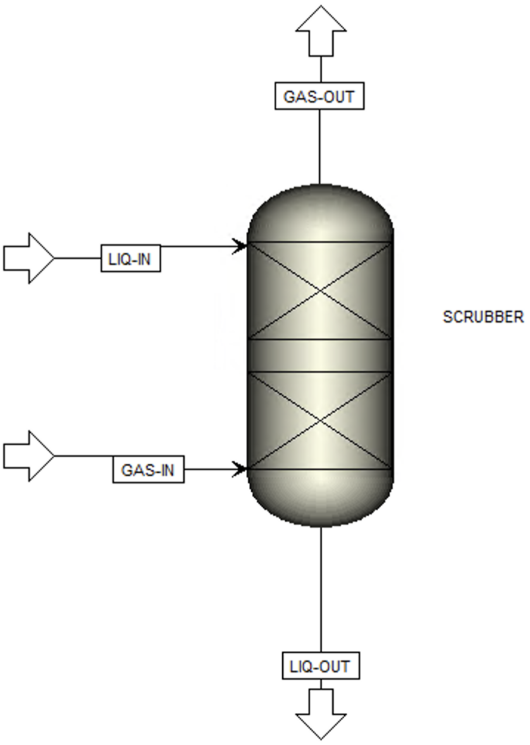

Carbon Capture Using White Liquor in a Kraft Pulping Plant

Simulation and Evaluation of a Scrubber

Master’s thesis in Sustainable Energy Systems

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CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

CO_2 emissions are a big part of the current discussion regarding global warming, and industries like pulp and paper play a large part in the aim to reduce global emissions. Implementing carbon capture technologies in pulp plants can significantly reduce CO_2 emissions from the plant and even make some plants negative CO_2 emitters.

In a suggested process, a scrubber was added to a Kraft pulp mill to capture CO_2 in the flue gases from the recovery boiler using white liquor as an absorbent. The project aimed to simulate and calculate the scrubber's cost and discuss the effects on the process and whether it was feasible to integrate the scrubber into the process.

The results suggested a scrubber that gave a 95% CO_2 capture rate from the recovery boiler flue gases, costing about 17 million SEK. It was concluded that sending the outlet liquor from the scrubber back to the process could affect the white liquor composition and overall chemical balance. There was also an increased load on the causticisation and lime kiln in the process and a risk of toxic H_2S leaving with the scrubbed flue gas.

Keywords: carbon capture, white liquor, pulp and paper industry, Kraft process, scrubber, simulation.

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Julia Cramstedt, Gothenburg, May 2023

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1

Introduction

CO_2 emissions are a big part of the current discussion regarding global warming. The pulp and paper industry accounted for just over 5% of greenhouse gas emissions from Swedish industries in 2021, with about 0.84 million tonnes of CO_2 equivalent emissions [1]. The pulp and paper industry has lowered its emissions during the last 25 years by moving away from oil as fuel [1], but still, a lot can be done.

Carbon capture and storage (CCS) is a promising technology to reduce emissions in the industry sector. It can potentially reduce 55% of global emissions by the end of this century [2]. There is a large potential for implementing carbon capture in the pulp and paper industry, and the industry could even become a net negative CO_2 emitter since the majority of the emissions are from biogenic sources [3].

IVL Svenska Miljöinstitutet AB (IVL) is working on a digital twin of a pulp mill, which hopes to help in optimising the daily operation of the pulp mill. In addition to this, IVL is also investigating the possibility of having zero CO_2 emissions from the pulp mill. A possible process has been imagined where IVL has investigated all CO_2 emitting units in the mill. This thesis will investigate one of the proposed carbon capture units, where CO_2 will be captured from flue gases using white liquor from the Kraft process.

1.1 Background

The primary sources of carbon emissions in a Kraft pulp mill can be found in the chemical recovery cycle [4]. The recovery boiler, the biomass boiler, and the lime kiln are the main emitters, where the recovery boiler accounts for over 75% of the CO_2 emissions [5]. Therefore, it is interesting to primarily investigate the emissions from the recovery boiler, which this project will focus on.

Previous studies on carbon capture in Kraft pulp mills have primarily been on post-combustion technologies since this does not require any reconstruction of the recovery boiler [6]. The most common post-combustion process is carbon capture by chemical absorption, such as using monoethanolamine (MEA) to capture CO_2, as it is a well-known and effective absorption technology [7]. Other theoretical suggestions exist where more substantial changes in the process are made, like substituting the recovery boiler with black liquor gasification and using different pre-combustion processes [8]. Studies have also suggested using oxy-combustion to capture CO_2 from the lime kiln [9].

Another common absorption chemical aside from MEA is NaOH which can be used to capture CO_2 from flue gases [10]. The theory investigated in this thesis is that white liquor, a chemical solution from the Kraft process containing mainly NaOH [11], could be used as an absorption medium in the same way as pure NaOH. White liquor as an absorption medium has been tried before to remove total reduced sulphur gases in non-condensable gases [12]. This study found a scrubbing efficiency of about 95% for total reduced sulphur gases. As for scrubbing flue gases with NaOH in a pilot scale, the absorption efficiency was 30-98% depending on operating conditions [13].

1.2 Aim and scope

The project mainly aims to do a simulation and cost calculation of a carbon capture unit. The objective is to evaluate the feasibility of using white liquor from the process as an absorption medium to absorb the CO_2 from the recovery boiler flue gas. The feasibility of returning the white liquor with absorbed CO_2 to the chemical recycling process will also be evaluated as a way to regenerate the solvent. The simulation will be done in ASPEN Plus, and Microsoft Excel will be used for the cost calculations. The result will be analysed, and a recommendation will be given if the carbon capture unit should be invested.

The second aim is to contribute to the digital twin that IVL is working on. In MODDE, a statistical model will be created that can be put into MATLAB Simulink and coupled to the digital twin IVL has done.

1.3 Research questions

To reach the aim of the thesis, the following questions are to be investigated:

- Which dimensions and operating conditions are needed to achieve good efficiency for the carbon capture unit?
- How much more white liquor is needed in the process when a carbon capture unit is integrated into the process?
- Can the outlet liquor flow from the carbon capture unit be sent to the causticisation process, and how will it affect the capacity?
- What are other possible effects on the process when integrating the carbon capture unit?
- What will be the cost of integrating the carbon capture unit?

1.4 Limitations

In the studied process, the captured CO_2 from the recovery boiler flue gas will react with NaOH in the white liquor and be sent back to the chemical recovery cycle. Therefore no storage or utilisation of the captured CO_2 will be studied.

In the proposed carbon capture process in the Kraft pulp mill, it has also been proposed to install an electric lime kiln to receive zero CO_2 emissions and to handle the potentially larger load of lime. Currently, this technology is not widely used in the pulp and paper industry. The installation and integration of an electric lime kiln fall outside of this project, and it is assumed that an electric lime kiln is already available to also account for the extra capacity needed in the lime kiln. The installation and integration of an electric lime kiln and what to do with the pure CO_2 stream is a suggested further study.

If something can be done with the flue gases from the current lime kiln is not something that will be studied in this project. Still, it could be interesting to investigate if this can be integrated with the carbon capture unit suggested in this report.

The addition of the carbon capture unit could give an increased energy demand. It will, however, be assumed that this energy is available, and a deeper study into potential energy sources will not be done.

Finally, the project will only simulate one type of carbon capture unit. The type of unit that would be the best fit will be decided from a literature study and using experience from engineers in the industry.

2

Theory

In the following chapter, all necessary theory for the thesis is presented. First, an overview of the Kraft pulping process is presented, and the relevant process stages are dived into more deeply. Then, some carbon capture technology is explained, and previous studies into carbon capture in the pulp and paper industry are presented. Finally, the theory behind absorption columns is presented to support the choice of carbon capture process in the thesis.

2.1 Kraft process overview

There are many different ways to obtain pulp from wood. The processes can fall into three overall categories; mechanical pulps, semi-chemical pulps or chemical pulps [14]. The plant of focus in this thesis is of the type chemical pulp, using the Kraft process.

The Kraft process, also known as the sulphate process, is the most common process for obtaining pulp [15]. This process is alkaline at high temperatures of around 140-180°C, and yields are about 45-50% [14]. Some of the advantages of the Kraft process, compared to other pulping methods, are that it has an excellent chemical recovery system, that it can be used on any wood type, that the cooking times are short, that it requires only half to a third of the electrical energy compared to mechanical pulps, and that the received pulp has great strength [14].

To remove most of the lignin, the wood chips are prepared in a digester with a chemical solution called white liquor, consisting mainly of sodium hydroxide and sodium sulphide. This process is called the cooking process. The lignin is removed to achieve better pulp quality. Out of the digester comes the cooked pulp and the spent cooking liquor, called black liquor. The pulp is washed before being sent to the paper mill or bleaching plant. The black liquor instead enters the chemical recovery process, which starts with the evaporation and then combustion of the black liquor in the evaporator and recovery boiler, respectively. Out of the recovery boiler comes green liquor, a solution of mainly sodium sulphide and sodium carbonate, which is sent to the final stage of the chemical recovery cycle, the causticising process [14]. In this process, the sodium carbonate reacts to form sodium hydroxide according to equation (2.1).

$$\mathrm{Na_2CO_3} + \mathrm{Ca(OH)_2} \longleftrightarrow 2\,\mathrm{NaOH} + \mathrm{CaCO_3} \tag{2.1}$$

The causticising process regenerates white liquor, which is sent to the digester and closes the chemical recovery cycle [14]. Since the reaction in equation (2.1) is an equilibrium reaction, it does not generate 100% conversion. In general, about 80% of the Na_2CO_3 is converted.

Coupled with the causticising process is another chemical cyle. In this cycle, the calcium carbonate in equation (2.1), also known as limestone, is sent to a lime kiln to convert into quicklime (CaO) according to equation (2.2).

$$CaCO_3 \longrightarrow CaO + CO_2 \tag{2.2}$$

The quicklime is then combined with water in the slaking process to form calcium hydroxide, also known as slaked lime, according to equation (2.3), which is then sent back to the causticising process [16].

$$CaO + H_2O \longrightarrow Ca(OH)_2 \tag{2.3}$$

A figure describing the two cycles in the Kraft process can be viewed below in figure 2.1.

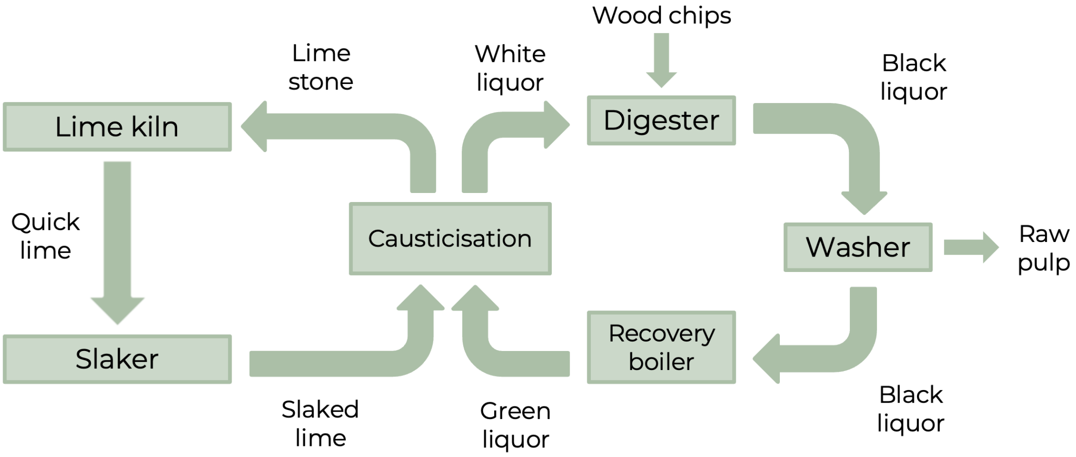
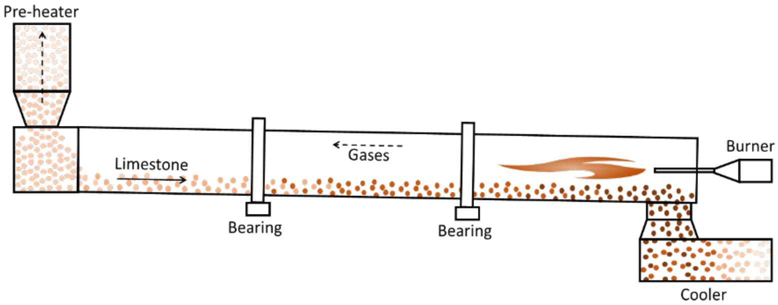


Figure 2.1: Overview of the Kraft pulping process (based on [14]).

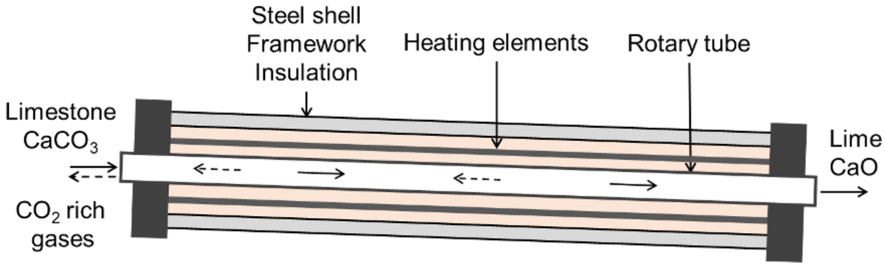
2.1.1 Electric lime kilns

Electric lime kilns are a relatively new technology and are currently in the piloting phase. In a traditional lime kiln, the limestone is heated with a flame and exhaust gases from burning fossil fuels. Heat is needed for the reaction in equation (2.2) to occur, and approximately 0.75 tonnes CO_2 is released per tonne of lime produced. Electrification, carbon capture, and utilisation or storage of the CO_2, have been deemed the most promising technologies for reducing CO_2 emissions from the lime kiln [17].

The limestone is indirectly heated with electric heating elements around a rotary tube in the electric lime kiln. A figure describing an electric and a traditional lime kiln can be seen in figure 2.2.



(a) Traditional lime kiln



(b) Electric lime kiln

Figure 2.2: An overview of (a) a traditional and (b) an electric lime kiln [17].

In the indirectly heated lime kiln, the produced gases are almost pure CO_2 since the limestone does not come in contact with other gases. This makes storing or utilising the CO_2 easier. Other advantages of an electric lime kiln are that the temperature profile is easier to control, the lime product will not be contaminated from the fuel, and the heat losses are smaller. However, the risk of recarbonation is higher, and the required energy is greater because of a higher partial pressure for CO_2 [17].

2.1.2 Na/S balance

In a Kraft pulping mill, keeping track of the sulphidity, or the sodium and sulphur balance, in the liquor is essential. This is because of the important role of the cooking chemicals and the white liquor in the preparation of the pulp. Usually, Scandinavian mills have a problem with low sodium and high sulphur concentrations, which can affect the pulp quality and increase emissions of sulphurous gases. Keeping track of the Na/S balance can minimise the production cost and ensure that the pulp is of sufficient quality. One problem, however, is that it can take time to notice changes in the sulphidity because of the large liquor flows in the mill. There are three main ways to keep track of the chemical balances in a mill - the sulphidity, the effective alkali, and the active alkali [18]. These are calculated by the following equations [19].

$$\text{Sulphidity [\%]} = \frac{\text{Na}_2\text{S}}{\text{NaOH} + \text{Na}_2\text{S}} \times 100\% \tag{2.4}$$

$$\text{Effective alkali [g/L]} = \text{NaOH} + \frac{\text{Na}_2\text{S}}{2} \tag{2.5}$$

$$\text{Active alkali [g/L]} = \text{NaOH} + \text{Na}_2\text{S} \tag{2.6}$$

2.2 Carbon capture technology

Carbon capture processes can be divided into three main types: pre-combustion, post-combustion, and oxy-fuel combustion processes. The pre-combustion process removes the carbon in the fuel before the combustion, post-combustion processes remove the CO_2 in the flue gas after the combustion, and in oxy-fuel combustion, the fuel is oxidised to create a purer stream of CO_2 [20]. Chemical looping should also be mentioned, which can be considered a type of oxy-fuel combustion. In the chemical looping process, oxygen is supplied to the fuel without contact with air with a metal oxide as an oxygen carrier. The stream will consist of pure water and CO_2 [2]. Out of these different carbon capture technologies, it is the easiest to implement post-combustion capture into existing Kraft pulping mills since it is only applied to the flue gas and, therefore, does not require any reconstruction of the recovery boiler [6]. It is also easy to retrofit into existing plants when it comes to energy and mass balances [21]. This is important to consider as capturing carbon dioxide will increase the site's energy demand [22].

For larger mills in Sweden, almost all the site carbon emissions are biogenic. This means the emissions could be considered negative if the carbon capture is implemented [22]. The recovery boiler and lime kiln make up about 90% of the total site emissions [22] where the recovery boiler is the largest emitter of carbon dioxide, representing around 75-80% of the total emissions [5]. Therefore, it is interesting to investigate carbon capture connected to the recovery boiler.

2.2.1 Carbon capture in pulp mills

Several studies have been done on carbon capture in the pulp and paper industry. A summary of some previous studies on carbon capture in pulp mills found during the literature study is presented below.

In a thesis by Hedström [8], they investigated three scenarios for reducing carbon emissions in pulp mills using simulation software. The first scenario applied a post-combustion capture technology to the recovery boiler flue gas, while the second and third scenarios replaced the recovery boiler with black liquor gasification with two different pre-combustion CO_2-capture processes; Selexol and Rectisol. Out of these, the first scenario showed the highest potential CO_2 reduction when applying Bioenergy with carbon capture and storage (BECCS), while the scenario using the Rectisol had the lowest capture cost [8].

In an article by Kuparinen et al. [23], BECCS using monoethanolamine (MEA) was studied as a reference case, which is a post-combustion capture process with a capture rate between 80-90%. In this case, calculations were done for several mills on energy balances, CO_2 emissions, and cost. The conclusion was that implementing carbon capture in pulp and paper mills could significantly reduce CO_2 emissions, and many mills could even become negative CO_2 emitters. The main reason for not adding BECCS into existing mills is because there are no incentives for negative emissions in the emission trade framework, making BECCS just a cost factor [23].

In a thesis by Kouri [24], they investigated thirteen different carbon capture technologies for the Finnish pulp and paper industry based on capture potential, cost, and technical maturity. Seven carbon capture technologies were applied to or replaced the recovery boiler, five capture technologies were investigated for the lime kiln, and one technology was applied to both the recovery boiler and the lime kiln. Of the investigated options, MEA absorption and lignin separation was the most technically mature concepts, and MEA absorption had the highest carbon capture potential. In general, technologies applied to the recovery boiler were more likely to be economically feasible. This thesis concluded that the feasibility of investing in carbon capture depends on incentives and other revenues [24].

Another way to reduce carbon emissions is to introduce an electric lime kiln, also called electric gas-plasma technology. Andersson and Skogström investigated this [25], where they recommend replacing the conventional lime kiln with an electric one at the end of its lifetime. Compared to the conventional lime kiln, the plasma technology results in a pure carbon dioxide stream that can be used in the process, sold, or stored without further concentration of the gas. It also has faster reaction times, an expected lower investment cost, is more energy efficient, and the equipment is smaller than the conventional lime kiln. Some suggested usage of the pure carbon dioxide stream is for the production of electro-fuels to replace fossil fuels, lignin extraction via the LignoBoost process to reduce the load of the recovery boiler, or it could be stored [25].

In summary, very few potential carbon capture technologies have been applied to mills, and there is currently low incentive to do so. In Sweden, a demonstration of black liquor gasification has been operated in Piteå [24], and Stora Enso has a pilot project for carbon capture in Skutskär [26]. Recently, Södra has joined a global project to reduce carbon emissions and, in the future, start using BECCS in their pulp mills [27]. The project between the pulp mill and IVL, which this thesis is a part of, is also a step in investigating new carbon capture technologies for pulp mills and how they can be integrated.

