In Figure 7.5 the transmittance profile throughout a certain wavenumber can be seen and analyzed with FTIR method. The initial part can be seen in light blue color. After running the experiment for half an hour, the profile of the remaining part can be seen in the orange curve. After letting the experiment run for another 45 minutes it seems that decomposition takes place and the peaks of the dark blue curve indicate the formation of formic acid. The yellow curve shows the formation of TMA. [70]

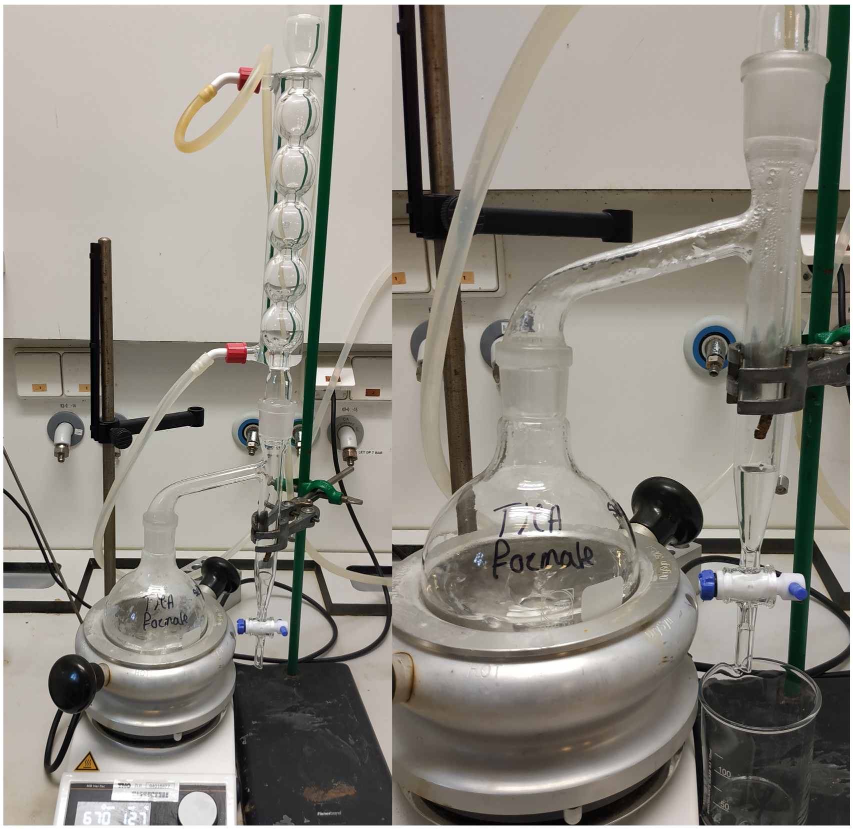


Figure 7.4: distillation column for decomposition of TMA formate.

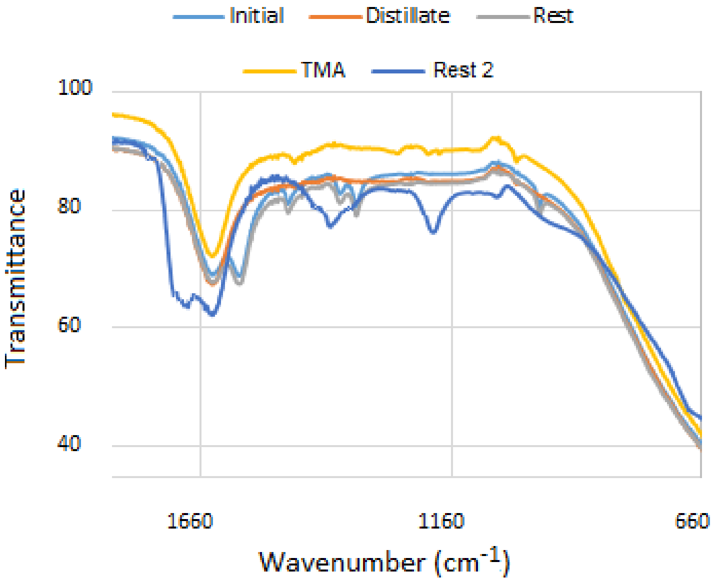


Figure 7.5: FTIR analysis for ammonium formate decomposition.

To sum up, further investigation on TMA as an indicated solvent appears to be an interesting added value of the research study. It is less volatile compared to ammonia, making the amine losses in the absorption step relatively low. TMA as a tertiary amine has similar chemical configuration as ammonia, resulting in similar behavior as aqueous ammonia in the proposed system. Further investigation on the techno-economic evaluation of the referred process design is worth doing, especially for the proposed top-closed absorption column.

