

# Evaluation of Excess Heat Driven Carbon Capture Integrated at a Swedish Pulp Mill

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## Abstract

As the atmospheric carbon dioxide keeps increasing, bioenergy with carbon capture and storage (BECCS) is getting increased attention as a measure to reduce the emissions of carbon dioxide. It is especially interesting in Sweden where the extensive paper and pulp industry constitutes point sources of biogenic carbon dioxide. As carbon capture requires energy, it is important to investigate the opportunity to use excess heat to cover the energy demand in order to avoid causing new emission which would counteract the purpose of implementing BECCS. In this thesis, integration of excess heat driven carbon capture was investigated on two flue gas streams at the Södra Cell Värö pulp mill in Sweden: the recovery boiler and lime kiln flue gases. Three different carbon capture technologies were investigated, which included the commercially available aqueous MEA (monoethanolamine) and HPC (hot potassium carbonate) as well as the novel technology of AMP (2-amino-2-methyl-1-propanol) in DMSO (dimethyl sulfoxide). Their energy demands were calculated through mass and energy balances. A mapping of sources of excess heat at the mill was also executed.

The results showed that the lime kiln flue gases would be more reasonable to treat due to the smaller flue gas stream with a higher CO<sub>2</sub> concentration. Partial carbon capture of the recovery boiler flue gases could also be an option worth considering. For the lime kiln flue gases, two components of the mill, the condensing turbine and the surface condenser, proved to be sources of excess heat that could cover the heat demand at the cost of some electrical power. The condensing turbine was more promising as it could cover the heat demand regardless of which technology is used while the surface condenser could only be used on the AMP in DMSO technology. In addition, a heat pump is required to make use of the heat from the surface condenser, making the electrical power demand higher for the surface condenser than for the condensing turbine. The MEA and AMP in DMSO technologies required much less energy supply than the HPC technology did but have higher cooling demands.

Further studies are needed which include more detailed process designs, management of the captured CO<sub>2</sub>, and evaluations of economical feasibility. This thesis gives a good indication on what to focus on going forward.



# Populärvetenskaplig sammanfattning

Genom att använda koldioxidinfångning som drivs av överskottsvärme på ett massabruk i sydvästra Sverige så kan mer än en tredjedel av de fossila utsläppen från hela pappers- och massaindustrin fångas in genom så kallade negativa utsläpp. Detta visar på hur snabbt Sveriges fossila utsläpp kan minska genom användning av koldioxidinfångning.

På ett massabruk används trä som den huvudsakliga råvaran i tillverkningen av pappersmassa, men det är också den främsta energikällan. Genom att förbränna resterna som inte behövs till pappersmassan så kan man producera ånga och elektricitet som används runt om på bruket, men även som säljs till fjärrvärme- och elnätet. Vid förbränningen produceras även koldioxid och andra gaser som kallas rökgaser. Dessa renas från partiklar och föroreningar och släpps sedan ut i atmosfären. Eftersom koldioxiden kommer från träd som nyligen fångat in koldioxid från atmosfären i takt med att de vuxit och inte från fossila källor som varit isolerade från kolets kretslopp i miljontals år, så benämns dessa utsläpp av koldioxid som biogena utsläpp.

De biogena koldioxidutsläppen står för ungefär 97% av de totala utsläppen från pappers- och massaindustrin. Resterande 3% är fossila utsläpp, och det är bara dessa utsläpp som syns i statistiken. Totalt 2% av Sveriges fossila koldioxidutsläpp kommer från pappers- och massaindustrin, vilket betyder att de totala utsläppen av koldioxid från pappers- och massaindustrin är nästan lika stora som alla fossila koldioxidutsläpp i hela Sverige. Genom att fånga in den i huvudsak biogena koldioxiden från pappers- och massaindustrin så kan vi snabbt kompensera för stora delar av de fossila utsläppen i Sverige. Då uppnår vi så kallade negativa utsläpp, eftersom mer koldioxid kan fångas in än vad som syns i utsläppsstatistiken. Att fånga in koldioxid kräver dock energi, främst i form av värme, och för att kunna uppnå verkligt negativa utsläpp är det viktigt att nya utsläpp inte uppstår för att den energin ska produceras. Därför är det viktigt att titta på hur överskottsvärme kan användas till att driva infångningen, det vill säga värme som redan finns på anläggningen men som inte utnyttjas.

I detta examensarbete undersöktes möjligheten att implementera koldioxidinfångning som drivs av överskottsvärme på Södras massabruk i Värö. Målet var att se hur mycket koldioxid som kan fångas in från brukets olika rökgasströmmar och sedan jämföra tre olika infångningstekniker baserat på deras energibehov. Teknikerna som inkluderades var de kommersiellt tillgängliga teknikerna MEA (monoetanolamin) och HPC (hot potassium carbonate) samt den nya tekniken AMP (2-amino-2-metyl-1-propanol) i DMSO (dimetylsulfoxid) som studeras på Institutionen för kemiteknik på LTH. AMP i DMSO är intressant att jämföra med de kommersiella teknikerna då värmen som behöver tillföras kan ha en lägre temperatur. Dessutom är den utformad så att en mindre andel lösningsmedel behöver värmas och den har därmed potential att kräva mindre energi per ton infångad koldioxid än de kommersiella teknikerna. Källor till överskottsvärme på bruket kartlades och utvärderades för att se hur väl de kunde täcka de olika teknikernas värmebehov.

Resultaten visade att AMP i DMSO var den minst energikrävande tekniken då den hade ett lägre värmebehov än MEA-tekniken och då HPC-tekniken inte bara har ett behov av värme utan också elektricitet. Källor till överskottsvärme hittades som kunde täcka behovet av värme oavsett teknik, men för HPC-tekniken kvarstår behovet av elektricitet som skulle behöva kompenseras för genom minskad leverans av el till elnätet. Examensarbetet gav därmed en bra indikation på vilka tekniker och källor till överskottsvärme som kan vara intressanta att titta vidare på. Det visade också att även om bara en av de mindre rökgasströmmarna på bruket behandlas så kan mer än en tredjedel av de fossila koldioxidutsläppen från hela pappers- och massaindustrin fångas in.





# Abbreviations and Symbols

## Abbreviations

AMP	2-Amino-2-methyl-1-propanol
BECCS	Bioenergy with carbon capture and storage
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
DMSO	Dimethyl sulfoxide
EU ETS	European Union emissions trading system
HPC	Hot potassium carbonate
LULUCF	Land use, land-use change, and forestry
MDEA	Methyl diethanolamine
MEA	Monoethanolamine
MVR	Mechanical vapor recompression
NMP	N-methyl-2-pyrrolidone
PZ	Piperazine
SHS	Secondary heat system

## Symbols

$\alpha$	Loading	[mol CO <sub>2</sub> /mol amine]
$C_{abs}$	Concentration of amine in solvent	[mol amine/kg sol]
$C_{Am}$	Concentration of amine in solution	[wt%]
$C_p$	Specific heat capacity	[kJ/(kg·K)]
$COP$	Coefficient of performance	[-]
$\Delta H$	Change in enthalpy	[J/mol]
$\Delta H_A^{cond}$	Condensation enthalpy of component A	[J/mol]
$\Delta H_A^{vap}$	Vaporization enthalpy of component A	[J/mol]

$\Delta T$	Change in temperature	[°C]
$H_V$	Enthalpy in vapor phase	[kJ/kg]
$M$	Molar mass	[g/mol]
$\dot{m}$	Mass flow rate	[kg/s]
$\dot{n}$	Molar flow rate	[kmol/s]
$P$	Pressure	[Pa]
$P_A$	Partial pressure of component A	[Pa]
$P_A^{sat}$	Saturation pressure of component A	[Pa]
$Q$	Heat added to a system	[J/kg]
$R$	Molar gas constant	[J/(mol·K)]
$T$	Temperature	[°C]
$\dot{V}$	Volumetric flow rate	[m <sup>3</sup> /s]
$V_m$	Molar volume	[m <sup>3</sup> /mol]
$W$	Work performed on a system	[J/kg]
$x_A$	Molar fraction of component A in liquid phase	[-]
$y_A$	Molar fraction of component A in gas phase	[-]

# Table of Contents

1	Introduction .....	1
1.1	Purpose and Objectives .....	2
1.2	Scope and Limitations .....	2
2	Södra Cell Värö .....	3
2.1	The Kraft Process.....	3
2.2	Energy System .....	4
2.3	CO <sub>2</sub> Emissions .....	4
3	Carbon Capture Technologies .....	6
3.1	Aqueous MEA .....	8
3.2	Aqueous HPC .....	9
3.3	Precipitating Non-Aqueous AMP in DMSO .....	10
4	Methods .....	12
4.1	Process Design .....	12
4.2	Data Collection .....	15
4.3	Calculations .....	16
4.4	Matching Heat Demands and Available Excess Heat .....	25
4.5	Sensitivity Analysis .....	25
5	Results and Discussion .....	27
5.1	Captured CO <sub>2</sub> and Absorbent Use .....	27
5.2	Energy Demands .....	28
5.3	Available Excess Heat .....	31
5.4	Matching Heat Demands and Available Excess Heat .....	33
5.5	Sensitivity Analysis .....	34
5.6	Flue Gas Stream.....	35
5.7	Energy Supply.....	35
5.8	Sources of Error .....	37
5.9	Limitations .....	38
6	Conclusions .....	39
7	Future Work.....	40
8	References .....	41
	Appendix A – Mass and Energy Balances .....	46
	Appendix B – Aspen Plus Models.....	55



# 1 Introduction

It is not new that the anthropogenic emissions of carbon dioxide and other greenhouse gases are causing an increase in the global temperature with climate change as a result. Already in 1938, it could be shown that increased levels of CO<sub>2</sub> in the atmosphere were connected to global warming [1], and in 1997, the first legally binding climate treaty aiming to reduce the greenhouse gas emissions was adopted, known as the Kyoto protocol [2]. In 2015, the Paris agreement was adopted replacing the Kyoto protocol with more ambitious goals [3] and yet, the emissions and the atmospheric CO<sub>2</sub> levels continue to increase every year. The CO<sub>2</sub> levels in the atmosphere averaged 415 ppm in 2021, compared to 280 ppm in pre-industrial times [4]. In order to stop this trend and limit the global warming to the 1.5°C increase stated in the Paris Agreement, the emissions of CO<sub>2</sub> need to be halved by 2030 and completely eliminated by mid-century [5]. To achieve the goals of the Paris agreement, focus has been put on phasing out fossil fuels and replacing them with renewable energy resources in order to reduce the emissions of greenhouse gases. But as time passes, the more urgent fast changes become, and all measures possible need to be considered. CO<sub>2</sub> reduction technologies are examples of methods receiving increasing attention, which includes carbon capture and storage (CCS) and carbon capture and utilization (CCU).

The technology needed for CCS is not new either. CO<sub>2</sub> removal has been used for decades in the upgrading of synthesis gas produced through gasification of coal [6, 7] as well as in the production of natural gas and hydrogen gas where acid gases like CO<sub>2</sub> must be removed in order to avoid corrosion on pipelines and equipment downstream [8, 9]. The underground storage of CO<sub>2</sub> is also already used in enhanced oil recovery, making the technologies necessary for CCS available [10]. The initial idea of CCS was to apply it on fossil fuel-fired power plants as it enables the continued use of fossil fuels while decreasing the CO<sub>2</sub> emissions [10] but in recent years the scope has grown bigger. Bioenergy with carbon capture and storage (BECCS) is gaining more interest with several projects around the world, including a Swedish project with Stockholm Exergi [11]. The prospect for BECCS in Sweden is promising with both the large pulp and paper industry and the extensive use of combined heat and power plants which are point source emissions of biogenic CO<sub>2</sub> [12, 13].

The pulp and paper industry stands for about 2% of the total greenhouse gas emissions in Sweden with 0.8 million tons CO<sub>2</sub>-equivalents in 2021 [14] and as an energy intensive industry it is included in the EU emissions trading system (EU ETS) [15]. However, only the fossil emissions are included in the statistics and in the EU ETS; the biogenic CO<sub>2</sub> is reported in the land use, land-use change, and forestry sector (LULUCF) as a decreased carbon sink when the biomass is harvested [16]. As the pulp and paper industry uses wood as the main feedstock as well as the biggest source of energy, about 97% of the emitted CO<sub>2</sub> is biogenic [17]. By using BECCS, significantly more CO<sub>2</sub> than the fossil fraction of the emissions could be captured, and hence negative CO<sub>2</sub> emissions could be obtained. The biggest obstacle for implementation of BECCS is that it at present is not economically feasible [12]. In 2021, the Swedish Energy Agency therefore proposed a state aid system for BECCS in order to make the technology economically feasible so that these negative CO<sub>2</sub> emissions can be achieved. That would be an important step towards the goal of net zero emissions by 2045 set by the Swedish government [12, 13].

Another important aspect of BECCS (and CCS in general) is the energy needed to power the capture process and how it is produced, as the effect of the negative emissions will decrease if more emissions are created in order to capture the already existing emissions. An investigation made on four large pulp mills in Sweden showed that if the carbon capture is to be powered by biomass fuels, the biomass demand will increase by 40-63% if 90% of the CO<sub>2</sub> emissions at the site are to be captured while the current production is maintained [18]. As the fossil fractions of the emissions are only 0.04-2.72%, the total amount of emitted CO<sub>2</sub> will increase almost as much as the biomass demand [18]. Making use of excess heat is therefore important in order to make the BECCS beneficial and to actually achieve negative emissions.

## 1.1 Purpose and Objectives

This thesis has been performed at the Department of Chemical Engineering at LTH, Lund University, together with Södra with the purpose of evaluating different technologies for carbon capture and their application at the Södra Cell Värö pulp mill in south-western Sweden. Three different technologies were included; the commercially available MEA and HPC, as well as the novel technology of AMP in DMSO that has been researched at the Department of Chemical Engineering at LTH. Simplified process designs were used and applied on the CO<sub>2</sub>-containing flue gas streams of the Värö pulp mill. From these, the heating, cooling, and electricity demands of the different technologies were estimated along with the amount of CO<sub>2</sub> that could be captured. In addition, sources of excess heat at the mill were investigated and evaluated to see whether they contain enough energy to power the carbon capture processes.

The objectives of this thesis are:

- To find how much CO<sub>2</sub> that could be captured from the recovery boiler and lime kiln flue gas streams at the Värö pulp mill
- To compare and evaluate three different technologies for carbon capture in terms of energy requirements and see which suits the mill best
- To map types and sizes of available excess heat at the mill that can be used to run the carbon capture processes and see how well they can cover the energy requirements
- To give recommendations of what carbon capture technology and source of excess heat to focus on moving forward

## 1.2 Scope and Limitations

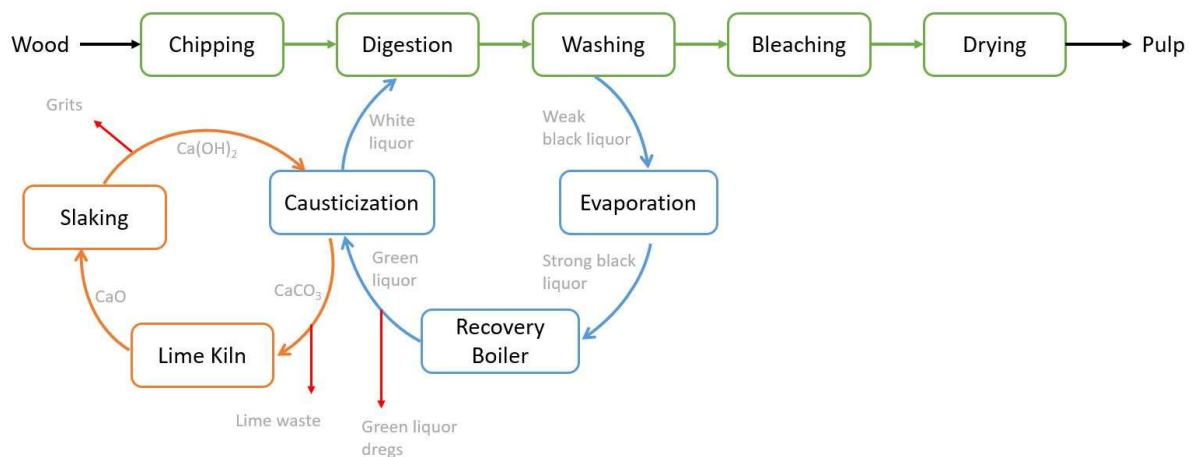
Three different technologies were compared in terms of energy requirements and the ability to cover them using excess heat from the mill. The designs of them were the simplest possible due to the limiting time frame of the thesis. In addition, only the capture of CO<sub>2</sub> was taken into consideration. The storage or utilization of CO<sub>2</sub> after separation was outside the scope as well as the design and cost estimation of the equipment needed. Furthermore, information about the flue gases and their composition was provided by Södra. The processes in their entirety were not modeled using a modeling software, instead calculations were performed using Excel. In addition, the thesis did not include an evaluation of whether the suggested technologies are technically possible or not. It did, however, include an investigation of sources of excess heat at the pulp mill and an evaluation of whether it will be enough to cover the heat demand of the different technologies or not. This was done using a previously performed mapping of the energy system. Thus, no thorough investigation of the current energy system was covered in this thesis.

## 2 Södra Cell Värö

In this section, a description of the Södra Cell Värö pulp mill is presented with emphasis on the origin of the CO<sub>2</sub> emissions. The energy system of the mill is also briefly described.

### 2.1 The Kraft Process

Södra Cell Värö is a pulp mill using the kraft process which uses white liquor, a mix of sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S), to digest the wood and release the cellulose fibers to produce pulp. Södra Cell Värö does not process the pulp further into paper products. A schematic overview of the process is shown in Figure 1.



**Figure 1:** A schematic overview of the kraft pulp mill process including the sodium recovery cycle (blue) and the calcium cycle (orange). Waste streams are marked in red. Adapted from [19, 20].

After the wood is washed and debarked, it is chopped into wood chips before entering the digesters where it is cooked together with white liquor. The cellulose fibers are liberated and then washed with water in several steps to remove the liquor, the lignin, and other unwanted substances. The mixture of used liquor, lignin, water, and other digestion products is called weak black liquor due to its dark color caused by the lignin. The cellulose fibers are then further processed through washing and bleaching in numerous steps before being dried, cut into sheets, and packaged.

The weak black liquor is processed in the sodium cycle in order to recover the cooking chemicals. The first step is evaporation where water is removed in a multi-effect evaporator plant, and the solids content of the liquor is increased from 15-20% to about 70-80% [21]. The now strong black liquor is then combusted in a recovery boiler to generate heat from the organic matter and to recover sodium and sulphur. A smelt settles at the bottom of the recovery boiler which is diluted with water and filtered to create green liquor. The solid reject from the filter is called green liquor dregs and is disposed of. The green liquor is further processed through causticization where slaked lime, or calcium hydroxide (Ca(OH)<sub>2</sub>), is reacted with green liquor to regain the white liquor which can be used in another cooking process.

When the Ca(OH)<sub>2</sub> has been used, it in turn can be recovered in the calcium cycle. In the causticization, calcium carbonate (CaCO<sub>3</sub>) is formed which is returned in a lime kiln to get

calcium oxide (CaO). The CaO is then slaked with water and the slaked lime is recovered to be reused in the causticization. Waste in the form of lime waste and grits is formed in the calcium cycle and are, like the green liquor dregs, disposed of.

## 2.2 Energy System

The Värö pulp mill is apart from being a pulp producer also a large energy producer. The heat generated in the recovery boiler and bark boiler is used to produce steam which is distributed and used for heating throughout the mill. Using turbines and pressure reduction stations, steam at different pressure levels can be obtained and the excess steam can be used to produce electricity in the turbines and hot water if the steam is condensed. The steam pressures used are 3, 8, 10, and 23 bar(g) [22]. At Värö, a back pressure turbine and a condensing turbine are available for electricity production and the mill is at present self-sufficient in electricity. Most of the time it is even a net electricity producer [23]. Excess heat from the production process is also utilized to provide the adjacent sawmill with heat and the city of Varberg with district heating.

During the 2016 expansion of the Värö mill, a new secondary heat system (SHS) was constructed. The purpose of the SHS is to recover heat from process streams throughout the mill and produce warm or hot water at different temperature levels between 50-90°C. The water can then be transported across the site to meet heat demands of other streams. Excess heat in the SHS is cooled using cooling towers. The water is then useful as cold water again and thus, the intake of fresh water can be reduced [22].

