The influence of partial capture conditions on CO₂ absorption in process industries

Master’s Thesis within the Sustainable Energy System programme

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Division of Heat and Power Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2016
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Cover:
Simplified flowsheet of the split-flow configuration

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ABSTRACT
The amount of carbon dioxide in the atmosphere is increasing rapidly which leads to serious climate damage if nothing is done to address this situation. This thesis evaluates the application of carbon capture to process industries to reduce emissions and decrease the atmospheric carbon dioxide concentration. The main focus is on partial carbon capture where waste heat or heat surplus is used to run the capture process leading to a lower capture rate but simultaneously the costs are reduced since no additional heat supply is needed.

The carbon capture processes are simulated using Aspen Plus where a standard set-up is first compared to an advanced split-flow configuration regarding the energy consumption. For both process designs a sensitivity analysis is conducted focusing on different parameters to optimize the carbon capture process. For comparison two different solvents, MEA and piperazine, are used for the sensitivity analysis of these two process configuration.

The optimized process design of the split-flow configuration using MEA as a solvent is used to investigate different partial capture cases. These investigated cases are applied to an existing industrial case, a pulp mill. Two stacks of the pulp mill can be used to capture CO2 from, the recovery boiler and the lime kiln. In the recovery boiler steam is produced which is primary used to satisfy the need of the pulping process, but there is a heat surplus which can be used to produce electricity or to run the capture process. First it is investigated how much CO2 can be captured from the two stacks by using this heat surplus instead of producing electricity. The electricity loss per unit of CO2 captured was determined for different cases. The electricity loss is investigated for the case where CO2 is only captured from one of the two stacks and a case where CO2 is captured from both stacks always using only the steam available.

In cooperation with an external partner, cost estimations for different partial capture cases, applied to the pulp mill, are conducted. First full scale capture, where the capture rate is 90 %, was applied to both stacks. For the second case, the capture rate is decreased to 75 % having partial capture and the third case uses partial capture where the flue gas flow is decreased to 75 %. The two latter ones were only applied to the recovery boiler.

Key words: partial carbon capture, chemical absorption, split-flow configuration, MEA, PZ, carbon capture process optimization, Aspen Plus, pulp mill, electricity loss
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Preface

In this study different partial carbon capture cases were investigated and applied to a pulp mill including cost estimations. The thesis has been carried out from January to June 2016. The work is part of a research project aiming to reduce the cost of industrial carbon dioxide capture processes. The project is performed in cooperation with different industrial and research partners where this thesis was carried out at the Department of Energy and Environment at the Division of Energy Technology, Chalmers University of Technology, Sweden. This part of the project has been performed with Stefánia Ósk Gardarsdóttir as supervisor and Fredrik Normann as examiner. The data of the pulp mill has been provided by Jens Wolf from Innventia AB and the cost estimations were conducted by Ragnhild Skagestad and her team from Tel-Tek which I would like to thank for their great cooperation and involvement.

I specially thank Stefánia Ósk Gardarsdóttir for always having time for me. Her support through the project by helping me with the simulations in Aspen Plus, giving feedback on the report and answering all my questions is highly appreciated and invaluable.

I am also thankful for the help by Fredrik Normann who always provided me with valuable input and helped in making decisions regarding the content of this thesis.

Göteborg, June 2016
Annabelle Berlinger
Notations

**Roman upper case letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q$</td>
<td>Energy</td>
<td>W</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>°C</td>
</tr>
<tr>
<td>$\dot{V}$</td>
<td>Volume flow rate</td>
<td>m³/h</td>
</tr>
</tbody>
</table>

**Roman lower case letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{\text{MEA}}$</td>
<td>MEA concentration</td>
<td>wt-%</td>
</tr>
<tr>
<td>$\text{loading}$</td>
<td>CO₂ loading</td>
<td>-</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>Mass flow</td>
<td>kg/s</td>
</tr>
<tr>
<td>$\dot{n}_i$</td>
<td>Mole flow of the component $i$</td>
<td>kmol/s</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure</td>
<td>bar</td>
</tr>
<tr>
<td>$x_i$</td>
<td>Mass concentration of the component $i$</td>
<td>-</td>
</tr>
</tbody>
</table>

**Greek upper case letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta h$</td>
<td>Enthalpy difference</td>
<td>kJ/kg</td>
</tr>
</tbody>
</table>
1 Introduction

This thesis investigates carbon capture processes in the process industry including cost estimations with the aim to find a techno-economical optimum. In this chapter an introduction is presented briefly as well as the aim and scope of the work.

1.1 Background

The global concentration of carbon dioxide (CO$_2$) in the atmosphere is increasing rapidly. CO$_2$ is the primary greenhouse gas (GHG) and causes global warming as well as serious climate change and damage. The CO$_2$ concentration in the atmosphere has been steadily increasing by 2 ppm/year in the last 10 years [1, 2]. This means that the GHG emissions have risen more rapidly from 2000 to 2010 than in the three decades before and reached 49 Gt CO$_2$ per year in 2010, although institutions and national policies are pursuing mitigation measures [3]. If nothing is done to address this situation, the CO$_2$ concentration would be almost doubled in 2100 compared to the amount present today in the atmosphere, which is around 400 ppm. [2, 4] The impact of the atmosphere’s amount of CO$_2$ on the average global temperature, commonly called climate sensitivity, is quite uncertain. In most cases experts assume a climate sensitivity of 3 °C which refers to an increase of the average global temperature by 3 °C if the CO$_2$ concentration in the atmosphere was doubled. [5] In consideration of this assumption, during the climate conference COP21 held in Paris in December 2015, the international target was reduced from 2 °C to 1.5 °C which aims to keep the earth’s rising temperatures within 1.5 °C of pre-industrial times. However, some experts suggest that even an increase by 1 °C would lead to serious climate damages [6].

To combat this trend of increasing atmospheric CO$_2$ concentration and to reach the target of 80 % CO$_2$ emissions reduction by 2050 for developed countries, effective abatement strategies are required [7]. These include improvements in energy efficiency as well as increasing use of renewable energy sources which, however, constitutes long processes. With an increasing use of renewable sources for energy supply meeting the varying demand and dealing with their intermittency have become major challenges. Whereas for example, coal-fired power plants have the advantage of a very flexible operation, wide availability, security in supply and competitiveness. Therefore a promising solution to satisfy the increasing energy demand and to simultaneously reach significant reductions in CO$_2$ emissions is carbon capture and storage (CCS). This process leads to a long-term elimination of CO$_2$ in the atmosphere by removing it from flue gas streams emitted by industrial and energy-related sources. The CO$_2$ then is transported to a storage point. [8] About one third of the global CO$_2$ emissions are caused by manufacturing industries of which two thirds are attributable to the large primary materials industries [9]. Therefore this thesis deals with carbon capture in industries with a special focus on pulp and paper industry. CCS has a huge potential in industries because of the large CO$_2$ emissions in this sector [10]. In line with the CCS technology fossil fuels can still be used to satisfy the energy demand while reducing CO$_2$ emissions significantly. CCS has the potential of almost zero-emissions from fossil fuel combustion [11] in the long term and even negative emissions by the use of biomass. The latter is called bio-energy carbon capture and storage (BECCS) and is based on the CO$_2$ neutral use of biomass as energy source since the released CO$_2$ during the combustion of biomass is captured while plants are growing. Nevertheless, the released CO$_2$ can be captured which leads to negative carbon emissions if the manufacturing of the biomass is considered to be carbon neutral. In general there are
three different types of CO₂ capture systems: post-combustion, pre-combustion and oxyfuel combustion [8]. In pre-combustion capture processes CO₂ is removed from fossil fuels before the combustion is completed by a gasification process. In oxyfuel combustion the fossil fuel is burned in oxygen rather in air producing a flue gas consisting mainly of CO₂ and water. This study focuses on post-combustion capture processes which are based on CO₂ removal from the flue gas after the combustion.

1.2 Aim and Scope

The aim of this thesis is to develop a cost effective carbon capture strategy for future CCS systems considering specific conditions of the pulp and paper industry as case study, in connection with industrial partners. The considered carbon capture processes are based on post-combustion capture since these processes are applicable to existing combustion technologies of all industrial cases without radical process modifications [2] which makes a retrofit option possible compared to the two other types of carbon capture. In general, relatively high capture rates of 85 % or more are achieved which is feasible in combination with power generation because there is enough access to energy to maintain the heat supply. Steam from the power plant is used to provide heat duty to power the capture process, which, however, becomes a limiting factor that causes about 20 % reduction of power generation in power industry applications [12]. In process industry such high rates of carbon capture mean higher additional cost because the capture process is energy intensive and the access to energy for the CO₂ capture is limited. Therefore this thesis deals with partial CO₂ capture which has the potential of cost reductions by using waste energy for the capture process. Partial capture is not about capturing as close to 100 % of the CO₂ as possible, but to find an economic and technological feasible optimum of CO₂ capture. This is explained more in detail in chapter 2.1.

In order to minimize the CO₂ capture costs a cost estimation of a post-combustion capture unit is performed based on a detailed process design, which includes dimensioning of process units, by using the simulation software Aspen Plus. Based on this simulated capture process including the dimensioned equipment, an investment cost analysis is performed in cooperation with an external partner. Also the heat supply for the carbon capture unit is taken into account which includes the use of waste heat but also external heat utility.
2 Carbon Capture

As mentioned in the previous section there are three different types of carbon capture processes. This study is based on post-combustion carbon capture, which is illustrated in a simple manner in Figure 1.

As can be seen, in Figure 1 CO₂ is removed from a gas stream after fuel is combusted in a post-combustion carbon capture process. The most promising method for the CO₂ separation in this type of carbon capture process is chemical absorption [13] which is explained in more detail in section 2.2. An advanced process configuration, a so-called split-flow configuration, was chosen as a base case for the CO₂ absorption process.

2.1 A global status of partial carbon capture

In October 2014 there were 22 operational or under construction carbon capture projects all over the world, 16 of which were located in North America (Figure 2). The size of the circles in Figure 2 imply the CO₂ capture capacity in a range of 0.7 to 14.6 Mt/year. Only three of these 22 projects are power stations, nine are industrial facilities and ten projects are natural gas processing facilities [14]. In line with the focus of this thesis, more detailed information on the nine carbon capture projects associated with industrial facilities is presented in Table 1.

