

Capture and utilization of carbon dioxide from the lime kilns of a Kraft pulp mill for bio-methanol production

Case study at the market pulp mill Södra Cell Mönsterås

Master's thesis in Sustainable and Innovative Chemical Engineering

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Department of Space, Earth and Environment Division of Energy Technology CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden 2023 Capture and utilization of carbon dioxide from the lime kilns of a Kraft pulp mill for bio-methanol production - Case study at the market pulp mill Södra Cell Mönsterås VENDELA LINDSTRÖM

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Abstract

Bio-methanol is a valuable product that can be used for a variety of applications. Södra Cell Mönsterås, a pulp mill situated in southern Sweden, currently produces bio-methanol as a byproduct from the pulping process. However, methanol could also be produced through carbon capture and utilisation (CCU), i.e. by capturing carbon dioxide from point emission sources at the plant site and reacting it with hydrogen. This master thesis aims to investigate the potential integration of such a CCU concept at Södra Cell Mönsterås, thus potentially increasing bio-methanol production on site.

The carbon dioxide was assumed to be captured through post-combustion capture using an amine-based absorption process. For energy-efficient carbon dioxide capture, a high concentration of carbon dioxide in the flue gas is favorable. Consequently, the lime kilns of the mill were selected as potential carbon dioxide sources, since they have the highest concentration of carbon dioxide in the flue gases of the emission sources at the pulp mill. A 90 % capture rate of carbon dioxide from the flue gases of both kilns was assumed, corresponding to a total of approximately 230 kton/year of captured biogenic carbon dioxide, which could be used to produce 170 kton/year of bio-methanol, requiring 30 kton/year of hydrogen.

For the energy balances, two levels of specific heating demands for the carbon capture process were evaluated. As a conservative estimate, a literature value for a standard capture process using a mono-ethanolamine (MEA) absorption solvent applied to typical combustion flue gases was considered, with a heating demand of 3600 kJ/kg carbon dioxide captured. To get an estimate of potential improvements with a more optimized process design and better performing solvents, a lower specific heating demand of 2900 kJ/kg carbon dioxide captured, which has been reported for the solvent blend amino-2-methyl-1-propanol/piperazine (AMP/PZ), was also evaluated. This resulted in a heating demands of 230 GWh/year and 186 GWh/year for the higher and lower value, respectively, when capturing 90 % of the carbon dioxide from the lime kilns.

The results also indicate that the heating demand for the whole CCU concept can be covered by steam that could be made available from the mill, more specifically by bypassing the condensing turbine. However, the electricity demand for the electrolyser seems to be a more limiting factor. Production of 30 kton/year of hydrogen requires an electrolyser with a total capacity of 260 MW of electric power input, corresponding to an electricity demand of 2.2 TWh/year. This can be compared to the current electricity consumption of the whole pulp mill, which was 0.7 TWh in 2021. One possibility could be to size the capture plant for maximum (90%) capture from both lime kilns, but only use part of the captured carbon dioxide for methanol production and sell the surplus or send it to permanent storage. Thus lowering the electricity demand for production of hydrogen at site.

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List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

ADt	Air Dried Ton
AMP	Amino-2-methyl-1-propanol
AEC	Alkaline Electrolysis
BECCS	Bio Energy Carbon Capture and Storage
BECCUS	Bio Energy Carbon Capture Utilization and Storage
DMSO	Dimethyld Sulfoxide
CaO	Calcium Oxide
$CaCO_3$	Calcium Carbonate
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
FEHE	Feed Effluent Heat Exchanger
HEX	Heat Exchanger
HPC	Hot Potassium Carbonate
HT	Steam Electrolyser
HTSE	High-temperature Steam Electrolysers
LHV	Low Heating Value
LK	Lime Kiln
MEA	Monoethanolamine
MeOH	Methanol
OCC	Oxy-combustion Carbon Capture
\mathbf{PFR}	Plug-flow Reactor
PEM	Polymer Electrolyte Cell
PRTR	Pollutant Release and Transfer Register
PCC	Post-combustion Carbon Capture
PrCC	Pre-combustion Carbon Capture
PZ	Piperazine
SCMS	Södra Cell Mönsterås
TRL	Technology Readiness Level

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1 Introduction

The Swedish climate policy framework states that in 2045, the greenhouse gas emissions should be zero and thereafter net negative [1]. Carbon dioxide (CO_2) is the largest source of greenhouse gas emissions. Thus, lowering the emissions of this gas is important for reaching the goal. There are upstream solutions to reach this, such as wind power and solar power. Additionally, there are downstream solutions, such as capturing of CO_2 . Carbon capture (CC) is a technology that emerged not so many decades ago. Up until now, application of CC has primarily involved the capture and storage (CCS) of fossil CO_2 . However, if the source of CO_2 is of biogenic origin and the origin of the biomass is sustainably regulated and managed, the use of biomass is recognized as carbon neutral [2] [3]. This is due to the fact that biomass absorbs CO_2 from the atmosphere whilst going through photosynthesis. If capturing and permanently storing CO_2 emissions where the carbon originates from biomass, the process would be considered carbon negative [4], i.e., permanently removing CO_2 from the atmosphere. Instead of storing the carbon, it can be utilized for production of various products. This is called carbon capture and utilization (CCU). Capture and utilization of biogenic CO_2 , is sometimes referred to by the abbreviation BECCU, bio energy carbon capture and utilization, and BECCS if the captured CO_2 is stored.

Sweden is well positioned for both BECCU and BECCS, since there are many large CO_2 emission sources in Sweden of biogenic origin. There are many large point sources from the pulp and paper industry, as well as from heat and power plants in the district heating sector. The pulp and paper industry is by far the largest CO_2 emitting industrial sector in Sweden (if including biogenic emissions). In 2021, the industry emitted 34600 kton of CO_2 , which is equivalent to 40 % of the total CO_2 emissions of all industrial plants listed in the Swedish Pollutant Release and Transfer Register (PRTR) [5]. This includes both biogenic and fossil based CO_2 emissions, where 98 % of the emitted CO_2 from the pulp and paper sector is of biogenic origin.

In the pulp and paper industry, a lot of steam is generated in the recovery boiler and power boiler [3]. In some mills more steam is generated than what is required to cover the steam demands of the pulping process. Since carbon capture requires a lot of energy in the form of steam and/or electricity, the potential availability of excess heat in such pulp mills is a favourable condition. The largest CO_2 sources in a pulp mill are the recovery boiler, the lime kilns and the power boiler. The lime kiln typically has the highest concentration of CO_2 in the flue gases since carbon is released not only from the combustion of fuels, but also from the calcination reaction. A higher CO_2 concentration generally requires a lower specific heat demand.

At Södra Cell Mönsterås (SCMS) there are two lime kilns with high concentrations of CO_2 in the flue gases, which makes them interesting to consider for the implementation of CCU. A CCU plant at Södra Cell Mönsterås could potentially open up many possibilities for production of new biobased products, such as electrofuels produced from the biogenic CO_2 .

Today, the mill already produces bio-methanol (bio-MeOH), by upgrading of a side stream from the pulping process. This bio-MeOH is mainly sold as a bio-fuel. In 2020, SCMS started production on site, then becoming the first producers of fossil free bio-MeOH in the world [6]. The pulp mill has a capacity of producing 5250 ton of bio-MeOH per year. In 2021, 3300 ton of bio-MeOH were produced. A future opportunity could be to also produce MeOH by reacting captured CO_2 with H_2 produced via electrolysis in a CCU concept. Integration of such a new process concept could (significantly) increase the production of MeOH at the mill.

MeOH produced from captured biogenic carbon has the potential to substitute the fossil based fuels existing on the market today. In this master thesis, the possibility to integrate a CCU plant to produce bio-MeOH at the pulp mill Södra Cell Mönsterås will be investigated.

1.1 Aim and objectives

The aim of this project is to analyse the potential for CCU for production of methanol at the pulp mill Södra Cell Mönsterås (SCMS). More specifically, the aim is to investigate a CCU concept, where carbon dioxide is captured from one or both of the lime kilns at site. The captured CO_2 is then to be utilized for synthesis of MeOH by reacting the CO_2 catalytically with H_2 , produced by electrolysis on site. The objectives of the project are formulated as:

- Mapping of available CO₂ emission sources at the pulp mill
- Extraction of process data from data logs to quantify heat sources and sinks at Södra Cell Mönsterås
- Collect relevant process data for production of MeOH and estimate corresponding specific energy demand
- Calculation of energy demand for production of H_2 using mass and energy balances
- Investigation of opportunities for heat integration of the CO₂ capture process and bio-MeOH production process at the pulp mill
- Provide a general overview of the energy demand for this CCU concept for evaluation on the order of magnitude of respective process

1.2 Limitations

This master thesis focuses on giving an overview of potential CCU integration at a pulp mill. Extracted data for calculation of mass and energy balances are therefore not site specific. However, calculations of captured CO_2 , produced MeOH and H_2 are based on mill data, such as CO_2 volumes in flue gases and heat sources for potential heat integration. However, overall energy and mass balances are calculated based on assumptions about typical yields and efficiencies to get a general idea of the potential scale of all processes included in the CCU concept. Hence, no site specific modelling and simulations have been executed.

The recovery boiler emits the most CO_2 in a Kraft pulp mill and has therefore been the subject of many other articles, reports and projects. However, in this study, lime kilns are in focus since they have a higher concentration of CO_2 in the flue gas and the size of the emissions is expected to be better scaled against reasonable sizes for the electrolyzer unit and demand for methanol. Therefore, estimations for capture from the flue gases of the bark boiler and recovery boiler have not been performed.

For the mass and heat balance estimations, only the most mature technology options for which performance data is publicly available in literature is considered. The CO_2 capture technology chosen for this master thesis is therefore the chemical absorption method with either monoethanolamine (MEA) or AMP/PZ (amino-2methyl-1-propanol and piperazine) as absorption solvent. Other amines, which could be used as solvents, such as AMP/DMSO (dimethyl sulfoxide) are not evaluated but described briefly, as well as capture using the hot potassium carbonate (HPC) process and membrane based technologies. Since MEA is a well-studied chemical solvent with plenty of data publicly available, it is the main solvent assumed in this thesis, and a literature value for MEA absorption applied to typical combustion flue gases was assumed. However, other solvents have been shown to have better performance, in particular when combined with more optimized process designs, applied to flue gases with higher CO_2 concentrations such as the flue gases from the lime kiln. The MEA assumption can therefore be considered a conservative estimate of the heating requirements needed for capture. To illustrate the potential of more advanced solvents, and optimized process designs in the pulp mill application, a value reported for AMP/PZ in industrial capture applications is assumed as a second scenario for the estimation of heating and cooling demands for capture. However, technologies in early development phases will not be included in the report and therefore not be further examined. Furthermore, possible future modifications of the pulp mill process (beyond the assessed CCU concept) will not be considered.