## 2.3 CO<sub>2</sub> Emissions

The CO<sub>2</sub> emissions of the pulp mill are mainly generated in two of the process steps: the recovery boiler and the lime kiln. The mill also has an auxiliary bark boiler in which bark from the pretreatment of the wood is occasionally combusted. The bark boiler is primarily used to produce additional steam when the recovery boiler cannot cover the steam demand of the plant [24]. It is however not considered in this work as it does not generate CO<sub>2</sub> emissions continuously like the recovery boiler and lime kiln do. As mentioned in section 2.1, the organic matter in the black liquor is combusted in the recovery boiler when sodium and sulphur is to be recovered. This results in the formation of CO<sub>2</sub> which leaves the recovery boiler in the flue gases. Before being emitted through the stack, the flue gases are cleaned from particulate matter using electric filters and they are also cooled down in flue gas coolers. The heat recovered in the flue gas coolers is used to pre-heat the feed water used in the recovery boiler.

In the lime kiln, heat is used to dry and calcinate the CaCO<sub>3</sub> that was formed in the causticization. In the calcination, CaCO<sub>3</sub> reacts to form CaO and CO<sub>2</sub> according to Reaction 1 and in order for this reaction to happen, temperatures of above 800°C are required [25].



Additional CO<sub>2</sub> is generated through combustion of biofuels which is necessary obtain the 800°C needed for the calcination. This generally leads to higher CO<sub>2</sub> concentrations in the generated flue gases than typical combustion flue gases have.

The CO<sub>2</sub>-containing flue gases leaving the lime kiln are first passing through a cyclone and then electrical filters to remove particles. Unlike the flue gases from the recovery boiler, the flue gases from the lime kiln are not cooled before being emitted through a stack.

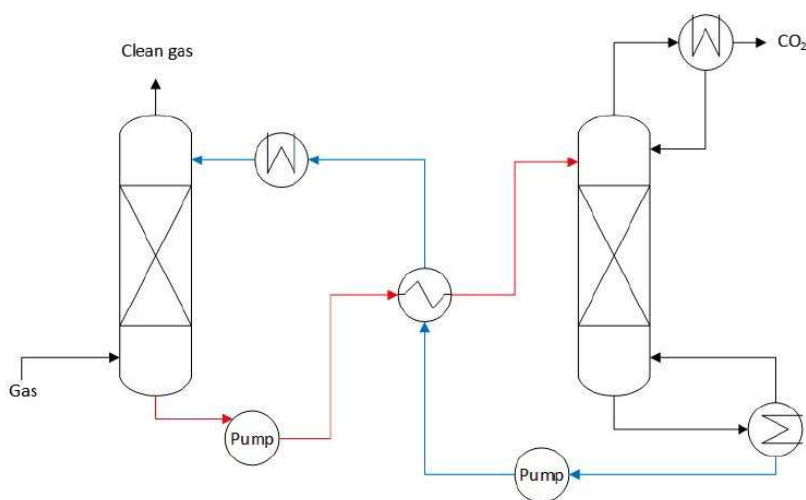


In total, the Värö mill emits about 1,860,000 tons of CO<sub>2</sub> per year, of which 10,000 comes from fossil sources [23]. These fossil sources include sodium formate used as sodium make-up, foam control agents and polymers used in the production process, and occasionally fossil oil. The fossil oil is sometimes used during shutdown of the mill to provide the adjacent sawmill with heat and during start-up a small amount is usually used to rinse the systems. Other than that, fossil oil would only be used if there is a deficiency of tall oil pitch.

### 3 Carbon Capture Technologies

Carbon capture can be performed using different techniques, including physical and chemical absorption, adsorption, and membrane separation. In absorption, a liquid absorbent in a solution with a solvent is used to separate the  $\text{CO}_2$  from the gas stream by dissolving and potentially reacting with it. The  $\text{CO}_2$ -rich phase is then transported to another container in which the conditions are changed, and the  $\text{CO}_2$  can be released and captured and potentially stored. Adsorption is based on the same principle except that a solid and porous adsorbent is used instead of a liquid absorbent. Membrane separation uses a membrane to separate the  $\text{CO}_2$  from the gas and is considered promising due to its energy efficiency and the simplicity of the operation [26]. This thesis will, however, only consider different types of absorption technologies.

Common absorbents for  $\text{CO}_2$ -capture are alkanolamines and carbonates. Alkanolamines are usually referred to as amines in literature related to carbon capture, which they will be in this thesis as well. Amines are selective to acid gases like  $\text{CO}_2$  and  $\text{H}_2\text{S}$  and have been used since the 1930's, originally to remove  $\text{CO}_2$  from natural gas or hydrogen [9]. Monoethanolamine (MEA) is an example of an amine that has been widely studied and used commercially. Others include methyldiethanolamine (MDEA), and the sterically hindered aminomethylpropanol (AMP). Carbonates that are used for carbon capture include potassium and sodium carbonates. The traditional Benfield process which uses hot potassium carbonate (HPC) has been used for the removal of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  from synthesis gas since the 1950's and is another example of a commercialized carbon capture technology [7].



**Figure 2:** Simple schematic of a typical amine absorption system.  $\text{CO}_2$ -rich streams are represented in red and  $\text{CO}_2$ -lean streams in blue [27].

A typical schematic of an amine absorption process for carbon capture is shown in Figure 2 [27]. The  $\text{CO}_2$ -containing gas enters the countercurrent absorption column at the bottom where it is contacted with the liquid amine solution that is entering at the top of the column. The  $\text{CO}_2$  reacts with the amine, transferring the  $\text{CO}_2$  from the gas phase into the liquid which exits the column at the bottom. The clean gas leaves at the top. The  $\text{CO}_2$ -rich amine solution from the bottom of the absorber is pre-heated in a heat exchanger before being transported to the top of the desorption column. The temperature is further increased to the regeneration

temperature at which the CO<sub>2</sub> is desorbed from the liquid and thus gaseous CO<sub>2</sub> is regenerated. The hot, now CO<sub>2</sub>-lean, amine solution exits the desorption column at the bottom and is cooled down by heat exchanging with the cold CO<sub>2</sub>-rich solution. It is further cooled before entering the absorption column where it is used in another cycle. A mixture of regenerated CO<sub>2</sub> and water vapor leaves at the top of the desorption column. They are separated by condensing the water which is returned to the desorption column while the purified CO<sub>2</sub> can be collected.

The amine solutions can be aqueous or non-aqueous, meaning that either water or an organic solvent can be used as solvent for the amine. A combination of the two is also possible, so-called water-lean systems [27]. For aqueous amine solutions, an absorption temperature of 40°C and a regeneration temperature of >120°C is typical [9, 27, 28]. Using a pressure swing instead of a temperature swing process to regenerate the gaseous CO<sub>2</sub> is also possible but is more common when using carbonates as absorbents.

The absorption of CO<sub>2</sub> in an aqueous amine system is an exothermic process, meaning that heat is released. The heat of absorption is determined by the heat of dissolution ( $\Delta H_{sol}$ ) and heat of reaction ( $\Delta H_{rxn}$ ) according to Equation 1 below [27].

$$\Delta H_{abs} = \Delta H_{sol} + \Delta H_{rxn} \quad \text{Equation 1}$$

The reversed process, the desorption and regeneration of CO<sub>2</sub>, thus instead requires heat. The regeneration heat is described in Equation 2 where  $\Delta H_{sens}$  is the heat needed to increase the temperature of the solution to the regeneration temperature, and  $\Delta H_{vap}$  is the vaporization heat of water [27].

$$\Delta H_{reg} = \Delta H_{abs} + \Delta H_{sens} + \Delta H_{vap} \quad \text{Equation 2}$$

The water vaporizes if the temperature needed for the regeneration of CO<sub>2</sub> is above the boiling point of water. Due to this, the regeneration can be very energy intensive for an aqueous amine solution and decreasing the energy needed is one of the major challenges with the technology. For sterically hindered amines, like AMP, the steric hindrance of the carbamates created in the absorption can prevent the formation of more stable products by using the right solvent. This means that lower regeneration temperatures are needed to reverse the absorption, around 80-90°C instead of 120°C [27]. The lower temperatures result in less solvent vaporizing, and if the water is additionally replaced by an organic solvent with a higher boiling point, the heat of vaporization can be removed altogether in Equation 2. Thus, the energy needed for regeneration can be significantly reduced when using a system with a sterically hindered amine in an organic solution.

In addition to this, the absorption systems can be phase changing which means that two phases are formed when CO<sub>2</sub> reacts with the homogeneous liquid absorbent solution. A CO<sub>2</sub>-rich phase is formed by the reaction products while the CO<sub>2</sub>-lean phase mostly consists of solvent and physically absorbed CO<sub>2</sub>. There are two types of phase-changing systems: precipitating systems where a solid phase is formed, and bi-phasic liquid systems where a second CO<sub>2</sub>-rich liquid phase is formed which is immiscible with the CO<sub>2</sub>-lean phase. For precipitating systems, the heat of phase change needs to be added to the heat of regeneration like Equation 3 shows [27].

$$\Delta H_{reg} = \Delta H_{abs} + \Delta H_{sens} + \Delta H_{vap} + \Delta H_{phase} \quad \text{Equation 3}$$

The advantage of this type of system is that the rich phase can be separated from the lean phase before entering the desorption column. Thereby only the rich phase needs to be regenerated while the lean phase can be sent directly to the absorption column. This reduces the amount of solution that needs go through the regeneration which in turn could decrease the energy requirement in the desorption column. However, it comes with challenges as well. Apart from the additional separation unit, other units might need to be designed differently in order to handle the second phase, particularly when solids are formed [27].

The solubility of CO<sub>2</sub> in the absorbent solution is a key parameter as the difference in solubility of CO<sub>2</sub> between the absorbing conditions and the desorption conditions is what enables the CO<sub>2</sub> capture. It is highly dependent on temperature and the CO<sub>2</sub> partial pressure in the gaseous phase, where the solubility decreases with increasing temperature and increases with increased partial pressure. It is usually presented as the loading ( $\alpha$ ) of the solution which is given in mol CO<sub>2</sub>/mol absorbent. The loading obtained through absorption is called the rich loading and the loading left after the regeneration is the lean loading. The difference in loading between the absorption and regeneration conditions is called the cyclic capacity, which represents the amount of CO<sub>2</sub> that can be captured by a system in each cycle.

The technologies chosen for this thesis are aqueous amine absorption using MEA, non-precipitating HPC in an aqueous solution, and precipitating non-aqueous AMP in DMSO. They will be described in further detail in the following subsections.

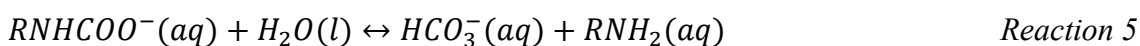
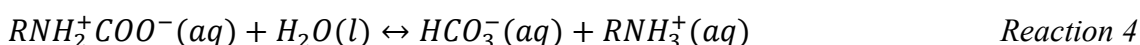
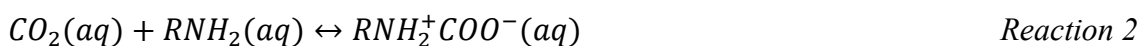
### 3.1 Aqueous MEA

As mentioned earlier, the use of MEA is a widely studied and commercialized carbon capture technology where the aqueous solution is the most common one. It is suitable for a range of applications as it has a high reactivity with CO<sub>2</sub> even at low CO<sub>2</sub> concentrations [28]. MEA is a primary amine, and its molecular structure is shown in Figure 3 below.

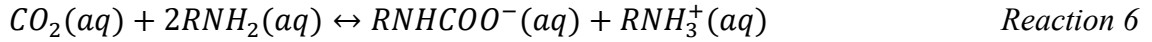


*Figure 3: The molecular structure of monoethanolamine (MEA).*

The exact mechanism of the absorption of CO<sub>2</sub> using primary amines (RNH<sub>2</sub>) is not known but is often described using the zwitterion mechanism [27, 29, 30]. The reactions involved in the zwitterion mechanism are presented as Reaction 2-5 below. After CO<sub>2</sub> has been physically absorbed into the aqueous solution, a zwitterion is formed as an intermediate when CO<sub>2</sub> reacts with the amine (Reaction 2). The zwitterion then reacts with another amine molecule to form carbamate (Reaction 3).



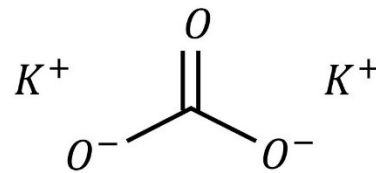
In Reaction 4 and 5 bicarbonate is formed, but the extent of the bicarbonate formation is limited for amines that form stable carbamates, like MEA [27, 30]. The overall reaction thus can be written according to Reaction 6, which also shows that the maximum theoretical loading is 0.5 mol CO<sub>2</sub>/mol MEA.



An advantage with using aqueous MEA is that it uses a relatively cheap absorbent [9]. A major disadvantage is, however, the high energy requirement that comes with the regeneration of the gaseous CO<sub>2</sub> in the desorption column which stands for about 80% of the total energy consumption [28]. Due to this, various advanced configurations have been researched in order to reduce it, including absorber intercooling [31], stripper interheating [32], and lean vapor compression [33, 34].

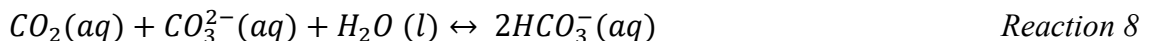
### 3.2 Aqueous HPC

HPC uses the inorganic salt potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) in a water solution to chemically absorb CO<sub>2</sub> from a gas stream. The molecular structure of K<sub>2</sub>CO<sub>3</sub> can be seen in Figure 4. Compared to traditional amine-based absorption, the use of inorganic salts, like K<sub>2</sub>CO<sub>3</sub>, has the benefit of having a more efficient regeneration process since the absorption can be run at a higher temperature. In addition, the absorbent costs are generally lower than for many amines. Other benefits include the fact that K<sub>2</sub>CO<sub>3</sub> is non-toxic and non-volatile resulting in reduced absorbent losses and replacement costs. It is also resistant to absorbent degradation at high temperatures and in the presence of components like oxygen, SO<sub>x</sub>, and NO<sub>x</sub> [7].

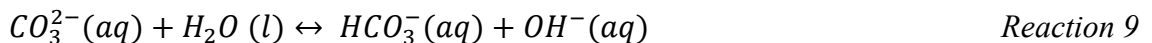


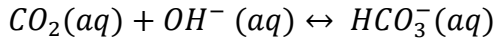
*Figure 4: The molecular structure of the ionic compound potassium carbonate (K<sub>2</sub>CO<sub>3</sub>).*

The overall reaction of the CO<sub>2</sub> absorption using K<sub>2</sub>CO<sub>3</sub> is presented below as Reaction 7. However, as the potassium carbonate and bicarbonate both are strong electrolytes they dissociate into ions where the K<sup>+</sup> ion most likely is not participating in the reaction. Reaction 8 thereby represents the same overall reaction in ionic terms, which is a more realistic representation [35, 36].



The overall reaction consists of a series of steps where the most prominent ones are presented as Reaction 9 and 10 below. First the carbonate ion reacts with water to form the hydroxyl ion in Reaction 9, which in turn reacts with CO<sub>2</sub> to form bicarbonate in Reaction 10 [35, 36].



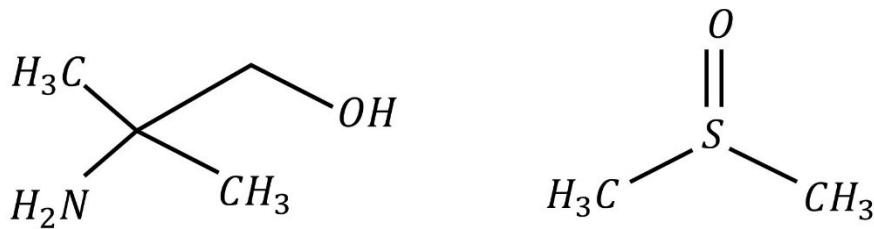


Reaction 10

As Reaction 9 is an instantaneous reaction, it leaves Reaction 10 to be the rate-controlling step [35, 36], and the kinetics for this absorption process are very slow compared to amine absorption systems [9]. Due to this, a wide range of promoters have been investigated in order to increase the absorption rate, and in addition, several different configurations have been suggested using different operation conditions. Letting the bicarbonate precipitate has also been researched as a way to improve the absorption capacity of the  $\text{K}_2\text{CO}_3$  solution [37], which is possible if the temperatures are low enough. However, the HPC technology is specifically designed to avoid the precipitation of bicarbonate by keeping the temperatures high both during the absorption and the desorption [7].

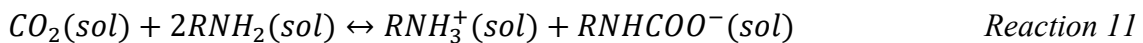
### 3.3 Precipitating Non-Aqueous AMP in DMSO

A novel  $\text{CO}_2$  absorption system has been studied at the Department of Chemical Engineering at Lund University which utilizes AMP in a non-aqueous solution with dimethyl sulfoxide (DMSO) as solvent [27]. AMP is a sterically hindered primary amine whose molecular structure can be seen to the left in Figure 5. To the right in the same figure the molecular structure of DMSO is presented. DMSO is an organic solvent that is commonly used in labs and in industry. Its characteristics include being aprotic, hygroscopic, relatively inert, nontoxic, and stable at high temperatures making it a good solvent for chemical reactions. It is also miscible with water and other organic solvents [38, 39].



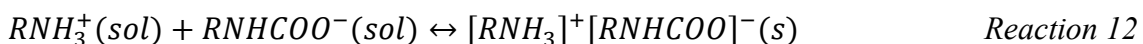
**Figure 5:** The molecular structure of 2-amino-2-methyl-1-propanol (AMP) to the left and dimethyl sulfoxide (DMSO) to the right.

The overall reaction of the absorption of  $\text{CO}_2$  in the AMP/DMSO solution is shown in Reaction 11, where the AMP carbamate is formed when dissolved  $\text{CO}_2$  reacts with AMP [27]. The theoretical maximum loading is 0.5 mol  $\text{CO}_2$ /mol AMP.



Reaction 11

If the solvent participates in the reaction, the theoretical loading can be increased. This is the case when alcohols are used as solvents, but not for DMSO. Instead, the steric hindrance of the AMP carbamate results in a solid precipitation of the carbamate salt in accordance with Reaction 12 [27].



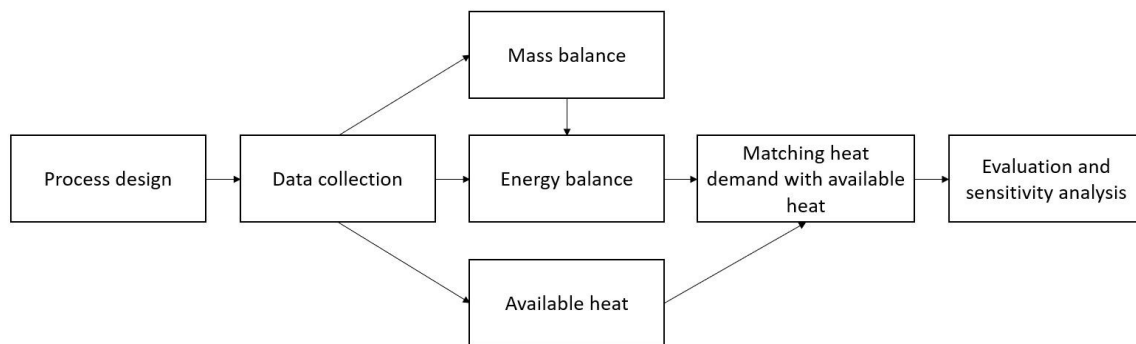
Reaction 12

As mentioned earlier, the precipitation can be beneficial as the  $\text{CO}_2$ -rich solid phase can be concentrated by removing a majority of  $\text{CO}_2$ -lean liquid phase, which results in a reduced amount of solution to regenerate. This, together with the fact that a lower regeneration tem-

perature is needed and that the boiling point of the organic solvent is higher than the needed regeneration temperature, can result in a significant reduction of the heat requirement of the regeneration compared to the conventional amine absorption systems. In addition, it can be easier to use excess heat to provide the desorption process with heat as the regeneration temperature is lower. The technology is however novel, meaning that the amount of literature and data available is limited.

## 4 Methods

The working process of this thesis is illustrated in Figure 6. First, a literature study was performed to find information about the chosen carbon capture technologies as well as the pulp mill. Simple designs of the three processes were created based on the information found. Data needed to perform calculations was then collected from different sources. The data obtained was then used to perform calculations on the mass balance of the processes which in turn were used to calculate the different heating, cooling, and electricity demands in the energy balance. In parallel, sources of available excess heat at the mill were identified and calculations were carried out to estimate the amount of available heat from each source. The results from the calculations of the energy demands and the available energy were then matched to see if the energy demand could be covered by the excess heat. Lastly, an evaluation of the resulting energy demands as well as the available excess heat was performed to assess whether the available excess heat could cover the heat demands of the capture processes or not. A sensitivity analysis was also made in order to evaluate the influence of incomplete data on the results. The work was performed iteratively. More information about the different parts of the working process is presented in the following subsections.



