Technical and Economic Assessment of Methanol Production from Biogas

MASTER’S THESIS
within
THERMAL ENERGY AND PROCESS ENGINEERING

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SYNOPSIS:
The importance of renewable fuel production has become significant in terms of supplying energy carriers for the transportation sector and storing electricity overflows from intermittent sources. Consequently, renewable methanol from electrolysis and a biogas origin is investigated. Two plant sizes have been established; farm and large scale. Three novel conceptual plant designs have been addressed and modeled through Aspen Plus®. An heat integration and economic assessment of capital and operational costs were established to estimate methanol production prices. The three designs have been subjected to a cost-optimization to minimize production costs.

It was found, that large scale methanol production is favored by economy of scale and that large plants based on partial oxidation reforming yielded the lowest cost. The methanol production price was found in the range of 418-687 USD/ton. Due to the competitive prices, the establishment of the novel schemes are projected to be an incentive to enhance biogas production. Despite the finding that methanol can be produced at competitive prices, basing a Danish methanol infrastructure entirely on synthesis of biogas is unlikely, due to low methanol conversion efficiencies.

By signing this document, each member of the group confirms that all participated in the project work and thereby all members are collectively liable for the content of the report.
Preface

This report is written during the 4th semester of the Master in Thermal Energy and Process Engineering at the Board of Studies of Energy at Aalborg University. The project was written in the period from 1st of February 2012 to 31st of May 2012. The report was supervised by Professor Søren Knudsen Kær, Associate Professor Mads Pagh Nielsen and PhD Fellow Jessica Hoffmann.

The thesis consists of several chapters describing different aspects of methanol production from biogas combined with co-electrolysis. Enclosed with the thesis is a CD with an electronic version in .pdf format of the report and the models made in Aspen Plus®.

References will appear throughout the report, and will listed in the back. The references are used according to the Harvard method, i.e. the references in the text will be given in the following way; [surname, year]. Furthermore, figures, tables and formulas are numbered according to the chapter, i.e. the first figure in Chapter 2, will be numbered 2.1, the next figure 2.2 etc. Explanatory text in attachment to figures and tables will be written below.

A nomenclature precedes the table of contents for the enclosure of all symbols and abbreviations appearing in the report. Moreover, all modeling assumptions are gathered in a list in the back of the report.
Summary

The purpose of this thesis is to address, model and assess economics of novel methanol production schemes from a biogas origin. It is envisioned, that the establishment of this Biomass To Liquid (BTL) process will enhance biogas production. The enhancement is based on creating a cost-effective alternative utilization method of biogas than combustion for co-production of heat and power. The benefits from the establishment are projected to be a reduction in Green House Gas (GHG) emissions from livestock waste and a biofuel contributor to renewable liquid energy carriers.

For the investigation, two plant sizes were chosen: A farm and a central large scale. The general production scheme assessed was based on biogas from degassed biowaste primarily in the form of animal manure. Two different biogas reforming technologies were investigated: Steam reforming (SR) and partial oxidation (POX). From a technological perspective a Solid Oxide Electrolysis Cell (SOEC) was adapted to the process schemes. The reason is, partly to improve composition of reactants for methanol synthesis and to enable a power peak shaving mechanism in a future energy system governed by intermittent power sources.

Based on a preliminary technical analysis, three different conceptual designs were addressed for further investigation. Overall process modeling of key components was accomplished in Aspen Plus®.

The feasibility of the proposed concepts was based on methanol production price, why an economic assessment was carried out. The assessment was divided into two parts; one for capital (CAPEX) and one for operational expenditures (OPEX).

A optimization routine was established upon a preceding sensitivity analysis of operational parameters to decrease the production price. The optimization parameters included both core component operational and size parameters.

From the results obtained through the technical and economic assessment the overall conclusion is, that methanol can be produced at a competitive price. The main results are shown in table 1.

<table>
<thead>
<tr>
<th>Methanol price, [USD/ton]</th>
<th>Farm scale</th>
<th>Large scale POX</th>
<th>Large scale SR</th>
<th>MNDRP (Hansen et al., 2011)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>687.03</td>
<td>418.56</td>
<td>452.57</td>
<td>459</td>
</tr>
</tbody>
</table>

Table 1: Methanol production price for the three production schemes compared to Methanex Non Discounted Reference Price (MNDRP, 28/5-2012) and [Hansen et al., 2011].
The biomass processing plant yielded the highest share of CAPEX on all three concepts. Hence, from a CAPEX point of view, enabling the possibly of producing methanol is a relatively cheap add-on investment. From a OPEX point of view the production price is highly sensitive to electricity prices, if the SOEC is a compulsory plant component.

A interesting finding was, that if the SOEC is not compulsory, the methanol production prices decrease for large scale production due to decreased OPEX. The yearly amount of produced methanol decreases especially for plants based on POX reforming. On farm scale it was found, that adapting a SOEC methanol production can be made more cost-effective.

It is evident from the work done, that all novel concepts presented have the makings of enhancing biogas production. To fully address the potential, it is recommended to evaluate especially large scale schemes in a time dependent context. Fluctuating electricity prices, seasonal district heating demand etc. have not been considered, since averaged values have been used. If electricity overproduction is allocated for Electricity To Liquid (ETL) processes for intermittent energy storage, the potential could be even higher.
## Nomenclature

