Post-Combustion CO2 Capture Using Chemical Absorption
Minimizing Energy Requirement

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Master of Science in Energy and Environment
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Problem Description

There is an increasing interest in CO2 capture and storage as a measure to reduce man-made emissions of the greenhouse gas CO2. Several methods have been proposed for how to do CO2 capture from power plants. It may seem that the post-combustion method including amine absorption is the most likely choice of technology in the short term. However, there is a significant efficiency penalty. When capturing the CO2, the use of fuel energy increases 15-25% per kWh of electricity produced.

The main focus of this master thesis will be modelling and simulation of a process for chemical absorption of CO2 from atmospheric exhaust gas coming from a gas turbine plant. In an absorption plant for gas separation there are many parameters which can be varied as well as there are many practical limitations. It is very important to have a good model representation of the solvent to be used. The impact on overall plant (including power plant) efficiency shall be quantified.

The objective of the work is to develop a computational model which with sufficient accuracy can predict performance with respect to energy requirement, and further to find optimal and realistic parameter values for low energy use.

The modelling and simulation shall be performed in Hysis, and will be built on the student’s previous project work in spring 2007. Aker Kværner Engineering & Technology will provide data for solvent characteristics beyond those in Hysis, if necessary. Issues to be considered are performance, safety and cost (CAPEX/OPEX) Aker Kværner Engineering & Technology can assist in obtaining cost data.

The following tasks should be considered in the project work:

1) Make a literature review of work done for modelling and simulation of absorption/desorption systems focusing on plant performance and the energy use.
2) A simulation model is to be made, on a level in line with the above stated objective, which is capable of a mass and heat balances of the process.
3) Parameters and configurations [as split stripper] with importance for the energy use in the process shall be identified, and realistic boundaries for parameter values shall be discussed.
4) Using simulations with energy use as guidance, an optimal combination of parameters as well as configuration choices shall be sought and found.

Within 14 days of receiving the written text on the diploma thesis, the candidate shall submit a research plan for his project to the supervisors. A planning with milestones should also be clearly
Norwegian University of Science and Technology NTNU

EPT-P-2007-79

MASTER THESIS
for
Henning Leisfen
Autumn 2007

Post-combustion CO₂ capture using chemical absorption - minimising energy requirement
Kraftproduksjon med CO₂-innfanging – teknologi for høy renhetsgrad for CO₂

Background and objective

There is an increasing interest in CO₂ capture and storage as a measure to reduce man-made emissions of the greenhouse gas CO₂. Several methods have been proposed for how to do CO₂ capture from power plants. It may seem that the post-combustion method including amine absorption is the most likely choice of technology in the short term. However, there is a significant efficiency penalty. When capturing the CO₂, the use of fuel energy increases 15-25% per kWh of electricity produced.

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When the thesis is evaluated, emphasis is put on processing of the results, and that they are presented in tabular and/or graphic form in a clear manner, and that they are analysed carefully.

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The candidate must follow the rules and regulations of NTNU as well as passive directions given by the Department of Energy and Process Engineering.

Three – 3 – copies of the thesis shall be submitted with a summary containing both the authors’ name and the title of the work, for use as reference in journals (max 1 page with double line-spacing).

A CD-ROM containing the thesis should also be submitted to the Department of Energy and Process Engineering.

Department of Energy and Process Engineering, 10.08.2007

Johan Hustad
Department Head

Olav Bolland
Academic Supervisor
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Abstract
Capture and storage from fossil fuel fired power plants is drawing increasing interest as a potential method for the control of greenhouse gas emissions. An optimization and technical parameter study for a CO₂ capture process of the flue gas of a commercial gas power plant, based on absorption/desorption process with MEA solutions, using HYSYS with the Amine Property Package fluid package, has been performed.

The optimization has aimed to reduce the energy requirement for solvent regeneration, by investigating the effects of circulation rate, cross-flow heat exchanger minimum approach, desorber operating pressure and the absorber diameter. In addition, an economic evaluation including investment cost has been performed for the first three parameters.

Major energy savings can be realized by optimizing the desorber pressure and the solvent circulation rate. The circulation rate will have a clearly defined optimal point, while for the desorber pressure the temperature will be a limiting factor. A too high temperature may lead to amine degradation and corrosion problems. The cross-flow heat exchanger minimum temperature approach will not affect the energy consumption significantly.

An optimum absorber column diameter was not found, but the column should be designed with a diameter large enough to prevent flooding through the column. A too large diameter will not favour the energy consumption very much, and other factors will be more decisive when the column diameter is chosen.

Indexing Terms: English

Group 1
CO₂, capture, MEA, optimization

Group 2

Selected by author

Indexing Terms: Norwegian

Group 1
CO₂, innfanging, MEA, optimalisering
Preface

CO₂-capture has a high priority on the agenda of the Norwegian government today. A collaboration between the government, Gassnova and several major industrial companies with Aker Kvaerner as one of the leading members has resulted in the project called “Just Catch”. The objective for Just Catch is to reduce the operating costs and improve the efficiency of CO₂-capturing plants. The aim is to offer a competitive technology for the Norwegian market as well as the international market.

This assignment was written in Trondheim for the Department of Energy and Process Engineering at the Norwegian University of Science and Technology (NTNU) autumn 2007. Aker Kvaerner supported the necessary cost data and helped with the making of a base model for simulation.

I would like to thank my supervisor professor Olav Bolland for his help and advices.

I would also like to thank Bjørn Magnus Berg at Aker Kvaerner for many helpful phone-meetings and for always being available for questions.

Trondheim, 21 day of December 2007

Henning Leifsen
Summary

Capture and storage from fossil fuel fired power plants is drawing increasing interest as a potential method for the control of greenhouse gas emissions. An optimization and technical parameter study for a CO₂ capture process of the flue gas of a commercial gas power plant, based on absorption/desorption process with MEA solutions, using HYSYS with the Amine Property Package fluid package, has been performed.

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An optimum absorber column diameter was not found, but the column should be designed with a diameter large enough to prevent flooding through the column. A too large diameter will not favour the energy consumption very much, and other factors will be more decisive when the column diameter is chosen.
Sammendrag

Innfanging og lagring av CO₂ fra kraftverk basert på fossil brensel har i økende grad vekket interesse som en mulig metode for å redusere drivhuseffekten. En optimalisering og teknisk parameter studie for en innfangingsprosess av CO₂ fra eksosen til et kommersielt gasskraftverk er gjennomført. Studien er basert på absorpsjon/desorpsjons-prosesser med MEA-løsninger, der HYSYS og medfølgene amine fluid-pakke er blitt benyttet.

Optimaliseringen har hatt som formål å redusere energiforbruket til regenereringen av amin ved å undersøke betydningen av sirkulasjonsrate, kryss-strøms varmevekslers minste temperaturdifferanse, driftstrykket til desorber og absorber diameter. I tillegg har det blitt gjennomført en økonomisk analyse av de tre førstnevnte parametrene hvor også invisteringskostnadene ble tatt hensyn til.


En optimal absorber diameter ble ikke funnet, men kolonnen bør designes med en diameter som er stor nok til å forebygge ”flooding” gjennom kolonnen. En for stor diameter vil ikke påvirke energiforbruket betydelig og andre faktorer vil ha større betydning når kolonnediameter skal velges.
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<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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<tbody>
<tr>
<td>A</td>
<td>area</td>
<td>m²</td>
</tr>
<tr>
<td>a</td>
<td>interfacial area</td>
<td>m²/m³</td>
</tr>
<tr>
<td>E</td>
<td>total mechanical work</td>
<td>MJ/kg CO₂</td>
</tr>
<tr>
<td>E_{env}</td>
<td>Murphree vapour efficiency</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>cost</td>
<td>NOK</td>
</tr>
<tr>
<td>c</td>
<td>concentration</td>
<td>kmol/m³</td>
</tr>
<tr>
<td>c_p</td>
<td>specific heat</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>F_c</td>
<td>total consumption of cooling water</td>
<td>m³/year</td>
</tr>
<tr>
<td>G</td>
<td>gas flux</td>
<td>kg/m²·h</td>
</tr>
<tr>
<td>G_M`</td>
<td>CO₂-free gas molar flow rate</td>
<td>kmol/s·m</td>
</tr>
<tr>
<td>H</td>
<td>enthalpy</td>
<td>kJ/kg</td>
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<tr>
<td>h</td>
<td>enthalpy</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>H_e</td>
<td>Henry’s law constant</td>
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<tr>
<td>I_e</td>
<td>enhancement factor</td>
<td>-</td>
</tr>
<tr>
<td>i</td>
<td>interest rate</td>
<td>%</td>
</tr>
<tr>
<td>K</td>
<td>equilibrium ratio</td>
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<td>K_G</td>
<td>overall mass-transfer coefficient for gas</td>
<td>kmol/s·m·Pa</td>
</tr>
<tr>
<td>K_L</td>
<td>overall mass-transfer coefficient for liquid</td>
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<td>k_G</td>
<td>gas absorption coefficient</td>
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<tr>
<td>k_L</td>
<td>liquid absorption coefficient</td>
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<td>L</td>
<td>liquid flux</td>
<td>kg/h·m²·Pa</td>
</tr>
<tr>
<td>L_M`</td>
<td>CO₂-free liquid molar flow rate</td>
<td>kmol/s·m</td>
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<tr>
<td>m</td>
<td>mass stream</td>
<td>kg/h</td>
</tr>
<tr>
<td>M</td>
<td>maintenance cost</td>
<td>NOK/year</td>
</tr>
<tr>
<td>M_w</td>
<td>molar weight</td>
<td>kg/kmol</td>
</tr>
<tr>
<td>N</td>
<td>flux</td>
<td>kmol/m²·s</td>
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<tr>
<td>n</td>
<td>molar stream</td>
<td>kmol/h</td>
</tr>
<tr>
<td>n</td>
<td>project life</td>
<td>years</td>
</tr>
<tr>
<td>P</td>
<td>pressure</td>
<td>bara</td>
</tr>
<tr>
<td>p</td>
<td>partial pressure</td>
<td>bara</td>
</tr>
<tr>
<td>P_{cl}</td>
<td>price of cooling water</td>
<td>NOK/m³</td>
</tr>
<tr>
<td>P_{el}</td>
<td>price of electricity</td>
<td>NOK/kWh</td>
</tr>
<tr>
<td>Q</td>
<td>heat duty</td>
<td>MJ</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>°C</td>
</tr>
<tr>
<td>U</td>
<td>overall heat transfer coefficient</td>
<td>kJ/C·h·m²</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
<td>m³</td>
</tr>
<tr>
<td>V_{cl}</td>
<td>volume stream of cooling water</td>
<td>M³/h</td>
</tr>
<tr>
<td>W</td>
<td>mechanical work</td>
<td>MJ</td>
</tr>
<tr>
<td>w_G</td>
<td>superficial gas velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>X</td>
<td>mole ratio component in liquid phase</td>
<td>-</td>
</tr>
<tr>
<td>x</td>
<td>mole fraction in liquid phase</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>mole ratio of component in gas phase</td>
<td>-</td>
</tr>
<tr>
<td>y</td>
<td>mole fraction in vapour phase</td>
<td>-</td>
</tr>
<tr>
<td>Z</td>
<td>mole fraction in feed stream</td>
<td>-</td>
</tr>
<tr>
<td>z</td>
<td>height of column</td>
<td>m</td>
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</table>
Greek Letters

\[\alpha = \text{CO}_2\text{-load} \quad \text{mole/mole}\]
\[\beta = \text{energy quality-factor}\]
\[\epsilon = \text{size exponent}\]
\[\eta = \text{capture coefficient}\]
\[\eta = \text{stage efficiency}\]
\[\rho = \text{density}\]
\[\nu = \text{kinematic liquid viscosity}\]

Indexes (superscript)

sat = saturation
vap = vapour

Indexes (subscript)

bc = base case
bp = boiling point
c = condenser
co = compression
diff = difference
e = equilibrium
g = gas
i = interface
i = component number
in = inlet
j = stage number
l = liquid
lm = log mean
p = constant pressure
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>CAPEX</td>
<td>Capital expenditures</td>
</tr>
<tr>
<td>HETP</td>
<td>Heat equivalent to a theoretical plate</td>
</tr>
<tr>
<td>LMTD</td>
<td>Logarithmic mean temperature difference</td>
</tr>
<tr>
<td>MDEA</td>
<td>Methyl-diethanolamine</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
</tr>
<tr>
<td>NPV</td>
<td>Net present value</td>
</tr>
<tr>
<td>NVE</td>
<td>Norges vassdrags- og energidirektorat</td>
</tr>
<tr>
<td>NTNU</td>
<td>Norwegian University of Science and Technology</td>
</tr>
<tr>
<td>OPEX</td>
<td>Operational expenditure</td>
</tr>
<tr>
<td>PR</td>
<td>Peng-Robinson</td>
</tr>
<tr>
<td>VLE</td>
<td>Vapour-liquid equilibrium representation</td>
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1 Introduction

Background
The climate change is the biggest environmental challenge the world face today. To avoid man-made climate changes it is necessary to reduce the CO₂ emissions drastically. Given the advantages inherent in fossil fuels, such as their availability, relatively low cost, and the existing infrastructure for delivery and distribution, they are likely to play an important role in the world wide energy production for at least the next 75 years. Therefore there is also an increasing interest in CO₂ capture and storage.

Several different methods have been proposed for how to perform CO₂ capture from power plants, but the maturity of the technologies differs. The most mature technology today is the post-combustion method including amine absorption. The major problem using this technology has been the high operational costs, mainly due to the regeneration of the amines. The operational costs are closely connected to the reduced efficiency of the power plant when capturing the CO₂.

Scope and Objective
The main area of investigation for this master thesis will be modelling and simulation of a chemical absorption process for CO₂ capture from atmospheric exhaust gas coming from a gas turbine plant. A simulation model which is capable of calculating mass and heat balances with sufficient accuracy will be presented and discussed.

In the CO₂ capture process there are many different parameters which can be varied. There are also many limitations. The objective of this thesis will be to find optimal and realistic parameter values for low energy use.

Four parameters will be presented and varied. The first parameter variation introduced is the solvent circulation rate, secondly the rich/lean heat exchanger minimum temperature approach and then the stripper column pressure. All these parameters will be presented with respect to both performance and cost. The fourth parameter is the absorber column diameter, where pressure loss, superficial gas velocity, diameter and height will be varied and discussed.

The structure of the thesis is listed below:

- Chapter two gives a short introduction to chemical absorption of CO₂.
- Chapter three explains the stripper heat demand for desorption.
- Chapter four describes the absorber column design.
- Chapter five is a short description of the Amine Property Package in HYSYS.
- Chapter six is a literature review of work done for modelling and simulation of absorption/desorption systems focusing on plant performance and the energy use.
- Chapter seven and eight describes how the different parameter variations were measured and compared in terms of energy use and cost.
- Chapter nine introduces the parameters examined in this thesis and includes assumptions, results and discussion.
- Chapter ten and eleven give the conclusion and recommendations for further work.
2 Description of a Typical Amine-based Absorption Process

Figure 2-1 depicts the operation of a typical amine-based absorption plant for recovery of CO₂ from flue gas. Before the flue gas enters the absorption column, it is cooled and treated for particles and other impurities such as SOₓ and NOₓ to tolerable levels. The flue gas is also compressed to a higher pressure in order to meet the absorber operational pressure.

In the absorber, the rising flue gas reacts with the lean amine solution flowing downwards. The amines selectively absorb CO₂ from the flue gas by chemically reacting with it. The absorber column typically operates within a temperature range of 40-45°C at the top and 50-60°C at the bottom[1], depending on column pressure and composition.

The treated flue gas exits from the top of the absorber, while the rich amine solution (rich on CO₂) from the bottom of the column is pumped to the cross-flow heat exchanger. Here the rich amine solution is preheated to about 105 ºC by heat integration with the lean amine solution[1].

The heated CO₂-rich amine then enters the upper section of the stripper column, which normally operates at a temperature of about 110 ºC at the top and 120 ºC at the bottom. The operation pressure in the bottom of the column and in the reboiler is typically 2 bara with a pressure drop across the column of about 0.2 bar[1].

In the stripper column, the CO₂ is desorbed from the amine solution and exits from the top of the column along with water vapour and some amines. The CO₂-rich vapour stream is passed through a reflux condenser where it is partially condensed. The bulk CO₂ is separated from the condensate, dried and further compressed to the required pressure for CO₂ sequestration, e.g., about 100 bara for injection into the ocean or a geological formation[1]. The condensate, which is mainly water, is fed back to the stripper.

Since the CO₂ desorption is an endothermic process, additional heat is required. This heat is normally provided by saturated steam at 3 bara or higher. Heating of the amine solution drives off some water which helps desorbing CO₂ from the rich amine solution[1].

The lean amine solution that leaves the bottom of the stripper is pumped up to the absorber pressure and cooled down to the absorber temperature before entering the absorber.
Figure 2-1 Schematic diagram for an amine absorption plant
3 Heat Requirements for the Stripper Column

The heat requirement for the stripper column could be divided into three:

- heat of absorption
- sensible heat
- dilution heat

By dividing the heat into three different types, it is easier to explain the pressure and flow dependency as well as load dependency for the desorption process. All numbers and equations in this chapter rest on work performed by Pernille Sire Seljom[2].