*Figure 6: Schematic illustration of the working process.*

### 4.1 Process Design

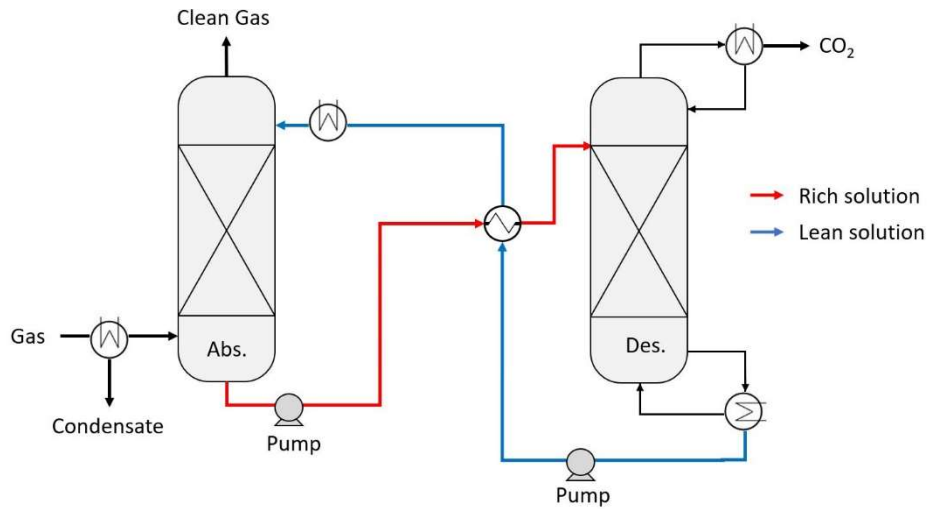
Literature was used to find information about the three different carbon capture technologies aqueous MEA, HPC, and AMP in DMSO. Google, Google Scholar, ScienceDirect, and LUB-search were the main data bases used to find literature and search worlds like *carbon capture*, *aqueous MEA*, *HPC*, *hot potassium carbonate*, and *potassium carbonate* were used. In turn, the information about the technologies was used to create simple process designs that would be comparable with each other. They are each presented under the respective subsections.

#### 4.1.1 Aqueous MEA

The chosen design for the technology using aqueous MEA is shown in Figure 7 below. The idea of this design is to use thermal-swing regeneration with typical temperatures of 40-50°C for the absorption and 120°C for the desorption [9, 27, 28]. The flue gases and the lean solution will enter the absorption column at 40°C, but as the absorption reaction is exothermic, temperatures of up to 50°C are expected for the rich solution leaving the absorber [28]. The pressure is atmospheric in the absorber while the desorption pressure is slightly increased to 2 bar(a) in accordance with what is reported in literature [28, 33, 34, 40]. The desorption for



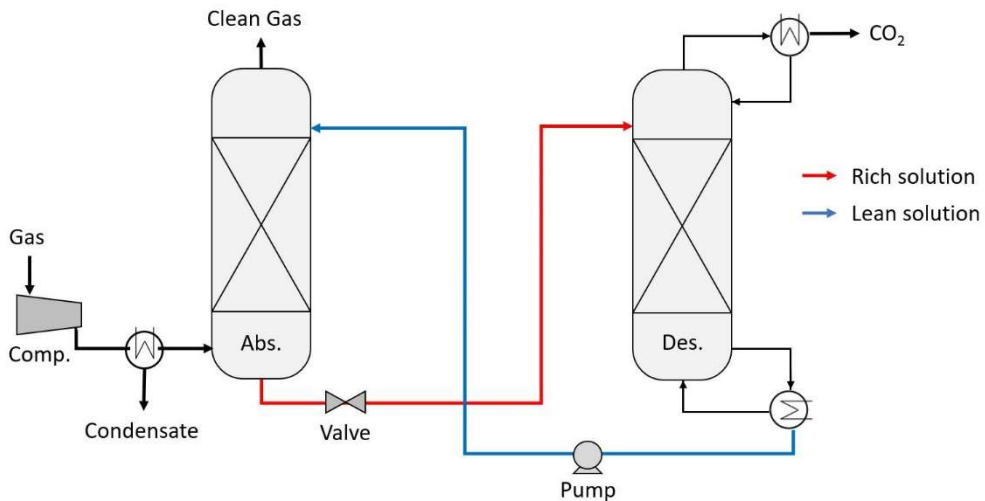
this system is performed in a stripper column. A concentration of 30 wt% MEA in water was used as this is the benchmark solution most often reported in literature [27, 41-43]. Based on this design, heat supply is required in the reboiler in the bottom of the stripper column and cooling is necessary for the gas and lean solution streams entering the absorption column as well as in the condenser at the top of the stripper column. Pumps are needed to transport the solutions between the columns and require electrical power.



**Figure 7:** A flow diagram of the simplified design for the carbon capture process using aqueous MEA as absorbent.

#### 4.1.2 HPC

In Figure 8 below, the chosen design for the HPC process is shown.



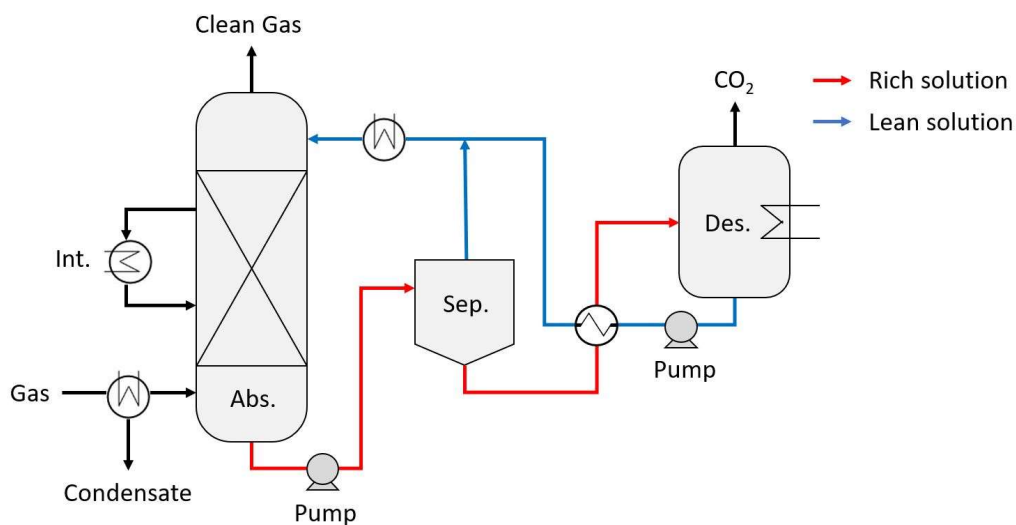
**Figure 8:** A flow diagram of the simplified design for the carbon capture process using aqueous HPC.

The design is a pressure swing process where the absorption is performed at a pressure of 7 bar(a) and the regeneration at 1.2 bar(a). The pressure of the flue gases and the lean solution thus need to be increased before entering the absorption column which is done by using a

compressor and a pump respectively, as shown in Figure 8. To decrease the pressure of the rich solution, a valve is used. The pressures chosen for this design were based on the information reported from the project performed by Stockholm Exergi [11]. The temperature is held constant and a temperature of at least 80°C is needed in order to prevent precipitation of potassium bicarbonate [11]. Temperatures of around 100°C are commonly used [9], but due to data availability, 90°C was chosen instead of 100°C [44]. In the Stockholm Exergi project, cooling of the flue gases is not performed before the absorption column [45], but it was added to this design in order to simplify the mass balance calculations as condensation of water otherwise would occur in the absorber. As for the MEA system, a stripper column is used for the desorption of CO<sub>2</sub>. In literature, concentrations of K<sub>2</sub>CO<sub>3</sub> in the aqueous solution of 15-40 wt% are reported and 20 wt% was chosen based on the information reported in the Stockholm Exergi project [11]. There is no heat exchange between the rich and lean solution in this design as the temperatures are quite similar in both streams. In order to keep the design simple, no promoters are used meaning that the kinetics will be slow. Similar to the MEA process, heat supply is required in the reboiler in the bottom of the stripper column and cooling is needed for the gas stream entering the absorber and in the condenser at the top of the stripper. The compressor as well as the pump requires electrical power.

#### 4.1.3 AMP in DMSO

A schematic figure of the chosen design for the process using AMP in DMSO can be seen in Figure 9.



**Figure 9:** A flow diagram of the simplified design for the carbon capture process using AMP solved in DMSO as absorbent in a precipitating system.

The design is similar to the design of the process using MEA as it also uses thermal-swing regeneration. However, the heat of absorption is higher due to precipitation of carbamate salt (see Equation 3). This results in more heat being released during absorption, and as higher temperatures decrease the solubility of CO<sub>2</sub> in the solution, the temperatures in the absorption column need to be reduced in order to maintain a high rich loading. Thus, the flue gas is cooled to 25°C and the lean solution to 30°C before entering the absorber. In addition, inter-cooling is used in the absorber in order to limit the temperature of the outgoing rich solution to 50°C. The precipitation is also separated from the CO<sub>2</sub>-lean solvent in the form of a con-

concentrated slurry containing the solid AMP carbamate salts. The CO<sub>2</sub>-lean solvent is sent directly to the lean stream entering the absorption column while the concentrated slurry enters the regeneration unit. The regeneration takes place at a temperature of 80°C and the pressure is kept atmospheric through the whole process. For this system the regeneration does not take place in a stripper column, but exact equipment has not been suggested yet and will hence be referred to as a desorber. A concentration of 25 wt% AMP in DMSO was chosen based on reported results showing that it is a good concentration to use in a precipitating system [27].

In this design, heat supply is needed in the regeneration unit and cooling for the gas and lean solution streams entering the absorption column as well as for the absorption intercooling. The pumps as well as the separation unit requires electrical power.

## 4.2 Data Collection

Information about the flue gases emitted by the pulp mill was provided by Södra. The values presented are estimated but realistic as some are measured while others are obtained from calculation models. This included the volumetric flows, temperatures, CO<sub>2</sub> content, water content, and occurrence of contaminants like NO<sub>x</sub> and SO<sub>x</sub>. The contaminant levels were considered to be low enough to be disregarded in the process design. The value of the CO<sub>2</sub> content of the recovery boiler flue gases is based on a measurement performed in 2018 showing a result of 16 vol% of CO<sub>2</sub> in dry flue gas i.e., the flue gas excluding the water content. As no similar measurement had been performed on the lime kiln flue gases, the CO<sub>2</sub> content was assumed to be similar to the corresponding flue gases of the Södra Cell Mönsterås pulp mill where calculations had been performed. The calculations showed a result of 17 vol% of CO<sub>2</sub> in wet flue gas, which corresponds to 26 vol% in dry flue gas [46]. The flue gas properties are summarized in Table 1 below.

**Table 1:** Properties of the flue gases from the recovery boiler and the lime kiln. Dry means that the water content of the flue gas is not included while wet means that the water is included.

Property	Unit	Recovery boiler	Lime kiln
Flow	Nm <sup>3</sup> /h (dry)	675,000	89,000
Temperature	°C	155	280
CO <sub>2</sub> content	Vol% (dry)	16	26
H <sub>2</sub> O content	Vol% (wet)	23	35

Data concerning the capture processes were obtained from literature. This included solubility data for CO<sub>2</sub> in the three different absorbent solutions, heat of absorption for the three different absorption systems, specific heat capacities at constant pressure ( $C_p$ ) for all components but water, and enthalpies for water at different temperatures that were used instead of  $C_p$ . Available example models of aqueous MEA systems in Aspen Plus were also used to find information that was not found elsewhere.

In order to find information about where excess heat is available at the mill, the previous work by Pedersén and Larsson was used [22]. Additional information about specific parts of the pulp mill energy system was provided by Södra.

### 4.3 Calculations

This section describes the calculations that were performed on the mass and energy balances of the processes as well as the available excess heat at the pulp mill. The mass and energy balance calculations were performed using the same method for both sources of flue gases: the recovery boiler and the lime kiln. They will only be handled as separate cases i.e., the possibility of using one facility to capture CO<sub>2</sub> from both flue gas streams will not be considered as it is less likely to be feasible. The mass and energy balance calculations will be presented separately, even though they to a large extent were performed simultaneously, in order to make the descriptions easier to follow. The energy balance part will have subsections for each capture technology while the mass balance part will not, and that is because the calculations for the different technologies were more similar in the mass balance calculations than they were in the energy balance calculations.

#### 4.3.1 Mass Balance

Based on information about the flue gas flow, CO<sub>2</sub> content, and water content provided by Södra, the total flow of CO<sub>2</sub> and water was calculated assuming that the gases behave like an ideal gas using Equations 4-5. The flue gases were assumed to only consist of CO<sub>2</sub>, water, and air and thus the total flow of air could also be calculated using Equation 6.

$$\dot{m}_{CO_2} = \frac{\dot{V}_{fluegas} \cdot y_{CO_2} \cdot M_{CO_2}}{V_m} \quad \text{Equation 4}$$

$$\dot{m}_{H_2O} = \frac{\dot{V}_{fluegas} \cdot y_{H_2O} \cdot M_{H_2O}}{V_m} \quad \text{Equation 5}$$

$$\dot{m}_{air} = \frac{(\dot{V}_{fluegas} - \dot{V}_{fluegas}(y_{CO_2} + y_{H_2O})) \cdot M_{H_2O}}{V_m} \quad \text{Equation 6}$$

Where  $\dot{m}$  is the mass flow rate,  $\dot{V}$  is the volumetric flow rate,  $y$  is the molar fraction in the gaseous phase,  $M$  is the molar weight, and  $V_m$  is the molar volume of an ideal gas. As could be seen in Figure 7, Figure 8, and Figure 9 the flue gases are cooled before entering the absorption column and calculations were performed to find the amount of water that would condense during the process. This was done by assuming that the cooled flue gases are saturated with water. As the liquid phase only contains water, the partial pressure of water in the cooled gases equals the saturation pressure of water, according to Raoult's law presented as Equation 7. Further, Dalton's law presented as Equation 8 could be used to calculate the water content in the cooled gas.

$$P_A = P_A^{sat} x_A \quad \text{Equation 7}$$

$$P_A = y_A P \quad \text{Equation 8}$$

Where  $P_A$  is the partial pressure of component A,  $P_A^{sat}$  is the saturation pressure of component A at a certain temperature,  $x_A$  is the molar fraction of component A in the liquid phase, and  $y_A$  is the molar fraction of component A in the gas phase. The CO<sub>2</sub> content could then be calculated using the resulting water content, as Equation 9 shows.

$$y_{CO_2} = \frac{\dot{n}_{CO_2}(1 - y_{H_2O})}{\dot{n}_{air} + \dot{n}_{CO_2}} \quad \text{Equation 9}$$

Where  $\dot{n}$  is the molar flow. Further, using Equation 10, the amount of water held in the cooled flue gases could be calculated. The difference between the mass flow of water before and after the cooling is the amount of water that condenses and is removed.

$$\dot{m}_{H_2O} = \frac{\dot{n}_{CO_2}}{y_{CO_2}} \cdot y_{H_2O} \cdot M_{H_2O} \quad \text{Equation 10}$$

In order to calculate the partial pressure of CO<sub>2</sub> in the absorption column, which is needed to find the rich loading of CO<sub>2</sub> in the absorbent solution, the molar fraction of water in the liquid phase was needed. For the MEA and HPC systems where water is used as solvent in the absorbent solution, the molar fraction of water in the solution could be calculated using Equation 11 below.

$$x_{H_2O} = \frac{(1-C_{abs}) \cdot M_{H_2O}}{(1-C_{abs}) \cdot M_{H_2O} - C_{abs} \cdot M_{abs}} \quad \text{Equation 11}$$

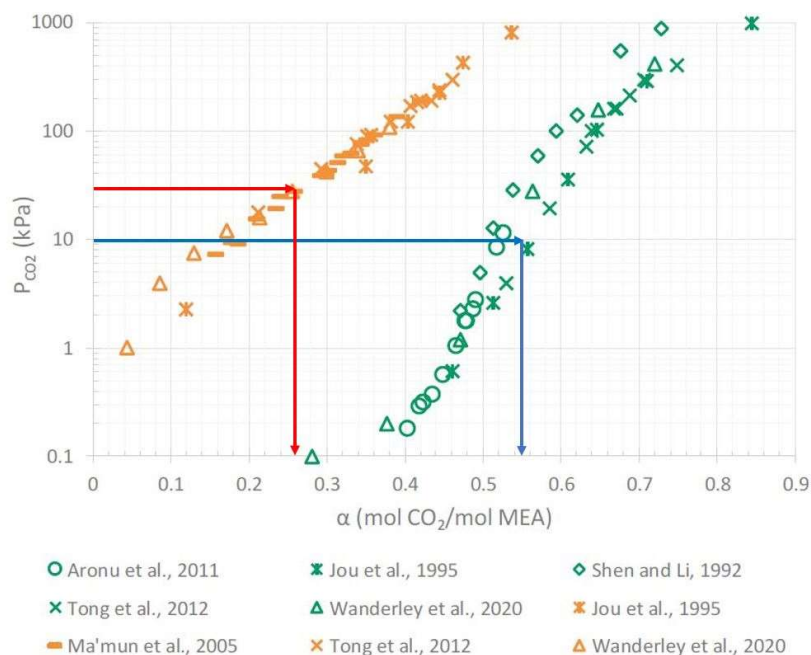
Where  $C_{abs}$  is the absorbent concentration given in wt%. Equation 7 could then be used to find the partial pressure of water, followed by Equation 8 to find the molar fraction of water in the gaseous phase. Further, Equation 9 was used to find the molar fraction of CO<sub>2</sub> and Equation 8 again to calculate the partial pressure of CO<sub>2</sub>. The same calculations were performed using the regeneration conditions in order to obtain the partial pressure of CO<sub>2</sub> in the stripper. As the temperature differs in the top and in the bottom of the stripper, two different partial pressures were calculated. The partial pressure at the bottom of the stripper was needed to find the lean loading of CO<sub>2</sub> in the absorbent solution, and the partial pressure at the top was needed to find the composition of the gas leaving at the top, entering the condenser.

For the AMP system, no water is present in the liquid phase. In addition, the volatility of the solution is low and can therefore be neglected. Hence, the partial pressure of CO<sub>2</sub> is only dependent on the composition of the cooled flue gas entering the absorber. The molar fraction of water in the gaseous phase is thereby known, and the molar fraction of CO<sub>2</sub> can be calculated using Equation 9. The partial pressure of CO<sub>2</sub> was then calculated using Equation 8. In the desorber, it is assumed that only CO<sub>2</sub> is present in the gas phase, making the CO<sub>2</sub> partial pressure equal to the total pressure.

Using solubility data of CO<sub>2</sub> in the different absorbent solutions [27, 41, 44], the obtained partial pressures could be used to find the rich and lean loadings. An example of how the loadings are found using solubility data is shown in Figure 10. The blue arrows show how to find the rich loading of a hypothetical absorption process at 40°C with a partial pressure of 10 kPa and the red arrows the lean loading of a regeneration process at 120°C with a partial pressure of 30 kPa. The cyclic capacity of the systems could thereby also be calculated as it is the difference between the rich and lean loadings.

It was assumed that 90% of the CO<sub>2</sub> in the flue gas streams is captured. Thus, the total amount of captured CO<sub>2</sub> could be calculated from the total mass flow of the flue gases. Further, the amount of absorbent needed could be calculated, as the captured CO<sub>2</sub> needs to be accommodated within the cyclic capacity. Mass balance calculations were then performed on the simplified processes presented in section 4.1. Several assumptions were made for these calculations:

- No water is added to the systems from the flue gases
- No losses of absorbent nor solvent occurs



**Figure 10:** Example of how to use solubility data to find the rich and lean loadings for an absorption system. The graph summarizes literature data for the solubility of CO<sub>2</sub> in 30 wt% aqueous MEA at 40°C (green) and 120°C (orange) [27]. The blue arrows show how to find the rich loading of a hypothetical absorption process at 40°C with a partial pressure of 10 kPa and the red arrows the lean loading of a regeneration process at 120°C with a partial pressure of 30 kPa. Reprinted with permission.

The water leaving with the regenerated CO<sub>2</sub> in the stripper for the MEA and HPC systems was however calculated to get a purity of the captured CO<sub>2</sub>, but it is assumed to be negligible in the overall mass balance. In the overall mass balance, it is thereby assumed that all water is condensed in the stripper condenser. The condensation of water at the top of the stripper for the MEA and HPC systems occurs at the same pressure as in the stripper itself and at 20°C, based on an available example model of a MEA system in Aspen Plus [47]. The CO<sub>2</sub> is thereby also cooled to 20°C.