7.3 Formate to oxalate

The formation of chemical routes towards higher carbon chains may lead to viable and valuable end-products of C2 through catalytic decomposition of formates to oxalates. In general, the production of multi-carbon chemicals derived initially from CO_2 can be assumed to be a sustainable way to produce valuable products. In this Chapter, another important chemical route that appears to be techno-economically attractive, as discussed in Chapter 2, is the chemical reaction of ammonium formate to ammonium oxalate as seen in the following reaction:

$$2NH_4COOH(l) \implies (NH_4)_2C_2O_4(s) + H_2(g) \tag{7.2}$$

The aforementioned reaction takes place at a temperature range of 310-410 °C and literature indicates the exceeding of 360 °C towards the formation of oxalate. It is highly selective towards the production of the solid oxalate and hydrogen by using alkali hydroxide or hydride catalysts and can also be characterized as simple, since the two main products can be separated spontaneously. [93]

Various studies indicate the different reaction conditions, including oxalate, carbonate, carbon monoxide and carbon dioxide, by varying the amount of the catalyst and temperature. [94], [95] The following mechanism is proposed and followed for the thermal decomposition of formate to oxalate with the intermediate production of carbonite $CO_2{}^{2-}$: [96]

$$2HCO_2^- \implies H_2 + CO_2 + CO_2^{2-} \tag{7.3}$$

$$CO_2^{2-} + CO_2 \iff C_2O_4^{2-} \tag{7.4}$$

The use of catalyst has great effect on the final oxalate yield. [93] Ammonium oxalate appears to be an interesting product, since it can be used as an intermediate product either for the production of oxalic acid or tartaric acid according to the following chemical reactions respectively:

$$(NH_4)_2C_2O_4 + 2HCl \implies C_2O_4H_2 + 2NH_4Cl \tag{7.5}$$

$$2(NH_4)_2C_2O_4 \implies C_4H_6O_6 + 2(NH_4)_2O \tag{7.6}$$

Oxalic acid can be a final product, since it has various applications, as referred in Chapter 2. Its production requires hydrogen chloride, as can be seen in Reaction 7.5. Tartaric acid can be used as an antioxidant. Also it can be found in many food products, such as baking powder. Additionally, its applications also include leather tanning and in medical applications for the measurement of glucose. [97]

Bibliography

[1] European Commission, "2050 energy strategy." *https://ec.europa.eu/energy/en/topics/energy-strategy-and-energy-union/2050-energy-strategy*, 2013.

[2] Ranjan M., Herzog H.J., *Feasibility of air capture*. Energy Procedia 4, 2869-2876, 2011.

[3] NASA - Global Climate Change, Vital Signs of the Planet, "Carbon Dioxide Measurement." *https://climate.nasa.gov/vital-signs/carbon-dioxide/*, 2018.

[4] DNV, *Carbon Dioxide Utilization Electrochemical Conversion of CO_2 – Opportunities and Challenges*. 2011.

[5] Quadrelli E.A., Armstrong K., Styring P., *Potential CO_2 Utilisation Contributions to a More Carbon-Sober Future: A 2050 Vision*. Carbon Dioxide Utilization, Closing the Carbon Cycle, 285-302, 2015.

[6] Narayanan H., Viswanathan B., Yesodharan S., *Photocatalytic reduction of carbon dioxide: Issues and prospects* . Current Catalysis 5, 79-107, 2016.

[7] Aulice Scibioh M., Viswanathan B., *Perspectives — CO_2 Conversion to Fuels and Chemicals* . Carbon Dioxide to Chemicals and Fuels - Chapter 10, 475-482, 2018.

[8] Chemical Book, "Cas database list - ammonium formate." *https://www.chemicalbook.com/ChemicalProductProperty_EN_CB3140017.htm*, 2017.

[9] Pérez-Fortes M., Schöneberger, Boulamanti A., Harrison G., Tzimas E., *Formic acid synthesis using CO_2 as raw material: Techno-economic and environmental evaluation and market potential*. International Journal of Hydrogen Energy 41, 16444-16462, 2016.

[10] TranTech Consultants Inc., "Chemical profile: formic acid." *http://chemplan.biz/chemplan_demo/sample_reports/Formic_Acid_Profile.pdf*, 2014.

[11] Mordor Intelligence, "Formic acid market - growth, trends, and forecasts (2019-2024)." *https://www.mordorintelligence.com/industry-reports/formic-acid-market*, 2019.

[12] Redondo A.B., Fodor D., Brown M.A., van Bokhoven J.A., *Formaldehyde, methanol and methyl formate from formic acid reaction over supported metal catalysts*. Catalysts Communications 56, 128-133, 2014.

[13] Foegeding P.M., Busta F.F., *Chemical food preservatives In: Disinfection, Sterilization and Preservation*. Philadelphia, PA: Lea & Febiger, 802-832, 1991.

[14] Formacare, "Applications: Formaldehyde's many applications." *https://www.formacare.eu/about-formaldehyde/applications/*, 2019.

[15] The Essential Chemical Industry - online, "Uses of methanal (formaldehyde)." *http://www.essentialchemicalindustry.org/chemicals/methanal.html*, 2016.

[16] Merchant Research & Consulting ltd, "Formaldehyde: 2010 world market outlook and forecast up to 2019." *https://mcgroup.co.uk/researches/formaldehyde*, 2010.

[17] IHS Annual Report 2015, *Letter to Stakeholders - Notice of 2016 Annual Stockholder Meeting*. Proxy Statement, 2015.

[18] Alvarado M., *Methanol - IHS Annual Report*. The Source for Critical Information and Insight, 2016.

[19] American Chemical Society, "Methyl formate: Applications." *https://www.acs.org/content/acs/en/molecule-of-the-week/archive/m/methyl-formate.html*, 2019.