Potential effects on cooling demands have not been of focus in this study. instead the integration of heating demand has been prioritized. Lastly, calculated values for site specific data are retrieved from the internal system INFOPLAN and based on the energy report from 2021. Seasonal variations have therefore not been included as a result or a topic of discussion. Instead the year of 2021 is the foundation for all results.

Additionally, an evaluation of economic feasibility and cost estimates is not included in this thesis. As well as a plant foot-print of the CCU concept, although it is an interesting topic for future evaluation.

Background

This chapter provides a concise background about the pulp and paper industry, as well as a description of the most common pulping method in Sweden, kraft pulping, also known as sulfate pulping. The pulp production process is introduced and the so called recovery cycle is explained. The recovery cycle contains three major sections: evaporation, recovery boiler and the causticization. The latter will be explained more thoroughly.

A key component of the causticizing process is the lime kiln. An introduction to the lime kilns and the potential of capturing CO_2 from their flue gases are also presented in this chapter, as well as different carbon capture technologies relevant for this purpose. Three companies providing carbon capture facilities will also be introduced. The last section of the background chapter introduces the subject of production of electro-MeOH.

2.1 Pulp and Paper Industry

The pulp and paper industry is a big industry in Sweden. According to the Swedish pollutant release and transfer register (PRTR) (2021) [5] paper and wood production and processing can be divided into subgroups of different industrial plants and production:

- Pulp from timber or similar fibrous materials
- Paper and board and other primary wood products
- Preservation of wood and wood products with chemicals

If a mill produces both pulp and paper on the same site, it is called an integrated pulp and paper mill. However, if the plant produce paper pulp only it is known as a stand-alone, or market pulp mill. Today there are 39 stand-alone pulp mills in Sweden producing pulp mechanically and chemically [7]. Mechanical pulping uses mechanical force to release cellulose fibres from the wood, whereas chemical pulping relies on chemicals to release the fibres. In this master thesis chemical pulping will be targeted, more specifically sulfate pulping.

2.1.1 Sulfate Pulping

Kraft pulping, also known as sulfate pulping, is the most common chemical pulp production method globally, as well as in Sweden, followed by other chemical and mechanical pulping methods [7][8]. The main purpose of the kraft cooking process, is to remove lignin from the wood material. Lignin makes up around 20-30 % of the chemical composition of different wood species [9]. The extraction of lignin is done by dissolution and this is possible due to chemical fragmentation that makes the lignin soluble. In Figure 2.1 an overview of a general chemical pulping plant is presented.



Figure 2.1: General blueprint of a paper and pulp mill [10].

To the left in Figure 2.1, the wood handling part of the process can be seen. At this part of the process, the wood is debarked and chipped. After the logs have been chipped, the wood chips are sent to an intermediate storage. The chips are then transferred to the digester. In the digester the wood chips are steamed and impregnated with white liquor that consists of sodium hydroxide (NaOH) and sodium sulphide (Na₂S). After the digester, the produced pulp is washed. After washing of the produced pulp, a mix of washing water, spent cooking chemicals and non-cellulosic components of the wood (mainly lignin), which is called black liquor, is obtained and sent to the chemical recovery cycle.

After the washing, the pulp is screened to detect any remaining lignin. Depending on the lignin content of the pulp, some is washed again. After the screening, oxygen delignification takes place, where most of the remaining lignin in the pulp is removed before it enters the bleaching plant and then is dried.

2.1.2 Chemical Recovery

In the chemical recovery cycle, the main purpose is to recover cooking chemicals from the black liquor and generate energy in the form of steam by combusting organic components (mainly lignin) in the black liquor. In Figure 2.2, a simplified overview of the chemical recovery process is presented.



Figure 2.2: An overview of a chemical recovery cycle at a paper and pulp mill.

The black liquor from the digester consists of lignin, aliphatic carboxylic acids, other organics and inorganics substances. These components originates from the spent cooking chemicals and the pars of the wood raw material that does not end up in the fibre line [8]. After the digester, the so called thin black liquor enters the evaporation plant, where large amounts of water are evaporated. The black liquor is then concentrated to a thick black liquor. The concentrated black liquor is fed into the recovery boiler where the organic components are combusted and steam is generated. In addition, sodium and sulfur is recovered. The chemicals form a smelt (of mainly Na₂S) in the bottom of the recovery boiler. From there, the smelt enters the smelt dissolver where green liquor is produced, containing many different salts, such as Na₂S, NaCl and Na₂CO₃. The green liquor then enters the the causticization vessels, where it reacts with calcium oxide (CaO) to produce white liquor and CaCO₃ (slaked lime), according to reaction 2.1 and 2.2.

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$
 (2.1)

$$Na_2CO_3(aq) + Ca(OH)_2 \rightarrow CaCO_3(s) + NaOH(aq)$$
 (2.2)

The white liquor, consisting of NaOH and Na₂S, is sent back to the digester. Both reactions are exothermic, $\Delta H = -64.5 \text{ kJ/mol}$ and $\Delta H = -5.3 \text{ kJ/mol}$ [11] respectively,

and the heat produced is recovered in the cooking process [12] [13]. The slaked lime on the other hand, is sent to the lime kiln where the lime is reburnt and CaO (burnt lime) is regenerated. See reaction 2.3.

$$CaCO_3(s) \to CaO(s) + CO_2(g)$$
 (2.3)

The burning of CaCO₃ is an endothermic reaction and requires a heat input of $\Delta H = 179.2 kJ/mol$ [11]. This heat is generated by combustion of different fuels, such as fossil based oil, bio based oil (such as tall pitch oil) or/and biomass (such as powdered bark). The reburning of CaCO₃ can be divided into four steps from beginning to end in the rotating lime kiln [8]:

- Drying of CaCO₃
- Heating of CaCO₃ to a temperature suitable for calcination
- Calcination of CaCO₃
- Sintering of the produced *CaO*

These four steps varies with temperature from where the $CaCO_3$ enters in the drying zone, to where the wanted product CaO leaves the kiln from the sintering zone. The temperature in the drying zone varies between 200-600°C and the heating zone around 600-1000°C. Additionally, the wanted calcination process occurs at around 1200°C [14]. See Figure 2.3 for an illustration of the temperature zones in a lime kiln.



Figure 2.3: Illustration of lime kiln and the four different zones. Figure adapted from Gellersted et. al [8].

The temperature of the lime varies from around 100°C in the drying zone, between 100-800°C in the heating zone, followed by around 850°C in the calcination zone and reaches it highest temperature around 1200°C in the middle of the sintering zone [8].

2.2 Carbon Capture

There are three principally different methods for carbon capture, post-combustion carbon capture (PCC), pre-combustion carbon capture (PrCC) and oxy-combustion carbon capture (OCC) [2][15][4]. Previous studies have shown that PCC is the best choice of method when the CCS/CCU plant is to be retrofitted into an already existing process, since it does not require any modifications of the boilers [16][2]. Thus, PCC is the only method considered in this master thesis.

PCC can be divided into different sub-classes, where CC with chemical absorption is acknowledged as the most common method today [2]. Consequently, only absorption solvent-based methods are elaborated on in this project. The methods depend on a reaction between CO_2 and the absorption solvent of choice. Solvents that are frequently studied or used are hot potassium carbonate (HPC), amino-2-methyl-1-propanol/piperazine (AMP/PZ), amino-2-methyl-1-propanol/ dimethyl sulfoxide (AMP/DMSO) and mono-ethanolamine (MEA).

For the energy balance estimations in this thesis, values for heating and cooling demands were chosen that have reported for MEA and AMP/PZ. MEA is a well studied solvent with performance data easily available, but could be seen as a conservative estimate of potential performance. Lower heating requirements reported for AMP/PZ are therefore also evaluated to get an indication of what could be achieved with a more advanced solvent.

Since MEA, AMP/PZ and AMP/DMSO are all amine-based chemical absorption methods, the principal function of the processes are similar. Thus, only the MEA based capture will be introduced in more detail and the latter two more briefly.

2.2.1 MEA

Mono-ethanolamine (MEA) is an amine based absorption and is one of the most studied chemical absorption techniques for carbon capture today. Compared to the HPC process that relies on a pressure swing, the MEA process depends on a temperature swing where CO_2 is captured at a low temperature and released at a higher temperature [17]. In Figure 2.4 an illustration of the MEA process is visualised.



Figure 2.4: An overview of a commercial chemical absorption process with MEA as an absorption agent. Based on a model by Onarheim et al. [3] and Wang et al. [18].

Prior to being fed into the absorber, the flue gas is quenched and cooled in a direct contact cooler (DCC) by use of cooling water [3]. The flue gas enters the absorption tower at the bottom, at around 40°C and at atmospheric pressure [3][19]. The MEA solvent is fed into the top of the absorber, where it absorbs CO_2 . The rich MEA solvent containing absorbed CO_2 leaves the absorber at the bottom and is heated in a heat exchange with lean solvent. Thereafter it is fed into the top of the desorber. Inside the desorber, heat is added from the reboiler at the bottom of the desorber. The heat duty of the reboiler is typically around 3600-4000 kJ/kg CO_2 [20] [21], but the duty depends on, e.g. inlet CO_2 concentration of the flue gases and temperature level of the reboiler and can have a reduced reboiler duty of around 3.0 GJ/ton CO_2 [22]. However, in this thesis a higher reboiler duty is assumed to gain an overview of the heating demand of the CCU process.

A low pressure steam is commonly used for heating, where temperature ranges from $120^{\circ}\text{C}-160^{\circ}\text{C}$ [3][19][20]. The heat drives the solvent to release the CO₂. The released CO₂ exits the stripper at the top and is thereafter condensed and sent either to liquefaction, further pressurization, or utilised for something else. Condensation of CO₂ from a capture process that uses MEA requires approximately 4.1 GJ cooling per ton CO₂. The lean absorption solvent leaves the stripper and is regenerated in the reboiler, thereafter enters the lean-rich heat exchanger before it is fed into the absorber again. The reboiler can regenerate certain amount of absorption agent, however some additional solvent make-up might be required du to solvent degradation, which is fed at the top of the absorber make up MEA is added.