<table>
<thead>
<tr>
<th>Acronym/Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pre-exponential factor</td>
<td>Varying</td>
</tr>
<tr>
<td>α</td>
<td>Relative volatility</td>
<td>[-]</td>
</tr>
<tr>
<td>A_{surface}</td>
<td>Cell surface area</td>
<td>[m^2]</td>
</tr>
<tr>
<td>AE</td>
<td>Alkaline electrolysis</td>
<td></td>
</tr>
<tr>
<td>ASR</td>
<td>Area Specific Resistance</td>
<td>[Ω · m^2]</td>
</tr>
<tr>
<td>ATR</td>
<td>Autothermal reforming</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Bottom flow rate</td>
<td>[kmol/s]</td>
</tr>
<tr>
<td>BTL</td>
<td>Biomass To Liquid</td>
<td></td>
</tr>
<tr>
<td>C_B</td>
<td>Base cost</td>
<td>[DKK]</td>
</tr>
<tr>
<td>C_C</td>
<td>Capital Cost</td>
<td>[DKK]</td>
</tr>
<tr>
<td>C_{electricity}</td>
<td>Electricity price</td>
<td>[DKK/MWhr]</td>
</tr>
<tr>
<td>C_{oxygen}</td>
<td>Cost of oxygen</td>
<td>[kr/m^3]</td>
</tr>
<tr>
<td>c_p</td>
<td>Specific heat capacity</td>
<td>[kJ/kg·K]</td>
</tr>
<tr>
<td>ć_p</td>
<td>Effective specific heat</td>
<td>[kJ/kg·K]</td>
</tr>
<tr>
<td>C_{SOEC}</td>
<td>Cost of SOEC</td>
<td>[USD/cm^2]</td>
</tr>
<tr>
<td>C_{water}</td>
<td>Cost of water</td>
<td>[kr/kg]</td>
</tr>
<tr>
<td>CAPEX</td>
<td>Capital expenditures</td>
<td></td>
</tr>
<tr>
<td>CEESA</td>
<td>Coherent Energy and Environmental Analysis</td>
<td></td>
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<tr>
<td>CH\textsubscript{3}OH</td>
<td>Methanol</td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>Methane</td>
<td></td>
</tr>
<tr>
<td>CHF</td>
<td>Combined Heat and Fuel</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
<td></td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>Carbon dioxide</td>
<td></td>
</tr>
<tr>
<td>CP</td>
<td>Heat capacity flow rate</td>
<td>[kW/K]</td>
</tr>
<tr>
<td>CSTR</td>
<td>Continuously stirred tank reactor</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Distillate flow rate</td>
<td>[kmol/s]</td>
</tr>
<tr>
<td>DKK</td>
<td>Danish currency</td>
<td></td>
</tr>
<tr>
<td>DME</td>
<td>Dimethyl Ether</td>
<td></td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct Methanol Fuel Cell</td>
<td></td>
</tr>
<tr>
<td>DT\textsubscript{min}</td>
<td>Minimum temperature difference</td>
<td>[K]</td>
</tr>
<tr>
<td>η</td>
<td>Efficiency</td>
<td>[-]</td>
</tr>
<tr>
<td>E\textsubscript{A}</td>
<td>Activation energy</td>
<td>[kJ/kmol]</td>
</tr>
<tr>
<td>E_{tn}</td>
<td>Thermo-neutral voltage</td>
<td>[V]</td>
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<td>F</td>
<td>Faraday constant</td>
<td>$96485 \text{ C/mol}$</td>
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<td>F</td>
<td>Feed flow rate</td>
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<tr>
<td>$f_M$</td>
<td>Material of construction capital cost factor</td>
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</tr>
<tr>
<td>$f_p$</td>
<td>Design pressure correction factor</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$f_T$</td>
<td>Design temperature correction factor</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$g_i$</td>
<td>Gibbs free energy</td>
<td>$[\text{J}]$</td>
</tr>
<tr>
<td>GHG</td>
<td>Green House Gases</td>
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<td>H</td>
<td>Enthalpy</td>
<td>$[\text{J/kg}]$</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Enthalpy of Reaction</td>
<td>$[\text{kJ/kmol}]$</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>Hydrogen</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{S}$</td>
<td>Hydrogen sulfide</td>
<td></td>
</tr>
<tr>
<td>HHV</td>
<td>Higher heating value</td>
<td>$[\text{MJ/kg}]$</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
<td>$[\text{A}]$</td>
</tr>
<tr>
<td>i</td>
<td>Current density</td>
<td>$[\text{A/cm}^2]$</td>
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<tr>
<td>$I_{\text{annual}}$</td>
<td>Annualized investment cost</td>
<td>$[\text{DKK/year}]$</td>
</tr>
<tr>
<td>$I_{\text{total}}$</td>
<td>Total investment cost</td>
<td>$[\text{DKK}]$</td>
</tr>
<tr>
<td>ICE</td>
<td>Internal Combustion Engine</td>
<td></td>
</tr>
<tr>
<td>IR</td>
<td>Interest rate</td>
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<td>Adsorption constant</td>
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<td>Driving force constants</td>
<td>Varying</td>
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<td>Specific heat ratio</td>
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<tr>
<td>$K_{\text{EQ}}$</td>
<td>Equilibrium Constant</td>
<td>Varying</td>
</tr>
<tr>
<td>L</td>
<td>Length of reactor</td>
<td>$[\text{m}]$</td>
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<tr>
<td>$\lambda$</td>
<td>Oxidizer to fuel ratio</td>
<td>$[-]$</td>
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<tr>
<td>LCFA</td>
<td>Long Chain Fatty Acids</td>
<td></td>
</tr>
<tr>
<td>LHHW</td>
<td>Langmuir-Hinshelwood Hougen Watson</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>Module/Stoichiometric number</td>
<td>$[-]$</td>
</tr>
<tr>
<td>M</td>
<td>Component specific exponent</td>
<td>$[-]$</td>
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<tr>
<td>$\dot{m}$</td>
<td>Mass flow</td>
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<td>MeOH</td>
<td>Methanol</td>
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<td>MNDRP</td>
<td>Methanex Non Discounted Reference Price</td>
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<tr>
<td>$\dot{n}$</td>
<td>Molar flow</td>
<td>$[\text{kmol/s}]$</td>
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<tr>
<td>NH$_3$</td>
<td>Ammonia</td>
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<td>O$_2$</td>
<td>Oxygen</td>
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</tr>
<tr>
<td>OP$_{hr}$</td>
<td>Hours of operation</td>
<td>$[\text{hr/year}]$</td>
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<tr>
<td>OPEX</td>
<td>Operational expenditures</td>
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</tr>
<tr>
<td>p</td>
<td>Purge fraction</td>
<td>$[-]$</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
<td>$[\text{bar}]$</td>
</tr>
<tr>
<td>p</td>
<td>Partial pressure</td>
<td>$[\text{bar}]$</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>Pressure change</td>
<td>$[\text{bar}]$</td>
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<th>Description</th>
<th>Unit</th>
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<tr>
<td>Pel</td>
<td>Electrical power consumption</td>
<td>[W]</td>
</tr>
<tr>
<td>PEME</td>
<td>Polymer Exchange Membrane Electrolysis</td>
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</tr>
<tr>
<td>POX</td>
<td>Partial oxidation</td>
<td></td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure Swing Adsorption</td>
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</tr>
<tr>
<td>$\dot{Q}$</td>
<td>Heat flow</td>
<td>[W]</td>
</tr>
<tr>
<td>q</td>
<td>Mole fraction of liquid in the feed</td>
<td>[-]</td>
</tr>
<tr>
<td>$Q_B$</td>
<td>Base capacity</td>
<td>[ton]</td>
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<tr>
<td>$Q_C$</td>
<td>Component capacity</td>
<td>[ton]</td>
</tr>
<tr>
<td>r</td>
<td>Reaction rate</td>
<td>[mol/kg·s]</td>
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<tr>
<td>R</td>
<td>Gas constant</td>
<td>$8.314 \text{ J/mol·K}$</td>
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<tr>
<td>R</td>
<td>Reflux flow rate</td>
<td>[mol/s]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>[kg/m$^3$]</td>
</tr>
<tr>
<td>$r_1$</td>
<td>Outer radius of reactor</td>
<td>[m]</td>
</tr>
<tr>
<td>$r_2$</td>
<td>Inner diameter of reactor</td>
<td>[m]</td>
</tr>
<tr>
<td>ROL</td>
<td>Rectifying operation line</td>
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<tr>
<td>RR</td>
<td>Reflux ratio</td>
<td>[-]</td>
</tr>
<tr>
<td>S/R</td>
<td>Steam to carbon ratio</td>
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</tr>
<tr>
<td>SOE</td>
<td>Solid Oxide Electrolysis</td>
<td></td>
</tr>
<tr>
<td>SOEC</td>
<td>Solid Oxide Electrolysis Cell</td>
<td></td>
</tr>
<tr>
<td>SOL</td>
<td>Stripping operation line</td>
<td></td>
</tr>
<tr>
<td>SQP</td>
<td>Sequential Quadric Programming</td>
<td></td>
</tr>
<tr>
<td>SR</td>
<td>Steam reforming</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>t</td>
<td>Reactor wall thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>Temperature change</td>
<td>[K]</td>
</tr>
<tr>
<td>$t_e$</td>
<td>Investment payback time</td>
<td>[year]</td>
</tr>
<tr>
<td>v</td>
<td>Specific</td>
<td>$[m^3]$</td>
</tr>
<tr>
<td>$\dot{V}$</td>
<td>Volume flow</td>
<td>$[m^3/s]$</td>
</tr>
<tr>
<td>VFA</td>
<td>Volatile fatty acid</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>Catalyst weight</td>
<td>[kg]</td>
</tr>
<tr>
<td>w</td>
<td>Weight of tubular reactors</td>
<td>[kg]</td>
</tr>
<tr>
<td>$w_{\text{comp}}$</td>
<td>Compressor work</td>
<td>[W]</td>
</tr>
<tr>
<td>$w_{\text{pump}}$</td>
<td>Pump work</td>
<td>[W]</td>
</tr>
<tr>
<td>WGS</td>
<td>Water Gas Shift</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>Molar fraction</td>
<td>[-]</td>
</tr>
<tr>
<td>$x$</td>
<td>Molar fraction of a component in liquid phase</td>
<td>[-]</td>
</tr>
<tr>
<td>y</td>
<td>Molar fraction of a component in vapor phase</td>
<td>[-]</td>
</tr>
<tr>
<td>z</td>
<td>Number of electrons</td>
<td>[-]</td>
</tr>
<tr>
<td>z</td>
<td>Mole fraction</td>
<td>[-]</td>
</tr>
</tbody>
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Introduction

1.1 Motivation

Towards the realization of a fossil free society, the energy supply and infrastructure are facing major challenges. If all fossil energy resources are to be phased out, the interaction between continuous and intermittent renewable resources must be optimized.

Combining an increasing penetration of intermittent renewables for electrical power production, with the existing power production could lead to periodic electricity overflows. These overflows are in worst case wasted, if they cannot be stored. [Jørgensen and Ropenus, 2008] states, that below a level of 20 % penetration of wind power in Denmark, the balancing between supply and demand can be controlled by conventional power plants. Above a level of 20 % the balancing must be done by export and/or additional balancing loads. In figure 1.1 the wind share development in the Danish power production is shown. It is evident that the threshold of 20 % has already been reached, and it is projected by [EnergiStyrelsen, 2011] that the wind share will increase to levels around 30 % already by 2015.

One way of balancing the demand and supply is to store the electricity overflows by generating hydrogen (H₂) in an electrolysis unit, which can be stored and later used in e.g. fuel cell applications. To obtain a good

Figure 1.1: Electricity production from distributed co-generation and wind power and their shares of total annual electricity production. Denmark 1972-2010. [Blarke, 2011]
1.1 Motivation

Volumetric energy density the hydrogen needs to be compressed to high pressures, be liquefied or absorbed on some solid material by physisorption or chemisorption. Since compression and liquefaction of hydrogen is very energy demanding, the conversion of electricity to hydrogen for storage has a poor efficiency. The absorption technologies have a higher volumetric energy density than both compressed and liquefied hydrogen [Olah et al., 2009]. One of the drawbacks of absorption is, that only 1-3% of the absorbent weight is usable hydrogen, why considerable extra weight is added to the storage system. This is undesirable especially for transportation purposes. Add the storage issues to the fact, that the whole infrastructure must be redesigned for a hydrogen society. This as a solution for a fossil free society is still facing major technological challenges.

Another storage possibility for energy storage is batteries, which are the ideal storage media for electricity with a high storage efficiency. Therefore, it might seem obvious to store the electricity overflow in large batteries. However, it is estimated that the price of storing the electrical overflows in 2050 is around 300 DKK/kWh, which will lead to a total price of 1000 billion DKK for a storage capable of handling the electricity fluctuations [Energinet.dk, 2011].

A third possibility proposed by the CEESA group [CEESA, 2011] and the Danish Methanol Association is by ETL (Electricity To Liquid) processes. Here unfavorable intermittent electricity is stored through utilization of electrolysis to produce syngas, which can be synthesized into energy liquids like methanol. Methanol as an energy carrier possesses several advantages. Since methanol is a liquid at atmospheric pressure, it can easily be stored in the same manner as gasoline and diesel with an volumetric energy density of roughly half of the energy content in gasoline and diesel.