[20] Easy & Intuitive Work Management Tool, "Ammonium oxalate formula." *http://www.softschools.com/formulas/chemistry/ammonium_oxalate_formula/384/*, 2019.

[21] The Chemical Company - Global Bonds in Chemistry, "Ammonium carbonate." *https://thechemco.com/chemical/ammonium-carbonate/*, 2019.

[22] MERCK - Sigma-Aldrich, "Formamide molecular biology reagent." *https://www.sigmaaldrich.com/technical-documents/articles/biology/formamide.html*, 2019.

[23] Acidpedia - Read All About Acids, "Oxalic acid -." *http://acidpedia.org/oxalic_acid/*, 2019.

[24] U.S. Natioanla Library of Medicine - National Center for Biotechnology Information, "Oxamide." *https://pubchem.ncbi.nlm.nih.gov/compound/oxamide*, 2019.

[25] Diefallah E.H.M., El-Bellihi A.A., Basahel S.N., Wahab M.A., Omran Z.A., *Kinetic analysis of thermal decomposition reactions. Radiation effects on the thermal decomposition of ammonium oxalate monohydrate*. Thermochimica Acta 230, 143-153, 1993.

[26] Radhakrishnan Nair M.N., Verneker V.R.P., *Incomplete Decomposition of Ammonium Oxalate*. Combustion and Flame 25, 301-307, 1975.

[27] Kenarsari S.D., Yang D., Jiang G., Zhang S., Wang J., Russell A.G., Fan M., *Review of recent advances in carbon dioxide separation and capture*. RSC Advances: The Royal Society of Chemistry, 2013.

[28] Boot-Handford M.E., Abanades J.C., Anthony E.J., Blunt M.J., Brandani S., Mac Dowell N., Fennell P.S., *Carbon capture and storage update*. Energy and Environmental Science: The Royal Society of Chemistry, 2014.

[29] A.J.Kidnay, M.J.Hiza, *Physical adsorption in cryogenic engineering*. Cryogenics 10 (4), 271-277, 1970.

[30] Yeh J.T., Pennline H.W., Resnik K.P., *Study of CO_2 Absorption and Desorption in a Packed Column*. Energy Fuels 15, 274-278, 2001.

[31] Separation Processes, "Type of absorbers - packed column." *http://www.separationprocesses.com/Absorption/Fig130.htm*, 2019.

[32] Hoff K.A., Svendesen H.F., *CO_2 absorption with membrane contactors vs. packed absorbers - Challenges and opportunities in post combustion capture and natural gas sweetening*. Energy Procedia 37, 952-960, 2013.

[33] Shim S.M., Lee S.J., Kim W.S., *A numerical evaluation of prediction accuracy of CO_2 absorber model for various reaction rate coefficients*. Thermal Science 16-3, 877-888, 2012.

[34] Han J.H., *Experimental Study on CO_2 Absorption Process by Using Aqueous Ammonia*. Department of Mechanical Engineering, Hanynag University, Seoul, 2012.

[35] Engineering ToolBox, "Ammonia - properties at gas-liquid equilibrium conditions." *https://www.engineeringtoolbox.com/ammonia-gas-liquid-equilibrium-condition-properties-temperature-pressure-boiling-curve-d_2013.html*, 2018.

[36] Darde V., Maribo-Mogenses B., Van Well W.J.M., Stenby E.H., Thomsen K., *Process simulation of CO_2 capture with aqueous ammonia using the extended UNIQUAC model*. International Journal of Greenhouse Gas Control 10, 74-87, 2012.

[37] Pismenskaya N., Laktionov E., Nikonenko V., Attar A.E., Auclair B., Pourcelly G., *Dependence of composition of anion-exchange membranes and their electrical conductivity on concentration of sodium salts of carbonic and phoshporic acids*. Journal of Membranes Science 181, 185-197, 2001.

[38] Chen P., Yu S., *CO_2 Capture and Crystallization of Ammonia Bicarbonate in a Lab-Scale Scrubber*. Crystals 8(1), 39, 2018.

[39] van de Runstraat A., Abu-Zahra M.R., Feron P.H.M., *CO_2 removal by aqueous ammonia scrubbing*. TNO Report, I&T-A R 2007/013, 2007.

[40] Gazzani M., Sutter D., Mazzotti M., *Improving the efficiency of a chilled ammonia CO_2 capture plant through solid formation: a thermodynamic analysis*. Energy Procedia 63, 1084–1090, 2014.

[41] Biscans B., *Crystallization reactors*. Master of Crystallography and Crystallization, Université de Toulouse, CNRS - Laboratoire de Génie Chimique UMR 5503 –FRANCE, 2012.

[42] Sutter D., Gazzani M., Pérez-Calvo J.F., Leopold C., Milella F., Mazzotti M., *Solid formation in ammonia-based processes for CO_2 capture – Turning a challenge into an opportunity*. Energy Procedia 114, 866–872, 2017.

[43] Sutter D., Gazzani M., Mazzotti M., *Kinetics of solid formationin the chilled ammonia system and implications for a 2^{nd} generation process*. Energy Procedia 63, 1957–1962, 2014.

[44] Sutter D., Gazzani M., Mazzotti M., *Formation of solids in ammonia-based CO_2 capture processes — Identification of criticalities through thermodynamic analysis of the CO_2–NH_3–H_2O system*. Chemical Engineering Science 133, 170–180, 2015.