2.2.2 AMP/PZ

Compared to MEA, AMP/PZ is an non-aqueous chemical absorption solvent. The methods resemble that of MEA as an absorption solvent, but studies have shown that AMP/PZ are likely to offer better performances in terms of lower specific heat requirements and lower temperature demands for the heat for regeneration [23] [24]. For example, AMP/PZ has been shown to have a cooling demand around 4.0 GJ/ton CO_2 and a heating demand of around 3.0 GJ/ton CO_2 [24] [22] for typical industrial capture applications, which is significantly lower than for MEA.

2.2.3 AMP/DMSO

AMP/DMSO is also a non-aqueous solution solvent for CO_2 capture with absorption. AMP/DMSO has mainly been studied at lab-scale, so performance data for industrial scale operation is not yet known. However, studies have shown that it would enable significantly lower regeneration temperatures, and the first pilot plant trials have recently been started up by Växjö Energi [25].

2.2.4 HPC

The potassium carbonate (HPC or K_2CO_3) method resembles the other chemical absorption techniques already mentioned. However, before the flue gas enters the CC plant, the gas is compressed. The flue gas is compressed to approximately 15 bar and 110°C [17]. The compressor is generally driven by electricity, hence the high electricity demand of around 0.7 GJ/ton CO₂ [26]. By increasing the pressure and temperature, the hot potassium solvent absorbs CO₂ and H₂O from the flue gases and forms bicarbonate (HCO₃⁻¹) in the absorber [19]. The bicarbonate is then fed into the desorber where it is reversed back into HPC, CO₂ and H₂O [27] at lower pressures. HPC is fed back into the absorber. After the desorber, the CO₂ is cooled and compressed.



Figure 2.5: An illustration of a hot potassium based carbon capture process, based on figure from Hammar (2022) [28].

The method enables usage of high temperature steam, suitable for heat and power plants, where the temperature demand reaches correct levels. However, since it is a process relying on a large amount of electricity, it would influence the net electricity production. Additionally, if the flue gases contains H_2S , the hot potassium solvent will react with it and hinder the absorption of CO_2 and increase the demand for HPC make-up [19].

2.3 MeOH Production

MeOH can be produced from natural gas, from biomass or from captured CO_2 reacting with H_2 . For production of MeOH with H_2 and CO_2 in a CCU concept, water and a large amounts of energy, in the form of heat and especially electricity (for hydrogen production via electrolysis), is needed. For an overview of the process, see Figure 2.6. The production of MeOH consists of a few steps and has four key components:

- An electrolyser for production of H_2
- (A H₂ storage unit)
- A CO_2 capture plant (see Section 2.2) and a
- A MeOH synthesis plant



Figure 2.6: A simplified flow sheet of an electro-fuel MeOH production process. Figure adapted from Jannasch et al. [29].

2.3.1 Water Electrolysis

One way of producing H₂ is by splitting H₂O through water electrolysis. The electrochemical reaction (Reaction 2.4) is endothermic and requires a high input of energy, in the form of electricity (Δ H=237 kJ/mol) and heat (Δ H = 49 kJ/mol).

$$H_2O(l) \to H_2(g) + 0.5O_2(g)$$
 (2.4)

Due to losses, significant shares of energy provided to the electrolysers require cooling. H_2 is an extremely flammable gas with a high energy content which makes the storage difficult [30]. Kuparinen (2019) [30] therefore argues that the electrolysers for production of H_2 ought to be located adjacent to the MeOH synthesis production. This to remove the need for storage and operate the electrolysers continuously.

There are currently a few different technologies for water electrolysis. Alkaline electrolysis (AEC), high temperature steam electrolysis (HTSE) and polymer electrolyte membrane electrolysis (PEM) are the most well-known technologies [29] [31]. All three technologies differ with regards to, for example, electrode materials, electrolyte solution, operating temperature, energy-to-hydrogen efficiencies, and technology readiness level (TRL).

2.3.1.1 AEC

AEC is the most used technology today. The electrolysers usually requires around $4.1-4.3 \text{ kWh/Nm}^3$ [32] of electricity at an approximate temperature around 60-90°C

[29]. Alkaline electrolysers have an energy-to-hydrogen efficiency around 60-70%. AEC has been on the market for a long time, and is thus a mature method.

2.3.1.2 HTSE

High temperature steam electrolysers (HTSE) operate at high temperatures around 400-800°C to split H₂O, thus consuming less electricity, but more high-temperature heat[31]. It is a technology with a potential electricity-to-hydrogen efficiency of around 90 %, with heat requirements of 2.6-3 kWh/Nm³ [33]. However, since HTSE uses steam as a feed material at such high temperatures, it is an option for H₂ production. However, since both PEM and AEC are two methods with a lot of commercial data available, HTSE is not the chosen method of water electrolysis for this project.

2.3.1.3 PEM

The polymer electrolyte cell (PEM) technology has the advantage of being the most dynamic technology with a short start-up time (a few seconds) and a wide operating range. Additionally, the electrolysers generally operate at a temperatures around 50-80°C [29]. A disadvantage with the technology is that it has not been on the market for as long as AEC. According to Jannasch et al. [29], the energy-to-hydrogen efficiency (on an LHV basis) is around 70%, which is similar to alkaline electrolysers. The specific energy consumption is around 4.75 kW/Nm³ according to Chi et al. [34]. The PEM technology will be assumed for estimation of the scale of the electrolyzers and their electricity demand, for the H₂ needed for production of MeOH in this project.

In PEM water electrolysis, water is fed to the anode, where H_2O is split into O_2 , protons (H⁺) and electrons (e⁻), according to reaction 2.5.

$$H_2 O \to 2H^+ + 0.5O_2 + 2e^-$$
 (2.5)

The protons moves through the membrane. At the cathode side, $2H^+$ and $2e^-$ re-attaches and forms H₂, as presented in reaction 2.6.

$$2H^+ + 2e^- \to H_2,$$
 (2.6)

2.3.2 MeOH Synthesis

MeOH is usually produced from syngas. But it can also be produced in a one-step process, where CO_2 is hydrogenated directly, as assumed in this project. Typical operation temperatures range between 200-300°C and the pressure between 30-50 bar, see equation 2.7 for the one-step reaction [29]. MeOH synthesis requires an input of heat and electricity, but some heat integraton is also possible within the process, where heat generated in the synthesis reactor can cover part of the heating demand for the downstream separation.

$$CO_2 + 3H_2 \to CH_3OH + H_2O \tag{2.7}$$

The reaction is exothermic ΔH =-49.16 kJ/mol [35] and the energy conversion efficiency for MeOH synthesis is generally between 70-80% (LHV) [29]. In Figure 2.7 an overview of a process for production of MeOH from H₂ and CO₂ is presented.



Figure 2.7: An overview of methanol production. Figure adapted from Kiss et al. [36].

The methanol process as described by Kiss et al. [36] and shown in Figure 2.7 is the production process assumed for the calculations for MeOH synthesis in this report. The process begins by mixing a feed stream of CO_2 with recycled stream from the recycle compressor. The mixed stream is fed to a feed-effluent-heat-exchanger (FEHE). In the FEHE, the gas mix is heated by the reactor outlet stream before being fed into a plug-flow reactor (PFR). The PFR is assumed to operate isothermically and the reaction is exothermic.

After cooling, the reactor outlet stream is flashed to separate the MeOH and water from the non-condensing gas components. The gas stream is compressed and recycled to the reactor. The liquid stream is fed into a desorption tower, where compressed wet H_2 feed stream is fed in the opposite direction compared to the liquid stream. This leads to a drying of the H_2 stream, which will be mixed with the recycled gas stream and fed to the reactor. The stream exiting from the bottom of the desorber (the liquid stream), is fed into a distillation tower, where H_2O and MeOH is separated.

2.4 Carbon Capture Suppliers

Today, there are equipment suppliers, which provide different carbon capture technologies. Three companies located in Norway and Sweden have been approached in this project: Aker Carbon Capture, Ocean Geoloop and Aqualung. The enterprises offer different technologies, for which an overview of energy consumption, disadvantages, advantages and current state of technology are presented in Table 2.1. The information was collected through interviews with the equipment suppliers.

Enterprise	Aker Carbon Capture [37]	Ocean Geoloop[38]	Aqualung [39]	
Technology	Amine absorption (ACCTM)	Amine free absorption	Membrane	
Energy needed	Heat	Electricity	Electricity	
Energy consumption	1000 kWh/ton CO_2	500 kWh/ton CO_2	200 kWh/ton CO_2	
Advantages	Provides a solvent (MEA-blend) with a low degredation compared to a MEA-based absorption. Less emissions than conventional amine scrubbing	Provides a possibility to capture CO ₂ from low levels of concentration of CO ₂ . Flexible and stable operations with poss- ibility to turn off and	Low sensitivity for Nox emissions. Functional for a broad variety of CO_2 concentration in flue	
Disadvantages	Sensitive towards high sulfur and Nox concentration in flue gas. Not optimal for low concentration of CO ₂ in flue gas.	on operation High electricity demand.	gas. High amounts of upkeep since membranes need to be constantly wet. Therefore a water dependent technology.	
Current state of technology	Pilot plant was successfully in operation 2020 at Preem Refinery working with SINTEF, Chalmers and Equintor.	Facility currently being installed at Nordkalk with SigmaRoc. Estimated to be in operation this year.	Pilot plant in operation in Arizona, America.	
Capacity of facilities	Plant in Lysekil will have a capture capacity of 600 kt CO ₂ /year.	Catch and release pilot with an aim of capturing $2000 \text{ ton } \text{CO}_2/\text{year}.$	Catch and release pilot with an aim of capturing 500 ton CO_2 /year.	

 Table 2.1: A selection of suppliers offering different carbon capture technologies.