The key challenge towards the realization of a fossil free society is the establishment of alternative fossil free fuels in the transport sector. Among the candidates, methanol in particular, seems to have a bright future. Firstly, the production of methanol is a well-established process and can be produced by synthesis from several renewable feed stocks e.g. biogas or diverse biomass sources. Secondly, methanol can easily be reformed into a hydrogen-rich syngas, from which multiple other compounds can be produced. Thirdly, methanol can almost directly be used as a substitute for gasoline or upgraded to DME as a substitute for diesel. Lastly, in a future transport sector predicted to be governed by fuel cells, methanol may play a significant role. Methanol is a promising high energy density hydrogen carrier, which through reforming can be used as a feed for hydrogen powered fuel cells or by direct conversion in DMFCs (Direct Methanol Fuel Cells). This means, that the existing infrastructure can be retrofitted to the use of methanol [Nowell, 1994].

A recently published report states, that methanol can be produced at the cost of current oil equivalents [Hansen et al., 2011] by combining ETL and BTL (Biomass To Liquid) processes. The methanol production scheme, based upon gasification of wood pellets, is combined with hydrogen or syngas production from electrolysis, which essentially can store periodic electrical overflows in liquid energy carriers. The plant combination with electrolysis results in a high methanol yield compared to traditional biomass based methanol plants.

However, the production scheme suffers from several issues. In 1989 it was decided by the Danish Parliament, that the forest area must be doubled by 2089, which may lead to the circumstances, that wood for gasification must be imported from neighboring countries. This in fact could lead to issues regarding the security of energy supply, and the price on imported biomass is highly uncontrollable. It was estimated, that over one third of the
annually operational expenditures is attributed to wood import. Therefore, even small variations in the biomass price can seriously affect the methanol production price. Also, the high methanol yield is dependent on the electrolysis and therefore on the electricity price. In fact, yet another third of the annual operating expenditures is represented by electricity consumption. These issues could perhaps be discarded, if other means of biomass are provided. Furthermore, the mentioned production price is dependent on several other factors like: process steam is already available, excess oxygen and heat can be sold etc.

Denmark is a country with a high animal density, which ultimately also leads to an abundant source of biomass mainly in the form of livestock slurry. Unfortunately, livestock slurry is not only a source of biomass but also a major contributor to Green House Gases (GHG) primarily due to formation of methane (CH\textsubscript{4}) and dinitrogen oxide (N\textsubscript{2}O). To reduce these GHG emissions, slurry management in the form of biogas production has been proposed as one of the best techniques for the purpose [Astrup et al. 2011].

In Denmark 20 large scale and 50-60 farm scale biogas plants are utilizing some of the biomass waste from the industry, manure, sewage plants etc. The Danish biogas potential is illustrated in the figure below by the blue columns.

![Biogas potential in Denmark](image)

*Figure 1.2: Biogas potential in Denmark (blue column) and utilized biogas in 2008 (red column) [EnergiStyrelsen, 2010].*

From figure 1.2 it is evident, that the main potential in Danish biogas production is in the utilization of manure from livestock animals, which holds 67% of the total potential. In total a biogas potential of 40 PJ was available in 2008, however only 4 PJ was utilized as indicated by the red columns. Due to the poor utilization, there is a large unused potential in biogas production and in the reduction of GHGs. The figure does not consider straw or any form of energy crops, which consequently will lead to an even higher biogas potential. Several initiatives have been taken in order to utilize more of the biogas potential. One of the main purposes of the “Green Growth”-agreement (Grøn Vækst aftalen) is to reduce the emissions in the agriculture by transforming up to 50% of the unused biomass into green energy by 2020.
Yet another issue arising for the biogas potential utilization is the fact, that all biogas produced today is combusted in gas engines for co-generation. Increasing the biogas production by co-generation will further increase power overflows in the future. Moreover, in order to obtain reasonable feasibility for the biogas plants, it has been a precondition, that the produced heat can be sold as district heating, when no notable heat is used in the production buildings [Hansen et al., 2011]. However, especially for farm scale biogas plants, often the production of heat exceeds the demand and thereby the biogas plants become infeasible, when the biogas is directly combusted. If the biogas utilization changes to e.g. methanol production, it could make up the incentive for establishing more biogas plants both on a farm and large scale.

Besides the large unused potential, biogas has a similar gas composition to natural gas and therefore holds the opportunity for storage in the existing natural gas network. By doing so the dependence between local production and consumption vanishes. Additionally, methanol can be produced from natural gas, why this similarity also introduce the opportunity for methanol production from biogas. Combining the methanol production scheme with the storage opportunity may lead to the advantage, that the methanol production yield is less dependent on electricity prices than when using wood pellets.

Finally, by the utilization of biogas combined with syngas generation from electrolysis introduces the possibility of poly-generation in form of heat, power and fuels.

### 1.2 Objectives

The aim of this thesis is to contribute with knowledge about alternative utilization of biogas from agricultural biowaste in the sense of pig and cattle manure, in contrast to direct combustion for district heating. The overall target of the project is to investigate, the feasibility of producing synthetic fuels in the form of methanol from production schemes based on traditional biogas production combined with electrolysis for high carbon utilization. Thereby, increasing the utilization of biogas and at the same time create a potential wind power peak shaving mechanism by a ETL process.

The more specific targets are:

- Investigate possible production schemes for both farm and large scale biogas plants.
- Develop overall process models for methanol production and identify the most sensitive parameters involved in the process.
- Do an economic assessment of the core components both in terms of investment and operational costs, to be able to estimate the methanol production price.
- Evaluate the feasibility of methanol production from biogas on farm and large scale levels.

### 1.3 Methodology

The following steps will be carried out for the achievement of the mentioned targets:

- Perform a technological description of system components.
• Through the technological description, develop conceptual process designs.
• Model the conceptual process designs in Aspen Plus® for process simulation.
• Perform a cost optimization of the process schemes to minimize production costs.
• Do a heat integration analysis to address needs for external utilities and possibilities for sales of district heating.

In Chapter 2 the plant size configurations will be presented together with the input feed for the different configurations. The assumptions presented in this chapter will be maintained throughout the report and therefore hold the basis for e.g. the biogas yield, the technical and economic assessment etc.

A short introduction to the Danish natural gas system and the aspects of cleaning and upgrading biogas to natural gas standards are given in Chapter 3.

Chapter 4 gives a short introduction to methanol and some general production perspectives. Biogas reforming is investigated from equilibrium models of steam and partial oxidation reforming and factors for high carbon utilization are examined.

The novel methanol production schemes to be assessed are presented in Chapter 5. These conceptual designs are the ones making up the basis for the methanol price estimations. The process schemes here presented are modeled in Aspen Plus®.

Chapter 6 presents the basic modeling assumptions of the core components present in the process scheme. Detailed modeling of the core components is given in Appendix A on page 101.

For the addressing of sensitive core component operational parameters, a sensitivity analysis is carried out in Chapter 7. The observations will be used as guide lines for the following process scheme optimization.

In Chapter 8 a short description to the optimization algorithm will be given. Afterwards the optimization parameters, their bounds and the objective function will be outlined.

Chapter 9 presents the heat integration analysis of the given process schemes. The heat integration analysis is used for calculating additional operational costs and sales.

The economic assessment is outlined in Chapter 10. All assumptions, the methodology for calculating investment and operational costs etc. are described.
1.3 Methodology

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1. Introduction
In this chapter the plant configurations will be described. These will be determining for the input biomass compositions and the amount of biogas to be processed. Firstly, to understand the conversion of biomass into biogas, the process will be described in short terms.

2.1 Biogas Production

Biogas is formed from anaerobic breakdown of organic material. The composition of biogas is dominated by \( \text{CH}_4 \) (55-70 %) and \( \text{CO}_2 \) (30-45 %) and some traces of \( \text{H}_2, \text{H}_2\text{S} \) and \( \text{NH}_3 \) (1-2 %). The \( \text{CH}_4 \) production is highly dependent on the type of organic material decomposed. If the organic material is rich in carbohydrates the \( \text{CH}_4 \) production is low, whereas if the organic material consists mainly of fats, the \( \text{CH}_4 \) production is high [Jørgensen, 2009].

In table 2.1 examples of the overall yields for total degradation of carbohydrates (cellulose and hemicellulose), proteins and fats are shown per kilo of biomass added. It is evident, that the degradation of fats provides the highest output of \( \text{CH}_4 \), over twice the amount of both carbohydrates and proteins.

<table>
<thead>
<tr>
<th>Organic material</th>
<th>L biogas/kg</th>
<th>L ( \text{CH}_4 )/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbohydrate</td>
<td>830</td>
<td>415</td>
</tr>
<tr>
<td>Proteins</td>
<td>793</td>
<td>504</td>
</tr>
<tr>
<td>Fats</td>
<td>1440</td>
<td>1014</td>
</tr>
</tbody>
</table>

*Table 2.1: Yield of biogas and \( \text{CH}_4 \) at total degradation of carbohydrates, proteins and fats [Jørgensen, 2009].*

The production of biogas from biomass is a complex degradation process in four phases named hydrolysis, acidogenesis, acetogenesis and methanogenic [Deublein and Steinhauser, 2008]. Most often the biogas reactor is a continuously stirred tank reactor (CSTR), where the biomass, in form of a mixture of manure, organic industrial waste etc. is pumped into the tank continuously. Bacteria are added to the reactor to act as a catalyst to speed up the four phases. Since some of the bacteria are obligatory anaerobic, it is important, that the reactor tank is sealed properly [Jørgensen, 2009].