3.1 Heat of Absorption

Heat of absorption is the energy needed to break the chemical bonds between the CO$_2$ and the amines. It is called the heat of absorption because it is the same heat that is released in the absorber when the amines react with CO$_2$. The heat of absorption is higher for primary amines (MEA) than for tertiary amines (MDEA).

3.2 Sensible Heat

The CO$_2$-rich amine solution that enters the stripper has a temperature below the boiling temperature of the solution. The heat that is required to heat the solution up to its boiling point is called the sensible heat. Mathematically it can be written as:

\[
Q_{\text{sensible}} = \frac{\rho(T_{\text{in}}, \alpha_{\text{rich}}) c_p(T_{\text{in}}, \alpha_{\text{rich}}) \Delta T}{(\alpha_{\text{rich}} - \alpha_{\text{lean}}) C_{\text{amine}} M_{\alpha,\text{CO}_2}}
\]

where

- $Q_{\text{sensible}}$ = energy needed to heat solution to boiling point (kJ)
- $m_{\text{CO}_2}$ = mass CO$_2$ (kg)
- $c_p$ = specific heat for rich amine solution (kJ/kg·C)
- $\rho$ = density of rich amine solution (kg/m$^3$)
- $\Delta T = T_{\text{in}} - T_{\text{bp}}$ = difference between inlet temperature and boiling temperature of CO$_2$ rich feed (°C)
- $(\alpha_{\text{rich}} - \alpha_{\text{lean}})$ = mole fraction CO$_2$ sent to compression per mole amine
- $C_{\text{amine}}$ = concentration of amine in rich amine solution (kmol/m$^3$)
- $M_{\alpha,\text{CO}_2}$ = moleweight CO$_2$ (kg/kmol)
### 3.3 Dilution Heat

In the stripper it is desirable that the CO₂ changes from liquid phase to gas phase. For this to happen it is necessary for the CO₂ saturation pressure in the amine solution flowing downwards to be greater than the CO₂ partial pressure of the gas solution rising.

The gas solution that rises in the stripper mainly consists of CO₂ and water. According to Dalton’s Law the partial pressure of CO₂ is a function of the total pressure and the molar portion of water, as shown in equation 3.2.

\[
p_{CO_2} = P - p_{H_2O} = P(1 - y_{H_2O})
\]

where

- \( P \) = total pressure (bar)
- \( p_{CO_2} \) = partial pressure of CO₂ (bar)
- \( p_{H_2O} \) = partial pressure of water (bar)
- \( y_{H_2O} \) = molar fraction of water

The purpose of the dilution heat is to increase the portion of water in the gas flowing upwards in the stripper column by evaporating some of the water in the amine solution. This will decrease the partial pressure of the CO₂.

As the gas stream rises in the column the partial pressure of CO₂ will increase. There are mainly two reasons for this; the CO₂ phase change from liquid to gas and the condensation of water caused by a decrease in temperature.

When the partial pressure exceeds the saturation pressure, CO₂ changes from gas to liquid. The dilution heat is the minimum heat requirement to keep the saturation pressure greater than the partial pressure, and make CO₂ change from liquid to gas, in the whole column.

Mathematically it can be written:

\[
\frac{Q_{\text{strip}}}{m_{CO_2}} = \frac{P_{\text{sat}}(T_w)x_{H_2O}}{p_{CO_2}(T_w)M_{CO_2}} \Delta H_{\text{vap}}^{H_2O}(T_w)
\]

where

- \( Q_{\text{strip}} \) = heat required to keep \( P_{\text{sat}} \) \( P_{CO_2} \) (kJ)
- \( m_{CO_2} \) = mass CO₂ (kg)
- \( \Delta H_{\text{vap}}^{H_2O} \) = energy required to evaporate water (kJ/kmol)
- \( x_{H_2O} \) = fraction of liquid water
- \( P_{\text{sat}} \) = saturation pressure water (bar)
- \( p_{CO_2} \) = partial pressure of CO₂ (bar)
- \( M_{CO_2} \) = moleweight for CO₂ (kg/kmol)
3.4 Stripper - Heat Pressure and Flow Dependency

The load, \( \alpha \), of the streams in the absorption process, is defined as mole CO\(_2\) per mole amine. The rich load is the mole CO\(_2\) per mole amine in the stream leaving the bottom of the absorber while the lean load is the mole CO\(_2\) per amine in the stream leaving the bottom of the stripper. The figure below shows the streams in and out of the absorber.

The figure shows the streams in and out of the absorption tower.

\[ n_{\text{amine}} = \frac{n_{\text{CO}_2} \cdot \eta_{\text{CO}_2}}{\alpha_{\text{rich}} - \alpha_{\text{lean}}} \quad (3.4) \]

where

- \( \eta_{\text{CO}_2} \) = capture coefficient for CO\(_2\)
- \( n_{\text{CO}_2} \) = moles of CO\(_2\) entering the absorption tower
- \( n_{\text{amine}} \) = moles of amines used for absorption
- \( \alpha_{\text{rich}} \) = rich load
- \( \alpha_{\text{lean}} \) = lean load

The rich load increases as the partial pressure of CO\(_2\) entering the absorber increases, assuming a constant temperature and capture coefficient in the absorption tower. Equation 3-4 shows that, with a given CO\(_2\) molar flow, capture coefficient and lean load, this lead to a smaller amount of amines needed. With less amines to be heated up to boiling temperature, the sensitive heat decreases. An increase in the rich load also increases the CO\(_2\) saturation pressure in the stream entering the stripper. A higher saturation pressure leads to a greater driving force between the CO\(_2\) partial pressure and saturation pressure, and less dilution heat is needed. Equation 3-3 shows that the dilution heat decreases with an increasing rich load.
By increasing the lean load the dilution heat will decrease. The higher the lean load is, the higher the CO₂ saturation pressure is at the bottom of the column. This means that less water vapour is needed to keep the saturation pressure higher than the partial pressure. However, equation 3-4 shows that by keeping the molar flow of CO₂, the capture coefficient and the rich load constant, the amount of amines necessary will increase when the lean load increases. Therefore the sensible heat will increase with an increasing lean load.

Figure 3-2 depicts the distribution between absorption heat, sensitive heat and dilution heat. The absorption heat is the largest and is independent of the partial pressure. Sensitive heat is larger than the dilution heat and they both decrease with an increase in partial pressure.

3.5 Primary Amines versus Tertiary Amines

The absorption heat is larger for primary amines than tertiary amines. In addition tertiary amines have got a higher load at low temperatures and a lower load at higher temperatures. Therefore tertiary amines have got a smaller heat demand in the stripper than primary amines. This difference in heat demand between the different amines increases as the partial pressure into the absorber increases.
3.6 Corrosion and Amine Degradation due to High Stripper Temperature

Amine solution corrosion is the corrosion of carbon steel in the presence of aqueous amine. Amine solution corrosion is most significant in the hot bottom section of the desorber column and is influenced by a number of factors. The most pronounced are high operating temperatures, high loadings, amine solution concentration, amine type and amine solution contaminants including amine degradation products and heat-stable salts[3].

Alkanolamines are subject to degradation by contact with free oxygen. Degradation products can reduce amine solution absorption capacity, increase solution viscosity, increase solution foaming tendency, and in some cases contribute to amine plant corrosion. MEA reacts with CO₂ to form substituted imidazolidone that later hydrolyzes to produce a diamine and release the CO₂. Both imidazolidone and the diamine degradation products can be removed from MEA solutions by thermal reclaiming. The amine-CO₂ degradation reactions are relatively slow, but do occur at a significant rate under the conditions prevailing in the regeneration section of an absorption plant. The extent of these reactions may be limited by avoiding elevated temperatures. Reboiler heat flux should be limited, and amine circulation through the reboiler should be kept high. Desorber column operating temperatures should be limited in order to minimize the rate of amine degradation.
4 Absorber Modelling

4.1 Design Principles
In the design of counter-current contactors, there are normally five major steps [3, 4]:

- Selection of contactor, including types of trays or packing based on process requirements and expected service conditions.
- Calculation of heat and material balances.
- Estimation of required column height (number of trays or height of packing) based on mass transfer analysis.
- Calculation of required column diameter and tray or packing parameters based on gas and liquid flow rates and hydraulic considerations.
- Mechanical design of the hardware.

4.2 Contactor Selection
The primary function for the contactor is to provide sufficiently large area for liquid surface in contact with the gas phase under the conditions favouring mass transfer. The three most commonly employed mechanisms for absorption/desorption are: bubble cap trays, spray chambers and packed columns. Although specific requirements and conditions may favour one over the other, they are interchangeable to a considerable extent. Packed columns are generally preferred over tray columns for small installations, corrosive service, liquids with a tendency to foam, very high liquid/gas ratios and applications in which a low pressure drop is desired [3]. Their use in larger sizes appears to be increasing, and there is also a growing use of packing to replace trays where an improvement in column performance is required. As packed column was found to be the best choice for the purpose of this thesis, only the packed column will be described in detail.

Packed columns are vertical columns which have been filled with packing or devices of large surface. One example of a randomly packed column is shown in figure 4-1.
The tower packing should offer the following characteristics [4]:

- Provide a large interfacial surface between liquid and gas.
- Process desirable fluid-flow characteristics. This ordinarily means that the fractional void volume, or fraction of empty space, in the packed bed should be large. The packing must permit passage of large volumes of fluid through small tower cross sections without loading and flooding (see below) and with low pressure drop for the gas.
- Be chemically inert to fluids being processed.
- Have structural strength to permit easy handling and installation.
- Represent low cost.

Packed columns could be packed randomly or structured. Random packings are simply dumped into the tower during installation and allowed to fall at random. The tower may first be filled with water to reduce the velocity of fall. Random packings most frequently used at present are manufactured, and some of the common types are shown in figure 4-2.
While random packing has been the most employed packing, the use of structured packing is expanding. These are of great variety. The structured packing offer the advantages of low pressure drop for the gas and greater possible fluid flow rates, usually at the expense of more costly installation than random packing. The use of packing in larger installations appears to becoming more common.
4.3 Material and Energy Balance

Figure 4-4 shows a simple model of an absorption column containing either trays or packing.

Equation 4.1 gives the material balance for the contactor column [3]:

\[ G_M' (Y - Y_2) = L_M' (X - X_2) \]  \hspace{1cm} \text{(4.1)}

Where

\[ G_M' = \text{CO}_2\text{-free gas molar flow rate} \left( \text{kmol}/(s \times m) \right) \]
\[ L_M' = \text{CO}_2\text{-free liquid molar flow rate} \left( \text{kmol}/(s \times m) \right) \]
\[ X = \text{mole ratio CO}_2 \text{ in the liquid phase} = \frac{x}{1 - x}, \text{ where } x = \text{mole fraction} \]
\[ Y = \text{mole ratio CO}_2 \text{ in the gas phase} = \frac{y}{1 - y}, \text{ where } y = \text{mole fraction} \]

The equation of the operating line is given by rearranging equation 4.1:

\[ Y = \frac{L_M'}{G_M'} (X - X_2) + Y_2 \] \hspace{1cm} \text{(4.2)}

On rectangular coordinate paper this equation will be a straight line with a slope of \( L_M' / G_M' \). The coordinates at the ends of the operating line represent conditions at the ends of the column. The known parameters are normally the feed gas flow rate \( G_M' \), the mole ratio of \text{CO}_2 \text{ in the feed gas} \( Y_1 \), the mole ratio of \text{CO}_2 \text{ in the lean solvent} \( X_2 \) and the required mole ratio of \text{CO}_2 \text{ in the product gas} \( Y_2 \). The objective is to estimate the required liquid flow rate and, finally, the dimensions of the column.
The performance of counter-current absorbers can best be visualised with a diagram. In figure 4-5 two possible operating lines has been drawn. Line A represents a typical design, while B represents the theoretical minimum liquid flow rate. The distance between the operating line and the equilibrium curve represents the driving force for mass transfer at any point in the column. Since line B actually touches the equilibrium curve at the bottom of the column, it would require an infinitely tall column, and therefore represents the limiting liquid flow rate.

Absorption increases the temperature within the column. It is therefore necessary to modify the equilibrium curve so that it corresponds to the actual conditions at each point in the column.

The amount of heat released between the liquid and gas streams is primarily determined by the ratio of the total heat capacities of the two streams, \( \frac{L_M C_q}{G_M C_p} \), where \( C_q \) and \( C_p \) are the heat capacities of the liquid and gas respectively. With a high ratio (higher than 2), the liquid carries the heat of reaction down the column, the product gas leaves at approximately the temperature of the liquid feed, and the product liquid leaves at an elevated temperature determined by the overall heat balance. The outgoing liquid is somewhat cooled by the feed gas which leads to a temperature bulge within the column. With a low ratio (lower than 0.5) the product gas carries most of the heat of reaction of the column. A ratio close to 1.0 splits the heat of reaction between the gas and liquid products and might increase the temperature well above that of the incoming streams [3].
4.4 Column Height

Counter-current packed columns operate in a different manner compared to trayed columns. In packed columns the fluids are in contact continuously in their path through the tower, rather than intermittently. The liquid and gas compositions therefore change continuously with height of packing. Every point on an operating line represents conditions found somewhere in the column. The “height equivalent to a theoretical plate” (HETP) is a frequently used approach to describe the mass transfer efficiency of packing. HETP is defined as height of packed zone divided by the number of theoretical plates achieved in packed zone. To estimate the packing height, the calculated number of theoretical plates required is simply multiplied by the HETP. If the efficiency of packing for a reason is not available, or a more detailed examination of the column height is necessary, the column height may be calculated with the use of absorption coefficients.

4.4.1 Absorption Coefficient

The absorption coefficient is based upon a two-film theory originally proposed by W. G. Whitman [3] where it is assumed that the gas and liquid are in equilibrium at the interface and that thin films separate the interface from the main bodies of the two phases. The liquid absorption coefficient, \( k_L \), is defined as the quantity of material transferred through the liquid film per unit time, per unit area, per unit of driving force in terms of liquid concentration. The gas absorption coefficient, \( k_G \), is defined as the quantity transferred through the gas film per unit time, per unit area, per unit of driving force in terms of pressure. The quantity of material transferred from the body of the gas to the interface must equal the quantity transferred from the interface to the body of the liquid. This balance is given as:

\[
N_{CO_2} = k_G (p - p_i) = k_G P (y - y_i) = k_L (c_i - c)
\]

where

\[
N_{CO_2} = \text{quantity of CO}_2 \text{ transferred per unit time, per unit area } \left( \frac{kmol}{m^2 \times s} \right)
\]

\[
k_G = \text{gas absorption coefficient } \left( \frac{kmol}{m^2 \times s \times Pa} \right)
\]

\[
k_L = \text{liquid absorption coefficient } \left( \frac{kmol}{m^2 \times s \times kmol/m^3} \right)
\]

\[
p = \text{partial pressure of CO}_2 \text{ in main body of gas (Pa)}
\]

\[
p_i = \text{partial pressure of CO}_2 \text{ in gas at interface (Pa)}
\]

\[
P = \text{total system pressure (Pa)}
\]

\[
y = \text{mole fraction of CO}_2 \text{ in main body of gas}
\]

\[
y_i = \text{mole fraction of CO}_2 \text{ in gas at interface}
\]

\[
c = \text{concentration of CO}_2 \text{ in main body of liquid } \left( \frac{kmol}{m^3} \right)
\]

\[
c_i = \text{concentration of CO}_2 \text{ in liquid at interface } \left( \frac{kmol}{m^3} \right)
\]

The partial pressure of CO\(_2\) at the interface is generated by the absorbed CO\(_2\) gas in the liquid solution that still has not reacted with the amines. It can be seen from equation 4.3 that the driving force for CO\(_2\) absorption and hence the mass flux of CO\(_2\) is greatest when the CO\(_2\) back pressure from the absorption liquid approaches zero and the partial pressure of CO\(_2\) in the gas stream is at a maximum.
4.4.2 The Gas-Liquid Interfacial Area

The gas-liquid interfacial area is an important factor for mass transfer in the gas absorption process. A larger interfacial area is required to achieve greater mass transfer efficiency. Determination of the mass-transfer area is considered to be the most extensive task in column design because it involves both experiments and rather complicated calculation steps. The calculations require a large number of fluid dynamic parameters and solvent physical properties, as well as the geometry of column internals that constantly vary from location within the column. In the case of CO₂ absorption into aqueous solutions these calculations can become even more difficult as the mass-transfer process involves exothermic chemical reactions, causing a significant variation in the column temperature. The gas-liquid interfacial area is defined as the transfer area divided by the volume:

\[
dz \frac{dA}{dz} = a
\]

Where
- \( dA \) = transfer area \((m^2)\)
- \( A_c \) = cross-sectional area of column \((m^2)\)
- \( \int_{0}^{h} dz = h \) = height of column \((m)\)