Figure 2: Worldwide location of carbon capture projects and their capacity [15]
### Table 1: Worldwide industrial facilities using carbon capture [15]

<table>
<thead>
<tr>
<th>Project</th>
<th>Industry</th>
<th>Capture method</th>
<th>Storage option</th>
<th>Captured CO$_2$ [Mtpa/%]</th>
<th>Start date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alberta Carbon Trunk Line, Canada</td>
<td>Fertilizer production</td>
<td>Solvent-based chemical absorption</td>
<td>Enhanced oil recovery</td>
<td>0,3-0,6/95 %</td>
<td>2016/2017</td>
</tr>
<tr>
<td>Enid Fertilizer, USA</td>
<td>Fertilizer production</td>
<td>Solvent-based chemical absorption</td>
<td>Enhanced oil recovery</td>
<td>0,7/NA</td>
<td>1982</td>
</tr>
<tr>
<td>Illinois Industrial CCS Project, USA</td>
<td>Chemical production</td>
<td>Fermentation</td>
<td>Dedicated geological storage</td>
<td>1,0/90 %</td>
<td>Early 2016</td>
</tr>
<tr>
<td>Coffeyville Gasification Plant, USA</td>
<td>Fertilizer production</td>
<td>Pre-combustion capture</td>
<td>Enhanced oil recovery</td>
<td>1,0/NA</td>
<td>2013</td>
</tr>
<tr>
<td>Great Plains Synfuel and Weyburn Midale project, Canada</td>
<td>Synthetic natural gas</td>
<td>Pre-combustion capture</td>
<td>Enhanced oil recovery</td>
<td>3,0/50%</td>
<td>2000</td>
</tr>
<tr>
<td>Quest, Canada</td>
<td>Hydrogen production</td>
<td>Solvent-based chemical absorption</td>
<td>Dedicated geological storage</td>
<td>1,0/35 %</td>
<td>2015</td>
</tr>
<tr>
<td>Air products steam methane reformer, USA</td>
<td>Hydrogen production</td>
<td>Vacuum swing adsorption</td>
<td>Enhanced oil recovery</td>
<td>1,0/90 %</td>
<td>2013</td>
</tr>
<tr>
<td>Abu Dhabi CCS project, United Arab Emirates</td>
<td>Iron and steel production</td>
<td>Solvent-based chemical absorption</td>
<td>Enhanced oil recovery</td>
<td>0,8/90 %</td>
<td>2016</td>
</tr>
<tr>
<td>Sinopec Qilu Petro-chemical CCS Project, China</td>
<td>Chemical production</td>
<td>Pre-combustion capture</td>
<td>Enhanced oil recovery</td>
<td>0,5/NA</td>
<td>2017</td>
</tr>
</tbody>
</table>
In 2013 the International Energy Agency stated that the number of operational projects should be increased to at least 30 by 2020 [16] while today, in 2016, there are already 35 projects in operation or planned to operate from 2020 or earlier. Two of these 9 industrial projects are based on partial carbon capture whereas for three projects no data on a capture rate could be found. The two partial carbon capture projects, greyed in Table 1, are both located in Canada where the Quest project is based on chemical absorption. This project is one of the first commercial-scale carbon capture projects in the world in which the CO$_2$ is permanently stored in a deep saline aquifer, located about 2 km below ground. [17] However, most of the carbon capture projects listed in Table 1 use the sequestrated CO$_2$ for enhanced oil recovery (EOR) which is a proven and effective method to improve oil production and can be applied to oil reserves under different geological conditions. [18]

As mentioned previously, the aim of partial carbon capture is to find an economic and technologically feasible optimum of carbon capture instead of capturing as much CO$_2$ as possible. In previous studies carried out by the International Energy Agency this concept was already recommended for power stations including multiple power generation units where two main options were mentioned: either capturing a low fraction of CO$_2$ in each power unit or capturing a high (85 % or more) fraction in one or more power units but disregarding other units. This is the case of the Quest carbon capture project; roughly 80 % of the CO$_2$ is captured from the three hydrogen manufacturing units which results in total capture rate of 35 % considering the total CO$_2$ emissions of the whole industrial facility. [17]

The advantage of this type of partial capture is that CO$_2$ capture processes can be added to the disregarded units without making changes to the other ones when stricter emission regulations are introduced [7].

### 2.2 Chemical absorption

In a chemical absorption process CO$_2$ is separated from the flue gas by chemically binding CO$_2$ in a liquid solvent. This technology was first patented in the 1930s and has been used for acid gas treating for more than 80 years. In the 1970s the technology was developed as a possible source of CO$_2$, mainly for EOR, using amine-based solvents. Today the focus of chemical absorption used for post-combustion technologies is on emission reduction. The most commonly used solvents are still aqueous amine solutions, as for example monoethanolamine (MEA), which have been deployed for decades since these systems are effective for dilute CO$_2$ streams and are a commercially available and proven technology. But there are also inherent disadvantages as the high heat of reaction requiring a large external heat input. In addition to the risk of equipment corrosion high regeneration energy is needed as well as large volume absorbers with expensive packings which results in high capital and operating costs. [19] Besides amine-based systems there are carbonate systems having the advantage of lower energy requirement for regeneration. Such a system was developed in which the solvent has been promoted with catalytic amounts of piperazine (PZ) which is a diamine, has a faster absorption rate than MEA and a better thermal stability but is more expensive. Although the energy requirement using PZ is approximately 5 % lower, compared to the use of MEA, the solvent concentration in the solution is typically higher which results in a similar economic impact [19]. Similar to amine-base systems are ammonia-based systems which have a significantly lower heat requirement and the potential for high CO$_2$ capacity. But ammonia has a higher volatility compared to MEA and the flue
gas must be cooled down to around 20 °C to facilitate the absorption of CO₂. Another CO₂ capture technology is a biologically based system using enzymes. These systems are based on natural reactions of CO₂ in living organisms and are currently under development. [19] Nevertheless, the benchmark amine-based solvent used in literature is MEA [20] because it is a suitable solvent for post-combustion CO₂ capture as it has a high reactivity and other advantages as low costs, high absorption capacity per mass, a decent thermal degradation rate [12], it is commercially available and well-known. Therefore MEA was chosen to be the basis for this study but additionally simulations are conducted using the more advanced solvent PZ. A simplified flow diagram of a conventional chemical absorption process is shown in Figure 3.

Figure 3: Simplified flowsheet of the conventional chemical absorption process

In the chemical absorption process the cooled flue gas and the solvent are brought into contact in the absorber at temperatures typically between 40 and 60 °C and at atmospheric pressure. The CO₂ is chemically bound by the solvent and separated from the flue gas which is further washed with water to remove any remaining solvent before it is released to the atmosphere. The solvent containing the bound CO₂, referred to as CO₂ rich, is pumped to the top of the stripper where it is regenerated after passing through a heat exchanger. For the regeneration process a higher temperature between 100 and 140 °C is required to remove the chemically bound CO₂ and to produce steam which acts as a stripping gas. These temperature conditions and a pressure slightly higher than atmospheric pressure are maintained by heat supplied to the reboiler which is the most energy consuming part of this chemical absorption process. Through a condenser the steam is recovered and fed back to the stripper whereas the CO₂ leaves the condenser for further conditioning before transportation to a storage site. The so-called lean solvent containing relatively small amounts of CO₂ is pumped back to the absorber, first passing through a heat exchanger for further cooling. [9]
The CO₂ leaving the condenser is pressurized in a compressor train to a pressure that ensures the CO₂ stays in the dense phase along the transportation pipeline.

### 2.2.1 Process equipment

**Flue gas fan/blower:** The flue gas has to overcome a pressure drop which occurs over the absorber. Therefore the flue gas pressure is increased before entering the absorber by the use of a blower.

**Direct contact cooler (DCC):** Flue gases coming from the source plant generally are of high temperature and have to be cooled down in order to improve the CO₂ absorption, to minimize solvent losses due to degradation and minimize moisture losses with the exhaust gases. [21]

**Absorber:** In the absorber column the flue gas rising from the bottom comes in contact with the solvent which is flowing downstream and absorbing part of the CO₂ in the flue gas. This countercurrent flow is used to achieve high-efficiency gas absorption. [22] Normally absorbers are packed columns with structured packing material which provides sufficient interfacial area and thus a suitable CO₂ absorption capacity. [23] The absorber contains a washing section in the upper part to remove solvent residues from the clean gas.

**Pump:** The rich solvent stream is transported to the heat exchanger by the use of a pump where the pressure is increased to the required pressure in the stripper.

**Lean/rich heat exchanger:** The temperature of the CO₂ rich stream needs to be increased for the stripping and regeneration process. To reduce the reboiler duty, this stream is pre-heated by using heat from the lean stream exiting the stripper. The lean stream is cooled down close to the temperature level in the absorber.

**Stripper:** In the stripper column heat is supplied by the reboiler to the rich solvent flow to separate the CO₂ from the solvent. The recovered CO₂ flows upwards and exits the top of the stripper. The required reboiler duty to strip off the CO₂ is directly related to the specific energy consumption per unit of CO₂.

**Valve:** Since the lean solvent flow coming from the stripper has a higher pressure than required for the absorber which operates at ambient pressure, the stream is depressurized by using a valve.

**Cooler:** The CO₂ lean solvent exiting the lean/rich heat exchanger is normally warmer than what is desired in the absorber. Thus the temperature is further decreased using a cooler before the solvent enters the absorber column.

**Compressor and intercoolers:** The CO₂ is transported via pipelines (or ships) to typically very long distances. To avoid corrosion in the pipelines it is preferable that it does not contain any moisture. To overcome the pressure losses during the transport, the CO₂ is liquefied by compressing it to very high pressures in a 4-stage compressor train with intercooling. [21] The discharge pressure depends on pipeline length, operating and storage conditions. [24]
2.2.2 Split-flow configuration

Since the chemical absorption process, especially the reboiler part, is very energy intensive, the process flowsheet can be modified in order to decrease this energy demand. In the literature, several advanced process configurations can be found, the base case for this thesis is a split-flow configuration which is explained subsequent. Different methods for split-flow configuration (SFC) have been suggested in the literature and the method considered in this work is the rich solvent splitting as it is relatively easy to implement and has little additional investment cost since no additional equipment except piping material is needed. This configuration is shown in Figure 4. The rich solvent stream exiting the absorber is split into two flows. The larger one is preheated by the lean/rich heat exchanger similar to the conventional configuration. The other flow is kept cold and injected in the top of the stripper. The hot stream is fed to the stripper at some distance below, depending on the temperature of the stream, the higher the stream temperature the lower the injection point. In the conventional process modification, vapour released from the hot rich stream, goes directly into the condenser without providing a benefit. The idea of the SFC is to provide stripping heat for the cold rich stream by using this vapour. Therefore less heat supply is needed in the reboiler and this arrangement leads to a reduction of the reboiler heat demand. Additionally the cooling duty in the condenser also is reduced.