In the hydrolysis process a breakdown of fats, carbohydrates and proteins into monomers occurs. The hydrolysis degradation time of the organic substance varies depending on the composition. The hydrolysis of proteins and fats takes a few days, whereas the degradation of carbohydrates only takes a few hours [Jørgensen, 2009]. Some substances like lignin and lignocellulose do not degrade or only degrade very slowly. Because some of
the cellulose and hemicellulose in plants is enclosed in lignin, the bacteria are unable to reach them. Therefore, only about 65% of the cellulose and hemicellulose in pig manure can be transformed into biogas.

In the acidogenic phase the monomers from the hydrolysis phase are decomposed by different facultative and obligatory anaerobic bacteria, into long chain fatty acids (LCFA) and volatile fatty acids (VFA). For a well-balanced process, 50% of the monomers and LCFA's are converted into acetic acid, 20% into $\text{H}_2$ and $\text{CO}_2$ and 30% to other VFA than acetic acid. In this process the partial pressure of $\text{H}_2$ is important, since the amount of reduced compounds is decreased with increasing $\text{H}_2$ partial pressure.

The bacteria in the acetogenic phase use the $\text{H}_2$ and $\text{CO}_2$ from the acidogenic phase to produce acetic acid.

In the last phase bacteria are added to create $\text{CH}_4$. They decompose the acetic acid to $\text{CH}_4$ and $\text{CO}_2$. The bacteria growth in the methanation phase is slower than both the hydrolysis and acidification phase; hence the methanation bacteria are the limiting bacteria of the $\text{CH}_4$ production [Deublein and Steinhauser, 2008].

The degree of degradation varies depending of the organic substance as shown in table 2.2. The rate of degradation is shown under normal process conditions. It is strongly dependent on the retention time in the reactor, and a total degradation of the biomass will often take very long time.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Degree of degradation, [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proteins</td>
<td>47</td>
</tr>
<tr>
<td>Fats</td>
<td>69</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>65</td>
</tr>
<tr>
<td>Cellulose</td>
<td>69</td>
</tr>
</tbody>
</table>

*Table 2.2: Degree of degradation under typical process conditions.*

Due to the high complexity of the degradation mechanisms, no further attention will be given to the biogas production mechanisms in this project. From now only the inputs and the outputs of the biogas tank are of concern. The dry matter compositions and biogas yields for different types of biomass are adopted from Pedersen et al. [2010] and shown in table 2.3. It must be noted, that the gas yield results are obtained from laboratory tests lasting for 90 days, why the yield may be higher than usual production.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Dry matter [%]</th>
<th>Gas yield Biogas/tonnes raw material [m$^3$/MT]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pig slurry</td>
<td>4.5</td>
<td>17.7/17.8</td>
</tr>
<tr>
<td>Cattle slurry</td>
<td>8.0</td>
<td>22.7/22.8</td>
</tr>
<tr>
<td>Manure fiber, pig</td>
<td>30.0</td>
<td>108/102</td>
</tr>
<tr>
<td>Manure fiber, cattle</td>
<td>30.0</td>
<td>101/95</td>
</tr>
<tr>
<td>Corn ensilage</td>
<td>29.0</td>
<td>177/180</td>
</tr>
</tbody>
</table>

*Table 2.3: Raw material, dry matter content and gas yield at mesophil / thermophil conditions.*
2.2 Plant Configuration

Regarding the biogas production capacity, it has been decided to follow two of the presented plant sizes and input compositions from [Pedesen et al., 2010]. The first one presented is a local farm scale size biogas plant with a biomass input of 18,500 MT/year. The second is a central large scale biogas plant with a biomass input of 500,000 MT/year.

From an economical point of view, digestion of only animal slurry is often infeasible, due to low CH₄ yields, as a consequence of the low amount of easily degradable carbon [Astrup et al., 2011]. Consequently, additional waste products, industrial waste, energy crops etc. are co-digested with the slurry to increase the carbon content. Corn ensilage is used as a supplement for farm scale. The input parameters for the farm scale case are shown in table 2.4.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Dry matter [%]</th>
<th>Quantity [MT/year]</th>
<th>Quantity share [%]</th>
<th>Biogas Share [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pig slurry</td>
<td>4.5</td>
<td>15,000</td>
<td>81</td>
<td>30</td>
</tr>
<tr>
<td>Corn ensilage</td>
<td>29.0</td>
<td>3,500</td>
<td>19</td>
<td>70</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>18,500</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

*Table 2.4: Input data for the farm scale size.*

As the amount of slurry increases, the availability and transportation of the supplements could turn out to be an issue. As an alternative to the supplements, slurry-separation into a dry (manure fibers) and liquid fraction is an option. Here the liquid fraction can be directly used as a fertilizer, and the manure fibers can substitute raw slurry to increase the biogas yield. This scenario is assumed for the large scale, for which the input parameters are shown in table 2.5.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Dry matter [%]</th>
<th>Quantity [MT/year]</th>
<th>Quantity share [%]</th>
<th>Biogas Share [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pig slurry</td>
<td>4.5</td>
<td>275,000</td>
<td>55</td>
<td>27</td>
</tr>
<tr>
<td>Cattle slurry</td>
<td>8.0</td>
<td>150,000</td>
<td>30</td>
<td>19</td>
</tr>
<tr>
<td>Manure fiber, pig,</td>
<td>28.0</td>
<td>25,000</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>chemical settling</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manure fiber, pig,</td>
<td>30.0</td>
<td>25,000</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>decanter centrifuges</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manure fiber, cattle</td>
<td>29.0</td>
<td>25,000</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>500,000</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

*Table 2.5: Input data for the central large scale size.*

The biogas yield from the farm and large scale plants can be calculated from table 2.3 on the preceding page, 2.4 and 2.5. The results are presented in table 2.6 on the following page.
2.2 Plant Configuration

Table 2.6: Biogas yield and composition at mesophil / thermophil condition. The biogas produced consists of 65% CH$_4$ and 35% CO$_2$.

<table>
<thead>
<tr>
<th>Scale</th>
<th>Biogas, [m$^3$/year]</th>
<th>CH$_4$, [m$^3$/year]</th>
<th>CO$_2$, [m$^3$/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farm Scale</td>
<td>885,000 / 897,000</td>
<td>575,250 / 583,050</td>
<td>309,750 / 313,950</td>
</tr>
<tr>
<td>Large Scale</td>
<td>17,920,000 / 15,610,000</td>
<td>11,648,000 / 10,146,500</td>
<td>6,272,000 / 5,463,500</td>
</tr>
</tbody>
</table>

2.2.1 Energy Consumption for Biogas Production

To estimate the price for methanol production, the energy consumption for biogas production needs to be stated. The heat consumption for both plant sizes will be based on heating the input biomass to the operational temperature of the biotank. This means, that if the biotank is operating at mesophil or thermophil conditions, the biomass must be heated to 310 [K] or 325 [K], respectively.

Regarding the power consumption, only the large scale plant will be dealt with, since a separation unit is needed for the slurry separation. According [Astrup et al., 2011], the internal electricity consumption from the separation unit corresponds to 5% of the net electricity production, provided that all biogas is combusted with an electrical efficiency of 40% and a heat efficiency of 46%. To calculate the electricity consumption for separation a HHV of 55 MJ/kg is used.
It was mentioned in the motivation, that biogas holds the opportunity for storage and distribution in the existing natural gas network. To be able to utilize these opportunities, requirements for the gas quality, injection pressure etc. need to be known. In this chapter, a short presentation to the Danish natural gas system will be given together with gas quality requirements. Finally, a description of upgrading and cleaning technologies to reach these requirements will be given.

3.1 The Danish Natural Gas Network

The Danish natural gas network consists of four different networks; transmission lines, allocation lines, distribution lines and service lines. The transmission lines are the main supply lines, transmitting natural gas at 80 bar from the offshore fields to land side for regional distribution and across national borders. M/R-stations reduce the transmission line pressure to 19-50 bar for transmission in the allocation lines, transmitting gas for urban areas or for industrial and power production usage. At these stations odorants are added to the natural gas to ease leakage detection. Finally, the pressure is reduced to 4-7 bar in the distribution and service lines for private end users.

![Danish natural gas network](Dansk Gasteknisk Center 2009)

It is obvious, that the closer to the end users the upgraded biogas is to be injected, the lower operational costs, as a consequence of the lower injection pressure. On the other hand, the less potential end users exist for the injected biogas. Another issue which must be considered is overproduction when considering the point of injection. Besides the two existing gas deposits in Denmark, small amounts of overproduction can be stored in the gas network, known as linepack, by increasing network pressure. But, if the overproduction exceeds the
3.2 Upgrading and Clean up of Biogas

storage capacity the gas must be flared. By injecting the gas close to the end users, it can be assumed that risk of flaring is higher.