[45] Ye Q., Wang X., Lu Y., *Kinetic behavior of potassium bicarbonate crystallization in a carbonate-based CO_2 absorption process*. Chemical Engineering Research And Design 93, 136–147, 2015.

[46] Su J., Yang L., Lin H., *Highly Efficient Hydrogen Storage System Based on Ammonium Bicarboante/Formate Redox Equilibrium over Palladium Nanocatalysts*. Chemistry & Sustainability, Energy & Materials 8, 816-816, 2015.

[47] Wang M., Zhang J., Yan N., *Transformation of sodium bicarbonate and CO_2 into sodium formate over NiPd nanoparticle catalyst*. Frontiers in Chemistry, 2013.

[48] Wiener H., Blum J., Feilchenfeld H., Sasson Y., Zalmanov N., *The Heterogeneous Catalytic-Hydrogenation of Bicarbonate to Formate in Aqueous-Solutions*. Journal of Catalysis 110, 184-190, 1988.

[49] Bulushev D., Ross J., *Heterogeneous catalysts for hydrogenation of CO_2 and bicarbonates to formic acid and formates*. Catalysis Reviwes 60:4, 566-593, 2018.

[50] Su J., Lu M., Lin H., *High yield production of formate by hydrogenating CO_2 derived ammonium carbamate/carbonate at room temperature*. Green Chemistry 17 (5), 2769-2773, 2015.

[51] Sutherland J.C., *Absorption & Stripping*. The University of UTAH SHR, Chapter 6, 2018.

[52] Wilson T.A., *Total and partial vapor pressures of aqueous ammonia solutions*. University of Illinois at Urbana Champaign, College of Engineering. Engineering Experiment Station, 1925.

[53] Liu Y., Wang Y., Zhang J., Shi S., Feng P., Wang T., *Observation of surface structural changes of Pt octahedron nanoparticles and its effect in electrocatalysis oxidation of methanol*. Catalysis Communications 10, 1244-1247, 2009.

[54] Zhou J., Huang L., Yan W., Li J., Liu C., Lu X., *Theoretical Study of the Mechanism for CO_2 Hydrogenation to Methanol Catalyzed by trans-$RuH_2(CO)(dpa)$*. Catalyst 8 (6), 244, 2018.

[55] Perez-Calvo J.F., Sutter D., Gazzani M., Mazzotti M., *Application of a chilled ammonia-based process for CO_2 capture to cement plants*. Energy Procedia 114, 6197-6205, 2017.

[56] Bonaventura D., Chacartegui R., Valverde J.M., Becerra J.A., Verda V., *Carbon capture and utilization for sodium bicarbonate production assisted by solar thermal power*. Energy Conversion and Management 149, 860-874, 2017.

[57] Physical and Theoretical Chemistry Textbook Maps, *The Equilibrium Constant, K*. Chemistry - Libretexts, 2019.

[58] Haynes H.W., *Thermodynamic solution model for trona brines*. AlChE Journal 49(7), 1883-1894, 2003.

[59] Yang N., Yu H., Li L., Xu D., Han W., Feron P., *Aqueous Ammonia (NH_3 Based Post Combustion CO_2 Capture: A Review*. Oil & Gas Science and technology - Revue d'IFP Energies nouvelles, Institut Français du Pétrole 69 (5), 931-945, 2014.

[60] Versteeg P., Rubin E.S., *A technical and economic assessment of ammonia-based post-combustion CO_2 capture at coal-fired power plants*. International Journal of Greenhouse Gas Control 5, 1596-1605, 2011.

[61] Budzianowski W.M., *Mitigating NH_3 vaporization from an aqueous ammonia process for CO_2 capture*. International Journal of Chemical Reactor Engineering 9-1, 1-27, 2011.

[62] Pinsent B.R.W., Pearson L., Roughton F.J.W., *The kinetics of combination of carbon dioxide with hydroxide ions*. Transactions of the Faraday Society 52, 1512-1520, 1956.

[63] Pinsent B.R.W., Pearson L., Roughton F.J.W., *The kinetics of combination of carbon dioxide with ammonia*. Transactions of the Faraday Society 52, 1594-1598, 1956.

[64] Zhou Q., Liu L., Croiset E., Tan Z., Liu Q., Yang J. , *Modeling study of the heat of absorption and solid precipitation for CO_2 capture by chilled ammonia*. RSC Advances 9 (35), 20075-20086, 2019.

[65] Qi G., Wang S., Yu H.,Feron P., Chen C., *Rate-Based Modeling of CO_2 Absorption in Aqueous NH_3 in a Packed Column*. Energy Procedia 37, 1968 – 1976 , 2013.

[66] European Commission, "Integrated pollution prevention and control: Best available techniques for large combustion plants." *https://eippcb.jrc.ec.europa.eu/reference/BREF/lcp_bref_0706.pdf*, 2006.

[67] Asif M., Kim W.S., *Process simulation of ammonia-based CO_2 capture and regeneration in packed column*. International Journal of Global Warming 8 (5), 401-414, 2015.

[68] Gaspar J., Waseem Arshad M., Ask Blaker E., Langseth B., Hansen T., Thomsen K., von Solms N., Lordrup Fosbøl P., *A low energy aqueous ammonia CO_2 capture process*. Energy Procedis 63, 614-623, 2014.