2.3 Chemical absorption

For post-combustion processes, chemical absorption is the most common and effective type of separation method [8]. This is because of many factors, including high absorption efficiency and low equipment cost [2]. In post-combustion processes, the CO_2 volume fraction in the flue gas is usually from 3-15%, which makes chemical absorption preferred compared to physical absorption because of lower costs [2].

The choice of absorption medium, also called absorbent or solvent, is very important in increasing efficiency and reducing costs. The choice of absorbent depends on the flue gas characteristics, such as the concentration and partial pressure of the carbon dioxide and the interaction between the fluid components. For chemical absorption, amine absorbents are the most common [2] such as monoethanolamine (MEA), piperazine (Pz), diethanolamine (DEA), and N-methyldiethanolamine (MDEA) [8]. MEA is the most common absorbent [8], and amine absorption is a well-known and widely used technology [2]. MEA can usually achieve a carbon capture rate of above 90%.

However, MEA, MDEA, and DEA can cause environmental problems since they decompose, which generates waste that has to be taken care of [2]. Flue gas treatment using amine absorbents can react and form ammonia, which is toxic when emitted in high concentrations. There is also a risk of the amines ending up in water streams, which could disrupt aquatic life [28]. Absorption with MEA also requires a lot of energy because of high reaction enthalpies [2].

2.3.1 White liquor as an absorbent

White liquor is one of the products in causticisation and an important chemical in the process. The solution consists of around 10% NaOH, 5% Na_2S and 3% Na_2CO_3 [19]. Not many studies have been done where white liquor has been used as an absorption medium. Only two studies have been found during the literature study where white liquor has been used as an absorption medium. One study was done at a pulp mill in Canada using white liquor in a scrubber to remove total reduced sulphur (TRS) gases in non-condensable gases. The study found that the white liquor successfully reduced some TRS, with efficiencies ranging from around 50% for the less effectively scrubbed gases. In contrast, the more effectively scrubbed gases had an efficiency of over 95% [12].

The other study was on sulphur recovery from syngas by Hruška et al. [29]. Here, syngas cleaning was investigated with two different absorption methods; MDEA and white liquor with a NaOH solution. The white liquor and NaOH solution was done in two steps, as solely using white liquor did not reach the targeted H_2S content of 20 ppmv. The study found that 16 772 kg/h CO_2 could be absorbed per 100 000 kg/h white liquor followed by a further 2 241 kg/h CO_2 per 21 500 kg/h NaOH solution, and to be able to calcinate the white liquor and NaOH solution the lime kiln had to expand its capacity by 22 000 kg CaO/h. The white liquor and NaOH solution had a total CO_2 absorption efficiency of 44,2% compared to the MDEA alternative, which had a 25,3% CO_2 absorption efficiency. Both alternatives had a 99,2% H_2S absorption efficiency. Because the study focused on sulphur recovery, it was concluded that the MDEA alternative was preferred because of its lower CO_2 capture efficiency, which does not require the addition of a new lime kiln. Therefore, they concluded that the white liquor and NaOH solution was economically infeasible. The CO_2 content in the syngas was about 62 w/w %, much higher than that of typical flue gas [29].

However, a known absorption medium is sodium hydroxide which can be used in CO_2 absorption. In theory, white liquor could work as an absorbent of CO_2 since it contains NaOH. The reactions between CO_2 and NaOH are called carbonation reactions, presented below. Since NaOH is very alkaline, the NaOH is split into its ions Na^+ and OH^- in water. First, the CO_2 is physically absorbed into the solution and becomes aqueous, and immediately reacts. Above pH 12,3, the following net reaction occurs where the OH^- ions react with the CO_2 to form CO_3^{2-} [30].

$$CO_{2(g)} + 2\,NaOH_{(aq)} \longleftrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \tag{2.7}$$

The pH decreases as the OH^- ions react with the CO_2, which happens fast in the beginning as the CO_3^{2-} ions are formed. That allows for the following reaction to occur.

$$Na_2CO_{3(aq)} + H_2O_{(l)} + CO_{2(g)} \longleftrightarrow 2\,NaHCO_{3(aq)} \tag{2.8}$$

The two reactions exist in equilibrium, dependent on pH.

One study done by Levantaki et al. [31] assessed the CO_2 absorption of NaOH in concentrations 1-8 w/w% with a CO_2 concentration of 30 v/v%. The experiments started at a pH between 12,4-13,5, dependent on NaOH concentration, and stopped at pH below 8 because of low CO_2 absorption. The inlet gas flow of 200 mL/min was injected into a 60 mL NaOH solution in a reactor. The absorption of the CO_2 was high at the beginning, and only the reaction in equation (2.7) occurred. At a certain point, the pH level dropped significantly and the reaction in equation (2.8) started increasing and equation (2.7) peaked. For a concentration of 4 w/w% NaOH, this occurred at a pH of about 12,3. It was also noted that the CO_2 absorption decreased over time as the pH dropped. The time for the pH to drop below 8 was increased with an increased NaOH concentration. Results suggested that the amount of OH^- ions were the driving force for the CO_2 absorption, and a NaOH concentration of 8 w/w% had the highest CO_2 absorption rate of 78,9 g/L [31].

In a study by Zhenqi et al. [32], they studied the CO_2 removal efficiency from a CO_2 and N_2 mixture in a spray scrubber using NaOH as a solvent. Effects of NaOH concentration, NaOH flow rate, gas flow rate, initial temperature and CO_2 inlet concentration were evaluated, looking at the change in CO_2. It was found that the NaOH concentration increased the CO_2 removal efficiency until the concentration reached a maximum of 95,5% at 10 w/w% NaOH, after which the CO_2 removal efficiency decreased again. The increase in NaOH flow rate steadily increased the CO_2 removal efficiency. In contrast, increasing the gas flow rate decreased the removal efficiency because of decreased contact time with the liquid. When it comes to the initial temperature in the scrubber, an increase in temperature increases the CO_2 removal efficiency because of the increased absorption rate, which is temperature dependent. Finally, an increase in CO_2 concentration in the inlet gas slightly decreased the CO_2 removal efficiency [32].

In a study by Yoo et al. [30], it was found that the CO_2 capture efficiency was between 35-58% with equation (2.7) and an extra 8-11% capture with equation (2.8) for solutions between 1-5 w/w% NaOH [30]. It could also be seen that equation (2.8) only started happening once the OH^- ions had been consumed in equation (2.7). It was concluded that equation (2.7) was a first-order reaction only dependent on available OH^- and that in the equilibrium stage of equation (2.7) and equation (2.8) the reactions were only dependent on CO_3^{2-} concentration [30].

2.4 Scrubbers

A scrubber is an effective way of removing particles or gases from the exhaust gas. In a wet scrubber, a liquid is used to absorb the unwanted particles in the gas, and it is typically very efficient [33].

To receive high absorption efficiency, it is essential to maximise the contact between the gas and the liquid [34]. This can be done in many different ways, mainly by using a packed tower or a plate tower, but there are also less common alternatives like spray towers and bubble columns [35]. Further, the operation of packed and plated columns will be introduced, as these are the most common wet scrubbers.

2.4.1 Packed columns

In a packed column, the gas enters from the bottom, and the liquid from the top, called counter-current absorption. The liquid is dispersed at the top over a plate holding the packing. It then flows over the packing as film or droplets, which creates a large surface area for the gas to interact with the solution. The gas flows upwards through the packing and exits at the top of the scrubber while the liquid is collected at the bottom [35]. In figure 2.3a, an overview of a packed column can be viewed.

The packing material can be either random or structured, and the mass-transfer efficiency between the liquid and gas decreases with the increase in the packing size. Metal packing is typically preferred for random packing because of its strength, but ceramic or plastic packing are less costly alternatives. Ceramic or plastic is preferred when working with corrosive liquids. Structured packing also comes in metal or plastic [35].

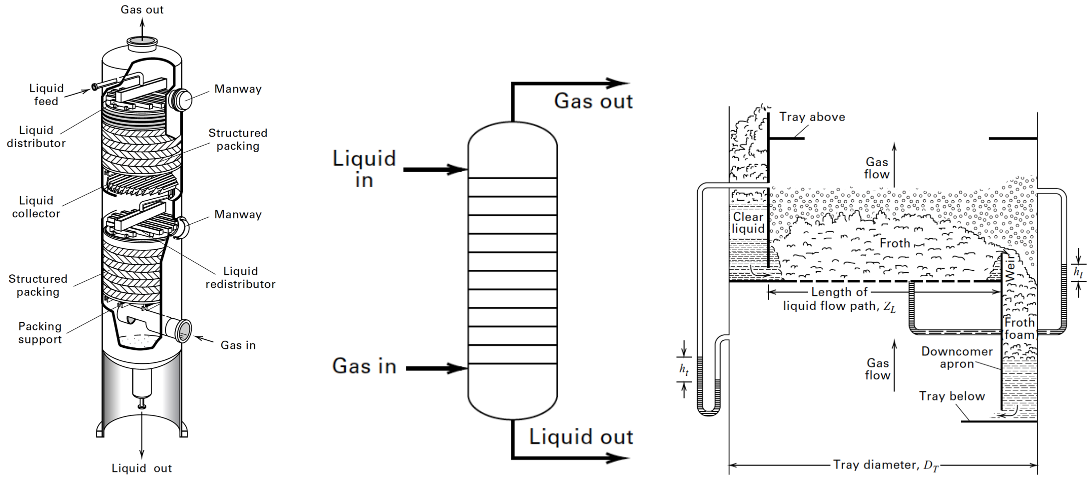
A common problem in packed columns is channelling, where the liquid falls along the walls, and the gas flows through the centre. This significantly reduces the mass transfer. The packing should be less than one-eighth of the column diameter to avoid channelling [35].

A packed column is typically preferred when the diameter of the column is less than 60 cm, the packing height is no more than 6 m, when working with corrosive fluids, when the low-pressure drop is needed, or when low liquid holdup is wanted, and when there is a high liquid velocity. In a packed column, the gas phase is usually mass-transfer limiting [35].

2.4.2 Plated columns

The flow in plated columns is also counter-current, where the liquid is dispersed over plates with holes through which the gas flows upwards. Some common plates are sieve trays, valve trays, and bubble-cap trays. Typically, sieve trays are preferred because of their low cost, but valve trays are preferred when flexibility in throughput is needed [35]. An overview and more detailed view of a plated column can be viewed in figure 2.3b and figure 2.3c.

Plated columns are typically more reliable and preferred when there are low liquid flows. In plated columns, the liquid phase is mass-transfer limiting [35].



(a) Packed column **(b)** Plated column **(c)** Plated column internals

Figure 2.3: Overview of (a) a packed column and (b,c) a plated column [35].

3

Methodology

This thesis was carried out by first doing a literature study. After that, a carbon capture unit was chosen and simulated using ASPEN Plus. A cost calculation was done for the simulated carbon capture unit, and after that, a statistical model was created, which could be coupled to the digital twin. Lab experiments were also performed using white liquor for CO_2 absorption. All parts are described in further detail below.

3.1 Literature study

To start with the project, a literature study was made. The Kraft pulping process was studied in detail to understand the process and chemistry involved. Next, different carbon capture technologies were studied, specifically coupled to pulp mills. Then, carbon capture technologies coupled with flue gas cleaning was studied to decide what type of technology to simulate. Finally, literature about sodium hydroxide and white liquor as absorption mediums were studied to find reference cases for the simulations and study the feasibility.

3.2 Design and simulation of scrubber

An overview of the proposed carbon capture process, coloured black, can be found in figure 3.1.

The flue gases from the recovery boiler are sent to the scrubber with part of the white liquor from the causticisation. The outlet liquid stream from the scrubber, called CC-liquor in the figure, is sent back to the causticising unit while the remaining flue gases are released into the air.

The flow of flue gases out of the recovery boiler was set to 232 kg/s, given by IVL and based on the operating conditions at the pulp mill. The flow and composition of the flue gas stream can be found in table 3.1. The composition was taken from another project done at a pulp mill [8] and combined with data given by the investigated pulp mill.

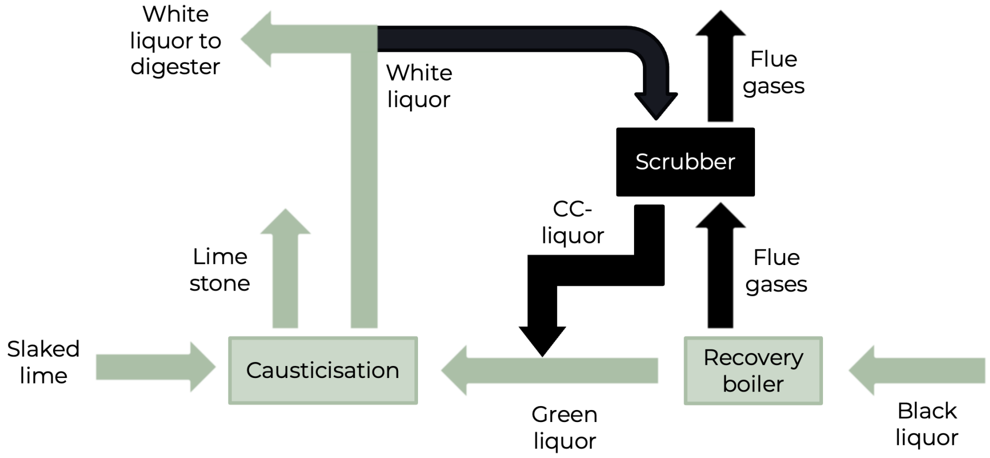


Figure 3.1: Overview of the proposed carbon capture process, coloured black.

Table 3.1: Flue gas composition out of the recovery boiler taken from [8] and the pulp mill.

Substance	**Composition [mole-%]**
CO_2	15
N_2	62
H_2O	19
O_2	4

The active components in the white liquor are the hydroxide ions (OH^-) and sulfur ions (HS^-) [11]. In the simulation, it was assumed that only the sodium hydroxide reacts with the carbon dioxide and that the rest of the substances are inert since H_2S will not form when the pH>9 [36]. Based on the following reaction, an initial guess of the mass flow of white liquor was calculated.

$$2\,NaOH(aq) + CO_2(g) \longrightarrow Na_2CO_3(aq) + H_2O(l) \tag{3.1}$$

The white liquor composition and mass flow are found in table 3.2, where water is the solvent.

Table 3.2: Typical white liquor composition, sulphidity, and alkali [19].

NaOH	100 g/L
Na_2CO_3	30 g/L
Na_2S	55 g/L
Sulphidity	35 %
Effective alkali	130 g/L
Active alkali	160 g/L

Assuming 100% conversion, the initial guess for the mass flow of white liquor was calculated to be just under 1000 kg/s, given the flue gas flow of 232 kg/s.

As for green liquor, the typical composition can be found in table 3.3. It was assumed that the green liquor flow out of the recovery boiler was 400 m3/h.

Table 3.3: Typical green liquor composition, sulphidity, and alkali [37]

NaOH	5 g/L
Na_2CO_3	130 g/L
Na_2S	50 g/L
Sulphidity	85 %
Effective alkali	35 g/L
Active alkali	60 g/L

The pH was calculated with equation (3.2), using the NaOH concentration in molarity, and was calculated to be pH 14,4 for white liquor and pH 13,2 for green liquor.

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{pH} - \log[\mathrm{OH^-}] = 14 \tag{3.2}$$

3.2.1 Reactions

Since white liquor consists mainly of sodium hydroxide, it was assumed to work similarly to a sodium hydroxide solution. Carbon dioxide absorption with sodium hydroxide has been widely studied, and reactive absorption occurs as follows. First, the sodium hydroxide is completely ionised into Na^+ and OH^- ions [30]. It was also assumed that the sodium carbonate and sodium sulfide are ionised into Na^+ and CO_3^{2-} as well as S^{2-} ions.

When the CO_2 flows through the solution, it is first physically absorbed into the solute. It can then react with the hydroxide ions in two steps, described in equation (3.3) and equation (3.4) [30].

$$\mathrm{CO_{2(aq)} + OH^-_{(aq)} \longleftrightarrow HCO^-_{3(aq)}} \tag{3.3}$$

$$\mathrm{HCO^-_{3(aq)} + OH^-_{(aq)} \longleftrightarrow CO^{2-}_{3(aq)} + H_2O_{(l)}} \tag{3.4}$$

The overall reaction that occurs is the following.

$$\mathrm{CO_{2(aq)} + 2\,NaOH_{(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}} \tag{3.5}$$

Equation (3.3) is the limiting reaction, but at high pH, both reactions are very fast and equation (3.4) occurs immediately after equation (3.3). At high pH, mostly CO_3^{2-} is formed [30].

The white liquor also contains sulphur in the form of Na_2S, which means that sulphur can react with water and form H_2S. H_2S is a very toxic and hazardous gas that has to be removed from the flue gas before it is released into the atmosphere [38]. The sulphur can exist in three forms, H_2S, HS^-, and S^{2-}, and the concentrations of the different forms are highly dependent on pH, which can be viewed in figure 3.2 [36].

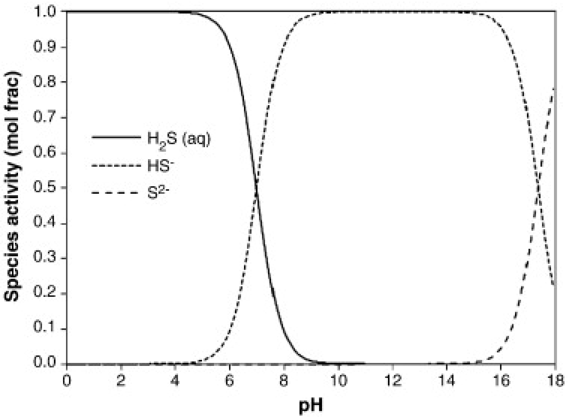


Figure 3.2: Sulphur forms dependence on pH [36].

It can be noted that H_2S is non-existent at pH>9 and that the sulphur exists almost only in the form of HS^- at pH 9 to 15. Removing H_2S from a gas can be done with filters or scrubbers [38].

3.2.2 Design in ASPEN Plus

An existing example for carbon capture with NaOH in ASPEN Plus was used as a basis for the reaction mechanisms. In the ASPEN Plus example, equation (3.4) was divided into two other reactions. Firstly, the self-ionisation of water in equation (3.6), and then the reaction of bicarbonate with water in equation (3.7).

$$2\,H_2O \longleftrightarrow H_3O^+ + OH^- \tag{3.6}$$

$$HCO^-_{3(aq)} + H_2O_{(l)} \longleftrightarrow CO^{2-}_{3(aq)} + H_3O^+_{(aq)} \tag{3.7}$$

The backward and forward reaction for equation (3.3) was set as kinetic reactions, and equation (3.6) and equation (3.7) were set as equilibrium reactions. For the kinetic reactions, the Arrhenius equation was used to calculate the kinetic rates of the reactions. In ASPEN Plus, the Arrhenius equation is defined as

$$K = kT^n e^{-\frac{E}{RT}} \tag{3.8}$$

where K is the kinetic rate of reaction, k is the pre-exponential factor, T is the temperature in Kelvin, n is a factor, E is the activation energy and R is the universal gas constant. The reactions and their constants were taken from the ASPEN Plus example and can be viewed in table 3.4 for the kinetic reactions.

Table 3.4: Kinetic constants for equation (3.3)

Reaction	**k**	**n**	**E [cal/mol]**
equation (3.3) forward	4,32e+13	0	13 249
equation (3.3) backward	2,83e+17	0	29 451

The built-in equilibrium reaction in ASPEN Plus, which has the form shown in equation (3.9), was used for the equilibrium reactions in equation (3.6) and equation (3.7), where A, B, C, and D are constants and T is the temperature in Kelvin. The constants were taken from the ASPEN Plus example for the equilibrium reactions and can be viewed in table 3.5.

$$ln(K_{eq}) = A + \frac{B}{T} + Cln(T) + DT \tag{3.9}$$

Table 3.5: Equilibrium reaction constants for equation (3.6) and equation (3.7).