Ocean Geoloop and Aqualung use alternative methods to the more well-known amine-based absorption methods. Membrane separation is used by Aqualung and non-amine absorption are used by Ocean Geoloop, as can be seen in Table 2.1. There are two types of membrane capture technologies: gas separation and gas absorption membranes. Aqualung utilises a technique by membrane absorption of CO_2 [39]. The company uses a patented absorbing coating on the membrane. Membrane absorption utilises a micro porous membrane, where flue gas enters one side of the membrane and the absorbent on the other side. Capturing the CO_2 in the through the membrane [2]. Ocean Geoloop operates with an amine free absorption method. Absorption with aqueous ammonia is an example of such amine free absorption solvent [38].

3

Case Study

This section presents an introduction to the studied pulp mill, Södra Cell Mönsterås (SCMS). It provides an overview of the CO_2 emissions from the mill, internally produced fuel and external fuel imported with CO_2 emission factors. Followed by an overview of the mill's steam system, particularly the condensing turbine (the largest electricity producer at the pulp mill).

3.1 Södra Cell Mönsterås

The pulp mill Södra Cell Mönsterås has been in operation since 1958 [40]. Today, the pulp mill has a capacity of producing 750 kton pulp per year. As can be seen in table 3.1, around 700 kton of pulp was produced at the mill in 2021. In Sweden the same year, a total of around 12 million tons of paper pulp was produced [7].

Table 3.1:	Produced	pulp	at	Södra	Cell	Mönsterås	in	2021.
------------	----------	------	---------------------	-------	------	-----------	----	-------

Hardwood	Softwood	Total	Share of hardwood	Share of softwood
[ton]	[ton]	[ton]	based pulp [%]	based pulp [%]
113700	586100	699600	16	84

Softwoods are the most common wood species in Sweden, with spruce and pine representing 80 % of the total share [7]. This also applies for southern Sweden, where the mills owned by Södra are located. In 2021, a vast majority of the pulp produced at Södra Cell Mönsterås was made from softwood, with a share of 84 %. The pulping method used at the pulp mill is the kraft process. In addition to pulp, the pulp mill also produces bio-MeOH as a byproduct, as mentioned in the introduction in chapter 1.

3.2 Carbon Dioxide Emissions at Södra Cell Mönsterås

In 2021, Södra Cell Mönsterås emitted around 1760 kton of biogenic CO_2 . The CO_2 emissions over the past 8 years at Södra Cell Mönsterås are presented in Table 3.2. Overall, 99 % of the CO_2 emissions at the mill are of biogenic origin.

Year	Amount	Unit	Amount	Unit
2014	1801	[kton/year]	4.9	[kton/day]
2015	1850	[kton/year]	5.1	[kton/day]
1016	1811	[kton/year]	5.0	[kton/day]
2017	1900	[kton/year]	5.2	[kton/day]
2018	1727	[kton/year]	4.7	[kton/day]
2019	1894	[kton/year]	5.2	[kton/day]
2020	1866	[kton/year]	5.1	[kton/day]
2021	1762	[kton/year]	4.8	[kton/day]

Table 3.2: CO_2 emitted at Södra Cell Mönsterås over the past 8 years [5].

3.3 Internal and External Fuels

The fuels used at Södra Cell Mönsterås are both from internal and external sources. In Table 3.3 and 3.4, the internal and external fuels are presented, including the emission factor for each fuel and ton of CO_2 emitted in 2021.

External	Emission	\mathbf{Unit}	\mathbf{CO}_2 emissions
fuels	factor		$[ton CO_2/year]$
Bark	96.0	[ton CO2/TJ]	97 300
E01	74.3	[ton CO2/TJ]	880
E03	76.2	[ton CO2/TJ]	9 300
LPG	65.1	[ton CO2/TJ]	5
Paraffin oil	3.10	[ton CO2/ton]	180
Bio oil	75.3	[ton CO2/TJ]	47 400
Alva mix	155	[ton CO2/TJ]	32 600
Formate	0.80	[ton CO2/ton]	1 000
Lime	0.40	[ton CO2/ton]	50
Polymer	1.70	[ton CO2/ton]	140
Foam damper	0.30	[ton CO2/ton]	40

Table 3.3: External fuels used in the pulp mill process and CO₂ emissions yielded.

Table 3.4: Internal fuels used in the pulp mill process and CO₂ emissions yielded.

Internal	Emission factor	\mathbf{CO}_2 emission
fuels	$[\mathrm{ton}~\mathrm{CO}_2/\mathrm{TJ}]$	$[\mathrm{ton}\ \mathrm{CO}_2/\mathrm{year}]$
Black liquor	96.0	1450 000
Solid biofuels	96.0	$221\ 000$
Tall oil	75.3	1 300
Bio sludge	78.0	3 400
Methanol	65.5	3 800

The largest emissions of CO_2 originate from the the black liquor and solid bio fuels. In the recovery boiler, almost 100 % of the fuel combusted is black liquor, derived from the digester. Apart from that, alvamix and bio sludge are combusted in smaller amounts. In the bark boiler, approximately 95 % of the combusted fuel is solid wood fuels and bark, 2 % is fuel oil (EO3) and 3 % process and fiber sludge.

Bio oil (tall oil pitch) and powdered bark are the main fuels combusted in the lime kilns at Södra Cell Mönsterås, corresponding to approximately 45 % of the CO_2 emitted in each kiln respectively. In addition to that, low volumes of EO3 and MeOH are combusted. The remaining 55 % CO_2 emission are produced during the calcination process in the lime kilns.

3.4 Overview of the Steam System

The pulp mill is self-sufficient in energy supply from the wood raw material. The recovery and bark boilers are two sources where heat is recovered. The steam from the recovery boiler and bark boiler reaches temperatures around 500°C at a pressure of approximately 60 bar. This steam is processed and converted to electrical energy and thermal energy is recovered.

The steam is expanded in four different turbines G3, G4, G5 and G6, see Figure 3.1, where G3, G4 and G5 are back-pressure turbines and G6 a condensing turbine. In the back-pressure turbines, the (super heated) high pressure steam is expanded to intermediate and low pressure steam ranging from 26 bar to 3 bar, thereby generating electricity, as can be seen in Figure 3.1. The different pressure steams are consumed in different sections of the pulp mill. In 2021, the pulp mill consumed a total of 4000 GWh of steam.



Figure 3.1: A detailed overview of the steam system of Södra Cell Mönsterås, visualized with the back pressure turbines G3, G4, G5 and the condensing turbine G6.

The 26 bar steam, around 260 $^{\circ}\mathrm{C}$ is, as an example consumed by the recovery boiler and 5 bar steam is consumed by the drying section. Both lime kilns consume 11 bar steam for drying of the flue gases.

In contrast to the back-pressure turbines, the condensing turbine is used for electricity generation only. In 2021, G6 consumed approximately 910 GWh steam, and produced 315 MWh of electricity. However, as can be seen in Figure 3.1, the turbine G6 has a steam extraction at 1.5 bar. This is since the condensing turbine was built to also recover 1.5 bar steam at around 145°C for usage internally [41], but this is not in operation today.

4

Methodology, input data and assumptions

This section is intended to give an overview of the work procedure of the project. The description starts with the first part of the project, the evaluation of carbon capture (CC) technologies in terms of advantages and disadvantages of carbon capture technologies offered by equipment suppliers in Sweden and Norway today. Thereafter, CO₂ emission sources at the pulp mill were identified and characterized. Heat and energy balances were established to calculate site specific requirements for electricity, heating and cooling for a CC plant targeting the flue gases from the mill's lime kilns. After the evaluation of the CC process, the production of H₂ and MeOH was evaluated in a similar way. Lastly, potential heat integration of CC and MeOH production at Södra Cell Mönsterås was investigated and different heat sources identified and compared.

4.1 Inventory of technology and process performance characteristics

The project was initiated by a preparation phase. Reading and researching the area of pulp and paper production and industry. Communication with pulp mill staff was also carried out where site specific questions were asked and answered regarding the pulping process, calcination cycle and the steam system at Södra Cell Mönsterås.

As part of the work with this thesis, different carbon capture suppliers have been contacted and three meetings with various companies were held. During these meetings, an introduction of this master thesis was held briefly, followed by an introduction by the company representative.

4.2 Mapping of emission sources at Södra Cell Mönsterås

Secondly, CO_2 emissions at Södra Cell Mönsterås section were mapped and characterized. Data for this, was collected from the internal system, INFOPLAN, and from the energy report of 2021 from the pulp mill. All data was taken to represent data for 2021. For calculation of CO_2 emissions and concentrations from both lime kiln 1 and 2, data from INFOPLAN was collected.

 CO_2 emissions from the different fuels combusted in the lime kilns, were calculated based on the energy content of fuel consumed and the emission factor (presented in Table 3.4 and 3.3) of respective fuel, see Table 4.1,

Fuel used	Lime kiln 1	Lime kiln 2	Total energy usage
ruei used	[MWh/year]	[MWh/year]	[MWh/year]
EO3	4 200	2 100	6 300
Tall oil pitch	120000	58000	170000
MeOH	500	200	700
Powdered bark	120000	56000	170000
Tall oil	3 200	1 600	4 800

Table 4.1: Fuels consumed in lime kiln 1 and 2.

The distribution of fuels between lime kiln 1 and lime kiln 2 in Table 4.1 was estimated based on the relative dimensions of the two lime kilns. The length, diameter and volume of both lime kilns are presented in Table 4.2.

 Table 4.2: Dimensions of both lime kilns and share of energy usage.

Lime kiln	Length [m]	Diameter [m]	Volume $[m^3]$	Share of fuel [%]
Lime kiln 1	106	3.8	1 200	67
Lime kiln 2	70	3.3	600	33

 CO_2 emissions from the calcination process was calculated by mass balances of produced CaO from $CaCO_3$, with an assumption of a 100 % conversion rate, this since no other value was retrieved from internal systems. See values presented in Table 4.3 for calculation of CO_2 emissions from both kilns. 355 days of operation in 2021 was assumed.

Table 4.3: Parameters for calculation of CO2 emissions from lime kiln 1 ar	d 2.
--	------

Lime kiln	CaO produced [ton/day]	Volumetric flow flue gas (wet) $[Nm^3/s]$	Temperature flue gas [°C]
Lime kiln 1	350	17	250
Lime kiln 2	190	8	215

By calculation of the volumetric flow of CO_2 and given measurements of total volumetric flow rates of the flue gases, the concentration of CO_2 in the flue gases was calculated, assuming the total flue gas flow as measured as wet flow.