[69] Ito K., Bernstein H.J., *The vibrational Spectra of the Formate, Acetate and Oxalate ions*. Canadian Journal of Chemistry 34(2), 170-178, 1956.

[70] NIST - National Institute of Standards and Technology, U.S. Department of Commerce, "Nist chemistry webbook, srd 69." *https://www.nist.gov/*, 2019.

[71] Commissione Europea Risultati della ricerca dell' UE - CORDIS, *Optimization of CO_2 Capture Technology Allowing Verification and Implementation at Utility Scale (OCTAVIUS)*. IFP Energies nouvelles, 2014.

[72] Razi N., Svendsen H.F., Bolland O., *Cost and energy sensitivity analysis of absorber design in CO_2 capture with MEA*. International Journal of Greenhouse Gas Control 19, 331-339, 2013.

[73] Towler G., Sinnott R., *Chemical Engineering Design, Principles, Practice and Economics of Plant and Process Design*. Elsevier - Second Edition, 2012.

[74] US Department of Energy, "Doe technical targets for hydrogen production from electrolysis." *https://www.energy.gov*, 2018.

[75] Nel ASA, "Wide spread adaption of competitive hydrogen solution." *http://nelhydrogen.com*, 2018.

[76] Rizzi F., Annunziata E., Liberati G., Frey M., *Technological trajectories in the automotive industry: are hydrogen technologies still a possibility?* Journal of Cleaner Production 66, 328–336, 2014.

[77] Kumar S.S., Himabindu V., *Hydrogen production by PEM water electrolysis - A review*. Materials Science for Energy Technologies 2, 442-454, 2019.

[78] IRENA, *Hydrogen from Renewable Power: Technology Outlook for the Energy Transition*. International Renewable Energy Agency, Abu Dhabi, 2018.

[79] E4tech - Strategic thinking in sustainable energy, *Study on development of water electrolysis in the EU*. Joint NOW / FCH JU Water Electrolysis Day, Brussels, 2014.

[80] Coulson & Richardson's Chemical Engineering, *Chemical Engineering*. R. K. Sinnott - Elsevier Volume 6 - Fourth Edition, 2005.

[81] Tennet, *Electricity market insights*. Annual Market Update 2018, 2019.

[82] Seider W.D., Seader J.D., Lewin D.R., Widagdo S., *Product and Process Design Principles: Synthesis, Analysis and Evaluation*. Wiley - Third Edition, Ch.22-23, 2009.

[83] Feenstra M., Monteiro J., van de Akker J.T., Abu-Zahra M.R.M., Gilling E.G., Goetheer E., *Ship-based carbon capture onboard of diesel or LNG-fuelled ships*. International Journal of Greenhouse Gas Control 85, 1-10, 2019.

[84] Carolyn Preston - CKP & Associates Consulting, *IEAGHG Summary Report of the Shell Quest Carbon Capture and Storage Project - (GHGT-14)*. 14th Greenhouse Gas Control Technologies Conference, Melbourne, 2018.

[85] Ulrich G.D., Vasudevan P.T., *How to estimate utility costs*. Chemical Engineering 113 (4), 66-69, 2006.

[86] Investopedia - Corporate Finance & Accounting Financial Ratios, "Net present value (npv)." *https://www.investopedia.com/terms/n/npv.asp*, 2019.

[87] Berhardsen I.M., Knuutil H.K., *A review of potential amine solvents for CO_2 absorption process: Absorption capacity, cyclic capacity and pKa*. International Journal of Greenhouse Gas Control 61, 27-48, 2017.

[88] Kolliopoulos G., Carlos M., Clark T.J., Holland A.M., Peng D.Y., Papangelakis V.G., *Chemical Modeling of the TMA-CO_2-H_2O System: A Draw Solution in Forward Osmosis for Process Water Recovery*. Journal of Chemical & Engineering Data 62 (4), 1214-1222, 2017.

[89] Liang Z., Rongwong W., Liu H., Fu K., Gao H., Cao F., Zhang R., Sema T., Henni A., Sumon K., Nath D., Gelowitz D., Srisang W., Saiwan C., Benamor A., Al-Marri M., Shi H., Supap T., Chan C., Zhou Q., Abu-Zahra M., Wilson M., Olson W.,Idem R., Tontiwachwuthikul P., *Recent progress and new developments in post-combustion carbon-capture technology with amine based solvents*. International Journal of Greenhouse Gas Control 40, 26-54, 2015.

[90] Boo C., Khalil Y.F., Elimelech M., *Performance evaluation of trimethylamine - carbon dioxide thermolytic draw solution for engineered osmosis*. Journal of Membrane Science 473, 302-309, 2015.

[91] Mani F., Peruzzini M., Stoppioni P., *CO_2 by aqueous NH_3 solutions: speciation of ammonium cabamate, bicarbonate and carbonate by a ^{13}C NMR study*. Green Chemistry 8 (11), 995, 2006.

[92] INCHEM - Internationally Peer Reviwed Chemical Safety Information, "Trimethylamine - acute hazards, prevention and fire fight." *http://www.inchem.org/documents/icsc/icsc/eics1484.htm*, 2003.