Based on the same Aspen Plus model [47], it was assumed that 4% of the liquid water is evaporating in the absorption tower for the MEA system. It is also assumed that it is condensed and brought back through an external water wash located at the top of the absorber, and no water is thereby lost. Energy is however consumed, which will be further addressed in the energy balance. In addition, the water that is added to the system through the water wash is assumed to be negligible in the overall mass balance.

For the AMP system, it is assumed that 90% of the DMSO is separated from the precipitate slurry and goes with the liquid stream from the separation unit [48]. The CO<sub>2</sub> which is physically absorbed in the DMSO goes with this stream as well, and the physical solubility of CO<sub>2</sub> in DMSO was found in [49]. The slurry fraction from the separation unit then contains all AMP, 10% of the DMSO, and the rest of the absorbed CO<sub>2</sub>.

### 4.3.2 Energy Balance

In the energy balance calculations, temperatures of the different streams and the heating and cooling requirements of the different units were calculated. A few general assumptions were made that apply to all three systems, and they are listed below:

- The pumps that are used to transport the rich and lean solutions are excluded from the calculations as their electrical power requirement is assumed to be negligible in the context. This includes the pump that is used to increase the pressure of the lean stream in the HPC system.
- The separation unit used in the AMP in DMSO system is excluded as there is no data available on the power requirement and as it is assumed that it is negligible in the context.
- The specific heat capacity at constant pressure ( $C_p$ ) of a compound whose temperature is changed through heat exchange is assumed to be the  $C_p$  of that compound at the average temperature of the interval, as described in Equation 12.
- If the  $C_p$  of a mixture is not available, it is assumed to be equal to the weighted average of the  $C_p$ :s of the individual compounds in the mixture, as described in Equation 13.

$$C_p(T_1 \rightarrow T_2) = C_p \left( \frac{T_1 + T_2}{2} \right) \quad \text{Equation 12}$$

$$C_{p,mix} = \frac{\sum C_{p,i} \cdot \dot{m}_i}{\dot{m}_{mix}} \quad \text{Equation 13}$$

Data that is recurring in the calculations of all three absorption systems include enthalpies of water and steam that was collected from Alveteg [50], and  $C_p$  of air and  $\text{CO}_2$  from online sources [51-53].

#### 4.3.2.1 MEA

As mentioned earlier, the MEA technology uses a cooler to decrease the temperature of the flue gases before they enter the absorption column and a fraction of the water content is condensed in the process. The cooling demand of this cooler was obtained by calculating the energy removed when cooling the  $\text{CO}_2$ , air, and water to  $40^\circ\text{C}$  and when condensing the fraction of water that is condensed.

In the absorption column, the energy released when absorbing  $\text{CO}_2$  was calculated based on the heat of absorption at  $40^\circ\text{C}$  [43] and the amount of  $\text{CO}_2$  absorbed, as Equation 14 shows. The released energy was then assumed to be distributed in the liquid and gas phase and on the water evaporating in the absorption column so that everything leaving the column has the same temperature. This temperature was calculated using Equation 15.

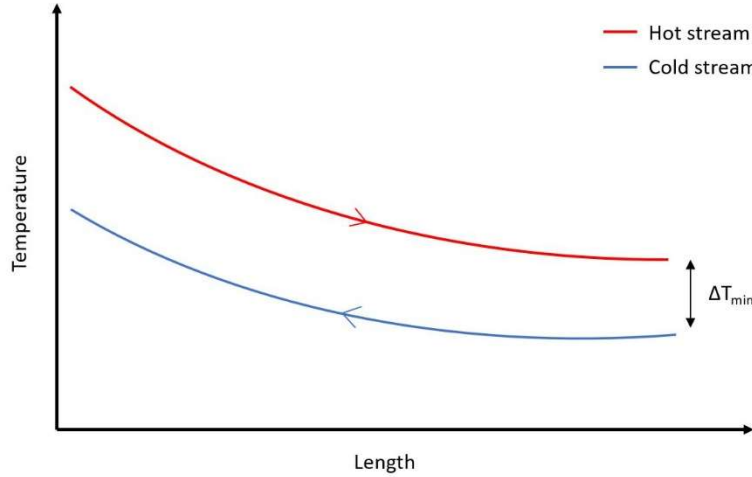
$$Q = \Delta H_{abs} \cdot \dot{m}_{\text{CO}_2,abs} \quad \text{Equation 14}$$

$$T_2 = T_1 - \frac{Q - \sum \Delta H_{\text{H}_2\text{O}} \cdot \dot{m}_{\text{H}_2\text{O}}}{\sum \dot{m}_i \cdot C_{p,i}} \quad \text{Equation 15}$$

Where  $Q$  is energy in the form of heat. Equation 15 shows that enthalpies were used for the water fractions, one evaporating and one non-evaporating fraction, and that  $C_p$  was used for the other compounds present in the absorber.

The heat exchanger used on the rich and lean streams was assumed to use countercurrent flow and a minimum temperature difference between the hot and the cold side,  $\Delta T_{\min}$ , of  $10^\circ\text{C}$ . This  $\Delta T_{\min}$  is assumed to occur where the cold stream enters and the hot stream leaves the exchanger, as Figure 11 shows. The  $\Delta T_{\min}$  was chosen based on a rule of thumb saying that above ambient temperatures typically use a  $\Delta T_{\min}$  of  $10^\circ\text{C}$  unless the heat transfer coefficients are low, then values up to  $20^\circ\text{C}$  can be used [54]. Gases generally have low heat transfer coef-

ficients compared to liquids, and hence 10°C will be used throughout this work when both sides in the heat exchange are liquids, 20°C when both sides are gaseous, and 15°C when one side is liquid and one side is gaseous. As the inlet temperatures of both streams was known, the assumptions made regarding the heat exchanger could be used to calculate the outlet temperatures of the streams.



**Figure 11:** A diagram showing the temperature changes in a heat exchanger using a countercurrent flow. The minimum temperature difference between the hot and cold streams occurs where the cold stream enters and the hot stream leaves the heat exchanger.

The heat required in the regeneration of gaseous CO<sub>2</sub> was calculated using Equations 16-19 below.

$$Q_{vap} = \frac{P_{H_2O}^{sat} x_{H_2O}}{P_{CO_2}} \Delta H_{H_2O}^{vap} \quad \text{Equation 16}$$

$$Q_{sens} = \frac{c_p \Delta T}{(\alpha_{rich} - \alpha_{lean}) C_{Am}} \quad \text{Equation 17}$$

$$Q_{des} = \Delta H_{abs,CO_2} \quad \text{Equation 18}$$

$$Q_{tot} = Q_{vap} + Q_{sens} + Q_{des} \quad \text{Equation 19}$$

Where  $P_{H_2O}^{sat}$  is the saturation pressure of water at the temperature in the top of the stripper column ( $T_{top}$ ),  $\Delta H_{H_2O}^{vap}$  is the enthalpy of evaporation for water at  $T_{top}$ ,  $P_{CO_2}$  is the partial pressure of CO<sub>2</sub> at  $T_{top}$  and at rich loading,  $C_p$  is the specific heat capacity of the solution entering the stripper column,  $\alpha$  is the CO<sub>2</sub> loading of the solution, and  $C_{Am}$  is the concentration of the amine given in mol amine/kg solution. Equation 19 shows the same thing as Equation 2 did in section 3.  $T_{top}$  is assumed to be the same as the temperature of the incoming rich solution and it is assumed to be taking the cold reflux water from the condenser into consideration. The heat of absorption ( $\Delta H_{abs,CO_2}$ ) used was specified for 120°C [43].

The condenser at the top of the stripper column is assumed to work at 20°C based on the available example model of a MEA system in Aspen Plus [47], and all water is assumed to be condensed. The cooling demand of the condenser was obtained by calculating the energy removed by cooling the gases to 20°C and condensing the water fraction.



As seen in Figure 7, a second cooler is used to get the temperature of the lean solution to 40°C before it enters the absorption column as the heat exchanger will not provide enough cooling. The cooling demand in this unit was calculated using the difference between the temperature of the lean solution leaving the heat exchanger and the required 40°C.

In the calculations just explained,  $C_p$  for loaded solution from Yun et al. [42] was used for the rich streams of aqueous MEA as it was based on a loading of 0.6 which was close to the resulting rich loading of the MEA system. For the lean streams, an average of the loaded and non-loaded  $C_p$  from the same source was used.

#### 4.3.2.2 HPC

In the aqueous HPC system, the flue gases are compressed before being cooled to the absorption temperature (see Figure 8). In the compressor, work is performed to increase the pressure to the 7 bar(a) wanted in the absorption column using electrical power. To calculate the power required to compress the flue gases and the temperature of the gas leaving the compressor, a model was created in Aspen Plus. Details on the Aspen Plus model can be found in Appendix B. Using the resulting temperature of the outgoing gas, the cooling demand needed to cool the flue gases to 90°C before it enters the absorption column could be calculated.

For the absorption column, the calculations were performed similarly to those made for the MEA system. The heat of absorption [9, 55] was used to calculate the heat generated which then was distributed on the liquid and gas phase so that everything leaving the column has the same temperature. However, few publications have reported on heat of absorption for the HPC system and the data that was found either did not specify the operating conditions of the absorption [9] or did not match the operating conditions of this work [55]. The latter was reported as an average value for temperatures between 40°C and 70°C, compared to the 90°C used in this work. As only one data point could be obtained from each source, an average value for the heat of absorption based on those data points was used for both the absorption and the desorption processes.  $C_p$  for the aqueous  $K_2CO_3$  solution from Kaur and Chen [44] was used. Unlike the MEA system, it was assumed that no water is evaporating as the heat of absorption is low and the temperatures hence will not increase enough to evaporate any water. The expanding valve used on the rich solution leaving the absorber was simulated in Aspen Plus to see how much the pressure drop to 1.2 bar(a) affects the temperature of the solution. Details on the Aspen Plus model can be found in Appendix B. The resulting temperature was then used in the regeneration calculations as the  $T_{top}$  in this system too was assumed to be the same as the temperature of the incoming rich solution. Equations 16-19 were used to calculate the heat required to regenerate the gaseous  $CO_2$ , similarly to the MEA system. The condenser on top of the stripper column was assumed to be identical to the one used in the MEA system and the same assumptions and calculations were hence made. The pump that is used to increase the pressure of the lean solution was assumed to not affect the temperature of the liquid.

#### 4.3.2.3 AMP in DMSO

In the AMP system, the cooling demand for the flue gas cooling was calculated in the same way as for the other systems. As mentioned in section 4.1.3, the flue gases are cooled to 25°C before entering the absorption column while the lean solution enters at 30°C. Like for the other systems, the heat developed from the absorption reaction was calculated using the heat of absorption for a precipitating system [27] and was assumed to be distributed on the liquid and

gas phase so that they both would have the same resulting temperature.  $C_p$  was only found for AMP and DMSO individually at standard conditions of 25°C and atmospheric pressure [56, 57] and the  $C_p$  of the mixture was thereby estimated using Equation 13. The cooling demand of the intercooling was calculated assuming that the liquid inside the absorption column is cooled to 50°C which then also is the temperature at which the liquid stream leaves the column. The heat exchanger used between the rich and lean streams is assumed to use a counter-current flow and a  $\Delta T_{\min}$  of 20°C that occurs where the cold stream enters and hot stream leaves (see Figure 11). 20°C was chosen as the exchanger is placed after the separation unit and the rich stream hence is a thick slurry, containing solid particles, which is assumed to have lower heat transfer coefficient than a liquid.

The heat demand of the regeneration was calculated using Equations 17-19 i.e., just like for the other systems except that  $Q_{vap}$  is excluded since there is no water evaporating during the regeneration. As the desorber looks different for the AMP system compared to the others (see Figure 9), it is assumed to have a uniform temperature profile making the  $T_{\text{top}}$  80°C. Like for the MEA technology, a cooler is used on the lean solution before it enters the absorption column. As the lean solution partly comes from the separation unit and partly from the heat exchanger, the cooling demand was calculated for the two separate streams and then summarized as they have different starting temperatures. Both streams are however cooled to 30°C.

### 4.3.3 Available Excess Heat

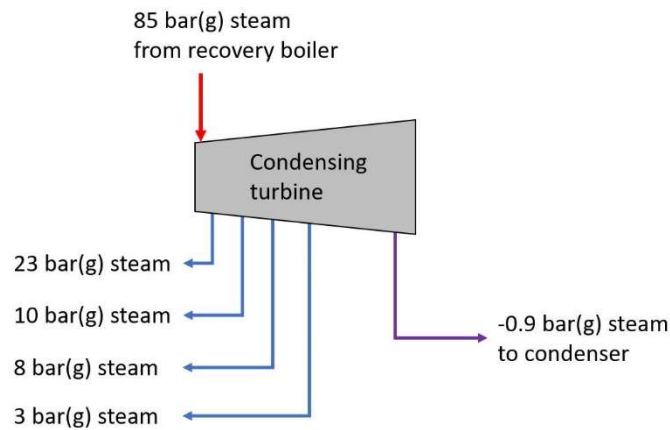
The previous work of Pedersén and Larsson [22] was used to find sources of available excess heat at the Värö mill. Changes that have been made at the mill since then are assumed to have small effects on the overall energy system. The sources of heat identified include the steam that is currently used in the condensing turbine, the surface condenser in the evaporation plant, and a stream of water containing excess heat in the SHS (secondary heat system). As the flue gases are cooled from high temperatures before entering the absorption column in all the carbon capture technologies, the heat that can be recovered from this cooling is also considered to be a potential heat source for the capture process.

In addition, the work of Pedersén and Larsson [22] used a heat integration targeting methodology to identify potential heat savings and efficiency improvements in the heat recovery system of the mill. The obtained results also visualize the potential availability and temperature level of excess heat from the pulp mill processes. The results show that some of the excess heat could be available above the required temperatures plus an additional  $\Delta T_{\min}$  of 10°C, while still holding temperatures that are too low to be useful for heat recovery improvements internally within the pulping process. Since the results are presented graphically, only the size and temperature of the available heat are easily identified and not the exact source. Furthermore, since the results were based on a theoretical targeting study, they also show an ideal case where heat exchangers are optimally integrated, which might not be representative for the actual energy system. Hence, the potentially available heat may consist of heat from several sources that are scattered across the site, making the heat difficult to utilize in practice. The previous thesis also contains results showing that 19.5 MW of steam at 3 bar(g) could be saved with a set of proposed investments in new heat exchanger arrangements which could be implemented at the mill. These 19.5 MW are also considered as a potential heat source.

Using the heat from the flue gas cooling is relevant for all technologies as the absorption temperatures required for MEA and AMP are very low compared to the flue gas temperatures and since the compression of the flue gases required for the HPC absorption causes the tempera-

ture to rise significantly making it necessary to cool them down again. All the heat available in the flue gases would, however, not be available for use. Due to impurities that would end up in the condensate requiring special handling, it was assumed that the cooling of the flue gases that is performed to extract useful energy is limited to 125°C and that no condensation occurs [58]. It was also assumed that a water loop with steam is used to transfer the heat from the flue gases to the desorber and that there are no losses along the way. A  $\Delta T_{\min}$  of 20°C was used for the first heat exchange step as it is performed between flue gases and steam, and 15°C for the second as the steam heat exchange with a liquid in the reboiler of the stripper column or in the AMP desorber. Based on these assumptions, the end temperature of the flue gases was determined as either 125°C or as the temperature needed in the regeneration plus the two  $\Delta T_{\min}$ , whichever was higher. Using enthalpies and  $C_p$  for the flue gas components, the available energy could be calculated.

The idea of the condensing turbine as a source of heat was to utilize the fraction of steam that at present goes all the way through the condensing turbine from a high pressure of 85 bar(g) to the turbine condenser. An illustration of the condensing turbine is presented in Figure 12. Instead of letting it go all the way through and leave the turbine at a pressure of about -0.9 bar(g) [59], it can be extracted as steam at 3 bar(g) where it contains more energy. This will be at the cost of losing some electrical power production.



**Figure 12:** A schematic illustration of the condensing turbine used for electricity production at the Värö pulp mill showing the different pressure levels at which steam is extracted.

To calculate the energy that would be made available in the form of steam at 3 bar(g) and the electricity production that would be lost, the flow rate of the steam going all the way through the condenser was needed. Data for the volumetric flow rate from the period May to November 2022 was provided by Södra and the average mass flow rate could be calculated using the ideal gas law and the molar weight of water, as Equation 20 shows.

$$\dot{m} = \frac{MP\dot{V}}{RT} \tag{Equation 20}$$

Where  $\dot{m}$  is the mass flow rate,  $M$  is the molar weight of water,  $\dot{V}$  is the volumetric flow rate, and  $R$  is the gas constant. The mass flow rate could then be used together with the condensation enthalpy for saturated steam at 3 bar(g) [50] in order to calculate the energy of the extracted 3 bar(g) steam, in accordance with Equation 21. The loss of electricity production was

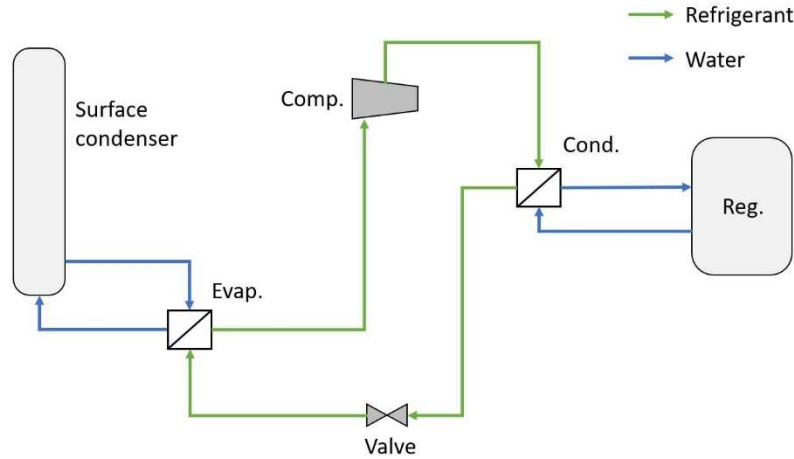
calculated using the enthalpy difference between steam at 3 and -0.9 bar(g) and the mass flow rate of the steam, in accordance with Equation 22.

$$Q_{steam} = \dot{m} \cdot \Delta H_{cond,3ba(g)} \quad \text{Equation 21}$$

$$W = \dot{m} \cdot (H_{V,3bar(g)} - H_{V,-0.9bar(g)}) \quad \text{Equation 22}$$

Where  $\Delta H_{cond}$  is the condensation enthalpy for steam at 3 bar(g),  $W$  is the electrical power, and  $H_V$  is the specific enthalpy for steam in vapor phase at different pressures.

In the GCC [22], the surface condenser was identified as a large source of low temperature heat with the potential of 69 MW at about 64°C. In order to make use of this heat, a heat pump could be used to upgrade it so that it can be useful in the regeneration of the AMP technology as it requires lower temperatures than the other technologies. A simple design of the heat pump system was created where two water loops and a heat pump are used to recover the heat from the surface condenser and use it in the regeneration of the AMP technology. The design can be seen in Figure 13.



**Figure 13:** A flow diagram of a simplified heat pump system upgrading heat from the surface condenser of the Värö pulp mill and use it to power the regeneration of the carbon capture technology using AMP in DMSO.

The temperatures at which the refrigerant needs to evaporate and condense were calculated by using the temperature of the surface condenser and the desorber respectively and assumed  $\Delta T_{min}$  for all four heat exchanges. All  $\Delta T_{min}$  were assumed to be 15°C except for the heat exchange between the right water loop and the desorber (see Figure 13) which was assumed to be 10°C as it involves two liquids. In the other heat exchanges both liquid and gas are present as they all are phase changing heat exchanges. The water used to evaporate the refrigerant is assumed to be cooled to 15°C and it is also assumed that no heat is lost in the system. The resulting temperatures were then used together with the regeneration heat demand or the maximum available heat in the surface condenser, whichever is lowest, to make an estimation of the electrical power input needed. Equations 23-25 below were used [60].

$$Q_2 = Q_1 + W \quad \text{Equation 23}$$

$$COP_{carnot} = \frac{T_2 + 273}{T_2 - T_1} \quad \text{Equation 24}$$

$$COP_{actual} = \frac{Q_2}{W} = \frac{Q_1}{W} + 1 \quad \text{Equation 25}$$

Where  $Q_1$  is the energy put into the heat pump system at the refrigerant evaporation,  $Q_2$  is the energy extracted at the refrigerant condensation,  $W$  is the electrical power input,  $T_1$  is the temperature of the refrigerant evaporation,  $T_2$  is the temperature of the refrigerant condensation and  $COP$  is coefficient of performance for the heat pump. It was assumed that  $COP_{actual}$  is 60% of  $COP_{carnot}$ .