Today, only one upgrading facility exists in Denmark. One of the reasons for this is caused by the way governmental subsidies for biogas have been allocated. Since Danish biogas production relies on direct combustion, subsidies have until recently only been allocated for co-generation biogas utilization. For upgrading of biogas to be feasible the current political framework conditions concerning subsidies must be changed from a utilization perspective to a production perspective.

3.2 Upgrading and Clean up of Biogas

If the biogas is to be distributed in the existing natural gas network or reformed into a syngas, it must be upgraded and cleaned. The upgraded biogas is sometimes referred to as bio-natural gas or bio-methane because the purity of CH$_4$ is high. From a distribution perspective several requirements of the distributed gas are directed by The Danish Safety Technology Authority. The upgrading process involves CO$_2$ removal in order to meet the required specification regarding a lower heating value (Wobbe-index), and the clean up process includes removal of toxic and corrosive species. Regarding the Wobbe-index, removal of CO$_2$ results in a bio-natural gas, which just exceeds the lower limit of the Wobbe-index. Occasionally, propane is added to ensure an acceptable heating value. Some of the specifications for the bio-natural gas are presented in table 3.1. The lower value of the Wobbe-index corresponds to an upgraded biogas with a CH$_4$ fraction of 97.3 % on a volume basis [Jensen, 2009].

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wobbe-index</td>
<td>50.8-55.8 [MJ/m$^3$]</td>
</tr>
<tr>
<td>CO$_2$ content</td>
<td>&lt;2.5 [%]</td>
</tr>
<tr>
<td>O$_2$ content</td>
<td>&lt;0.1 [%]</td>
</tr>
<tr>
<td>H$_2$S and COS content</td>
<td>&lt;5 [mg/m$^3$] (6 ppm)</td>
</tr>
</tbody>
</table>

*Table 3.1: Requirements for natural gas to be distributed in the natural gas network.*

Biogas produced from manure has a high content of hydrogen sulphides (H$_2$S) [Jørgensen, 2009], which can cause corrosion in the upgrading equipment and degradation in catalyst activity. Therefore, a desulfurization step is necessary prior to upgrading and reforming. Some different clean up technologies are presented in table [3.2 on the facing page] which are divided into primary and precision desulfurizers depending on the output concentration. For distribution and for later reforming of the biogas a precision desulfurizer is needed to meet the sulfur requirements.

After the clean up step, CO$_2$ must be removed from the mixture. The different upgrading technologies differ in the physical way CO$_2$ is captured. A general division of upgrading technologies is given in figure [3.3 on the next page] [Beil and Hoffstede, 2010].
### Figure 3.2: Different cleaning technologies [Beil and Hoffstede 2010].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Internal biological H2S reduction (In the digester)</td>
<td>50 - 200 ppm</td>
<td>Yes</td>
<td>Internal</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>External biological H2S reduction (Out of the digester in a sprinkling filter)</td>
<td>50 - 200 ppm</td>
<td>Yes</td>
<td>External</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Combination of external biological H2S reduction with lye scrubber</td>
<td>20 - 100 ppm</td>
<td>Yes</td>
<td>External</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Chemical precipitation using iron salts (Sulphide precipitation)</td>
<td>100 - 150 ppm</td>
<td>No</td>
<td>Internal</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Chemical precipitation using iron hydroxide</td>
<td>100 - 150 ppm</td>
<td>No</td>
<td>Internal</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Iron oxide or iron hydroxide (In an external column)</td>
<td>&lt; 1 ppm</td>
<td>Yes</td>
<td>External</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Adsorption / catalytic oxidation using impregnated activated carbon</td>
<td>&lt; 1 ppm</td>
<td>Yes</td>
<td>External</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Zinc oxide</td>
<td>&lt; 1 ppm</td>
<td>No</td>
<td>External</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

- Adsorption, the different adsorptivities of the gas mixture components are utilized. For pressure swing adsorption CO2 is captured on the surface of a third body i.e. activated carbon.

- By absorption, CO2 is captured in the bulk of a third body, regularly water or a liquid organic solvent. Physical absorption technologies, which include water scrubbing, are like the adsorption technologies carried out at elevated pressure. Oppositely, the chemical absorption technologies are carried out at near standard pressure but proceed at elevated temperatures.

- Permeation is the utilization of selective membranes and is often divided by high or low pressure technologies depending on the dryness of the mixture.

---

3. Biogas Distribution and Storage
In cryogenics the difference in dew points of the different species is utilized. In [Beil and Hoffstede, 2010] the above mentioned CO₂ removal technologies are described and estimates on the required power inputs are presented. This is shown in figure 3.4. Additionally, some specific operational parameters and requirement for different technologies are presented in table 3.2.

![Figure 3.4: Upgrading energy demands for a plant capacity of 250 m³/h.](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PSA</th>
<th>Water scrubbing</th>
<th>Organic physical scrubbing</th>
<th>Chemical scrubbing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-cleaning needed</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Working pressure, [bar]</td>
<td>4-7</td>
<td>4-7</td>
<td>4-7</td>
<td>Standard</td>
</tr>
<tr>
<td>CH₄ loss</td>
<td>&lt;3 % / 6-10 %&lt;sub&gt;1&lt;/sub&gt;</td>
<td>&lt;1 % / &lt;2 %&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2-4 %</td>
<td>&lt;0.1 %</td>
</tr>
<tr>
<td>CH₄ content in upgraded gas</td>
<td>&gt;96 %</td>
<td>&gt;97 %</td>
<td>&gt;96 %</td>
<td>&gt;99 %</td>
</tr>
<tr>
<td>Electricity consumption, [kWh/Nm³]</td>
<td>0.25</td>
<td>&lt;0.25</td>
<td>0.24-0.33</td>
<td>&lt;0.15</td>
</tr>
<tr>
<td>Heat requirement [K]</td>
<td>No</td>
<td>No</td>
<td>328-353</td>
<td>433</td>
</tr>
<tr>
<td>Controllability compared to nominal load</td>
<td>10-15 %</td>
<td>50-100 %</td>
<td>10-100 %</td>
<td>50-100 %</td>
</tr>
</tbody>
</table>

Table 3.2: Different upgrading technologies. 1) <3 % CarboTech / 6–10 % QuestAir, 2) < 1 % Malmberg / <2 % Flotech. [Petersson and Weelinger, 2009]

The different upgrading technologies differ significantly in their power input. All of the technologies are dependent on electricity, for which all technologies but chemical absorption is used to pressurize the system, why chemical absorption also yields the lowest electricity requirement. The lowest electricity requirement for the chemical absorption technology is accompanied by the highest heat input.

According to [Jensen, 2009], the power consumption for PSA and water scrubbing accounts for roughly 4 % and 0.5 % of the energy content in the raw biogas.
The heat consumption for chemical absorption accounts for about 7 % of the energy content of the raw biogas.

Which technology is the most suitable dependents on the application, total system in question i.e. excess heat or electricity, availability, economics etc. This will further be discussed in Chapter 10 on page 61.
3.2 Upgrading and Clean up of Biogas
It has been emphasized in the introduction, that the project aims to investigate the production of synthetic fuels in the form of methanol from biogas. As an initiation, this chapter gives a short introduction to methanol followed by a search for methanol production schemes.

Methanol has been proven an attractive compound both as a direct fuel for the fuel cell and automotive industry. Today, it is mainly used as a feedstock for chemical synthesis for the production of various compounds as illustrated in figure 4.1. Methanol can be produced from fossil resources such as coal, oil and natural gas or by conversion of biomass. Today, more than 75 % of the methanol produced is based on a natural gas origin. Common for all resources is the intermediate production of syngas, which is synthesized into methanol.

Methanol demand in 2007 [Olah et al., 2009].

Methanol is not an energy source but an energy carrier with a higher heating value of approximately 23 MJ/kg. The energy content is only half of common transportation fuels like gasoline and diesel as shown in table 4.1 [on the following page] However, the high octane number of methanol causes the mileage of ICE-driven vehicle comparable to conventional fuels, due to higher compression ratios. Especially for the transportation sector, the major issue is an energy carrier problem not an energy problem [Danish Methanol Association 2011].

Methanol is a liquid at standard conditions and can be retrofitted to the existing transportation sector, either as a blend or as a complete substitute. The many advantages of methanol have made the phrase methanol economy, proposed by several authors [Olah et al. 2009].
4.1 Methanol Production

<table>
<thead>
<tr>
<th>Fuel</th>
<th>HHV MJ/kg</th>
<th>LHV MJ/kg</th>
<th>Density kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>22.9</td>
<td>20.1</td>
<td>794</td>
</tr>
<tr>
<td>Dimethyl ether (DME)</td>
<td>31.7</td>
<td>28.9</td>
<td>665</td>
</tr>
<tr>
<td>Ethanol</td>
<td>29.8</td>
<td>27.0</td>
<td>789</td>
</tr>
<tr>
<td>Gasoline, conventional</td>
<td>44.9</td>
<td>44.9</td>
<td>745</td>
</tr>
<tr>
<td>Diesel, conventional</td>
<td>46.5</td>
<td>43.4</td>
<td>837</td>
</tr>
<tr>
<td>Diesel, Fisher-Tropsch</td>
<td>45.5</td>
<td>43.2</td>
<td>797</td>
</tr>
</tbody>
</table>

*Table 4.1:* Various fuels are their heating values.