[93] Lakkaraju P., Askerka M., Beyer H., Ryan C., Dobbins T., Bennett C., Kaczur J., Batista V., *Formate to Oxalate: A crucial Step for the Conversion of Carbon Dioxide into Multi-carbon Compounds*. ChemCatChem 8, 3453-3457, Wiley Online Library, 2016.

[94] Meisel T., Halmos Z., Seybold K., Pungor E., *The thermal decomposition of alkali metal formates*. Journal of Thermal Analysis 7, 73-80, 1975.

[95] Canning R., Hughes M.A., *The thermal decomposition of alkaline earth formates*. Thermochimica Acta 6, 399-409, 1973.

[96] Górski A., Kraśnicka A.D., *Formation of oxalates and carbonates in the thermal decompositions of alkali metal formates*. Journal of Thermal Analysis 32, 1895-1904, 1987.

[97] The Chemical Company - Global Bonds in Chemistry, "Tartaric acid." *https://thechemco.com/chemical/tartaric-acid/*, 2019.

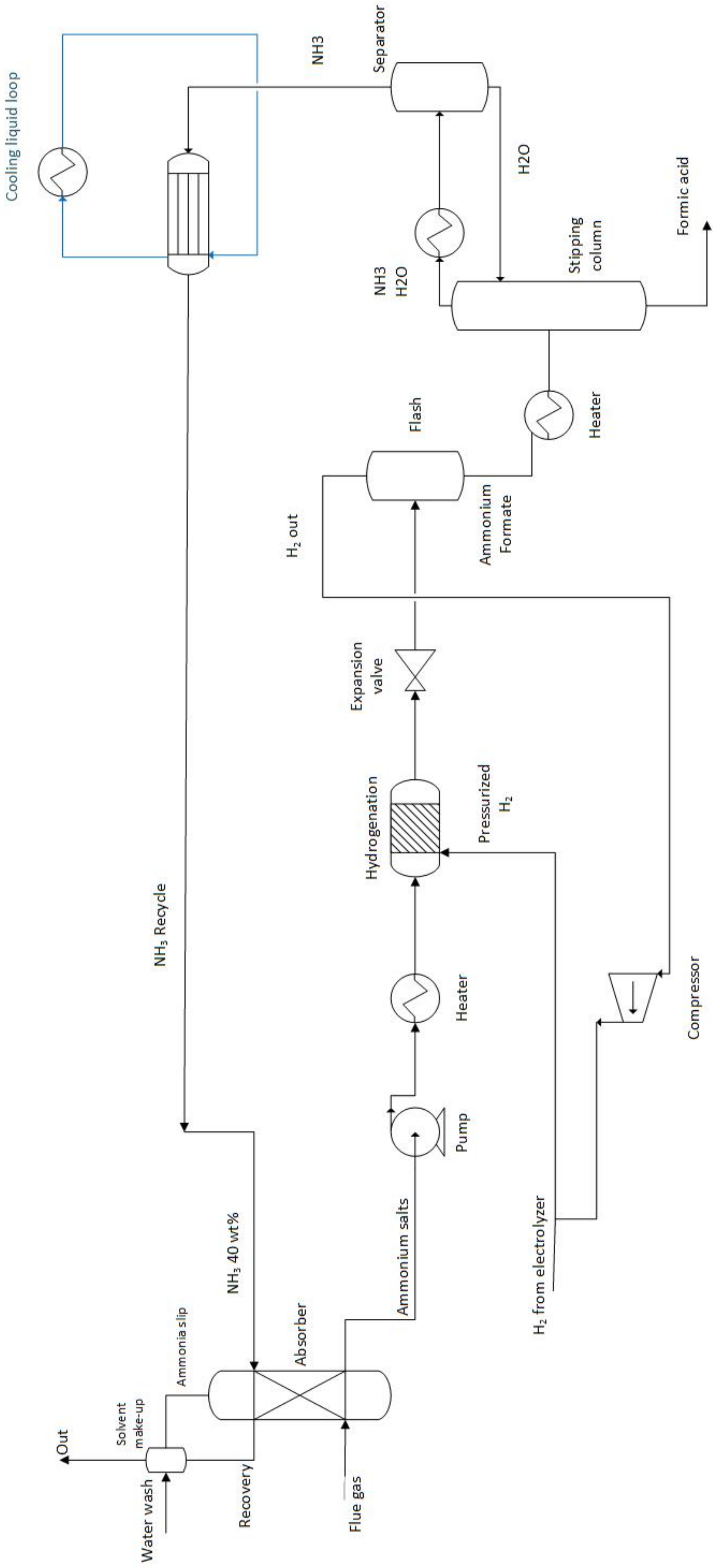
[98] The Linde Group, "Specialty Gases & Specialty Equipment - High performance liquid chromatography (HPLC)." *http://hiq.linde-gas.com/en/analytical_methods/liquid_chromatography/high_performance_liquid_chromatography.html*, 2019.