4.4.3 Height of Column

The absorption coefficient data are used to express the height of the column. It is then necessary to consider the changes in liquid and gas compositions that occur over the length of the column. The quantity of material transferred to the quantity indicated to be transferred on the basis of the absorption coefficient and driving forces has to be equated and integrated over the length of the column as shown in equation 4.5 [3]:

\[
h = G' M \int_{p_c}^{p} a k'(P(1 - y))y y_p L \rho L \int_{c_p}^{c} \frac{dc}{k_c a(c - c_p)}
\]

Where
- \( h \) = height of packed zone \((m)\)
- \( G' M \) = superficial molar mass flux of inert gas \((kmol/(h \times m^2))\)
- \( a \) = interfacial area per unit volume of absorber \((m^2/m^3)\)
- \( y_c \) = mole fraction of CO₂ in equilibrium with a solution having the composition of main body of liquid \((Pa)\)
- \( c_c \) = concentration of CO₂ in a solution in equilibrium with main body of gas \((kmol/m^3)\)
- \( p_{lim} \) = log mean of inert gas pressures
- \( k'G = k_G (p_{lim}/p) \) = special mass-transfer coefficient which is independent of gas composition \((kmol/(h \times m^2 \times Pa))\)
- \( L \) = liquid flux \((kmol/(h \times m^2))\)
- \( \rho_L \) = liquid density (assumed constant) \((kg/m^3)\)

The subscript 1 refers to the bottom of the column, while the subscript 2 refers to the top of the column.
4.4.4 Volumetric Overall Mass-transfer Coefficient

The use of equation 4.5 for design requires knowledge of both $k_G$ and $k_L$ as well as the equilibrium relationship and the interfacial area per unit volume of absorber. Usually it is more practical to use overall coefficients which are based on the total driving force from the main body of the gas to the main body of the liquid. These overall coefficients relate directly to the contactor volume rather than to the interfacial area:

$$N_{co,ad}dV = k_G a P(y - y_i)dV = k_L a (c_e - c)dV$$

(4.6)

Where

- $k_G a = \text{overall mass-transfer coefficient for gas (} kmol/(s \times m \times Pa))$
- $k_L a = \text{overall mass-transfer coefficient for liquid (} kmol/(s \times m \times (kmol/m^3)))$
- $V = \text{volume of packing (} m^3)$

The relationship between the individual film coefficients and the overall coefficients is given as:

$$\frac{1}{k_G a} = \frac{1}{k_G a} + \frac{He}{k_L a}$$

(4.7a)

$$\frac{1}{k_L a} = \frac{1}{k_L a} + \frac{1}{He k_G a}$$

(4.7b)

$He$ is the Henry’s law constant and is commonly defined as:

$$He = \frac{p_i}{c_i}$$

(4.8)

In cases where Henry’s law does not apply, $(p_i - p_e)/(c_i - c_e)$ is used instead. The overall coefficients are only valid where the equilibrium line is straight over the operating region but, nevertheless, they are widely used in reporting test data due to their convenience.

When chemical absorption takes place, as in the case for CO2 absorption by amines, the liquid side mass transfer is improved. To describe the influence of this chemical reaction an enhancement factor, $I_e$, can be added to equation 4.7[5]:

$$\frac{1}{k_G a} = \frac{1}{k_G a} + \frac{He}{I_e k_L a}$$

(4.9a)

$$\frac{1}{k_L a} = \frac{1}{I_e k_L a} + \frac{1}{He k_G a}$$

(4.9b)

Where

- $k_{L,ref} = \text{liquid side mass transfer coefficient without chemical reaction (} kmol/(m^2 \times s \times kmol/m^3))$
- $I_e = \text{enhancement factor}$

(4.9b)
4.4.5 **Height of Column Using Overall Mass-Transfer Coefficient**

More simplified forms of equation 4.5 are developed and are more commonly employed to design the height of columns. These forms are sufficiently accurate for most engineering-design calculations, particularly for gas purification with low gas and liquid concentrations. For these equations to apply, the following assumptions must be valid [3]:

- The equilibrium curve is linear over the range of concentrations encountered, which means that overall coefficients can be applied.
- The partial pressure of the inert gas is essentially constant over the length of the column.
- The CO₂ content of gaseous and liquid phases are sufficiently low so that the partial pressure and liquid concentration values may be assumed proportional to the corresponding values when expressed in terms of mole of CO₂ per mole of inert gas.

The column height can then be estimated, in terms of the overall gas coefficient and gas-phase composition, by equation 4.10a, or by equation 4.10b if the overall liquid absorption coefficient is available:

\[ h = \frac{G_M}{K_o a P} \int_{y_e}^{y} dy \quad (4.10a) \]
\[ h = \frac{L_M}{P_0 K_L a} \int_{x_e}^{x} dx \quad (4.10b) \]

Where

- \( x \) = mole fraction of solute in the liquid streams
- \( x_e \) = mole fraction of solute in the liquid streams at equilibrium
- \( G_M \) = molar flow rate value of gas per cross-sectional area \( (kmol/s \times m^2) \)
- \( L_M \) = molar flow rate of liquid per cross-sectional area \( (kmol/s \times m^2) \)

If a dilute mixture (<10% CO₂) and a constant \( G_M \) along the column is assumed, a simpler expression for the mass balance can be given as:

\[ -\frac{d(G_M y)}{dz} \cong -G_M \frac{dy}{dz} = K_o a P(y - y_{eq}) \quad (4.11) \]

The height of the column can then be obtained by rearranging equation 4.11:

\[ \int_{0}^{z} dz = h = \int_{y_{eq}}^{y} -\frac{G_M}{K_o a P(y - y_{eq})} dy = \frac{G_M}{K_o a P} \ln \frac{y_{1} - y_{eq}}{y_{2} - y_{eq}} \quad (4.12) \]
4.4.6 Selecting the Volumetric Overall Mass-Transfer Coefficient

The volumetric overall mass-transfer coefficient, \( K_{G,a} \), is a combination of three contributions associated with mass transfer, i.e., thermodynamics, kinetics, and hydrodynamics of the CO\(_2\) absorption system.

The value of the volumetric mass transfer coefficient is unaffected by the gas flow rate through the absorber over a range of 30-100 kmol/(h\(\times\)m\(^2\))[6]. A constant mass flow rate of CO\(_2\) is absorbed despite the increased mass flow rate of CO\(_2\) molecules at a higher gas flow rate. Therefore the liquid phase mass transfer to the gas-liquid interface, which depends upon diffusion of reagent molecules within the liquid phase, is considered to be the major controlling factor.

If the CO\(_2\) concentration of the gas stream is increased to values up to 15%, it is found to reduce the value of \( K_{G,a} \) for the system. However, the increase in CO\(_2\) partial pressure causes the mass flux of CO\(_2\) absorbed in the system to remain relatively constant [6].

The increase in value of \( K_{G,a} \) on the basis of the increase of liquid flow rate is the result of two different effects. Firstly, increasing the liquid flow rate increases the liquid phase mass transfer rate to the gas-liquid interface, which directly increases availability of the amine at this location and the liquid side mass transfer coefficient component of \( K_{G,a} \). Secondly, increasing the liquid flow rate can improve the liquid distribution on the packing surface leading to an increase in the effective interfacial area component of \( K_{G,a} \). The figure below shows the effect of liquid flow rate on overall mass-transfer coefficient for the structured packing Mellapak 500Y [7].

![Figure 4-6 Effect of liquid flow rate on overall mass-transfer coefficient](image_url)

It is important to note that the impact of liquid flow rate varies considerably from packing to packing. This can be observed in figure 4-7 [7], which gives \( K_{G,a} \) values for three different packings under the range of liquid flow rate.
The temperature of the absorbing reagent solvent is found to have a complex effect on the value of the mass transfer coefficient\[6\]. Figure 4-8 shows that an increase in liquid temperature from 20°C to 30°C causes an increase in $K_{Ga}$. However, as the temperature of the solution is increased from 40°C to 65°C the value of $K_{Ga}$ decreases. It is proposed that this effect is caused by an increase in the Henry’s Law coefficient with temperature which then limits the capability of CO2 to transfer from the gas phase to the solution. If the liquid temperature is further increased towards temperatures close to 120°C the CO2 absorption reaction will reverse as in the regenerator. The maximum $K_{Ga}$ value in a 3 kmol/m$^3$ MEA system with a CO2 loading of 0.36 mol/mol is found to occur at approximately 36°C\[6\].

The amine concentration within the absorbing liquid has a straightforward effect on the CO2 absorption performance. An increase in the amine concentration provides a higher number of amine molecules per unit volume and therefore a greater ability to absorb the gas-liquid interface. This will increase the value of $K_{Ga}$ and thereby improve the CO2 removal performance of the system. However, it is important to balance factors such as corrosion and the operating cost with this improvement in CO2 removal performance.
The CO₂ loading of the system is expressed as the number of moles of CO₂ per moles of amines in solution. The CO₂ loading is therefore directly linked to the amine concentration and yields an equally straightforward relationship between the CO₂ loading and the mass transfer coefficient of the system. An increase in the CO₂ loading reduces the concentration of active reagent molecules in the liquid and hence the $K_Ga$ value decreases.

4.5 Column Diameter

The diameter of packed columns is usually based on flooding correlations (see below). The Eckert correlation [3] below is a widely used correlation for estimating pressure drop in structured packing. The Y axis is called the Flow Capacity Factor and the X axis the Relative Flow Capacity. The flow capacity factor includes a packing factor, $F$, which is a characteristic of the packing configuration. For most packings acceptable packing factor values are made available by the packing vendor or the open literature. The equations for the Flow Capacity Factor and Relative Flow Capacity are given below as:

\[
\text{Flow Capacity Factor} = \frac{G_{G}^{0.2} F \nu^{0.1}}{32.2 \rho_v (\rho_e - \rho_v)} \tag{4.14}
\]

\[
\text{Relative Flow Capacity} = \frac{L \left[ \frac{\rho_v}{\rho_e} \right]}{G} \tag{4.15}
\]

Where
- $F$ = packing factor
- $G$ = gas flux \( ((lb/ft^2 \times s) = \frac{1}{1.356 \times 10^{-3}} \times kg/(m^2 \times s)) \)
- $G_{G}^{0.2}$ = gas flux \( ((lb/ft^2 \times s) = \frac{1}{1.356 \times 10^{-3}} \times kg/(m^2 \times s)) \)
- $L$ = liquid flux \( ((lb/ft^2 \times h) = \frac{1}{1.356 \times 10^{-3}} \times kg/(m^2 \times h)) \)
- $\nu$ = kinematic liquid viscosity \((cst)\)
- $\rho_G$ = gas density \( ((lb/ft^3) = \frac{1}{16.019} \times kg/m^3) \)
- $\rho_L$ = liquid density \( ((lb/ft^3) = \frac{1}{16.019} \times kg/m^3) \)
It is normally considered good practice to design for a gas rate that gives a pressure drop of less than about 3.3 mbar per meter of packing. Many gas purification absorbers have a high L/G ratio. The pressure drop may then exceed the above value, but the gas rate should not exceed 85% of the rate that results in a pressure drop of 12.5 mbar per meter of packing. Systems that tend to foam should be operated to give a low pressure drop and vacuum systems may require an even lower pressure drop to minimize overall column pressure drop.

4.6 Flooding

When the inlet gas flow rate is so high that it interferes with the downward flow of the solvent liquid, it may cause an upward flow of the liquid through the tower. This is known as flooding [8]. Most absorbers are designed to operate at no more than 70% of the maximum gas velocity that can cause flooding. Besides a high inlet gas flow rate, low circulation rates and small diameter towers could also lead to flooding. Flooding conditions in random packings depend on the method of packing (wet or dry) and settling of packing. Flooding velocities for structured packings will generally be considerably greater than for random packing[4], i.e. structured packing is more resistant to flooding.


4.7 Number of Equilibrium Stages

In order to determine the number of equilibrium stages required in a cascade, the equilibrium characteristics of the system and material-balance calculations are required. The design of absorbers and strippers typically involves a computer-assisted, tray-by-tray (or section-by section of packing) heat- and material-balance calculation to determine the required number of equilibrium stages. The required number of equilibrium stages is related to the required number of actual trays based on an estimated tray efficiency. Tray efficiencies are available for various services in literature.

4.8 Tray Efficiency

The number of actual trays in an absorber is related to the number of theoretical trays by a factor known as the “tray efficiency”. The “overall tray efficiency” is defined as the ratio of theoretical to actual trays required for a given separation[3]. The overall tray efficiency can only be used after the total number of theoretical trays has been calculated using a graphical or analytical technique. To relate the actual performance to the theoretical trays for individual trays, the Murphree vapour efficiency is used. This is defined as:

\[ E_{mr} = \frac{y_p - y_{p+1}}{y_{pe} - y_{p+1}} \]  

Where

\[ y_p \] = average mole fraction of solute in gas leaving tray
\[ y_{p+1} \] = average mole fraction of solute in gas entering tray (leaving tray below)
\[ y_{pe} \] = mole fraction of solute in gas in equilibrium with liquid leaving tray

Murphree tray efficiency values can be used to correct the individual steps in graphical analysis of the number of trays required.

4.9 Residence Time Requirement

The time of contact is closely connected to the stage efficiency, whereas for continuous-contact equipment the time leads ultimately to the volume or length of the required device. There are several factors which help establish the time necessary. Material balances permit calculation of the relative quantities required of the various phases. The equilibrium characteristics of the system establish the ultimate concentrations possible, and the rate of transfer of material between phases depends upon the departure from equilibrium which is maintained. The rate of transfer is also depending on upon the physical properties of the phases as well as the flow regime within the equipment.
5 Amines Property Package in HYSYS

The Amines Property Package in HYSYS is a property package designed especially for modelling of alkanolamine treating units in which H₂S and CO₂ are removed from gas streams. The package contains data to model the absorption/desorption process where aqueous solutions of single amines and aqueous solutions of blended amines are used. The Amine Property Package uses technology developed by D. B. Robinson and Associates Ltd. [9] to model the equilibrium solubility of acid gases in aqueous solutions. A non-equilibrium stage model which is based on the tray efficiency concept is used to simulate the performance of contactors and regenerators.

The generalized stage model as shown in figure 5-1 gives the flow geometry and nomenclature for an individual stage in a column. The fundamental concept used is that the rate of absorption/desorption of acid gases to/from the amine solution must be considered as a mass-transfer rate process.

![Figure 5-1 Stage j in a column simulated in HYSYS](image)

where

\[
\begin{align*}
F & = \text{stage feed stream (kmole/h)} \\
L & = \text{liquid stream travelling to stage below (kmole/h)} \\
V & = \text{vapour stream travelling to stage above (kmole/h)} \\
SL & = \text{liquid side draw from stage (kmole/h)} \\
SV & = \text{vapour side draw from stage (kmole/h)} \\
Q & = \text{energy stream entering stage (kJ/h)} \\
H & = \text{enthalpy (kJ/h)} \\
h & = \text{enthalpy (kJ/h)} \\
Z & = \text{mole fraction in feed stream} \\
x & = \text{mole fraction in liquid phase} \\
y & = \text{mole fraction in vapour phase} \\
j & = \text{stage number} \\
i & = \text{component number}
\end{align*}
\]
The rate process depends on the equilibrium and kinetic parameters that describe the acid gas/amine system. This model uses a modified Murphree-type vapour efficiency to account for the varying mass-transfer rates of individual acid gas components. The acid gas stage efficiencies are, in turn, functions of mass-transfer coefficients and the mechanical design of the tray.

A modified Newton-Raphson method is used to solve the rigorous non-linear stage equations simultaneously for temperature, composition and phase rates on each stage in a column.

The Amines property package defines the stage efficiency as:

\[
\eta = \frac{(V_i + SV_j)y_j - V_{j+1}y_{j+1}}{(V_i + SV_j)K_{ij}x_j - V_{j+1}y_{j+1}}
\]

Where

- \( \eta \) = stage efficiency
- \( K \) = equilibrium ratio

The stage efficiency is a function of the kinetic rate constants for the reactions between each acid gas and the amine, the physico-chemical properties of the amine solution, the pressure, the temperature and the mechanical tray design variables such as tray diameter, weir height and weir length. The stage efficiencies could be specified or calculated by HYSYS.

The range of applicability for the amines in the Amine Property Package is given as 25-126.7°C (77-260°F). To avoid physical amine degradation into corrosive products, HYSYS recommends a maximum reboiler temperature of 137.8°C (280°F).

The most important equations for the non-equilibrium stage model in the Amine Property Package are shown in appendix B.
6 Minimizing the Energy Consumption in Amine-Based Absorption Plants

The operational cost of the overall gas sweetening process is mainly determined by the regeneration of the loaded liquid in the desorber. Several parameters have been identified and varied over a given span in order to see the performance effects of the regeneration system. This chapter gives the results of previous work in order to minimize the energy consumption in amine-based absorption plants.