Reaction	**A**	**B**	**C**	**D**
equation (3.6)	132,899	-13 445,9	-22,4773	0
equation (3.7)	216,049	-12 431,7	-35,4819	0

In ASPEN Plus, the Radfrac block was chosen for the scrubber. The inlet white liquor (LIQ-IN) and inlet flue gas (GAS-IN) were first specified according to the given data by the pulp mill, using the compositions from table 3.1 and table 3.2. The initial inlet conditions can be viewed in table 3.6.

Table 3.6: Initial inlet conditions for the white liquor and flue gas.

Stream	**Temperature [°C]**	**Pressure [Pa]**	**Flow rate [kg/s]**
LIQ-IN	102	101 325	232
GAS-IN	200	101 325	1 000

An overview of the absorber flowsheet can be seen in figure 3.3.

After designing the inlets and overall scrubber, the column internals were designed. An initial guess was made with 25 stages and pall ring packing. The stages were numbered from top to bottom, and the feed streams were put as *On-stage*. The first stage pressure was set equal to the liquid inlet pressure of 101 325 Pa. The packing was initially put as pall rings, and ASPEN Plus calculated the column diameter to be 12,1083 m. The packing size was set to 50 mm, by industry recommendations [39]. A summary of the initial guess for the dimensions can be viewed in table 3.7.

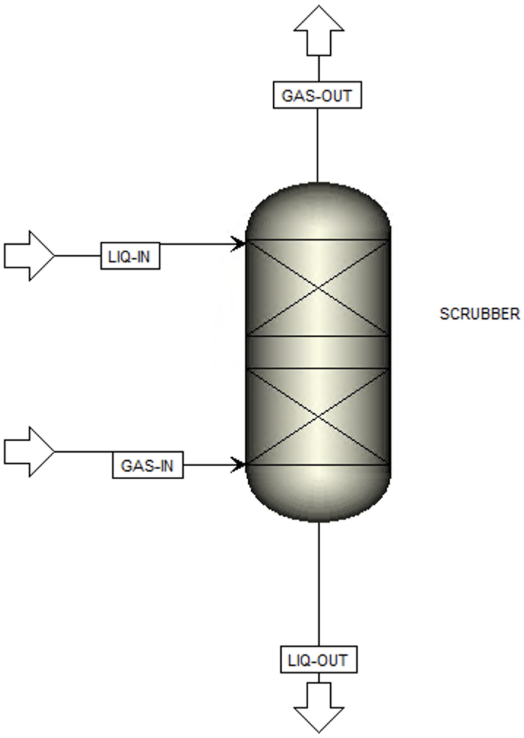


Figure 3.3: Overview of the scrubber flowsheet in ASPEN Plus.

Table 3.7: Initial guess for the scrubber dimensions.

Diameter [m]	12,1083
Stage height [m]	1
Number of stages	25
Pressure [Pa]	101 325

First, equilibrium calculations with interactive sizing mode for the packing were performed to ensure convergence. This was achieved easily, so rate-based calculations were then performed with rating mode for the packing. For the rate-based calculations, film reactions were included for both the liquid and gas phase. For fast reactions, the reaction occurs in the film, and in the CO_2-NaOH system they occur in the liquid film [40]. Since the reactions are deemed fast at high pH, the film resistance was set to *Film reactions* for both the liquid and gas phases. The flow model was set to mixed, assuming that the packing created good contact between the liquid and gas phases.

3.2.3 Sensitivity analysis and optimisation

After designing the scrubber, a sensitivity analysis was performed. While a sensitivity analysis was performed, the other parameters that were not investigated were kept at their value of the initial design, respectively. The parameters and range of values evaluated and the initial design values can be viewed in table 3.8.

Table 3.8: Initial operating conditions and start and end value for the performed sensitivity analyses.

Parameter	**Unit**	**Initial design**	**Start value**	**End value**	**Step size**
White liquor inlet flow	kg/s	1 000	100	2 000	10
White liquor inlet temperature	°C	102	20	300	5
Flue gas inlet temperature	°C	200	20	300	5
Scrubber inlet pressure	Pa	101 325	50 000	500 000	5 000
Scrubber inner diameter	m	12,1083	4	20	0,1
Number of stages	-	25	5	65	5
Stage height	m	1	0,2	10	0,1

All of these parameters were analysed using the built-in sensitivity analysis tool in ASPEN Plus, except for the number of stages, which was evaluated manually. This was due to the value being changed at three different places in the simulation - the number of ideal stages, the packing stages, and the gas inlet stage.

Different types of packing were also tested manually. The tested packing and sizes can be viewed in table 3.9. The packaging was chosen randomly based on wanting to try an assortment of random and structured packing in different sizes, to ensure that the model acted according to theory and to evaluate which packing to use for the final design. For the structured packing, the number denotes the surface area of the packing per unit volume [41] and X or Y denotes the corrugation angle, which is 45° for Y and 60° for X [42]. The requirement was that the packing was available in either plastic or ceramic and that no additional information had to be supplied to ASPEN Plus regarding the packing. The tests of the different packings were done after the scrubber dimensions had been chosen. In the initial design and for the sensitivity analysis, metal pall rings size 50-MM were used because the corrosivity of white liquor had not been researched yet.

The flue gas flow was set to the constant value of 232 kg/s which is the approximate flue gas flow at normal operating conditions for the plant. The scrubber height was determined by multiplying the number of stages with the stage height and adding 1 m to accommodate the top and bottom fluid distribution and collection.

The carbon capture efficiency of the scrubber was calculated by subtracting the outlet mole flow of CO_2 in the gas from the inlet mole flow of CO_2 and dividing by the inlet mole flow of CO_2, according to equation (3.10), with the unit mol-%.

$$\text{Carbon capture efficiency [mol-\%]} = \frac{F_{CO2,in} - F_{CO2,out}}{F_{CO2,in}} \times 100\% \tag{3.10}$$

After the sensitivity analysis had been performed for all parameters, a final design

Table 3.9: Different packing materials and sizes evaluated in ASPEN Plus.

Packing name	Type	Material	Void factor	Sizes
Pall ring	Random	Metal	0,96	50-MM
Pall ring	Random	Plastic	0,9 0,91 0,92 0,92	25-MM 38-MM 50-MM 75-MM
Raschig ring	Random	Ceramic	0,64 0,74 0,73 0,75	13-MM 25-MM 38-MM 75-MM
Berl saddle	Random	Ceramic	0,68 0,71 0,72	25-MM 38-MM 50-MM
Mellapak	Structured	Plastic	0,988 0,987 0,987	125Y 250X 250Y

was decided based on the sensitivity analysis result, the carbon capture efficiency, and the equipment cost described in section 3.3. The general aim for the final design was to be around 80% flooding to ensure that the scrubber was used at a good capacity.

3.3 Cost calculations

The method for the cost calculations will be presented below. The calculations consisted of estimating capital costs, operating costs, and potential profits. However, no product will be sold in the proposed carbon capture process, so no revenues are associated with the process.

3.3.1 Capital cost

Capital costs consist of many things, mainly designing, constructing and installing the new equipment. To calculate the equipment costs, the following correlation was used where C_e is the purchased equipment cost, a and b are constants depending on the equipment type, S is a size parameter, and n is an exponent dependent on the equipment type [43].

$$C_e = a + b * S^n \tag{3.11}$$

In Chemical Engineering Design by Towler [43], an absorption column is calculated with the values for a pressure vessel. For vertical pressure vessels, the constants in table 3.10 were used.

Table 3.10: Constants for pressure vessels for equation (3.11) for two different scrubber wall materials [43].

Material	**S$_{lower}$ [kg]**	**S$_{upper}$ [kg]**	**a**	**b**	**n**
Carbon steel	160	250 000	11 600	34	0,85
Stainless steel	120	250 000	17 400	79	0,85

To calculate the mass of the wall material, the absorption column was estimated as a cylinder with a wall thickness that was calculated according to equation (3.12) where t is the wall thickness, P_i is the internal pressure, D_i is the internal diameter, and S is the maximum allowable stress.

$$t = \frac{P_i D_i}{2S - P_i} \tag{3.12}$$

The maximum allowable stress for carbon steel is 12 900 psi at 300°F (159°C) and 16 700 psi for stainless steel [43]. An extra height of 0,5 m was added to the top and bottom of the column in the calculations. The density of carbon steel was put as 7 850 kg/m^3 and 8 000 kg/m^3 for stainless steel [44].

The packing cost was also estimated using tabulated data from Chemical Engineering Design [43]. The costs for different packings can be viewed in table 3.11. For packing, S in equation (3.11) is the packing volume in m^3. The void factor given by ASPEN plus for all the packings was used to calculate the packing volume. These can be viewed in table 3.9. The volume of the packing, V_P, is then calculated by multiplying the bulk volume, V_B, of the cylindrical scrubber in m^3 by one minus the void factor, as in equation (3.13) [45].

$$V_P = V_B \times (1 - \epsilon) \tag{3.13}$$

Table 3.11: Constants for different packings for equation (3.11) [43].

Packing	**a**	**b**	**n**
Ceramic Intalox saddles	0	2 000	1
304 ss Pall rings	0	8 500	1
PVC structured packing	0	5 500	1

For the calculations, the price for the Intalox saddle was used to calculate the cost of Berl saddles, assuming a similar price.

When choosing material for the scrubber and packing, the material had to be chosen considering the solvent and flue gas properties. White liquor contains mainly sodium hydroxide, which is strongly alkali and very corrosive [46]. Previous studies have recommended stainless steel, which is more resistant to corrosion. Carbon steel has low corrosion resistance. North American carbon steel tanks storing Kraft liquors usually experience high corrosion, while the stainless steel tanks used in Scandinavia experience very little corrosion [47]. Stainless steel is also more resistant to high temperatures [48]. For 10 w/w% NaOH, stress cracking has been reported over 80°C and above 120°C for stainless steel, but for white liquor, when sulphide is present, cracking and corrosion can occur at lower temperatures [49]. As for packing, plastic or ceramic is cheaper than metal packing, and they are also more resistant to corrosion [40].

All cost estimation constants are based on the U.S. Gulf Coast in January 2010, which has a CEPCI index of 532.9. To calculate the cost for the year 2023, the following equation can be used [43].

$$\text{Cost in year A} = \text{Cost in year B} * \frac{\text{Cost index in year A}}{\text{Cost index in year B}} \tag{3.14}$$

For 2022, the CEPCI index was 813,0 [50], used to calculate the cost. During 2022, the average exchange rate from U.S. Dollar to Swedish Krona was 10.1198 SEK/USD [51].

3.3.2 Operating costs

The operating costs are associated with the everyday running of the plant, like consumed materials and chemicals, utilities, maintenance, operating labour and disposal.

In the process, it is assumed that there is no cost for heat utilities since the entire pulp mill has a heat surplus. There is also no electricity shortage since the mill produces electricity at the plant which is used in the mill. The pulp mill is in Elområde 2, Sweden's electricity price area 2. In this area, there is generally an excess of electricity, and the demand is lower, so the price is generally lower [52].

To control the Na/S balance, sodium hydroxide or sulphur can be added to the liquor. The annual average price for sodium hydroxide was 0,41 US$/kg in 2022 [53]. The price for sulphur was 150 US$/ton in 2022 [54].

In Sweden, there is no carbon dioxide tax for biogenic CO_2 emissions, as is the case for a Kraft pulping mill [55]. Therefore, no carbon avoidance cost will be added to the operational costs.

3.4 Simulink model

After deciding on the scrubber's dimensions, a statistical model was created using ASPEN Plus and MODDE that could be put into MATLAB Simulink. The factors needed for the statistical model were deemed to be the gas and white liquor inlet flows and the white liquor temperature, based on the sensitivity analysis and general understanding of the process and MATLAB Simulink model. The outputs were put as the carbon capture efficiency, the outlet liquor temperature and outlet liquor composition for NaOH, Na_2CO_3, and Na_2S.

The statistical model was created by deciding on a minimum and maximum value for each factor and a central point, which was put as the point in the middle of the minimum and maximum value for the factor. This simple linear statistical model has three factors or axes, creating eight corner points. The middle point was run twice to ensure the same result. The ASPEN Plus model was then run at each experiment according to the run order, and data for each experiment were collected.

After this, it was noted that the model was not linear, and seven additional experimental points were added to create a non-linear model. All 17 experiments and the run order can be seen in table 3.12.

Table 3.12: Experimental setup of statistical model in ASPEN Plus.

Exp No	**Run Order**	**White liquor temp. [°C]**	**Vhite liquor flow [kg/s]**	**Flue gas flow [kg/s]**
N1	4	20	400	125
N2	9	110	400	125
N3	11	20	400	250
N4	16	110	400	250
N5	1	20	1200	125
N6	2	110	1200	125
N7	12	20	1200	250
N8	10	110	1200	250
N9	5	20	800	187,5
N10	15	110	800	187,5
N11	3	65	800	125
N12	13	65	800	250
N13	17	65	400	187,5
N14	8	65	1200	187,5
N15	7	65	800	187,5
N16	6	65	800	187,5
N17	14	65	800	187,5

After the results were generated for each experimental point, one equation for each output was created using MODDE, totalling five equations. These equations were validated against the ASPEN Plus model using the inputs and results for the final design of the scrubber. The equations were then coupled with the MATLAB Simulink model. In the Simulink model, the lime kiln had an outlet flow of 17,1 kg CaO/s. Assuming 100% conversion in the lime kiln, that means a flow of 30,5 kg $CaCO_3$/s out of the causticisation.

3.5 Experiments with white liquor

The lab at the pulp mill performed lab experiments using white liquor as an absorption medium for CO_2. The results from the experiments will be used to discuss the feasibility of implementing the suggested carbon capture unit at the mill.

The experiments used white liquor from the mill, with approximate composition as in table 3.2. White liquor was put into a clear cylinder of 78 mm and placed in a fume hood on a scale; see figure B.1 in appendix B. The total weight of the cylinder and white liquor was noted before the experiments. Pure CO_2 was then made to flow through the white liquor from the bottom of the cylinder for a set time. After this, the total weight of the cylinder and liquor was once again noted down to calculate the CO_2 absorption of the white liquor. The white liquor and CO_2 gas had the same temperature as the ambient temperature of the lab at the start of the experiments.

Three experiments were done, first with a CO_2 flow of 72,5 mL/min for 20 minutes and secondly with a CO_2 flow of 29,0 mL/min for 20 minutes and for 10 minutes. After noting the weight increase, the CO_2 absorption could be calculated.

4

Results

Below are the results for the design, sensitivity analysis, cost calculations, and the statistical model. These results are then discussed in chapter 5.

4.1 Sensitivity analyses

The outlet mole flows and outlet temperatures were looked at for all sensitivity analyses of the scrubber in ASPEN Plus. The mole flows presented in the diagrams are for the CO_2 in the outlet flue gas, and the OH^-, CO_3^{2-}, HCO_3^-, HS^- ions and H_2S in the outlet liquor.

For all sensitivity analyses, one dimension or operating condition was analysed at the time. The other parameters that were not analysed were kept constant according to the specified conditions presented in table 3.7 and table 3.8.

First, the scrubber diameter was analysed. The sensitivity analysis of the diameter can be viewed in figure 4.1.

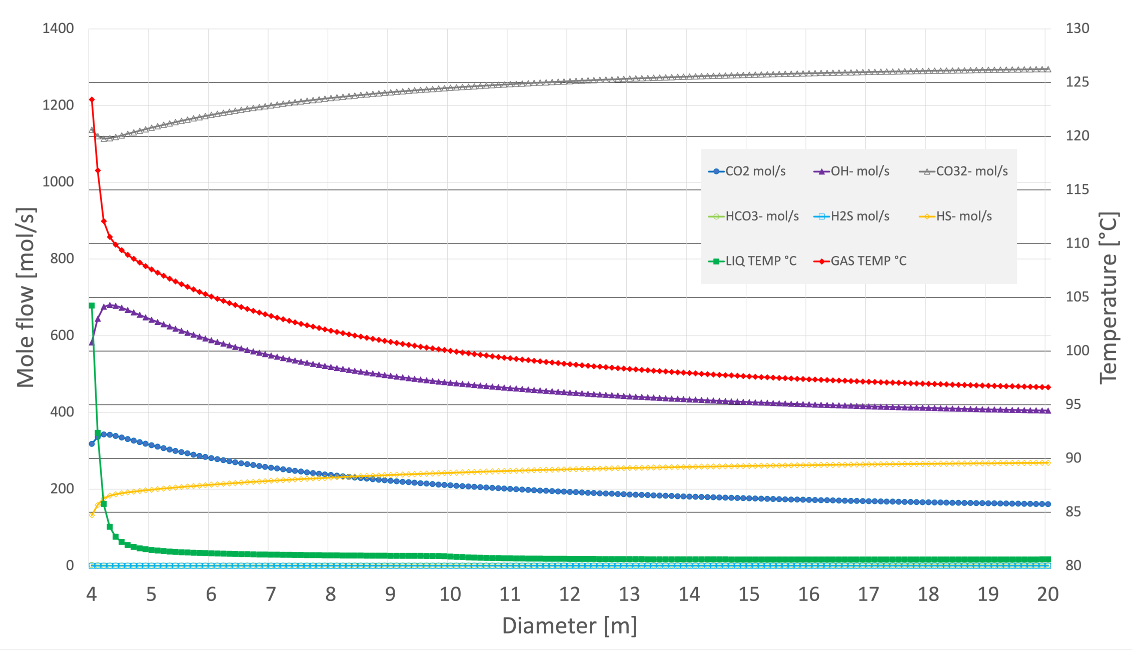


Figure 4.1: Variations in outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures depending on scrubber diameter.

The diameter was analysed between 4 and 20 meters. Four meters was the smallest diameter the ASPEN Plus model could handle without errors. From figure 4.1, it can be seen that the outlet temperatures, especially the liquor temp, fast reach a steady temperature of around 81°C for the liquor and around 100°C for the gas. The CO_3^{2-} flow increases with diameter, which means that the CO_2 in the outlet gas flow as well as the OH^- in the liquor decreases. Looking just at the CO_2 flow, it can be seen that after 4,2 meters, the difference in the flow between each step gets smaller. The carbon capture efficiency ranges from 74% to 87% and steadily increases with the diameter. It reaches 80% carbon capture efficiency at 7,7 meters and 85% at 13,8 meters in diameter.

Moving on to the packing stage height. The stage height was changed between 0,2 and 10 meters. The sensitivity analysis can be viewed in figure 4.2.