Appendix

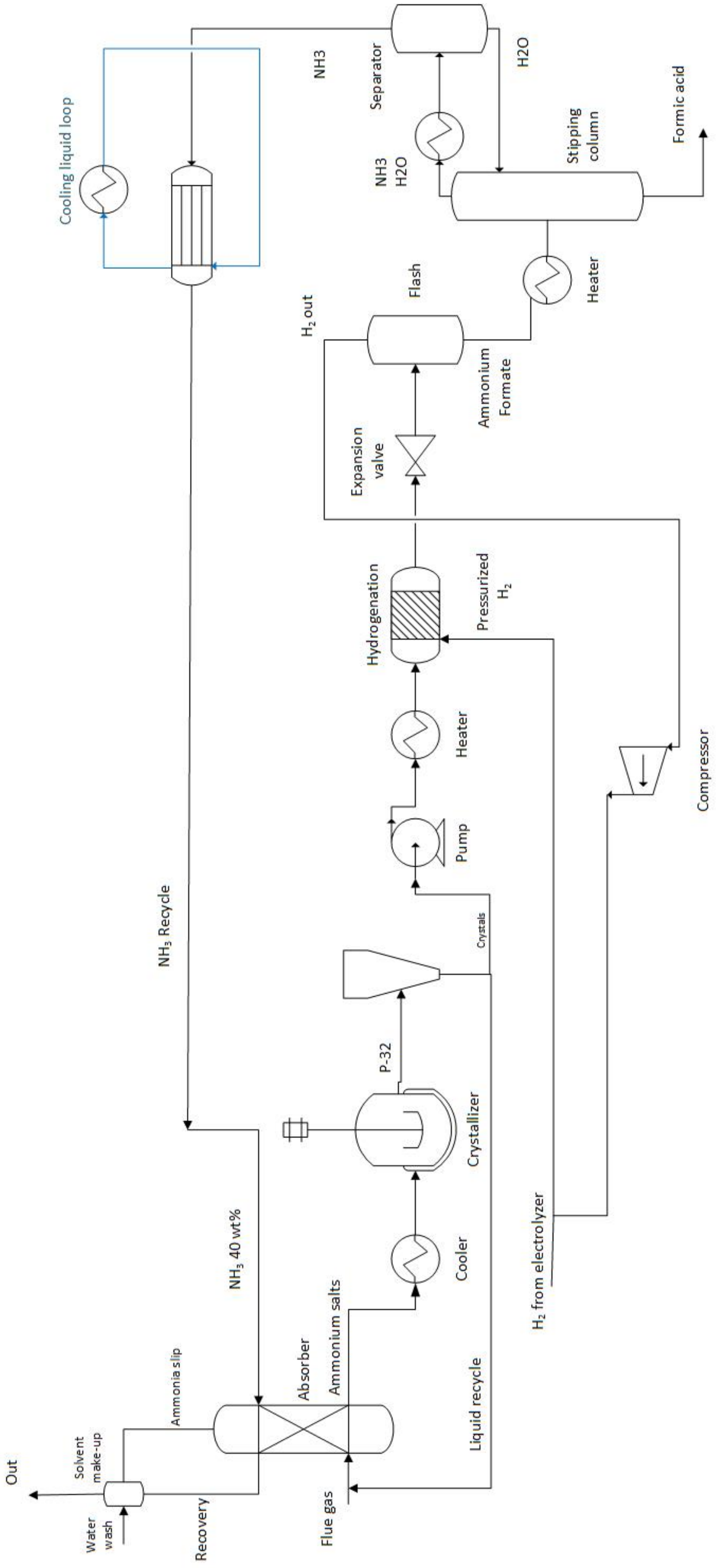
A. List of alternative products and their properties

#	Chemical Formula	Density [g/cm^3]	Molar mass [g/mol]	Melting point [°C]	Std enthalpy of formation ΔH^0_{298K} [kJ/mol]	Solubility in water [g/L] (at 20^{o}C)	Price [€/tn]
1	**Ammonium bicarbonate** NH_4HCO_3	1.58	79	41.9	-853.19	216	650-750
2	**Ammonium formate** $HCOONH_4$	1.26	63	116	-556.18	1.42	800-1000
3	**Formic acid** $HCOOH$	1.22	46	8.3	-425	1000	550-650
4	**Formaldehyde** CH_2O	0.81	30	-92	-108.6	400	300-350
5	**Methanol** CH_3OH	0.79	32	-98	-238.6	1000	350
6	**Methyl formate** $CHOOCH_3$	0.98	60	-100	-362	300	2500
7	**Ammonium oxalate** $(NH_4)_2C_2O_4$	1.5	124	70	-1243.9	45	1200-2000
8	**Ammonium carbonate** $NH_{42}CO_3$	1.5	96	58	-938.9	10	150-250
9	**Formamide** $HCONH_2$	1.13	45	2	-257.6	Miscible	80,000
10	**Oxalic acid** $(COOH)_2$	1.9	90	190	-825.7	90-100	450-510
11	**Oxamide** $(CONH_2)_2$	1.67	88	350	-237.2	Soluble	8,000
a	**Sodium bicarbonate** $NaHCO_3$	2.1	84	50	-950.8	87	110
b	**Sodium formate** $HCOONa$	1.92	68	253	-666.5	970	300-450
c	**Sodium oxalate** $Na_2C_2O_4$	2.34	134	260	-1318	37	1000
d	**Sodium carbonate** Na_2CO_3	2.54	106	851	-1130.7	300	280-290

B. Process flow diagram for production of formic acid



C. Process diagram for production of formic acid with crystallization



D. Experiments in the rotovap

For this reaction an experimental test took place in a rotovap at 60-65°C. For the experiment different solutions were prepared with ammonium formate and water and in Table 7.4 the measurement of the pH values is illustrated for the different initial concentrations and the pH values of both the distillate/-condensed part and the rest of the solution. The experiment itself is done in vacuum conditions and the whole set up can be seen in Figures in Index 1.