Figure 4: Simplified flowsheet of the split-flow configuration
3 Methodology

In a literature review, the chemical absorption of CO₂ was studied, especially advanced process modifications. As mentioned in the previous section the base case was decided to be the rich split-flow configuration. Based on the standard set-up and split-flow configuration a sensitivity analysis was conducted to get an optimized process design. The optimized advanced split-flow configuration was applied to an existing industrial plant to investigate different partial capture cases as described below. For selected process configurations the equipment was dimensioned and sent to an external partner for the cost estimations.

3.1 Process simulation

By the use of flue gas data from a cement plant the standard chemical absorption process and the split-flow configuration, using MEA and PZ as a solvent, were simulated in Aspen Plus V8.8. A sensitivity analysis was performed to optimize these processes regarding their energy use which is described in detail below. The use of these two different solvents serve as a comparison where the investigation of different partial capture cases and the cost estimations use only MEA as solvent.

In the simulation a rate-based approach was applied which is based on chemical engineering principles and therefore includes chemical reactions and mass transfer rates which results in a more accurate and reliable process model. [25] The simulated models include all required equipment except for operation pumps. These pumps are necessary to overcome pressure drops but are left out in the model as a simplification.

A model pulp mill was used as case study to apply the results from the sensitivity analysis to an existing industrial process. A more detailed description of the industrial process and the emission sources focused on are shown in section 5.

To evaluate the effect of partial carbon capture on the cost for capturing CO₂, different cases were considered using the SFC which are explained in section 3.1.2.

3.1.1 Sensitivity analysis

The performance of the carbon capture process is dependent on the interaction of several parameters which have been identified as important design parameters in previous studies [26, 27]. The parameters were varied to gain a good performance in terms of a low specific reboiler duty per unit of CO₂ captured. The considered parameters in this analysis are described below.

Stripper pressure

When achieving higher temperatures in the reboiler part of the stripper, the stripper process can be facilitated. At high temperatures the intermediate containing solvent and CO₂ is splitted where the CO₂ molecule is released. Additionally the water vaporization is suppressed by increasing the stripper pressure which reduces the heat of water vaporization and therefore the heat loss in the remaining liquid. [27] When determining the optimal operating pressure it had to be considered that too high temperatures may lead to amine degradation and corrosion problems. [26] This feasible temperature range depends on the solvent which is used where for example for MEA and PZ temperatures up to 125 °C and 150 °C respectively can be applied.
Solvent concentration

The solvent concentration is measured in weight percent and calculated by using the components' mass concentrations in the solution as follows:

\[
c_{\text{MEA}} = \frac{x_{\text{MEA}} + x_{\text{MEAH}}^+ + x_{\text{MEACOO}}^-}{x_{\text{MEA}} + x_{\text{MEAH}}^+ + x_{\text{MEACOO}}^- + x_{\text{H}_2\text{O}}^- + x_{\text{H}_2\text{O}}^+} \cdot 100
\] (1)

\[
c_{\text{PZ}} = \frac{x_{\text{PZ}} + x_{\text{PZH}}^- + x_{\text{HPZCOO}}^- + x_{\text{PZCOO}^-}}{x_{\text{PZ}} + x_{\text{PZH}}^- + x_{\text{HPZCOO}}^- + x_{\text{PZCOO}^-} + x_{\text{H}_2\text{O}}^- + x_{\text{H}_2\text{O}}^+} \cdot 100
\] (2)

Where

- \( c_{\text{MEA}} \) MEA concentration [wt-%]
- \( c_{\text{PZ}} \) PZ concentration [wt-%]
- \( x_i \) Mass flow of the component \( i \) [kg/s]

Lean CO\(_2\) loading

The CO\(_2\) loading specifies the number of moles of CO\(_2\) per moles of solvent in the solution and is calculated for MEA and PZ as can be seen in equation (3) and (4). Since PZ has the capacity to absorb two moles of CO\(_2\) per mole of PZ the loading has to be divided by 2.

\[
\text{loading}_{\text{MEA}} = \frac{\dot{n}_{\text{CO}_2} + \dot{n}_{\text{HCO}_3}^- + \dot{n}_{\text{CO}_2}^- + \dot{n}_{\text{MEACOO}^-}}{\dot{n}_{\text{MEA}} + \dot{n}_{\text{MEAH}}^+ + \dot{n}_{\text{MEACOO}^-}}
\] (3)

\[
\text{loading}_{\text{PZ}} = \frac{\dot{n}_{\text{CO}_2} + \dot{n}_{\text{HCO}_3}^- + \dot{n}_{\text{CO}_2}^- + \dot{n}_{\text{HPZCOO}}^- + \dot{n}_{\text{PZCOO}^-} + \dot{n}_{\text{PZCOO}^-}}{2 \cdot (\dot{n}_{\text{PZ}} + \dot{n}_{\text{PZH}}^- + \dot{n}_{\text{HPZCOO}} + \dot{n}_{\text{PZCOO}^-} + \dot{n}_{\text{PZCOO}^-})}
\] (4)

Where

- \( \text{loading} \) CO\(_2\) loading [-]
- \( \dot{n}_i \) Mole flow of the component \( i \) [kmol/s]

Ideally all the CO\(_2\) is stripped off, but in reality the solvent contains some CO\(_2\) residues. To reach a very low lean loading, which means that a great amount of CO\(_2\) is stripped off in the reboiler, a great amount of stripping steam is required leading to a high absolute reboiler duty which also results in a high specific reboiler duty. [27]

Parameters for the SFC

In comparison to the standard set-up the SFC has two more parameters to consider for an optimal process performance. First there is the split fraction which determines how much of the rich solvent flow is sent through the heat exchanger and how much is kept cold. The second parameter to consider is the stripper stage in which the rich stream after the heat exchanger is inserted. As mentioned in the previous section this height should be the lower the higher the stream temperature is, but since no reference values...
were available the optimum injection height was identified by performing a sensitivity analysis.

3.1.2 Investigated cases

Three cases where investigated which differ in the CO₂ capture rate, the amount of waste heat used for the capture process or the flue gas flowrate.

Case 1: Full capture

First full scale of CO₂ capture was investigated. For this case no partial capture was considered and the aim was to capture 90% of the CO₂ available in the flue gas. The remaining 10% are assumed to be released to the atmosphere. The specific reboiler duty which is necessary to run this capture process was determined.

Case 2: Partial capture – reduced capture rate

This case refers to the use of only waste heat to operate the reboiler which leads to a lower capture efficiency. To keep the process in a general framework and to make it comparable to the full capture case the process was simulated with a CO₂ capture rate of 75% and 50% respectively. For both cases the specific reboiler duty was identified under the assumption that there is enough waste heat to reach these capture rates.

Case 3: Partial capture – reduced flue gas flow

Similarly to the previous case, this case also considers the use of only free waste heat to supply the reboiler heat demand. But instead of lowering the capture rate the flue gas flow was decreased. Here it is assumed that the flue gas stream is split and just a part is sent through the capture process while the capture rate of this branch stream is 90%.

3.1.3 Investigation on the pulp mill

The aim in this case study is to determine how much CO₂ can be captured from two stacks by using the energy of an existing steam cycle. Here the three cases, investigated in section 3.1.2, are applied by using the SFC with MEA and the optimized process designs. The dimensioning of all cases is sent to the external partner for cost estimations.

Additionally, the loss in electricity due to the carbon capture unit was determined. Therefore, part of the steam turbine, that is, the low pressure section after which all steam needed in the pulp making process has been extracted, was simulated in Aspen Plus which is shown in section 5.3. The produced electricity is then compared to the electricity which is lost when using (part of) the steam for the reboiler in the capture process.

3.2 Dimensioning

In most cases Aspen Plus provides the characteristic variables of the equipment. For the electrically driven equipment, as pumps and compressors, the capacity and flow can be taken from the simulation results as well as the diameters of the absorber and the stripper. Aspen Plus estimates the heating and cooling duties as well as the areas of the coolers, the lean/rich heat exchanger and the reboiler just as the required capacity of the buffer and make-up tanks.
As mentioned in the previous section, operation pumps weren’t included in the process design. Therefore they have to be added in a last step as well as buffer tanks and tanks for the make-up stream. Buffer tanks are needed to respond to variation in production and to enable a simplified process control. They are located in-between the absorber and the stripper. In total two tanks for make-up streams are needed, one for the solvent and one for water.
This data is collected and summarized for each unit as a basis for the cost estimations.
4 Process modelling

As mentioned in section 3.1, the flue gas data for the processes undergoing the sensitivity analysis was taken from a stack of a cement plant and is shown in the table below.

Table 2: Flue gas data used in the sensitivity analysis

<table>
<thead>
<tr>
<th></th>
<th>( \dot{V} ) [m³/h]</th>
<th>( P ) [bar]</th>
<th>( T ) [°C]</th>
<th>( H_2O ) [mole-%]</th>
<th>( CO_2 ) [mole-%]</th>
<th>( N_2 ) [mole-%]</th>
<th>( O_2 ) [mole-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>339307</td>
<td>1</td>
<td>118</td>
<td>0,131</td>
<td>0,126</td>
<td>0,630</td>
<td>0,113</td>
</tr>
</tbody>
</table>

For the simulations in Aspen Plus the property method Electrolyte NRTL is employed. This method enables the modelling of aqueous electrolytes and mixed solvent electrolytes for a wide range of solvent concentrations. Aspen Plus provides a template for the rate-based approach and the use of MEA and PZ as a solvent respectively which already contains the necessary property data as well as the following reaction kinetics.

\[
\begin{align*}
\text{MEAH}^+ + H_2O & \leftrightarrow \text{MEA} + H_3O^+ \quad & \text{R1} \\
2H_2O & \leftrightarrow H_3O^+ + OH^- \quad & \text{R2} \\
HCO_3^- + H_2O & \leftrightarrow CO_2^{2-} + H_3O^+ \quad & \text{R3} \\
CO_3^{2-} + OH^- & \rightarrow HCO_3^- \quad & \text{R4} \\
HCO_3^- & \rightarrow CO_2 + OH^- \quad & \text{R5} \\
\text{MEA} + CO_2 + H_2O & \rightarrow \text{MEACOO}^- + H_3O^+ \quad & \text{R6} \\
\text{MEACOO}^- + H_3O^+ & \rightarrow \text{MEA} + CO_2 + H_2O \quad & \text{R7} \\
2H_2O & \leftrightarrow H_3O^+ + OH^- \quad & \text{R8} \\
HCO_3^- + H_2O & \leftrightarrow CO_2^{2-} + H_3O^+ \quad & \text{R9} \\
\text{PZ}^+ + H_2O & \leftrightarrow \text{PZ} + H_3O^+ \quad & \text{R10} \\
\text{HPZCOO} + H_2O & \leftrightarrow \text{PZCOO}^- + H_3O^+ \quad & \text{R11} \\
CO_3^{2-} + OH^- & \rightarrow HCO_3^- \quad & \text{R12} \\
HCO_3^- & \rightarrow CO_2 + OH^- \quad & \text{R13} \\
\text{PZ} + CO_2 + H_2O & \rightarrow \text{PZCOO}^- + H_3O^+ \quad & \text{R14} \\
\text{PZCOO}^- + H_3O^+ & \rightarrow \text{PZ} + CO_2 + H_2O \quad & \text{R15} \\
\text{PZCOO}^- + CO_2 + H_2O & \rightarrow \text{PZCOO}^{2-} + H_3O^+ \quad & \text{R16} \\
\text{PZCOO}^{2-} + H_3O^+ & \rightarrow \text{PZCOO}^- + CO_2 + H_2O \quad & \text{R17}
\end{align*}
\]
The reactions R1 – R3 as well as R8 – R11 are assumed to be at equilibrium whereas the reactions R4 – R7 and R12 – R17 are kinetic reactions. [28]
In the following sections the general assumptions and parameters for the process design, which are not manipulated in the sensitivity analysis, are explained for the standard set-up as well as the SFC.

