

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Ammonia-Based Post-Combustion Capture of Carbon Dioxide

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ABSTRACT

Post-combustion capture of carbon dioxide is one of the measures to reduce emissions of carbon dioxide from large point source emitters. In post-combustion capture the carbon dioxide is absorbed from the flue gas by means of a liquid absorbent. In this thesis, ammonia is evaluated as absorbent of carbon dioxide in a post-combustion capture application. The major energy penalty for capturing carbon dioxide is, in the case of post-combustion capture, the heat required to release the carbon dioxide from the absorbent, also called the heat of regeneration. The overall aim of this thesis is to determine the heat requirement of ammonia regeneration and to evaluate the consequences of integrating post-combustion capture with an existing coal-fired power plant.

The primary evaluation tool in this work is equilibrium-based thermodynamic modeling. Three thermodynamic models proposed in literature for the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system are evaluated. A literature review in this work revealed missing data for equilibrium partial pressures of carbon dioxide and ammonia at 0 - 20°C, which is the typical temperature range for post-combustion capture with ammonia.

An experimental methodology was therefore established in Paper I in which the aim was to determine the partial pressures of ammonia and carbon dioxide at 10 and 20°C. The experimental setup consisted of an equilibrium cell connected to a gas chromatograph. The experimental conditions included 5.7 and 10.7 wt% NH_3 and CO_2 -loadings between 0.15 - 0.75. The results provide additional data points in the partial pressure range 0.1 - 20 kPa and 0.01 - 10 kPa for ammonia and carbon dioxide, respectively.

In Paper II the CO_2 capture cycle is simulated in the process simulation software Aspen Plus. The thermodynamic models form the foundation for the flow sheet process modeling. The heat requirement for regeneration is evaluated for NH_3 concentrations ranging from 2 to 20% and the lean CO_2 -loading is varied between 0.2 - 0.5. The specific heat requirement was determined to be 2500 kJ/kg CO_2 captured. There is a minimum of 2100 kJ/kg CO_2 captured at a CO_2 -loading of 0.5, just where solid precipitation starts. However, at these conditions the equilibrium sets a limit to the capture efficiency of 50%. Furthermore, it is concluded that the major reason for the low heat requirement for ammonia regeneration is not a low heat of reaction but a low heat of vaporization, due to the pressurized desorption.

In Paper III, the ammonia-based post-combustion technology “Chilled Ammonia Process” is thermally integrated with a coal-fired power plant. It is concluded that the electric efficiency of the power plant will decrease with 9.2%-points. Yet, this figure depends strongly on the available cooling water temperature. Access to low temperature cooling water greatly enhances the performance of the capture process. A 10°C higher cooling water temperature could increase the energy penalty of the power plant with almost one percentage point.

LIST OF PUBLICATIONS

This thesis is based on the following papers:

- I. H. Jilvero, K.J. Jens, F. Normann, K. Andersson, F. Johnsson, D. Eimer, *Equilibrium partial pressures for ammonia and carbon dioxide at low temperature*, To be submitted for publication
- II. H. Jilvero, F. Normann, K. Andersson and F. Johnsson, *Thermal integration and modeling of the chilled ammonia process*, Energy Procedia 2011, 4, 1713-1720.
- III. H. Jilvero, F. Normann, K. Andersson and F. Johnsson, *Heat requirement for regeneration of aqueous ammonia in post-combustion carbon dioxide capture*, International Journal of Greenhouse Gas Control 2012, 11, 181-187.

Henrik Jilvero is the main author for all three papers. Dr Fredrik Normann, Dr Klas Andersson and Professor Filip Johnsson have contributed with discussions and writing to all papers. Professor Klaus-Joachim Jens and Professor Dag Eimer at Telemark University College have contributed with the guidance on the operational aspects of the experiments and the writing of Paper I.

ACKNOWLEDGEMENTS

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I would also like to extend my thanks to all the people who have helped me and made me feel welcome during my stay in Porsgrunn, Norway. Especially, I would like to thank Professor Klaus-Joachim Jens at Telemark University Collage, who made my stay there possible. His enthusiasm for chemistry is unmatched and really contagious. My gratitude also goes to the people at Tel-Tek, especially Dag Eimer who has shared his vast experience and Chameera Jayarathna for teaching me how a gas chromatograph is operated and making a mechanical engineer feel comfortable in a chemistry lab.

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Henrik Jilvero

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OUTLINE

This thesis is divided into 7 chapters and 3 attached papers. This first chapter briefly explains the concept of Carbon Capture and Storage and defines the aim and scope of the work as well as introducing the concept of post-combustion capture. A summary of previous work using ammonia as an absorbent of carbon dioxide is described in Chapter 2. This chapter also gives the theoretical background for the modeling work. Chapter 3 describes the experimental setup used in this work and the operating conditions and assumptions of the modeling work. In Chapter 4, the results from the three attached papers are presented and put into a common context. The conclusions and suggestions for future work are given in Chapter 5 and 6.

Paper I presents a validation of existing thermodynamic models by comparing with new experimentally derived data of the partial pressures of ammonia and carbon dioxide for temperatures between 10-20°C. The two following papers focus on modeling of the capture process. Paper III use equilibrium based process modeling to evaluate how the chilled ammonia process can be integrated into an existing power plant. Much like Paper III, Paper II is based on process modeling, but it also offers a more in-depth evaluation of the heat requirement for regeneration.

1 Introduction

Global warming due to anthropogenic emissions of greenhouse gases (GHG) may be the most significant environmental problem that our society has faced so far. The major GHG component is CO₂; the emission result mainly from fossil fuel combustion. Fossil fuels stood for 81% of the world's primary energy in 2010. As seen in Figure 1, there is a steady increase in the use of fossil fuels and the trend seems to continue due to the abundance of fossil fuels, especially of coal. Even though the use of fossil fuels in OECD countries has stagnated, emerging economies are responsible for a rapid increase in fossil fuel demand [1]. According to *World Energy Outlook 2012*, the use of coal is still expected to increase in the near future unless very stringent policies are applied [2].

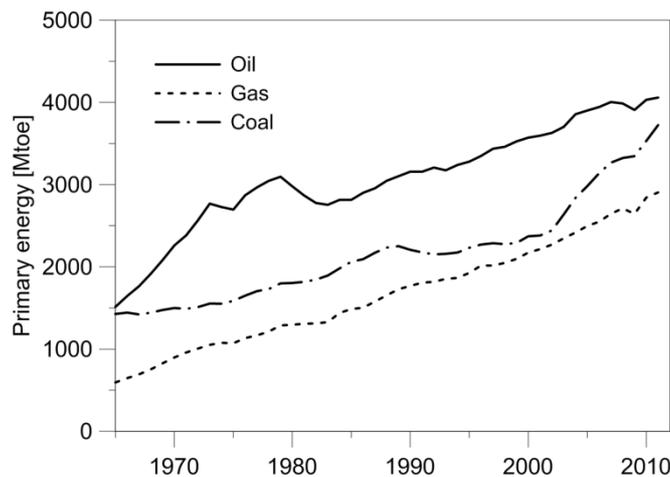


Figure 1 The world's primary energy consumption (Mtoe) of the fossil fuel, oil, gas and coal for the years 1965-2011. [1]

One measure to meet the future energy demand allowing continued use of fossil fuels while making required cuts in CO₂ emissions is to apply Carbon Capture and Storage (CCS). The concept of CCS is to capture CO₂ from large point source emitters (mainly in the power and industrial sectors), to compress the CO₂ and transport it to a geological formation for storage. CCS is often referred to as a bridging technology, to be applied until renewable technologies and other mitigation options such as energy savings can be applied at the required scale. Several ways to separate ("capture") the carbon dioxide from large point sources are presently being investigated. Three options have emerged as the most feasible carbon capture techniques: oxy-fuel combustion, pre-combustion capture and post-combustion capture. This work focuses on the post-combustion capture technique.

1.1 Post-combustion capture

Post-combustion capture refers to the process in which CO₂ is removed from flue gases or process gas streams. As the name indicates the capturing process is located after the main process, such as e.g. combustion, gasification or natural gas extraction. Post-combustion capture can be used as an end-of-pipe solution, meaning that no retrofit of the existing process is required. The process design is built on a two column setup (absorber/stripper) where the temperature difference between the two columns acts as the driving force for the separation of CO₂, see Figure 1. The concept of absorbing gaseous CO₂ into an alkanolamine-based liquid is widely used in the process industry [3]. The first patent of using an alkanolamine to absorb

acidic gases is from 1930. The main application of this process is the removal of H₂S and CO₂ from industrial gases, such as natural gas. As a result of the interest in reducing CO₂ emissions, this technology has emerged as one of the most promising CO₂ capture options. Figure 2 show a schematic of a post-combustion capture process integrated with a power plant. The dashed box indicates the post-combustion process.