6.1 Effect of Condenser Temperature

The condenser temperature determines the amount of steam that follows along with CO₂ to the compression unit as well as the temperature of the liquid reflux returning to the column. The higher this temperature is, the more amines and water follows the CO₂ leaving the condenser. On the other hand, less steam is required for heating the liquid flowing down the column. Figure 6-1 shows the effect of varying the condenser temperature between 45-75°C, with respect to reboiler duty and the total amount of steam that follows at the CO₂ out of the reboiler with a fixed CO₂ pickup of 0.32[10].

![Figure 6-1 Condenser temperature versus reboiler duty][10]

The figure shows that an increase in condenser temperature from 45°C to 75°C only reduces the reboiler duty marginally. The amount of steam following the exit CO₂ is on the other hand increased from about 50 to 200kmol/h. This occurs because only a small amount of the total liquid that flows down the main packing is refluxed liquid. A 30°C change in condenser temperature will only change the temperature of the liquid meeting the main packing after being mixed with the reflux with about one degree. As the temperature increases, the amount of MEA following the CO₂ will become more significant. At 60°C, the amine loss is calculated to about 0.4 kg MEA/ton CO₂ recovered. At 45°C the loss of MEA is reduced to the half, but the energy consumption is higher. An economic optimum between these two factors is possible to calculate. It is also important to take the environmental concerns regarding MEA loss into account as well as the steam content of the exit CO₂ steam.
6.2 Effect of Cross-Flow Heat Exchanger Performance

Varying Temperature Approach

The rich amine inlet temperature to the desorber is determined by the performance of the rich/lean cross-flow heat exchanger. This performance can be defined by the temperature on the pinch side, which in this case is the cold side. The minimum acceptable temperature approach is normally set to 10-15°C, but more modern heat exchangers can bring this minimum approach down to less than 5°C[10]. The results for all three temperature approaches are given in table 6-1.

<table>
<thead>
<tr>
<th>Simulation.HEX</th>
<th>HEX pinch ΔT</th>
<th>HEX duty ΔQ</th>
<th>T rich inlet desorber °C</th>
<th>Loading after flash [-]</th>
<th>T reboiler °C</th>
<th>Reboiler heat duty</th>
<th>Condenser heat duty</th>
<th>Specific Steam consumption GJ/t CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash_D15</td>
<td>15</td>
<td>101.1</td>
<td>101.5</td>
<td>0.45</td>
<td>121.1</td>
<td>144.9</td>
<td>-71.8</td>
<td>4.53</td>
</tr>
<tr>
<td>BASE_D10</td>
<td>10</td>
<td>110.2</td>
<td>102.1</td>
<td>0.42</td>
<td>121.2</td>
<td>143.5</td>
<td>-79.6</td>
<td>4.49</td>
</tr>
<tr>
<td>Flash_D05</td>
<td>5</td>
<td>119.3</td>
<td>102.8</td>
<td>0.39</td>
<td>121.2</td>
<td>142.0</td>
<td>-87.3</td>
<td>4.44</td>
</tr>
</tbody>
</table>

Rich loading = 0.48, Lean loading = 0.16 Reboiler pressure 200 kPa, pressure drop column 25 kPa, Rich bubble point T = 100.9 °C

When the pinch is reduced from 15°C to 5°C, less steam is needed for desorption in the tower at the same pressure and less water is condensed in the tower. The loading is also reduced from 0.45 to 0.38, while the inlet rich feed temperature to the desorber increases with about one degree. Furthermore, the overall steam consumption parameter is lowered from 4.53 to 4.44 GJ/t CO₂ and both the liquid and vapour flow in the desorber are lower.

Interaction Between Cross-Flow Heat Exchanger and Desorber Column

As the heat exchanger duty is increased the vapour fraction will increase and the use of a flash separator will reduce the loading significantly. When the feed, which is at its equilibrium, meets the water wash reflux, the solvent is cooled and diluted. This could result in a drop in the equilibrium partial pressure below the partial pressure of the vapour phase in the tower. To keep desorption occurring throughout the column, the cross-flow heat exchanger should only have a limited duty. The duty should be chosen so that the inlet rich feed to the desorber column, after being mixed with the reflux, is close to the desorber exit gas phase equilibrium. In other words, the more efficient the heat exchanger is, the higher the chances are for the desorber to be performing below optimum. The size of the heat exchanger should therefore be chosen depending on the desorber size and efficiency[10].

If a larger and more efficient heat exchanger is used, the temperature of the rich stream to the desorber will not increase as much. This is because the bubble point is exceeded. Instead CO₂ and other vapours will start desorbing. By promoting turbulence and increasing local heat transfer this might serve the heat exchanger favourably. If the vapour fraction becomes too large, however, it can decrease the heat transfer coefficient and give a reduced total heat transfer. This can be prevented by boosting the rich amine pressure to above the bubble point before the cross-flow heat exchanger and followed by a pressure reduction and flash.
6.3 Effect of CO₂ Capture Efficiency

Thermal Energy
The thermal energy required for the regeneration of the amines is a function of the design and operating parameters of the CO₂ capture system, including amine concentration, CO₂ mole fraction, lean loading and CO₂ capture efficiency. The heat in power-plant applications is usually supplied in the form of low-pressure steam extracted from the steam turbine. The steam extraction leads to a loss in power generation and the thermal energy requirement can therefore be expressed in terms of an equivalent electrical energy penalty. Figure 6-2 shows the amine regeneration energy requirement per unit of CO₂ captured, and the equivalent loss in power generation [11]. The numbers are based on detailed studies of LP steam extraction points for modern steam turbines. Higher capture efficiency requires more efficient use of the loading capacity of the amines and, hence, more regeneration energy. The specific thermal energy requirement increases therefore as the CO₂ removal efficiency increases.

![Figure 6-2 Sorbent regeneration heat requirement (kJ/kg CO₂), and the equivalent loss in power generation (MWh/tonne CO₂) as a function of CO₂ capture efficiency [11].](image)

Electrical Energy
The gain in CO₂ capture efficiency by building a higher absorber column is found to be quite low [11]. However, by keeping the column height and increasing the liquid/gas ratio a higher CO₂ capture efficiency is achieved. This requires a larger column diameter. Since there is a practical limit on column diameter size (also in terms of available column vendors), the flue gas flow rate must be reduced to increase the liquid/gas ratio further. Thus, it may be required to increase the number of trains to achieve higher CO₂ removal for a given flue gas flow rate.

The flue gas blower power requirement will remain constant if the column height is unchanged. However, a higher capture efficiency will increase the sorbent pumping power requirement. Overall, the total electrical energy requirement per unit of CO₂ captured decreases as the capture efficiency increases, as shown in figure 6-3.
Figure 6-3 Electrical energy requirement for capture and compression (MWh/tonne CO₂), and comparison to the equivalent thermal loss in power generation (MWh/tonne CO₂) [11].

Figure 6-4 combines the two results in figure 6-3 to show the total energy penalty of the amine-based CO₂ capture system in terms of MWh/tonne CO₂. This graph includes both the electrical energy requirement and the equivalent power loss that is due to the solvent regeneration heat requirement. At a 90% capture efficiency 53% of the total energy comes from sorbent regeneration. The electrical energy requirements for capture and compression are 37% and 10% of the total respectively [11]. The minimum overall energy requirement is observed to be at a capture efficiency of about 86%.

Figure 6-4 Total energy requirement (MWh/tonne CO₂) of the amine-based CO₂ capture system, as a function of CO₂ capture efficiency.
The net power output of a power plant with CO₂ capture as a function of CO₂ capture efficiency is shown in figure 6-5. Although the curves may appear linear at the scales presented, the slope of the line gradually increases with higher capture efficiency.

![Figure 6-5 Net power output of a power plant with amine-based CO₂ capture system as a function of CO₂ capture efficiency (MWg = gross power plant size) [11].](image)

**Capital Cost of the CO₂ Capture System**

Figure 6-6 and 6-7 show how the total capital cost varies with an increasing CO₂ capture efficiency. The minimum capital cost in both figures is different from the 86% capture efficiency at which the total energy requirement of the system was determined to be minimum given in figure 6-4. Although the energy penalty strongly affects the net capital cost via its impact on net power output, other factors (especially the number of operating trains for CO₂ capture and compression) also influence the location of the minimum capital cost per unit of CO₂ removed.

![Figure 6-6 CO₂ capture system capital cost as a function of the CO₂ capture efficiency for two plant sizes.](image)
6.4 Effect of Rich and Lean Amine Level

The amount of steam needed for the desorber is highly dependent on the lean amine loading. A higher lean amine loading results in higher desorber driving forces, which reduces the steam consumption per ton CO₂. The lean amine load can be increased in two ways, either by keeping the rich amine loading and increasing the liquid circulation rate, or by increasing both the rich and lean amine loadings such that the cyclic capacity, and circulation rate, remains the same.

Increasing Circulation Rate and Lean Loading Level

Table 6-2 gives the results of varying the lean loadings from 0.16 to 0.20 and 0.24, while increasing the circulation rate so that the CO₂ production rate is kept constant. The table shows that the steam consumption reduces radically as the circulation rate and lean loading is increased. Even though this will have a negative effect on the absorber operation, the driving force at the top of the absorber will still be very high. The additional cost associated with the increase in pump energy required is very small compared to the overall energy requirement for steam production. An increase in the liquid flow rate of 30% will give a negligible efficiency penalty compared to the energy required for steam production.
Table 6-2 Effect of: a. Increasing circulation rate and lean loading level and b. Increasing the rich and lean levels simultaneously[10]

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Circulation rate</th>
<th>y rich from abs</th>
<th>y lean from des</th>
<th>T rich inlet</th>
<th>T desorber</th>
<th>Loading after flash</th>
<th>T reboiler</th>
<th>Specific Steam consumption</th>
<th>GJ/ton CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Sim_cr_24</td>
<td>26546</td>
<td>0.48</td>
<td>0.24</td>
<td>101.4</td>
<td>0.45</td>
<td>115.7</td>
<td>106.7</td>
<td>3.34</td>
<td></td>
</tr>
<tr>
<td>Sim_cr_20</td>
<td>22754</td>
<td>0.48</td>
<td>0.20</td>
<td>101.9</td>
<td>0.43</td>
<td>119.4</td>
<td>122.2</td>
<td>3.78</td>
<td></td>
</tr>
<tr>
<td>b. Sim_52_20</td>
<td>19910</td>
<td>0.52</td>
<td>0.20</td>
<td>94.3</td>
<td>0.39</td>
<td>119.4</td>
<td>106.3</td>
<td>3.32</td>
<td></td>
</tr>
<tr>
<td>Sim_50_18</td>
<td>19910</td>
<td>0.50</td>
<td>0.18</td>
<td>98.5</td>
<td>0.41</td>
<td>120.3</td>
<td>122.8</td>
<td>3.84</td>
<td></td>
</tr>
<tr>
<td>Base_48_16</td>
<td>19910</td>
<td>0.48</td>
<td>0.16</td>
<td>102.1</td>
<td>0.42</td>
<td>121.27</td>
<td>143.5</td>
<td>4.49</td>
<td></td>
</tr>
</tbody>
</table>

Product rate CO₂ = 726.4 kmol/h, Reboiler pressure 200 kPa, pressure drop column 25 kPa, y (loading)

**Increasing the Rich and Lean Levels Simultaneously**

Part b of table 6-2 shows that the steam consumption is drastically reduced as the rich and lean loads are increased.

Table 6-2 shows that an increase in the amine loading by either one of the two methods reduces the desorber energy consumption very effectively, and should be considered when optimizing a removal plant. However, it is also important to take the effect on the absorber into account.

**6.4.1 Effect of Different Lean Solvent Loading Including the Effect of the CO₂-Removal Percentage**

Figure 6-8 shows that the thermal energy requirement decreases with increasing lean loading until a minimum is reached. If the lean load is further increased, the thermal energy requirement will increase as well. Figure 6-8 also shows that decreasing the degree of regeneration will decrease the thermal energy requirement. Furthermore, at very low degrees of regeneration the amount of solvent needed increases considerably and this would require more regeneration energy. Therefore, an optimal lean loading will exist. The figures of this chapter are based on a bituminous coal fired plant (CF), and the numbers would differ from a natural gas combined circle (NGCC).
Figure 6-8 Thermal energy requirement at various CO$_2$/amine lean loadings for different CO$_2$ removal (CF) [12]

Since the lean load is varied by varying the solvent circulation rate, a high lean load also represents a high solvent circulation rate as shown below.

Figure 6-9 Solvent flow rate requirement at various CO$_2$/amine lean solvent loadings for different CO$_2$ removal [12]

The amount of thermal cooling water decreases with increasing lean solvent loadings as shown in figure 6-4. The reason that the amount of cooling water remains constant for a loading between 0.26 and 0.33 mol CO$_2$/mol MEA in this graph, is that the temperature for high lean solvent loadings was allowed to increase to meet the requirement of a closed water balance[12]. The consequence of this is that the absorber operates at a higher temperature which allows evaporation of water at the top of the absorber to maintain a closed water balance in the complete process. If the lean solvent temperature was kept constant at high solvent flow rates, this would have led to excessive condensation in the absorber. This water would have to be removed in the stripper.
6.4.2 Effect of Different Lean Solvent Loading Including the Effect of the MEA Weight%

The thermal energy requirement decreases substantially with increasing MEA concentration in the absorption solution. The increasing MEA concentration will however have a corrosive effect on the process equipment. This problem could be solved by adding corrosion inhibitors to the process. Figure 6-12 shows that there are clear benefits by increasing the MEA concentration in the solvent. By increasing the MEA concentration from 30 to 40 wt% the thermal energy requirement is decreased with 5-8% [12]. The cooling water and solvent consumption are also decreased as a result of a higher MEA concentration as shown in figure 6-13 and figure 6-14.
Figure 6-12 Thermal energy requirement at various CO2/amine lean loadings for different MEA wt%.
(for a bituminous coal fired plant) [12]

Figure 6-13 Solvent flow rate requirement at various CO2/amine lean solvent loadings for different MEA (wt.%)

Figure 6-14 Cooling water consumption at various CO2/amine lean solvent loadings for different MEA (wt.%)

6.5 Effect of Reboiler Pressure

By increasing the pressure in the reboiler, one will increase both temperature and pressure profiles of the column. The effect of varying the reboiler pressure between 180 and 220 kPa is shown in table 6-3.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Reboiler Pressure</th>
<th>Reboiler heat duty</th>
<th>Specific Steam consumption</th>
<th>T reboiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press_180kPa</td>
<td>180</td>
<td>157.5</td>
<td>4.93</td>
<td>118.2</td>
</tr>
<tr>
<td>Base_200kPa</td>
<td>200</td>
<td>143.5</td>
<td>4.49</td>
<td>121.2</td>
</tr>
<tr>
<td>Press_220kPa</td>
<td>220</td>
<td>132.8</td>
<td>4.15</td>
<td>123.9</td>
</tr>
</tbody>
</table>

Rich loading 0.48, lean loading 0.16

The table shows that an increase in pressure will enhance stripping and reduce CO₂ compression cost, if compression is required. By increasing the pressure, more steam condenses and the CO₂ mass transfer throughout the column will increase. As shown in table 6-3 an increase in pressure from 180 to 220 kPa will lead to a reduction of 15% in the reboiler duty. The disadvantage of increasing the pressure is that the boiling point of the amine solution will increase also, which may lead to higher amine degradation rates and to increased corrosion problems.

6.6 Effect of Varying Reboiler Equilibrium Efficiency

Larger reboiler units may operate at different equilibrium stages. This has an effect on the performance on the regenerator. Equilibrium efficiency is defined as the approach to phase-equilibrium of CO₂ that can be achieved in the reboiler by reducing the equilibrium value of \( Y_{CO2} \) by a certain percentage. Table 6-4 shows the effect of varying the reboiler equilibrium efficiency with a constant rich and lean loading of 0.48 and 0.16 respectively.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>( T_{rich inlet desorber} )</th>
<th>Reboiler heat duty</th>
<th>( T_{reboiler} )</th>
<th>% CO₂ approach to eq. in reboiler</th>
<th>Specific Steam consumption</th>
<th>CO₂ mass transfer packing</th>
<th>Steam/CO₂ ratio out of reboiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base_100_i</td>
<td>102.12</td>
<td>143.5</td>
<td>121.17</td>
<td>100</td>
<td>4.490</td>
<td>314.3</td>
<td>10.6</td>
</tr>
<tr>
<td>Pst_90_i</td>
<td>102.17</td>
<td>149.3</td>
<td>121.59</td>
<td>90</td>
<td>4.670</td>
<td>339.9</td>
<td>12.6</td>
</tr>
<tr>
<td>Pst_80_i</td>
<td>102.22</td>
<td>155.3</td>
<td>121.97</td>
<td>80</td>
<td>4.858</td>
<td>365.6</td>
<td>15.5</td>
</tr>
<tr>
<td>Pst_70_i</td>
<td>102.27</td>
<td>161.6</td>
<td>122.32</td>
<td>70</td>
<td>5.054</td>
<td>391.7</td>
<td>18.5</td>
</tr>
</tbody>
</table>

P = 200 kPa, initial loading 0.48, lean loading = 0.16.