4.1 Standard set-up

In Figure 5 the flowsheet for the standard set-up modelled in Aspen Plus is shown. This process design was used for both solvents, MEA and PZ. The flue gas enters the process at ambient pressure and a temperature of 118 °C. Before it is fed into the absorber it is cooled down in a direct contact cooler (DCC) which is explained in section 2.2.1. For simplicity the DCC is modelled as a cooler (COOL-1) where the flue gas is cooled down to 40 °C and a flash (FLASH-1) to separate the flue gas from the condensed water. After that it enters the absorber (ABS-1) in the bottom stage. The liquid solvent enters the top stage of the absorber also at 40 °C. The absorber is modelled as a packed column with 20 stages using a “RadFrac” block. The packing material used is Mellapak 250Y.

Diffusion resistance with reactions in the film is assumed for the liquid phase where 6 discretization points were used for the liquid film whose location is shown in Table 3. For the vapour phase diffusion resistance with no reactions in the film is assumed.

Table 3: Discretization points in the liquid film

<table>
<thead>
<tr>
<th>Point</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance</td>
<td>0,00001</td>
<td>0,0001</td>
<td>0,001</td>
<td>0,01</td>
<td>0,1</td>
<td>0,5</td>
</tr>
</tbody>
</table>

A design mode is used to calculate the diameter of the absorber and the stripper which is based on flooding. Flooding is the condition when the diameter is so small, that the liquid flowing through the packing is held voids between the packing. This problem could be eliminated by using a large diameter, however that would also increase costs.
Therefore this flooding approach is used by choosing the stage with the highest liquid and vapour flow as the base stage and setting the base flood to 0.8. The diameter is then calculated so that it is operating at 80% of the flooding velocity which is the flooding limit.

There are two streams leaving the absorber. One is the CO$_2$ lean gas stream (CLEANGAS) which is exiting in the top stage. In the process shown in Figure 5 the washing section to remove solvent residues is modelled as a separate column and is designed the same way as the absorber but with only two stages and a height of 2 m. After the washing section the CO$_2$ lean gas is let into the atmosphere. For the water going into the washer the water stream from FLASH-1 can be used, which is a sufficient amount as the target concentration of solvent in the CO$_2$ lean stream was set to less than 1 ppm but even a concentration in a range of 0.21 ppm to 0.24 ppm could be reached in all processes using MEA and PZ for the standard set-up and also the SFC. Table 4 shows the design parameters and dimensions of the absorber and the washer.

Table 4: Design parameters and dimensions of the absorber and the washer

<table>
<thead>
<tr>
<th>Column</th>
<th>Packing material</th>
<th>Stages</th>
<th>Pressure [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorber</td>
<td>Mellapak 250Y</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>Washer</td>
<td>Mellapak 250Y</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

As mentioned in section 2.2.1 a pressure drop occurs over the absorber and the washer which is possible to overcome by the use of a flue gas blower which has to be placed before the COOL-1. But since these pressure drops are unknown at a preliminary process design the flue gas blower is simulated separately after knowing the pressure drops by the use of the flowsheet below. The flue gas blower is designed as a compressor while the outlet pressure is 1 bar plus the total pressure drop over the absorber and the washer.

Figure 6: Aspen Plus flowsheet of the flue gas fan

The second stream leaving the absorber is the solvent containing the absorbed CO$_2$. Through the PUMP the pressure is increased to the required stripper pressure and enters the lean/rich heat exchanger (HEX) where the temperature is increased. For the HEX,
the HeatX block is used and set to countercurrent flow direction. The temperature difference between the hot outlet and the cold inlet temperature is assumed to be 10 K, but the minimum temperature approach is set to 5 K. After the HEX the heated stream enters the stripper at the second stage since the reflux is inserted to the first stage. The stripper is modelled with the same assumptions for the liquid film and the same design specifications, the only difference is the pressure and the height which is further investigated in section 6.1.

The CO₂ product gas is cooled down to 20 °C and the condensed water removed from the gas stream before it is compressed. To simplify the convergence the CO₂ condenser is modelled as a cooler and a flash. The compression section is modelled separately for simplicity and shown in Figure 7.

\[ \text{Figure 7: Aspen Plus flowsheet of the CO}_2 \text{ compression section} \]

The CO₂ rich stream is compressed to 80 bar in a multistage compression section (4 stages in total) with intercooling to 25 °C. Through a pump after the compressor the pressure is increased to 110 bar for transportation and storage. The three streams L1, L2 and L3 in Figure 7 are condensed water.

After stripping the CO₂ off the solvent in the reboiler, the CO₂ lean stream leaves the stripper. The LEAN-1 stream enters the HEX where the temperature is decreased. The pressure is lowered to the absorber pressure of 1 bar through the VALVE and then mixed with make-up water and solvent to obtain the mass balance in the system. This is modelled by using a balance block. The water, containing small amounts of solvent, coming out from the washer can be used as make-up stream. For simplicity this recycling is not taken into account in the process shown in Figure 5. Before entering the absorber once again, the regenerated solvent is cooled down to 40 °C in the block COOL-3. The selector is only used to ease the convergence to have the possibility of running the simulation first as an open loop, before having a closed loop configuration.

### 4.2 Split-flow configuration

The SFC is similar to the standard set-up where the main difference is that the rich stream exiting the absorber is split before entering the HEX as explained in section 2.2.2. The flowsheet is shown in Figure 8. The rich stream is split by having the larger fraction going through the HEX and the rest is kept cold and fed into the top of the stripper.
4.3 Design specifications

For all models two design specifications are implemented. The first one is set in the stripper block to control the lean loading. Therefore the type of the design specification is set to “Mole ratio” and the target value is specified. The components to calculate the mole ratio are selected according to equation (4) and (5) as well as the stream LEAN-1. The varied parameter to reach a specific lean loading is the reboiler duty.

The second design specification is set as specification of the flowsheet to have a certain capture rate by specifying the mole flow of CO₂ in the CLEANGAS. For a capture rate of 90 % this flow is 10 % of the CO₂ mole flow available in the flue gas entering the absorber. Here the manipulated variable is the flow rate of the LEANIN stream entering the absorber.
5 Case study: Pulp mill

Pulp, and eventually paper, are produced from raw materials like containing cellulose fibres, which normally is wood, recycled paper or agricultural residues. The pulp mill and the paper mill can exist separately which means that pulp must be brought to the paper mill from an outside source. This specific pulp and paper mill is an integrated case where the auxiliary systems can be used commonly.

5.1 Pulp making process

There are several different pulping processes but the most common one is chemical pulping which is the one used for this case study. The process is based on extracting the specific part of the raw material by means of cooking it in chemicals while the recovery of the cooking chemicals is responsible for the emissions. The main part of these emissions comes from combusting the unusable part of the raw material. The chemical recovery loop is shown in Figure 9 by the box with dashed lines. More information on this process can be taken from the master thesis [29].

![Figure 9: A schematic overview of the kraft pulping process](image)

As can be seen in Figure 9 there are two stacks from which CO₂ is to be capture, the recovery boiler (RB) and the lime kiln (LK). There is steam produced in the recovery boiler which is expanded in a back pressure steam turbine to produce electricity. To cover the need of the pulping process MP-steam and LP-steam is extracted. In a modern pulp mill there is often a steam surplus which can be further expanded in a condensing turbine. This produced electricity can be sold to the grid or, in this case, used for the reboiler of the carbon capture unit. Further data on the flue gases and the available steam is provided in the next section.
5.2 Emissions and steam data from the pulp mill

Table 5 shows the data of the flue gas coming from the recovery boiler and the lime kiln. In Table 6 the data of the saturated steam which can be used for the capture process is shown while the enthalpy was taken from a steam table [30].

*Table 5: Flue gas data of the pulp mill*

<table>
<thead>
<tr>
<th>Stack</th>
<th>$\dot{V}$ [m$^3$/s]</th>
<th>$P$ [bar]</th>
<th>$T$ [°C]</th>
<th>$H_2O$ [wt-%]</th>
<th>$CO_2$ [wt-%]</th>
<th>$N_2$ [wt-%]</th>
<th>$O_2$ [wt-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery boiler</td>
<td>255</td>
<td>1</td>
<td>118</td>
<td>0,187</td>
<td>0,194</td>
<td>0,590</td>
<td>0,029</td>
</tr>
<tr>
<td>Lime kiln</td>
<td>16,5</td>
<td>1</td>
<td>118</td>
<td>0,174</td>
<td>0,347</td>
<td>0,460</td>
<td>0,018</td>
</tr>
</tbody>
</table>

*Table 6: Steam data of the pulp mill*

<table>
<thead>
<tr>
<th>Alternative</th>
<th>$P$ [bar]</th>
<th>$\dot{m}$ [t/h]</th>
<th>$h$ [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4,5</td>
<td>173</td>
<td>2744,03</td>
</tr>
<tr>
<td>2</td>
<td>2,8</td>
<td>172</td>
<td>2722,96</td>
</tr>
</tbody>
</table>

The goal is to capture CO2 in the pulp mill with the existing infrastructure and capacity. There are two different alternatives which can be taken into consideration for the steam available at the pulp mill. Alternative 1 uses steam at 4,5 bar for the capture process while in alternative 2 the steam is first expanded in a turbine from 4,5 bar to 2,8 bar producing electricity and using steam at 2,8 bar for the capture process. When providing heat for regeneration in the reboiler of the stripper the steam is condensed in both cases to saturated water at 2,8 bar which has an enthalpy of 551,5 kJ/kg. The available heat can be calculated as follows:

$$Q = \dot{m} \cdot \Delta h$$  \hspace{1cm} (5)

Where

- $Q$ energy [W]
- $\dot{m}$ mass flow [kg/s]
- $\Delta h$ enthalpy difference [kJ/kg]
\[ Q_1 = 173 \text{ t/h} \cdot \frac{1}{3.6} \cdot (2744.0 - 551.5) \text{ kJ/kg} = 105.4 \text{ MW} \]
\[ Q_2 = 172 \text{ t/h} \cdot \frac{1}{3.6} \cdot (2723.0 - 551.5) \text{ kJ/kg} = 103.7 \text{ MW} \]

### 5.3 Modelling

As mentioned in section 3.1.3 the condensing part of the steam turbine was simulated in Aspen Plus. The flowsheet is shown in Figure 10.