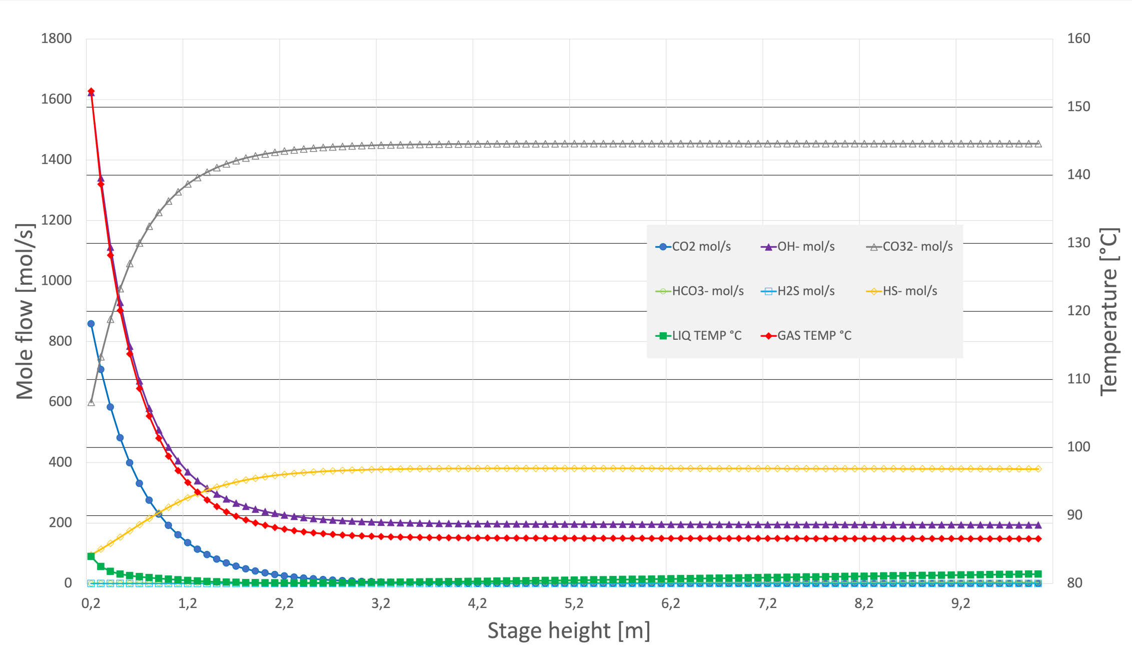


Figure 4.2: Variations in outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures depending on stage height.

The figure shows that most of the effect is between 0,2 and 2 meters. After that, the flows and temperatures stay constant with increasing stage height. The carbon capture increases from 29,3% to 97,1% between 0,2 and 2 meters, reaching 90% at 1,3 meters. At 2,7 meters, the carbon capture reaches 99%. However, increasing the stage height will increase the cost of the scrubber. This result will be presented further in section 4.2.

The inlet white liquor flow impact was analysed between 100 kg/s and 2 000 kg/s, and the results for the component mole flow and outlet temperatures can be viewed in figure 4.3.

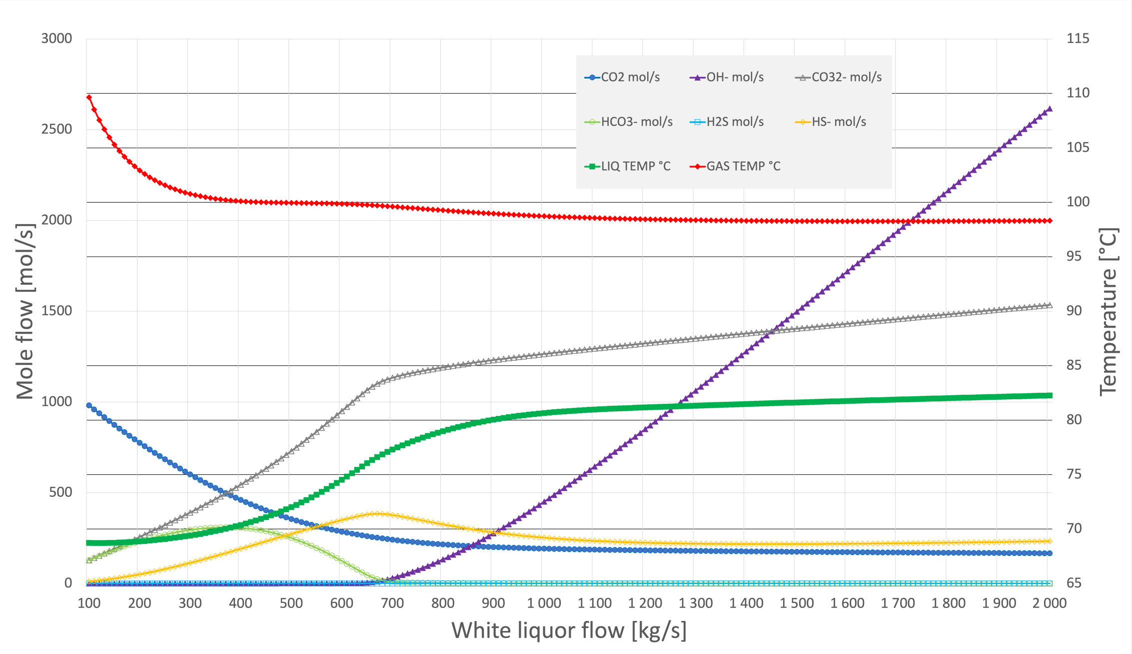
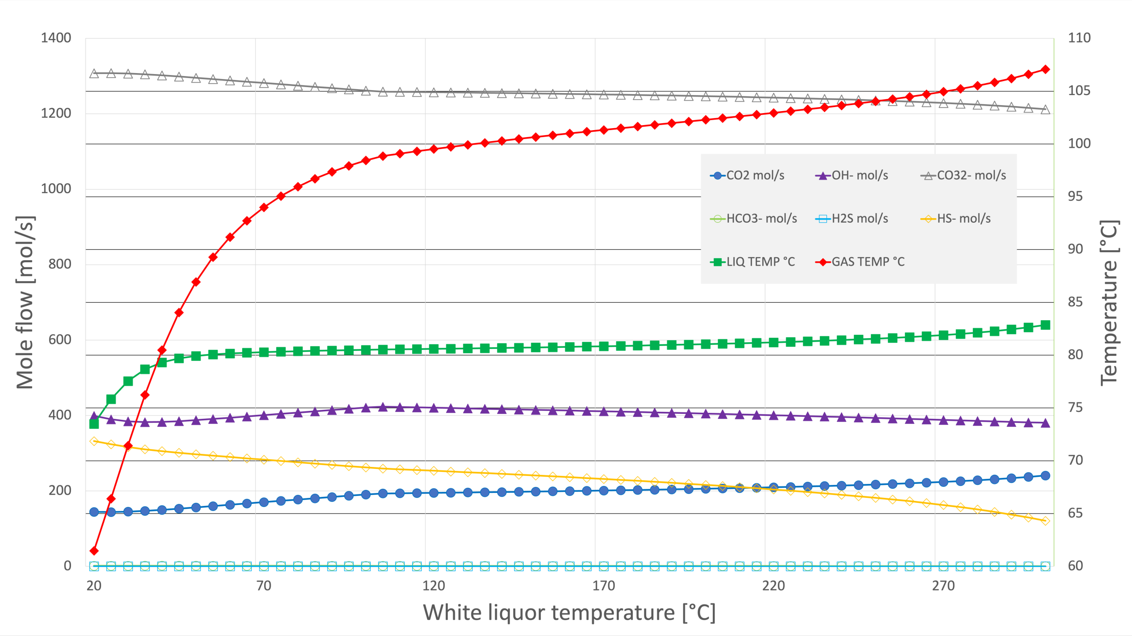


Figure 4.3: Variations in outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures depending on white liquor inlet mass flow.

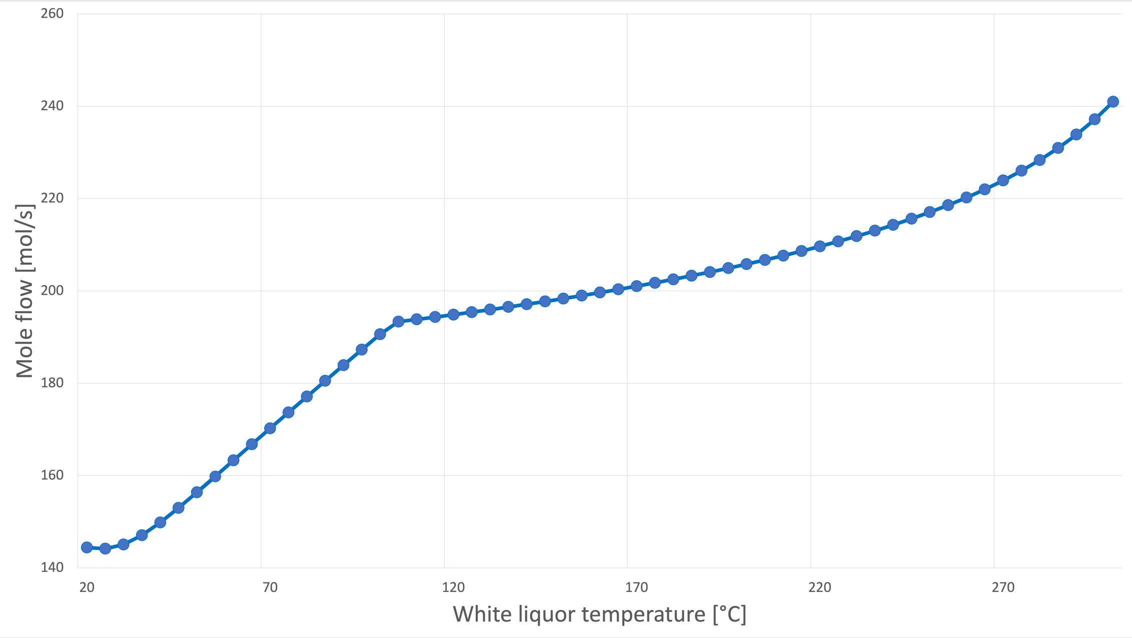
The white liquor mass flow seems to have a significant impact. The outlet flue gas temperature reaches a steady temperature of around 100°C at around 400 kg/s. The outlet liquor temperature is affected differently and reaches a steady temperature of about 83°C at around 1 000 kg/s. The H_2S concentration is almost zero for the entire analysed spectrum, but it does decrease with increasing white liquor flow. The HS^- flow is also affected by the white liquor flow and reaches a peak at 670 kg/s, which is around when the OH^- flow starts increasing. After this, the HS^- decreases slightly and reaches a steady flow of around 230 mole/s. When the OH^- starts increasing, the slope of the CO_3^{2-} increase becomes lower. Since the OH^- flow continues to increase after 700 kg/s, it can be concluded that some sort of maximum carbon capture is reached, which can also be seen in the outlet flow of CO_2 which reaches a plateau around the same flow. The reason for the continual increase in CO_3^{2-} could be because there is CO_2 solved in the liquid that has not reacted, and the increase in OH- drives the reaction in equation (3.5) to produce the products on the right. The carbon capture efficiency increases a lot in the beginning and then starts plateauing at around 700 kg/s. The efficiency is 19% at the minimum white liquor flow, then goes over 80% at 700 kg/s, and then reaches a maximum of around 85%.

Next, the effect of the white liquor inlet temperature was analysed. This was analysed between 20°C and 300°C, and the results can be viewed in figure 4.4. The inlet flue gas temperature was constant at 200°C during the analysis.

It can be concluded that the amount of CO_2 in the outlet gas increases with increasing white liquor temperature, meaning that the carbon capture efficiency is decreased with increased white liquor temperature. The carbon capture rate varies between 88% to 80%. Increasing the white liquor temperature has a significant effect on the outlet gas temperature, while the outlet liquor temperature stays relatively constant between 75-85°C.



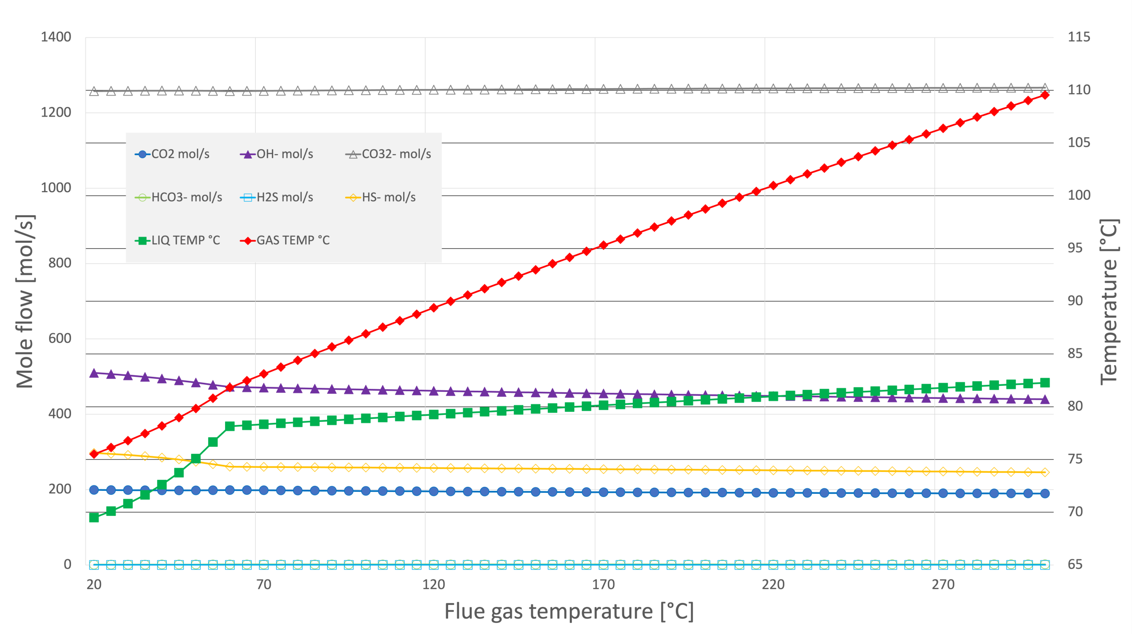
(a) Outlet mole flows and temperatures.



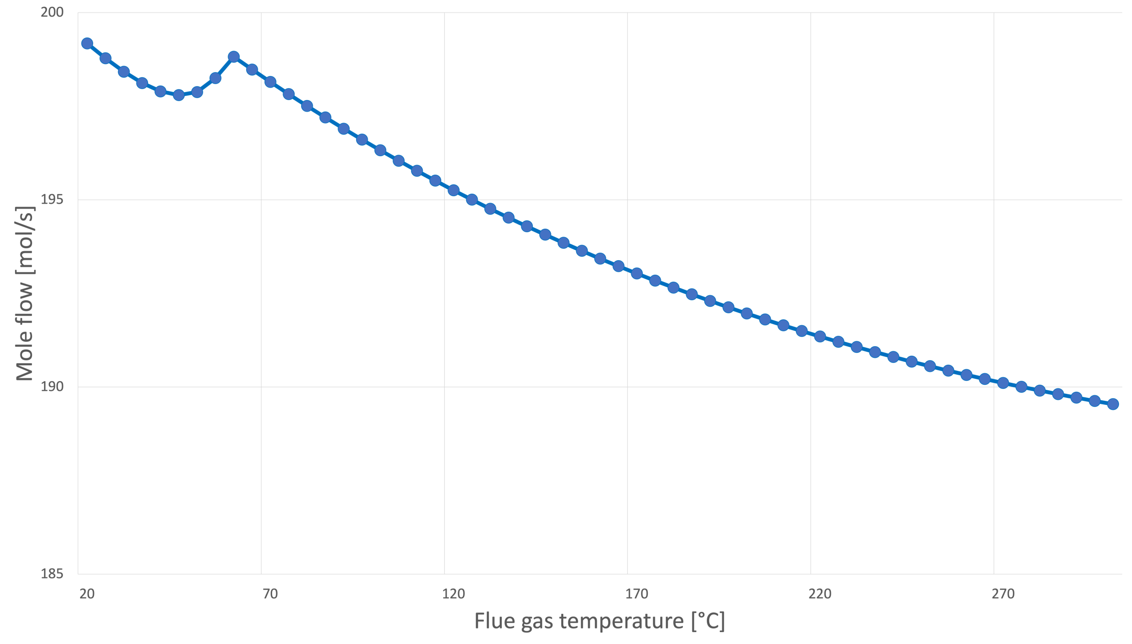
(b) CO2 outlet flow

Figure 4.4: Variations in (a) outlet flue gas CO$_2$ flow, outlet liquor component flows and outlet liquor and flue gas temperatures and (b) outlet flue gas CO$_2$ flow, depending on white liquor inlet temperature diameter.

The flue gas inlet temperature was also analysed between 20°C and 300°C, where the results can be viewed in figure 4.5.



(a) Outlet mole flows and temperatures.



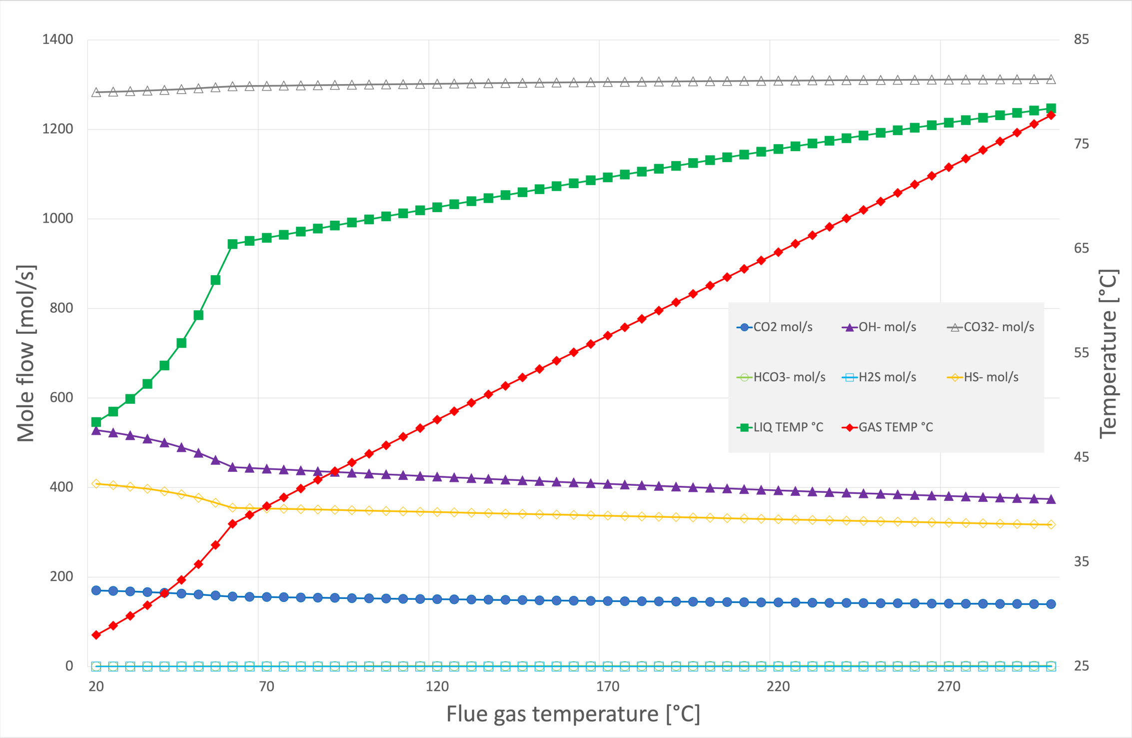
(b) CO2 outlet flow

Figure 4.5: Variations in (a) outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures and (b) outlet flue gas CO_2 flow, depending on flue gas inlet temperature.