By reducing the reboiler efficiency, the CO₂ gas concentration out of the reboiler will reduce proportionally. The total CO₂ leaving the desorber does however not decrease by the same magnitude. The table shows that with a 70% approach to equilibrium the amount CO₂ stripped in the column packing is 391.7 kmol/h, while its only 314.3 kmol/h at 100%. Thus, there are two counteracting effects: a more efficient reboiler indicated by a high outgoing CO₂ partial pressure will be counteracted by the effect of a less efficient CO₂ mass transfer in the desorber column and vice versa.
The steam consumption is lower with a reboiler that approaches equilibrium, and the efficiency is therefore an important element in the optimization process. Reducing the efficiency from 100 to 70% will however only increase the steam consumption by 10% and it is thus not the most important factor.

### 6.7 Importance of the Accuracy of the Equilibrium Model

The accuracy of the vapour-liquid equilibrium representation (VLE) is very important for the results of the simulation as these models always depend on experimental data to which they have been fitted. At high CO₂-loading the equilibrium partial pressure increases very rapidly with loading, especially at high temperatures. The deviations in this area might therefore be significant. Figure 6-15 gives an example of this.

![Figure 6-15 Tuned vapour liquid equilibrium (VLE) data for 30 wt% MEA at stripper conditions. a. normal plot, b. log-log plot [10]](image-url)
Table 6-5 shows how the result of the simulation is affected by the equilibrium model when the equilibrium curves are adjusted at high temperatures. The curve Eq1_3 gives higher equilibrium partial pressures for CO\textsubscript{2} as the temperature is increased at a given loading compared to the base case Eq1_5. This yields a higher driving force for desorption, which again yields higher desorption fluxes. This is the case in both the flash drum (if a flash drum is used), reboiler and in the column since all these units operate at a high temperature. To reach a desired lean loading of 0.16, however, a higher temperature in the reboiler is needed. This leads to a higher lean temperature in the cross-flow heat exchanger, which gives a higher inlet rich temperature or a higher vapour phase fraction in the flash unit. An accurate VLE description at desorber temperatures is therefore critical for the models performance. A 2\% shift in the equilibrium line at 120°C changes the overall steam consumption in the simulations with more than 15%.

<table>
<thead>
<tr>
<th>Simulation_eq</th>
<th>(T) rich inlet desorber (^\circ\text{C})</th>
<th>Reboiler heat duty (\text{GJ/h})</th>
<th>(T) reboiler (^\circ\text{C})</th>
<th>Steam out of reboiler (\text{kmol/h})</th>
<th>(\text{CO}_2) out of reboiler (\text{kmol/h})</th>
<th>(\text{CO}_2) out of desorber (\text{kmol/h})</th>
<th>Specific Steam consumption (\text{GJ/ton CO}_2)</th>
<th>Loading after flash [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq1_3</td>
<td>100.6</td>
<td>122.3</td>
<td>120.34</td>
<td>2456.6</td>
<td>303.9</td>
<td>574.8</td>
<td>3.83</td>
<td>0.409</td>
</tr>
<tr>
<td>Eq1_4</td>
<td>101.4</td>
<td>132.4</td>
<td>120.81</td>
<td>2730.8</td>
<td>292.3</td>
<td>586.6</td>
<td>4.14</td>
<td>0.413</td>
</tr>
<tr>
<td>Eq1_5</td>
<td>102.1</td>
<td>143.5</td>
<td>121.17</td>
<td>3022.5</td>
<td>284.4</td>
<td>598.7</td>
<td>4.49</td>
<td>0.417</td>
</tr>
<tr>
<td>Eq1_6</td>
<td>102.8</td>
<td>155.7</td>
<td>121.46</td>
<td>3332.3</td>
<td>279.2</td>
<td>610.8</td>
<td>4.87</td>
<td>0.421</td>
</tr>
</tbody>
</table>

Product rate \(\text{CO}_2\) = 726.4 \(\text{kmol/h}\), Reboiler pressure 200 kPa, rich loading 0.48, lean loading 0.16
7 Modelling Theory

In simulation modelling there are a few important things to be aware of. There are several different simulation programmes, but not all the programmes are designed for the same purpose. The first step will be to find the right programme.

All process simulation programmes use preinstalled thermodynamic models that include a predefined set of unit operational modules. To be able to choose the correct package it is necessary to know the process behind the simulation. Sometimes more than one fluid package can be used, and the engineer has to decide which one to choose.

For two cases to be comparable it is necessary that they use the same basis. If the subject is to find a way of reducing the energy consumption, the quality of the energy used needs to be taken into consideration. Just as important is it that the product from the process is the same for all cases. If not a comparison of the energy consumption would be useless.

7.1 Selection of Process Simulation Programme

A chemical process simulator calculates a thermodynamic consistent solution for a process flow diagram based on input from the user. The simulator contains an input and an output section, a library of unit operation models, a database for physical properties, a solver library and an administrative section. The simulator performs calculations based on the instructions of an engineer and helps the engineer making decisions by providing the necessary information. The three most well-known commercial process simulators are:

- ASPEN Plus
- PRO-II/Provision
- HYSYS

ASPEN and PRO-II are steady state process simulators with process optimization features, while HYSYS provides both steady state and dynamic simulation features. ASPEN has the largest number of users followed by PRO-II and then HYSYS. They all have an extensive database of compounds for physical properties and a large collection of unit operation models and thermodynamic models. All the three simulators have Windows-based PC-versions.

7.2 Selection of Thermodynamic Package

Fluid packages contain all necessary information regarding pure component flash and physical property calculations. By using a fluid package it is possible to define all the required information in a single location, making the information easy to modify. The fluid packages can be imported and exported as completely defined packages for use in any simulation. It is also possible to use multiple fluid packages within one simulation. The choice of fluid package is depending on the fluid or mixture of fluids as well as pressure regime used in the process.
7.3 Heat versus Mechanical Work

The total mechanical energy used per kg CO₂ sent to compression is a valuable benchmark for evaluating the efficiency of a capturing process.

Heat at a certain temperature can only be partially converted into work/electricity. Generally heat is considered as having a lower energy quality than mechanical work. To be able to calculate the total mechanical work for the capturing process, the heat duty from the reboiler has to be corrected for the difference in energy quality. This factor can be found from the graph below, which is based on a combined power plant with a condenser pressure of 0.04 bara. The graph is calculated for heat, in the form of saturated steam, which is taken from the power plant steam turbine and returned at a temperature of 70°C [14].

![Graph showing the ratio (β) between reduced electricity production and heat outlet from a power plant.]  

The value of β depends on the temperature of the steam used. The steam from the power production is however not used directly. First it has to be transported from the power plant to the sweetening plant. Even though the distance usually is short, this will lead to an additional pressure drop. It is necessary to account for this when the interaction with the graph is made.

A general equation for the mechanical work in a sweetening process is given below [5].

\[
E = \frac{\dot{Q} \times \beta + \dot{W}_{\text{CO₂}} + \dot{W}_{\text{blower}} + \dot{W}_{\text{pumps}}}{\dot{m}}
\]

(7.2)

where

- \( E \) = total mechanical work (MJ/kg CO₂)
- \( \dot{Q} \) = heat from saturated steam used for separation (MJ/h)
- \( \beta \) = factor that describes the different energy quality between electricity and heat
- \( \dot{W}_{\text{CO₂}} \) = CO₂ compression work (MJ/h)
- \( \dot{W}_{\text{blower}} \) = blower compression work (MJ/h)
- \( \dot{W}_{\text{pumps}} \) = pump work (MJ/h)
- \( \dot{m} \) = mass of CO₂ sent to compression (kg/h)
8 Methodology for Economic Evaluation

Even though a parameter variation could improve the energy efficiency of a process, it might still not be the optimum solution. As the main objective for a company is to increase the profit, optimum technical solutions have to be weighted against the extra investment expenses (CAPEX) and operational expenses (OPEX).

There are several different methods for making an economic evaluation of a project. The choice of method depends on which information is available and what the project is compared to. Usually more than one method is chosen.

8.1 Investment Expenses (CAPEX)

The investment expenses depend on the size and type of equipment needed, as well as the amount of equipment needed. The choice of equipment is based on several different parameters. The choice of equipment material is usually the cheapest material that is good enough. In other words, it is not practical to build a process plant that would last for 150 years if it is meant to be in operation for 15 years. It is however important that the equipment fulfils the safety requirements and performs satisfactory.

The main investment items for the absorption system are the two towers, the inlet cooler, and the lean/rich cross-flow heat exchanger.

Estimating Cost by Scaling

The different equipment is measured differently when a cost calculation is performed. During screening of process alternatives it is for example normal to scale the heat exchangers and columns by area, while the weight of the separators is more interesting. For scale-up purposes, the following equation can be used to determine the scaled base unit cost.

\[ C_2 = C_1 \times \left( \frac{\text{size}_2}{\text{size}_1} \right)^\epsilon \]  

where

- \( C_2 \) = scaled base unit cost (MNOK)
- \( C_1 \) = base unit cost (MNOK)
- \( \text{size}_1 \) = base unit size
- \( \text{size}_2 \) = scaled base unit size
- \( \epsilon \) = size exponent
Simulation programs like HYSYS can help calculating many of the necessary parameters, but sometimes some additional calculations are necessary. Equation 8.2 shows how the area of heat exchangers can be calculated using $Q$ and LMTD found in HYSYS and a $U$ found from tables [15].

$$A = \frac{Q}{U \times LMTD} \quad (8.2)$$

where
- $A = \text{area (m}^2\text{)}$
- $Q = \text{heat duty (kJ/h)}$
- $U = \text{overall heat transfer coefficient (kJ/C\cdot h\cdot m}^2\text{)}$
- $LMTD = \text{logarithmic mean temperature difference (°C)}$

The necessary column area can be calculated based on a maximum superficial gas velocity. This maximum velocity is depending on type of packing and this information is available from the vendor for most packings. The column area is calculated as a function of the largest volume flow of gas in the column and a specified maximum gas velocity as shown below.

$$A_{\text{column}} = \frac{\dot{V}}{w_G} \quad (8.3)$$

where
- $A_{\text{column}} = \text{column area (m}^2\text{)}$
- $\dot{V} = \text{maximum volume flow through column (m}^3/\text{s)}$
- $w_G = \text{maximum superficial gas velocity (m/s)}$

### 8.2 Operating Expenses (OPEX)

The main operating expenses for a CO$_2$ sweetening plant are connected to the consumption of steam and electricity. Electricity only amounts to about 10-20% of the total energy required, and the largest consumers are the product CO$_2$ compressors, the inlet flue gas blower, and to a minor extent, the two pumps for amine recycling.

The main thermal energy for separation is added to the process as low pressured steam to the stripper reboiler. The steam might be extracted from the gas power plant, or from a separate steam generating boiler as a part of a utility system. This is by far the major energy sink in the process and amounts to about 80-90% of the total energy requirement. The steam can be converted to equivalent mechanical energy by multiplying it with a factor found from figure 7-1. The operating expenses for the steam can then be calculated by multiplying the steam equivalent mechanical energy with the price of electricity.
The amount of cooling water used is also an important parameter when the operating cost is being calculated. The largest sources are the stripper condenser, the compressor intercoolers, the lean liquid cooler, and the flue gas cooler (if a flue gas cooler is included). The total consumption of cooling water is found by summing all the cooling water in all heat exchangers used for cooling, and the cost of the cooling water is calculated by equation 8.4:

\[ P_c = F_c \times P_{col} \]  

Where

- \( P_c \) = price of cooling water (NOK/year)
- \( F_c \) = total consumption of cooling water (m\(^3\)/year)
- \( P_{col} \) = price of cooling water per volume (NOK/m\(^3\))

The cost of operating an absorption plant varies with the complexity of the technology used. A more complex technology might involve more maintenance and thereby the need of more operators on the plant. If there is not an extensive change in technology applied, the maintenance can be calculated as a percentage of the investment cost.

### 8.3 Profitability Analysis

#### Net Present Value

A standard method for the financial appraisal of long-time projects is the net present value (NPV). In this method, a discount interest rate \( i \) is specified. This may be based on the average rate of return that the company is currently obtaining on its capital, or the bank prime lending rate. The NPV can be calculated using equation 8.5[16].

\[ NPV = \sum_{j=0}^{n} \frac{(\text{cash flow})_i}{(1 + i)^j} \]  

where

- \( NPV \) = net present value (NOK)
- cash flow = annual cash flow (NOK/year)
- \( i \) = interest rate (%)
- \( n \) = project life (year)


9 Simulation Cases

In all aspects of industrial activity, one must continuously try to improve the performance and it is common to aim at a target for ultimate or “best” operating point. In almost all engineering problems, the functions and variables can be converted into NOK. Hence, most engineering optimization problems can be reduced to a minimization of cost or maximization of profit.

The basis for this master thesis was a post-combustion capture plant using amine absorption. The parameters and dimensions were similar to a commercial plant intended to recover CO₂ from flue gas from a gas power plant at atmospheric pressure. The simulations were performed in HYSYS. The choice of process simulation programme was stated in the scope of work. HYSYS is also widely used for amine process simulation in industry and it is known as one of the best programmes for simulation with MEA amines[15].

Since gas based power plants exhaust flue gas at atmospheric pressure, MEA was chosen as the preferred amine. MEA amines have a high reaction rate and are therefore the most used amines for absorption at atmospheric pressure. The amine fluid package was used for all streams that contained amines, while the Peng-Robinson fluid package was used for cooling water.

The first and most time-consuming part of this master thesis was the making of a base case simulation model. It was desired to make a model with realistic parameters and simple solutions.

The scope of work left the choice of parameters to be optimized open. As the major energy consumption in a capture plant is in the desorption process, the main focus was set on parameters that affected the desorber column directly. The aim was to find an optimum operating point in terms of energy consumption and economy. In order to make an economical evaluation both the difference in operational costs and investment costs were included.

Three parameters were varied with respect to achieve an optimum operating point;
- the solvent circulation rate,
- the rich/lean cross-flow heat exchanger minimum temperature approach and
- the desorber pressure.

All these parameters have a significant effect on the desorber operation and an optimization of these parameters can reduce the expenses of a capture plant greatly. For each parameter variation the other parameters were kept constant at the base case value. In the end the optimal point for each varied parameter were included in the same model. This will not necessarily be the optimized solution since these parameters depend on each other. It will however give an indication of the possible improvement in energy consumption and economy.

A fourth parameter, the absorber diameter, was varied to get a better understanding of column design. For this purpose HYSYS has its limitations and an additional programme and calculations by hand were necessary. It was found difficult to include these results in the optimization of the other parameters. The variation of the absorber diameter was therefore presented as a separate part of the results.
9.1 Base Case Model

The base case for the simulation in HYSYS is shown in figure 9-1 and figure 9-3. Since some of the water and amines followed the flue gas out of the absorber and the CO₂ to compression, two additional streams were added to the simulation, keeping the circulation rate of water and amines constant. The streams were added right before the absorber inlet. To simplify the simulation model, a water scrubber was not included in the absorber. Neither was an amine filter or a reclamer. This lead to a relatively high consumption of amines. The consumption of amines did however not vary significantly for the different cases.

![Diagram of absorber and stripper](image)

Figure 9-1 Base case for simulation

The columns both used packing material. The number of stages in the absorber and the stripper was set to 11 and 32 respectively, based on results from a simulation model with similar parameters[15].

The total pressure drop for the absorber was for the base case set to 0.05 bar. The determination of this pressure drop was based on a similar model which included a washing section [15]. The stripper pressure drop was set to 0.138 bar based on the same model as the absorber. The flue gas was blown up to a pressure of 0.01 bar above the absorber bottom pressure and entered with temperature of 107.9°C. To reduce the investment cost, a flue gas cooler was not included.

To simulate the height of the absorber and the stripper, two valves were added to decrease the pressure of the streams entering the top of the columns. The pressure drops through the valves were about 5 bar.

The lean liquid entering the absorber was cooled to 21°C by the lean amine cooler, while the condenser outlet temperature was kept constant at 28°C. The condenser and lean amine cooler both used water at 8°C and 4 bara as coolant. The pressure loss for the cooling water was set to 0.5 bar and the water was specified to exit with a temperature of 18°C.

The capture rate was set to 85%, which for the base case was attained by an amine wt% of 30%, a solvent circulation rate of 2358 ton/h and a reboiler duty of $8 \times 10^8$ kJ/h. An accuracy of ± 0.1% for the capture rate was used for all cases.
A total mechanical work, which included the equivalent mechanical energy for the reboiler steam, was calculated to easily compare the different cases in terms of energy consumption and operational cost. To calculate the total mechanical work equation 7.2 was employed. The value of $\beta$ was found from figure 7-1. The condensing temperature of the steam used in the reboiler was 143°C. With an additional pressure drop in the steam transportation, $\beta$ was chosen to be 0.23. The same value was used for all cases since it was assumed that all cases used the same steam. This resulted in a total mechanical work of 1.441 MJ/kg CO$_2$ for the base case.