To determine the loss in electricity the two alternatives, shown in Table 6, are considered while the discharge pressure in both cases is 0.1 bar.

![Aspen Plus flowsheet of the steam turbine](image)

*Figure 10: Aspen Plus flowsheet of the steam turbine*
6 Results and discussion

6.1 Sensitivity analysis

While changing one parameter, as explained in section 3.1.1 the other parameters are kept constant to perform a sensitivity analysis. The values of these constant parameters are listed in the table below for the processes using MEA and PZ respectively. As can be seen, the only difference between the use of MEA and the use of PZ is the solvent concentration, which was taken from literature [31, 32] and in the split fraction. The reason for the difference in the latter is a temperature crossover which appears in the heat exchanger when having a split fraction of less than 0.8 for the process using PZ.

Table 7: Constant values for the sensitivity analysis

<table>
<thead>
<tr>
<th>Parameters</th>
<th>MEA</th>
<th>PZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stripper pressure [bar]</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>solvent concentration [wt-%]</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Lean CO₂ loading [-]</td>
<td></td>
<td>0.27</td>
</tr>
<tr>
<td>Parameters for the SFC [-]</td>
<td>Split fraction</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Stage</td>
<td>5</td>
</tr>
<tr>
<td>Height [m]</td>
<td>Absorber</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Stripper</td>
<td>15</td>
</tr>
<tr>
<td>Capture rate [%]</td>
<td></td>
<td>90</td>
</tr>
</tbody>
</table>

Since all these parameters are dependent on one another an optimal process design can’t be distinguished by only changing one parameter, but it helps to identify the influence of different parameters on the process performance which is shown in the following sections as well as the interaction of different parameters. The sensitivity analysis for the stage where the hot split stream is inserted to the stripper and the size of the split fraction which are necessary parameters for the SFC are shown in the appendix A.
6.1.1 Monoethanolamine

Stripper pressure

The reboiler duty as a function of the stripping pressure as well as the change in the reboiler temperature is shown in Figure 11. As can be seen, the higher the stripper pressure, the higher the reboiler temperature while at the same time, the required reboiler duty decreases. Having a low pressure means almost the same reboiler duty for both process configurations. That’s because having a low temperature in the reboiler results in just a small difference between the rich inlet and the lean outlet stream so there is not much gained from splitting the stream. But with an increasing pressure, the difference in the reboiler duties increases as the reboiler temperature increases. While the reboiler duty is decreasing more rapidly in the range of lower pressures, the curves flatten when it comes to a higher pressure. That shows that the reactions are already very fast at these pressures, so there is not much to gain from increasing the pressure or the temperature further. It can be clearly stated that the reboiler temperature is tied directly to the stripper pressure. If the temperature in the reboiler is increased the conditions are favourable for transfer of CO\textsubscript{2} to the gas phase and therefore less steam per mole CO\textsubscript{2} is required [33]. Increasing the stripper pressure therefore means higher temperature and lower reboiler duty, however, there is a practical limit to the temperature increase because of thermal MEA degradation. In the modelling degradation is not taken into account and thus the effect cannot be seen directly from the simulation results, nevertheless, it has to be considered. There are more factors influencing the degradation rate, but the reboiler temperature has the largest effect on it. [34] The temperature should be 125 °C or less in the reboiler [33]. In this case a stripper pressure of 2 bar was chosen which corresponds to a temperature of 121 °C.

![Figure 11: Effect of stripper pressure on reboiler duty and temperature in MEA-based absorption](image)

Solvent concentration

The MEA concentration not just influences the reboiler duty but also the solvent flow rate. As can be seen in Figure 12, the higher the MEA concentration the less solvent is
required to reach a desired capture rate. When having a low MEA concentration a clear difference between the reboiler duty of the standard set-up and the SFC can be stated. But as the MEA concentration increases this difference is decreasing while for both processes an optimum can be identified. For the standard configuration the reboiler duty is at its minimum when having a MEA concentration of 30 wt-% which leads to a solvent flow rate of approximately 300 kg/s, resulting in a liquid-to-gas (L/G) ratio of 3.68. To reach a minimum reboiler duty for the SFC the MEA concentration should be 25 wt-%, according to Figure 12, which results in a solvent flow rate of 352 kg/s and a L/G ratio of 4.32.

![Figure 12: Effect of MEA concentration on reboiler duty and solvent flow rate in MEA-based absorption](image)

**Lean CO₂ loading**

Figure 13 shows the influence of lean CO₂ loading on the reboiler duty and the solvent flow rate. It can be seen that for a lean loading of 0.2 the reboiler duty is similar for both process designs while it differs more with increasing lean loading. The minimum for the standard set-up is at 0.28 while this value is 0.32 for the SFC design. For low lean loadings, although the solution provides more free MEA for faster CO₂ absorption and a lower solvent flow rate, the reboiler duty increases since more stripping steam is required to regenerate such a low loading [35]. As the lean loading increases also the solvent flow rate is increasing to ensure a certain capture rate.
Figure 13: Effect of lean CO₂ loading on reboiler duty and solvent flow rate in MEA-based absorption

**Optimal process values**

In Figure 14 the influence of the lean CO₂ loading and the MEA concentration on the reboiler duty is shown for the standard set-up. All the other parameters are kept constantly having the values listed in Table 7.
When comparing Figure 14 to Figure 12 and Figure 13, it can be seen that the combination of both parameters has another influence than just varying the value of one parameter. When having a small lean loading the reboiler duty is the lower the lower the MEA concentration is. But this is the opposite when having a high lean loading leading to a small reboiler duty as the MEA concentration is increasing. In general, as the MEA concentration is increasing the lean loading should also be increased to have a low regeneration duty. The optimum design distinguished in Figure 14 is a MEA concentration of 40 wt-% and a lean loading of 0.32. But in general a MEA concentration of more than 30 wt-% shouldn’t be used in order to prevent equipment corrosion and solvent degradation. Therefore, and because the minimum when having a concentration of 35 % is not significantly smaller than the minimum when having a 30 % concentration, a MEA concentration of 30 wt-% was chosen together with a lean loading of 0.28 resulting in a reboiler duty of 3826 kJ/kg CO₂.

Similar curve progressions can be distinguished for the SFC which is shown in Figure 15. Compared to the standard set-up, shown in Figure 14, the minimums in reboiler duty for the SFC are slightly shifted towards higher lean loadings. In this case as well the minimum reboiler duty can be reached by having a MEA concentration of 40 wt-% but with a lean loading of 0.36. Similar to the standard set-up a MEA concentration of 30 wt-% was chosen to obviate corrosion which leads to a lean loading of 0.32 to reach the minimum reboiler duty of 3253 kJ/kg CO₂.

![Figure 15: Effect of lean CO₂ loading and MEA concentration on reboiler duty in MEA-based absorption for the SFC](image_url)

Due to the changed values for the MEA concentration and the lean loading also the optimum stripper stage for inserting the hot rich CO₂ stream changes which is shown in appendix A.

For the sensitivity analysis a stripper height of 15 m was used, while the optimal height was investigated as can be seen in Figure 33 in appendix A. Finally a height of 12 m
was chosen. For the absorber height 20 m were chosen at the beginning, when conducting the sensitivity analysis. However, Figure 34 in appendix A shows that a height of 10 m for the absorber is sufficient.

6.1.2 Piperazine

Stripper pressure

In contrast to MEA, PZ can be used in a temperature range up to 150 °C without having thermal degradation [32]. This results in a very high stripper pressure of 13 bar as can be seen in Figure 16 for the standard set-up. The curve progression of the reboiler duty looks similar to the one using MEA: the higher the pressure the lower the reboiler duty, while the curve flattens in the range of very high pressures. As expected, the reboiler temperature is increasing as the pressure is increasing.

![Figure 16: Effect of stripper pressure on reboiler duty and temperature in PZ-based absorption using the standard set-up](image)

The SFC has a different behaviour than the process using the standard set-up shown in Figure 16. When having a pressure higher than 4 bar a temperature cross over occurs in the heat exchanger. Since a higher pressure also means higher temperature the heat exchanger can’t handle this as also the mass flow of this stream is higher than the one which is heated up. Therefore a pressure of 4 bar was chosen which results in a reboiler temperature of 125 °C.
The effect of the PZ concentration on the reboiler duty and the solvent flow rate is shown in Figure 18.

As can be seen, no clear minimum for the PZ concentration can be stated but the curve progressions look similar as for MEA, since the curve for the standard set-up and the one for the SFC are converging when it comes to high concentrations. But a different trend is observed for the flow rate since there is a minimum, which means that although the concentration is increasing the amount of solvent flow required for having a specific capture rate (here 90%) is also increasing. This minimum occurs at a PZ concentration...
of 40 % which is the value used and recommended in literature [32, 36, 37]. When comparing Figure 12 and Figure 18, it can be seen that in general the L/G ratio using PZ is higher than for the process using MEA because of the poorer CO₂ loading capacity of PZ compared to MEA.

**Lean CO₂ loading**

When using PZ as solvent there is also a minimum in the reboiler duty when varying the lean CO₂ loading which occurs at a loading of 0,22. To avoid solids precipitation a loading below 0,26 should not be used [32] which leads to a solvent flow rate of 527 kg/s.

![Figure 19: Effect of lean CO₂ loading on reboiler duty and solvent flow rate in PZ-based absorption](image)

**Optimal process values**

In Figure 18 it was shown that there is a minimum in the solvent flow rate at a PZ concentration of 40 wt-% although no minimum in the concentration could be stated. Also in the literature a PZ concentration of 40 wt-% is commonly used and recommended [32, 36, 37]. Figure 19 shows that a lean loading of 0,26 has the lowest reboiler duty if considered that the loading shouldn’t be less. Therefore a concentration of 40 wt-% and a lean loading of 0,26 was chosen for the standard set-up as well as the SFC in connection with the optimal values for the stripper pressure identified before. In Figure 20 the influence of the stripper height on the regeneration duty is shown for the standard set-up as well as the SFC.
When having as very small stripper of 2 m the reboiler duty is almost the same for both processes. While this value is quite constant for the standard set-up, one can identify a small decrease in reboiler duty for the SFC until a height of 6 m is reached. When the stripper is higher than 6 m the reboiler duty is almost constant, therefore a stripper height of 6 m was identified as the optimal value.