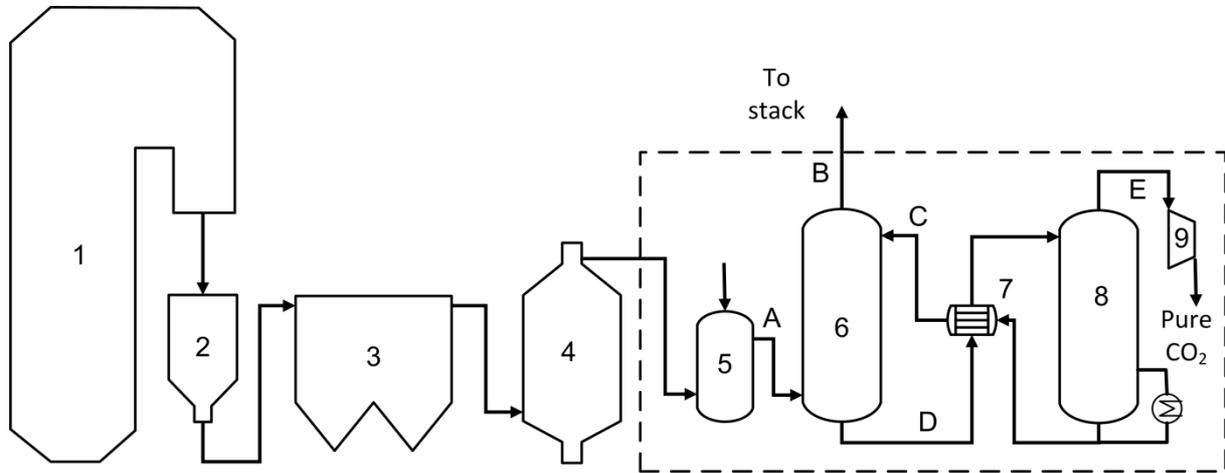


Figure 2. Schematic of a post-combustion capture process integrated with a power plant. 1. Furnace 2. Selective Catalytic Reduction 3. Electrostatic precipitator 4. Flue gas desulphurization 5. Flue gas conditioning 6. Absorber 7. Rich/lean heat exchanger 8. Stripper 9. CO₂ compression. The striped line indicates the post-combustion capture units.

To avoid absorbent degradation due to flue gas impurities (NO_x, SO_x, particles) the post-combustion facility is placed between the flue gas cleaning system (units 2-4 in Figure 2) and the stack. The flue gases first enter a conditioning unit (unit 5) where water vapour is condensed and the temperature is regulated. After the conditioning unit the flue gas is introduced into the bottom of an absorption column (unit 6). In the top of the absorber a CO₂ absorbent mixed with water is injected. The absorbent is distributed over a packing material to increase gas-liquid contact area. A common design target is that about 90% of all the carbon dioxide in the flue gases is absorbed into the liquid. Before the unreacted gases exits through the stack, they are washed to remove residual chemicals from the capture process. The absorption reactions are exothermal. The liquid exiting the absorber is called the CO₂-rich solution. The CO₂-rich solution is pumped through a rich/lean heat exchanger (unit 7), where the temperature of the solution is elevated. After the heat exchanger the rich solution is fed to a stripper (regenerator/desorber in Paper III) column (unit 8). At the bottom of the stripper column, heat is added to a reboiler to reverse the absorption reaction and to strip the carbon dioxide from the solvent. The heat is usually supplied to the reboiler in the form of low pressure steam. The production of this steam is the major energy penalty associated with post-combustion capture. The heat requirement of post-combustion capture is given as the specific heat required for regeneration in kJ/kg CO₂ captured. At the top of the stripper a gas mainly consisting of CO₂ is cooled to remove water. The almost pure CO₂ is now pressurized in a multi-stage compressor (unit 9) until it is liquefied and ready for transport to the storage location. Liquefaction usually requires a pressure of about 100 bar at ambient temperature conditions. The nomenclature for parameters associated with post-combustion capture is given in Table 1.

Table 1. The nomenclature for parameters used in post-combustion capture. The stream notation corresponds to Figure 1.

Variable	Definition	Unit
Lean CO ₂ -loading	$\dot{n}_{CO_2}/\dot{n}_{NH_3}$ (Stream C)	-
Rich CO ₂ -loading	$\dot{n}_{CO_2}/\dot{n}_{NH_3}$ (Stream D)	-
CO ₂ capture efficiency	\dot{n}_{CO_2} Stream B/ \dot{n}_{CO_2} Stream A	[%]
Ammonia slip	\dot{n}_{NH_3} Stream B/ \dot{n}_{tot} Stream A	[ppm]
CO ₂ flue gas/NH ₃ liquid	\dot{n}_{CO_2} Stream C/ \dot{n}_{NH_3} Stream A	-
Heat requirement for regeneration	$Q_{reboiler}/\dot{m}_{CO_2}$ Stream E	[kJ/kg CO ₂]
Heat requirement for ammonia stripping	$Q_{NH_3, stripper}/\dot{m}_{CO_2}$ Stream E	[kJ/kg CO ₂]
Energy penalty	$P_{el,loss} + P_{CO_2 comp.} + P_{refrige} + P_{aux}$	[MW]

The choice of carbon dioxide absorbent is an important area of research for the development of post-combustion capture, since the the choice of absorbent has a strong impact on the process design and performance. Several absorbents have been evaluated for post-combustion capture. The benchmark absorbents today are primary, secondary and tertiary alkanolamines (amines). The most important amines are; monoethanolamine (MEA, primary), diethanolamine (DEA, secondary) and methyl diethanolamine (MDEA, tertiary). Primary amines are characterized by fast reaction kinetics and a high heat requirement of regeneration. The opposite is valid for the tertiary amines. Thus, mixtures of different amines can offer positive synergies. A novel absorbent is the sterically hindered version of MEA, 2-Amino-2-Methyl-1-Propanol (AMP), which offers a lower heat requirement of regeneration and a higher loading capacity. Other suggested absorbents are, potassium carbonate (K₂CO₃), ionic liquids (IL), piperazine (PZ) and ammonia (NH₃). Absorbents are assessed with respect to the following parameters:

- Absorption kinetics
- Heat requirement for regeneration
- Persistence to degradation
- CO₂-loading capacity
- Corrosiveness
- Volatility
- Price
- Toxicity

1.2 Aim and scope

The focus of this work is to evaluate ammonia-based post-combustion capture. The concept of using ammonia for CO₂ capture is not yet tested in industrial scale units. However, initial experimental work indicates that ammonia could offer several positive aspects compared to more conventional absorbents. The aim of this work is to evaluate ammonia as a possible absorbent in post-combustion capture of carbon dioxide. The main focus is on the thermal performance, where the most important issue is the heat requirement for regeneration of the absorbent.

Even though ammonia mixed with carbon dioxide and water is a known system, post-combustion capture is a new application and there is a need for additional data and further evaluation under conditions of interest. The vapour-liquid equilibrium data at low

temperatures is sparse and thus, decreases the accuracy of modeling predictions at these conditions. In order to provide additional data to be used for thermodynamic modeling an experimental methodology to determine equilibrium partial pressures of carbon dioxide and ammonia is presented in Paper I. The methodology is limited to equilibrium-based modeling and experiments. Equilibrium-based process modeling is used to determine the heat requirement for regeneration (Paper II) and the effect that this has on the performance of a power plant equipped with a post-combustion capture process (Paper III).

2 Ammonia as absorbent of carbon dioxide

Ammonia has been proposed as a promising absorbent of carbon dioxide. The use of ammonia in post-combustion capture has since 2006 been investigated on pilot plant scale in a number of projects. The most important actor is Alstom, who pursue the commercialization of what they call the Chilled Ammonia Process (CAP) [4]. Furthermore, Powerspan promote a similar concept called ECO₂ [5]. Other organizations that have evaluated ammonia on a pilot scale are the Research Institute of Industrial Science and Technology (RIST) in Korea [6] and the Commonwealth Scientific and Industrial Research Organization (CSIRO) [7]. Table 2 lists the major efforts to investigate and demonstrate post combustion capture using ammonia. Many of the demonstration scale plants have been canceled due to unclear future policies with respect to emission targets or lack of funding [8].

Table 2. A compilation of pilot plants and planned demonstration plants and that use ammonia as absorbent. Source: MIT CCS project database [8]. (n.i.o. = not in operation)

Location/Project	Supplier	Inauguration year	Capacity	Status
Växjö	Alstom	2006	0.25 MW _{th}	n.i.o.
Pleasant Prairie	Alstom	2008	5 MW _{th}	n.i.o.
Berger	Powerspan	2008	1 MW _{th}	n.i.o.
Pohang Steel Works	RIST	2008	50 Nm ³ /h	n.i.o.
AEP Mountineer	Alstom	2009	58 MW _{th}	n.i.o.
Karlshamn	Alstom	2009	5 MW _{th}	n.i.o.
Munmorah	CSIRO	2009	1000 kg/h	n.i.o.
Pohang Steel Works	RIST	2011	1000 Nm ³ /h (0.5 MW _{th})	Running
Mongstad TCM	Alstom	2012	40 MW _{th}	Running
AEP Mountineer	Alstom	-	250 MW _{el}	Cancelled
Transalta	Alstom	-	450 MW _{el}	Cancelled
Getica – CET Turceni	Alstom	Planned 2015	330 MW _{el}	Planning

Figure 3 shows a schematic of an ammonia-based post-combustion capture facility. The operating conditions and process design of ammonia-based post-combustion capture differ somewhat from the regular post-combustion process described in Chapter 1.3. This is illustrated by comparing Figures 2 and 3. The incentive to pursue ammonia instead of MEA is that it has lower heat of regeneration, a lower cost, and is much less prone to degrade than amines [9]. MEA has a significant tendency to loose performance due to degradation products formed by flue gas impurities. Degradation of MEA is also sensitive to oxidizing or high temperature environments. The consumption of MEA due to degradation could be as high as 1.4 kg MEA/ton CO₂ captured [10]. In contrast, none of the pilot plants studies have shown any ammonia degradation during operation. Several studies have evaluated the specific heat requirement of ammonia regeneration; however, there is a large discrepancy between sources as can be seen from Table 3. Paper II discusses this discrepancy. As reference, the corresponding heat requirement of MEA regeneration is 3700 kJ/kg CO₂ captured. All of the sources in Table 2 that are based on modeling have used an equilibrium-based approach. Thus, the influence of reaction kinetics on the heat of regeneration is yet to be investigated (further discussed below).