Worldwide, methanol is produced by over 90 methanol plants having a total annual capacity of more than 50 million tons. The price of methanol, is daily pronounced by Methanex Corporation, the major producer of methanol. The price development is illustrated in figure 4.2. This price only affects methanol produced from fossil resources and may not be comparable to methanol produced from renewables.

*Figure 4.2: Methanex Non Discounted Reference Price (MNDRP) [Methanex 2012].

4.1 Methanol Production

The methanol production involves three processing steps [Aasberg-Petersen et al., 2009]:

- Synthesis gas preparation (Reforming)
- Methanol synthesis
- Methanol purification

In the search for possible methanol production schemes with a biogas feed, the scheme shown in figure 4.3 on the facing page serves as a basis scheme [Lee et al., 2007]. The reason for this is twofold. The first reason is the available CO₂ from the biogas as explained in section 2 on page 7. From [Hansen et al., 2011] it is known that the availability of CO₂ reduces the energy consumption to approximately 29 GJ/MT compared to 30-32 GJ/MT produced methanol for other optimized designs. The second reason is, that this concept with one-step reforming for the syngas production has traditionally been dominating plants with a capacity up to 2,500 MTPD (Metric Ton Per Day) [Aasberg-Petersen et al., 2009].
4.1.1 Synthesis Gas Preparation

Methanol production is subjected to a thermodynamic equilibrium, that limits the methanol produced per reactor pass. This leads to a high fraction of unconverted gas. In the production scheme, especially the synthesis gas preparation and methanol synthesis step must therefore be examined carefully, to ensure a feasible gas composition in order to maximize the methanol conversion per pass.

The gas composition for methanol synthesis is aimed for the ratio presented in equation 4.1 known as the module or stoichiometric number, \( M \) [Lee et al., 2007].

\[
M = \frac{x_{H_2} - x_{CO_2}}{x_{CO} + x_{CO_2}} \approx 2
\]  

The ideal gas composition is process dependent and must be determined by kinetics, process temperature and pressure etc. All though steam is not included in the module, it must be present for a high methanol production [Lee et al., 2007]. Even though a module of 2 can be obtained by a gas mixture consisting of only \( H_2 \) and \( CO \), traces of \( CO_2 \) must be present to prevent carbon deposition. However, too high concentrations lead to slow reaction rates. Therefore, the \( CO_2 \) content often varies in the interval of 2-8 % on a molar basis [Lee et al., 2007]. Despite the module process dependency, for a process topology investigation, the module as it appears in equation 4.1 serves sufficient information for a preliminary study of the gas composition from different reforming technologies.

Next the module and the \( CO_2 \) content interval will act as general process targets and boundaries for different production schemes and varying process parameters. Methanol synthesis is generally carried out in the temperature range of 500-550 K and is a trade off between high yield and fast kinetics. The pressure ranges typically from 50-100 bar.

For production of synthesis, gas generally three types of reforming processes exist; steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR). A description of the three different processes is given

4. Perspectives of Methanol Production
4.1 Methanol Production

in [Liso et al., 2018], from which Table 4.2 is presented. Autothermal reforming will not be considered in this study, because it is usually not used for one-step reforming. It is rather used downstream a steam reformer as a secondary reformer, in order to reform unreacted CH$_4$ [Lögdberg and Jakobsen, 2010].

<table>
<thead>
<tr>
<th>Type of process</th>
<th>Steam reforming</th>
<th>Partial oxidation</th>
<th>Autothermal reforming</th>
</tr>
</thead>
<tbody>
<tr>
<td>System complexity</td>
<td>Endothermic</td>
<td>Exothermic</td>
<td>Neutral</td>
</tr>
<tr>
<td>Outlet H$_2$ content</td>
<td>70-80%</td>
<td>35-45%</td>
<td>40-45%</td>
</tr>
<tr>
<td>Carbon yield</td>
<td>9% CO, 15% CO$_2$</td>
<td>19% CO, 1% CO$_2$</td>
<td>3% CO, 15% CO$_2$</td>
</tr>
<tr>
<td>System configuration</td>
<td>Complex</td>
<td>Simple</td>
<td>Complex</td>
</tr>
<tr>
<td>$M$</td>
<td>≈3</td>
<td>≈1.8</td>
<td>≈2</td>
</tr>
</tbody>
</table>

**Table 4.2:** Different reforming processes and specifications.

It is evident, that partial oxidation produces a more feasible syngas composition than steam reforming when comparing their resulting module. But it must be kept in mind, that the presented numbers in Table 4.2 are based on natural gas reforming. The natural gas composition differs from that of biogas; higher hydrocarbons are present, higher CH$_4$ and lower CO$_2$ concentrations than biogas. Table 4.3 shows the composition of Danish natural gas and the biogas composition assumed in this project.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Danish natural gas</th>
<th>Biogas</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>91.13</td>
<td>65</td>
</tr>
<tr>
<td>Ethane</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.5</td>
<td>35</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.3:** Composition of Danish natural gas and biogas [Mads Pagh Nielsen, 2001].

The higher concentration of CO$_2$ will decrease the module, why biogas reforming will generate modules lower than that of natural gas reforming. The more feasible gas composition of partial oxidation probably then vanishes when reforming biogas. It is also evident, that steam reforming of CH$_4$ produces CO$_2$, which could lead to a significantly higher concentration of CO$_2$ than favorable for methanol synthesis. These issues of biogas reforming will next be addressed through equilibrium models of biogas steam reforming and partial oxidation in a topology context.

### 4.1.2 Equilibrium Models for Syngas Investigation

As a consequence of a high CO$_2$ molar fraction in biogas, the risk of high CO$_2$ concentrations for methanol synthesis exist, if the CO$_2$ fraction must be within the interval mentioned above. It can be seen from the basis
scheme in figure 4.3 on page 19, that the possibility of purging some CO\textsubscript{2} from the biogas exists. By purging, some of the CO\textsubscript{2} can be interpreted as wasted matter for potential additional methanol production. To reduce this waste, it is desirable to obtain both feasible values of M, CO\textsubscript{2} concentrations and at the same time achieve high carbon utilization. To investigate how to achieve these targets, and how the reforming gas composition is affected for varies reforming processes, an equilibrium steam reforming model and a partial oxidation reforming model will be used for the purpose. In-depth reforming and synthesis explanations and calculations will be not be considered in this section, but further information can be found in Appendix A on page 101.

The necessity for purging will next be explained from a mass balance point of view, if this option did not exist as illustrated in figure 4.4. If the cleaned biogas is directly steam reformed considering a fixed reactor temperature and pressure, the only way to change the gas mixture composition is by changing the steam to carbon (S/C) ratio. However, it was found that both the module M and the CO\textsubscript{2} molar fraction are almost constants for varying S/C-ratios and that the values of these are in the infeasible region. The CO\textsubscript{2} molar fraction was found to approximately 20%.

![Figure 4.4: Simplified methanol production scheme. Direct reforming of cleaned biogas.](image)

To decrease the amount of CO\textsubscript{2} to a more desirable level, purging can be used. A simplified view of figure 4.3 on page 19 is given in figure 4.5 where purging is an option.

![Figure 4.5: Simplified methanol production scheme with possibility of CO\textsubscript{2} purging.](image)

The fraction of purged CO\textsubscript{2} is given by the parameter p as expressed in 4.2.

\[
\dot{n}_{\text{CO}_2,\text{purge}} = \dot{n}_{\text{CO}_2,\text{biogas}} \cdot p
\]  

(4.2)

If the reforming pressure and temperature are fixed parameters, the gas composition can be changed by the S/C-ratio and the purging parameter. The resulting module M and the fraction of CO\textsubscript{2}, from such variations are shown in figure 4.6 and 4.7 on the next page.

4. Perspectives of Methanol Production
4.1 Methanol Production

The molar fraction of CO\textsubscript{2} entering the synthesis is given by equation 4.3:

\[
x_{\text{CO}_2} = \frac{n_{\text{CO}_2,\text{sr, outlet}} + n_{\text{CO}_2,\text{biogas}} \cdot (1 - p)}{n_{\text{total, sr, outlet}} + n_{\text{CO}_2,\text{biogas}} \cdot (1 - p)}
\]

By increasing \(p\), \(M\) increases and the CO\textsubscript{2} molar fraction decreases as expected. It can also be seen that \(M\) is almost constant with varying S/C-ratio, but the CO\textsubscript{2} molar fraction decreases as the S/C-ratio decreases. To obtain a \(M\) of 2, slightly more than 10% must be purged. But at a \(p \approx 0.1\) the CO\textsubscript{2} molar fraction is still unfeasible with a fraction of around 10% at a S/C-ratio of 1.

Often the steam reformer is operated at a S/C-ratio of 2.5 [Grue, 2005], to avoid the risk of carbon deposition. If the S/C-ratio is assumed fixed at 2.5, the syngas composition can only be changed by varying \(p\). In figure 4.8 the CO\textsubscript{2} the molar fraction is illustrated as a function of purging.

\[\textbf{Figure 4.8:} \text{CO}_2 \text{ molar fraction as a function of } p. \text{ S/C-ratio } = 2.5.\]
From the figure it is observed, that only by purging, it is possible to utilize approximately 40 % of the CO$_2$ when constrained by the CO$_2$ molar fraction. At this point M is equal to 2.2.