To evaluate the feasibility in the calculated values, a dry volumetric flow of CO_2 was calculated with an assumption of a 29 % H₂O concentration in the flue gas of both lime kilns. According to Onarheim et. al [3], a typical concentration of H₂O content

of in flue gas from lime kiln is 30.9. In a feasibility study by Stora Enso AB [19], a dry CO_2 concentration varies between 20-28 % with a H₂O conent of 28 %. In order to evaluate and compare these values with the values calculated, an assumption of a H₂O concentration of 28 % was used to calculate the CO_2 concentrations in the flue gases on dry basis.

 CO_2 emissions from the recovery boiler and power boiler was calculated similarly as the lime kiln, based on fuel usage and energy content for comparison. The concentration of CO_2 in the flue gases were not calculated from the bark and recovery boiler.

4.3 Carbon Capture

Thereafter, investigation of different carbon capture technologies was carried out. From the mapping of available CO_2 flows as mentioned in 4.2, different CO_2 capture volumes corresponding to varying capture rates were calculated. Values for specific heating and cooling demands per ton captured CO_2 were extracted from literature. In Table 4.4, specific heating and cooling demands that have been reported for MEA (30 wet-%) and AMP/PZ (approximately 33 wet-% AMP and 12 wet-% PZ [22]) solvents are presented. In reality, the heating and cooling demands depend on process specific conditions such as flue gas CO_2 concentration and reboiler temperature. Since the concentration of CO_2 in the flue gases of the lime kilns is relatively high (due to process-related emissions from the calcination reaction), specific heat requirements are expected to be lower than the typical values (representing normal combustion-related emissions) reported in Table 4.4. However, in this study, the literature values were used, without any adjustment, to estimate the demand for heat needed to cover the reboiler duty in the CC process.

Table 4.4: Specific energy demand from literature for MEA and AMP/PZ as chemical absorbents for carbon capture.

Specific energy demand	MEA	AMP/PZ	Reference
Heating $[GJ/ton CO_2]$	3.6	2.9	[21][24]
Cooling $[GJ/ton CO_2]$	4.1	4.0	[24]

In this master thesis, the cooling demand is assumed not to be a limiting factor, with various cooling systems at disposal, including water from the local river, Emån, as well as cooling towers at the pulp mill. However, the cooling demand can potentially be a limiting factor and should be further investigated.

4.4 MeOH Production

Section 4.4.2 and 4.4.1 provides assumptions and values used for calculations of MeOH production with CO_2 and H_2 as feedstock. Additionally, collected data for

energy and heating demand calculations are presented. The production is based on mass balances over Reaction 2.7 and 2.4, where the reactions are assumed to occur consecutively.

4.4.1 MeOH Synthesis

The potential production of MeOH from a given flow of CO_2 , and the corresponding amount of water produced, were estimated by mass balances over the methanol synthesis reaction according to Reaction 2.7. According to Lande [38], 140 kton of CO_2 can produce approximately 100 kton of MeOH. In a feasibility study by RISE [29], mentioned in section 5.1, 133 kton CO_2 produces approximately 97 kton of MeOH. According to the same study, a conversion rate of 99 % can be assumed. However, in this thesis a 100 % conversion rate is assumed since the difference is minimal. Other assumptions based on the feasibility study by RISE, 2019 [29] are here presented:

- An excess of 5 % H₂ is necessary
- All produced heat in the reactor, where MeOH synthesising occurs, visible in Figure 2.7 is used to cover part of heating demand in the reboiler
- Additionally heat required is covered by excess heat from pulp mill
- Heat leaving with the cooling water is wasted energy

These assumptions, as well as values from Kiss et. al [36] in Table 4.5, were used to calculate the energy consumption (heating and cooling demand) for the MeOH production. In Kiss et. al [36], calculations were based on a production of 100 kton/year of MeOH and calculations of energy demand were scaled based on this.

Table 4.5: Key energy performance data for a 100 ktron MeOH production plant, based on Kiss et. al [36].

Parameter	Value	Unit
Heat generated in reactor	-4450	[kW]
Heat duty of reboiler (disstilation boiler)	7620	[kW]
Electricity usage (per ton MeOH)	550	[kWh/ton MeOH]

4.4.2 Electrolyis

The required production of H_2 was estimated based on to the H_2 demand for MeOH production, with an assumption as stated in the study by RISE (2019), an excess of 5 % of H_2 , as mentioned in 4.4.1. The technology assumed in this master thesis is PEM, as mentioned in Section 2.3.1.3. Table 4.6 presents values used for calculations of electricity demand for the electrolyser and water demand for the required amount of H_2 . There are different specific electricity consumption values presented in Table 4.6. These represent different scenario assumptions about the electricity demand, due to uncertainties in this value.

Parameter	Value	Unit	Source
Total specific	4 5	$[kWh/Nm^3]$	[34]
energy consumption	1.0		
Total specific	4.75	$[kWh/Nm^3]$	[42]
energy consumption		L / J	
energy consumption	5.5	$[kWh/Nm^3]$	[34]
Evaporation of			
charged water	5.0	[%]	[29]
charges mater			

Table 4.6: Values used for calculations of electricity demand of hydrogen production, along with H_2O demand with PEM.

4.5 Heat Integration

Heat integration possibilities at the pulp mill were investigated. Steam from the condensing turbine (G6) and excess heat from flue gases from both lime kilns and the recovery boiler were considered. For calculation of potential heat integration from the flue gas from lime kiln 1 and 2, a $\Delta T_{min} = 10^{\circ}$ C was assumed with a T_{target} of 140°C. Although, to cover the reboiler duty, a requirement of a temperature around 120°C is necessary, a temperature of 140°C was assumed to be a good temperature. This to avoid unwanted condensation and avoid precipitation of unwanted substances from the flue gas. For calculation of available heat recovery, data, presented in Table 4.7, were extracted. More specifically, the supply temperature, target temperature, mass flow rate of the flue gas and the specific heat capacities.

Table 4.7: Potential recovered heat from flue gases emitted from lime kiln 1 and 2 with a $\Delta T_{min} = 10$ °C.

Lime kiln	\mathbf{T}_{in} [°C]	\mathbf{T}_{target} [°C]	$\mathbf{F} \ [\mathbf{Nm}^3/s]$	F [kg/s]	$\mathbf{C}_p \; (\mathbf{kJ/kg} \; \mathbf{K})$
Lime kiln 1	250	145	17	15	1.02
Lime kiln 2	270	145	8	7	1.02

The specific heat capacity (C_p) for the flue gas was assumed to be equal to the C_p value of air. Available heat from the recovery boiler was retrieved from the master thesis written and executed by Mauhmoud and Nihlmark [43] and is presented in Section 5.4.

For estimation of potential excess steam that could be extracted from turbine G6, it was assumed that steam could be extracted from the turbine at low pressure (3 bar) instead of being expanded all they way to the turbine condenser. The potential extraction of 3 bar steam was estimated by taking the total steam consumption in G6 minus the energy used for power generation when the steam expands from high pressure (60 bar) to low pressure (3 bar). This calculation was highly simplified to get an overview of potential heat integration. In 2021 the steam consumption in G6 was 900 GWh with a steam flow rate of 39.7 kg/s. The temperature of the steam in

 (T_{in}) to the turbine was 475°C and the temperature at the low pressure (LP) steam header at the pulp mill is around 160 °C. See given values in Table 4.8 utilised for calculations.

Table 4.8: Parameters for calculation of steam production between 60 to 3 barprocessed in the steam turbine.

Unit	Turbine inlet	Assumed turbine	\mathbf{F}
	pressure [bar]	extraction pressure [bar]	[kg/s]
Condensing turbine	60	3	40

5

Results

This section provides an overview of the results. Firstly, estimated CO_2 emissions from each of the Lime kilns are presented. This is followed by results on the concentration of CO_2 in the flue gases. Thereafter, the heating and cooling demands of an amine-based carbon capture process applied on these sources are presented. For these results, two scenarios have been considered representing specific thermal loads that have been reported for MEA and AMP/PZ absorbents, respectively.

Thereafter, potential MeOH production from the captured CO_2 is presented as well as the energy demand for the selected MeOH production process. Since H_2 is a reactant for MeOH synthesis, the H_2 demand and the correspondig electricity demand for water electrolysis is presented as well.

Lastly, heat integration opportunities at the pulp mill for carbon capture and MeOH synthesis is presented. Heat recovery potentials from the condensing turbine and from flue gas cooling are evaluated.

5.1 Carbon dioxide emissions, concentrations and carbon capture

A majority of the CO_2 emissions from the Lime kilns are produced from the calcination process, approximately 60 %. See Table 5.1 for an overview of the calculated CO_2 emissions.

${f CO}_2 \ {f emissions}$	Lime kiln 1	Lime kiln 2
Fuel emissions [kton/year]	71	36
Lime emissions [kton/year]	97	52
Total emission [kton/year]	168	88
Share of total mill emissions $[\%]$	10	5

Table 5.1: CO_2 emissions from respective Lime kiln.

The total emissions from both Lime kilns were 256 kton CO_2 per year, equivalent to 15 % of the total CO_2 emission at Södra cell Mönsterås, in 2021. Furthermore, the CO_2 emissions from the recovery boiler and the bark boiler were calculated. The total CO_2 emissions from the recovery boiler were approximately 1 342 kton/year and from the bark boiler they were 164 kton/year. In Figure 5.1 the share of CO_2

emitted from the three largest emitting sources at Södra Cell Mönsterås in 2021, is presented.



Figure 5.1: Share of total CO_2 emissions from the Lime kilns, recovery boiler and bark boiler at Södra Cell Mönsterås.

In Table 5.2, the estimated concentrations of CO_2 in the flue gases from each Lime kiln and the total volumetric flow from both Lime kilns are presented.

Table 5.2: Dry and wet CO_2 concentration in flue gases of both Lime kilns as well as the total volumetric flow.

Parameters	Lime kiln 1	Lime kiln 2
Wet volume- $\%$	17	18
Dry volume- $\%$	23	27
Volumetric flow (wet) $[m^3/s]$	2.8	1.5
Volumetric flow (dry) $[m^3/s]$	2.0	1.0

At a maximum capture rate of 90 % from both Lime kilns, the potential capture amounts to approximately 230 kton of CO_2 per year. This is equivalent to 151 kton/year of CO_2 from Lime kiln 1 and 79 kton/year CO_2 from Lime kiln 2.