The excess stream of water found in the mapping of the SHS [22] keeps a temperature of 72°C and could be used in a system similar to that of the surface condenser, except that the water stream could be heat exchanged with the refrigerant without a water loop. As the flow of the excess water stream was limited to 64 kg/s, it was assumed that the refrigerant evaporates and condenses at the same temperatures as in the case of the surface condenser and that  $\Delta T_{min}$  is 15°C in order to calculate the available energy in this stream. Equations 23-25 were then used to estimate the power input needed to recover this energy.

#### 4.4 Matching Heat Demands and Available Excess Heat

The resulting heat demands of the different capture technologies applied on the two flue gas streams were compared with the different available heat sources in order to see if the demand could be covered by available heat in any of the cases. It was assumed that using more than one source of available heat would be rather complicated and thereby increase the capital costs enough to make the carbon capture economically infeasible. The resulting heat and cooling demands obtained were also compared with values reported in literature in order to assess the validity of the results.

#### 4.5 Sensitivity Analysis

A sensitivity analysis was performed in order to assess the influence of incomplete data on the results. The incomplete data included the data on heat of absorption for the HPC system and the  $C_p$  of AMP in DMSO. In addition, an alternative design of the heat pump system used on the surface condenser was made in order to evaluate how the design affects the performance of the heat pump.

##### 4.5.1 Heat of Absorption for the HPC System

As mentioned in section 4.3.2.2, few publications have reported on heat of absorption for the HPC system and the data that was found either did not specify the operating conditions of the absorption or did not match the operating conditions of this work. In the data found for heat of absorption for aqueous MEA, it could be seen that the heat of absorption changed with temperature [43] and thus the use of data for a different temperature could influence the results. As no data was found showing how the heat of absorption for HPC changes with temperature, it was assumed that it behaves similarly to the heat of absorption for aqueous MEA. The potential error was estimated by comparing the resulting reboiler heat demands of the MEA technology when using the heat of absorption for 120°C and when using the heat of absorption for 40°C.

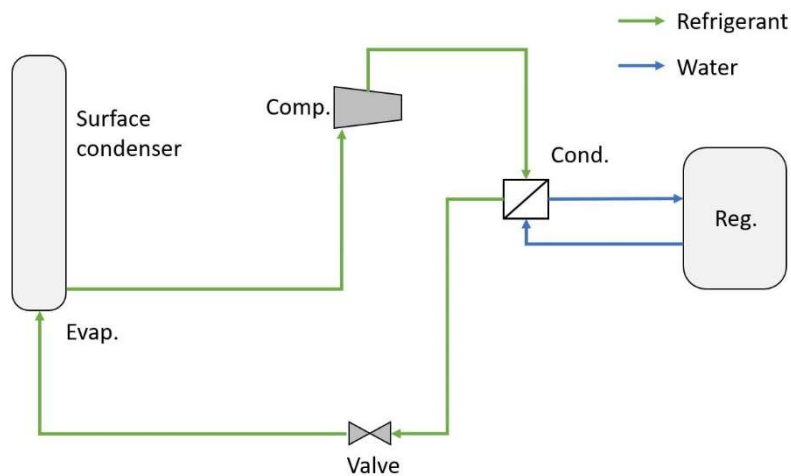
##### 4.5.2 Specific Heat Capacity of AMP in DMSO

AMP in DMSO is the only absorbent solution for which  $C_p$  could not be found. In addition, the values of  $C_p$  found for the individual compounds were only applicable for standard conditions of atmospheric pressure and 25°C. Hence, the  $C_p$  of the mix was both assumed to be the

weighted average of the  $C_p$  of the individual compounds and to be independent of temperature. To estimate the error that could come with these assumptions, the  $C_p$  of the MEA solution was first calculated as a weighted average of the  $C_p$  of the individual compounds and compared to the  $C_p$  found for the mixture in literature [42]. Secondly, as the data for  $C_p$  of the MEA solution shows that  $C_p$  is dependent on temperature, the calculations of the heat demand in the desorber were repeated with a  $C_p$  of  $\pm 0.5$  kJ/(kg·K). The value of 0.5 was chosen based on how much the  $C_p$  for the MEA solution changes when the temperature is varied from 25°C to 80°C. The resulting heat demands were then compared.

### 4.5.3 Heat Pump System of the Surface Condenser

An alternative design of the heat pump system to the one presented in Figure 13 was made and it is presented in Figure 14 below. Instead of using a water loop to transport heat from the surface condenser to the heat pump refrigerant, they are directly heat exchanged with each other. Thus, one heat exchanger is removed and hence the temperature lift performed by the heat pump is decreased. The lower working temperature of the heat pump is thereby increased which affects the power input and efficiency of the heat pump. The same calculations were performed as for the original design to find the power input needed for the new design in order to compare the performances of the two designs.



**Figure 14:** A flow diagram of an alternative heat pump system upgrading heat from the surface condenser of the Värö pulp mill and use it to power the regeneration of the carbon capture technology using AMP in DMSO. Instead of using a water loop to transport heat from the surface condenser to the heat pump refrigerant, they are directly heat exchanged with each other.

## 5 Results and Discussion

In this section, results from the calculations of the mass and energy balances as well as the matching of heat demand and available energy are presented and discussed. The mass and energy balances are presented in their entirety in Appendix A. The results are then discussed regarding the limitations of the method potential sources of error.

### 5.1 Captured CO<sub>2</sub> and Absorbent Use

Capturing 90% of the CO<sub>2</sub> in the flue gases from the recovery boiler and lime kiln results in captured flow rates of 185 tons and 41 tons per hour of operation, respectively. It is the same for all technologies as all mass balance calculations are based on the same assumption about the fraction of CO<sub>2</sub> that will be captured. The difference in amount of CO<sub>2</sub> captured between the recovery boiler and lime kiln is caused by the much higher flow rate of the recovery boiler flue gases, even though the concentration of CO<sub>2</sub> is higher in the lime kiln flue gases (see Table 1). Whether these captured flow rates are manageable or not is dependent on what the CO<sub>2</sub> will be used for and the costs that come with handling it. However, Romeo et al. [61] summarized parameters from four different simulation studies where the flow rates of captured CO<sub>2</sub> range from about 200-700 tons per hour, which gives an indication that the flow rates of captured CO<sub>2</sub> in this work are not unreasonably large to handle and transport. The purities of the captured CO<sub>2</sub> are similar for all capture technologies according to the calculations made with a purity of 98.1 mol% or higher after the condensation of water. The lowest acceptable purity of CO<sub>2</sub> might depend on whether it will be utilized or stored, but according to Wetenhall et al. [62], impurities of up to 2 mol% do not affect the relative cost per kilometer of transportation in pipelines.

The flows of absorbent and solvent needed to capture CO<sub>2</sub> at these rates are presented in Table 2 below. Note that this only shows the flow rate at which the solution is circulating between the absorber and desorber, as potential losses and need of make-up was not included in the calculations.

**Table 2:** Mass flow rates of absorbent and solvent for the MEA, HPC and AMP technologies necessary in the circulating system if 90% of the CO<sub>2</sub> in the flue gases from the recovery boiler and lime kiln are captured.

Component	Recovery boiler		Lime kiln	
	[kg/s]	[kg/kg CO <sub>2</sub> ]	[kg/s]	[kg/kg CO <sub>2</sub> ]
MEA	297	5.78	60.7	5.34
H <sub>2</sub> O	693	13.5	142	12.5
K <sub>2</sub> CO <sub>3</sub>	1340	26.2	178	15.7
H <sub>2</sub> O	5370	105	714	62.8
AMP	520	10.1	105	9.21
DMSO	1560	30.4	314	27.6

As Table 2 shows, the HPC technology requires much more absorbent and solvent compared with the MEA and AMP technologies in order to capture the same amount of CO<sub>2</sub>. Not only will the costs for chemical purchase hence increase, but also for the equipment as the dimensions of pipes and unit operations needs to be larger. These differences in need of absorbent and solvent are dependent on the cyclic capacities of the different technologies, which are presented in Table 3. As the cyclic capacity represents the amount of CO<sub>2</sub> that will be captured in each cycle, a small cyclic capacity will require more absorbent in order to capture the pre-determined 90% of the CO<sub>2</sub> in the flue gas stream, which is the case for HPC. MEA, which has a much higher cyclic capacity therefore has a lower absorbent requirement, and AMP is somewhere in between HPC and MEA. The amount of solvent needed is of course also dependent on the concentration of absorbent chosen for the solution. It can also be seen in Table 3 that HPC has much higher lean loading compared to the other technologies, which leads to a larger amount of CO<sub>2</sub> being trapped in the absorbent solution further increasing the flow rate and dimensions of the equipment.

Another thing that can be observed in Table 2 is that the amount of absorbent and solvent per kg of captured CO<sub>2</sub> is lower when the technologies are applied to the lime kiln flue gases compared to the recovery boiler flue gases. This is connected to the higher cyclic capacities obtained with the lime kiln flue gases (see Table 3). The higher cyclic capacities are enabled by the higher CO<sub>2</sub> concentration in the lime kiln flue gases which increases the partial pressure of CO<sub>2</sub> in the absorption tower. The solubility of CO<sub>2</sub> in the absorbent solution is thereby increased which determines the rich loading. The lean loading is the same for both flue gas streams as it ultimately is determined by the composition in the liquid phase in the regeneration step, which is only dependent on the concentration of absorbent in solvent and the concentration is the same regardless of the flue gas source.

**Table 3:** The lean loadings, the rich loadings, and the cyclic capacities of the different carbon capture technologies when applied on the recovery boiler and lime kiln flue gases. All numbers are given in mol CO<sub>2</sub>/mol absorbent.

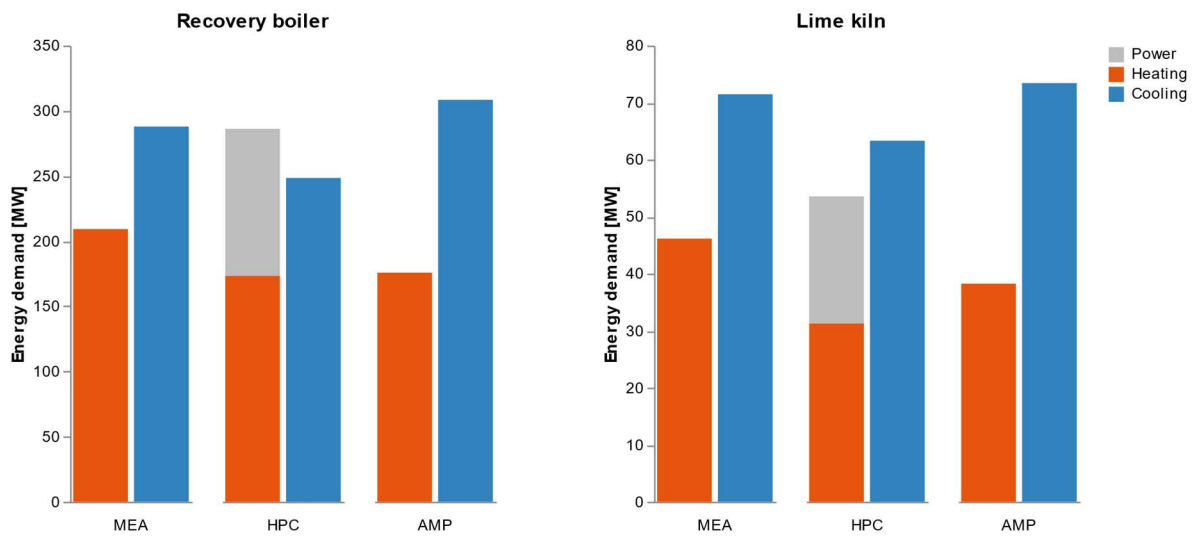
Property	Recovery boiler [mol CO <sub>2</sub> /mol abs.]			Lime kiln [mol CO <sub>2</sub> /mol abs.]		
	MEA	HPC	AMP	MEA	HPC	AMP
Lean loading ( $\alpha_{lean}$ )	0.26	0.68	0.12	0.26	0.68	0.12
Rich loading ( $\alpha_{rich}$ )	0.50	0.80	0.32	0.52	0.88	0.34
Cyclic capacity ( $\alpha_{lean} - \alpha_{rich}$ )	0.24	0.12	0.20	0.26	0.20	0.22

## 5.2 Energy Demands

In Figure 15 below, the resulting energy demands given in MW are presented for the different carbon capture technologies when applied on the two flue gas streams. This includes the de-



mands for heating, cooling, and electrical power. It can be seen that the heating demand is highest for the MEA technology with 209 MW and 46 MW for the recovery boiler and lime kiln flue gases respectively, and it is lowest for the HPC technology with 173 MW and 31 MW respectively. Note that the temperature of the heating required is different for the different capture technologies. The demand is much higher for the recovery boiler flue gases than for the lime kiln flue gases due to the much higher flow rate of flue gases and captured CO<sub>2</sub>. Although the heating demand is lower for the HPC technology, this technology has an additional demand of electrical power to drive the pressure swing, which the MEA and AMP technologies do not. This makes the total energy supply requirements for HPC (286 MW and 54 MW for recovery boiler and lime kiln respectively) higher than those of MEA and AMP. The AMP technology hence stand for the lowest total energy supply demand with 176 MW and 38 MW for the recovery boiler and lime kiln flue gases respectively. It is, however, important to remember that electrical power is a more valuable form of energy than heat is.



**Figure 15:** Energy demands including heating, cooling, and electrical power requirements for the three different carbon capture technologies. The left chart shows the results for the recovery boiler flue gases and the right chart shows the results of the lime kiln flue gases. The heating is required at temperatures of 120°C, 90°C, and 80°C for the MEA, HPC, and AMP technologies respectively.

It can also be seen that, in general, the cooling demand is higher than the heating demand, and the AMP technology has the highest cooling demand while HPC has the lowest. This could be explained by the fact that the flue gases and lean absorbent solution enters the absorption column at lower temperatures in the AMP technology than in the other technologies and that AMP uses intercooling in the absorption column. Meanwhile, HPC is the technology with the highest absorption temperature and additionally, it has fewer coolers than AMP and MEA as the absorption and desorption are operated at the same temperature and thus the lean solution does not need cooling.

When comparing the size of the heat demands with other flows of heat at the Värö pulp mill, it is clear that the heat needed for carbon capture on the recovery boiler flue gases is relatively high. The additional heat needed corresponds to about 35% of the steam production at the mill when assuming that the mill is operating 7500 hours per year [23]. This agrees well with the 40-63% increase in biomass demand reported by Karlsson et al. [18] as that included 90% capture in both the recovery boiler and lime kiln flue gas streams simultaneously. In contrast, the heat demands when capturing the CO<sub>2</sub> from the lime kiln flue gases are corresponding to

an increase in steam production of less than 10%. In addition, the electricity demand of the HPC technology when applied to the recovery boiler flue gases is almost double the amount of electricity used at the entire mill at present, also assuming 7500 operation hours per year [23]. The electricity demand of the HPC technology alone exceeds the total electricity production of the mill. In contrast, the electricity demand of the HPC technology when applied on the lime kiln flue gases is about a third of the current electricity use of the mill and would consume about half of the produced surplus electricity.

Table 4 below shows the same energy demands that are shown in Figure 15 but put in relation to the flow rate of the captured CO<sub>2</sub>. What can be observed in Table 4 is that the total demand of energy supply is generally lower per ton captured CO<sub>2</sub> when the technology is applied to the lime kiln flue gases compared to the recovery boiler flue gases, while the cooling demand is higher. Applying carbon capture on the lime kiln flue gases is hence more energy efficient when it comes to energy supply, which can be explained by the higher concentration of CO<sub>2</sub> in the lime kiln flue gases compared to the recovery boiler flue gases which increases the cyclic capacity and decreases the amount of absorbent solution needed, as discussed in section 5.1. The difference is especially large for the HPC technology, which could be explained by the fact that the increased pressure in the absorber of the HPC technology is enhancing the effect. The molar fraction of CO<sub>2</sub> in the gas phase in the absorber is very similar for the different technologies for both flue gas streams, hence the difference in CO<sub>2</sub> content between the two flue gas streams is similar for all technologies as well. However, the difference in partial pressure between the recovery boiler and lime kiln flue gases becomes seven times higher if the total pressure is 7 bar(a), as it is for the HCP technology, instead of 1 bar(a), as it is for the MEA and AMP technologies (see Equation 8). This also explains the difference in rich loading between the flue gas streams for the HPC technology, which can be seen in Table 3. The increased cooling demand when applying the technologies on the lime kiln flue gases on the other hand, can mainly be explained by the fact that the lime kiln flue gases keep a higher temperature than the recovery boiler flue gases and thereby more cooling is needed before they enter the absorption column.

**Table 4:** The energy demands of the three different carbon capture technologies when applied on the recovery boiler and lime kiln flue gases, all given in GJ/ton captured CO<sub>2</sub>.

Energy type	Recovery boiler [GJ/ton captured CO <sub>2</sub> ]			Lime kiln [GJ/ton captured CO <sub>2</sub> ]		
	MEA	HPC	AMP	MEA	HPC	AMP
Heating	4.08	3.38	3.42	4.06	2.75	3.37
Electricity	-	2.20	-	-	1.96	-
Cooling	5.61	4.84	6.01	6.29	5.57	6.46

In literature, heat demands of 3.57-4.0 GJ/ton CO<sub>2</sub> [61, 63, 64] have been reported for 30 wt% MEA. These numbers only include the heat needed in the reboiler of the stripper column, similarly to this work. The results of 4.06 and 4.08 GJ/ton CO<sub>2</sub> are in the upper range of the val-

ues found in literature, meaning that they are in a reasonable size range even though the estimations might be a bit conservative. For HPC, heat demands for the regeneration of 2.0-2.5 GJ/ton CO<sub>2</sub> [65] were found for a precipitating system using thermal swing regeneration, which is not directly comparable with the system used in this work. The resulting heat demands were higher than those found in literature, 3.38 and 2.75 GJ/ton CO<sub>2</sub> for the different flue gas streams. This could be explained by the fact that a separation unit was used for the precipitating system [65], similarly to the AMP in DMSO system, which allows for a smaller fraction of the rich solution to be regenerated and thereby lower heat demand. However, the results show a lower heat demand for HPC than for MEA which is in accordance with the literature.

Since the AMP in DMSO technology is novel, no literature was found that has reported the heat demand of the process. What was found, however, was numbers from modelled systems of AMP in NMP (N-methyl-2-pyrrolidone) showing heat demands of 1.4 GJ/ton CO<sub>2</sub> [66] and 9.89 GJ/ton CO<sub>2</sub> [67]. Since they are neither close to each other nor very comparable with the AMP in DMSO system, it is difficult to validate of the results for the AMP technology. However, the results of 3.42 and 3.37 GJ/ton CO<sub>2</sub> are lower than the corresponding results for MEA which is in accordance with the expectations (see section 3).

It was also difficult to find comparable numbers of the cooling demands. 3.01-4.4 GJ/ton CO<sub>2</sub> was found for a simulation of a PZ (piperazine) and AMP blend using a much more advanced process design than those in this work and flue gases holding temperatures of 40-85°C [68]. Measurements from a pilot plant using MEA showing cooling demands of 3.2-3.9 GJ/ton CO<sub>2</sub> were also found, which had a process design that was more similar to those made in this thesis. The biggest difference is that the flue gases were not cooled before entering the absorption column in the pilot plant [64]. The resulting cooling demands of this work are much higher for all technologies than the ones found in literature, which partially could be explained by the differences in the designs as the number of coolers and their placement differ. In particular, the flue gas cooling is a big part of the resulting cooling demands of this work as it stands for almost half of the demand in the MEA and AMP technologies and around 80% in the HPC technology, and no or very little cooling was performed on the flue gases in the literature found.

### 5.3 Available Excess Heat

In Table 5 below, the heat that can be recovered from flue gas cooling to cover the heat demand of the regeneration unit is presented for the different technologies when applied on the two flue gas streams.

**Table 5:** Recoverable heat from cooling of flue gases when the different carbon capture technologies are applied to the recovery boiler flue gases and lime kiln flue gases.

Source	Available heat from flue gas cooling [MW]		
	MEA	HPC	AMP
Recovery boiler	0.00	124	9.62
Lime kiln	4.91	31.6	6.40

The amount of heat that can be recovered differs considerably with no heat recovery possible when MEA is used on the recovery boiler flue gases up to 124 MW of recoverable heat when HPC is applied on the same flue gas stream. These vast differences are caused by the different start temperatures for recovery boiler and lime kiln flue gases, the fact that HPC uses flue gas compression before cooling while the other technologies do not, and different temperature requirements for the heat needed for regeneration depending on the capture technology used. For instance, the high values of the HPC technology are caused by the very high temperatures of the flue gases, about 460°C and 640°C for recovery boiler and lime kiln flue gases respectively, resulting from the flue gas compression (see Appendix A). In addition, the fact that the regeneration temperature is 90°C compared to the 120°C needed in the MEA technology makes it possible to cool the flue gases to 125°C for utilization while the MEA technology only can cool to 155°C for utilization due to the  $\Delta T_{\min}$  necessary to transport the heat to the stripper reboiler.