The CO$_2$ compression was done in 3 stages with intermediate cooling as shown in figure 9-3. An equal pressure ratio was used, based on the pressure into the first compressor stage and a specification of 80 bara out of the third compressor stage. A pump further raised the pressure to 110 bara. The adiabatic efficiencies were set to 85%, 85% and 80% for compressor stage 1, 2 and 3 respectively. The pump adiabatic efficiency was set to 75%.

The pressure losses through all 3 heat exchangers were set to 0.3 bar for both the gas stream and the coolant. As a coolant, water at 8°C and 4 bara was chosen. The water was specified to heat up to 18°C, while the temperature of the CO$_2$ was specified to be 20°C out of all three heat exchangers.
Two separators were included in the model to extract the majority of the remaining water from the CO\textsubscript{2} gas. This water is usually returned to the capturing process so that less water has to be added.

Appendix A gives the specifications for the model.

**Discussion of the Base Case Model**

**Flue Gas Cooler**
The chemical absorption between the CO\textsubscript{2} and the amines is favoured by a relatively low temperature and a pre-cooler at the gas inlet to the absorber is often included in an absorption plant. Inserting a flue gas cooler does however not a cause significant improvement in operational cost\textsuperscript{[17]}.

The flue gas of a traditional gas power plant will have a water content of approximately 5wt\%. At atmospheric pressure this will lead to a saturation temperature of about 43°C. The flue gas leaving a gas power plant will have a temperature of 90-100°C. When the flue gas enters the absorber it will instantly vaporize some of the water in the absorber, and this vaporization will cool down the flue gas.

If a flue gas cooler is employed the vaporization process occurs before the flue gas enters the absorber. The flue gas will then be saturated with water and will not experience the cooling effect of the vaporization in the absorber. Therefore the absorber temperature will not differ much from the case without pre-cooling. As pre-cooling involves a higher investment cost and a higher use of cooling water, it was found reasonably to exclude the flue gas cooler.

**Impact on Power Plant**
The blower duty was unchanged when the circulation rate, the rich/lean minimum temperature approach and the stripper pressure was varied, and the flue gas composition was kept constant for all cases. Therefore the only matter that affected the efficiency of the power plant was the low pressured steam employed in the reboiler, which was assumed to be extracted from the gas power plant. As the power plant was not included in the simulation model, the impact on the power plant efficiency can only be discussed on general level.

The steam specifications were kept constant for all cases and the steam mass flow was the only variable. As less steam was consumed, a higher efficiency was obtained for the power production.

**Total Mechanical Work**
The steam employed in the reboiler was converted into an equivalent mechanical energy, where it was assumed that the condensate was returned to the power plant at 70°C. In more modern power plants, however, it is possible to return the condensate at a lower temperature, meaning a less conservative factor could be applied to convert the reboiler duty to mechanical work.
Water Consumption
The water consumption was not regulated or fixed in the base case model. The only parameter that had a significant effect on the water consumption was the solvent circulation rate. For this purpose the temperature out of the lean loading cooler was adjusted so that a more or less constant mass flow of water followed the cleaned flue gas out of the absorber. Although a more accurate way of regulating the water consumption will be favourable, this simplification was found to be sufficient for the purpose of this thesis.

Pressure Loss through Valves
The valves for the streams entering the absorber and the stripper were given rather higher pressure losses. This will not have a significant effect on the absorber, other than a slightly increased lean pump duty. For the stripper column, however, a very high pressure loss may change the phase of the stream entering the column. This will affect the regeneration process in the stripper column.

9.2 Circulation Rate
Varying the circulation rate also changes the CO\textsubscript{2} recovery rate, because the circulation rate affects the thermal energy requirement in the desorber. To account for this the reboiler duty was adjusted so that a constant recovery rate of 85\% was kept.

There is also a close connection between the circulation rate, the temperature of the lean amine stream entering the absorber and the water consumption. To keep the water consumption at a constant level, the temperature of the lean amine stream entering the absorber was adjusted for the different circulation rates. This resulted in a maximum change in water consumption of 1.5\%.

The lean amine loading varies with the circulation rate and the reboiler duty. The variation in lean amine loading was therefore also presented as a function of the total mechanical work.

Results
Figure 9-4 and figure 9-5 shows that the optimal circulation rate in terms of total mechanical work and reboiler duty per kg CO\textsubscript{2} with a capture rate of 85\% is about 2500 ton/h.
The lean loading as a function of total mechanical work varies in a similar manner as the circulation rate, and the minimum for total mechanical work was found for a lean loading of about 0.22 as shown in figure 9-6. The rich loading was kept constant at 0.45 since the number of stages in the absorber column and the recovery rate was unchanged.
When the circulation rate was increased the necessary cooling of the lean amine stream decreased with about 1°C for every increase in flow rate of 100 ton/h. Figure 9-7 shows that for a variation in circulation rate of 1800 ton/h, the temperature out of the lean amine cooler was varied with 17°C.

The consumption of cooling water varied in the same way as the energy consumption, leading to a minimum consumption for a circulation rate of 2500-2600 ton/h.
The composition and flow rate of out of the top of the desorber column varies very little with the circulation rate, but the flow rate will decrease a little when the circulation rate is increased.

**Discussion of Results**

At low circulation rates, the dilution heat is dominant in the thermal energy requirement as a higher driving force is needed. At high circulation rates more amines has to be heated up before entering the desorber, and the sensible heat will be dominant in the thermal energy requirement. Therefore a minimum is expected. Figure 9-4 and figure 9-5 show that the thermal energy requirement decreases with increasing circulation rate until a minimum is attained. The point at which the energy requirement is lowest will be defined to be the optimum lean solvent loading.

The results from figure 9-4 and 9-5 show a lower optimum circulation rate and lean loading than what was found by Abu-Zahra, Niederer, Feron and Versteeg given in chapter 6.5. The reason for this is most likely that the results are based on two different feed gas compositions and a slightly different mass flow.

**9.3 Minimum Temperature Approach for Rich/Lean Heat Exchanger**

The rich/lean heat exchanger minimum temperature approach was varied between 3°C and 15°C to observe the effect on the total energy consumption. The composition and flow rate in and out of the stripper were also observed. The reboiler duty was adjusted so that a constant recovery rate of 85% was kept.

**Results**

A variation in the rich/lean minimum temperature approach results in a linear change in total mechanical work per kg CO₂. It is also shown that a change from 15°C to 3°C changes the total mechanical work per CO₂ with less than 1.5%.
The reboiler duty varied with about 2% between 3°C and 15°C favouring a low temperature approach.

With a higher temperature after the rich/lean heat exchanger the vapour fraction in the stripper inlet stream increases. A change from 15°C to 3°C almost triples the vapour fraction. A minimum temperature approach of 3°C resulted in a 5.7°C higher stripper inlet temperature than with a minimum temperature approach of 15°C. This again resulted in a difference in stripper top temperature of 5.4°C and more water and amines followed the CO₂ out of the stripper. The extra water and amines were however flashed in the overhead receiver and sent back to the process. The composition and mass flow sent to CO₂ compression therefore remained constant. This resulted however in a higher flow rate in the stripper reflux pump and the lean amine pump for low temperature approaches. It was also observed that both the vapour and liquid flow increased throughout the column.
The total consumption of cooling water decreased with lower minimum approaches. The difference between 3°C and 15°C was however less than 2%. The lean amine stream from the bottom of the stripper, the blower duty and the CO₂ compression were not affected by the temperature approach in the rich/lean heat exchanger.

**Discussion of Results**

The rich/lean minimum temperature approach was found to have little impact on the energy consumption for absorption processes. It will therefore not be the most important parameter in a parameter optimization.

At low temperature approaches the vapour fraction in the rich stream entering the stripper increases. A flash separator after the rich/lean heat exchanger can reduce the loading significantly. Although a flash separator was not used in the simulation model of this masters thesis, the distillation columns of HYSYS have a flash included and the separation will occur before it interacts with flows of the column.

When the feed, at its equilibrium, meets the water wash reflux, the solvent is cooled and diluted. As explained in chapter 6.2.2 this could result in a drop in the equilibrium partial pressure below the partial pressure of the vapour phase in the tower. The cross-flow heat exchanger should therefore only have a limited duty to keep desorption occurring throughout the column. The duty should be chosen so that the inlet rich feed to the desorber column, after being mixed with the reflux, is close to the desorber exit gas phase equilibrium. In other words, the more efficient the heat exchanger is, the higher the chances are for the desorber to be performing below optimum. The size of the heat exchanger should therefore be chosen depending on the desorber size and efficiency.

### 9.4 Stripper Pressure

The stripper column pressure was varied between 1.462 bara and 3.462 bara at the bottom of the column with a constant pressure drop of 138 mbar. For every increase in column pressure an equal increase in outlet pressures were set for the reboiler reflux pump, the rich amine pump, the condenser reflux pump and the valve in front of the stripper. The reboiler duty was adjusted so that a constant recovery rate of 85% was kept.

The specifications for the steam used to heat up the reboiler were constant for all pressures and the reboiler duty was varied by the mass flow of the steam only.

**Results**

Figure 9-11 and 9-12 show that the energy consumption per kg CO₂ can be reduced by increasing the stripper column pressure. The graphs are steep for an increase in column bottom pressure up to about 2 bara and stabilizes more to a linear decrease if the pressure is further increased. Figure 9-13 shows that the consumption of cooling water will vary with the stripper pressure in the same manner as the energy consumption.
The lean loading decreases and the recovery rate increases with an increased column pressure. Since a constant recovery rate was desired and the reboiler duty was adjusted for the different pressures, the lean loading was constant.
At a bottom pressure of 3.46 bara (3.32 bara in the top) two liquid phases were observed in the top stage of the stripper column and HYSYS had trouble converging. The solution temperature after the reboiler will also be relatively high if the pressure is further increased. With a stripper bottom pressure of 3.46 bara the solution temperature after the reboiler is 140.9°C. The variation in temperature after the reboiler is shown below.

The amount of water following the CO₂ out of the stripper tower decreases with a higher stripper pressure. For bottom pressures up to about 2 bara the amount of water vapour out of the stripper tower decreases rapidly but decreases with a lesser degree for higher pressures. The amount of amines following the CO₂ and water out of the stripper decreases up to a pressure of 2.162 bara and start to increase again for higher pressures.
Discussion of Results
When the stripper pressure is increased more CO₂ is stripped. This can be explained based on the effect of temperature on vapour pressures. The vapour pressure of CO₂ over an amine solution generally increases with temperature more rapidly than does the vapour pressure over the water/amine mixture over the same solution. As a result, stripping to the same mole fraction CO₂ in the vapour phase means stripping to a lower mole fraction in the liquid if the pressure (and thereby the temperature) is increased[3]. This also explains why less water vapour followed the CO₂ out of the stripper when the pressure was increased. It should however be noted that this phenomenon is a characteristic for CO₂ in MEA and will not necessarily occur with other amines. In addition to a decrease in reboiler duty, the CO₂ compression work will decrease with higher stripper pressure leading to an even lower total work per kg CO₂.

The energy consumption decreases very rapidly for an increase in desorber bottom pressure up to about 2 bara before it decreases linearly and more gently for higher pressures. A good explanation for this was not found and should be examined more closely.

A lower energy consumption due to a higher stripper pressure is in accordance with the results of Tobiesen, Svendsen and Hoff shown in chapter 6.7.

With a column bottom pressure above 3.462 bara two liquid phases were found in the top stage of the stripper column, and the simulation model had problem converging. This may be connected to the limitations on the amine temperature in the amine package in HYSYS. For a column bottom pressure of 3.462 bara, a temperature of almost 141°C was observed on the outlet of the reboiler. The range of applicability for the amines in the Amines Property Package in HYSYS is given as 25°C-126.7°C. It is also noted in the simulation basis manual for HYSYS that the reboiler temperature should not exceed 137.8°C to avoid physical degradation of the amines into corrosive by-products. HYSYS will therefore not be a suitable programme for simulating high stripper pressures. The optimum operational pressure will be a trade-off between the gain in decreased operational cost and the increased operational problems due to degradation and corrosion.

9.5 Economic Evaluation
Investment Expenses (CAPEX)
Only the equipment that differed from the base case was included in the investment calculations, and all results are given as a cost difference from base case. The investment cost data were supported by Aker Kvaerner. The prices were scaled based on the AKET Just Catch CO₂ capture plant. Due to a request by Aker Kvaerner for keeping the economic background data undisclosed, these numbers were not included in the thesis.

The different equipment was scaled differently. The heat exchangers and columns were scaled by area, the separators by weight, the compressors by duty and the pumps by volume flow. The areas, duties and volume flows were found by the student. The separator weight was calculated based on flow rate and operational pressure, and was calculated in co-operation with Aker Kvaerner.
Heat exchanger areas were calculated using equation 8.2, while the absorber and stripper areas were calculated using equation 8.3. A superficial gas velocity of 3 m/s through the columns were used for all cases. This was the number recommend by Sulzer for the Mellapack 2X packing [18].

Operational Expenses (OPEX)
The operational expenses were calculated as the sum of mechanical energy cost, cooling water cost and maintenance. The mechanical energy cost was calculated with an electricity cost of 0.36 NOK per kWh, while the cost of cooling water was calculated with a price of 0.1 NOK per m³ seawater. The maintenance was calculated as 2.5%/year of investment costs. These numbers were based on a report from NVE [19] written in December 2006, which included an economic evaluation of a future CO₂ capture plant at Kårstø, Norway.

To compare the total cost for the different cases from start to end, the net present value (NPV) was calculated, using equation 8.5. It was assumed that the project life was 25 years, and that the plant was running for 8000 hours a year[19]. In the report from NVE an interest rate of 5% was used, while interest rates of 3% and 7% were included in the sensitivity analysis. The reason for applying three different interest rates was that all numbers were calculated on an early stage and the uncertainties regarding their accuracy were high. The same interest rates were applied in this thesis, and it was assumed a real interest rate.

Results
Circulation Rate
Table 9-1 and 9-2 compares different circulation rates with the base case of 2358 ton/h in terms of investment cost, operational cost and net present value. It is found that a circulation rate of 2500 ton/h will be the best economical option. It has the lowest investment cost and operational cost and the highest net present value.

<table>
<thead>
<tr>
<th>[ton/h]</th>
<th>∆Investment Cost [mill. NOK]</th>
<th>∆Operational Cost [thousand NOK/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2200</td>
<td>3.26</td>
<td>6037</td>
</tr>
<tr>
<td>2300</td>
<td>0.46</td>
<td>986</td>
</tr>
<tr>
<td>base case (2358)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2500</td>
<td>-0.40</td>
<td>-809</td>
</tr>
<tr>
<td>2600</td>
<td>0.01</td>
<td>-515</td>
</tr>
<tr>
<td>2700</td>
<td>0.92</td>
<td>497</td>
</tr>
<tr>
<td>2800</td>
<td>2.80</td>
<td>2125</td>
</tr>
<tr>
<td>2900</td>
<td>3.55</td>
<td>2274</td>
</tr>
<tr>
<td>3000</td>
<td>5.50</td>
<td>4693</td>
</tr>
<tr>
<td>3250</td>
<td>8.70</td>
<td>7474</td>
</tr>
<tr>
<td>3500</td>
<td>11.72</td>
<td>9969</td>
</tr>
<tr>
<td>4000</td>
<td>19.48</td>
<td>16748</td>
</tr>
</tbody>
</table>
Table 9-2 Difference in net present value (NPV) for different circulation rates compared to base case of 2358 ton/h

<table>
<thead>
<tr>
<th>Cases</th>
<th>∆NPV (i=3%)</th>
<th>∆NPV (i=5%)</th>
<th>∆NPV (i=7%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2200</td>
<td>-108,4</td>
<td>-88,4</td>
<td>-73,6</td>
</tr>
<tr>
<td>2300</td>
<td>-17,6</td>
<td>-14,4</td>
<td>-12,0</td>
</tr>
<tr>
<td>base case (2358)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2500</td>
<td>14,5</td>
<td>11,8</td>
<td>9,8</td>
</tr>
<tr>
<td>2600</td>
<td>8,9</td>
<td>7,2</td>
<td>6,0</td>
</tr>
<tr>
<td>2700</td>
<td>-9,6</td>
<td>-7,9</td>
<td>-6,7</td>
</tr>
<tr>
<td>2800</td>
<td>-39,8</td>
<td>-32,7</td>
<td>-27,6</td>
</tr>
<tr>
<td>2900</td>
<td>-43,2</td>
<td>-35,6</td>
<td>-30,1</td>
</tr>
<tr>
<td>3000</td>
<td>-87,2</td>
<td>-71,6</td>
<td>-60,2</td>
</tr>
<tr>
<td>3250</td>
<td>-138,8</td>
<td>-114,0</td>
<td>-95,8</td>
</tr>
<tr>
<td>3500</td>
<td>-185,3</td>
<td>-152,2</td>
<td>-127,9</td>
</tr>
<tr>
<td>4000</td>
<td>-311,1</td>
<td>-255,5</td>
<td>-214,7</td>
</tr>
</tbody>
</table>

Rich/Lean Minimum Temperature Approach

Table 9-3 and 9-4 compare different minimum temperature approaches in the rich/lean heat exchanger with the base case temperature of 8.5°C in terms of investment cost, operational cost and net present value. It is found that a minimum temperature approach of 5°C will be the best economical option based on the highest net present value.