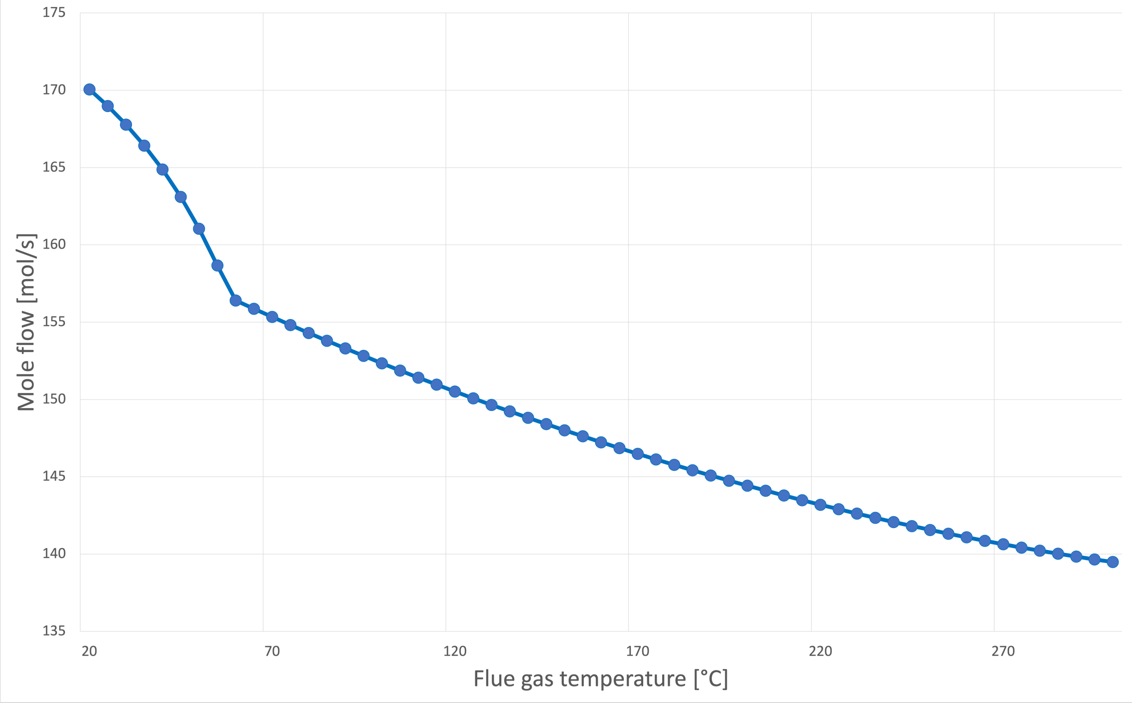
It can be concluded that the carbon capture efficiency increases with increasing flue gas temperature. However, the effect is minimal, with the efficiency only varying one percentage point around 84%. It can also be concluded that the white liquor temperature has a more significant effect on carbon capture than the flue gas temperature. It can also be noted in figure 4.5 that the CO_2 mole flow has a local maximum. This could be a result of the constants and the temperature dependence in equation (3.8) and equation (3.9).

Since a lower white liquor temperature was favourable and gave a higher carbon capture efficiency, the effect of the flue gas temperature outlet was evaluated when the inlet white liquor temperature was constant at 20°C instead of 102°C. These results can be viewed in figure 4.6.

The difference in the CO_2 mole flow is larger at the lower white liquor temperature than at the higher. However, the efficiency only varies between 86% and 89%, so the difference is still not much. A lower inlet temperature requires cooling, which will increase operating costs, while not bringing much difference in the carbon capture efficiency.



(a) Outlet mole flows and temperatures.



(b) CO2 outlet flow

Figure 4.6: Variations in (a) outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures and (b) outlet flue gas CO_2 flow, depending on flue gas inlet temperature when the white liquor inlet temperature is 20°C.

The internal scrubber pressure was also investigated between 50 kPa and 5 MPa; the result can be viewed in figure 4.7.

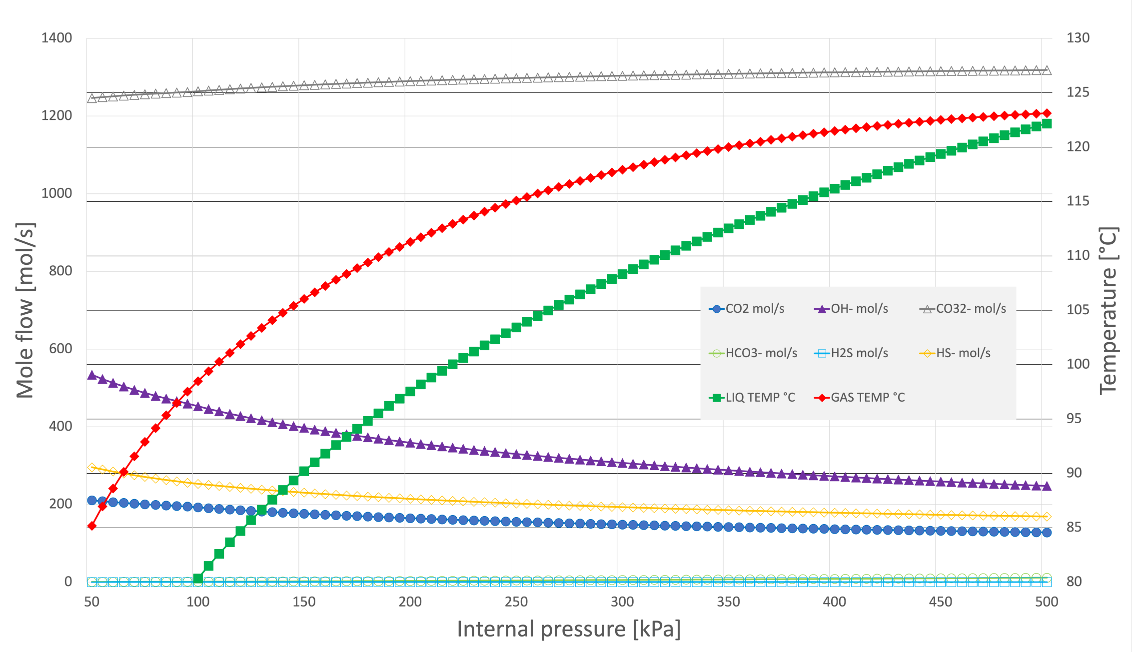


Figure 4.7: Variations in outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures depending on internal scrubber pressure.

It can be seen that increasing the pressure increases the carbon capture efficiency, which varies between 83% and 89%. It can also be noted that the outlet temperatures are increasing with increasing pressure, which is reasonable when one looks at the ideal gas law.

The number of stages was also investigated, which was done manually. The results can be seen in figure 4.8.

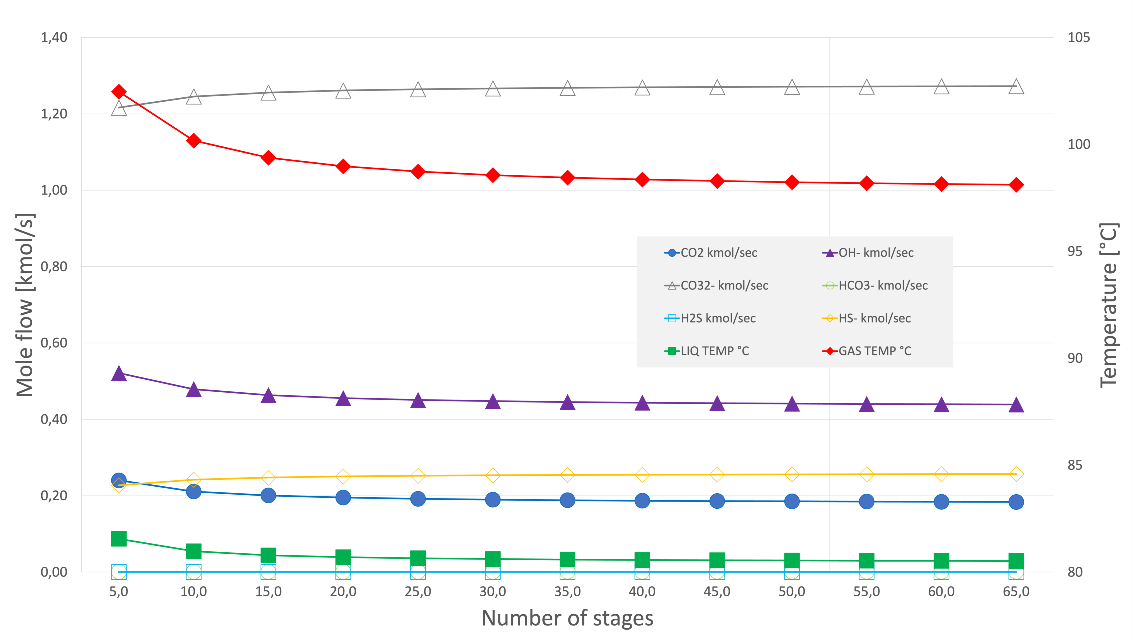


Figure 4.8: Variations in outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures depending on the number of stages.

The carbon capture increases with the number of stages, but the effect of increasing the number of stages gets less after around 25 stages, and the carbon capture efficiency varies between 80% and 85%. An increase in the number of stages significantly affects the investment cost and should therefore be increased carefully. This will be presented further in section 4.2.

For all sensitivity analyses, it could be seen that the H_2S and HCO_3^- flows are close to zero. This corresponds to theory, where no H_2S should be formed at such high pH, and the fast reactions and high pH should only form CO_3^{2-} ions.

Finally, different random and structured packing was tested, and the result for the carbon capture efficiency for the different packings can be viewed in table 4.1.

Table 4.1: Carbon capture efficiency depending on packing type and size.

Packing	**Material**	**Sizes**	**CO_2 capture efficiency [mol-%]**
Pall ring	Metal	50-MM	0,92
Pall ring	Plastic	25-MM 38-MM 50-MM 75-MM	0,96 0,91 0,84 0,63
Raschig ring	Ceramic	13-MM 25-MM 38-MM 75-MM	0,98 0,98 0,96 0,81
Berl saddle	Ceramic	25-MM 38-MM 50-MM	0,98 0,94 0,90
Mellapak	Plastic	125Y 250X 250Y	0,79 0,95 0,97

It can be seen that for smaller random packing sizes, the carbon capture efficiency increases. However, smaller packings give an increased risk of flooding in the scrubber. For the structured packing, the corrugation angles and surface area impacted carbon capture, receiving a higher capture efficiency with a larger surface area.

To ensure that the sensitivity analyses performed for the metal pall ring were representative, the same analyses were performed on Mellapak and 250X and Berl saddles, and they had the same visuals for the graphs but a slight difference in the value of the carbon capture efficiency and concentrations. Some results for the Mellapak can be viewed in appendix A.

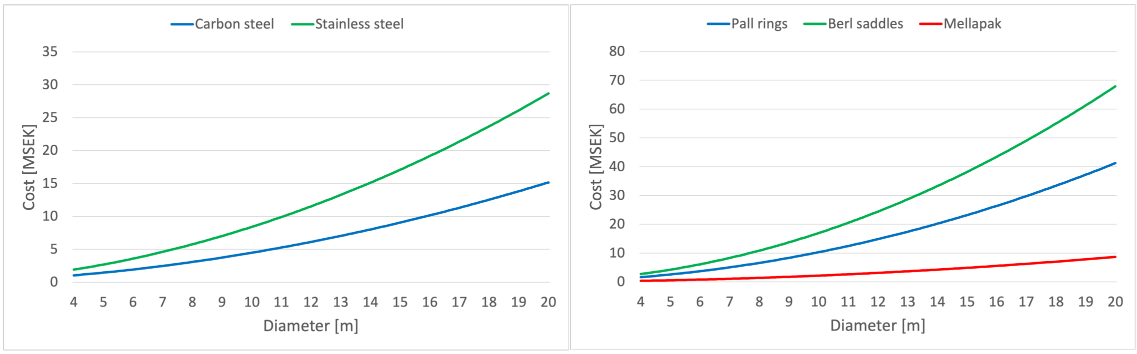
4.2 Investment cost

When calculating the cost of the scrubber, the inlet temperatures and the white liquor flow did not affect the investment cost. For the cost calculations of the packings, the void factor for 50 mm structured packing and 250 structured packings were used, respectively, according to industry recommendations. The cost for the initial design for the scrubber and different packings can be seen in table 4.2.

Table 4.2: Initial design costs for scrubber walls and different packings.

Stainless steel scrubber cost [SEK]	11 706 530
Metal pall rings cost [SEK]	15 109 760
Ceramic berl saddles cost [SEK]	24 886 664
Plastic Mellapak cost [SEK]	3 177 494

The cost for the scrubber with increasing diameter can be seen in figure 4.9.



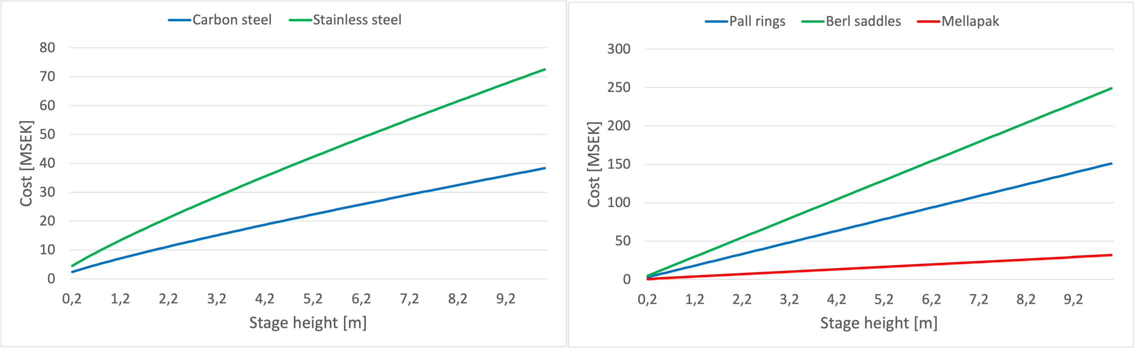
(a) Different scrubber material. **(b)** Different packing types.

Figure 4.9: Variation in cost for (a) scrubber wall material and (b) different packing types, depending on scrubber diameter.

It can be seen that increasing the diameter increases the cost exponentially for both the scrubber material and packing types. The stainless steel scrubber cost varies between 1,9 million SEK and 28,7 million SEK. At the initial design of 12,1 m diameter, the cost for the scrubber is 11,7 million SEK.

For all cost calculations, the plastic, structured Mellapak packing was significantly cheaper than ceramic and metal random packing. The plastic Mellapak varies between 350 000 SEK and 8,7 million SEK, while the metal pall rings vary between 1,6 and 41,2 million SEK.

Next, the scrubber stage height was varied, and the cost variation for the scrubber and packing can be seen in figure 4.10.



(a) Different scrubber material. **(b)** Different packing types.

Figure 4.10: Variation in cost for (a) scrubber wall material and (b) different packing types, depending on stage height.

The cost of the scrubber almost increases linearly with increasing stage height. The stainless steel scrubber cost varies between 4,5 million SEK and 72,6 million SEK.

The packing cost increases linearly with increasing stage height. Again Mellapak is significantly cheaper than the other types.

Increasing the pressure only had an effect on the scrubber wall thickness and no effect on the packing cost. The change in scrubber cost with varying pressure can be seen in figure 4.11.

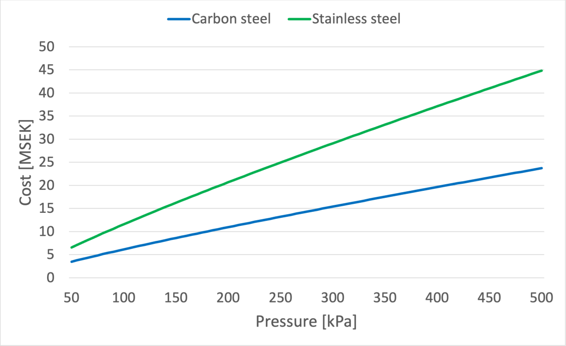
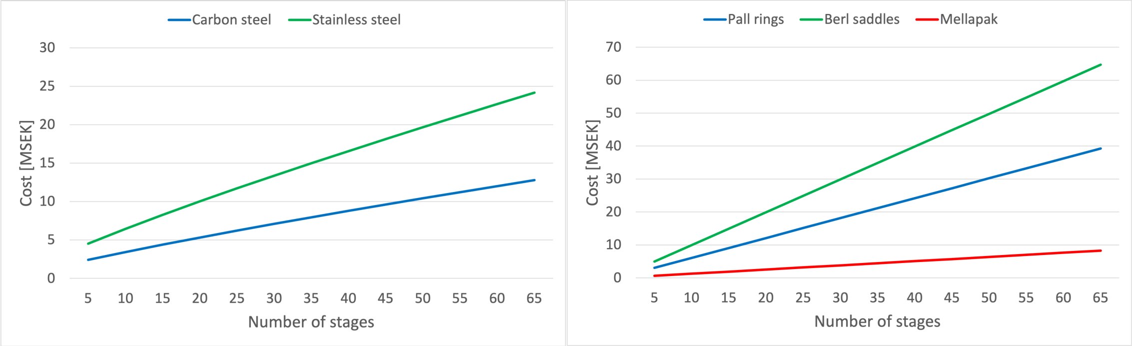


Figure 4.11: Variation in cost for scrubber wall material depending on the scrubber's internal pressure .

The scrubber cost increases almost linearly with pressure and varies between 6,5 million SEK and 44,8 million SEK for the tested pressure interval.

Finally, the effect of increasing the number of stages on the scrubber and packing cost was tested. These results can be viewed in figure 4.12.



(a) Different scrubber material.

(b) Different packing types.

Figure 4.12: Variation in cost for (a) scrubber wall material and (b) different packing types, depending on the number of stages.

The cost of the scrubber and packing material increases linearly with an increasing number of stages.

As for the cost of the packing, the smaller the packing, the higher the cost. This is because the decrease in the void factor increases the packing volume and, therefore, the cost according to equation (3.13).

4.3 Final dimensions and cost

After evaluating the sensitivity analysis and cost calculation results, a final dimension of the scrubber was chosen. The final dimensions of the scrubber can be seen in table 4.3. How these were chosen can be read about in the discussion in section 5.1.

Table 4.3: Suggested scrubber dimensions.

Dimension	Unit	Value
Diameter	m	12,0
Stage height	m	1,5
Number of stages		20
Total height	m	31
Structured plastic Mellapak		250X

The design factors for normal operating conditions, with a flue gas flow of 232 kg/s, are presented in table 4.4. The results for the outlet temperatures, the carbon capture efficiency, the concentrations in the outlet liquor, the outlet liquor sulphidity, alkali, and pH, as well as investment cost, including packing, can be viewed in table 4.5.

Table 4.4: Suggested operating conditions for the scrubber during normal plant operation.

Operating condition	Unit	Value
White liquor inlet temperature	°C	102
Flue gas inlet temperature	°C	200
White liquor flow	kg/s	800
Pressure	Pa	101 325

Using the results in table 4.3, table 4.4, and table 4.5, an estimation of the increased load for the causticisation and lime kiln was calculated, assuming an efficiency of 80% for equation (2.1) and 100% for equation (2.2). The load was estimated to increase with 104,5 kg $CaCO_3$/s for the causticisation and 58,5 kg CaO/s for the lime kiln. Assuming 80% conversion of the Na_2CO_3, the outlet white liquor from the causticisation will have the composition as shown in table 4.6 when the liquor from the scrubber is mixed with the green liquor from the recovery boiler before the causticisation. The sulphur in the form of HS^- is not included in the equations for calculating sulphidity and alkali, but when one includes the HS^-, assuming that the HS^- ion reacts and forms Na_2S, the sulphidity becomes 32,2%, the effective alkali becomes 144,5 g/L and the active alkali is 172,4 g/L.

Table 4.5: Results for final scrubber design at normal operating conditions.

Parameter	**Unit**	**Value**
Liquor outlet temperature	°C	78,41
Flue gas outlet temperature	°C	89,29
Carbon capture efficiency	mol-%	95,17
Liquor NaOH concentration	g/L	0,539
Liquor Na_2CO_3 concentration	g/L	201,304
Liquor Na_2S concentration	g/L	1,841
Liquor H_2S concentration	g/L	0,0005
Liquor HS^- concentration	g/L	23,029
Liquor sulphidity	%	77,36
Liquor effective alkali	g/L	1,46
Liquor active alkali	g/L]	2,38
Liquor pH		12,13
Flue gas outlet H_2S	ppm	294
Total investment cost	SEK	16 898 574

Table 4.6: White liquor (WL) composition, sulphidity, and alkali out of the causticisation when the scrubber liquor is returned to the chemical recovery cycle, compared to typical white liquor composition.