By purging the remaining 60 % of the CO$_2$ can be interpreted as a waste for potential additional methanol production. Therefore, it is desirable to change the gas composition by other means than the purging parameter, p.

One way of changing the composition is by adding H$_2$ to the methanol reactor as seen from equation 4.1 on page 19. Adding H$_2$ will increase M but also decrease the CO$_2$ molar fraction, since the total number of moles increases. The extra H$_2$ could be supplied by H$_2$ recovery from the methanol outlet stream or by using an electrolyzer. A simplified overview of a configuration, where an electrolyzer is utilized is shown in figure 4.9. The produced O$_2$ from the electrolysis can be used as an oxidant for fuel combustion to provide heat for the endothermic steam reforming reactions of steam reforming.

In figure 4.10 and 4.11 on the following page equation 4.4 and 4.5 are plotted as a function of p for two different values of M; 2 and 3. From an equilibrium standpoint of steam reforming with a S/C-ratio of 2.5, it is not possible to obtain a M of 2, while at the same time keeping the CO$_2$ content within the given boundaries. It is seen, that in order to keep the CO$_2$ concentration in the feasible region, removal of H$_2$ is needed to obtain a M on 2. If allowing M = 3 as indicated in the figure, the utilization of CO$_2$ may reach levels of 60 % before violating the CO$_2$ constraint. It corresponds to an almost 50 % increase in CO$_2$ utilization, than the case without added H$_2$. The added H$_2$ at this point, amounts approximately to 22 % of the total moles entering from the reformer and from purging.
Through this preliminary investigation it is evident, that the synergy between M, CO\textsubscript{2} molar fraction and the purging parameter makes it impossible to obtain a M = 2, when constraint by the CO\textsubscript{2} molar fraction. Moreover, the utilization can be increased if the composition is not directed by a M = 2. At M = 3 a 60 % CO\textsubscript{2} utilization can be obtained.

From equation 4.1 on page 19 it can be seen, that M is also a function of CO\textsubscript{2}. For steam reforming the fraction of H\textsubscript{2} to CO (H\textsubscript{2}/CO) is 4-5 for a S/C-ratio of approximately 2.5. If this ratio can be lowered, M will decrease. Adding H\textsubscript{2} to this scenario will again decrease the CO\textsubscript{2} molar fraction, which will enable the possibility for a higher CO\textsubscript{2} utilization.

### 4.1.3 Partial Oxidation Syngas Investigation

To increase the carbon utilization even further, the two following concepts can be considered: Add CO as with H\textsubscript{2} to the effluent gas stream from the steam reforming or reforming by partial oxidation (POX) of the biogas.

POX is contrary SR an exothermic process, which produces a CO rich syngas. A simplified scheme of this configuration is shown in figure 4.12.

---

**Figure 4.10:** CO\textsubscript{2} molar fraction and added H\textsubscript{2} for M = 2 as a function of p. S/C-ratio = 2.5.

**Figure 4.11:** CO\textsubscript{2} molar fraction and added H\textsubscript{2} for M = 3 as a function of p. S/C-ratio = 2.5.

**Figure 4.12:** Simplified scheme of partial oxidation of CH\textsubscript{4} with added electrolysis unit.
The input parameter for the POX reactor is defined as an oxidizer to fuel ratio as shown in equation 4.6.

\[ \lambda = \frac{\dot{n}_{O_2}}{\dot{n}_{CH_4}} \]  

([4.6])

In figure 4.13, the equilibrium composition of H\(_2\) and CO is shown as a function of \(\lambda\). The syngas conversion peaks at approximately \(\lambda = 0.5\) at a value close to 90 \%. At \(\lambda = 0.5\), CO\(_2\) utilization is investigated for \(M = 2\) and \(M = 3\) as a function of the purging parameter. The results are shown in figure 4.14 and 4.15.

The main observation from these figures is, that at \(M = 3\) a full utilization of the available CO\(_2\) is possible. It must thus be kept in mind, that the high utilization is at the cost of a higher concentration of added H\(_2\), which must be supplied by the electrolyser. The added H\(_2\) at this point, amounts to more than 75 \% of the total moles entering from the reformer and from purging.
4.2 Methanol Synthesis

The investigation of synthesis gas preparation was initiated by the thermodynamic equilibrium limits of methanol conversion, introducing a high fraction of unconverted gas. To deal with this unconverted gas, several conversion trains have been proposed, for which three are illustrated in figure 4.16. The first one is a once-through process, where a series of subsequent reactors with interstage methanol separation is used to avoid recycling of unconverted gas. The separation can be done e.g. by flashing or absorption in liquid solvents. Recycling of unconverted gas is avoided, but the recycle loop is substituted by a larger and more complex system. If methanol is flashed, interstage cooling/heating and compression/expansion is still needed, and if solvents are used, these must be regenerated after separation. Also, the gas composition through each reactor may change, why this could introduce interstage addition of H$_2$ to maintain feasible gas compositions. Once-through concepts though exhibit advantages for co-production schemes of methanol and H$_2$ production. [Hamelinck and Faaij, 2002] showed, that once-through concepts perform better in terms of fuel production price than the concepts aiming for only liquid fuel production. This functionality is however, not a part of this project and will not be discussed any further.

\[\text{Reforming syngas} \rightarrow \text{MeOH} \]

\[\text{Flash} \rightarrow \text{syngas recycle} \rightarrow \text{MeOH} \]

\[\text{Flash} \rightarrow \text{purge gas} \]

\[\text{MeOH} \rightarrow \text{flash} \rightarrow \text{MeOH} \]

(A) Series of subsequent reactors (B) Membrane reactor with recycle loop (C) Recycle loop with flashing

Figure 4.16: Methanol trains.

To avoid large energy duties by compression/expansion and cooling/heating when flashing, in situ methanol separation by the use of a membrane reactor has also been proposed. The method has its limitations, since it is expected to have fairly high investment costs [Lange, 2001]. The last concept for recovering of unconverted gas is simply to recycle the gas back to the methanol reactor. This concept is fairly simple, but loop concepts introduce the disadvantage of purging some of the gas to avoid inert gasses accumulation in the synthesis loop.

4.3 Reforming Economics

The above mentioned statements have only been based upon qualitative observations in terms of methanol synthesis gas preparation from specific synthesis parameters and utilization of carbon. Decision-making of process schemes for methanol production can not be done entirely on such qualitative numbers and basic
intuition. Economics of several different methanol schemes have been broken down into the most important partitions and compared relative to a base scheme based on steam reforming of natural gas followed by a synthesis loop. The comparison is shown in figure 4.17.

![Figure 4.17](image)

**Figure 4.17**: Relative capital costs. (1) Steam reformer and conversion in recycle reactor (2) Partial oxidation and conversion in recycle reactor (3) Partial oxidation and conversion in reactor series (4) Air-blown partial oxidation (44 % O$_2$) and conversion in reactor series. [Lange, 2001]

It is clear from the figure, that turning from steam reforming to partial oxidation the capital cost on the reformer decreases, but the saving is offset by an expensive air separation unit. It is also evident by comparing option (3) and (4), that O$_2$ blown reformers decreases the capital cost compared to air-blown oxidation. Finally, using a recycle loop the capital cost on the methanol reactor is lower, than when using a series of reactors.

### 4.4 Summary

From this preliminary equilibrium study, it was evident, that a full CO$_2$ utilization is not achievable only by reforming of CH$_4$. It was also found, that by supplying additional H$_2$ to the methanol reactor a 50 % higher CO$_2$ utilization is possible for SR and a full utilization is possible for POX. Though it has not been investigated through the equilibrium models, it is also evident, that adding CO or dissociate some of the CO$_2$ into CO, an even higher carbon utilization is achievable for the SR based scheme.

From the economics it was shown, that using partial oxidation, significant savings is obtained on the reformer, but an expensive air-separation unit is needed for the O$_2$ supply. Also, the schemes based on a recycle loop yield the lowest synthesis reactor capital cost.

The preconditions for this study was an equilibrium model, constrained by some general values of the parameter M and CO$_2$ molar fraction. For true operation, steam from the outlet stream of the reformer will be knocked out before the methanol synthesis. This will in fact alter the molar fraction and possibly the actual CO$_2$ utilization predicted by this preliminary equilibrium study.
Non-equilibrium conditions may arise due to catalytic selectivity and short residence times, why knowledge about the reaction kinetics must be obtained to calculate the optimal input composition for the highest methanol yield. Reaction kinetics for the reforming processes and the methanol synthesis is the topic of Appendix A on page 101.
Novel Methanol Production Concepts

In this chapter, the plant configurations of the farm and large scale cases will be outlined. The decision-making will be based partly on qualitative observations from previous chapters, partly on statements from work done by other authors on similar subjects and partly on basic argumentation. It was stated in the motivation, that this project aims to enhance knowledge on how to increase the utilization of biogas produced from agricultural waste by a BTL-process, and at the same time enable a wind power peak shaving mechanism by a ETL-process. These objectives will be consistent throughout the chapter.