The rest of the excess heat sources are presented in Table 6, which shows the amount of available heat together with electricity required to make that heat available. Note that if not all the available heat is used, the electricity demand will also decrease. The available excess heat based on the excess heat identified from the theoretical energy targeting study [22], which has a high enough temperature to be used for regeneration without the use of a heat pump, was identified to only hold 1-2 MW. The AMP technology is the only technology that could make use of this heat as it was found to be available at temperatures between 95°C and 105°C. In addition, as mentioned in section 4.3.3, this energy is most likely not coming from a single source which could make it hard to locate and utilize in practice. Due to the uncertainties associated with this theoretical target, and the risk of a potential overlap with other identified excess heat sources, it has been neglected.

**Table 6:** The available excess heat from different sources at the Värö pulp mill and the electricity production demand (lost electricity production from turbine extraction or electricity demand for heat pumping) when making this heat available.

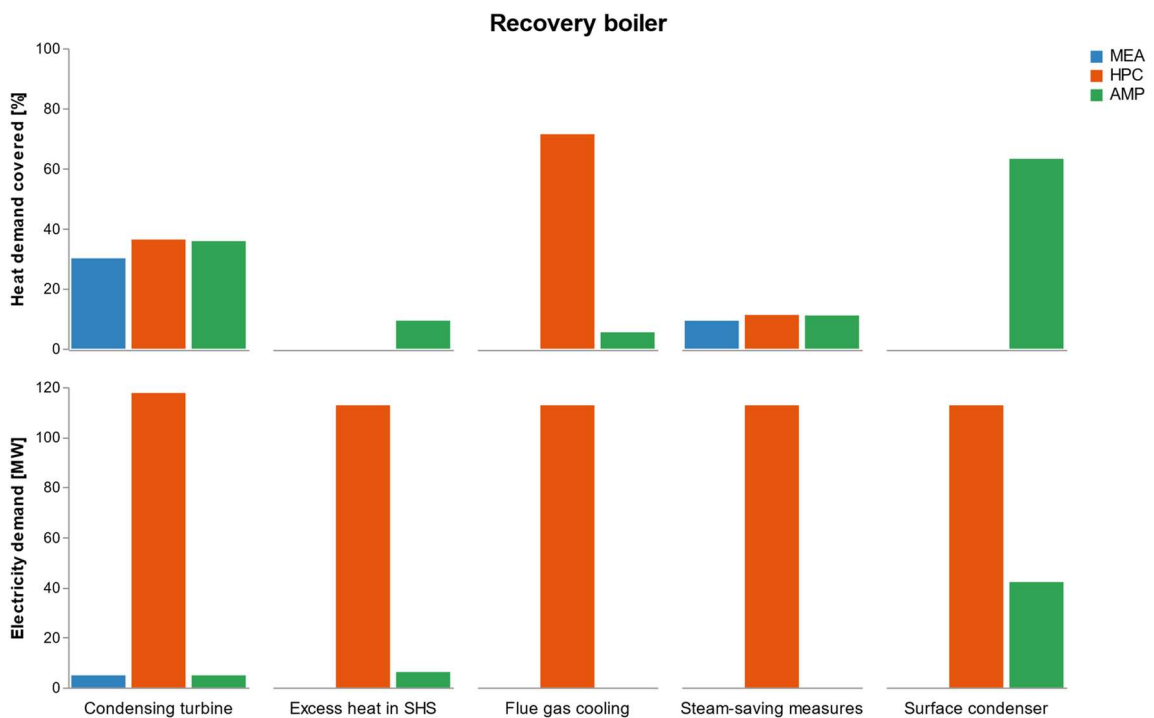
Source	Available heat [MW]	Temperature [°C]	Electricity demand [MW]
Condensing turbine	63.0	144	4.91
Surface condenser	111	80	42.1
Excess in SHS	16.5	80	6.24
Steam-saving measures	19.5	144	-

The most promising sources of excess heat are the condensing turbine and the surface condenser as they hold the largest amount of available heat. However, utilizing heat from the surface condenser results in a larger electricity demand than for the condensing turbine, since a heat pump would be needed to raise the temperature of the heat. The heat pump needs electricity supply and as it contains two water loops (see Figure 13) that both have large  $\Delta T_{\min}$ , the temperature lift of the heat pump system is significant. Extraction of steam from the condensing turbine causes a loss in electricity production, but as the last part of the turbine is the least efficient part of the turbine, the production loss is limited to under 5 MW when 63 MW of steam is obtained (see Table 6).

## 5.4 Matching Heat Demands and Available Excess Heat

Figure 16 shows the results from matching the heat demands of the different carbon capture technologies with the different sources of excess heat when applied to the recovery boiler flue gases. In the top chart, the percentage of the heat demand that can be covered is presented and the chart at the bottom shows the corresponding electricity demand. The electricity demand includes electricity production that is lost in order to make the excess heat available, electricity demand of heat pumps, as well as the electricity demand of the carbon capture process.

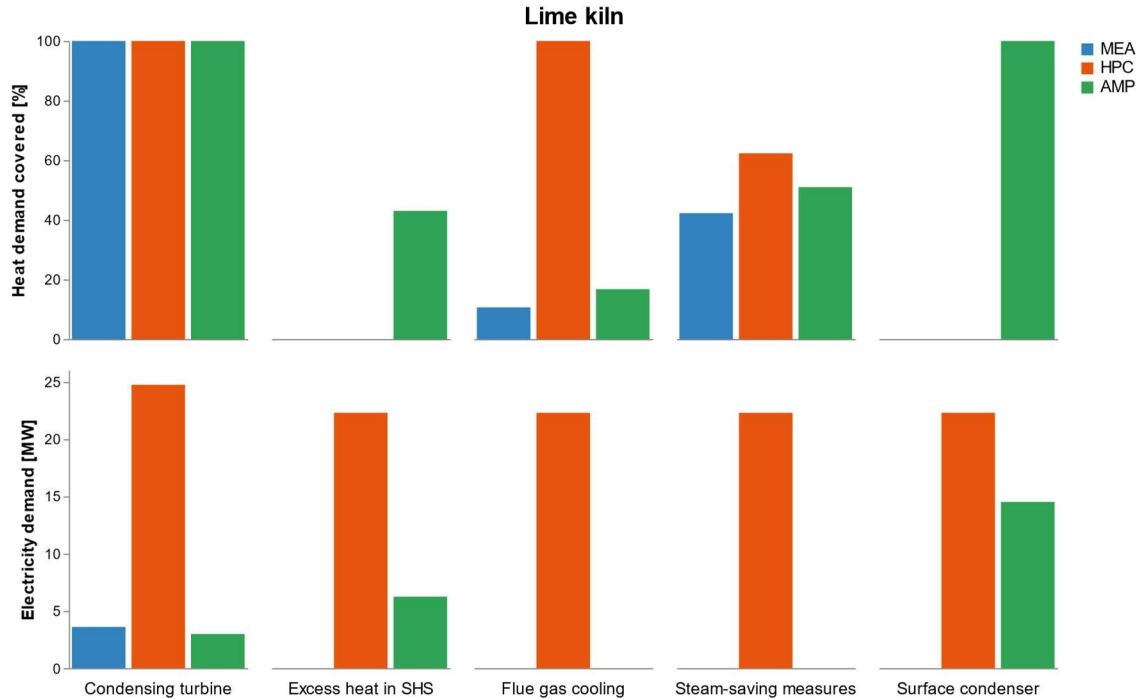
It can be seen that the heat demand cannot be completely covered in any of the cases presented in Figure 16. The largest coverage is obtained when using the flue gas cooling to provide heat for the HPC technology with 71%, but it is also one of the cases with the biggest electricity demands. Due to the HPC technology requiring a large amount of electrical power for the compression of the flue gases, all cases using HPC result in a large electricity demand. Another match standing out in terms of the electricity demand is the AMP/DMSO technology combined with the surface condenser, which would consume 42 MW of electricity due to the heat pump.



**Figure 16:** The top chart shows the percentage of the heat demand that is covered by the different sources of excess heat when the different carbon capture technologies are applied to the recovery boiler flue gases. The bottom chart shows the corresponding electricity demand, which includes the electricity production lost in order to make the excess heat available and the electrical power needed in the carbon capture process.

Figure 17 shows the results from the same matchings but when the carbon capture technologies are applied on the lime kiln flue gases. It can be seen that five of the matches result in complete coverage of the heat demands: the flue gas cooling combined with HPC, the condensing turbine combined with any of the three carbon capture technologies, and the surface condenser combined with AMP. All other cases result in 62% coverage or lower.

Among the matches that resulted in complete heat coverage, the condensing turbine combined with the MEA and AMP technologies have a low electricity demand, 3.60 and 2.98 MW respectively. As mentioned before, the HPC technology comes with an electricity demand resulting in much higher total electricity demand. The combination of AMP with the surface condenser also results in a relatively high electricity demand of 14.5 MW which is caused by the use of a heat pump.



**Figure 17:** The top graph chart shows the percentage of the heat demand that is covered by the different sources of excess heat when the different carbon capture technologies are applied to the lime kiln flue gases. The bottom chart shows the corresponding electricity demand, which includes the electricity production lost in order to make the excess heat available and the electrical power needed in the carbon capture process.

## 5.5 Sensitivity Analysis

An alternative design was made for the heat pump used when recovering heat from the surface condenser to use in the desorber of the AMP technology (see Figure 14) in order to evaluate how the design affects the performance of the heat pump. By removing the water loop between the surface condenser and the heat pump letting them heat exchange directly with each other, the required power input could be decreased significantly. The new electricity demand was 23 MW when upgrading 69 MW of heat from the surface condenser, compared to 42 MW for the original design. This is a decrease in electricity demand of 46%.

To estimate the potential error that could be caused by using the heat of absorption for the wrong temperature for the HPC system, the resulting reboiler heat demands of the MEA technology when using the heat of absorption for two different temperatures, 40°C and 120°C, were compared. The results showed that the reboiler heat demand decreased with 6% when incorrectly using the heat of absorption for 40°C instead of 120°C. The temperature interval used in the calculations is most likely larger than the real difference for the HPC technology, as the reported data accounting for the operation conditions was an average value for temperatures between 40°C and 70°C [55] while the HPC system of this work used a temperature of 90°C. Thus, the estimated error is likely to be conservative.

The  $C_p$  for the aqueous MEA solution calculated as a weighted average of the  $C_p$  of the individual components resulted in 3.7 kJ/(kg·K), compared to the 3.6 kJ/(kg·K) found in literature [43]. The weighted average thereby results in a lower error than what was estimated for the temperature difference. Further, when varying the  $C_p$  with  $\pm 0.5$  kJ/(kg·K), the resulting heat demand of the desorber varies with  $\pm 4\%$ .

## 5.6 Flue Gas Stream

Looking at the results, it is quite clear that applying carbon capture on the reboiler flue gases with the ambition to capture 90% of the CO<sub>2</sub> would result in a large facility in relation to the rest of the mill, especially in terms of energy consumption. Finding excess heat to cover the need would most likely be difficult and lead to high investment costs as many sources would need to be combined. The alternatives would be to increase the heat production to cover all or parts of the heat demand, which would lead to increased emissions and counteract the purpose of implementing the carbon capture in the first place, or to bypass the turbines to extract more steam at the cost of a reduced electricity production. By applying carbon capture on the lime kiln flue gases instead, it would be possible to cover the heating demand using only excess heat, according to the results. In some cases, the sources of excess heat are even larger than the demand of heat, like for the condensing turbine, which would leave excess heat unused as it probably would be hard to achieve a capture rate higher than 90%. An alternative could therefore be to perform partial capture on the recovery boiler flue gases in order to maximize the amount of captured CO<sub>2</sub> while making use of all available excess heat from one source. Partial capture can be performed in two ways; either only a part of the flue gas stream is led to the carbon capture facility where the capture rate is kept at 90% while the rest is bypassed, or all flue gases are passed through the carbon capture but a smaller fraction of the CO<sub>2</sub> is captured, decreasing the capture rate [69].

The results did, however, show that the energy efficiency is higher when applying carbon capture on the lime kiln flue gases, and the captured CO<sub>2</sub> that the lime kiln flue gases would result in would compensate for far more than the fossil CO<sub>2</sub> emissions of the Värö pulp mill. If it is assumed that the carbon capture facility would operate for 7,500 hours per year, about 300,000 tons of CO<sub>2</sub> could be captured from the lime kiln each year, compared to the 10,000 tons of fossil CO<sub>2</sub> emissions at Värö pulp mill and about 800,000 tons of fossil CO<sub>2</sub> from the entire pulp and paper industry in Sweden [14]. More than a third of the fossil emissions of the Swedish pulp and paper industry can thus be captured from the flue gas stream of the lime kiln only, and this shows how quickly the emissions could be decreased by implementing BECCS at point source emitters of biogenic CO<sub>2</sub>. It is, however, important to note that in order to achieve true negative emissions, it is not only crucial that the emissions are not increased when implementing the carbon capture but also that the carbon sinks of the forests do not decrease.

## 5.7 Energy Supply

As mentioned in the results, the condensing turbine and the surface condenser are considered to be the most promising sources of excess heat as these sources have enough heat available to cover the heat demands of the different carbon capture technologies when applied to the lime kiln flue gases. However, the availability of the heat from the surface condenser is worth discussing. It was found as an available source of heat in the theoretical energy efficiency targeting study [22], but when looking at its location at the mill, it could be seen that it currently is condensing against the SHS (secondary heat system) providing it with warm water at

approximately 60°C. As an investigation of the SHS was not within the scope of this thesis, it was assumed that the heat from the surface condenser could be made available by finding other ways to produce the warm water, but in practice this might require substantial rearrangements of the heat exchangers connected to the SHS which could mean that it is not practically or economically feasible. Thus, a more thorough investigation of its availability is necessary.

It was also observed that using the available excess heat from the surface condenser would result in a rather large electricity demand due to the electricity required for the heat pump. The alternative design of the heat pump system presented in Figure 14 resulted in a 46% decrease in electricity demand, which shows the importance of the design. It is therefore important to include the equipment design when further evaluating the different sources of excess heat. Another option that was considered was using mechanical vapor recompression (MVR) instead of a heat pump. In that case, the vapor condensing in the surface condensers would be compressed to a higher pressure before being condensed. The condensation would then be performed at a higher temperature at which the heat would be useful. This would result in fewer heat exchange steps with less temperature loss due to  $\Delta T_{\min}$ . This option was however excluded because of the vapor going into the surface condenser being below atmospheric pressure. The volumes would thereby be very large, leading to expensive equipment, and the risk of air leaking in is high, which would affect the condensing temperature negatively.

In regard to this, the condensing turbine appear to be a more convenient source of excess heat. It is more easily accessible as the steam already exists and only needs to be extracted at a higher pressure at the cost of some electricity production. As the results show, this loss in electricity production would be far less than the electricity demand of a heat pump, regardless of the design. In addition, the heat can be transported using the already existing steam network, which probably would result in less new equipment being required compared to other sources of excess heat. The heat that can be extracted can also be applied to any of the suggested carbon capture technologies due to the temperature of the 3 bar(g) steam, and the heat demands can be covered for all of them if applied to the lime kiln flue gases. However, as the condensate from the condensing turbine is used to provide the recovery boiler with feedwater, the condensate would need to be led back to the feedwater tank in order to not lose feedwater. How this could be arranged would also need to be included in further investigations.

Another interesting source of excess heat is the flue gas cooling, as it is an opportunity to integrate heat within the carbon capture facility, since the flue gases need to be cooled whether the heat is utilized or not. Due to the source of heat already being present in the carbon capture facility, it might be easier to combine it with an external source of heat than it would be to combine two external sources. The process design would, however, be more complex when using heat integration since two stages of flue gas cooling then would be needed because of the impurities in the condensate that need special handling. The possibility to utilize heat integration in this way is also dependent on the amount of available heat. If it can only cover a small portion of the heat demand or if another source can cover the entire heat demand, it might not be worth the additional equipment needed to make use of the heat from the flue gas cooling. According to the results presented in Table 5, the HPC technology would probably be the only one where enough heat is available when cooling the flue gases for it to be an interesting option. However, the large amount of available heat is caused by the high temperatures of the flue gases after compression, which might be unrealistically high. As can be seen



in Appendix B, the temperatures of the recovery boiler and lime kiln flue gases are 460°C and 640°C respectively after the flue gas compression. Consequently, the process design of the HPC technology need to be amended to prevent the flue gases from reaching temperatures as high as these, which in turn could affect the amount of heat available for utilization.

Due to the need of electricity for the compression of flue gases in the HPC technology, a large portion of the energy supply cannot be covered by the use of excess heat, and it also results in a higher energy demand in total, compared to the other technologies. The plausibility of the energy demand results is however hard to assess, considering the very simplified process design that most likely would not be used in practice due to the slow kinetics. It would most likely be possible to utilize a promoter, a more advanced process design, or both, in order to increase the cyclic capacity and thereby decrease the amount of absorbent and solvent needed, which in turn would affect the heating and cooling demands. In addition, since the electricity demand single-handedly comes from the compression of the flue gases, it is only the amount of treated flue gas and the pressure used in the absorption column that can affect the electricity demand. Changing them in order to achieve a lower electricity demand would lead to a decreased amount of captured CO<sub>2</sub> and thereby only affect the total energy demand, not increase the energy efficiency of the capture. In addition, excess electricity is a source of income for the mill while excess heat is more difficult to make use of, and therefore it would probably be more beneficial to use the MEA or AMP technologies where only heat is needed for the capture process and the losses in net electricity production are much lower. Furthermore, if HPC were to be used, the design of the compressor would need to be investigated as the characteristics of the flue gases with acid gases and impurities might make it difficult to implement in practice due to the risk of corrosion.

## 5.8 Sources of Error

Apart from the process designs, the calculations performed were also simplified with numerous assumptions, as stated in section 4.3. With these assumptions come sources of error which can affect the results to a varying extent. For instance, it was assumed that no water is added to the carbon capture systems from the flue gases. For the MEA and HPC technologies, the effects of the assumption are insignificant as water is used as solvent. It thereby only affects the mass balance in which the potential losses are also assumed to be non-existent. For AMP on the other hand, addition of water can affect the system to a greater extent due to the system being non-aqueous. Since DMSO is hygroscopic [39], water from the flue gases will be absorbed in the solution. With water present, the formation of bicarbonate is increased, which could affect the precipitation of carbamates and further the cyclic capacity of the system [27]. However, this effect seems to be small as long as the accumulation of water is below 10 wt% [27]. Additionally, there is a risk of increased heat demand in the desorber, as the bicarbonate requires a higher regeneration temperature than the carbamate, and since water might evaporate which would consume energy [27]. Studies on other water-lean absorption systems have reported on high tolerance for water as the water load reaches steady-state during operation [70], but the extent of the accumulation of water and the effects of it on the AMP/DMSO system need to be further studied before the influence of added water can be evaluated.

The different  $\Delta T_{\min}$  used throughout the energy balance calculations are also assumptions which are potential sources of errors. High values of  $\Delta T_{\min}$  are used in order to achieve conservative results, as the real  $\Delta T_{\min}$  are not known. The real  $\Delta T_{\min}$  is a trade-off between equipment cost and heat transfer, as a larger heat exchanger can maximize the heat transfer with a lower  $\Delta T_{\min}$  but will also be more expensive. The chosen  $\Delta T_{\min}$  can have a large influ-

ence on the resulting heating and cooling demands and can thereby be a partial explanation to the high heat and cooling demands seen in the results when compared with values from literature. However, as all  $\Delta T_{\min}$  are based on the same principle, the potential errors are similar for all cases.

The availability of data differed for the different carbon capture technologies. Even though data for the MEA and HPC technologies has been widely reported, different operating conditions have been used making it difficult to find data that corresponds to the designs made in this work. For MEA, solubility data for 60°C had to be used as data was not found for 50°C, at which the absorption takes place according to the energy balance (see Appendix A). However, as the solubility did not differ much between 40°C and 60°C [41], this probably did not affect the results in a remarkable way. For HPC, few publications have reported data on the heat of absorption and the data that was found either did not specify the operating conditions of the absorption or did not match the operation conditions of this work. Through the sensitivity analysis, the error that this might have caused was estimated to be lower than 6%, which is small enough to be considered insignificant in the comparison of the different carbon capture technologies. The same conclusion can be drawn for the estimation of  $C_p$  for the AMP in DMSO, where the biggest estimated errors of  $\pm 0.5$  kJ/(kg·K) resulted in changes of  $\pm 4\%$  in the heat demand of the desorber.