The maximum capture rate, here assumed to be 90 % capture from both kilns, would reduce the biogenic CO_2 emissions from the pulp mill by 13 %. See Appendix A for various capture rates from both Lime kilns.

5.1.1 Energy Demand

With a reboiler duty of $3.6 \text{ GJ/ton } \text{CO}_2$ and a condenser duty of 4.1 GJ/ton captured CO₂, the calculated energy demands with MEA as an absorption agent are presented in Table 5.3. Different capture rates are presented in Appendix B.

Energy demand &	Lime kiln 1	Lime kiln 2	Lime kiln
captured carbon			1 & 2
Captured carbon [kton/year]	151	79	228
Reboiler duty [GWh/year]	151	79	230
Cooling [GWh/year]	172	90	262

Table 5.3: Captured carbon from Lime kiln 1 and 2 with respective reboiler duty and cooling demand for 90% capture rate of CO_2 with MEA as absorption solvent.

The reboiler requires LP steam at around 3 bar. This increase in steam demand at the mill, for capture of 90 % CO_2 from both Lime kilns, would be 17 % for the whole mill.

Alternatively, if a solvent blend of AMP/PZ would be used, the reboiler would utilise 22 % less heat compared to MEA. See Table 5.4 for calculated heating and cooling demands for AMP/PZ, assuming a heating demand of 2.9 GJ/ton CO_2 and a cooling demand of 4 GJ/ton. For alternative capture rates of CO_2 , see Appendix B.

Table 5.4: Reboiler duty and cooling demand for Lime kiln 1 and 2 with a capture rate of 90 % with AMP/PZ as absorption solvent.

Energy demand	Lime kiln 1	Lime kiln 2	Lime kiln
			1 & 2
Reboiler duty [GWh/year]	122	64	186
Cooling [GWh/year]	169	88	257

5.2 MeOH Production

Based on a 90 % capture rate of CO_2 , the potential production of MeOH, and the corresponding demand for H_2 , are presented in Table 5.5. Where scenario 1, is a 90 % capture rate from Lime kiln 1, scenario 2, a 90 % capture rate from Lime kiln 2 and scenario 3, a maximum capture rate from both Lime kilns.

Table 5.5: Potential MeOH production for the three scenarios of captured CO_2 with corresponding H_2 demand.

Reactants & products	Scenario 1	Scenario 2	Scenario 3
Produced MeOH [kton/year]	110	57	168
Produced MeOH $[m^3/h]$	16	9	25
H_2 demand [kton/year]	22	11	33
Produced H ₂ O [kton/year]	62	32	94
Produced H ₂ O $[m^3/h]$	7	4	11

Besides MeOH, H_2O is also produced. Since water electrolysis demands high amounts of water, this can potentially cover part of the H_2O requirement (see reaction 2.4). For different MeOH production rates, see Appendix C.

5.2.1 Energy Demand for Methanol Synthesis

The production of MeOH requires a high amount of heat in the reboiler of the distillation column. Table 5.6 presents the calculated heating and electricity demands for a methanol plant sized to utilize all CO_2 captured from the Lime kilns, according to the scenarios introduced in Section 5.2.

Table 5.6: Reboiler duty, heat produced in the reactor and electricity demand forthe produced MeOH based on the different scenarios presented.

Parameter	Scenario 1	Scenario 2	Scenario 3
Produced MeOH [kton/year]	110	57	168
Reboiler duty [GWh/year]	72	64	135
Heat produced reactor [GWh/year]	-42	-37	-79
Electricity demand [GWh/year]	61	32	92

In the reactor, where the MeOH synthesis occurs, heat is generated. This heat is assumed to be recovered within the MeOH process and cover approximately half of the heat required in the reboiler. The synthesis occurs in the reactor at approximately 250°C, therefore partially cover the heating demand for the reactor that requires heating from approximately 30°C to 225°C [36]. Additional heat needed (approximately 30 GWh/year for Scenario 1 and 26 GWh/year for Scenario 2) must be covered by external heat, i.e. by steam from the pulp mill steam system, see Section 5.4.

5.3 Water Electrolysis

This section presents the mass and heat balances for an electrolyzer plant producing the amount of H_2 needed for methanol synthesis according to the results presented in Section 5.2. For water electrolysis a great amount of water is needed to produce H_2 . Besides the H_2O demand, the amount of O_2 generated as a by-product of the H_2 is presented in Table 5.7.

Table 5.7: Mass balances for a water electrolysis plant producing the amount of H_2 required to convert all captured CO_2 to MeOH from the scenarios presented.

Reactant & products	Scenario 1	Scenario 2	Scenario 3
H_2 required for MeOH	22	11	33
synthesis [kton/year]			
H_2O demand [kton/year]	186	97	283
H_2O demand $[m^3/h]$	50	26	76
O_2 produced [kton/year]	165	86	251

5.3.1 Energy Demand

Based on different assumptions regarding the specific electricity demand for electrolysis (see Section 4.4.2, Table 4.6), the electricity required for water electrolysis was calculated, see Table 5.8, for the specific electricity demand with a total specific energy consumption of 4.75 kWh/Nm³. The electricity demand for an energy consumption of 4.5 and 5.5 kWh/Nm³ are presented in Appendix D.

Table 5.8: Electricity demand of the electrolyser for production of the required amount of H_2 to meet the demand for MeOH synthesis with an energy consumption of 4.75 kWh/Nm³.

Electricity demand & H_2 production	Scenario 1	Scenario 2	Scenario 3
H_2 produced [kton/year]	22	11	33
Electricity demand [GWh/year]	1500	800	2300

In 2021, the pulp mill consumed approximately 530 GWh of electricity. With a MeOH synthesis plant based scenario 1, the corresponding demand for H_2 production would require that the mill triple its electricity consumption.

5.4 Heat Integration Opportunities

The reboiler duty for the carbon capture and the bio-MeOH production, in the form of low-pressure steam (3 bar), can be covered by excess heat that could be made available from the existing processes at Södra Cell Mönsterås. In Table 5.9, heat that could be recovered from the Lime kiln flue gases and from the recovery boiler flue gases is presented together with low-pressure steam that could be extracted from the condensing turbine.

Table 5.9: Potential heat that could be recovered from the flue gases of Lime kiln 1 and 2 and the recovery boiler, as well as from steam extractions from the condensing turbine (ΔT_{min} is assumed to be 10 °C).

Flue gas	\mathbf{T}_{start}	\mathbf{T}_{target}	\mathbf{F}	FCp	\mathbf{Q}
location	$[^{\circ}C]$	$[^{\circ}C]$	[kg/s]	[MW/K]	$[\mathbf{MW}]$
Flue gases from	255	145	15	0.02	2
Lime kiln 1					
Flue gases from	275	145	7	0.01	1
Lime kiln 2					
Flue gases from	200	145	190	188	11
the Recovery boiler					

From Table 5.9, it is evident that the steam that could be generated by recovering heat from the flue gases of the lime kilns would not be enough to cover the heating demand for carbon capture for any of the capture scenarios presented in Table 5.3.

Approximately 90 GWh/year heat can be recovered from the flue gas from the recovery boiler. This would be enough to cover, for example, the heat demand for 90 % capture rate from Lime kiln 2 (scenario 2) only, which corresponds to a capture of roughly 79 kton CO_2 per year (with MEA as an absorption solvent). However, heat would then also be required for the methanol synthesis process. Capture of 79 kton CO_2 per year would allow for a production of 57 kton/year of MeOH (see Table 5.5) with corresponding heat demands as indicated in Table 5.6. Assuming internal recovery of heat from the synthesis reactor, the results show that it would be possible to cover the remaining net heat demand by heat recovered from scenario 2.

However, if the pulp mill aims at producing a maximum volume of MeOH according to scenario 3, approximately 290 GWh/year of heat is required in total for both the MeOH production process and the CC process. Table 5.10 presents the possibility to either completely bypass the condensing turbine or to extract steam from the turbine at low pressure. By bypassing all steam, a maximum production of bio-MeOH (scenario 3) can be achieved.

Table 5.10: Potential heat extracted for CCU concept by bypassing all steam consumed by the condensing turbine or by extracting low pressure steam at a pressure at 3 bar.

Potential ways to extract steam from condensing turbine	${f Q} ~[{ m GWh}/{ m year}]$
Bypassing steam	315
Extraction of low pressure steam	122

If all steam from the condensing turbine is utilized for the CCU concept, a production of approximately 300 GWh/year of electricity would be lost.

5.5 Summarizing Evaluation

In Table 5.11, a summary of all data calculated for the processes included in the CCU concept investigated in this master thesis are presented. A 90 % capture rate for either Lime kiln 1 or 2, or for both is evaluated, introduced as scenarios in Section 5.2.

Table 5.11: A summary of three scenarios for potential production of MeOH atSödra Cell Mönsterås.

Parameter for bio-MeOH	Scenario 1	Scenario 2	Scenario 3
production			
$CO_2 \ {f captured} \ [{f kton/year}]$	151	79	230
Heating demand CC	151	70	220
(MEA) [MWh/year]	101	19	230
Cooling demand CC	179	00	262
(MEA) [MWh/year]	112	90	202
MeOH production [kton/year]	110	57	168
H_2O production [kton/year]	62	32	94
Net heating demand [GWh/year]	30	26	56
Electricity demand MeOH	61	20	0.2
production [GWh/year]	01	32	92
H_2 production		11	2.2
electrolyser [kton/year]		11	.
O_2 production	165	96	951
electrolyser [kton/year]	105	00	201
H_2O demand	196	07	002
electrolyser [kton/year]	180	97	200
Electricity demand	1464	764	0000
electrolyser [GWh/year]	1404	/04	2220
Total heating demand	101	105	207
CC concept [GWh/year]	101	105	201
Total electricity demand	1595	705	0000
CC concept [GWh/year]	1525	795	2320
Total steam consumption		4000	
pulp mill 2021 [GWh/year]		1000	
Total electricity demand		526	
pulp mill 2021 [GWh/year]	J2U		

Based on Table 5.11, it is apparent that electricity demand for the electrolyser seems to be a critical limiting factor for the sizing of the CCU concept. A maximum capture rate, according to scenario 3 (90% capture from both Lime kilns) would imply an electricity requirement approximately four times as high as the electricity consumption at the pulp mill today. The heating demand for all scenarios in Table 5.11 can be covered, from the heat recovered from the flue gases or the condensing turbine, as mentioned in Section 5.4. However, that would lead to a considerably lower electricity production at the pulp mill.