After preparing the solutions the initial values of pH were measured in order to observe the difference in these values after the thermal decomposition of the reactant, compared to the distillated stream and the final product. So the portion coming out after condensation taking place is basically the ammonia that is condensed, making the pH value high at around 9.

Experiments in the rotovap were carried out for both 64 °C and 84 °C with different concentrations of the examined solution, ammonium formate, including 1, 1.5 and 2 M and the results of the aforementioned reaction are gathered in Table 7.4.

Table 7.4: Measurement of pH values for the different temperatures tested.

T = 64 ° C	**M**	**mL**	**moles**	**gr**	**pH_i**	**$pH_{distillate}$**	**pH_{rest}**	**$Vol_{distillate}$**	**Vol_{rest}**
	1	200	0.2	12.61	6.42	9.61	5.63	60	120
	1.5	200	0.3	18.91	6.44	9.79	5.46	70	115
	2	200	0.4	25.22	6.4	9.85	5.4	85	110
T = 84 ° C	**M**	**mL**	**moles**	**gr**	**pH_i**	**$pH_{distillate}$**	**pH_{rest}**	**$Vol_{distillate}$**	**Vol_{rest}**
	1	200	0.2	12.61	6.17	9.55	5.69	170	15
	1.5	200	0.3	18.91	6.20	9.61	5.63	160	20
	2	200	0.4	25.22	6.37	9.8	5.57	150	30

After the completion of the experimental part, both the solutions of the *rest* and the *distillate* part have been going through a procedure called HPLC (High Performance Liquiq Chromatography) in order to measure the amount of formic acid that was formed during the reaction. [98] For this procedure samples were taken and have been diluted 5 times and afterwards the concentration of the sample in formic acid was measured. An already existing calibration line was used for the measurement of formic acid, as can be seen in Figure 7.6.

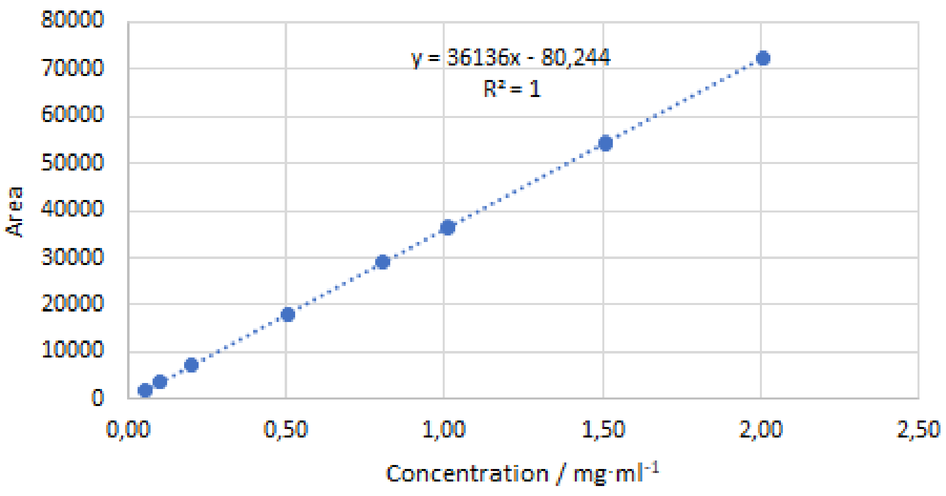


Figure 7.6: Calibration curve for the estimation of concentration of formic acid.

In Table 7.5 the results of the HPLC are presented and the calculation of the % conversion of the final product is calculated. Thus, in the HPLC only the formic acid can be detected, which is obvious by observing the areas indicated in the Table below. A correction of the amounts of ammonium formate, formic acid and ammonia by taking into account the different amounts of volume that correspond to each reactant and products. In this term, the final conversion is calculated as the ratio of moles of formic acid to moles of ammonium formate, since the Reaction 3.7 has stoichiometric ratio 1:1.

Table 7.5: Calibration results and conversion measurement.

T = 64 ^{o} C	**Area rest**	**Area distil**	**mg/mL rest**	**mg/mL distil**	**mol/L rest**	**mol/L distil**	**moles**	**Conversion %**
	3.73e+05	782.9	51.6	0.12	1.12	0.0026	0.13	**67.3**
	2.35e+05	924.8	64.9	0.14	1.41	0.0031	0.16	**54.1**
	8.83e+05	868.8	122.2	0.13	2.65	0.0029	0.29	**73.1**
T = 84 ^{o} C	**Area rest**	**Area distil**	**mg/mL rest**	**mg/mL distil**	**mol/L rest**	**mol/L distil**	**moles**	**Conversion %**
	3.21e+06	1,213	444.3	0.18	9.65	0.0039	0.14	**72.4**
	3.53e+06	1,980	488.8	0.29	10.62	0.0062	0.21	**70.8**
	2.3e+06	5,745	318.2	0.81	6.91	0.0175	0.20	**51.9**