Even though the individual effects of assumptions and simplifications are rather small, they have the potential to amplify the effect when being stacked on top of each other. However, all the designs are simplified to the fundamental principle of each technology and the calculations are performed as similarly as possible for all the technologies. In addition, the orders of magnitude of the energy demand results seem reasonable when compared to literature, even if they might be a bit conservative. This indicates that the energy demand results are representative for the basic functionalities of the carbon capture technologies and are comparable to each other.

## 5.9 Limitations

It is important to remember that not all electricity consumers are included in the calculations made in this thesis. Equipment like pumps and the separation unit of the AMP technology will contribute to an increased demand of electricity, even though the contributions are small in the context. It would therefore need to be included in further studies on how carbon capture can be implemented at the Värö pulp mill. In addition, compression of the captured CO<sub>2</sub> will probably also be necessary regardless of whether it will be utilized or stored underground, which will also increase the demand of electrical power. Moreover, if the flue gases are to be treated in a carbon capture facility, the temperature at which they are emitted will decrease significantly, which can affect the spreading of the flue gases when emitted through the stack. An additional heater could be required in order to reheat the flue gases to a temperature at which they can be spread properly. This also needs to be further investigated and added to the heat demand if it is required.

## 6 Conclusions

The results of the study provide an indication on what technologies and sources of excess heat that is worth looking closer into in future studies. Due to the simplifications of the method, the results should not be interpreted as absolute truths. Based on the results, it seems more reasonable to focus on the lime kiln flue gases than on the recovery boiler flue gases if a capture rate of 90% is the ambition. The size of the carbon capture facility when applying it on the recovery boiler flue gases would make it hard to cover the heat needed using only excess heat. An alternative to investigate further could be to apply partial carbon capture on the recovery boiler flue gases as that has the potential to maximize the amount of CO<sub>2</sub> captured while making use of all available excess heat from one source.

The technologies requiring the least amount of energy supply seems to be the amine-based technologies MEA and AMP as they would have a much lower need of electric power than the HPC technology. The energy efficiency is highest for the AMP technology, but it comes with a higher demand of cooling and possible technical challenges as it is a novel technology in comparison to the MEA and HPC technologies.

The condensing turbine seems like a promising source of excess heat, as the electricity production loss is very small in comparison to the energy that can be extracted in the form of 3 bar(g) steam. It also has the potential to be used with any of the suggested technologies where it can cover the heat demand for all of them if the carbon capture is applied to the lime kiln flue gases. In addition, it might not require as much reconstruction and new equipment as some of the other sources of excess heat would, as the heat would be produced and transported using the already existing steam network onto which the carbon capture facility would need to be connected.

Ultimately, using BECCS on the Värö pulp mill has great potential to rapidly decrease the fossil emissions of the pulp and paper industry in Sweden through negative emissions as long as no additional emissions are created by the implementation of BECCS and the carbon sinks of the forest do not decrease.

## 7 Future Work

Moving forward, more detailed investigations need to be performed on the technologies and the sources of excess heat that seem to be a promising fit for the Värö mill. First of all, more realistic designs of the technologies would need to be made based on what is used in research and industry. This could mean to include the use of promoters, a mix of absorbents, and more advanced process designs. In addition, more detailed calculations would need to be performed which, for instance, includes the losses and make-up of absorbent and solvent, the electricity demand of all equipment, and takes into consideration that water from the flue gases is added to the system. More research would also need to be performed on the AMP in DMSO system in order for more data to be available and to be able to evaluate the performance of this technology. Further, investigations are required to determine the consequences that the use of excess heat would imply on the energy system of the pulp mill.

It is also necessary to look beyond the carbon capture process and investigate what the captured CO<sub>2</sub> can be used for, if storage is needed on site, and how the CO<sub>2</sub> would need to be processed in order to be transportable. Another master thesis was performed in parallel to this thesis which was investigating the utilization of the CO<sub>2</sub> when captured at the pulp mill of Södra Cell Mönsterås [46] which constitutes the start of this subject. Moreover, equipment design, facility placement at the mill, and cost estimations would need to be included in order to evaluate the feasibility of implementing a carbon capture facility at the Värö pulp mill.

## 8 References

- [1] H. Shaftel, S. Callery, R. Jackson, D. Bailey, and S. Callery. "Evidence - How Do We Know Climate Change Is Real?" NASA Global Climate Change. <https://climate.nasa.gov/evidence/> (accessed 2023-01-03).
- [2] "Kyoto Protocol." Encyclopedia Britannica. <https://www.britannica.com/event/Kyoto-Protocol> (accessed 2023-01-05).
- [3] "Paris Agreement." Encyclopedia Britannica. <https://www.britannica.com/topic/Paris-Agreement-2015> (accessed 2023-01-05).
- [4] R. Lindsey. "Climate Change: Atmospheric Carbon Dioxide." NOAA Climate.gov. <https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide> (accessed 2023-01-03).
- [5] "2100 Warming Projections: Emissions and expected warming based on pledges and current policies." Climate Action Tracker. <https://climateactiontracker.org/global/temperatures/> (accessed 2023-01-03).
- [6] J. A. Moulijn, M. Makkee, and A. v. Diepen, *Chemical Process Technology*. Wiley-Blackwell, 2013.
- [7] K. H. Smith, N. J. Nicholas, and G. W. Stevens, "7 - Inorganic salt solutions for post-combustion capture," in *Absorption-Based Post-combustion Capture of Carbon Dioxide*, P. H. M. Feron Ed.: Woodhead Publishing, 2016, pp. 145-166.
- [8] T. E. Rufford *et al.*, "The removal of CO<sub>2</sub> and N<sub>2</sub> from natural gas: A review of conventional and emerging process technologies," *Journal of Petroleum Science and Engineering*, vol. 94-95, pp. 123-154, 2012/09/01/ 2012, doi: <https://doi.org/10.1016/j.petrol.2012.06.016>.
- [9] G. T. Rochelle, "3 - Conventional amine scrubbing for CO<sub>2</sub> capture," in *Absorption-Based Post-combustion Capture of Carbon Dioxide*, P. H. M. Feron Ed.: Woodhead Publishing, 2016, pp. 35-67.
- [10] P. H. M. Feron, "1 - Introduction," in *Absorption-Based Post-combustion Capture of Carbon Dioxide*, P. H. M. Feron Ed.: Woodhead Publishing, 2016, pp. 3-12.
- [11] "Testanläggning för BECCS vid kraftvärmeverk," Stockholm Exergi AB, 2020.
- [12] "State aid for BECCS." Swedish Energy Agency. <https://www.energimyndigheten.se/en/sustainability/carbon-capture-and-storage/state-aid-for-beccs/> (accessed 2023-01-04).
- [13] "Första, andra, tredje... Förslag på utformning av ett stödsystem för bio-CCS," ER 2021:31, 2021. [Online]. Available: <https://www.regeringen.se/4b0191/contentassets/d232104ea40d4234a5ffde3fe7d48b37/forsta-andra-tredje-forslag-pa-utformning-av-ett-stodsystem-for-bio-ccs.pdf>
- [14] "Industri, utsläpp av växthusgaser." Swedish Environmental Protection Agency. <https://www.naturvardsverket.se/data-och-statistik/klimat/vaxthusgaser-utslapp-fran-industrin/> (accessed 2023-01-04).
- [15] "EU Emissions Trading System." European Commission. [https://climate.ec.europa.eu/eu-action/eu-emissions-trading-system-eu-ets\\_en#sectors-and-gases-covered](https://climate.ec.europa.eu/eu-action/eu-emissions-trading-system-eu-ets_en#sectors-and-gases-covered) (accessed 2023-01-05).
- [16] "Biogena koldioxidutsläpp och klimatpåverkan." Swedish Environmental Protection Agency. <https://www.naturvardsverket.se/amnesomraden/klimatomstallningen/omraden/klimat-et-och-skogen/biogena-koldioxidutslapp-och-klimatpaverkan/> (accessed 2023-01-04).

- [17] "Utsläpp av växthusgaser från industrin efter växthusgas, bransch och år." Statistikdatabasen. <https://www.statistikdatabasen.scb.se/sq/133787> (accessed 2023-01-31).
- [18] S. Karlsson, A. Eriksson, F. Normann, and F. Johnsson, "Ccs in the Pulp and Paper Industry – Implications on Regional Biomass Supply," *Proceedings of the 15th Greenhouse Gas Control Technologies Conference 15-18 March 2021*, 2021, doi: <http://dx.doi.org/10.2139/ssrn.3820355>.
- [19] P. Bajpai, "Chapter 14 - Production of Dissolving Grade Pulp," in *Biermann's Handbook of Pulp and Paper (Third Edition)*, P. Bajpai Ed.: Elsevier, 2018, pp. 375-388.
- [20] "Kraft Pulp Mill Process." Scholarly Community Encyclopedia. [https://encyclopedia.pub/entry/history/compare\\_revision/7865/-1](https://encyclopedia.pub/entry/history/compare_revision/7865/-1) (accessed 2023-01-31).
- [21] P. Bajpai, "Chapter 3 - Evaporation of Black Liquor," in *Pulp and Paper Industry*, P. Bajpai Ed.: Elsevier, 2017, pp. 39-66.
- [22] A. Pedersén and A. Larsson, "Energy Efficiency Study at a Softwood Kraft Pulp Mill," Master Thesis, Department of Energy and Environment, Chalmers University of Technology, Gothenburg, 2017.
- [23] K. Strandberg, ed. Södra, personal communication, January 4, 2023.
- [24] K. Strandberg, ed. Södra, personal communication, January 10, 2023.
- [25] P. Bajpai, "Chapter 6 - Reburning of Lime Mud," in *Pulp and Paper Industry*, P. Bajpai Ed.: Elsevier, 2017, pp. 131-146.
- [26] K. Y. Shin-ichi Nakao, Kazuya Goto, Teruhiko Kai, Hidetaka Yamada, *Advanced CO2 Capture Technologies*, 1 ed. (SpringerBriefs in Energy). Springer Cham, 2019, pp. VII, 83.
- [27] H. Karlsson, "Precipitating Amine Absorption Systems for Carbon Capture," Doctoral Thesis, Chemical Engineering, Lund University, Lund, 2021.
- [28] J. Jung, Y. S. Jeong, Y. Lim, C. S. Lee, and C. Han, "Advanced CO2 Capture Process Using MEA Scrubbing: Configuration of a Split Flow and Phase Separation Heat Exchanger," *Energy Procedia*, vol. 37, pp. 1778-1784, 2013/01/01/ 2013, doi: <https://doi.org/10.1016/j.egypro.2013.06.054>.
- [29] B. Lv, B. Guo, Z. Zhou, and G. Jing, "Mechanisms of CO2 Capture into Monoethanolamine Solution with Different CO2 Loading during the Absorption/Desorption Processes," *Environmental Science & Technology*, vol. 49, no. 17, pp. 10728-10735, 2015, doi: 10.1021/acs.est.5b02356.
- [30] P. D. Vaidya and E. Y. Kenig, "CO2-Alkanolamine Reaction Kinetics: A Review of Recent Studies," *Chemical Engineering & Technology*, vol. 30, no. 11, pp. 1467-1474, 2007, doi: 10.1002/ceat.200700268.
- [31] H. Chang and C. M. Shih, "Simulation and Optimization for Power Plant Flue Gas CO2 Absorption-Stripping Systems," *Separation Science and Technology*, vol. 40, no. 4, pp. 877-909, 2005, doi: 10.1081/ss-200048014.
- [32] D. H. Van Wagener and G. T. Rochelle, "Stripper configurations for CO2 capture by aqueous monoethanolamine and piperazine," *Energy Procedia*, vol. 4, pp. 1323-1330, 2011/01/01/ 2011, doi: <https://doi.org/10.1016/j.egypro.2011.01.190>.
- [33] M. Karimi, M. Hillestad, and H. F. Svendsen, "Capital costs and energy considerations of different alternative stripper configurations for post combustion CO2 capture," *Chemical Engineering Research and Design*, vol. 89, no. 8, pp. 1229-1236, 2011/08/01/ 2011, doi: <https://doi.org/10.1016/j.cherd.2011.03.005>.

- [34] M. Karimi, M. Hillestad, and H. F. Svendsen, "Investigation of the dynamic behavior of different stripper configurations for post-combustion CO<sub>2</sub> capture," *International Journal of Greenhouse Gas Control*, vol. 7, pp. 230-239, 2012/03/01/ 2012, doi: <https://doi.org/10.1016/j.ijggc.2011.10.008>.
- [35] D. Sanyal, N. Vasishtha, and D. N. Saraf, "Modeling of carbon dioxide absorber using hot carbonate process," *Industrial & Engineering Chemistry Research*, vol. 27, no. 11, pp. 2149-2156, 1988, doi: 10.1021/ie00083a032.
- [36] M. R. Rahimpour and A. Z. Kashkooli, "Enhanced carbon dioxide removal by promoted hot potassium carbonate in a split-flow absorber," *Chemical Engineering and Processing: Process Intensification*, vol. 43, no. 7, pp. 857-865, 2004/07/01/ 2004, doi: [https://doi.org/10.1016/S0255-2701\(03\)00106-5](https://doi.org/10.1016/S0255-2701(03)00106-5).
- [37] Y. Wu, N. R. Mirza, G. Hu, K. H. Smith, G. W. Stevens, and K. A. Mumford, "Precipitating Characteristics of Potassium Bicarbonate Using Concentrated Potassium Carbonate Solvent for Carbon Dioxide Capture. Part 1. Nucleation," *Industrial & Engineering Chemistry Research*, vol. 56, no. 23, pp. 6764-6774, 2017, doi: 10.1021/acs.iecr.7b00699.
- [38] "Dimethyl sulfoxide." American Chemical Society. <https://www.acs.org/molecule-of-the-week/archive/d/dimethyl-sulfoxide.html> (accessed 2022-12-13).
- [39] R. G. LeBel and D. A. I. Goring, "Density, Viscosity, Refractive Index, and Hygroscopicity of Mixtures of Water and Dimethyl Sulfoxide," *Journal of Chemical & Engineering Data*, vol. 7, no. 1, pp. 100-101, 1962/01/01 1962, doi: 10.1021/je60012a032.
- [40] R. Khalilpour and A. Abbas, "HEN optimization for efficient retrofitting of coal-fired power plants with post-combustion carbon capture," *International Journal of Greenhouse Gas Control*, vol. 5, no. 2, pp. 189-199, 2011/03/01/ 2011, doi: <https://doi.org/10.1016/j.ijggc.2010.10.006>.
- [41] S. H. Park, K. B. Lee, J. C. Hyun, and S. H. Kim, "Correlation and Prediction of the Solubility of Carbon Dioxide in Aqueous Alkanolamine and Mixed Alkanolamine Solutions," *Industrial & Engineering Chemistry Research*, vol. 41, no. 6, pp. 1658-1665, 2002, doi: 10.1021/ie010252o.
- [42] S. Yun, Y. Kim, j. h. Choi, S. Nam, J. Chang, and Y. Yoon, "CO<sub>2</sub> absorption, density, viscosity and vapor pressure of aqueous potassium carbonate+2-methylpiperazine," *Korean Journal of Chemical Engineering*, vol. 33, 08/24 2016, doi: 10.1007/s11814-016-0210-7.
- [43] I. Kim, K. A. Hoff, and T. Mejdell, "Heat of Absorption of CO<sub>2</sub> with Aqueous Solutions of MEA: New Experimental Data," *Energy Procedia*, vol. 63, pp. 1446-1455, 2014/01/01/ 2014, doi: <https://doi.org/10.1016/j.egypro.2014.11.154>.
- [44] H. Kaur and C.-C. Chen, "Thermodynamic modeling of CO<sub>2</sub> absorption in aqueous potassium carbonate solution with electrolyte NRTL model," *Fluid Phase Equilibria*, vol. 505, p. 112339, 2020/02/01/ 2020, doi: <https://doi.org/10.1016/j.fluid.2019.112339>.
- [45] E. Dahlén, ed. Stockholm Exergi, personal communication, November 3, 2022.
- [46] V. Lindström, "Capture and utilization of carbon dioxide from the lime kilns of a Kraft pulp mill for bio-methanol production," Master Thesis, Department of Earth, Space and Environment, Chalmers University of Technology, Gothenburg, 2023.
- [47] *Rate-Based Model of the CO<sub>2</sub> Capture Process by MEA using Aspen Plus*. (2008). Aspen Technology, Inc., Bedford, MA. [Online]. Available: <http://www.aspentech.com>
- [48] H. Svensson, ed. Lund University, personal communication, November 14, 2022.

- [49] H. K. Karlsson, P. Drabo, and H. Svensson, "Precipitating non-aqueous amine systems for absorption of carbon dioxide using 2-amino-2-methyl-1-propanol," *International Journal of Greenhouse Gas Control*, vol. 88, pp. 460-468, 2019/09/01/ 2019, doi: <https://doi.org/10.1016/j.ijggc.2019.07.001>.
- [50] M. Alveteg, *Handbook*. Department of Chemical Engineering, Lund University, 2021.
- [51] "Air - Specific Heat vs. Temperature at Constant Pressure." Engineering ToolBox. [https://www.engineeringtoolbox.com/air-specific-heat-capacity-d\\_705.html](https://www.engineeringtoolbox.com/air-specific-heat-capacity-d_705.html) (accessed 2023-01-03).
- [52] B. Wischniewski. "Calculation of Thermodynamic State Variables of Carbon Dioxide." Peace Software. [http://www.peacesoftware.de/einigewerte/co2\\_e.html](http://www.peacesoftware.de/einigewerte/co2_e.html) (accessed 2023-01-03).
- [53] "Carbon Dioxide - Specific Heat of Gas vs. Temperature." Engineering ToolBox. [https://www.engineeringtoolbox.com/carbon-dioxide-d\\_974.html](https://www.engineeringtoolbox.com/carbon-dioxide-d_974.html) (accessed 2023-01-03).
- [54] R. Smith, *Chemical Process Design and Integration*, 2nd ed. Chichester: John Wiley & Sons, Inc., 2016.
- [55] J. T. Cullinane and G. T. Rochelle, "Thermodynamics of aqueous potassium carbonate, piperazine, and carbon dioxide," *Fluid Phase Equilibria*, vol. 227, no. 2, pp. 197-213, 2005/01/25/ 2005, doi: <https://doi.org/10.1016/j.fluid.2004.11.011>.
- [56] H. L. Clever and E. F. Westrum, "Dimethyl sulfoxide and dimethyl sulfone. Heat capacities, enthalpies of fusion, and thermodynamic properties," *The Journal of Physical Chemistry*, vol. 74, no. 6, pp. 1309-1317, 1970, doi: 10.1021/j100701a027.
- [57] "1-Propanol, 2-amino-2-methyl-." National Institute of Standards and Technology, U.S. Department of Commerce. <https://webbook.nist.gov/cgi/cbook.cgi?ID=C124685&Units=SI&Mask=FFF> (accessed 2023-01-26).
- [58] E. Svensson, ed. Chalmers University of Technology, personal communication, November 24, 2022.
- [59] K. Strandberg, ed. Södra, personal communication, October 5, 2022.
- [60] T. D. Eastop and A. McConkey, *Applied thermodynamics for engineering technologists*, 5. ed. Longman, 1993.
- [61] L. M. Romeo, I. Bolea, and J. M. Escosa, "Integration of power plant and amine scrubbing to reduce CO<sub>2</sub> capture costs," *Applied Thermal Engineering*, vol. 28, no. 8, pp. 1039-1046, 2008/06/01/ 2008, doi: <https://doi.org/10.1016/j.applthermaleng.2007.06.036>.
- [62] B. Wetenhall, J. M. Race, and M. J. Downie, "The Effect of CO<sub>2</sub> Purity on the Development of Pipeline Networks for Carbon Capture and Storage Schemes," *International Journal of Greenhouse Gas Control*, vol. 30, pp. 197-211, 2014/11/01/ 2014, doi: <https://doi.org/10.1016/j.ijggc.2014.09.016>.
- [63] M. Bui *et al.*, "Carbon capture and storage (CCS): the way forward," *Energy & Environmental Science*, vol. 11, no. 5, pp. 1062-1176, 2018, doi: 10.1039/c7ee02342a.
- [64] J. N. J. J. N. Knudsen, P. Vilhelmsen, "First year operation experience with a 1 t / h CO<sub>2</sub> absorption pilot plant at Esbjerg coal-fired power plant," in *European Congress of Chemical Engineering*, September 2007, pp. 16-20.
- [65] C. Anderson *et al.*, "Developments in the CO<sub>2</sub>CRC UNO MK 3 Process: A Multi-component Solvent Process for Large Scale CO<sub>2</sub> Capture," *Energy Procedia*, vol. 37, pp. 225-232, 2013/01/01/ 2013, doi: <https://doi.org/10.1016/j.egypro.2013.05.106>.