Figure 21 shows the reboiler duty and the L/G ratio as a function of the absorber height for the standard set-up and the SFC using PZ.

The same as before, when having MEA as solvent, can be stated for the use of PZ: While the reboiler duty is only influenced by the absorber height in the range of small
values, the L/G ratio is decreasing as the height is increasing. But in comparison to Figure 34 the L/G ratio is also changing when having a high absorber which could be related to the higher solvent rate in general. As well as for the use of MEA 10 m were distinguished as the optimal height.

6.1.3 Partial capture

Since the main part of this thesis are different partial capture conditions, a small sensitivity analysis was conducted to compare the influence of the solvent concentration and the lean CO\textsubscript{2} loading when having different capture rates. This analysis was based on CO\textsubscript{2} absorption using MEA as solvent and SFC. In Figure 22 the results for the sensitivity analysis using 90 \% and 75 \% (marked with p.c.) are shown. It can be seen that the curve progression for both capture rates are almost parallel which would result in the same optimum parameter values, if more than these three points would be considered. In general the reboiler duty, when having a capture rate of 75 \%, is slightly smaller than with a capture rate of 90 \%.

![Graph showing the effect of lean CO\textsubscript{2} loading and MEA concentration on reboiler duty in MEA-based absorption for the SFC with 90 \% and 75 \% capture rate](image)

In Figure 23 and Figure 24 the influence of the absorber height on the reboiler duty are shown for different lean loadings and solvent concentrations with a capture rate of 90 \% and 75 \% respectively. Again it can be seen that the curve progressions are similar for both capture rates. The optimum absorber height in all these cases is 10 m as already determined in the previous section. The influence of the absorber height is discussed more in detail in appendix A2.
Figure 23: Effect of absorber height on reboiler duty for different values in lean loading and solvent concentration in MEA-based absorption for the SFC with 90% and capture rate.

Figure 24: Effect of absorber height on reboiler duty for different values in lean loading and solvent concentration in MEA-based absorption for the SFC with 75% and capture rate.
### 6.1.4 Results of sensitivity analysis

Table 8 shows the optimized process conditions for the four investigated processes namely the standard set-up of chemical absorption and the SFC each with MEA and PZ as solvent.

*Table 8: Results of sensitivity analysis*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MEA</th>
<th>PZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard set-up</td>
<td>SFC</td>
</tr>
<tr>
<td>Stripper height [m]</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>Absorber height [m]</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Stripper pressure [bar]</td>
<td>2</td>
<td>13</td>
</tr>
<tr>
<td>Stripper diameter [m]</td>
<td>4,24</td>
<td>4,30</td>
</tr>
<tr>
<td>Absorber diameter [m]</td>
<td>6,91</td>
<td>7,07</td>
</tr>
<tr>
<td>Solvent concentration [wt-%]</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Lean CO2 loading [-]</td>
<td>0,28</td>
<td>0,32</td>
</tr>
<tr>
<td>Rich CO2 loading [-]</td>
<td>0,535</td>
<td>0,530</td>
</tr>
<tr>
<td>L/G ratio [-]</td>
<td>3,87</td>
<td>4,74</td>
</tr>
<tr>
<td>Stage [-]</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Split fraction [-]</td>
<td>-</td>
<td>0,7</td>
</tr>
<tr>
<td>Reboiler duty [kJ/kg CO₂]</td>
<td>3880</td>
<td>3093</td>
</tr>
</tbody>
</table>

As can be seen, when using PZ the stripper height is half as big as with the use of MEA whereas the absorber height was decided to be the same for all four cases. A relatively large difference can be identified in the pressure for the stripping. Both processes using MEA have the same pressure of 2 bar whereas the standard set-up using PZ has a stripper pressure of 13 bar which is possible since solvent temperatures up to 150 °C can be used. For the SFC this was not possible as explained in section 6.1.2, therefore a pressure of 4 bar is used. The stripper diameter for the process using MEA is similar, while this diameter is slightly smaller when using PZ, also the absorber diameter is in the same range for all four processes. The solvent concentration are different for the use of MEA and PZ while the standard set-up and the SFC using PZ have the same lean loading as well as the same rich loading of 0,26 and 0,33 respectively. For the standard
set-up using MEA a lean loading of 0.28 was identified to be the optimal one whereas this value is 0.32 for the SFC. The rich loading in these two processes is 0.535 and 0.530 respectively which is almost the same. In general the processes using PZ have a higher solvent flow rate and therefore a higher L/G ratio while in both cases this ratio is bigger for the SFC. For the SFC using MEA stage 10 was identified to be the optimal one where the hot split fraction is inserted to, while this one is stage 7 for the use of PZ. The split fraction was chosen to be 0.7 for the use of MEA and 0.8 for the use of PZ. All these parameters result in different reboiler duties and different L/G ratios as can be seen in Figure 25. The MEA standard process is the most energy intensive one with a reboiler duty of 3880 kJ/kg CO$_2$. When having the MEA SFC even 20% of reboiler duty can be saved. The PZ standard process requires a regeneration duty of 2739 kJ/kg CO$_2$ which actually is 28% less than the standard process using MEA as solvent. The least energy intensive process is the SFC using PZ, whereas only 6% can be saved compared to the PZ standard process design and 16% in comparison to the MEA SFC. In Figure 25 it can also be noticed that the lower the reboiler duty, the higher the L/G ratio, which means the more solvent is needed to reach a specific capture rate, here 90%. But as mentioned before, there is also the fundamental difference between MEA and PZ with respect to CO2 carrying capacity, which results in a higher L/G ratio when using PZ compared to MEA.

Figure 25: Results in reboiler duty and L/G ratio for the MEA- and PZ-based absorption each with standard set-up and SFC

### 6.2 Pulp mill

#### 6.2.1 Investigated cases

As mentioned in section 5.3 for the pulp mill the different partial capture cases are investigated for the two stacks (recovery boiler and lime kiln). First it was proved if the optimum values for the solvent concentration and the lean loading also apply for this case by using full scale capture and a capture rate of 75% respectively. Capturing 75% of the CO$_2$ available in the flue gases leads to a reduction in reboiler duty which is, however, diminutive as shown in Figure 35 for the recovery boiler and Figure 38 for
the lime kiln in appendix B. The optimum values are chosen to be the same as for the MEA SFC shown in Table 8 which is reasonable for the recovery boiler and the lime kiln. When decreasing the capture rate, the L/G ratio is automatically decreasing since the absorber height was kept constant, which is shown in Figure 36 and Figure 39 in appendix B. By contrast, the capture rate could also be decreased by decreasing the absorber height which, however, is not recommended because that leads to an increase in reboiler duty and besides a capture rate of less than 85 % can’t be reached as can be seen in Figure 37 and Figure 40 in appendix B.

The results for the three different capture rates capturing from the flue gas coming from the recovery boiler and the lime kiln are shown in Table 9.

Table 9: Results for the recovery boiler and the lime kiln when varying the capture rate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Capture rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Recovery boiler</td>
</tr>
<tr>
<td></td>
<td>90</td>
</tr>
<tr>
<td>Stripper height [m]</td>
<td></td>
</tr>
<tr>
<td>Absorber height [m]</td>
<td></td>
</tr>
<tr>
<td>Stripper pressure [bar]</td>
<td></td>
</tr>
<tr>
<td>Stripper diameter [m]</td>
<td>5.69</td>
</tr>
<tr>
<td>Absorber diameter [m]</td>
<td>8.93</td>
</tr>
<tr>
<td>Solvent concentration [wt-%]</td>
<td></td>
</tr>
<tr>
<td>Lean CO2 loading [-]</td>
<td>0.32</td>
</tr>
<tr>
<td>Rich CO2 loading [-]</td>
<td>0.53</td>
</tr>
<tr>
<td>L/G ratio [-]</td>
<td>5.48</td>
</tr>
<tr>
<td>Stage [-]</td>
<td></td>
</tr>
<tr>
<td>Split fraction [-]</td>
<td></td>
</tr>
<tr>
<td>Reboiler duty [MW]</td>
<td>116</td>
</tr>
<tr>
<td>Spec. reboiler duty [kJ/kg CO2]</td>
<td>3119</td>
</tr>
</tbody>
</table>

As can be seen the column diameters are decreasing when lowering the capture rate and also the solvent flow rate is decreasing which leads to a lower L/G ratio for a 50 % capture rate compared to 90 %. The reboiler duty is decreasing when having a lower capture rate, however, the specific reboiler duty is only decreased by 3 %, for both
stacks, when having a capture rate of 75 % while the decrease is 7 % for the recovery boiler and 8 % for the lime kiln when the capture rate is 50 %.

When looking at case 3, explained in section 3.1.2, where partial capture is applied by decreasing the flue gas flow going through the capture process, it can be seen that the specific reboiler duty remains constant, which was expected. The equipment is getting smaller in size, especially the absorber and stripper diameters, when having less flue gas coming in. Furthermore a smaller solvent flow is needed, but the L/G ratio remains the same. These results are shown in Table 10.

Table 10: Results for the recovery boiler and the lime kiln when varying the flue gas flow

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bypass [%]</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Recovery boiler</td>
<td>Lime kiln</td>
<td>Recovery boiler</td>
<td>Lime kiln</td>
<td>Recovery boiler</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>25</td>
<td>50</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>Stripper height [m]</td>
<td></td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorber height [m]</td>
<td></td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stripper pressure [bar]</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stripper diameter [m]</td>
<td>5.69</td>
<td>4.93</td>
<td>4.02</td>
<td></td>
<td>3.01</td>
<td>2.61</td>
</tr>
<tr>
<td>Absorber diameter [m]</td>
<td>8.93</td>
<td>7.74</td>
<td>6.32</td>
<td></td>
<td>3.84</td>
<td>3.33</td>
</tr>
<tr>
<td>Solvent concentration [wt-%]</td>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lean CO2 loading [-]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Rich CO2 loading [-]</td>
<td>0.53</td>
<td>0.53</td>
<td>0.53</td>
<td></td>
<td>0.53</td>
<td>0.53</td>
</tr>
<tr>
<td>L/G ratio [-]</td>
<td>5.48</td>
<td>5.48</td>
<td>5.46</td>
<td></td>
<td>9.62</td>
<td>9.62</td>
</tr>
<tr>
<td>Stage [-]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Split fraction [-]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Reboiler duty [MW]</td>
<td>116</td>
<td>83</td>
<td>50</td>
<td></td>
<td>23</td>
<td>19</td>
</tr>
<tr>
<td>Spec. reboiler duty [kJ/kg CO2]</td>
<td>3119</td>
<td>3119</td>
<td>3120</td>
<td></td>
<td>3198</td>
<td>3197</td>
</tr>
</tbody>
</table>
6.2.2 Loss in electricity when applying partial capture

To determine the loss in electricity, both alternatives shown in Table 6, which differ from the steam pressure were taken into consideration. The results are shown below.