Table 9-3 Difference in investment cost and operational cost for different minimum temperature approaches compared to base case at 8.5°C

<table>
<thead>
<tr>
<th>°C</th>
<th>∆Investment Cost</th>
<th>∆Operational Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>7,70</td>
<td>-503</td>
</tr>
<tr>
<td>5</td>
<td>3,94</td>
<td>-414</td>
</tr>
<tr>
<td>7</td>
<td>1,50</td>
<td>-160</td>
</tr>
<tr>
<td>base case (8,5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>-2,07</td>
<td>373</td>
</tr>
<tr>
<td>13</td>
<td>-3,72</td>
<td>696</td>
</tr>
<tr>
<td>15</td>
<td>-5,12</td>
<td>1293</td>
</tr>
</tbody>
</table>

Table 9-4 Difference in net present value (NPV) for different minimum temperature approaches compared to base case at 8.5°C

<table>
<thead>
<tr>
<th>°C</th>
<th>∆NPV (i=3%)</th>
<th>∆NPV (i=5%)</th>
<th>∆NPV (i=7%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1,1</td>
<td>-0,6</td>
<td>-1,8</td>
</tr>
<tr>
<td>5</td>
<td>3,3</td>
<td>1,9</td>
<td>0,9</td>
</tr>
<tr>
<td>7</td>
<td>1,3</td>
<td>0,8</td>
<td>0,4</td>
</tr>
<tr>
<td>base case (8,5)</td>
<td>0,0</td>
<td>0,0</td>
<td>0,0</td>
</tr>
<tr>
<td>11</td>
<td>-4,4</td>
<td>-3,2</td>
<td>-2,3</td>
</tr>
<tr>
<td>13</td>
<td>-8,4</td>
<td>-6,1</td>
<td>-4,4</td>
</tr>
<tr>
<td>15</td>
<td>-17,4</td>
<td>-13,1</td>
<td>-10,0</td>
</tr>
</tbody>
</table>
Stripper Column Pressure

Table 9-5 and 9-6 compare different stripper column pressures with the base case of 1.862 bara in terms of investment cost, operational cost and net present value. It is found that a bottom pressure of 3.262 bara will give the highest net present value and will therefore be considered as the best economical option.

Table 9-5 Difference in investment cost and operational cost for different stripper column bottom pressures compared to base case of 1.862 bara

<table>
<thead>
<tr>
<th>Cases</th>
<th>△Investment Cost</th>
<th>△Operational Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,462</td>
<td>45,45</td>
<td>23,4</td>
</tr>
<tr>
<td>1,562</td>
<td>30,85</td>
<td>16,0</td>
</tr>
<tr>
<td>1,662</td>
<td>18,64</td>
<td>9,2</td>
</tr>
<tr>
<td>1,762</td>
<td>8,48</td>
<td>4,0</td>
</tr>
<tr>
<td>base case (1,862)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1,962</td>
<td>-7,15</td>
<td>-2,7</td>
</tr>
<tr>
<td>2,062</td>
<td>-12,32</td>
<td>-4,2</td>
</tr>
<tr>
<td>2,162</td>
<td>-17,33</td>
<td>-5,2</td>
</tr>
<tr>
<td>2,262</td>
<td>-22,09</td>
<td>-6,2</td>
</tr>
<tr>
<td>2,362</td>
<td>-25,94</td>
<td>-7,1</td>
</tr>
<tr>
<td>2,462</td>
<td>-28,89</td>
<td>-7,6</td>
</tr>
<tr>
<td>2,562</td>
<td>-32,36</td>
<td>-8,3</td>
</tr>
<tr>
<td>2,662</td>
<td>-34,55</td>
<td>-8,9</td>
</tr>
<tr>
<td>2,762</td>
<td>-37,14</td>
<td>-9,6</td>
</tr>
<tr>
<td>2,862</td>
<td>-39,24</td>
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</tr>
<tr>
<td>2,962</td>
<td>-39,62</td>
<td>-10,7</td>
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<td>3,062</td>
<td>-40,23</td>
<td>-11,3</td>
</tr>
<tr>
<td>3,162</td>
<td>-39,41</td>
<td>-11,8</td>
</tr>
<tr>
<td>3,262</td>
<td>-40,22</td>
<td>-12,2</td>
</tr>
<tr>
<td>3,362</td>
<td>-33,49</td>
<td>-12,5</td>
</tr>
<tr>
<td>3,462</td>
<td>-26,52</td>
<td>-12,8</td>
</tr>
</tbody>
</table>
Table 9-6 Difference in net present value (NPV) for different stripper column bottom pressures compared to base case of 1.862 bara, given for interest rates of 3%, 5% and 7%.

<table>
<thead>
<tr>
<th>bara</th>
<th>∆NPV (i=3%)</th>
<th>∆NPV (i=5%)</th>
<th>∆NPV (i=7%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,462</td>
<td>-452,9</td>
<td>-375,2</td>
<td>-318,1</td>
</tr>
<tr>
<td>1,562</td>
<td>-310,0</td>
<td>-256,8</td>
<td>-217,7</td>
</tr>
<tr>
<td>1,662</td>
<td>-179,0</td>
<td>-148,4</td>
<td>-125,9</td>
</tr>
<tr>
<td>1,762</td>
<td>-78,4</td>
<td>-65,1</td>
<td>-55,3</td>
</tr>
<tr>
<td>base case (1,862)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1,962</td>
<td>53,7</td>
<td>44,8</td>
<td>38,3</td>
</tr>
<tr>
<td>2,062</td>
<td>84,9</td>
<td>71,1</td>
<td>60,9</td>
</tr>
<tr>
<td>2,162</td>
<td>108,0</td>
<td>90,7</td>
<td>78,0</td>
</tr>
<tr>
<td>2,262</td>
<td>130,5</td>
<td>109,8</td>
<td>94,6</td>
</tr>
<tr>
<td>2,362</td>
<td>149,0</td>
<td>125,5</td>
<td>108,3</td>
</tr>
<tr>
<td>2,462</td>
<td>161,2</td>
<td>136,0</td>
<td>117,4</td>
</tr>
<tr>
<td>2,562</td>
<td>177,1</td>
<td>149,5</td>
<td>129,2</td>
</tr>
<tr>
<td>2,662</td>
<td>190,1</td>
<td>160,4</td>
<td>138,6</td>
</tr>
<tr>
<td>2,762</td>
<td>204,2</td>
<td>172,4</td>
<td>149,0</td>
</tr>
<tr>
<td>2,862</td>
<td>218,4</td>
<td>184,2</td>
<td>159,1</td>
</tr>
<tr>
<td>2,962</td>
<td>225,9</td>
<td>190,4</td>
<td>164,3</td>
</tr>
<tr>
<td>3,062</td>
<td>237,3</td>
<td>199,7</td>
<td>172,1</td>
</tr>
<tr>
<td>3,162</td>
<td>244,9</td>
<td>205,8</td>
<td>177,0</td>
</tr>
<tr>
<td>3,262</td>
<td>253,5</td>
<td>212,8</td>
<td>182,9</td>
</tr>
<tr>
<td>3,362</td>
<td>250,5</td>
<td>209,1</td>
<td>178,7</td>
</tr>
<tr>
<td>3,462</td>
<td>249,1</td>
<td>206,7</td>
<td>175,5</td>
</tr>
</tbody>
</table>

Combining the Optimum Results
An optimal point was found for a circulation rate of 2500 ton/h, for a rich/lean minimum temperature approach of 5°C and for a stripper column pressure of 3.262 bara in the bottom. These results were combined in a new model. Table 9-7 shows how much the investment cost is improved compared to base case, including all equipment that changes with the three parameters above.

Table 9-7 Difference in investment cost for a sub-optimal operating point compared to base case

<table>
<thead>
<tr>
<th>Unit</th>
<th>[mill. NOK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂-compressor</td>
<td>-45,18</td>
</tr>
<tr>
<td>rich lean exchanger</td>
<td>-0,52</td>
</tr>
<tr>
<td>stripper</td>
<td>-20,35</td>
</tr>
<tr>
<td>stripper condenser</td>
<td>-1,84</td>
</tr>
<tr>
<td>seperator CO₂-compression 1</td>
<td>0,50</td>
</tr>
<tr>
<td>seperator CO₂-compression 2</td>
<td>0,20</td>
</tr>
<tr>
<td>stripper overhead receiver</td>
<td>0,80</td>
</tr>
<tr>
<td>stripper reflux pump</td>
<td>-0,09</td>
</tr>
<tr>
<td>stripper reboiler</td>
<td>27,82</td>
</tr>
<tr>
<td>lean amine pump</td>
<td>0,66</td>
</tr>
<tr>
<td>lean amine cooler</td>
<td>-2,06</td>
</tr>
<tr>
<td>total cost</td>
<td>-40,06</td>
</tr>
</tbody>
</table>
The investment cost for the three parameters varied, where all equipment that differed is specified, is shown in appendix C.

**Discussion of Results**

In many design situations, it is possible to have small increments in capacity; hence the possibility of small increments in capital investment. By providing more surface area for heat transfer in a co-current heat exchanger, greater heat transfer may be obtained. But each m² of heat transfer area provides a diminishing heat transfer flux. On the other hand, the cost of the heat exchanger goes up as the area is increased.

The areas of the condenser, the lean amine cooler, the reboiler and the rich/lean cross-flow heat exchanger vary as a consequence of the difference in minimum temperature approach in the rich/lean heat exchanger. The reboiler and the lean amine cooler areas both decreased with a lower minimum approach, while the condenser and rich/lean heat exchanger increased. The major difference was however for the rich/lean heat exchanger which became very large for a minimum approach of 3°C.

An optimal stripper pressure in terms of net present value (NPV) was found for a bottom pressure of 3.262 bara. The reason that the net present value was higher at this pressure than for higher pressures, even though higher pressures resulted in a lower energy consumption, is connected to the increased investment cost of the reboiler. The specifications for the steam employed in the simulations of this thesis were kept constant at 4 bara and 270°C. For an increased pressure (and temperature) of the amine solvent, the temperature difference between the steam and the amine solvent will become smaller and the necessary surface area will increase. Therefore, if the stripper column pressure is increased, the pressure of the steam employed should also be increased. This means that the optimal point in terms of net present value can be higher than 3.262 bara. However, it is very important to be aware of the increased operational problems due to an increased pressure (and temperature), and most likely a significantly lower pressure will be more realistic.

Table 9-7 shows that the major reduction in investment costs are found for the stripper column and the CO₂-compressor. The increased investment cost due to a large reboiler at higher pressures is the main reason that the reduction in investment costs is not greater.

### 9.6 Absorber Column Diameter

The absorber column diameter was found to be a difficult parameter to vary. Varying the column diameter changes the gas velocity, and thereby the pressure drop, through the column. The pressure drop again affects the necessary column height and the energy consumption of the absorption plant. The value of the pressure drop is also highly dependent of the type of packing in the column.

To get an understanding of how the pressure drop through the absorber affects the energy consumption a simple test in HYSYS was performed, where the pressure drop was varied with constant absorber specifications. The result is shown in figure 9-15.

The connection between the superficial gas velocity and the absorber column diameter can be described by rearranging equation 8.3:
With a constant volume flow the superficial gas velocity will be a function of the diameter alone. Figure 9-16 gives the result of varying the column diameter in terms of superficial gas velocity using the maximum volume flow from the base case simulation model.

For column design HYSYS has its limitations. The absorber product depends on the number of stages, inlet flows, pressure drop, diameter and type of internal material (packing, sieve, valve etc.). All these parameters have to be given to HYSYS as inputs. Based on these HYSYS calculates the outlet streams. HYSYS does not calculate the absorber height and it is not possible to specify the height or type of packing.

It turned out that a variation of the absorber column diameter using HYSYS alone will not give any interesting results. Therefore a second programme, SULCOL, was used in order to determine the variation in column pressure as a result of varying the diameter.

SULCOL is a sizing program designed for distillation, stripping and absorption columns with Sulzer mass transfer products. The sizing procedure leads to estimated values for the product specific design figures like capacity, pressure drop, holdup etc., based on the specified liquid and gas flow rates and physical properties at a given column diameter. The column height can also be specified. However, this programme does not account for the chemical reactions inside the column.

To be able to determine the necessary height for different diameters the use of an additional program or calculations by hand was necessary. Other programmes like PROTREAT has the ability to calculate column height, but due to the time limit it was found better to do some simplifications and calculate the column height by hand rather than learning to use a third programme.

The column height was calculated using equation 9.2, which is modification of equation 4-12. The mole fraction of CO₂ in equilibrium, \( y_e \), was assumed to be a lot lower than the CO₂ mole fraction at the top and bottom of the column, and was as a simplification neglected. Since the type of packing, temperature and pressure were kept constant, the overall mass transfer coefficient, \( K_Ga \), was also assumed constant. With a constant overall mass transfer coefficient, a constant column pressure and constant inlet streams, the necessary column height to keep the CO₂ capture rate constant for different diameters could be calculated.

\[
\frac{w_G}{D^2} = \frac{4}{\pi} \frac{\dot{V}}{G}
\]  

(9.1)

\[
h = \frac{G_u}{K_G a P} \ln \left( \frac{y_e}{y} \right)
\]  

(9.2)

The overall mass transfer coefficient was found by calculating backwards, using the specifications of a model with similar specifications[15] where the absorber height was known.

The diameter was varied between 13 and 30 meters, and for each diameter a new height was calculated. These specifications were given as inputs to SULCOL along with the inlet and outlet specifications of the streams entering and leaving the absorber column and the number of stages in the absorber. The stream specifications and number of stages were found from the
base case simulation model in HYSYS. The packing type chosen for the absorber column design was Mellapack 2X from Sulzer. This is the same type of packing recommended to Aker Kværner by Sulzer. Based on this information the pressure drop through the column was calculated using SULCOL. The diameter with the corresponding height as a function of pressure loss is shown in figure 9-17.

The pressure drop calculated in SULCOL for each diameter was returned to the simulation model in HYSYS along with the diameter. The pressure drop of 0.05 bar was used for the base case with a column diameter of 17 meters. The other pressure drops were adjusted to make the difference in pressure drop as calculated in SULCOL. As the recovery rate increases with a lower pressure drop, the reboiler duty was varied to keep the recovery rate constant. The energy consumption as a function of the column diameter is shown in figure 9-18. Since the overall mass coefficient was applied, the volume of the absorber did not vary and an economic evaluation was not included.

Results
As shown below the energy consumption varies linearly with the pressure drop through the absorber column. This mainly due to the change in blower duty.

![Total Mechanical Work VS Pressure Drop Absorber](image)

Figure 9-15 Total mechanical work as a function of pressure drop in absorber column

Figure 9-16 shows that for a maximum superficial gas velocity of 3 m/s the minimum column diameter will be about 17 meters.
The overall mass transfer coefficient, $K_G a$, was calculated to be 0.0155 kmol/(m×bar×s) for a superficial gas velocity of 3m/s, a height of 12m and the specifications in the base case simulation model.

The diameter and the corresponding height as a function of the absorber pressure drop is shown in figure 9-17. It is shown that increasing the diameter to more than 19 meters will affect the pressure loss through the column very little. If the diameter is decreased to below 15 meters however, the pressure loss will differ significantly.

As the pressure drop varied very little for column diameters above 19 meters, the difference in energy consumption varied very little as well. A diameter below 17 meters will increase the energy consumption significantly, while increasing the diameter from 17 meters to 19 meters can give favourable results.
Discussion of Results

Figure 9-15 shows that the pressure drop in the absorber will affect the energy consumption significantly if the pressure loss becomes high. This is mainly due to the increased duty of the flue gas blower. The pressure loss will however not differ as much as in figure 9-15 for different diameters, and was only included as an illustration.

The maximum acceptable superficial gas velocity is a quality of the packing in terms of at which velocity flooding can occur. For the Mellapack 2X a maximum velocity of 3 m/s was recommended. This leads to a minimum diameter of about 17 meters with the gas volumetric flow rate in the model of this thesis. The diameters for Mellapack are given for 0.08m up to 17m, depending on type[18]. If it is desirable to increase the diameter more, a different type of packing might be more favourable. An increase in diameter to more than 19m did however not result in much difference in total mechanical work for the absorption plant.

The value of \( y_{\text{eq}} \) was neglected in equation 9.2. This means that no back pressure was expected or that the reaction was irreversible. In reality the column will be significantly taller than the calculated height.

It was found that HYSYS is not a suitable programme for column design. On the basis of the simplifications and uncertainties regarding the calculations of diameter and height, the degree of accuracy of the results found for the absorber design has to be taken into consideration. The column diameter should therefore be examined to a greater extent if an optimal diameter is to be found.
10 Conclusion

A simulation model for a CO$_2$ capturing plant using MEA amines has been made, and a base case with similar parameters as a commercial regeneration plant was determined. Three parameters were varied in terms of improving the overall energy efficiency of the plant and thereby reduce operating costs. The parameters varied were the solvent circulation rate, the rich/lean heat exchanger minimum temperature approach and the desorber pressure. An economical evaluation has been performed, where investment costs were included in the calculations. In the end, the optimal values for the three parameters were included in one new model.