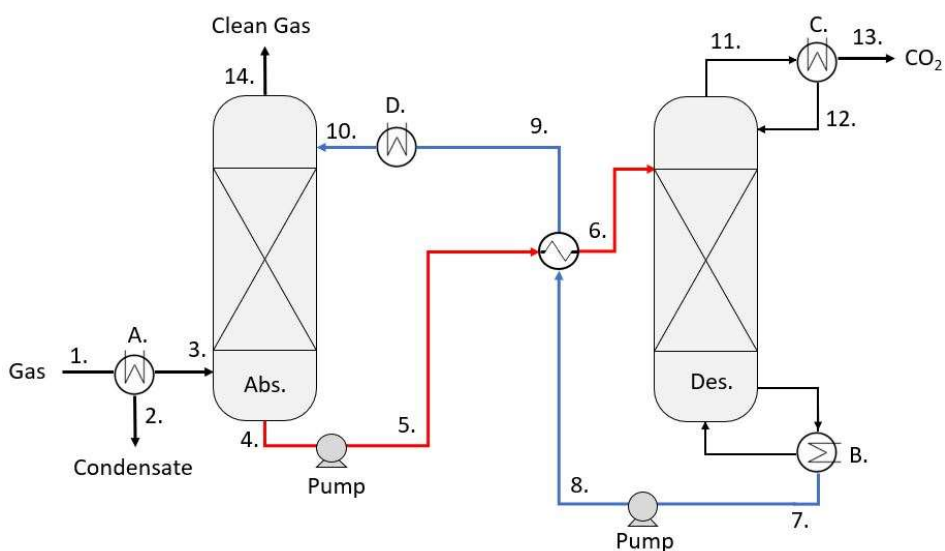


- [66] C. Hulteberg, H. Svensson, M. Sanku, and H. Karlsson, "Energy efficient CO<sub>2</sub> removal," Institutionen för kemiteknik, Lunds Universitet, Swedish Energy Agency, 2017.
- [67] R. G. Calle, "Modelling of an Amine-Organic Solvent based Carbon-Capture Process for Efficient Excess Heat Utilization," Master Thesis, Department of Space, Earth and Environment, Chalmers University of Technology, Gothenburg, 2018.
- [68] P. H. M. Feron, A. Cousins, K. Jiang, R. Zhai, and M. Garcia, "An update of the benchmark post-combustion CO<sub>2</sub>-capture technology," *Fuel*, vol. 273, p. 117776, 2020/08/01/ 2020, doi: <https://doi.org/10.1016/j.fuel.2020.117776>.
- [69] M. Biermann, "Partial CO<sub>2</sub> capture to facilitate cost-efficient deployment of carbon capture and storage in process industries," Doctoral Thesis, Department of Space, Earth and Environment, Chalmers University of Technology, Gothenburg, 2022.
- [70] D. J. Heldebrant, P. K. Koech, V.-A. Glezakou, R. Rousseau, D. Malhotra, and D. C. Cantu, "Water-Lean Solvents for Post-Combustion CO<sub>2</sub> Capture: Fundamentals, Uncertainties, Opportunities, and Outlook," *Chemical Reviews*, vol. 117, no. 14, pp. 9594-9624, 2017, doi: 10.1021/acs.chemrev.6b00768.

# Appendix A – Mass and Energy Balances

In this appendix, the mass and energy balances for the three different carbon capture technologies are presented in their entirety. Figure A1, A2, and A3 illustrates the process designs and have all streams marked with numbers and all units requiring energy supply marked with letters. The supplementary tables present the information concerning mass and energy for all streams and units.

## MEA



**Figure A.1:** A flow diagram of the process design for the carbon capture using aqueous MEA as absorbent. All streams are marked with numbers and all units are marked with letters.

**Table A.1:** Mass balance for the streams included in the carbon capture technology using aqueous MEA as absorbent together with the corresponding temperatures and pressures of the streams. The streams are illustrated in Figure A.1 above.

Stream	Mass flow [kg/s]		Temperature [°C]		Pressure [kPa]
	Recovery boiler	Lime kiln	Recovery boiler	Lime kiln	
<b>1</b>					
CO <sub>2</sub>	57.04	12.63			
H <sub>2</sub> O	45.05	10.72	155.0	279.6	101.3
Air	204.8	23.67			
<b>2</b>					
H <sub>2</sub> O	33.21	9.162	40.00	40	101.3
<b>3</b>					
CO <sub>2</sub>	57.04	12.63			

	H <sub>2</sub> O Air	11.83 204.8	1.562 23.67	40.00	40	101.3
<b>4</b>	CO <sub>2</sub> MEA H <sub>2</sub> O	106.9 296.8 692.6	22.73 60.67 141.6	48.43	50.94	101.3
<b>5</b>	CO <sub>2</sub> MEA H <sub>2</sub> O	106.9 296.8 692.6	22.73 60.67 141.6	48.43	50.94	200.0
<b>6</b>	CO <sub>2</sub> MEA H <sub>2</sub> O	106.9 296.8 692.6	22.73 60.67 141.6	111.1	110.9	200.0
<b>7</b>	CO <sub>2</sub> MEA H <sub>2</sub> O	55.61 296.8 692.6	11.37 60.67 141.6	120.0	120.0	200.0
<b>8</b>	CO <sub>2</sub> MEA H <sub>2</sub> O	55.61 296.8 692.6	11.37 60.67 141.6	120.0	120.0	101.3
<b>9</b>	CO <sub>2</sub> MEA H <sub>2</sub> O	55.61 296.8 692.6	11.37 60.67 141.6	58.43	60.94	101.3
<b>10</b>	CO <sub>2</sub> MEA H <sub>2</sub> O	55.61 296.8 692.6	11.37 60.67 141.6	40.00	40	101.3
<b>11</b>	CO <sub>2</sub> H <sub>2</sub> O	51.33 2.042	11.37 8.146	111.1	110.9	200
<b>12</b>	H <sub>2</sub> O	2.042	8.146	20.00	20.00	200.0
<b>13</b>	CO <sub>2</sub>	51.33	11.37	20.00	20.00	200.0
<b>14</b>	CO <sub>2</sub> H <sub>2</sub> O Air	5.704 11.83 204.8	1.263 1.562 23.67	48.43	50.94	101.3

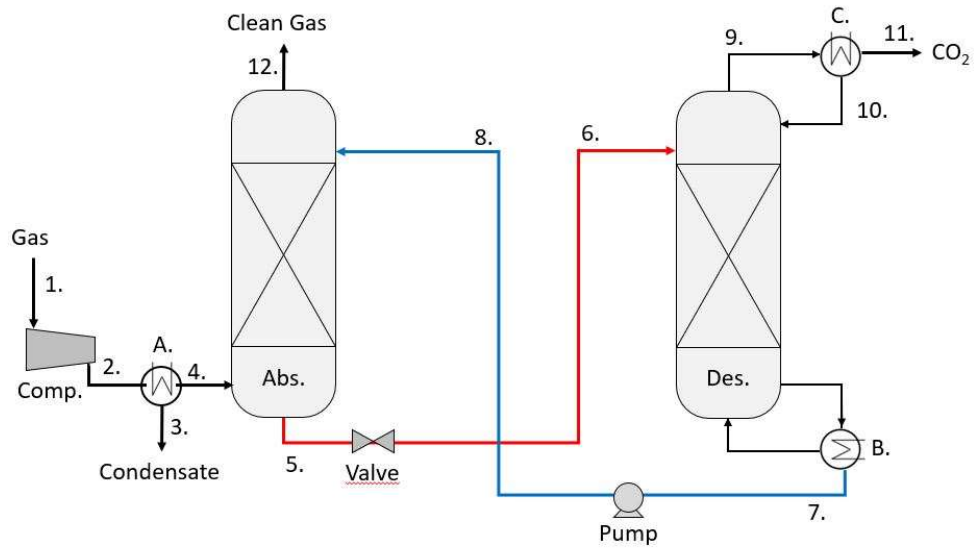
**Table A.2:** Heat and cooling duties of the units used in the carbon capture technology using aqueous MEA as absorbent. The units are illustrated in Figure A.1 above. Negative values indicate cooling duty.

Unit	Duty [MW]	
	Recovery boiler	Lime kiln
A	-117.8	-33.00
B	209.3	46.15
C	-100.1	-22.15
D	-70.09	-16.31

**Table A.3:** The types of heat included in the heat demand of the reboiler (unit B in Figure A.1) of the MEA technology.

Type of heat [MW]	Recovery boiler	Lime kiln
Vaporization	82.03	18.16
Sensible	16.42	3.456
Absorption	110.8	24.53
<b>Total</b>	<b>209.3</b>	<b>46.15</b>

# HPC



**Figure A.2:** A flow diagram of the process design for the carbon capture using aqueous HPC. All streams are marked with numbers and all units marked with letters.

**Table A.4:** Mass balance for the streams included in the carbon capture technology using aqueous HPC together with the corresponding temperatures and pressures of the streams. The streams are illustrated in Figure A.2 above.

Stream		Mass flow [kg/s]		Temperature [°C]		Pressure [kPa]
		Recovery boiler	Lime kiln	Recovery boiler	Lime kiln	
<b>1</b>	CO <sub>2</sub>	57.04	12.63	155.0	279.6	101.3
	H <sub>2</sub> O	45.05	10.72			
	Air	204.8	23.67			
<b>2</b>	CO <sub>2</sub>	57.04	12.63	462.5	636.0	700.0
	H <sub>2</sub> O	45.05	10.72			
	Air	204.8	23.67			
<b>3</b>	H <sub>2</sub> O	28.26	8.509	90.00	90.00	700.0
<b>4</b>	CO <sub>2</sub>	57.04	12.63	90.00	90.00	700.0
	H <sub>2</sub> O	16.79	2.215			
	Air	204.8	23.67			
<b>5</b>	CO <sub>2</sub>	342.2	50.01	92.00	93.32	700.0
	K <sub>2</sub> CO <sub>3</sub>	1343	178.4			

	H <sub>2</sub> O	5373	713.8			
<b>6</b>	CO <sub>2</sub> K <sub>2</sub> CO <sub>3</sub> H <sub>2</sub> O	342.2 1343 5373	50.01 178.4 713.8	83.45	83.67	120.0
<b>7</b>	CO <sub>2</sub> K <sub>2</sub> CO <sub>3</sub> H <sub>2</sub> O	290.9 1343 5373	38.64 178.4 713.8	90.00	90.00	120.0
<b>8</b>	CO <sub>2</sub> K <sub>2</sub> CO <sub>3</sub> H <sub>2</sub> O	290.9 1343 5373	38.64 178.4 713.8	90.00	90.00	700.0
<b>9</b>	CO <sub>2</sub> H <sub>2</sub> O	51.33 18.42	11.37 4.078	83.45	83.67	120.0
<b>10</b>	H <sub>2</sub> O	18.42	4.078	20.00	20.00	120.0
<b>11</b>	CO <sub>2</sub>	51.33	11.37	20.00	20.00	120.0
<b>12</b>	CO <sub>2</sub> H <sub>2</sub> O Air	5.704 16.79 204.8	1.263 2.215 23.67	92.00	93.32	700.0

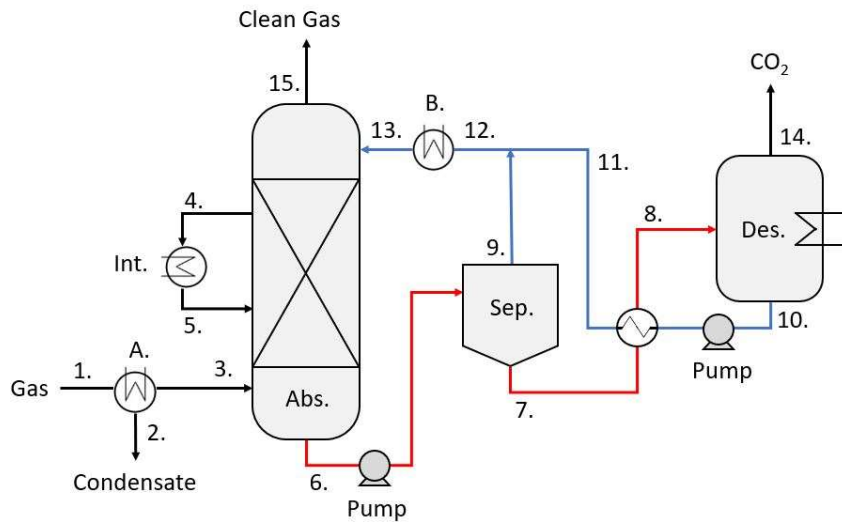
**Table A.5:** Heat and cooling duties of the units used in the carbon capture technology using HPC. The units are illustrated in Figure A.2 above. Negative values indicate cooling duty.

Unit	Duty [MW]	
	Recovery boiler	Lime kiln
Comp.	112.8	22.28
A	-198.4	-52.23
B	173.4	31.29
C	-50.12	-11.10

**Table A.6:** The types of heat included in the heat demand of the reboiler (unit B in Figure A.2) in the HPC technology.

<b>Type of heat [MW]</b>	<b>Recovery boiler</b>	<b>Lime kiln</b>
Vaporization	51.96	11.50
Sensible	74.75	9.454
Absorption	46.66	10.33
<b>Total</b>	<b>173.4</b>	<b>31.29</b>

# AMP



**Figure A.3:** A flow diagram of the process design for the carbon capture using AMP in DMSO as absorbent in a precipitating system. All streams are marked with numbers and all units are marked with letters.

**Table A.7:** Mass balance for the streams included in the carbon capture technology using AMP in DMSO as absorbent together with the corresponding temperatures and pressures of the streams. The streams are illustrated in Figure A.3 above. The temperature of stream 10 was not calculated as the temperature of stream 11 was calculated directly from stream 7 and 9.

Stream		Mass flow [kg/s]		Temperature [°C]		Pressure [kPa]
		Recovery boiler	Lime kiln	Recovery boiler	Lime kiln	
1	CO <sub>2</sub>	57.04	12.63	155.0	279.6	101.3
	H <sub>2</sub> O	45.05	10.72			
	Air	204.8	23.67			
2	H <sub>2</sub> O	40.18	10.08	25.00	25.00	101.3
3	CO <sub>2</sub>	57.04	12.63	25.00	25.00	101.3
	H <sub>2</sub> O	4.865	0.6420			
	Air	204.8	23.67			
4	CO <sub>2</sub>	82.13	17.56	59.51	63.18	101.3
	AMP	519.9	104.6			
	DMSO	1560	313.9			
5	CO <sub>2</sub>	82.13	17.56			



	AMP DMSO	519.9 1560	104.6 313.9	50.00	50.00	101.3
<b>6</b>	CO <sub>2</sub> AMP DMSO	82.13 519.9 1560	17.56 104.6 313.9	50.00	50.00	101.3
<b>7</b>	CO <sub>2</sub> AMP DMSO	82.13 519.9 156.0	17.56 104.6 31.39	50.00	50.00	101.3
<b>8</b>	CO <sub>2</sub> AMP DMSO	82.13 519.9 156.0	17.56 104.6 31.39	59.74	59.72	101.3
<b>9</b>	CO <sub>2</sub> DMSO	0.7906 1404	0.3183 282.5	50.00	50.00	101.3
<b>10</b>	CO <sub>2</sub> AMP DMSO	30.01 519.9 156.0	5.881 104.6 31.39	80.00	80.00	101.3
<b>11</b>	CO <sub>2</sub> AMP DMSO	30.01 519.9 156.0	5.881 104.6 31.39	70.00	70.00	101.3
<b>12</b>	CO <sub>2</sub> AMP DMSO	30.80 519.9 1560	6.199 104.6 313.9	-	-	101.3
<b>13</b>	CO <sub>2</sub> AMP DMSO	30.80 519.9 1560	6.199 104.6 313.9	30.00	30.00	101.3
<b>14</b>	CO <sub>2</sub>	51.33	11.37	80.00	80.00	101.3
<b>15</b>	CO <sub>2</sub> H <sub>2</sub> O Air	5.704 4.865 204.8	1.263 0.6420 23.67	59.51	63.18	101.3

**Table A.8:** Heat and cooling duties of the units used in the carbon capture technology using AMP in DMSO as absorbent. The units are illustrated in Figure A.3 above. Negative values indicate cooling duty.

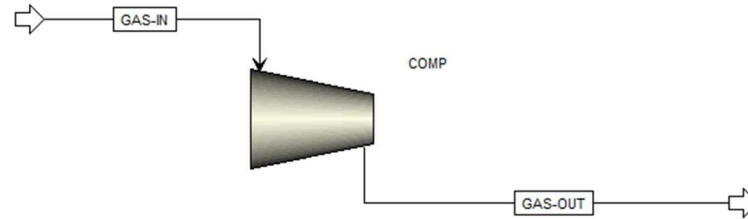
Unit	Duty [MW]	
	Recovery boiler	Lime kiln
A	-141.0	-36.36
Int.	-43.41	-12.12
Des.	175.8	38.26
B	-124.0	-24.95

**Table A.9:** The types of heat included in the heat demand of the desorber in the AMP technology.

Type of heat [MW]	Recovery boiler	Lime kiln
Vaporization	-	-
Sensible	33.50	6.752
Absorption	142.3	31.51
<b>Total</b>	<b>175.8</b>	<b>38.26</b>

## Appendix B – Aspen Plus Models

The flue gas compressor used to increase the pressure of the flue gas in the HPC technology was modeled as an isentropic compressor using Aspen Plus. Figure B.1 below shows the flowsheet diagram of the model.



**Figure B.1:** Flowsheet diagram of the flue gas compressor used in the HPC technology which was modeled using Aspen Plus.

The input data and settings used in the model for the different flue gas streams are presented in Table B.1 below. The isentropic efficiency ( $\eta_{IS}$ ) was estimated using Equations B.1 and B.2 [54].

$$\eta_{IS} = 0.1091(\ln r)^3 - 0.5247(\ln r)^2 + 0.8577 \ln r + 0.3727 \quad \text{Equation B.1}$$

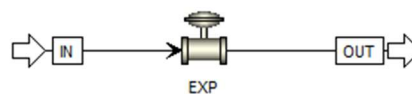
$$r = \frac{P_{out}}{P_{in}} \quad \text{Equation B.2}$$

Where  $P_{out}$  is the pressure of the gas leaving the compressor and  $P_{in}$  is the pressure of the gas entering the compressor. Table B.1 also presents the resulting outlet temperature of the flue gases and the work required in the form of electrical power that were both used in the energy balance calculations.

**Table B.1:** Input data and settings used in when modeling the flue gas compressor illustrated in Figure B.1 in Aspen Plus together with the resulting outputs.

<b>Input data</b>	<b>Units</b>	<b>Recovery boiler</b>	<b>Lime kiln</b>
<b>GAS-IN</b>			
Material			
CO <sub>2</sub>	[kg/s]	57.0	12.6
H <sub>2</sub> O		45.0	10.7
O <sub>2</sub>		43.0	5.0
N <sub>2</sub>		161.8	18.7
Temperature	[°C]	155	280
Pressure	[bar(a)]	1.01325	1.01325
<b>COMP</b>			
Type	-	Isentropic	Isentropic
Discharge pressure	[bar(a)]	7	7
Isentropic efficiency	-	0.858	0.858
Mechanical efficiency	-	1	1
<b>Output data</b>	<b>Units</b>	<b>Recovery boiler</b>	<b>Lime kiln</b>
Outlet temperature	[°C]	462.534	636.03
Net work required	[MW]	112.775	22.2753

The expansion valve used to decrease the pressure of the rich absorbent solution in the same technology was also modeled using Aspen Plus and the flowsheet is presented in Figure B.2.



**Figure B.2:** Flow sheet diagram of the expander valve used to decrease the pressure of the rich absorbent solution in the HPC technology which was modeled using Aspen Plus.

The input data and settings used in the model are presented in Table B.2 together with the resulting outlet temperature of the rich absorbent solution. The outlet temperature was used in the energy balance calculations.

**Table B.2:** Input data and settings used in when modeling the expander valve illustrated in Figure B.2 in Aspen Plus together with the resulting outputs.

<b>Input data</b>	<b>Units</b>	<b>Recovery boiler</b>	<b>Lime kiln</b>
<b>GAS-IN</b>			
Material			
H <sub>2</sub> O	[kg/s]	5373.2	713.8
CO <sub>2</sub>		342.2	50.0
K <sub>2</sub> CO <sub>3</sub>		1343.3	178.4
Temperature	[°C]	92.00	93.32
Pressure	[bar(a)]	7	7
<b>EXP</b>			
Type	-	Adiabatic flash	Adiabatic flash
Outlet pressure	[bar(a)]	1.2	1.2
Valid phases	-	Vapour-Liquid	Vapour-Liquid
<b>Output data</b>	<b>Units</b>	<b>Recovery boiler</b>	<b>Lime kiln</b>
Outlet temperature	[°C]	83.4534	83.6743