**Alternative 1: Steam at 4,5 bar**

As explained in section 5.3, in a first step the electricity produced when expanding the steam from 4,5 bar to 0,1 bar was determined by using Aspen Plus. The electricity produced in the turbine for alternative 1 is 22,57 MW. If this steam is extracted from the turbine instead of producing electricity, this corresponds to available steam for the reboiler of 105,36 MW as calculated in section 5.2. There are two different possibilities to apply partial capture to the pulp mill which are shown below:

1. **First capturing from the recovery boiler**

   In this case it was examined how much CO₂ can be captured from the flue gas coming from the recovery boiler by only using the available steam which corresponds to 105,36 MW. The results are shown in Table 11.

   *Table 11: Results for the electricity loss when first capturing from the recovery boiler using steam at 4.5 bar*

<table>
<thead>
<tr>
<th>Remaining electricity [kW]</th>
<th>Capture rate [%]</th>
<th>Specific reboiler duty [kJ/kg CO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>82,85</td>
<td>3069</td>
</tr>
</tbody>
</table>

   It can be seen that all of the available steam has to be used to capture from the recovery boiler while a capture rate of almost 83 % is reached.

2. **First capturing from the lime kiln**

   In this case the available steam which can be used and the electricity produced is the same as before. The results are shown in Table 12.

   *Table 12: Results for the electricity loss when first capturing from the lime kiln using steam at 4.5 bar*

<table>
<thead>
<tr>
<th>Stack</th>
<th>Remaining electricity [kW]</th>
<th>Capture rate [%]</th>
<th>Specific reboiler duty [kJ/kg CO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime kiln</td>
<td>5371</td>
<td>90,00</td>
<td>3197</td>
</tr>
<tr>
<td>Recovery boiler</td>
<td>0</td>
<td>66,51</td>
<td>2973</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>84,03</td>
</tr>
</tbody>
</table>
When first capturing CO\textsubscript{2} from the flue gas coming from the lime kiln a full scale capture (90 % capture rate) can be reached for the lime kiln while 5371 kW of electricity remain which corresponds to a steam duty of 81939 kW. This remaining steam can be used to capture from the recovery boiler while a partial capture rate of 66.51 % is reached for the flue gas coming from the recovery boiler and no electricity is remaining. The total capture rate when capturing from both stacks is calculated by using the total amount of CO\textsubscript{2} from the recovery boiler and the lime kiln as well as the total amount of CO\textsubscript{2} captured which leads to a total capture rate of 84.03 %.

**Alternative 2: Steam at 2.8 bar**

For this alternative steam at 4.5 bar is first expanded to 2.8 bar and further to 0.1 bar while the latter expansion can be replaced by using the steam for the reboiler. Due to the first expansion step to 2.8 bar 3821 kW of electricity is produced. As before, there are two possibilities which differ in stack order.

1. **First capturing from the recovery boiler**

   In this case it was also examined how much CO\textsubscript{2} can be captured from the flue gas coming from the recovery boiler by only using the available steam which corresponds to 103.75 MW. The results are shown in Table 13.

<table>
<thead>
<tr>
<th>Remaining electricity [kW]</th>
<th>Capture rate [%]</th>
<th>Specific reboiler duty [kJ/kg CO\textsubscript{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3821</td>
<td>81.77</td>
<td>3062</td>
</tr>
</tbody>
</table>

   It can be seen that all of the available steam at 2.8 bar has to be used to capture from the recovery boiler while a capture rate of almost 82 % is reached.

2. **First capturing from the lime kiln**

   The available steam which can be used and the electricity produced is the same as before. As well as before a full scale capture (90 % capture rate) can be reached when first capturing CO\textsubscript{2} from the flue gas coming from the lime kiln while 7976 kW of electricity remain which also contains the 3821 kW produced by the first turbine step. The remaining steam can be used to capture from the recovery boiler while a partial capture rate of 65.34 % is reached and again 3821 kW of electricity remain. For this alternative the total capture rate when capturing from both stacks is 83.12 %.
Table 14: Results for the electricity loss when first capturing from the lime kiln using steam at 2,8 bar

<table>
<thead>
<tr>
<th>Stack</th>
<th>Remaining electricity [kW]</th>
<th>Capture rate [%]</th>
<th>Specific reboiler duty [kJ/kg CO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime kiln</td>
<td>7976</td>
<td>90,00</td>
<td>3197</td>
</tr>
<tr>
<td>Recovery boiler</td>
<td>3821</td>
<td>65,34</td>
<td>2967</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>83,12</td>
</tr>
</tbody>
</table>

Comparison of the different alternatives

In Figure 26 the electricity loss per kg of CO₂ captured is shown for the different alternatives. As can be seen, when applying alternative 2, using steam at 2,8 bar, the electricity loss is always smaller than compared to alternative 1 because of the remaining electricity due to the expansion in two steps which was shown before. Therefore alternative 2 using steam at 2,8 bar is more reasonable to apply partial capture than alternative 1. It can also be noticed that capturing only from the lime kiln leads to the highest loss in electricity per kg of CO₂ captured for both alternatives while this value is the lowest for the recovery boiler.

Figure 26: Electricity loss per kg of CO₂ captured for the different alternatives
6.2.3 Estimated costs

The costs were estimated for some of the investigated cases. For the recovery boiler all three cases, explained in section 3.1.2, were taken into consideration while for the lime kiln it was just case 1 using full scale capture, since this is the only case for the lime kiln which comes into consideration as shown in the previous section. For simplicity the cases and there specifications used in the following figures are given in Table 15.

Table 15: specifications of the cases used for the cost estimations

<table>
<thead>
<tr>
<th>Case</th>
<th>Capture rate [%]</th>
<th>Flue gas stream [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>case 1</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>case 2</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>case 3</td>
<td>90</td>
<td>75</td>
</tr>
</tbody>
</table>

The result for the operational expenditures (Opex), the capital expenditures (Capex), the cost for electricity loss and the total cost as sum of opex and capex and electricity loss, each one per kg of CO$_2$ captured and per year, are shown in Figure 27. For the cost estimations a life time for the capture plant of 25 years was assumed. The cost for electricity loss recovery boiler using full scale capture also takes into account the additional cost associated with providing the remaining steam needed to capture 90%. As can be seen, for each of the four cases the operational cost are higher than the capital cost. If only looking into the reboiler, full scale capture (case 1) leads to the highest total cost but is similar to case 3. Having a lower capture rate (case 2) for the recovery boiler means almost the same operation cost as in case 1 but slightly higher capital cost while for case 3 the operation cost are the highest. The reason for the lower operational cost in case 2 compared to case 3 is the cooling water which accounts for the biggest part of the operational cost and is the smallest for case 2 in absolute terms, as shown in Figure 42 in appendix C. The costs per kg of CO$_2$ captured for the lime kiln are clearly higher for all three types of cost since the flue gas stream is significantly smaller, although the absolute costs are only slightly smaller than for the recovery boiler. These costs in absolute terms are shown in Figure 41 in appendix C for the four cases. It can be seen that the more CO$_2$ is captured the lower are the cost which doesn’t account for the recovery boiler case 1 since here also the additional steam is considered. Figure 27 shows that the cheapest way, in specific terms, is to capture only from the flue gas coming from the recovery boiler using partial capture with decreased capture rate.

The flue gas stream coming from the lime kiln and especially the amount of CO$_2$ is too small for this relatively big system which leads to very high specific cost for this case. When comparing with section 6.2.2 it becomes reasonable to capture as much CO$_2$ as possible from the flue gas coming from the recovery boiler which leads to a capture rate of 82% having annual specific cost in between case 1 and case 2, shown in Figure 27, which is approximately 48 €. This case leads to the smallest electricity loss and also to the lowest total cost per kg of CO$_2$ captured.
Figure 27: Total cost per CO$_2$ captured for different cases
Conclusion and future work

In this thesis different partial capture conditions were evaluated by means of their cost and applicability to process industries with a special focus on a pulp mill as case study. For the capture process MEA was chosen as solvent since this is the benchmark solvent in literature and a proven technology, even though the use of piperazine could lead to a reduction in reboiler duty of 28%. Further on a rich split-flow configuration was used since this advanced modification reduces the reboiler duty by 20% compared to the standard set-up when using MEA.

First a sensitivity analysis was conducted to optimize the process values and reach a minimum reboiler duty, which is the most energy consuming part. The considered parameters were stripper pressure, lean loading, solvent concentration as well as absorber and stripper height. For the SFC two more parameters, the split fraction and the stripper stage, where the hot split stream is inserted, were considered. This sensitivity analysis was also conducted for a partial capture case having a capture rate of 75%. The capture rate was decreased by decreasing the solvent flow rate. Another possibility could have been to reduce the absorber height, but a capture rate of less than 85% couldn’t be reached.

The optimum process values for a capture rate of 75% are the same as for full scale capture capturing 90% of the CO₂, where the reboiler duty could be slightly reduced by approximately 3%.

By applying this capture process with optimum process values to a pulp mill, different partial capture cases, but also a full scale capture case, were investigated for the two stacks, the recovery boiler and the lime kiln. The flue gases from these two stacks differ in the size of the streams and also in the amount of CO₂, where the flue gas coming from the lime kiln is much lower, but the CO₂ fraction is higher compared to the recovery boiler. First partial capture was applied by reducing the capture rate to 75% and 50% respectively. The column diameters are decreasing when lowering the capture rate and also the solvent flow rate is decreasing which leads to a lower L/G ratio. The reboiler duty is decreasing similar to the results from the sensitivity analysis. Another possibility to apply partial capture is to reduce the flue gas flow. In this case the specific reboiler duty per unit of CO₂ captured remains constant. The equipment is getting smaller in size, especially the absorber and stripper diameters, when having less flue gas coming in, and a smaller solvent flow is needed, but the L/G ratio remains the same.

In a next step the electricity loss for the pulp mill was investigated when applying partial capture instead of using the available steam to produce electricity. Two different alternatives were taken into consideration for the steam which can be used to run the capture process. The first alternative is to use steam at 4,5 bar where the second alternative also uses steam at 4,5 bar which is first expanded to 2,8 bar producing electricity of 4 MW and then it is further on used for the capture process.