Table 3. Data from literature on the heat requirement of regeneration. (Eq. = Equilibrium, Estimate = The overall process is estimated to be governed by the reaction between ammonium carbonate and ammonium bicarbonate, reaction R1)

Source	Year	Method	Heat requirement (kJ/kg CO ₂ captured)	Ammonia concentration [wt%]	Lean CO ₂ -loading
EPRI [9]	2006	Estimate	930	-	-
McLarnon et al. [5]	2009	Estimate	1000	-	-
Valenti et al. [11]	2009	Estimate	1536	11.5	
Darde et al. [12]	2009	Eq. modeling	2050	28	0.33
Dave et al. [13]	2009	Eq. modeling	2900	7	-
Mathias et al. [14]	2009	Eq. modeling	2377	26	0.35
Jilvero et al. (Paper III)	2010	Eq. modeling	2200	26	-
Powerspan [15]	2010	Pilot plant	2326	-	-
Yu et al. [7]	2010	Pilot plant	4000 - 4200	0 - 6	0 - 0.6
Valenti et al. [16]	2010	Eq. modeling	2460	20	0.25
A. Kothandaraman [17]	2010	Eq. modeling	2400	17 - 31	0.4
Darde et al. [18]	2011	Eq. modeling	2533	7.8	0.33

One issue with ammonia is that it is volatile. This has the effect that the stream exiting the top of the absorber can contain several percent of ammonia. This ammonia is referred to as slip. A common design parameter for ammonia emissions is that the discharge ammonia concentration in the stack may not exceed 10 ppm. The gaseous emission of ammonia is reduced with a water wash (unit 5 in Figure 3) before discharge. The ammonia containing solution is regenerated to recover most of the ammonia to the CO₂ capture cycle (units 6). This cycle is called the “ammonia abatement cycle” (process C in Figure 3). The heat required in the ammonia stripper has also been evaluated, see Table 4, but not to the same extent as the heat requirement of regeneration. When the performance of capture processes is evaluated both the heat requirement of the stripper and the ammonia recovery should be included. As seen in Table 4, the heat required for the ammonia recovery may be in the same order as the ammonia regeneration and, thus, could lower the total process performance. To reduce the slip of ammonia the absorber should operate at a low temperature. Low temperatures decrease the partial pressure of ammonia and, thus, the slip. Low-temperature absorption is a main feature of the CAP, where refrigeration maintains the absorber at a temperature of 0 - 20°C (process A).

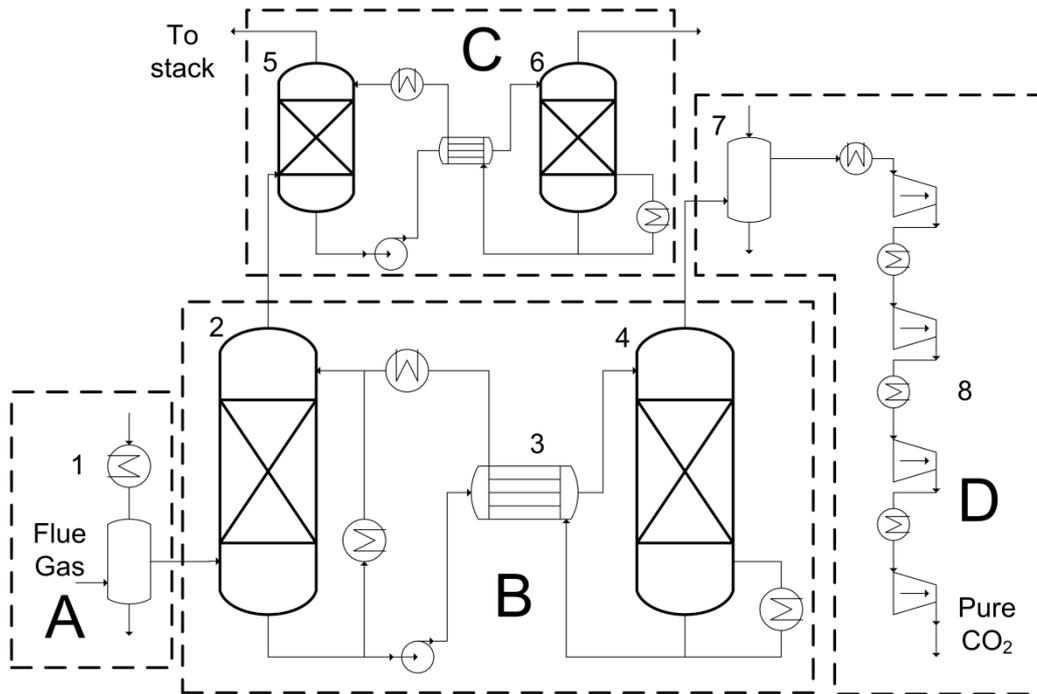


Figure 3. A detailed schematic of an ammonia-based post-combustion process. A. Flue gas conditioning and cooling system B. CO₂ capture cycle C. Ammonia abatement cycle D. CO₂ compression. 1. Flue gas conditioning 2. Absorber 3. Rich/lean heat exchanger 4. Stripper 5. Water wash 6. Ammonia stripper 7. CO₂ wash 8. Multi-stage compression.

Another potential issue with ammonia is that at low temperatures and high ammonia and carbon dioxide concentrations, the solubility limit of solids can be reached and solid precipitation can occur in the liquid. A slurry may form in the absorber and be present all the way to the rich/lean heat exchanger. The slurry may dissolve before or in the heat exchanger. In the CAP, precipitation is desired as it increases the capture capacity (kg CO₂/kg solvent) of the solvent. However, slurries are much harder to handle and have a risk of plugging process equipment.

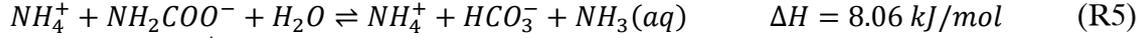
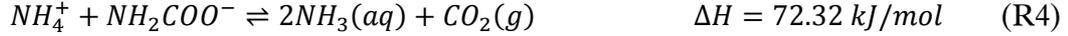
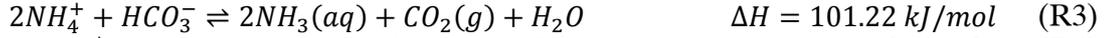
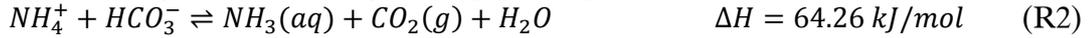
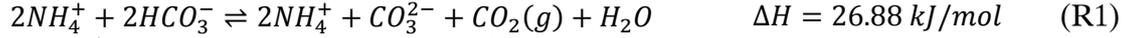
There is also a possibility to use higher CO₂-loadings with ammonia than with MEA. The lean and rich CO₂-loading for ammonia is 0.25 - 0.5 and 0.5 - 1, respectively, which is compared with 0.15 - 0.2 and 0.4 - 0.5 for MEA. Thus, less absorbent is required when using ammonia. The MEA concentration in regular operation is usually 30wt%, while a wide range of ammonia concentrations have been evaluated; 5 - 30%wt. There are two reasons to use a lower ammonia concentration: to decrease the ammonia slip and to prohibit precipitation. The ammonia concentration is an important design parameter.

Table 4. Data from the literature on the heat requirement of the ammonia stripper.

Source	Year	Method	Ammonia slip (ppm)	Heat requirement (kJ/kg CO ₂ captured)
Mathias et al. [14]	2010	Eq. modeling	250-2200	700-2350
Jilvero et al. (Paper III)	2011	Eq. modeling	500-30000	73 ^a
Darde et al. [18]	2011	Eq. modeling	5000-19000	200-800

^aAssumed reduction to 200 ppm NH₃, while the remaining is removed in an acid wash.

The Reactions R1 - R6 are expected to occur in the liquid phase during the absorption process [19, 20]. In the aqueous ammonia solution, gaseous CO₂ may be absorbed through any of the Reactions R1 - R4. Carbon dioxide may be bound as carbonate (CO₃²⁻), bicarbonate (HCO₃⁻), and carbamate (NH₂COO⁻) depending on the operational conditions of the absorber. For the CAP, the governing reaction involves the absorption of CO₂ with carbonate, to form bicarbonate, i.e., Reaction R1 [9]. This reaction has a low heat of reaction, although the absence of free ammonia has a negative effect on the absorption kinetics. Reactions R2, R3 and R4, which involve the absorption of CO₂ by free ammonia, entail significantly higher heats of reaction than Reaction R1.