	Unit	**New WL**	**Typical WL**
NaOH	g/L	116,7	100
Na_2CO_3	g/L	38,2	30
Na_2S	g/L	9,0	55
HS^-	g/L	19,8	-
Sulphidity	%	7,1	35
Effective alkali	g/L	121,1	130
Active alkali	g/L	125,6	160

4.4 Statistical model

A statistical model was created after deciding on the final dimensions of the scrubber and the packing material. The experiments presented in table 3.12 were performed, and the results can be viewed in table C.1 in appendix C.

It can be seen that experimental points 15-17 all have the same results. That is because they are the middle point and were done multiple times to ensure the same results were achieved.

From the results in table C.1, five equations were created using MODDE, one for each output. The generated equations had the form shown in equation (4.1), where T_{WL} is the inlet white liquor temperature in °C, F_{WL} is the white liquor inlet flow in kg/s, and F_{RG} is the inlet flue gas flow in kg/s. The constants a-j for each equation can be seen in table 4.7.

$$\begin{aligned} Output = & a + b \times T_{WL} + c \times F_{FG} + d \times F_{WL} + e \times T_{WL}^2 + \\ & + f \times F_{FG}^2 + g \times F_{WL}^2 + h \times T_{WL} \times F_{FG} + \\ & + i \times T_{WL} \times F_{WL} + j \times F_{WL} \times F_{FG} \end{aligned} \tag{4.1}$$

Table 4.7: Constants for each output in equation (4.1).

Output	**CO_2 capture efficiency**	**Outlet liquor temp. [°C]**	**CO_3^{2-} conc. [g/L]**	**S^{2-} conc. [g/L]**	**OH^- conc. [g/L]**
a	1,112	61,79	79,31	-14,31	6,132
b	1,439E-04	0,1422	-0,3218	-2,935E-02	4,728E-02
c	-2,368E-03	8,586E-02	-6,272E-02	7,837E-02	-0,1666
d	2,585E-04	4,387E-03	5,710E-02	2,945E-02	2,958E-02
e	-1,148E-06	-3,166E-04	4,099E-03	1,479E-04	-4,371E-04
f	-1,786E-06	-4,497E-04	-7,833E-04	-2,036E-04	6,093E-04
g	-3,517E-07	-3,411E-05	-1,054E-04	-5,095E-06	1,543E-05
h	1,778E-07	-1,133E-03	1,970E-04	-9,700E-05	2,124E-05
i	-1,903E-07	2,486E-04	-1,395E-04	7,625E-05	1,690E-05
j	2,569E-06	1,973E-04	5,422E-04	-4,354E-05	-1,829E-04

Because of a miss with the factors, the outputs from the equations are the ions for all concentrations instead of the entire components. The concentrations for the components can easily be calculated using molar masses for the components and ions.

To validate the statistical model against the model in ASPEN Plus, the conditions of the flue gas flow and white liquor temperature and flow for the final design in section 4.3 were put into the equations. The results are shown in table 4.8.

Table 4.8: Results for the statistical model compared to the results for the final design conditions in ASPEN Plus.

Result	**Unit**	**Stat.model**	**ASPEN design**
Carbon capture efficiency	mol-%	91,61	95,17
Liquor outlet temperature	°C	80,5	78,41
Liquor Na_2CO_3 concentration	g/L	184,7	201,3
Liquor Na_2S concentration	g/L	18,5	1,841
Liquor NaOH concentration	g/L	4,8	0,539

It can be seen that the model underestimates the carbon capture and, therefore, the conversion of NaOH to Na_2CO_3. It also overestimates how much Na_2S that is left in the liquor. The temperature is close to that of the ASPEN Plus model.

4.5 Experiments with white liquor

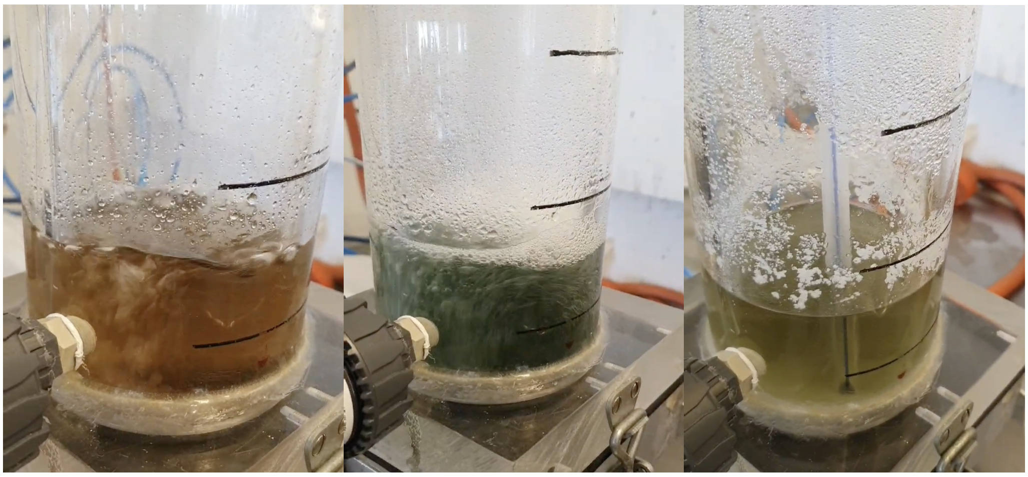
The results from the three experiments can be seen in table 4.9.

Table 4.9: Results from lab experiments with white liquor [56][57].

CO_2 flow [mL/min]	**Time [min]**	**CO_2 absorption [g/kg white liquor]**	**Temperature [°C]**
72,5	20	46,6	53
29,0	20	39,6	49
29,0	10	35,0	53

It can be seen that an increased CO_2 flow and increased experiment time increase the absorption of CO_2. The temperature for the second experiment was different compared to the other experiments, which could be due to human error in not giving the thermometer enough time to reach 53°C. Since the temperature is higher at the end of the experiments than at the beginning, it can be concluded that the reactions occurring during the absorption give a temperature increase.

In figure 4.13, some pictures can be seen from the experiment with a CO_2 flow of 72,5 mL/min. They are captured just at the beginning of the experiments, sometime in the middle, and at the end. It was noted that there was salt precipitation during the experiments, which can be seen as the white pieces on the walls of the cylinder in figure 4.13c and also in the bottom. This was most likely $NaCO_3$. Salt precipitation was only noted in the experiments with a 20 minute running time, not in the 10 minute experiment. In figure 4.13b, the liquor reaches a maximum green colour before the salt starts precipitating. This green colour is similar to that of green liquor. It can also be seen that there is some foaming of the liquor in figure 4.13b.



(a) Start: white liquor **(b)** Middle of experiments **(c)** End: salt precipitation

Figure 4.13: Pictures from lab experiments with white liquor and a CO_2 flow of 72,5 mL/min [58].

5

Discussion

This chapter will discuss the results in more detail, and the process behind selecting the final model will be presented and discussed. The research questions will also be answered. The effects on the plant and the feasibility of adding a carbon capture scrubber will be discussed based on theory and the results. Some potential further research will also be presented.

5.1 Sensitivity analyses and costs

This section discusses the results of the sensitivity analyses and cost calculations in more detail. When arriving at the final design, a balance between the cost and the efficiency of the scrubber was considered. There was an aim to reach above 90% carbon capture since that is comparable to other carbon capture solvents, like MEA.

5.1.1 Scrubber dimensions

Starting with the diameter, the effect on the carbon capture slowly decreases with increasing diameter, but the cost increases exponentially. The diameter does not help increase the carbon capture above 90%, so having too large of a diameter is not beneficial, especially above 13,8 meters. Since ASPEN Plus recommended 12,1 meters in diameter, it is probably not reasonable to increase the diameter above that, especially considering the increased cost and barely increasing the carbon capture. Other scrubber dimensions had a more significant effect on carbon capture. However, it should be noted that too small of a diameter means a lower liquid range and the risk of too much liquid hold-up, which can cause problems with the scrubber.

Moving on to the stage height, between 0,2 and 2 meters, there was a significant effect on the carbon capture when just increasing the stage height a few decimeters, up until about 1,3 meters. After this, the slight increase in carbon capture compared to the total scrubber cost was less favourable. Just increasing the stage height from 1 meter to 1,3 meters increases the cost of the scrubber shell by almost 2,5 million SEK and increases the carbon capture by 6,5 percentage points. But the effect on the carbon capture by increasing the stage height is more significant than increasing the diameter. Therefore it is more beneficial to increase the stage height.

As for increasing the number of stages, it had less of an effect than increasing the stage height. It was similar to that of the diameter, that increasing the stages did not give much increase in the efficiency, while the cost increased a lot. Since there was barely any effect after 25 stages, the final design was given 20 stages to keep the cost lower.

5.1.2 Operating conditions

When it comes to the inlet white liquor flow, it can be seen that it significantly affects the carbon capture efficiency until a point where a maximum capture efficiency is reached, at around 700 kg/s. It is, therefore, reasonable not to have too large of a white liquor flow for a few reasons, partly because the carbon capture efficiency does not increase and partly because of the risk of too much liquid hold-up in the scrubber, which could decrease the carbon capture efficiency. However, it could be good to slightly over-dimension the white liquor flow to capture potential peaks of CO_2 in the flue gas. Increasing the white liquor flow might also give an outlet composition closer to that of green liquor. When it comes to the cost of the white liquor, there will be an initial cost of adding white liquor to the process, and after that, there will only be operational costs, such as keeping the Na/S balance in the process and pumping the liquor to the scrubber.

The inlet temperatures of the flue gas and white liquor were also analysed. It was noted that the white liquor temperature had a more significant effect than the flue gas temperature. It was also noted that a lower white liquor temperature was favourable for carbon capture. However, that would require the white liquor to be cooled before entering the scrubber since it leaves the process at 102°C. Considering that the carbon capture is 84,2% at 102°C and only increases to 88,1% when being cooled to 20°C, it was deemed better to change another parameter that adds to the investment cost of the scrubber than adding a cooling unit with an investment cost and an operational cost. The carbon capture also only increases from 84,2% to 88,1% when the gas is at its normal inlet temperature of 200°C and the white liquor temperature is decreased to 20°C.

The figures for varying inlet temperatures, figure 4.4 and figure 4.5, show a plateau or a local minimum or maximum for the carbon capture efficiency. This most likely has to do with the reactions and the reaction constants. When looking at the carbon capture efficiency and temperature, it can be seen in figure 4.1, figure 4.2, figure 4.3, figure 4.4, and figure 4.5 that the liquor outlet temperature stabilises at just above 80°C, while the outlet gas temperature is a bit more unpredictable. Since the reactions occur in the liquid film, the temperature of 80°C is probably where the reactions occur at maximum capacity. From the figures, it can be concluded that the overall reaction is most likely endothermic since the liquor leaves at a lower temperature than it enters. Since the flue gas is hotter than the white liquor and no reactions occur in the gas, heat is transferred to the liquid, which helps with the reactions. This can be seen in figure 4.5 and figure 4.6, where increasing the temperature difference between the fluids also increases the carbon capture efficiency. There will be a point in the scrubber where the liquor and gas are almost the same temperatures, and no more heat transfer can occur, thus ceasing the increase in carbon capture. However, this result is different compared to the lab experiments which showed a temperature increase, pointing to exothermic reactions. But when looking at an inlet temperature of 20°C for both the liquor and the gas, it could be seen in figure 4.6 that the outlet liquor had a temperature of just under 50°C, close to the temperature reached in the lab experiments. It could be that other reactions, that are endothermic, occur in the solution at higher temperatures.

The scrubber's internal pressure was also analysed, but it did not affect the carbon capture efficiency much, especially compared to the increase in cost when increasing the pressure.

5.1.3 Choice of packing

The last design parameter that was decided on was the packing type and material. The structured packing Mellapak was the best and most obvious choice regarding cost and carbon capture efficiency. The packing is made from plastic which is more corrosion-resistant to the white liquor. However, based on the results of the experiments done by the lab, presented in section 4.5, it is relevant to discuss the choice of a packed column instead of a plated column. One thing that speaks in favour of plated columns is that they are much easier to clean than packed columns. With the results from the experiments, there seems to be a risk of salt precipitation in the liquor, which will likely build up on the packing material and on the scrubber wall. Therefore, it could be advantageous to choose column internals that are easier to clean if it has to be cleaned often. However, plated columns only come in metal, so the corrosion risk is high since NaOH is very corrosive, as previously mentioned. Thus, it might be cheaper to replace the plastic structured packing when it is needed, than it is to replace the trays. There is also a very high liquid flow, which argues for choosing a packed column to minimise liquid hold-up.

5.1.4 Risks with the design

For all sensitivity analyses, the sulphur should be discussed. When it comes to the formation of H_2S and the risk of it leaving the gas, it can be seen that there is H_2S leaving the scrubber in the flue gas. According to theory, there should mainly exist HS^- ions in the liquor at high pH, but it can be seen in the results from the ASPEN Plus model that some H_2S leaves with the gas. It could be that sulphur in the liquor reacts with the flue gas to form H_2S. Because H_2S is a very toxic gas, it must be taken care of somehow. One way could be to run it through a filter or another absorption column to remove the H_2S. Potentially, the flue gas could be sent through already existing filters at the plant. Since sulphur is transferred from the liquor to the gas, it also leaves the chemical recovery system. Although sodium is usually low in Scandinavian mills, sulphur leaving continuously with the flue gas could mean it must also be added to the liquor, which would add an operating cost for the makeup chemicals.

5.2 Final design and model reliability

The final design of the scrubber was based on sensitivity analyses and cost calculations. The considerations and thought process for the results of the sensitivity analysis and cost were discussed in section 5.1, which resulted in the dimensions presented in section 4.3 and suggests a total investment cost of 16,9 million SEK for the scrubber. In addition to that, costs for installation will be added. The suggested scrubber will minimise the total plant emissions by more than 75%.

5.2.1 Choice of final design

The main thing that was difficult to choose was the number of stages. There was a difference of about three percentage points in the carbon capture efficiency between 15 and 20 stages, but it increased the total cost of the scrubber by over two million SEK. It was decided that it was better to have a higher column to account for any potential future increase in plant capacity. The same was done for the scrubber diameter which was decided between 10 and 12 meters, where the higher diameter of 12 meters was chosen to account for future capacity increase. It was also better to have a larger diameter because of the decrease in the liquid hold-up.

When deciding on the inlet temperatures, it was decided that keeping the temperatures of the fluids as they come from the plant was the best, to not add any operational costs. The higher temperatures might also help the reactions that seem to require energy. It was decided that having a higher investment cost was better than adding a cooler. But the plant could easily add a cooler in the future if that is wanted. Temperature variations of the liquor are also accounted for in the statistical model for the scrubber, which can affect the efficiency.

The final design recommends a liquor flow of 800 kg/s for normal operating conditions of the plant. That is how much more liquor must be added to the process flow and sent to the causticisation. Adding even more white liquor will barely increase carbon capture, but the suggested design can handle an increased liquor flow in case of future increased capacity needs. Because of the slight over-dimensioning of the scrubber, it is also a possibility to send other flue gases through the scrubber, for example, the flue gases from the lime kiln.

5.2.2 Comparison with MEA scrubber

The suggested design has a carbon capture of 91,5%, which is comparable to using MEA as a solvent. Because of that, using white liquor from the plant is better in terms of cost, as there is no cost for the solvent if one excludes the possible cost of makeup chemicals. Using another solvent would also most likely mean that a stripper must be invested in, for regenerating the solvent. That is also an additional cost which supports carbon capture using white liquor, since in the suggested design, the already existing process will be used to regenerate the solvent through the causticisation. That is, as long as it is possible to send the outlet liquor back to the causticisation to regenerate the solvent. Having a separate solvent regeneration unit will also take up more space at the plant and add an extra element of complexity.

5.2.3 Model reliability

The model designed and simulated in ASPEN Plus generally represents a real-life scenario well. Comparing the results of the sensitivity analyses done in ASPEN Plus with the study done by Zhenqi et al. [32] on CO_2 removal with NaOH, the results are similar. Increasing the amount of white liquor, or NaOH, increases the CO_2 removal efficiency, and increasing the temperature of the flue gas increases the CO_2 removal efficiency. However, one result which differs from the study by Zhenqi et al. is that in ASPEN Plus, decreasing the white liquor temperature increases the CO_2 removal efficiency. In contrast, the study found that increasing the inlet temperatures gave a higher CO_2 removal efficiency. However, the study changed both inlet temperatures simultaneously, while in the ASPEN Plus model, the inlet temperatures were analysed separately. The temperatures in ASPEN Plus were also much higher than what the study looked at, which could impact the reactions quite significantly. The difference could also be because of the reactions in ASPEN Plus, which consists of both equilibrium and kinetic reactions. A laboratory scale column could be set up to verify the model in ASPEN Plus. When the ASPEN Plus model had a low inlet white liquor temperature, it could be seen that the outlet liquor temperature was higher than the inlet. This corresponds to the results from the lab experiments, which showed that the liquor increased with temperature. Since several reactions are occurring, it is reasonable that one reaction is favoured above another at a certain point since the reactions are all temperature dependent.

Regarding the number of stages, stage height, and scrubber diameter, the results are reasonable since increasing these parameters increases the contact between the liquid and gas, which in turn increases carbon capture efficiency. The smaller packing sizes also give a higher carbon capture efficiency, which corresponds to the theory.

When it comes to the formation of H_2S, it is unsure if this is actually a reasonable result. Since the theory suggests that only HS^- ions should form in the liquor and no H_2S, this result might not be valid. This should be studied further. It could be good to analyse how the outlet H_2S in the flue gas varies with different parameters. It should also be verified with lab experiments, to see if H_2S actually leaves the scrubber.

5.3 Statistical model

As noted in the statistical model results, there were differences between the statistical model and the model in ASPEN Plus. The main difference was for the concentrations of the components in the outlet liquor. The goal of the digital twin in MATLAB Simulink is to continuously operate the pulp mill. Thus, if the model estimates the liquor composition wrong, there could be consequences for the entire MATLAB Simulink model for the plant. The liquor and its composition is essential to the pulp mill and influences the entire operation of the plant. If the statistical model predicts the liquor composition inaccurately, the operating engineers might make the wrong move when operating the pulp mill. Having real-life simultaneous measurements of the liquor composition will help when operating the mill against the Simulink model. However, having inaccurate parts in the digital model for the pulp mill will create mistrust in the model and therefore be of little use. To ensure a better digital model in Simulink, the ASPEN Plus model could be verified against a lab-scale model. Then more data points should be taken to create the statistical model for Simulink.

It is difficult to say if the statistical model is more reliable than the model in ASPEN Plus, but it is an okay representation of the ASPEN Plus model. Some errors can be accepted since there are very few data points. To increase the accuracy of the statistical model in predicting the ASPEN Plus model, more data points have to be taken from the ASPEN Plus model. That will most likely bring a more accurate prediction of the coefficients for the equations.

5.4 Effect on the plant

Since the outlet liquor from the scrubber would be sent back to the causticisation and enter the process again, there are several potential effects on the process as a whole. Starting with the causticisation, it will have to handle a significantly increased load, going from a production of 30 kg $CaCO_3$/s, according to the MATLAB Simulink model, to 135 kg $CaCO_3$/s. That will increase the lime kiln load from 17 kg CaO/s to 76 kg CaO/s. A solution for the increased lime kiln load has already been presented by IVL, which is adding an electric lime kiln. That is because an electric lime kiln will give an almost pure stream of CO_2 which can be used in the process, sold, or stored. With the calculated increased load, the lime kiln will produce a flow of about 59 kg CO_2/s. In the future, when the regular lime kiln needs replacing, an electric lime kiln could be invested in. Therefore, it is advisable to invest in an electric lime kiln that can handle the total capacity of the process. However, the load increase is a lot compared to the current load in the causticisation. Most likely, the current causticisation unit cannot handle the increased load, and it will become a bottleneck when regenerating the white liquor. It would be costly to invest in a larger causticising unit, so a deeper study has to be done into the capacity of the causticising unit and if it can handle the increased load caused by the scrubber. It is also important to note that the pulp mill has not supplied the actual loads for the causticisation, and the values from the MATLAB Simulink model are just estimations.