In Figure 5.2 an overview of mass balances resulting in a maximum MeOH production (scenario 3) is presented.



Figure 5.2: A simplified overview of the mass balances calculated over the CCU concept for production of 168 kton of bio-MeOH based on a 90 % CO₂ capture rate from both Lime kilns (scenario 3).

The corresponding energy balances over the CCU concept for scenario is presented in Figure 5.3. The values for Figure 5.2 and Figure 5.3 are presented in Table 5.11.



Figure 5.3: A simplified overview of the energy balances calculated over the CCU concept for production of 168 kton of bio-MeOH based on a 90 % CO₂ capture rate, with MEA as an absorption agent, from both Lime kilns (scenario 3).

6

Discussion

This chapter discusses the final results of this master thesis.

Firstly, the assumptions and results regarding CO_2 emissions and concentrations of the lime kilns are discussed, followed by a discussion regarding which postcombustion carbon capture method could be the most suitable for Södra Cell Mönsterås based on currently publicly available information. Thereafter the assumptions and results regarding the MeOH synthesis and water electrolysis processes are examined. This chapter is then concluded by discussing the heat integration opportunities and available heat sources at the pulp mill.

6.1 CO₂ Emissions and Concentration

A higher CO_2 concentration in the flue gas simplifies capture and absorption of CO_2 and is advantageous. Thus the lime kilns were the emission sources of choice in this master thesis. The concentration of CO_2 was estimated based on information about fuels used and related CO_2 emissions factor. A more accurate CO_2 concentration could be achieved if the flue gas composition were to be determined by measurements. The CO_2 concentration fluctuates over the year and varies according to production campaigns and also depending on fuels combusted. The exact composition of pulverized bark, for example, depends on the dryness level of the bark and the wood species utilized.

The concentration of other emitted substances in the flue gas ought to be measured as well. Post-combustion carbon capture by aqueous absorption solvent, such as MEA, is sensitive towards certain levels of sulfide compounds, such as H_2S , as well as nitric oxide (NO) and nitrogen (NO₂). With the knowledge of this, the flue gas entering the CO₂ capture plant can be better monitored and unwanted substances can be removed.

6.2 Carbon Capture

In this thesis, MEA is briefly compared to AMP/PZ as a absorption agent in Section 5.1.1 to get an indication of the potential improvement that could be achieved compared to the conservative estimate represented by the MEA assumption. According to the assumed reboiler duties, AMP/PZ would be a significantly better option. However, in a feasibility study conducted by Preem (in cooperation with Chalmers, SINTEF, Aker Carbon Capture and Equinor) [22], the reboiler duty does not differ as much between MEA and AMP/PZ as presented in this report. In the feasibility study mentioned, a reboiler duty of $3.16 \text{ GJ/ton } \text{CO}_2$ is found for MEA and $2.95 \text{ GJ/ton } \text{CO}_2$ for AMP/PZ [22]. This further confirms that the heating demand assumed in this report when using MEA is conservative, and better performance could likely be achieved, not only with better solvents, but also with process design improvements and by considering the higher CO₂ concentration in the lime kiln flue gases.

In addition to amine-based capture technologies, there are also other technologies and solvents being developed by various companies, see, e.g., Table 2.1. For amine free CO_2 capture, the process is electricity demanding, and therefore not the most optimal method at Södra Cell Mönsterås presently. There are also membrane-based capture processes being developed, with a lower electricity demand but a high water demand. A high water demand could potentially be a challenge in the future, with water scarcity being an increasingly important issue, and therefore not an optimal method to depend on.

Capturing the maximum amount of CO_2 (90 % capture rate from both lime kilns) is equivalent to a heat demand corresponding to about half of the steam produced in the bark boiler in 2021 (423 GWh of high-pressure (60 bar) steam). Availability of steam is not directly a limiting factor, since the pulp mill is self sufficient in steam supply, and currently has an excess, which is used for electricity generation in a condensing turbine. However, using this steam to coverthe significant heat demand of a capture processs would change the internal energy balance considerably and have a major effect on the electricity production at the mill.

Since the aim of the study was to investigate capture of CO_2 for the purpose of utilising it for production of MeOH, the amount of captured CO_2 should, preferably, be determined based on the amount of MeOH desired. However, if more CO_2 is captured than required for the MeOH production, the excess CO_2 could be sold or utilised internally for other purposed. Biogenic carbon is likely to become a valuable product on a market when looking for alternatives to fossil carbon in products such as many chemicals and plastics. CO_2 is also needed when extracting lignin from the black liquor of a pulp mill. Lignin extraction is still uncommon in pulp mills, but is receiving increasing interest, since lignin would also be a bio-based carbon source with a great potential to replace fossil alternatives.

Data publicly available for heating and cooling demands for CO_2 capture are mainly based on CCS cases, where CO_2 is captured, liquefied and then transported for permanent storage. Liquefaction of CO_2 requires a lot of energy, more specifically for cooling. However, producing MeOH by reacting H₂ and CO₂, also requires CO₂ in a liquefied form at a temperature around 20°C [36]. Therefore, data retrieved are assumed to be valid for this CCU concept.

During the liquefaction process and condensation of CO_2 , H_2O is removed, which could potentially be used for the H_2 production or in other processes at site. However, since the direct contact cooler (DCC) removes a high amount of H_2O before entering the absorption tower, more water could potentially be recovered from there. This was not evaluated and included in the report. Nevertheless it is an interesting topic for potential water scarcity in the future and a possible partial solution if the pulp mill is to be self sufficient in water supply in the future.

6.3 MeOH Production

As mentioned in Section 1, a total amount of 3.3 ktons of bio-MeOH was produced at Södra Cell Mönsterås in 2021, which was sold as a bio-fuel [44]. By producing the potential maximum amount of MeOH from CO_2 from the lime kilns (with 90% capture rate), equivalent to 168 kton/year, Södra Cell Mönsterås would significantly increase its production of a fossil free (assuming non-fossil lime kiln fuels and fossilfree electricity supply) alternative for transportation fuels or chemical feedstock. This is a market worth exploring.

6.3.1 MeOH Synthesis

The estimation of potential MeOH production with an assumption of 100 % conversion of CO_2 through direct hydrogenation (see Reaction 2.7 [29]) is a simplification to give an indication of how much MeOH could be produced. A 100 % conversion rate is a high estimate whereas in reality this rarely occurs. For methanol synthesis (for example) there are other competing reactions that were not taken into consideration in this study These two competing reactions can also occur [29]:

$$CO + 2H_2 \rightarrow CH_3OH$$
 (6.1)

$$CO_2 + H_2 \to CO + H_2O \tag{6.2}$$

Competing reactions can cause a higher energy demand and unwanted side products. This is an important factor to consider if MeOH synthesis is implemented at the pulp mill. Besides, a side product from MeOH synthesis is H_2O , at around $100^{\circ}C$ [29]. Not an immense amount of H_2O is produced, but since H_2O is needed in large volumes for the water electrolysis for production of H_2 , it will become increasingly

important to house keep with water resources at the mill. It is potentially possible to recover the water generated in the MeOH synthesis for use in the water electrolysis plant (or the rest of the mill), thus, lowering the H₂O demand from other sources. The electrolyser operates around 50-80°C [29][31] and would have to be heat exchanged.

Additionally, since the heating demand for the heat exchanger was calculated based on an Aspen Model introduced by Kiss et. Al [36], the result is to be evaluated with caution. Models differ and are site specific. However, since the purpose of this thesis is to give an overview of potential energy demands, this will suffice and is considered valid. For future evaluation and calculations this should be considered and additionally modelling is needed.

6.3.2 Water Electrolysis

In Table 5.8 it is evident that for an electricity demand between 4.5-5.5 kWh/Nm³ of H₂ [31], the maximum MeOH production based on 90% CO₂ capture from both lime kilns (168 kton/year) seems unrealistic based on the required electricity for electrolysis, which is estimated to approximately 2.2 TWh/year. Södra Cell Mönsterås today consumes approximately 0.7 TWh of electricity per year. Instead, a capture rate of 50 % from lime kiln 1, corresponding to a MeOH production of 61 kton/year, would require an electricity demand of approximately 0.7 TWh/year (assuming a specific electricity demand of 4.75 kWh/Nm³), which is more likely to fall within the capacity of existing grid connections.

It is clear that for an electrolysis plant sized to match the capture of a significant share of the CO_2 of the lime kilns, the electricity consumption would to the most extent have to be covered by external sources. For the overall site, the change in electricity balances would result in a loss of income from electricity sales, and the self sufficiency of energy supply would be lost as well. Furthermore, since the electricity price fluctuates considerably today, there are large uncertainties in the costs of operating the electrolysis process. One solution could be to operate the H₂ production plant flexibly depending on the price of electricity. This would require that either the rest of the CCU processes can also operate flexibly or that a hydrogen storage solution is also implemented. Water electrolysis is by far the limiting process in this CCU concept.

As mentioned in Section 2.3.1, there are other electrolyser technologies, which could be relevant for H_2 production other than the PEM electrolysers assumed in this study. Alkaline electrolysis (AEC) has a lower electricity demand, around 4.2 kWh/Nm³ H₂ [32], but a higher temperature demand at around 60-90 °C [29], and could potentially be more suitable for a pulp mill with excess heat in this temperature range. According to the results of this study, the recovery boiler emits five times as much CO_2 as both lime kilns at Södra Cell Mönsterås. Capture and utilisation of this large amount of CO_2 is assumed to not be feasible today. One of the main reasons for this is that the corresponding on-site production of H₂ for the MeOH synthesis would require extremely high demands for electricity.

 O_2 is generated as a by-product in water electrolysis. Today O_2 is a valuable product in numerous industries and applications. It is utilized in the steel industry, chemical industry as well as pulp an paper industry and can therefore be used at site or sold.

6.4 Heat Sources and Integration

Various heat sources at the mill that could potentially be integrated with the CCU plant have been investigated. The results show that bypassing steam over the condensing turbine, 315 GWh/year of steam can be utilized to cover the specific heating demand of the capture process for scenario 3 (capturing 90 % of emissions from both lime kiln 1 and lime kiln 2). Additionally, the steam can cover the heat demand for the MeOH synthesis. By extracting low pressure steam instead, 122 GWh/year of steam can be utilized. If utilizing the low pressure steam extracted from the condensing turbine, it can cover the heating demand for scenario 2 (capturing 90% of CO_2 from lime kiln 2). Hence produce 57 kton bio-MeOH per year.