Another important issue with using ammonia as absorbent is the absorption rate. Many studies have identified the carbamate formation (Reaction R4) to be rate determining for the absorption [21, 22]. The carbamate formation can be represented by a two-step reaction with a zwitter-ion intermediate (Reactions R7-R8) [23-25] or an Arrhenius expression [21, 22]. In Reaction R8 the zwitter-ion is deprotonated by any present base (H₂O or NH₃).

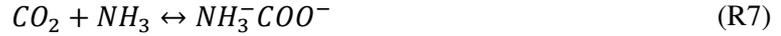


Figure 5 shows the apparent kinetic rate of the carbamate formation reaction of five investigations as a function of temperature. The apparent reaction rate for the MEA-based absorption as given by Versteeg et al. [26] is also included in Figure 5. The operating conditions are a CO₂-free solution with an ammonia concentration of 1 kmol/m³. It is apparent from Figure 5 that there is no consensus with respect to the apparent reaction rate, or even the temperature dependence, of the carbamate reaction. However, the absorption rate of ammonia is likely to be slower than of MEA.

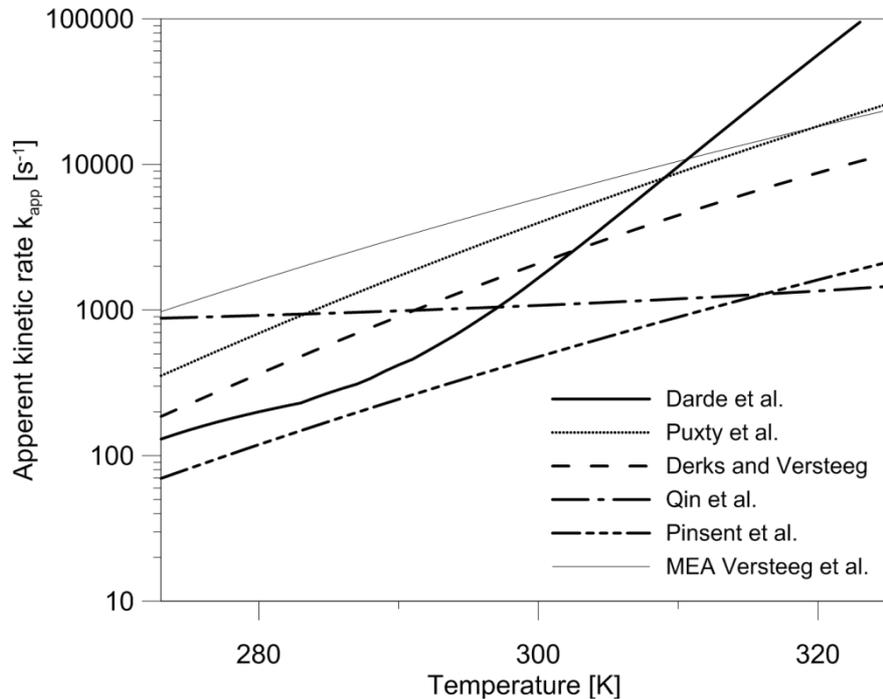


Figure 5. The apparent kinetic reaction rates for the carbamate formation (Reaction R4) as a function of temperature. The conditions are a CO₂-free solution with an ammonia concentration of 1 kmol/m³. The reaction rates by Puxty et al. [22] and Pinsent et al. [21] use an Arrhenius expression while the remaining are expressed as two-step zwitter-ion mechanisms [23-25]. The apparent kinetic reaction rate for MEA are taken from Versteeg et al. [26]

2.1 Equilibrium-based experiments and modeling

The mixture of ammonia and carbon dioxide in water is a volatile, weak-electrolyte solution. As the solution is a mixture of molecular species and non-volatile ionic compounds, a complex thermodynamic model is required to determine its phase behavior and composition. The liquid phase of an electrolyte solution requires an activity coefficient model to describe the interionic forces and the non-ideal behavior of the solution. An equation of state is also required to describe the vapor phase behavior, i.e., to calculate the fugacity coefficients. These electrolyte models depend strongly on experimental data for accurate predictions. Figure 4 shows a graphical representation of at which experimental conditions species distribution data exists in the liquid phase (Fig. 4a) [27-29] and vapour phase respectively (Fig. 4b) [9, 30-39]. Each measurement data point is represented by one symbol for the ammonia concentration (cross) and one for the carbon dioxide concentration (triangle). The shaded areas at (0 - 20°C) and at (100 - 150°C) represent the operating conditions of the absorber and the stripper, respectively. The operating concentrations can range from 2 - 23 moles/kg H₂O. It is clear that there is more experimental data available for the conditions of the stripper than of the absorber. Hence, less predictive capabilities of the thermodynamic models are expected for the absorber. However, in Paper I additional data points are added at 3.6 and 7 moles NH₃/kg H₂O. The CO₂-loading for these data points are 0.15 - 0.75 and the operating temperature are 10 and 20°C. There is also a clear difference between Figures 4a and b. The vapour phase is more thoroughly investigated than the liquid phase. More experimental data for the liquid phase is an area of interest for future research.

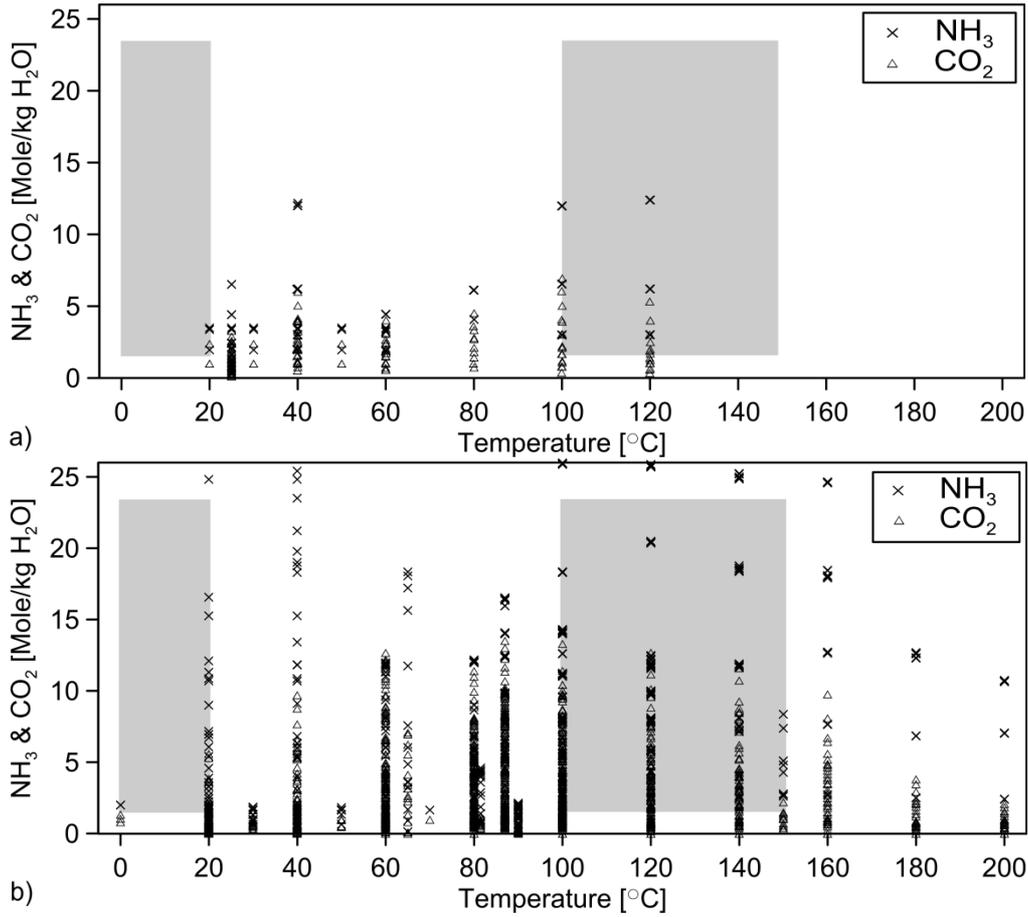
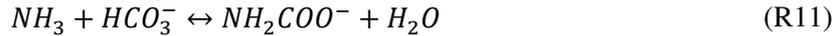


Figure 4. Graphical representation of at which conditions experimental species distribution data exist in the liquid phase (a) and gas phase (b). The shaded areas, 0-20°C, and, 100-150°C, represent the operating conditions of the absorber and the stripper, respectively. The ammonia concentration is represented by a cross and the carbon dioxide concentration is represented by a triangle. Source: Paper I.