The thermal energy requirement in the desorber is highly dependent on the circulation rate. At low circulation rates a higher driving force in terms of steam is needed, and for high circulation rates the thermal energy required for heating of amines, the sensible heat, will be dominant. An optimum can be found, where the combination of sensible, absorption and dilution heat is at its lowest. This circulation rate was found to be 2500 ton/h and it was also this option that gave the highest net present value.

The minimum temperature approach for the rich/lean cross-flow heat exchanger has little impact on the overall energy consumption of the absorption plant. The ideal minimum temperature approach is found to be low but not too low. With a lower minimum temperature approach, the vapour fraction in the rich amine stream will be higher and the saturation pressure of the CO$_2$ in the rich amine stream will decrease. If the saturation pressure becomes too low, it will have a bad affect on the regeneration process in the desorber. An optimal temperature in terms of net present value was found for a temperature of 5°C, mainly due to the increased investment cost with a lower minimum temperature approach.

Increasing the desorber pressure can give favourable results. A higher pressure may reduce the energy consumption significantly as well as reduce the investment costs, especially for the stripper column and the CO$_2$-compressor. However, since the temperature will increase with the pressure, the temperature of the column will be a limiting factor. If the temperature becomes too high this may lead to operational problems like amine degradation and corrosion.

By including the optimal values for the three parameter variations, a sub-optimal model was made. It was found that optimizing the reboiler pressure and the circulation rate will result in a significant reduction in both investment cost and operating cost.

A fourth parameter, the absorber column diameter, was also varied in order to see the connection between the diameter and height of the column, the pressure loss through the column and the energy consumption of the absorption plant. It was found that for a packed column, the pressure loss will be low, and the gain in increased efficiency for the absorption plant due to an optimization of the absorber diameter is limited. The absorber diameter should therefore be determined based on flooding correlations rather than pressure drop.
11 Recommendations for Further Work

The temperature of the amine solution is the limiting factor for an increase in desorber column pressure as a high temperature will lead to degradation of amines and corrosion problems. Since there are many uncertainties regarding the amine behaviour at higher temperatures and pressures this should be investigated in more detail. Problems to be investigated may be the cause for the amine degradation, the optimum trade-off between additional operational problems and the reduced energy consumption, and the possibility of minimizing the degradation and corrosion problems by changing the basis for the absorption process (amine type, column material etc.).

A constant pressure for the reboiler steam was applied for all cases and made the reboiler area very large for high pressures. A similar simulation should be performed where the pressure of the steam is increased along with the stripper pressure.

The energy consumption decreases very rapidly for an increase in desorber bottom pressure up to about 2 bara before it decreases linearly and more gently for higher pressures. The reason for the shape of this graph should be investigated further.
12 References

Appendix A: Base Case Data

**Flue Gas Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>100°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.013 bara</td>
</tr>
<tr>
<td>Mass flow</td>
<td>2.471×10^4 kg/h</td>
</tr>
<tr>
<td>Composition</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.060941 (mass fraction)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.743124</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.143219</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.052716</td>
</tr>
</tbody>
</table>

**Loading and Recovery**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Rich load</td>
<td>0.4559 mol/mol</td>
</tr>
<tr>
<td>Lean load</td>
<td>0.2045 mol/mol</td>
</tr>
<tr>
<td>Recovery rate</td>
<td>84.94%</td>
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</table>

**Energy Use**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Mechanical Work</td>
<td>1.441 MJ/kg CO₂</td>
</tr>
<tr>
<td>Reboiler Duty</td>
<td>4.086 MJ/kg CO₂</td>
</tr>
<tr>
<td>Duty CO₂ compression</td>
<td>0.307 MJ/kg CO₂</td>
</tr>
</tbody>
</table>

**Compressors**

**Blower**

<table>
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<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet pressure</td>
<td>1.013 bara</td>
</tr>
<tr>
<td>Outlet pressure</td>
<td>1.073 bara</td>
</tr>
<tr>
<td>Duty</td>
<td>5.74 MW</td>
</tr>
<tr>
<td>Adiabatic efficiency</td>
<td>75%</td>
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</tbody>
</table>

**CO₂ Compressor**

<table>
<thead>
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<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Inlet pressure</td>
<td>1.672 bara</td>
</tr>
<tr>
<td>Outlet Pressure</td>
<td>80.00 bara</td>
</tr>
<tr>
<td>Stages</td>
<td>3</td>
</tr>
<tr>
<td>Duty</td>
<td>10.89 MW</td>
</tr>
<tr>
<td>Adiabatic efficiency</td>
<td>85%, 85% and 80%</td>
</tr>
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</table>
### Streams

#### Rich Amine Stream Leaving Absorber

<table>
<thead>
<tr>
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<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Temperature</td>
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</tr>
<tr>
<td>Pressure</td>
<td>1.063 bara</td>
</tr>
<tr>
<td>Mass flow</td>
<td>$2.557 \times 10^6$ kg/h</td>
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<tr>
<td>Composition (mass fraction)</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.090635</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.000008</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.000003</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.633410</td>
</tr>
<tr>
<td>MEA-amine</td>
<td>0.275944</td>
</tr>
</tbody>
</table>

#### Lean Amine Stream Entering Absorber

<table>
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<tbody>
<tr>
<td>Temperature</td>
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</tr>
<tr>
<td>Pressure</td>
<td>1.070 bara</td>
</tr>
<tr>
<td>Mass flow</td>
<td>$2.462 \times 10^6$ kg/h</td>
</tr>
<tr>
<td>Composition (mass fraction)</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.042184</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.670471</td>
</tr>
<tr>
<td>MEA-amine</td>
<td>0.287345</td>
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</table>

#### Condenser Reflux

<table>
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<tr>
<td>Temperature</td>
<td>28.15°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>6.5 bara</td>
</tr>
<tr>
<td>Mass flow</td>
<td>$7.773 \times 10^4$ kg/h</td>
</tr>
<tr>
<td>Composition (mass fraction)</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.002184</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.995596</td>
</tr>
<tr>
<td>MEA-amine</td>
<td>0.002220</td>
</tr>
</tbody>
</table>

#### Reboiler Reflux

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>122.20°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.94 bara</td>
</tr>
<tr>
<td>Mass flow</td>
<td>$1.406 \times 10^4$ kg/h</td>
</tr>
<tr>
<td>Composition (mass fraction)</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.042953</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.665379</td>
</tr>
<tr>
<td>MEA-amine</td>
<td>0.291668</td>
</tr>
</tbody>
</table>
Absorber and Stripper Tower

Stripper Tower
Internal type: Packed
Number of stages: 32
Pressure bottom: 1.862 bara
Pressure top: 1.724 bara
Rich amine inlet stage: 2 (from the top)

Absorber Tower
Internal type: Packed
Number of stages: 11
Pressure bottom: 1.063 bara
Pressure top: 1.013 bara
Lean amine inlet stage: 1 (from the top)

Heat Exchangers

Condenser
Heat exchanger model: End Point
Pressure loss cooling water: 5 bara
Pressure loss CO₂: 3% of inlet pressure
Reflux pump outlet pressure: 6.5 bara

Reboiler
Heat exchanger model: Weighted
Pressure loss Steam: 0.8 bara
Pressure loss amine stream: 0.6 bara
Reboiler duty specification: 594000000 kJ/h
Steam pressure: 4 bara
Steam temperature: 270°C

Rich/Lean Heat Exchanger
Heat exchanger model: Weighted
Pressure loss lean stream: 4 bara
Pressure loss rich stream: 4 bara
Specified pinch: 8.5°C

Lean Amine Cooler
Heat exchanger model: End point
Pressure loss cooling water: 4 bara
Pressure loss lean solvent: 5 bara
Appendix B: Non-Equilibrium Stage Model in HYSYS

Overall Material Balance

\[ F_j + L_{j-1}(L_j + SL_j) - (V_j + SV_j) = 0 \]  \hspace{1cm} (b.1)

Component Material Balance

\[ F_j x_{j0} + L_{j-1} x_{j0} + V_{j+1} y_{j+1} - (L_j + SL_j)x_j - (V_j + SV_j)y_j = 0 \]  \hspace{1cm} (b.2)

Energy Balance

\[ F_j H_f + Q_j + L_{j-1} h_{j-1} + V_{j+1} H_{j+1} - (L_j + SL_j)h_j - (V_j + SV_j)H_j = 0 \]  \hspace{1cm} (b.3)

Equilibrium Relationship

\[ \eta \xi x_{j0}(V_j + SV_j) - (V_j + SV_j)y_j + (1 - \eta) V_{j+1} y_{j+1} = 0 \]  \hspace{1cm} (b.4)
Appendix C: Difference in Investment Cost

Table C-1: Difference in investment cost for different circulation rates compared to base case of 2358 ton/h, including all equipment that differs.

<table>
<thead>
<tr>
<th>Unit</th>
<th>2200</th>
<th>2300</th>
<th>2500</th>
<th>2600</th>
<th>2700</th>
<th>2800</th>
<th>2900</th>
<th>3000</th>
<th>3250</th>
<th>3500</th>
<th>4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich amine pump</td>
<td>-0.71</td>
<td>-0.26</td>
<td>0.61</td>
<td>1.05</td>
<td>1.48</td>
<td>1.91</td>
<td>2.34</td>
<td>2.75</td>
<td>3.79</td>
<td>4.82</td>
<td>6.82</td>
</tr>
<tr>
<td>rich lean exchanger</td>
<td>-0.89</td>
<td>-0.20</td>
<td>0.71</td>
<td>1.20</td>
<td>1.27</td>
<td>2.07</td>
<td>2.45</td>
<td>2.97</td>
<td>3.93</td>
<td>4.87</td>
<td>6.94</td>
</tr>
<tr>
<td>stripper</td>
<td>1.19</td>
<td>0.22</td>
<td>-0.24</td>
<td>-0.34</td>
<td>-0.26</td>
<td>-0.07</td>
<td>-0.14</td>
<td>0.18</td>
<td>0.43</td>
<td>0.63</td>
<td>1.34</td>
</tr>
<tr>
<td>stripper condenser</td>
<td>2.06</td>
<td>0.55</td>
<td>-0.48</td>
<td>-0.64</td>
<td>-0.71</td>
<td>-0.59</td>
<td>-0.76</td>
<td>-0.57</td>
<td>-0.70</td>
<td>-0.65</td>
<td></td>
</tr>
<tr>
<td>stripper reflux pump</td>
<td>0.35</td>
<td>0.08</td>
<td>-0.11</td>
<td>-0.14</td>
<td>-0.15</td>
<td>-0.13</td>
<td>-0.16</td>
<td>-0.12</td>
<td>-0.15</td>
<td>-0.14</td>
<td></td>
</tr>
<tr>
<td>stripper reboiler</td>
<td>0.94</td>
<td>0.24</td>
<td>-0.14</td>
<td>-0.22</td>
<td>-0.17</td>
<td>-0.06</td>
<td>-0.11</td>
<td>0.10</td>
<td>0.30</td>
<td>0.44</td>
<td>0.99</td>
</tr>
<tr>
<td>lean amine pump</td>
<td>-0.79</td>
<td>-0.29</td>
<td>0.68</td>
<td>1.17</td>
<td>1.65</td>
<td>2.14</td>
<td>2.61</td>
<td>3.07</td>
<td>4.24</td>
<td>5.37</td>
<td>7.61</td>
</tr>
<tr>
<td>lean amine cooler</td>
<td>1.12</td>
<td>0.11</td>
<td>-1.43</td>
<td>-2.06</td>
<td>-2.19</td>
<td>-2.47</td>
<td>-2.68</td>
<td>-2.90</td>
<td>-3.29</td>
<td>-3.56</td>
<td>-3.43</td>
</tr>
<tr>
<td>total cost</td>
<td>3.26</td>
<td>0.46</td>
<td>-0.40</td>
<td>0.01</td>
<td>0.92</td>
<td>2.80</td>
<td>3.55</td>
<td>5.50</td>
<td>8.70</td>
<td>11.72</td>
<td>19.48</td>
</tr>
</tbody>
</table>

Table C-2: Difference in investment cost for different minimum temperature approaches compared to base case of 8.5°C including all equipment that differed.

<table>
<thead>
<tr>
<th>Unit</th>
<th>3°C</th>
<th>5°C</th>
<th>7°C</th>
<th>11°C</th>
<th>13°C</th>
<th>15°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich lean exchanger</td>
<td>4.76</td>
<td>2.04</td>
<td>0.68</td>
<td>-0.79</td>
<td>-1.25</td>
<td>-1.63</td>
</tr>
<tr>
<td>stripper condenser</td>
<td>2.84</td>
<td>1.77</td>
<td>0.75</td>
<td>-1.31</td>
<td>-2.43</td>
<td>-3.50</td>
</tr>
<tr>
<td>stripper reflux pump</td>
<td>0.20</td>
<td>0.20</td>
<td>0.10</td>
<td>0.00</td>
<td>-0.10</td>
<td>-0.10</td>
</tr>
<tr>
<td>stripper reboiler</td>
<td>0.52</td>
<td>0.33</td>
<td>0.14</td>
<td>-0.24</td>
<td>-0.44</td>
<td>-0.63</td>
</tr>
<tr>
<td>lean amine cooler</td>
<td>-0.09</td>
<td>-0.07</td>
<td>-0.03</td>
<td>0.06</td>
<td>0.11</td>
<td>0.18</td>
</tr>
<tr>
<td>total cost</td>
<td>7.70</td>
<td>3.94</td>
<td>1.50</td>
<td>-2.07</td>
<td>-3.72</td>
<td>-5.12</td>
</tr>
</tbody>
</table>
Table C-3: Difference in investment cost for different reboiler bottom pressures compared to base case of 1,862 bara including all equipment that differed.

<table>
<thead>
<tr>
<th>Unit</th>
<th>1,462</th>
<th>1,562</th>
<th>1,662</th>
<th>1,762</th>
<th>1,962</th>
<th>2,062</th>
<th>2,162</th>
<th>2,262</th>
<th>2,362</th>
<th>2,462</th>
</tr>
</thead>
<tbody>
<tr>
<td>rich lean exchanger</td>
<td>0.24</td>
<td>0.16</td>
<td>0.1</td>
<td>0.05</td>
<td>-0.05</td>
<td>-0.09</td>
<td>-0.14</td>
<td>-0.18</td>
<td>-0.22</td>
<td>-0.26</td>
</tr>
<tr>
<td>stripper condenser</td>
<td>6.29</td>
<td>4.35</td>
<td>2.5</td>
<td>1.06</td>
<td>-0.76</td>
<td>-1.21</td>
<td>-1.51</td>
<td>-1.79</td>
<td>-2.02</td>
<td>-2.23</td>
</tr>
<tr>
<td>seperator (CO₂-compression) 1</td>
<td>-0.4</td>
<td>-0.2</td>
<td>-0.2</td>
<td>-0.1</td>
<td>0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>seperator (CO₂-compression) 2</td>
<td>-0.1</td>
<td>-0.2</td>
<td>-0.1</td>
<td>-0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>stripper overhead receiver</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>stripper reflux pump</td>
<td>1.02</td>
<td>0.71</td>
<td>0.4</td>
<td>0.17</td>
<td>-0.11</td>
<td>-0.17</td>
<td>-0.21</td>
<td>-0.24</td>
<td>-0.26</td>
<td>-0.28</td>
</tr>
<tr>
<td>stripper reboiler</td>
<td>-1.16</td>
<td>-1</td>
<td>-0.82</td>
<td>-0.46</td>
<td>0.69</td>
<td>1.6</td>
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<td>3.78</td>
<td>5.02</td>
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<td>lean amine cooler</td>
<td>-0.06</td>
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<td>-0.04</td>
<td>-0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.07</td>
<td>0.07</td>
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<tr>
<td>total cost</td>
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<td>30.85</td>
<td>18.64</td>
<td>8.48</td>
<td>-7.15</td>
<td>-12.32</td>
<td>-17.33</td>
<td>-22.09</td>
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<td>-28.89</td>
</tr>
</tbody>
</table>

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<tr>
<th>Unit</th>
<th>2,562</th>
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<th>2,862</th>
<th>2,962</th>
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<th>3,162</th>
<th>3,262</th>
<th>3,362</th>
<th>3,462</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂-compressor</td>
<td>-25.85</td>
<td>-28.43</td>
<td>-31.89</td>
<td>-35.17</td>
<td>-37.23</td>
<td>-40.1</td>
<td>-42.44</td>
<td>-44.9</td>
<td>-47.46</td>
<td>-50.08</td>
</tr>
<tr>
<td>rich lean exchanger</td>
<td>-0.3</td>
<td>-0.33</td>
<td>-0.37</td>
<td>-0.41</td>
<td>-0.43</td>
<td>-0.46</td>
<td>-0.49</td>
<td>-0.52</td>
<td>-0.55</td>
<td>-0.58</td>
</tr>
<tr>
<td>seperator (CO₂-compression) 1</td>
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