The outlet composition of the liquor is not close to that of green liquor, which is the other flow that enters the causticisation. Since about 80% of the Na_2CO_3 is converted in the causticisation, the outlet composition of the white liquor will be as presented in table 4.6. As can be seen, the NaOH concentration is regenerated to above that of typical white liquor composition of the pulp mill, while the Na_2S concentration is much lower than that of typical white liquor. However, not all sulphur is lost to the flue gas in the scrubber, as much of it is in the form of HS^- in the liquor. When including all the sulphur in the liquor, the sulphidity is almost the same as typical white liquor, while the effective and active alkali is higher than that of typical white liquor. It is also noted that the $NaCO_3$ is higher, which is reasonable since NaOH reacts with CO_2 and forms $NaCO_3$. It is difficult to determine whether sodium or sulphur is lost in the process, but most likely, both have to be kept track of more closely. However, the active component in the white liquor, NaOH, is very close to its typical value, which means that there will most likely be little effect on the process as a whole. But since the white liquor will be sent back to the scrubber and then back to the causticising, the scrubber is likely to accumulate the NaOH and Na_2CO_3 concentration in the white liquor. This could perhaps be solved by having a white liquor tank, where the solution is diluted with water before being sent to the scrubber and digestor.

5.5 Feasability of integrating the scrubber at the plant

Based on the simulation and experiment results, using white liquor from the process as an absorption medium for CO_2 seems possible. However, further studies have to be done on the effects on the plant if the scrubber was to be integrated with the chemical recovery cycle.

The current most common carbon capture solvent is MEA. A more in-depth comparison of investing in a scrubber using MEA compared to white liquor could be made, comparing the efficiency, cost, solvent regeneration, and feasibility. The MEA scrubber must have a separate solvent regeneration unit that the white liquor scrubber does not require. The environmental problems of MEA were brought up in the theory, and comparing the two solvents MEA and white liquor, they both possibly cause environmental problems if released into nature and when coming in contact with humans. The risk of H_2S formation in white liquor is, however, unique to the solvent and has to be considered when investing in this scrubber.

However, there are currently few incentives for adding carbon capture in the pulp and paper industry since there is no economic loss from releasing biogenic carbon dioxide. In the future, it is possible that this could change if the climate crisis requires more action. However, the suggested scrubber as a component has a reasonably low cost and does not come with any operational costs for the solvent. But there is uncertainty if the current pulp mill can handle the increased load on the causticisation and lime kiln. The solution with the electric lime kiln is also not in place at the moment, and if the current lime kiln at the pulp mill cannot handle the increased load, the scrubber cannot be put into operation before that is solved. A deeper study into the effects on the plant as a whole will be needed to more confidently suggest implementing the white liquor scrubber.

5.6 Comments on method

Some development of the method is mainly on what is analysed in the sensitivity analyses. A better understanding of how the pH, the sulphidity, and effective and active alkali changes in the liquor in the scrubber, as well as keeping track of the H_2S in the flue gas, could give better recommendations and might have changed the suggested final design of the scrubber to make a lower impact on the pulp mill operation.

By doing a more developed economic calculation, including piping, installation, and actual operational cost, a better recommendation could have been given on whether to invest in the scrubber.

In the statistical model, the ions were modelled instead of the components. To make a better statistical model that is more accurate and also works better with IVL's model, more data points should have been modelled, and the actual components should have been modelled instead of the ions. If there had been more time, it would also have been beneficial to couple the statistical model with the whole model in MATLAB Simulink to better understand how the entire pulp mill is affected by adding a scrubber.

5.7 Further research

Potential further research is suggested below, partly with the scrubber and partly with the digital model of the pulp mill.

When it comes to the scrubber, to confirm that the ASPEN Plus model represents reality, a lab-scale and then a pilot-scale model of a scrubber could be experimented on, using white liquor as an absorption medium. That could give better insight into how white liquor acts as an absorption medium, and any potential complications could better be addressed. This could also give better insight into the results achieved in experiments done by the lab at the pulp mill and how the white liquor acts in a continuous model when it comes to salt precipitation, temperature increase and reactions.

It would also be beneficial to analyse how the H_2S forms in the liquor and gas and how this can be minimised or handled, or if it even happens in real life.

For IVL and the pulp mill, there should also be an interest in investigating how the scrubber impacts the whole plant and the chemical and energy balances through the digital MATLAB Simulink model. They should also want to investigate the increased load on the causticisation and lime kiln and if that is feasible. Adding an electric lime kiln is also of interest in a future study and whether the almost pure carbon dioxide stream can be used in the pulp mill or how it can be stored. One use of interest is lignin extraction, where CO_2 is needed.

6

Conclusion

This project aimed to simulate and calculate the cost for a scrubber using white liquor as an absorption medium to capture CO_2 from flue gases. The final design of the scrubber was given the dimensions 12 meters in diameter and 31 meters in height, with 20 stages, giving a carbon capture efficiency of 95%. The total investment cost was about 17 million SEK, using carbon steel for the scrubber walls and plastic Mellapak as packing material.

The sensitivity analyses showed that increasing the diameter, height, inlet white liquor flow, and inlet flue gas temperature increased the carbon capture efficiency while increasing the white liquor inlet temperature decreased the efficiency. A decreased packing size gave a higher carbon capture efficiency but increased the risk of flooding. Because of the risk of corrosion, packing material in plastic or ceramic had to be chosen, and the scrubber walls had to be in stainless steel, which has better corrosion resistance. Increasing the scrubber size increased the cost, so a balance between efficiency and cost had to be considered when deciding on the final dimension.

Lab experiments performed with pure CO_2 gas flowing through white liquor showed that increased gas flow and experiment time gave increased CO_2 absorption. It could be concluded that the experiments increased the temperature of the white liquor. Salt precipitation and foaming were also observed during the experiments.

The ASPEN model seems to perform as expected, in agreement with the theory and previous studies, and white liquor works well as an absorption medium for capturing CO_2 from flue gases. Experiments with a lab-scale scrubber could be performed to validate the model further.

Some possible risks are the formation of toxic H_2S in the scrubber, which could be released with the flue gas, as well as salt precipitation which could lower the scrubber's efficiency and require cleaning the scrubber more often. The outlet liquor flow can be returned to the chemical recycling loop and causticisation. However, there is a risk of NaOH and Na_2CO_3 being accumulated in liquor over time and a decrease in the sulphur content, affecting the entire plant.

Implementing the scrubber in the plant is currently not feasible, as the plant cannot handle the increased load that the scrubber adds to the causticisation and lime kiln. There is also no economic incentive to invest in the scrubber at the moment, as releasing biogenic CO_2 does not have any economic consequences.

In conclusion, the scrubber works well on its own and white liquor can be used as an absorption medium, but there are some questions about the effects on the plant and increased loads that must be solved before the scrubber can be integrated with the plant.

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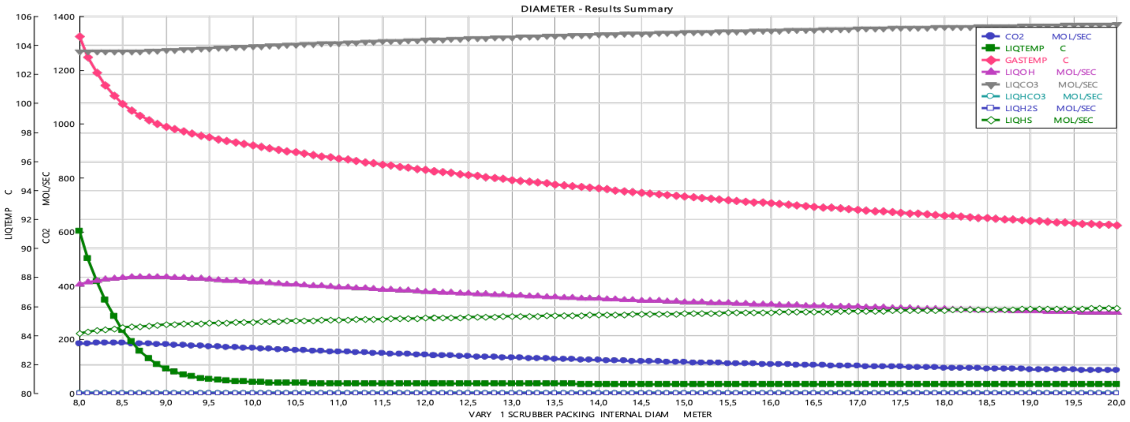
A

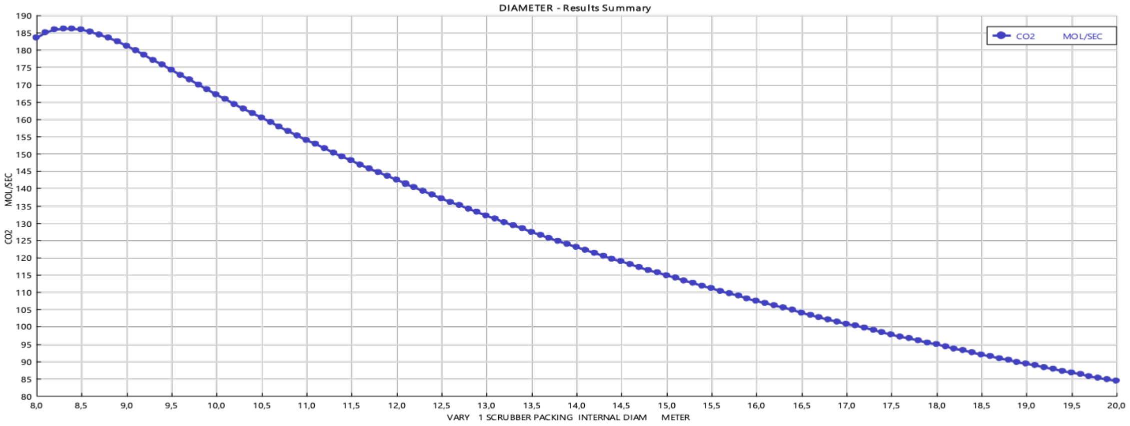
Appendix A

Sensitivity analyses were performed with Mellapak structured plastic packing in size 250X. When a sensitivity analysis was performed, all other parameters were constant according to the given values in table 3.7 and table 3.8.

The results for the variation of the scrubber outlet liquor component flows for each of the sensitivity analyses with Mellapak, as well as the variation in the outlet flue gas CO_2 mole flow and outlet flow temperatures, can be viewed in the figures below.

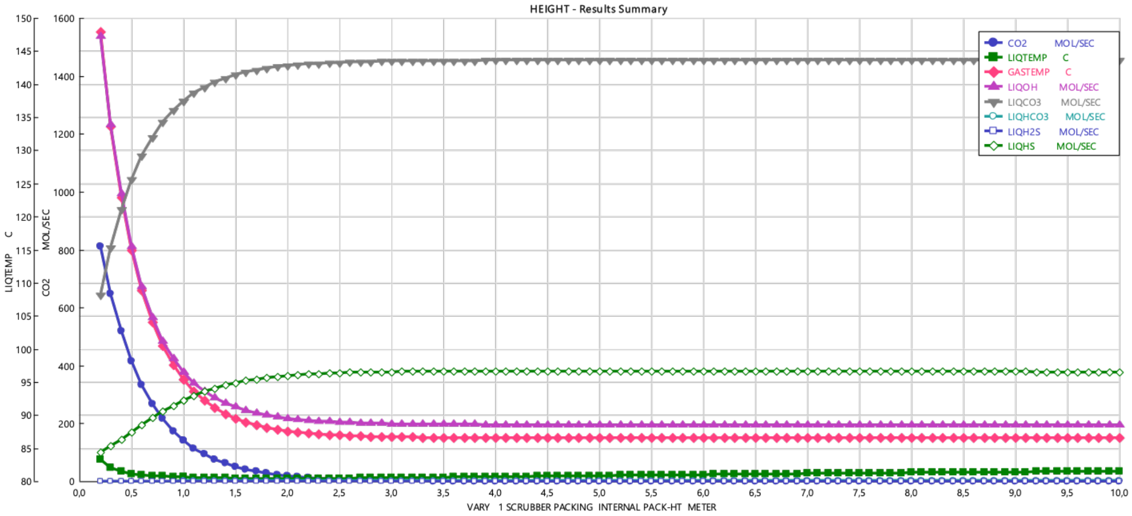


(a) Outlet mole flows and temperatures.

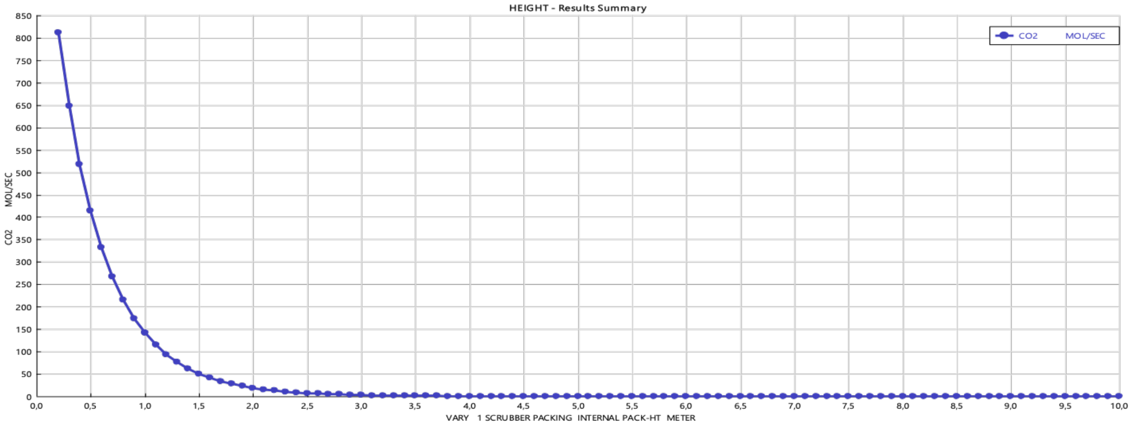


(b) CO2 outlet flow

Figure A.1: Variations in (a) outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures and (b) outlet flue gas CO_2 flow, depending on scrubber diameter, using Mellapak structured plastic packing 250X.

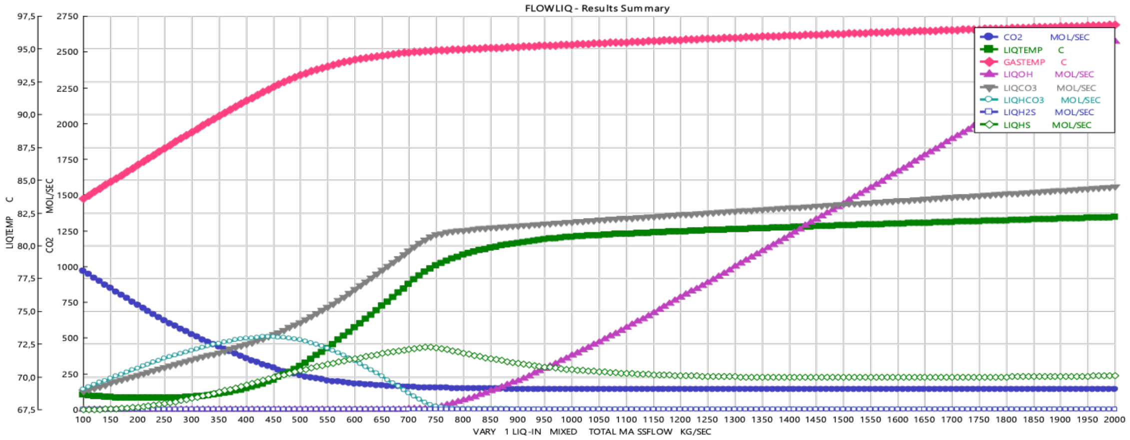


(a) Outlet mole flows and temperatures.

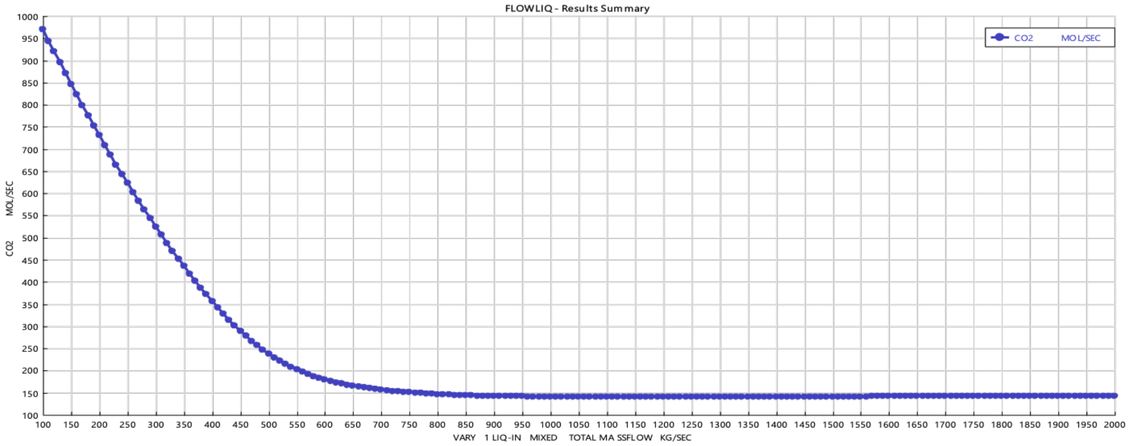


(b) CO2 outlet flow

Figure A.2: Variations in (a) outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures and (b) outlet flue gas CO_2 flow, depending on scrubber stage height, using Mellapak structured plastic packing 250X.

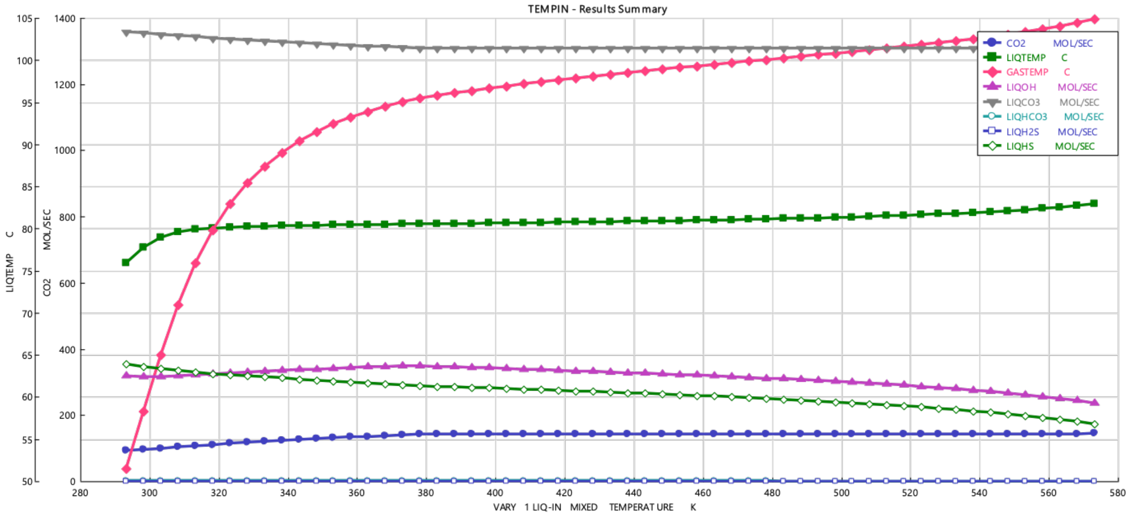


(a) Outlet mole flows and temperatures.