Thermodynamic models describing the NH₃-CO₂-H₂O system have been established by Darde et al. [40], Kurz et al. [38], and Que and Chen [41]. Common to all these thermodynamic models is the treatment of the vapor-liquid equilibrium (VLE) of ammonia, carbon dioxide and water. In general, the liquid phase chemistry includes the following five ionic equilibrium-based reactions:



The precipitation of ammonium bicarbonate $NH_4HCO_3(s)$ is included in all the models. However, the model developed by Darde et al. [40] also include the solid state of ammonium carbonate $(NH_4)_2CO_3(s)$, ammonium carbamate $NH_2COONH_4(s)$, and ammonium sesquicarbonate $(NH_4)_2CO_3 \cdot NH_4HCO_3(s)$. The thermodynamic model presented by Darde et al. [40] is based on the extended UNIQUAC electrolyte model developed by Thomsen and Rasmussen [42], and has been used to model the CAP [12]. The Pitzer-based [43] thermodynamic model described by Kurz and co-workers has been used in Paper III to

determine the energy penalty of a coal-fired power plant equipped with a CAP. However, the model derived by Kurz et al. [38] has been shown to predict the liquid species concentrations inaccurately [44]. The thermodynamic model of Que and Chen [41], which is used in Paper II, employs the electrolyte NRTL model, developed by Chen et al. [45]. The electrolyte NRTL is the default electrolyte model used by the Aspen Plus v7.3.2 [46] process simulation software.

2.2 Equilibrium- and rate-based process modeling

There are two different approaches that can be used in process modeling, equilibrium- and rate-based modeling. Only equilibrium-based results are presented in this work. Figure 6 shows equilibrium- and rate-based simulations of the absorber capture efficiency of CO₂ as a function of the absorber height. The process modeling setup is similar to the one described in Paper II. In Figure 6 the heat of regeneration is given for 3 process simulations with different absorber models (indicated by 3 dots): equilibrium and rate-based with both the reaction rates by Puxty et al. [22] and Pinsent et al. [21]. The ratio between the carbon dioxide in the flue gases and the ammonia in the CO₂-lean stream is set to 0.5. The ammonia concentration is set to 5% and the lean stream CO₂-loading is 0.25. The equilibrium-derived capture efficiency for a mole ratio of 0.5 is close to 100%, represented by a dashed line in Figure 6.

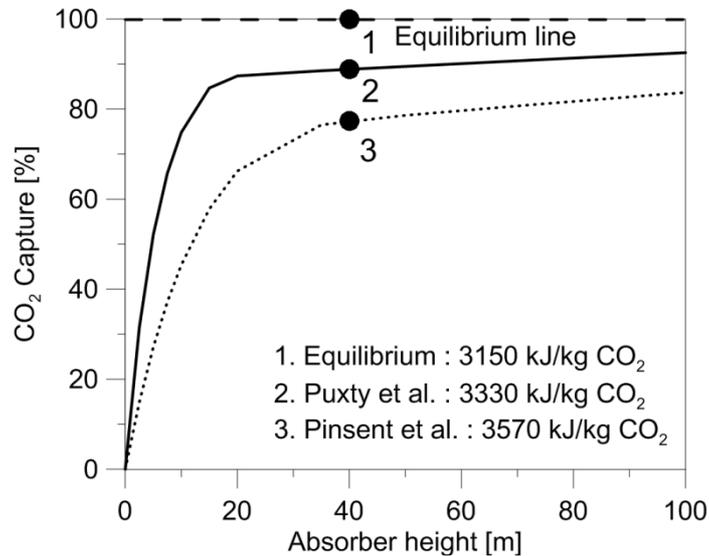


Figure 6. The carbon dioxide capture efficiency of the absorber as a function of column height. The dashed line represents the equilibrium capture efficiency at the CO₂/NH₃-ratio of 0.5. The heat requirement of regeneration is given when the equilibrium and the rate-based assumption is used. The carbamate reaction is represented by the reaction rates by Pinsent et al. [21] and Puxty et al. [22]. The absorber height is 40m in the calculations of the heat of regeneration.

In an actual capture process the residence time will not be sufficient to reach equilibrium. Thus, the reaction kinetics and the mass and heat transfer need to be accounted for, to make a realistic simulation of the capture process. There are however situations where the scope of study allows for an equilibrium assumption. As a result of the high temperature in the stripper, the desorption reactions will be fast and the conditions in the stripper are close to equilibrium. As the heat requirement of regeneration is associated with the stripper, this parameter may be evaluated by an equilibrium-based approach. As seen in Figure 6 the heat requirement of regeneration, there is not such a large difference between the equilibrium- and rate-based approaches. However, if the equilibrium assumption is applied to the absorber, the CO₂ absorption will be overestimated and the ammonia slip will be underestimated.

In rate-based modeling the columns are discretized along the height in a number of stages. In equilibrium based modeling each stage is assumed to be in equilibrium. Both the bulk liquid phase and the vapour phase are assumed to be perfectly mixed and in equilibrium. In the rate-based approach two extra zones are introduced at each stage, the vapour interface and the liquid interface, also known as a two-film model. These zones account for mass transfer, heat transfer and reaction rate resistance. The bulk liquid and vapour phase are still considered to be in equilibrium. The reaction kinetics are treated by introducing rate expressions for certain reactions in the liquid interface. The standard rate-based model for the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system in Aspen Plus uses the reaction rates given by Pinsent et al. [21] for both the carbamate and the bicarbonate formation reactions. The carbamate reaction is much faster than the bicarbonate reaction [21]. The carbamate reaction is represented by the reaction rates given by Puxty et al. [22] and Pinsent et al. [21]. The bicarbonate reaction is the same for all cases. The reaction rate has a profound impact on the design of the absorber, especially when it comes to the height where a clear correlation can be identified. The relation between the ammonia in the liquid feed stream and carbon dioxide in the flue gases is also important for the reactivity. The process simulation conditions shown above represent a non-optimized case since the rate-based approach resulted in significant convergence problems, especially at running conditions where precipitation ought to occur in the absorber. It is also noteworthy that there are two distinct reaction zones in the column. Below 40 meters, the reactions are fast in both cases, but in the remaining height of the column the absorption is clearly much slower. This is probably due to that first the carbamate reaction occurs and when the liquid is saturated with carbamate the bicarbonate reaction takes over. Even though the reactions occur simultaneously, they appear to react sequentially due to the high difference in reaction rates. A measure to increase the reactivity is to increase the ratio between the ammonia in the CO_2 -lean stream and the CO_2 in the flue gases to higher values than for the equilibrium-based cases. This while keeping the ammonia concentration at the same level. Thus, the liquid flow-rate is in this case much higher. However, this results in a very high ammonia slip, and also that almost all CO_2 is bound as carbamate and the sensible heat requirement increases.

3 Methodology

The thermal performance of the ammonia-based carbon capture is evaluated by determining the specific heat requirements of the regeneration process and by assessing the energy penalty of the entire capture process integrated with coal-fired power plant. Furthermore, the work gives new experimental data at low temperatures for validation of the thermodynamic models in the typical operating region of the absorption process (cf. shadowed areas in Figure 4). The methodology is divided into experimental work (Paper I) and modeling work (Paper II and III).

3.1 Experimental work

The purpose of the experimental work is to determine the partial pressures of carbon dioxide and ammonia partial pressure. The experimental conditions are set to those of the absorber, with a temperature ranging from 0 - 20°C. The ammonia concentration ranges from 5 - 30wt% and the lean CO₂-loading are in the range 0.25 - 0.5 and the rich CO₂-loading is in the range of 0.5 - 1. The experimental data series is distributed to cover this range of operating conditions. It is concluded in Paper II that an ammonia concentration between 5 and 10% is a promising operating condition due to a low heat requirement for regeneration in these ranges. Thus, this range was in focus during the experimental procedure in this work. There is also a possibility that solid precipitation can be avoided in this range. The experimental matrix covers data points at ammonia concentrations of 5.7%, 10.7wt%, temperatures between 10 - 20°C and CO₂-loadings between 0.15 - 0.75.

The experimental setup consists of an equilibrium cell and a gas chromatograph (GC), as shown in Figure 7. An equilibrium cell is used to reach the correct pressure and temperature of the vapour and liquid phase. The equilibrium cell consists of three flasks connected in series, which form a closed loop. There are two valves connected to the closed loop, one for gas injection (N₂ and CO₂) and one to extract gas samples to the GC. The first two flasks are empty and have a volume of 500ml. The purpose of these flasks is to supply sufficient volume in the equilibrium cell, to ensure a low pressure drop when a gas sample is extracted. In the third flask, a known amount of ammonia and water (200ml) is injected. More details of the experimental setup are given in Paper I.

The analytical instrument used in this work is a GC with a Thermal Conductivity Detector (TCD). It is calibrated to measure both the ammonia and carbon dioxide concentrations in the vapour phase. The experimental specifications and operation conditions are described in detail in Paper I. The results from the experiments are compared with previous VLE-data from the literature. The existing equilibrium-based thermodynamic models representing the NH₃-CO₂-H₂O system by Darde et al. [40], Kurz et al. [38] and Que and Chen [41] are evaluated with respect to the new data in Paper I.