The condensing turbine is already equipped with a possibility to extract steam at 1.5 bar [41]. This could possibly be utilized for extraction of the low pressure steam discussed for the capture process, thus avoiding the need to reconstruct G6 entirely.

Since the heating demand is assumed not to be a limiting factor when targeting the lime kilns only, CO_2 could potentially be captured at a high capture rate (90%). However, due to the high electricity demand of H₂, it seems unrealistic to use all of the captured CO_2 for MeOH production on site. Instead, excess CO_2 captured could be sold. If an even higher amount of CO_2 is desired, the recovery boiler can be considered an other source. However, that would require additional heat supply to cover the reboiler duty is needed, potentially a new bark boiler. This is somehow contradictory if the purpose is to reduce CO_2 emissions from the mill.

Instead of depending on extraction steam from G6, integration of CO_2 capture is possible from other excess heat sources. As can be seen in Table 5.9, waste heat from the flue gases of the lime kilns and the recovery boiler are potential heat sources. These heat sources are interesting since they would not affect the energy self sufficiency demand at the pulp mill today. However, there is not enough heat in the flue gases to cover a maximum capture rate, but it would cover a capture rate of approximately 90 % from lime kiln 2 or 70 % capture rate from lime kiln 1, for the CO_2 capture process, as well as the MeOH synthesis (ca 57 kton/year of MeOH). This would require 90 MW electricity, approximately the electricity consumption at the pulp mill today, as mentioned previously.

6. Discussion

7

Conclusion

This study set out to investigate the potential integration of CCU (Carbon Capture and Utilisation) for production of bio-MeOH, at Södra Cell Mönsterås. The potential for integration of the CCU plant was evaluated on the basis of available heat sources at Södra Cell Mönsterås. The heating demand for CO₂ capture was investigated for two different values of the specific reboiler duty, representing values that have been reported for two different CO₂ absorption solvents: MEA and AM-P/PZ. With specific heating demands of 3600 kJ/kg CO₂ captured and 2900 kJ/kg CO₂ captured, respectively. With the assumption of a lower reboiler duty, a heating requirement of 186 GWh/year was obtained for capture of 230 kton/year of CO₂ (a 90 % capture rate from both lime kilns). Capturing this amount of CO₂ would enable a production of MeOH of 168 kton/year. Capture assuming the higher reboiler duty would require 230 GWh/year of heating, which could be seen as a more conservative estimate of the heating requirements.

Water electrolysis, on the other hand, is an electricity demanding process, and was therefore evaluated with regards to the required electricity consumption and how that compares to the current electricity consumption of the mill. A total production of 168 kton/year of MeOH would require around 30 kton/year of H₂, which corresponds to an electricity demand of approximately 2.2 TWh/year (151 GW). For comparison, this is equivalent to three years of electricity production at the pulp mill.

Furthermore, MeOH synthesis of 168 kton MeOH/year requires 135 MWh/year of heat. The total heating demand for MeOH synthesis and CO₂ capture can, according to the results, be covered with steam bypassed from the condensing turbine at the pulp mill. Bypassing of the condensing turbine would lead to significant loss of electricity production, therefore an alternative is to capture only around 70 kton/year CO_2 from lime kiln 1, in which case the heat demand for CO₂ capture and MeOH can be covered by heat from the flue gases of both lime kilns and the recovery boiler. With 70 kton/year of CO_2 , a production of 9 kton/year of H₂ is required for MeOH synthesis, resulting in an electricity demand of 0.6 TWh/year. Although this is a significant electricity demand, it is in the same range as the electricity consumption of the existing mill processes.

To summarize, this thesis suggests that based on mass and energy balances, the integration of a CCU concept at Södra Cell Mönsterås should be feasible. However, it will have a substantial impact on the energy consumption at the pulp mill, resulting

in a shift from being self sufficient supply of energy to relying on external supply, where electricity is a limiting factor.

7.1 Future Work

There are potential areas for further investigation of CCU concepts at Södra Cell Mönsterås. These include more detailed evaluation of energy demands for different methods of CO_2 capture based on modelling of the capture processes using assumptions about mill-specific flue gas compositions, as well as an economic evaluation. AMP/PZ based capture is a fairly new method and supposedly not the sole option for decreasing energy demand in the forthcoming future and likely not the most economically feasible method. An evaluation based on plant footprint and cost estimations is a necessity for potential implementation in the future.

Additionally, cooling and/or water demand is a potential limiting factor of increasing importance. Water can potentially be recovered from flue gas condensation and during MeOH synthesis. These are interesting topics to evaluate further.

As introduced in Section 6.4, if a higher amount of CO_2 would be desired for capture, the recovery boiler can be of interest to investigate further. With a flow rate of around 190 kg/s of the flue gas and approximately 1 340 kton of CO_2 emitted in 2021, a significantly higher amount of CO_2 can potentially be captured. Capturing more CO_2 would require more heat, hence a new heat source could be required, such as a new power boiler.

Finally, production of H_2 should be further investigated. Other electrolysis processes than the PEM technology, such as those mentioned in Section 2.3.1, might be better suited. Potentially it would be more profitable to invest in potential suppliers of H_2 and not produce it on site.

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A Carbon Capture

Table A.1: Amount of captured carbon ranging from 90 % to 10 % from lime kiln 1 and 2.

Share of captured CO_2	Lime kiln 1	Lime kiln 2	Lime kiln 1 & 2	Unit
90%	151	79	230	[kton CO_2 /year]
80%	134	70	205	[kton CO_2 /year]
70%	118	61	179	[kton CO_2 /year]
60%	101	53	154	[kton CO_2 /year]
50%	84	44	128	[kton CO_2 /year]
40%	67	35	102	[kton CO_2 /year]
30%	50	26	77	[kton CO_2 /year]
20%	34	18	51	[kton CO_2 /year]
10%	17	9	26	[kton CO_2 /year]

A. Carbon Capture

В

Heating and Cooling Demand CC

Heating and cooling demand for MEA as an absorption agent for carbon capture.

Table B.1: Reboiler duty for CO_2 capture with a capture rate of 90 % to 10 % from lime kiln 1 with MEA as an absorption solvent.

Share of captured	Captured	Heating demand
CO_2 [%]	CO_2 [kton/year]	$[{ m GWh}/{ m year}]$
90	151	151
80	135	135
70	118	118
60	101	101
50	84	84
40	67	67
30	50	50
20	34	34
10	17	17

Table B.2: Condenser cooling demand for CO_2 capture with a capture rate of 90 % to 10 % from lime kiln 1 with MEA as an absorption solvent.

Share of captured	Captured	Cooling demand
CO_2 [%]	CO_2 [kton/year]	[GWh/year]
90	151	172
80	135	153
70	118	134
60	101	115
50	84	96
40	67	77
30	50	57
20	34	38
10	17	19

Heating and cooling demand for AMP/PZ as an absorption agent for carbon capture.

Share of captured	Captured	Heating demand
CO_2 [%]	CO_2 [kton/year]	$[{ m GWh}/{ m year}]$
90	151	122
80	135	108
70	118	95
60	101	81
50	84	68
40	67	54
30	50	41
20	34	27
10	17	14

Table B.3: Reboiler duty for CO2 capture with a capture rate of 90 % to 10 % from lime kiln 1 with AMP/PZ as an absorption solvent.

Table B.4: Condenser duty for CO2 capture with a capture rate of 90 % to 10 % from lime kiln 1 with AMP/PZ as an absorption solvent.

$\begin{array}{c c} CO_2 \ [\%] & CO_2 \ [kton/year] & [GWh/year] \\ \hline 90 & 151 & 169 \end{array}$	Share of captured	Captured	Cooling demand
90 151 169	CO_2 [%]	CO_2 [kton/year]	$[{ m GWh}/{ m year}]$
	90	151	169
80 135 150	80	135	150
70 118 131	70	118	131
60 101 112	60	101	112
50 84 94	50	84	94
40 67 75	40	67	75
30 50 56	30	50	56
20 34 37	20	34	37
10 17 19	10	17	19

С

Bio-Methanol Production

Potentially produced bio-MeOH based on captured CO_2 from lime kiln 1.

Table C.1: Produced bio-MeOH from lime kiln 1 with a capture rate varying from 90 % to 10 %.

Captured CO_2	Produced bio-MeOH	Produced H_2O
Lime kiln 1 [kton/year]	[kton/year]	$[\mathrm{kton}/\mathrm{year}]$
151	110	62
135	98	55
118	86	48
101	73	41
84	61	34
67	49	28
50	37	21
34	24	14
17	12	69

Potentially produced bio-MeOH based on captured CO_2 from lime kiln 2.

Table C.2: Produced bio-MeOH from lime kiln 2 with a capture rate varying from 90 % to 10 %.

Captured CO_2	Produced bio-MeOH	Produced H_2O
Lime kiln 2 [kton/year]	[kton/year]	[kton/year]
79	57	32
70	51	29
61	45	25
53	38	22
44	32	18
35	26	14
26	19	11
18	13	7
9	6	4

D Hydrogen Production

Electricity demand of the electrolyser from production of H_2 with an energy consumption of 4.50 and 5.50 kWh/Nm^3 based on the three different scenarios defined in Section 5.2 where scenario 1 is based on 90 % CO₂ capture from Lime kiln 1, scenario 2 a 90 % capture rate from Lime kiln 2 and scenario 3 a maximum capture rate with a CO₂ capture rate of 90 % from both Lime kilns.

Table D.1: Electricity demand of the electrolyser for production of the required amount of H_2 to meet the demand for MeOH synthesis with an energy consumption of 4.50 kWh/Nm^3 .

Electricity demand & H_2 production	Scenario 1	Scenario 2	Scenario 3
H_2 produced [kton/year]	22.0	11.0	33.0
Electricity demand [TWh/year]	1.4	0.7	2.1

Table D.2: Electricity demand of the electrolyser for production of the required amount of H_2 to meet the demand for MeOH synthesis with an energy consumption of 5.50 kWh/Nm^3 .

Electricity demand & H_2 production	Scenario 1	Scenario 2	Scenario 3
H_2 produced [kton/year]	22.0	11.0	33.0
Electricity demand [TWh/year]	1.70	0.90	2.6

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