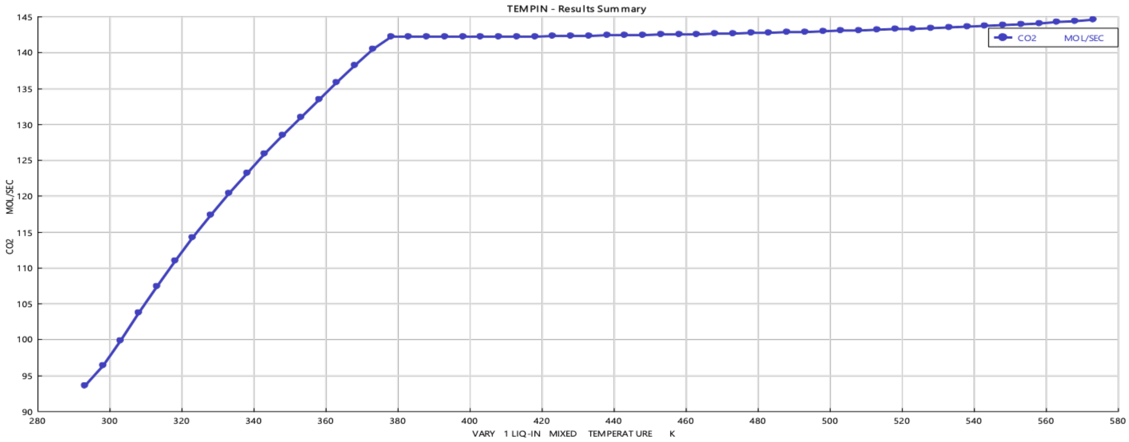


(b) CO2 outlet flow

Figure A.3: Variations in (a) outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures and (b) outlet flue gas CO_2 flow, depending on inlet white liquor flow, using Mellapak structured plastic packing 250X.

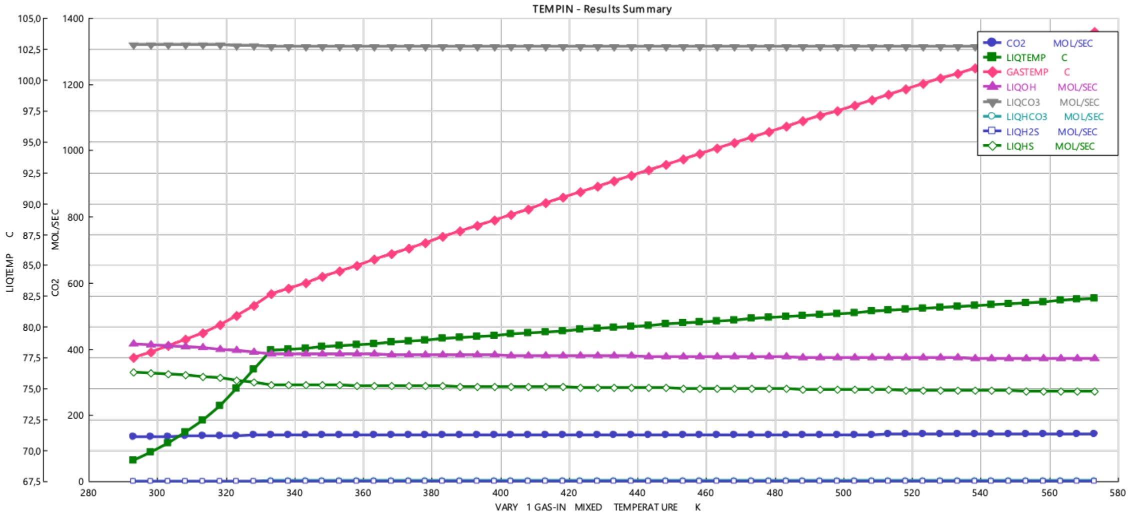


(a) Outlet mole flows and temperatures.

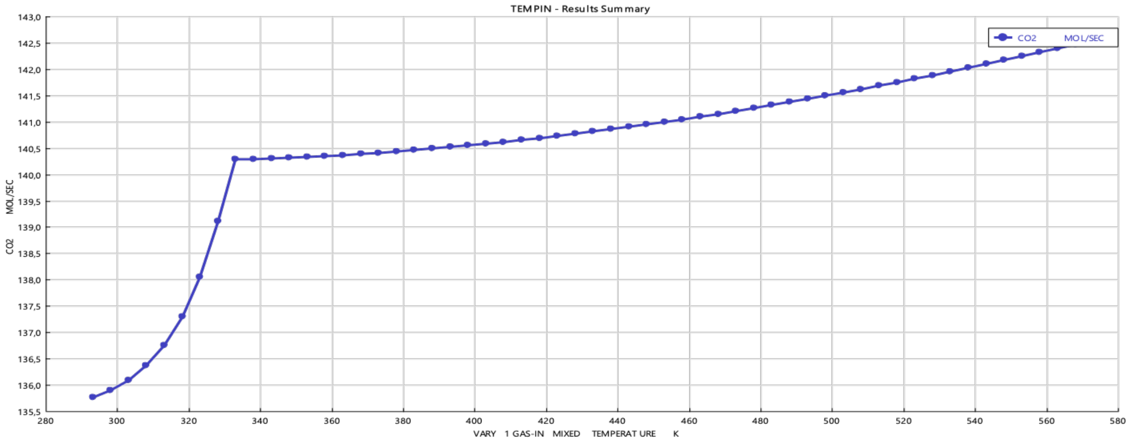


(b) CO2 outlet flow

Figure A.4: Variations in (a) outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures and (b) outlet flue gas CO_2 flow, depending on inlet white liquor temperature, using Mellapak structured plastic packing 250X.

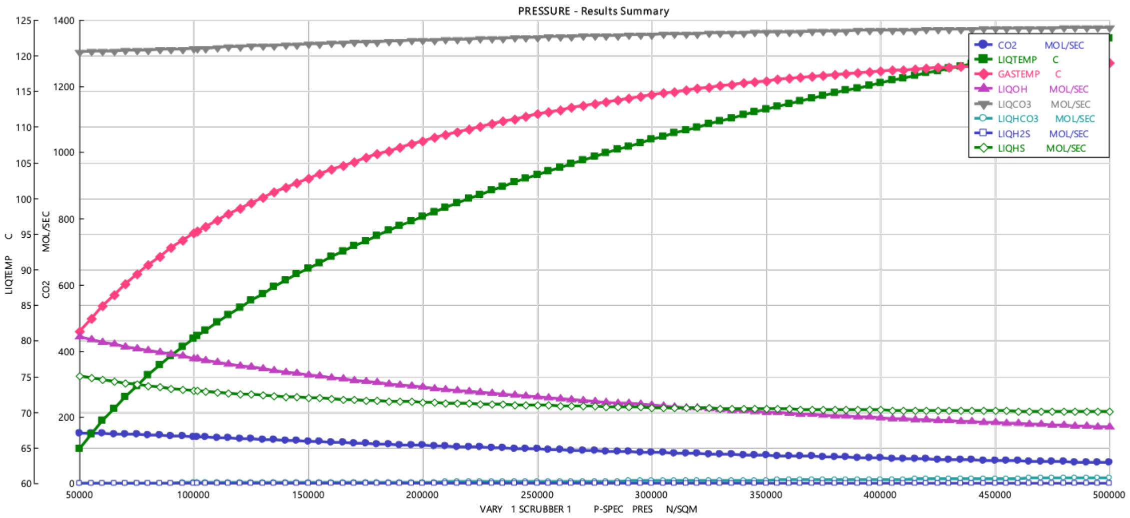


(a) Outlet mole flows and temperatures.

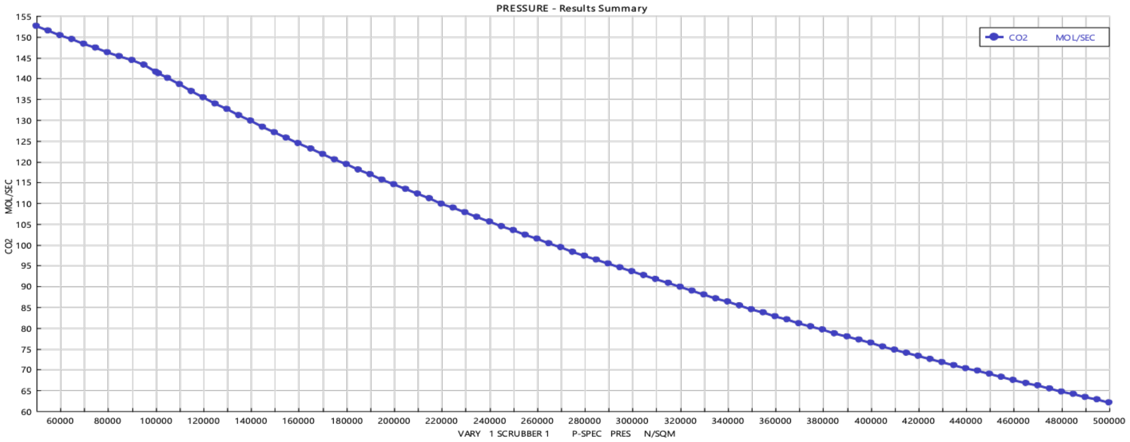


(b) CO2 outlet flow

Figure A.5: Variations in (a) outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures and (b) outlet flue gas CO_2 flow, depending on inlet flue gas temperature, using Mellapak structured plastic packing 250X.

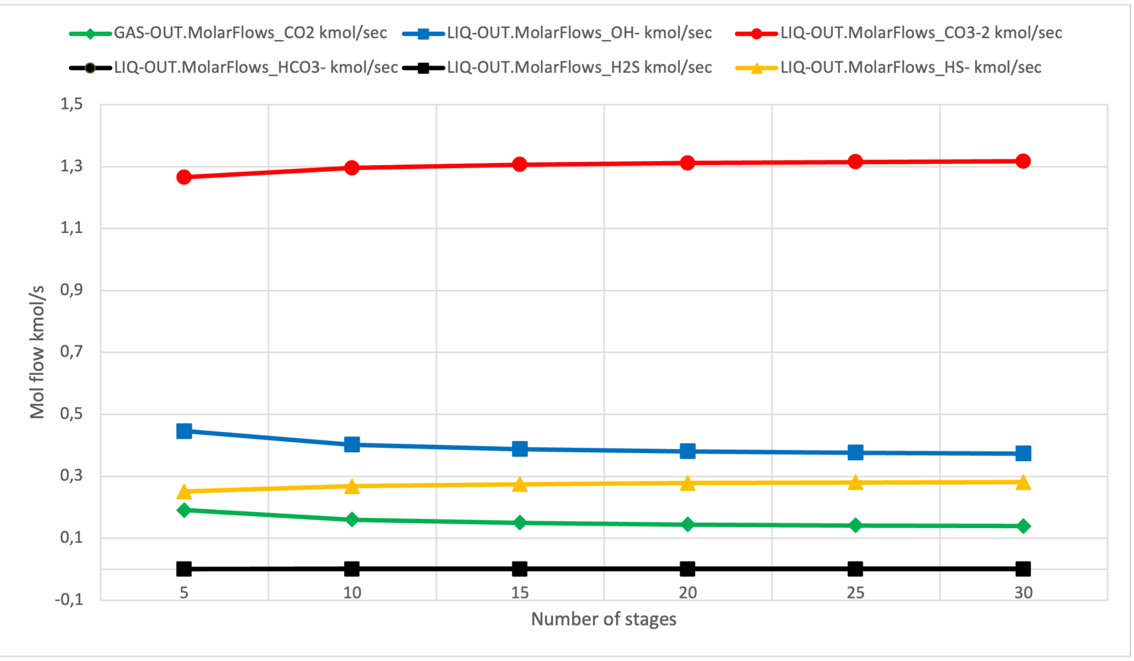


(a) Outlet mole flows and temperatures.

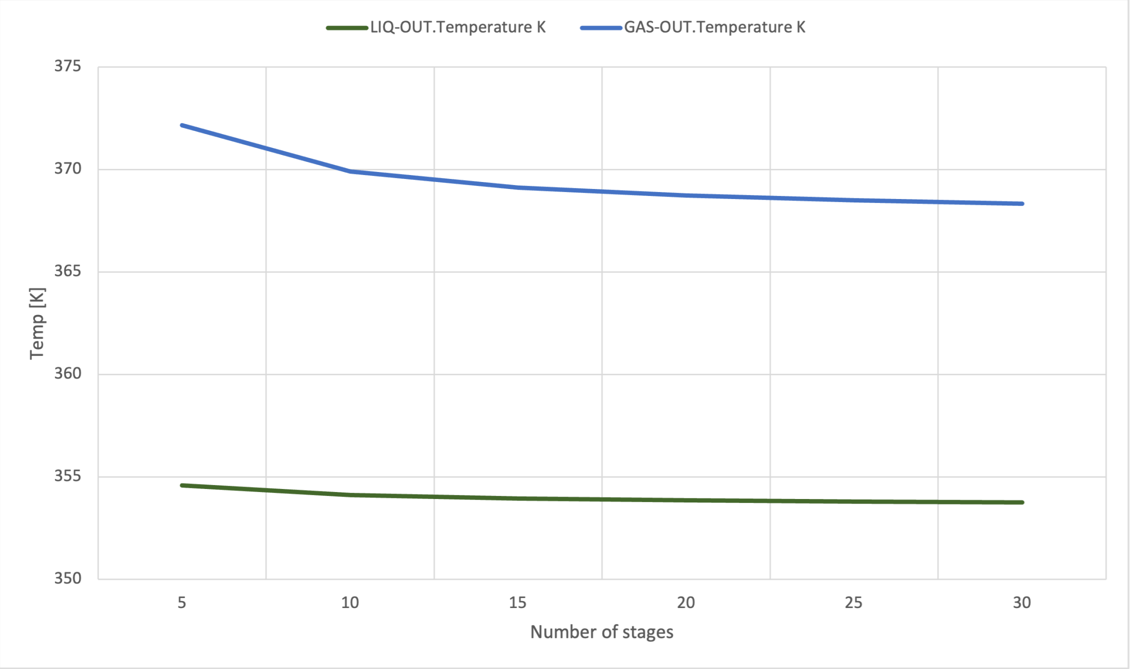


(b) CO2 outlet flow

Figure A.6: Variations in (a) outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures and (b) outlet flue gas CO_2 flow, depending on scrubber internal pressure, using Mellapak structured plastic packing 250X.



(a) Outlet mole flows and temperatures.



(b) Outlet temperatures.

Figure A.7: Variations in (a) outlet flue gas CO_2 flow, outlet liquor component flows and outlet liquor and flue gas temperatures and (b) outlet flue gas CO_2 flow, depending on number of stages in scrubber, using Mellapak structured plastic packing 250X.

B

Appendix B

Figure B.1: Setup for the lab experiments using white liquor to capture CO_2 [58].

C

Appendix C

Table C.1: Results for the experiments in table 3.12, performed in ASPEN Plus

Exp No	**CO2 capture efficiency [mol-%]**	**Outlet liq. temp. [°C]**	**Outlet liq. CO_3^{2-} [g/L]**	**Outlet liq. S^{2-} [g/L]**	**Outlet liq. OH^{-} [g/L]**
N1	97,43	76,4291	90,5766	0,0783	0,0349
N2	96,69	77,0764	108,6187	0,1309	0,0424
N3	69,70	68,1575	70,9495	0,0044	0,0074
N4	69,74	68,5274	87,4999	0,0059	0,0075
N5	98,73	51,2702	52,0114	13,2012	25,9005
N6	97,20	82,2835	56,3010	19,7840	26,8785
N7	97,27	75,1975	82,9007	9,8136	7,3386
N8	95,36	80,9950	93,1149	14,2649	8,8019
N9	97,56	79,0706	90,1894	7,0607	3,8071
N10	96,11	80,5816	102,4713	10,6854	4,9386
N11	97,73	81,1805	70,2809	15,4455	15,2331
N12	95,01	76,2406	99,6610	0,1111	0,0434
N13	85,92	68,8598	72,4644	0,0087	0,0075
N14	96,96	81,1601	69,8611	15,5078	15,4451
N15	96,61	80,2431	95,2063	8,3826	4,1478
N16	96,61	80,2431	95,2063	8,3826	4,1478
N17	96,61	80,2431	95,2063	8,3826	4,1478

With the achieved data in table C.1, the results were checked against the predicted result from the generated statistical model. The observed versus the predicted results can be seen in figure C.1.

In both of the figures below, note that the concentrations are for the CO_3^{2-}, S^{2-}, and OH^{-} ions and not the entire component as it says in the figures.

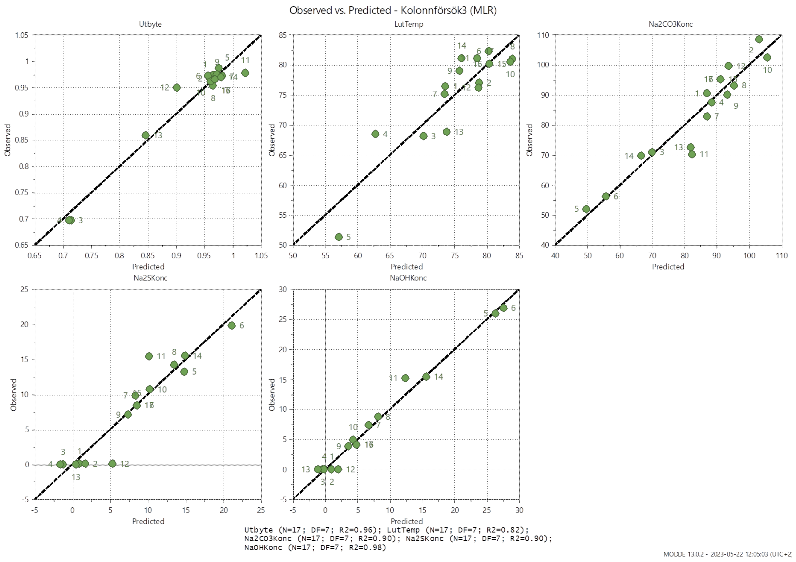


Figure C.1: Plots for observed vs predicted results for the statistical model.

Based on figure C.1, it can be seen that the outlet white liquor temperature has the most inaccurate prediction since the experimental data points are far from the black line.

In figure figure C.2, contour plots for all the outputs, based on the white liquor and flue gas flow inputs, can be seen. The plots should be interpreted in the following way - for an inlet white liquor flow of 900 kg/s (x-axis) and a flue gas flow of 160 kg/s (y-axis), the CO_2 capture efficiency is about 0,98 (orange field, between 0,95 and 1).

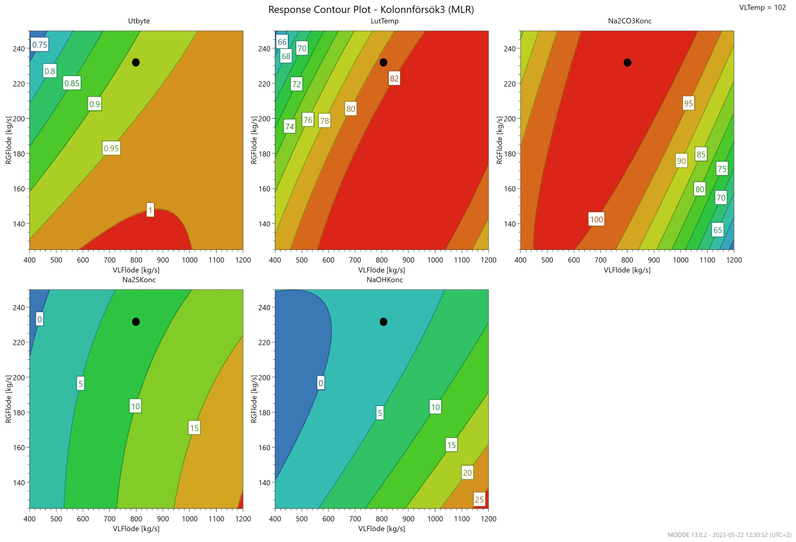


Figure C.2: Contour plots for flue gas and white liquor with white liquor temperature 102°C. The black dot indicates the design conditions of the final design in ASPEN Plus.

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