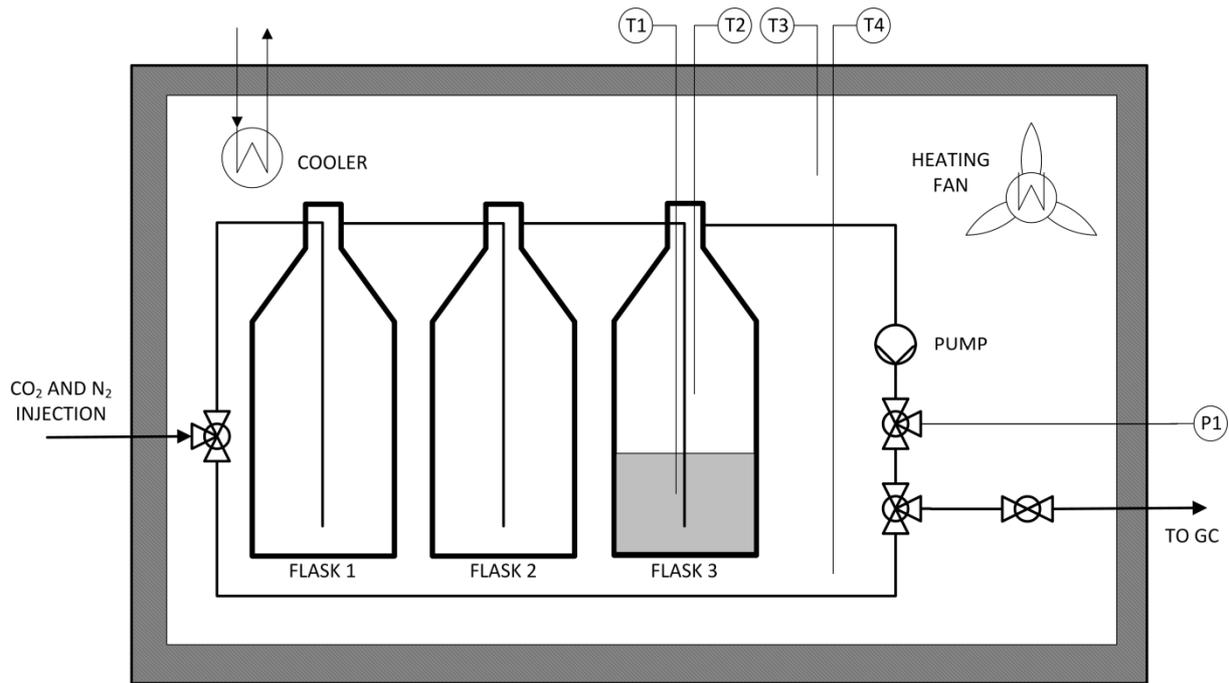


Figure 7. Schematic setup of the equilibrium cell. The equilibrium cell is inserted in an insulated box. T1-T4 denotes the temperature measurement positions. P1 denotes the pressure measurement. Source: Paper I

3.2 Modeling work

The modeling work is divided into two different parts. Paper II evaluates the heat requirement of regeneration, while the energy penalty of the whole capture process is considered in Paper III. The common basis for both papers is that they are based on equilibrium-based process modeling in the process simulation software Aspen Plus. In Paper III the thermodynamic model by Kurz et al. is used, while in Paper II the model by Que and Chen is used. The reason why the thermodynamic model of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system was changed between Paper III and Paper II was due to that, Que and Chen [41] presented a new model which more accurately predicts the liquid phase, which is a central issue in Paper II. As the aim of Paper II is to evaluate the heat requirement of regeneration, only the CO_2 capture cycle is modeled. The operating conditions of the capture process are presented in Paper II. The heat requirement for regeneration is evaluated by changing the operating conditions of the capture process. The lean stream ammonia concentration is varied between 2 - 20% and the lean stream CO_2 -loading is varied between 0.2 - 0.5. The heat requirement of regeneration and the equilibrium CO_2 capture efficiency is evaluated for each operating condition. As an equilibrium-based approach is used, the CO_2 capture efficiency represents the maximum possible. In the patent of the CAP [47], the heat of reaction is assumed to be significantly lower than for MEA. This presumption is in this work evaluated by decomposing the heat requirement of regeneration, into its three contributions; heat of reaction, sensible heat and heat of vaporization. In Paper III the energy penalty of the entire capture process is evaluated, including flue gas conditioning, CO_2 capture cycle, ammonia abatement cycle, and the CO_2 compression. The energy penalty of the whole capture process will result in the efficiency decrease of reference power plant. The operating conditions of the CAP used in the simulations are presented in Paper III. The Danish power plant, Nordjyllandsværket, is used as reference plant. Nordjyllandsværket is a state-of-the-art pulverized coal-fired plant with

combined heat and power generation. In condensing mode the power plant generates an electrical output of 408 MW with an electric efficiency of 47%. The steam to power the reboiler and ammonia stripper is extracted from the intermediate pressure turbine outlet. The main result of Paper III is the energy penalty of the existing coal-fired power plant. The major contribution to the energy penalty, the heat that is extracted from the steam cycle to the reboiler, is treated most thoroughly. The smaller contribution to the energy penalty such as the CO₂ compression, refrigeration and pump work are also included.

4 Thermal performance of ammonia-based post combustion

The performance evaluation is divided into three parts, each corresponding to the results from the included papers: validation of thermodynamic models (Paper I), heat requirement for regeneration (Paper II), and thermal integration of the chilled ammonia process (Paper III). The thermodynamic models used in the thermal evaluation are evaluated with respect to new VLE data in Chapter 4.1. In Chapter 4.2 the thermodynamic model by Que and Chen [41] is used to determine the heat requirement for regeneration at different process conditions. In Chapter 4.3 all energy penalties of the capture process is accounted for when the chilled ammonia process is integrated into an existing power plant. Apart from the heat requirement for regeneration, the heat requirement of the ammonia stripper, refrigeration, CO₂ compression and the pump work is included in this work.

4.1 Validation of thermodynamic models

Figures 8 a-d and 9 a-d show the partial pressures of ammonia and carbon dioxide, respectively. The experimental conditions are 10 and 20°C and at ammonia concentrations of 5.7 and 10.7wt% NH₃. The CO₂-loadings are varied between 0.15 - 0.75. All the experimental data is summarized in Paper I. The experimental data is compared with the thermodynamic models by Que and Chen [41], Kurz et al. [38] and Darde et al. [40]

Partial pressures of carbon dioxide

In Figure 8 the partial pressure of carbon dioxide is given as a function of CO₂-loading. Both experiments from this work and the predictions from the above mentioned thermodynamic models are included. The general trend is that at low CO₂-loadings the partial pressure of CO₂ is underestimated by the thermodynamic models. The saturation point for solid ammonium bicarbonate is also higher than suggested by the thermodynamic models, see Reaction R6. As mentioned in the previous chapter, the model by Darde et al. [40] includes the possibility of more solids than ammonium bicarbonate to precipitate. However, in the investigated range only ammonium bicarbonate is present. This is most evident at low ammonia concentrations (5.7wt%) and low temperature (10°C) where the precipitation starts at 0.7 - 0.74 whereas the model predicts the precipitation to start at just above 0.6. The most evident difference between the different models is that the prediction for the CO₂ partial pressure at low CO₂-loading is most accurately predicted by the model by Que and Chen [41].