When capturing from the flue gas coming from the recovery boiler all the available steam is needed which leads to a capture rate of 83% for alternative 1 and 82% for alternative 2 respectively. For the lime kiln full scale capture with a capture rate of 90% can be applied while there is still steam available to capture 67% and 65% respectively from the flue gas coming from the recovery boiler.

When applying alternative 2, using steam at 2,8 bar, the electricity loss is always smaller compared to alternative 1, because of the remaining electricity due to the expansion in two steps. Therefore alternative 2 using steam at 2,8 bar is more reasonable to apply partial capture than alternative 1. Capturing only from the lime kiln leads to the highest loss in electricity per unit of CO₂ captured for both alternatives.
For some of the investigated cases costs were estimated in cooperation with an external partner. For the recovery boiler full scale capture and partial capture by reducing the capture rate to 75% and alternatively by reducing the flue gas stream to 75% were taken into consideration. For the lime kiln only case 1, using full scale capture, was investigated, since this is the only reasonable case for this stack. The full scale capture case for the recovery boiler leads to higher cost per unit of CO₂ captured compared to the partial capture, since additional steam is needed to capture 90%. However, the cost is still similar to the cost for the partial capture case with reduced flue gas stream. Having a lower capture rate for the recovery boiler leads to the lowest specific cost. The costs per unit of CO₂ captured for the lime kiln are clearly higher since the flue gas stream is too small for this relatively big system which leads to very high specific cost for this case.

In general, the more CO₂ is captured the higher are the cost which doesn’t account for the recovery boiler using full scale capture since here also the additional steam is considered. The cheapest way, in specific terms, is to capture only from the flue gas coming from the recovery boiler using partial capture with decreased capture rate and using steam at 2.8 bar. With this solution 82% of the CO₂ in the flue gas coming from the recovery boiler can be captured leading to total annual cost of approximately 48 € per kg of CO₂ captured which already includes the electricity loss.

All these cases do not take into consideration the savings in cost for CO₂ emissions. This could be done in a next step which would be interesting from an economic point of view. Another step is to apply this optimized process to other industrial plants to investigate the possibility of partial capture and to find a techno-economical optimum.
8 References


A  Additional sensitivity analysis
A1  Parameters for the split-flow configuration

Monoethanolamine

The sensitivity analysis for the split fraction in the SFC design is shown in Figure 28 for the use of MEA while the split fraction refers to the hot stream which going through the HEX.

![Figure 28: Effect of hot stream split fraction on reboiler duty in MEA-based absorption](image)

Having a split fraction of 1.0 means that the whole stream is going through the HEX. As can be seen the regeneration duty is decreasing as the split fraction of the hot stream increases. When having a lower split fraction than 0.7 a temperature crossover occurs because the HEX can’t handle such small cold stream compared to the hot stream coming from the reboiler. Therefore the minimum hot stream split fraction which is possible is 0.7.

Figure 29 shows the influence of the stripper stage, to which the hot stream is inserted, on the reboiler duty. As mentioned before this is dependent on the temperature of the hot stream while in a clear minimum can be stated at the stripper stage 5.
Figure 29: Effect of the stage the hot split stream is inserted on reboiler duty in MEA-based absorption using optimized values.

Figure 30 shows the influence of the stage on the reboiler duty when using optimum process values. It can be seen that the lowest reboiler duty can be reached when inserting this stream to stage 10 instead of stage 5.

Figure 30: Effect of the stage the hot split stream is inserted on reboiler duty in MEA-based absorption using optimized values.
**Piperazine**

In Figure 31 the influence of the split fraction on the reboiler duty of the process using PZ as solvent is shown.

![Figure 31: Effect of hot stream split fraction on reboiler duty in PZ-based absorption](image)

As mentioned before at the beginning of section 6.1 a temperature crossover occurs in the HEX when having a split fraction lower than 0.8 which therefore was chosen to be the optimum value.

In Figure 32 the reboiler duty of the process using PZ dependent on the stage where the hot split stream is inserted is shown. As can be seen, the regeneration duty is almost constant when inserting the stream below stage 7.

![Figure 32: Effect of the stage the hot split stream is inserted on reboiler duty in PZ-based absorption using optimized values](image)
When looking into the stage where the hot split stream is inserted using optimal process values for the SFC, the results are the same as shown in Figure 32. Therefore stage 7 is chosen.

**A2 Absorber and stripper height**

For the sensitivity analysis a stripper height of 15 m was used, while the optimal height was investigated as can be seen in Figure 33. The required reboiler duty is increasing as the stripper height is decreasing, but it is almost constant in the range of 12 m to 18 m and is increasing faster when having a height of less than 12 m, which means that around 12 m an equilibrium is reached. Therefore 12 m was chosen for the stripper height instead of 15 m since the packing material is a very costly part of the capital cost. For the absorber height 20 m were chosen at the beginning, when conducting the sensitivity analysis. However, Figure 34 in shows that a height of 10 m for the absorber is sufficient since the reboiler duty and the L/G ratio are not decreasing when having an absorber higher than 10 m while the desired capture rate of 90 % is reached by varying the solvent flow rate. The reboiler duty is almost constant if the absorber is higher than 6 m while also the L/G ratio doesn’t change much when having more than 10 m of absorber height. Therefore a height of 10 m was chosen for the absorber to cut down on cost for the packing material.

![Figure 33: Effect of stripper height on reboiler duty in MEA-based absorption](image)
Figure 34: Effect of absorber height on reboiler duty and L/G ratio in MEA-based absorption.
B  Pulp mill – sensitivity analysis

Recovery boiler

The influence of the MEA concentration and the lean loading on the reboiler duty is shown in Figure 35. The dotted lines show the partial capture case capturing 75 % of the CO$_2$ in the flue gas.

As can be seen, having a capture rate of 75 % leads to a reduction in reboiler duty which is, however, diminutive. When having a small MEA concentration the difference between full and partial capture is bigger in the range of low lean loadings but decreases as the loading is increased. The opposite can be identified when having higher solvent concentrations.

![Figure 35: Effect of lean CO$_2$ loading and MEA concentration on reboiler duty for the flue gas from the recovery boiler having a capture rate of 90 % and 75 % respectively](image)

As expected, the L/G ratio is decreasing as the capture rate is decreasing since the absorber height is kept constantly at 10 m for the three different cases shown in Figure 36. Another possibility to lower the capture rate could be a decrease in absorber height which is shown in Figure 37. As can be seen, the capture rate is decreasing when lowering the absorber height but not significantly. When the absorber height is decreased from 10 m to 2 m the capture rate is decreasing by 5,22 % while the reboiler duty actually is increasing. Therefore, and since the target capture rate of 75 % can’t be reached by only lowering the absorber height, decreasing the absorber height is not recommended. Instead the solvent flow rate is decreased to lower the capture rate as shown in Figure 36.
Figure 36: Results of reboiler duty and L/G ratio using different capture rates (90 %, 75 %, 50 %) for the flue gas from the recovery boiler

Figure 37: Effect of absorber height on reboiler duty and capture rate for the flue gas from the recovery boiler

Lime kiln

In Figure 38 the reboiler duty as a function of the lean CO₂ loading is shown for the flue gas coming from the lime kiln for different MEA concentrations. The same trends can be seen as before for the recovery boiler shown in Figure 35. Having a capture rate of 75 % (dashed lines) reduces the reboiler duty slightly compared to the full scale capture with a capture rate of 90 %. Again it can be stated that having a high concentration means more reboiler duty can be saved by partial capture as the lean loading is increasing, while this is the other way around when having a low MEA concentration. The only difference to the recovery boiler and also the sensitivity analysis based on the cement plant is, that having a MEA concentration of 30 % leads
to a minimum reboiler duty at a lean loading of 0.34 for both capture cases. But since the difference in the reboiler duty is negligible the optimum values were chosen to be the same as for the other cases.

Figure 38: Effect of lean CO2 loading and MEA concentration on reboiler duty for the flue gas from the lime kiln having a capture rate of 90 % and 75 % respectively

As stated for the recovery boiler, also for the lime kiln it can be seen that the L/G ratio is decreasing as the capture rate is decreasing which is shown in Figure 39.

Figure 39: Results of reboiler duty and L/G ratio using different capture rates (90 %, 75 %, 50 %) for the flue gas from the lime kiln
In Figure 40 the reboiler duty and the capture rate are shown as a function of the absorber height. The reboiler duty is also increasing when the absorber height is increased, and the capture rate is decreasing. For the lime kiln this capture rate is only decreasing by 2.85 % when decreasing the height of the absorber from 10 to 2 m which is even less then for the recovery boiler.

Figure 40: Effect of absorber height on reboiler duty and capture rate for the flue gas from the recovery boiler
C  Additional cost analysis

In Figure 41 the operational and capital expenditures, cost for electricity loss as well as total cost per year for the four different cases are shown. As can be seen, for each of the four cases the operational cost are higher than the capital cost. If only looking into the recovery boiler, full scale capture (case 1) leads to the highest capital and operational cost as well as the highest cost for electricity loss since here the additional steam cost is included. Therefore also the total cost are higher than for the other cases, which was expected. Having a lower capture rate (case 2) for the recovery boiler means lower operation cost but slightly higher capital cost than having partial capture using a lower flue gas stream (case 3). The reason for the lower operational cost in case 2 compared to case 3 is the cooling water which accounts for the biggest part of the operational cost and is the smallest for case 2 as shown in Figure 42. The costs for the lime kiln are clearly smaller for all three types of cost since the flue gas stream is also smaller. Also the capital cost differ slightly in all cases, while the biggest influence here are the heat exchangers, especially the lean/rich heat exchanger and the reboiler which have similar cost for case 2 and case 3. This can be seen more in detail in Figure 43.

![Figure 41: Operational and capital expenditures, cost for electricity loss as well as total cost per year for different cases](image)

In Figure 42 the cost for electricity, maintenance and cooling water is shown for the four different cases. It can be seen that the electricity and the steam have the smallest influence of the total operational cost while the cost for cooling water accounts for most of the total cost. When looking into the recovery boiler the cost for the three cases don’t differ as much for electricity and maintenance, but there is a bigger difference in the cost for cooling water between case 2 and case 1 or case 3 respectively. The operational costs for the lime kiln are much smaller than for the recovery boiler for all four categories.
The capital cost, namely costs for pumps, vessels and heat exchangers, are shown in Figure 43.

It can be seen that the main cost are the heat exchangers, especially the lean/rich heat exchanger and the reboiler. For the vessels there is not much difference in cost for the four cases. The cost for pumps are similar when looking into the recovery boiler but for the lime kiln these costs are almost half as big as for the recovery boiler.