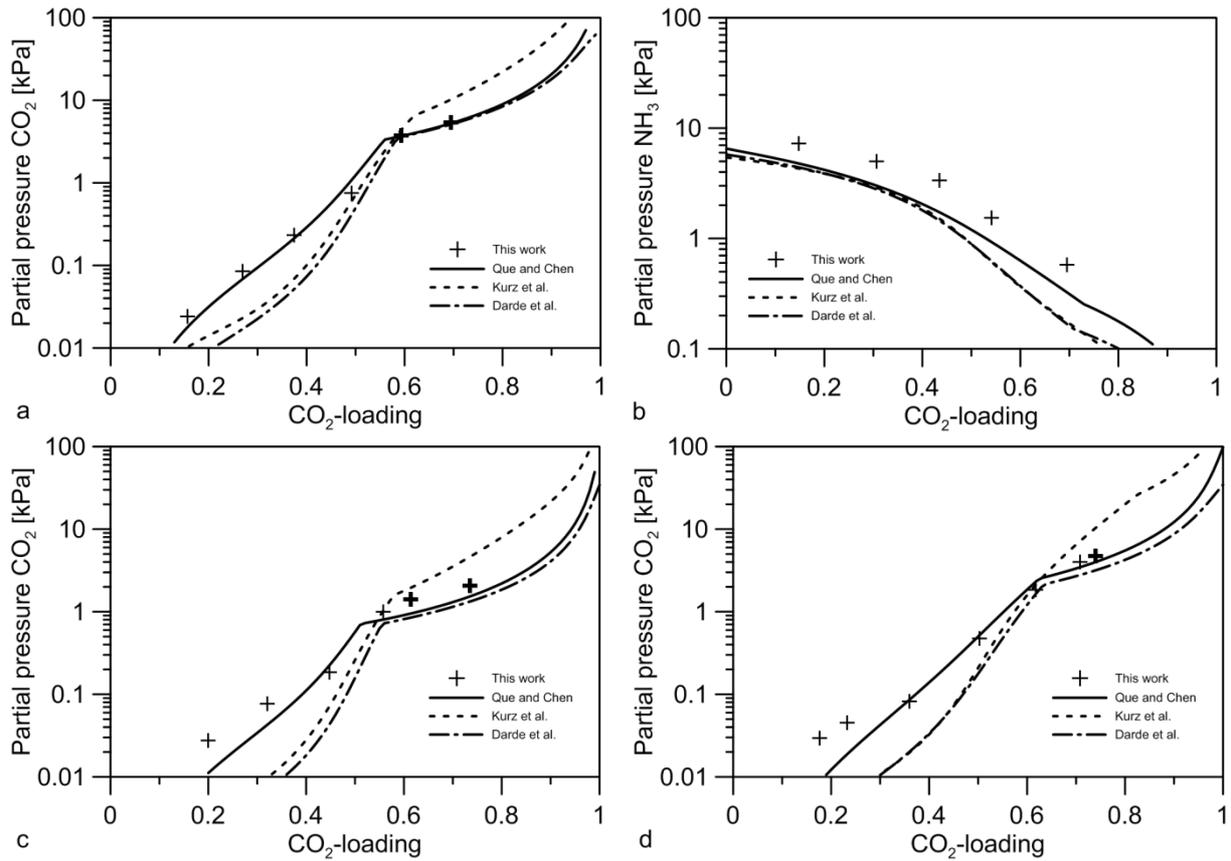


Figure 8. The partial pressures of carbon dioxide as a function of CO_2 -loading. Figures 8 a) represent 10.7wt% NH_3 and 20°C , b) 5.7wt% NH_3 and 20°C , c) 10.7wt% and 10°C and d) 5.7wt% NH_3 and 10°C . The crosses represent the experimental work in this work. Bold crosses represent measurement points where precipitation occurs. The continuous lines represent the thermodynamic models by Darde et al. [40], Kurz et al. [38] and Que and Chen [41] The sudden trend change in the model prediction at 0.5 - 0.7 CO_2 -loading is due to solid ammonium bicarbonate precipitation. Source: Paper I

Partial pressures of ammonia

Figure 9 show the partial pressure of ammonia when varying the CO_2 -loading. The partial pressure of ammonia is generally higher than the thermodynamic models for all CO_2 -loadings, even though they share the same shape. Only after a CO_2 -loading of 0.5 some real differences between the models are identified. The more rapid decrease in partial pressure at a CO_2 -loading of 0.5 is due to that more of the carbon dioxide is bound as bicarbonate, which reacts according to the stoichiometric relation 1:1 with ammonia, see Reaction R2. Carbon dioxide can also be absorbed through reaction R1 to form bicarbonate, however it is shown in Paper II that little CO_2 is actually captured through this reaction. Before a CO_2 -loading of 0.5 most of the carbon dioxide is bound as carbonate and carbamate, which reacts according to the stoichiometric relation 1:2 (R3 and R4).

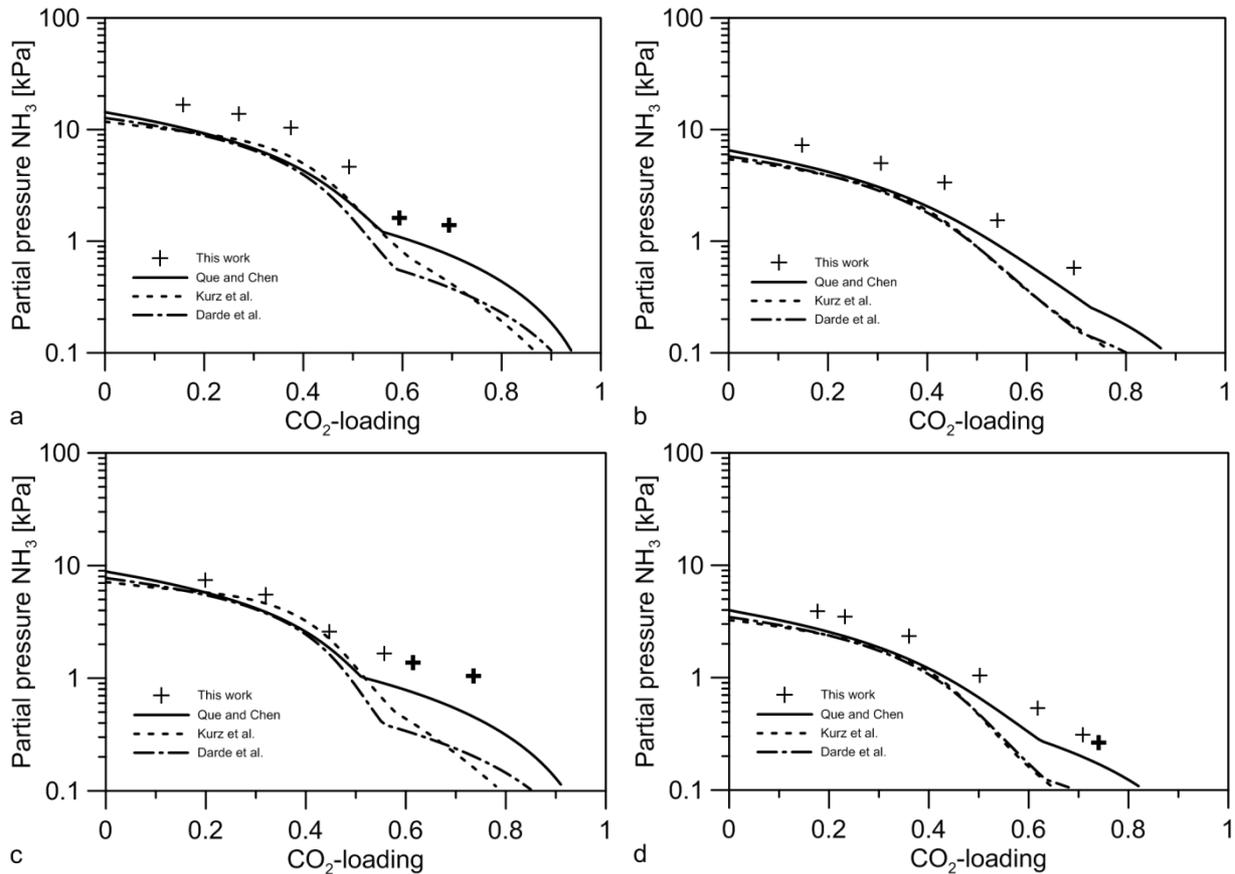


Figure 9. The partial pressure of ammonia of as a function of CO_2 -loading. Figures 9 a) represent 10.7wt% NH_3 and 20°C , b) 5.7wt% NH_3 and 20°C , c) 10.7wt% and 10°C and d) 5.7wt% NH_3 and 10°C . The crosses represent the experimental work in this work. Bold crosses represent measurement points where precipitation occurs. The continuous lines represent the thermodynamic models by Darde et al. [40], Kurz et al. [38] and Que and Chen [41] The sudden trend change in the model prediction at 0.5 - 0.7 CO_2 -loading is due to solid ammonium bicarbonate precipitation. Source: Paper I

4.2 Heat requirement for regeneration

To determine the effect of how CO_2 is bound in the liquid on the heat requirement of the ammonia regeneration, the model is run at different ammonia concentrations at a fixed lean CO_2 -loading. Figures 10a and b show the specific heat requirements and the CO_2 capture efficiencies for lean CO_2 -loadings between 0.2 - 0.5, and ammonia concentrations between 2 - 20%. For a lean solution with a CO_2 -loading of 0.5, there is a minimum heat requirement of 2100 kJ/kg CO_2 at 5% ammonia (Figure 10a). Under these conditions, the solubility limit of ammonium bicarbonate is reached and it starts to precipitate. However, the CO_2 capture efficiency is low under these conditions (Figure 10b), and a capture efficiency of only approximately 50% is achieved. As shown in Figure 10a there is no incentive to run the process with solid formation from a thermal performance perspective. The decrease in heating due to lower liquid flow-rate is counteracted by the heat required to dissolve the solids.

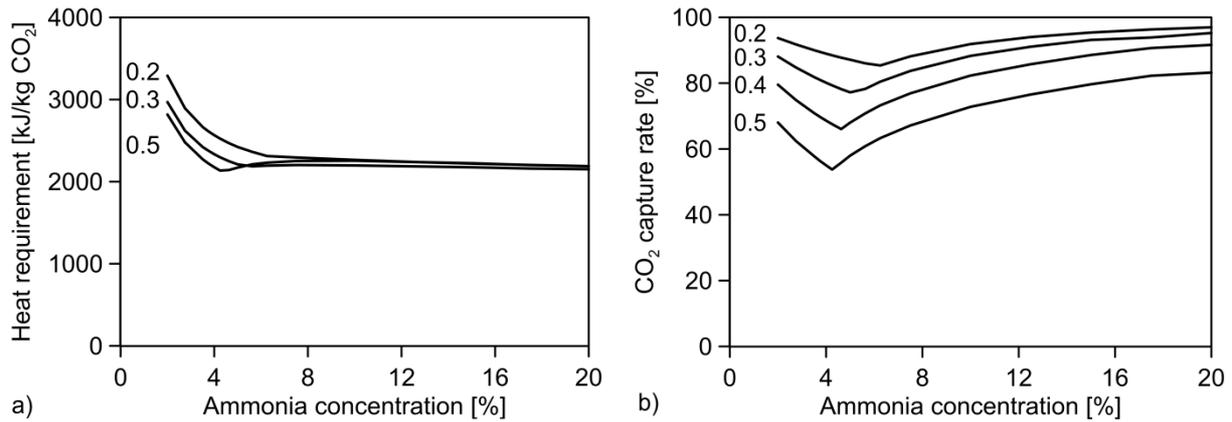


Figure 10. a) The specific heat requirements and b) CO₂ capture efficiencies at different ammonia concentrations. The curves represent the influences of the lean CO₂-loadings (0.2, 0.3, 0.4 and 0.5) Source: Paper II

Table 6 shows the heat requirement for regeneration, divided into heat of reaction, heat of vaporization, and sensible heat, for an ammonia concentration of 10% and a lean CO₂-loading of 0.3. The decomposition of the heat requirement for MEA has been described by Dave et al. [48], in a similar manner to that of the present work, and their data are presented in Table 6. It is mainly the heat contribution of water vaporization that makes absorption of CO₂ by ammonia beneficial compared to absorption by MEA. The reason for the higher heat requirement for the vaporization of water in the MEA process is the low pressure desorption, which leads to an increase of the water content in the off-gas. The lower sensible heat requirement of ammonia is due to the higher loading capacity. The CO₂-rich stream loading capacity of MEA is up to 0.5, whereas a loading of up to unity is possible for ammonia. It is also worth noting that the difference in heat of reaction between ammonia and MEA is not as significant as might have been expected. This is because the absorption and desorption of CO₂ by ammonia are governed by Reaction R2 rather than by Reaction R1, as concluded in Paper II.

Table 6. The specific heat requirement for MEA and ammonia. The running conditions for the ammonia cases are taken for a lean CO₂-loading of 0.3 and an ammonia concentration of 10%.

Specific heat requirement (kJ/kg CO ₂ captured)	MEA ([25])	Ammonia Source: Paper II
Heat of vaporization	1190	50
Sensible heat	1450	1170
Heat of reaction	1400	980
Total	4040	2200

4.3 Thermal integration of the chilled ammonia process

Figure 11 shows the energy penalty of an existing coal-fired power plant integrated with the CAP, applying the thermodynamic model by Kurz et al. [38]. The energy penalty is given as the decrease in percentage points of electric efficiency. In Figure 11, the electric efficiency is given as a function of ammonia concentration, including (solid line) and excluding (dashed line) the impact of the ammonia stripper. The electric efficiency of the power plant with chilled ammonia-based capture is directly connected to the heat requirement for the regeneration shown in Figure 10a. However, a high ammonia concentration leads to a high ammonia slip and thus also significantly higher heat requirement for the ammonia stripper. The heat requirement of regeneration estimated in Paper III corresponds well with the results of Paper II, even though different thermodynamic models are used.

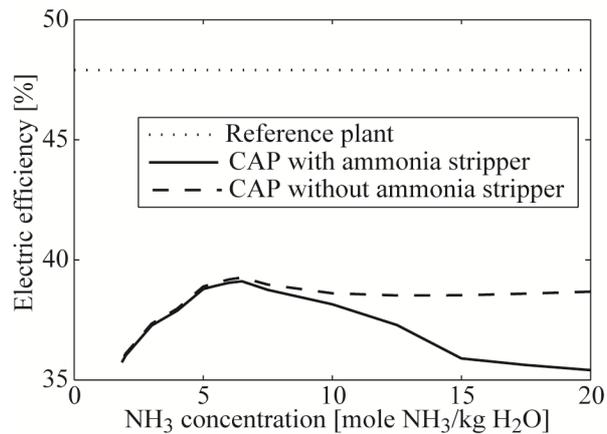


Figure 11. Electric efficiency of the reference power plant when equipped with a CAP for different ammonia concentrations. Reference electric efficiency is estimated to 47.9% at 10°C cooling water. Source: Paper III

The CAP is highly dependent on large amounts of cooling water mainly to reject the excess heat formed during the exothermic absorption reaction, but, also to cool the solvent and flue gas down to the operating temperature of the absorber. The impact of cooling water temperature on the electric efficiency is shown in Figure 12. If cooling water of 5°C is available, it is assumed that no refrigeration is required, due to a sufficient temperature difference between the cooling water temperature and the absorber operating temperature (10°C). This is the reason for the distinct change in energy penalty between a cooling water temperature of 5 and 10°C. The energy penalty is 9.2% at a cooling water temperature of 10°C. However, as shown in Figure 12, the energy penalty can range from 8 - 11% depending on the cooling water temperature. The electric output of the power plant drops from 408 to 362 MW_{el} when equipped with a post-combustion capture process.

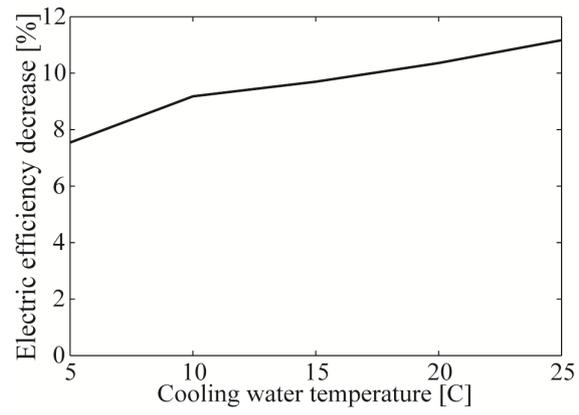


Figure 12. The electric efficiency of the reference plant when the cooling water temperature is varied between 5-25°C. The efficiency decrease is given in percentage points. Source: Paper III

5 Conclusions

In the present work ammonia is evaluated as absorbent of carbon dioxide to be used in post-combustion carbon capture. The evaluation is based on modeling of the thermal performance of the capture process. A literature review of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system of available experimental data is performed.

In this work, an experimental procedure is presented to determine the equilibrium partial pressures of ammonia and carbon dioxide. In Paper I, new experimental data points are produced for regression of thermodynamic models of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system. The partial pressures of ammonia and carbon dioxide were determined at the temperatures 10 and 20°C, ammonia concentrations 5.7 and 10.7wt% and CO_2 -loadings between 0.15 - 0.75. Three different thermodynamic models for the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system are evaluated with respect to the new experimental data in this work. The evaluated models are those by, Que and Chen [41], Kurz et al. [38] and Darde et al. [40] The results from the measurements of the ammonia partial pressure in this work proved to be higher than previous work, while the carbon dioxide partial pressures concurred with previous findings. The model by Que and Chen provided the most accurate prediction over the investigated range.

In this work, the heat requirement of ammonia regeneration from CO_2 capture is evaluated. An electrolyte-based thermodynamic model was used to represent the properties of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system, and a process model analyzed relevant operational conditions. The simulations verify that, compared to MEA, ammonia has a lower heat requirement to capture CO_2 from flue gases. The simulations show that the heat requirement of ammonia regeneration could be less than 2500 kJ/kg CO_2 captured. The main reason for the lower heat requirement for ammonia compared to MEA is that the thermodynamic properties of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system allow for pressurized regeneration, which results in significantly lower water vaporization. Thus, it is not the lower heat of reaction that results in the lower heat requirement. We found that a specific heat requirement below 2100 kJ/kg CO_2 captured is achievable, albeit at capture efficiencies that are undesirably low. Furthermore, equilibrium modeling shows that the precipitation of solids in the absorber does not enhance the thermal process performance. The incentives of a lower sensible heat requirement and higher loading capacity are counteracted by the energy that is required to dissolve the solids. In conclusion, an ammonia concentration close to the solubility limit of the solid phase is preferable from a thermal performance point of view. Though, the CO_2 -loading should not be too high due to a low capture efficiency.

The thermal integration of the coal-fired power plant shows that the energy penalty of installing the CAP for CO_2 capture on a state-of-the art power plant (with 47% electric efficiency) is in the range 8 - 11% percentage points. The large range is mainly caused by the great importance of the investigated cooling water temperatures. Thus, one prerequisite for the ammonia process to be competitive is the access to large amounts of cooling water at a low temperature.

6 Future work

From the present work a number of areas of interest have emerged, where one of the most obvious is the impact of the absorption reaction rate. As indicated in Chapter 2.2, the reaction rate is a high impact parameter for which a large uncertainty remains. Efforts should be put into narrowing down this uncertainty or to evaluate the real impact of this parameter and how it affects the process design and the heat requirement. Though, it should be mentioned that a slow reaction rate was used in this case and the heat requirement should therefore be interpreted as the maximum possible heat requirement. Likewise, the results from the equilibrium-based approach should be interpreted as the minimum heat requirement.

Another important aspect is the penalty of avoiding the ammonia slip. This is indicated by the large discrepancy in Table 3, where the heat requirement for the ammonia recovery is presented from different sources. This is confirmed by Figure 11 where the contribution from the ammonia stripping at different operating conditions is far from negligible. If the heat requirement for ammonia stripping exceed the difference between the heat requirement for MEA (3700 kJ/ kg CO₂) and the ammonia CO₂ capture cycle (2500 kJ/kg CO₂), there is a significantly smaller incentive to pursue ammonia for post-combustion capture. In this work only the ammonia abatement cycle is mentioned as a possible measure to decrease the ammonia slip. However, there are other options that should be investigated, such as upstream SO_x reduction, acid wash and vapour suppressing additives.

When it comes to vapour-liquid equilibrium data there are a lot of vapour phase data for a wide range of operational conditions. The liquid phase at all investigated to the same extent as indicated by the difference between Figure 4a and b. There are no data for higher concentrations and low temperatures. This data can be obtained by experimental techniques such as Nuclear Magnetic Resonance (NMR) or Raman spectroscopy.

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