5.1 High Biogas to Methanol Conversion

It has been a prerequisite for the feasibility of biogas plants, that both heat and power produced from combustion of biogas could be sold. This fact could also be essential when developing concepts for methanol production. In [Hansen et al. 2011], about 8 percent of the annual expenditures of methanol production are recovered by selling excess heat as district heating. For farm scale plants, high heat recovery within the methanol production scheme is a key factor, since excess heat sold as district heating can not be guarantied due to decentralized locations.

In the previous chapter, it was observed that the syngas composition produced from biogas reforming does not yield ideal conditions for methanol synthesis. Adding either H\textsubscript{2}, CO or a combination of both can increase carbon utilization. Optimizing the gas composition increases the methanol produced for each syngas pass, therefore reduces matter in the syntheses loop. Without adding any matter a shift reactor can be used to alter the gas composition by utilization of the Water Gas Shift (WGS) reaction in equation 5.1.

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = -41157 \quad \frac{kJ}{kmole}
\] (5.1)

The forward shift reaction produces desirable surplus H\textsubscript{2} but simultaneously produces carbon dioxide. Ultimately, a carbon dioxide extraction is needed to deal with the excess carbon dioxide.

A second possibility is by separation of specific compounds of the methanol reactor effluent stream. The separated compounds are then recycled to the synthesis inlet. This again may lead to purged matter and a decrease in carbon utilization.
5.2 Introducing an Electrolyser

To handle future fluctuations in electricity production, higher grid flexibility is needed. H\textsubscript{2} and syngas production from electrolysis has been proposed as a technology for surplus electricity shaving. Through the conversion of electricity to synthesis fuels, energy is stored in chemical bonds. Due to the need of intermediate syngas production for methanol synthesis, these conditions create the possibility of linking reforming of biogas with H\textsubscript{2} or syngas production from electrolysis.

[Hansen et al., 2011] showed, that by combining traditional gasification of wood pellets with a subsequent syngas composition optimization by introducing an electrolyser, a higher methanol conversion efficiency was obtained, than for a traditional methanol plant with a shift reactor. Additionally [Mignard and Pritchard, 2008] found, that the concentration of inerts from H\textsubscript{2} addition from an electrolyser was lower than when using a shift reactor. The reason is that a CO\textsubscript{2} extraction step is needed after the shift reactor due to the additional formation of CO\textsubscript{2}.

Finally, when searching for possible production scheme options, not only do the investment and operational costs have to be considered, but also the possibility for valuable by-products. Incorporating an electrolysis unit, does not only produce valuables for the methanol synthesis. It also produces O\textsubscript{2}, which can be sold, used for partial oxidation or used for combustion. In the case of partial oxidation, this can reduce the production scheme, since an air-separation unit is no longer necessary.

For all the above mentioned reasons, an electrolyser will be present in all proposed production schemes.

5.2.1 Choice of Electrolyser

To evaluate the choice of electrolysis technology, three different technologies are considered: Alkaline Electrolysis (AE), Polymer Exchange Membrane Electrolysis (PEME) and Solid Oxide Electrolysis (SOE). AE is the most well established commercialized technology and SOE is still in the research phase [Jensen et al., 2008]. Different specific technology parameters are presented in table 5.1 on the next page. Choosing the most suitable electrolysis technology depends on the operational conditions, price and availability.

From Chapter 4 on page 17 it was found, that adding H\textsubscript{2} increased the carbon utilization for steam reforming and resulted in a possible full utilization for partial oxidation. Adding CO or dissociate CO\textsubscript{2} into CO could further increase the carbon utilization for the case of steam reforming. From table 5.1 on the next page it is observed, that all technologies are able to produce H\textsubscript{2}, but the SOE technology is the only one suitable for co-electrolysis. Using a SOEC makes it possible to produce H\textsubscript{2}, CO or a syngas simultaneous with O\textsubscript{2} in situ. Moreover, it has been projected, that the SOE technology will become the cheapest both in terms of investment and operation [Hansen et al., 2011]. This is illustrated in figure 5.1 on the facing page by the future expected price movement [Partnerskabet for brint og brændselsceller, 2009].

One disadvantage of the SOE technology is the need for demineralized H\textsubscript{2}O, which possesses an extra expense [Rokni, 2012].
Due to these facts, SOE is the choice of electrolysis whether the production scheme is based upon steam reforming or partial oxidation.

<table>
<thead>
<tr>
<th>AE</th>
<th>PEME</th>
<th>SOE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>333-353 K</td>
<td>333-353 K</td>
</tr>
<tr>
<td></td>
<td>373-473 K under development</td>
<td>1023-1223 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>32 bar in large scale industrial plants</td>
<td>Potential for high</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pressure (100 bar) due to solid electrolyte</td>
</tr>
<tr>
<td>Stage of development</td>
<td>Commercial for industrial H₂ production.</td>
<td>Commercial for industrial H₂ production.</td>
</tr>
<tr>
<td></td>
<td>Potential for development into energy plant.</td>
<td>Potential for development into energy plant.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Under development</td>
</tr>
<tr>
<td>Maximum demonstrated stack size</td>
<td>3.4 MW</td>
<td>45 kW</td>
</tr>
<tr>
<td>Products</td>
<td>H₂</td>
<td>H₂</td>
</tr>
</tbody>
</table>

Table 5.1: Different electrolysis technologies and specific parameters.

![Figure 5.1: Price movement of H₂ production for the three electrolysis technologies compared to reforming of natural gas.](Partnerskabet for brint og brændselsceller 2009).

5.3 Syngas Preparation

For syngas preparation only two technologies are in consideration: Steam reforming and partial oxidation. For medium sized methanol plants with a maximum single train capacity limited to about 2500 MTPD, conventional steam reforming is economically applied [Haid and Koss 2001]. Steam reforming produces considerable amounts of steam, which from a methanol production purpose is not desirable, since steam acts as an inert in
the synthesis. For large scale plants steam is not necessarily an undesirable compound since it makes up the possibility for combined heat and fuel (CHF) production. It can recover waste heat to be sold as district heating and thereby acts as a valuable by-product.

It has been stated by [Lögdberg and Jakobsen, 2010] that partial oxidation is frequently used in farm scale. One of the major advantages of using partial oxidation is the simple design and operation. A second advantage is when CH$_4$ is entirely oxidized by O$_2$ hardly no steam is formed. Hence, only small amounts of inerts are produced. One of the disadvantages of partial oxidation is the exothermic nature combined with an exothermic synthesis, which could lead to a significant excess heat production, which must be cooled by some external utilities.

For the same reasons as with district heating, the opportunity for periodical CH$_4$ hold up in the natural gas system is not a wide spread option on farm scale, because the natural gas network is generally concentrated around urban areas. This means, that farm scale plants have to operate continuously at nominal load, if some gas hold up tank is not present, since the feed input is assumed constant.

### 5.4 Farm Scale Concept Presentation

Based on above mentioned assertions, the base concept for the farm scale size plant is presented in figure 5.2. Due to the equilibrium limit of methanol production, it is necessary to extract produced methanol to enhance the production. From 4.17 on page 27 it was found, that the synthesis loop yields the lowest investment, and will therefore be integrated in the production schemes. To avoid inert accumulation in the synthesis loop, some of the recycled gas is purged.

![Diagram of farm scale methanol production concept](image)

**Figure 5.2:** Base farm scale methanol production concept.
5.5 Large Scale Concept Presentation

It is evident that a high system efficiency is preferable, but if an increase in system efficiency is at the expense of even higher investment and/or operational cost it may not be cost-effective. Due to the high share of electricity consumption on the operational costs, tariff operation could be an option for large scale plants, where part load operation is adjusted according to the electricity price. The fluctuation power tariff, as a result of mismatched power supply and demand, leads to speculations on operation strategies to decrease operational costs:

- Operate the electrolyser in balanced mode to ensure optimized synthesis gas composition.
- Operate the electrolyser in an on/off mode depending on the electricity price.
- Operate the electrolyser at decreased load, when the electricity price is sufficiently high.
- Expand the production scheme with a shift reactor. When the electricity price is high the shift reactor is operating, when low the electrolyser is operating.

The different strategies have different benefits in terms of investment and operational costs. If the life time of the SOEC is assumed constant, the operation and investment cost on the SOEC will be the highest for option one. On the other hand, the methanol production per reactor pass will always be maximized by this option. This could lead to the scenario, that the inlet composition is a more sensitive parameter than the electricity price on the methanol production price.

5.5.1 Electrolysis considerations

[Fu et al., 2010] investigated the sensitivity of unit lifetime of SOE syngas production. It was found that above 20,000 hours of lifetime, operational cost was dominating syngas production price, and therefore not sensitive to the investment cost. From [Jensen et al., 2008] it is expected that the lifetime is more than 40,000 hours. With a life time of 40,000 hours, it is therefore predicted, that the electrolysis price will be highly dominated by electricity consumption.

[Hansen et al., 2011] evaluated different operation strategies and concluded, that operating at balanced mode, for optimized synthesis gas composition, yielded the minimum methanol production price.

For these reasons, it has been chosen not to expand the production scheme with additional components to enable on/off operation. Tariff operation will still be possible by upgrading the biogas for natural gas standards, and then store the gas when electricity prices are high.

Though it has been stated by [Haid and Koss, 2001] that steam reforming is economically applied, two base production schemes for large scale methanol production will be presented. One for steam reforming and one for partial oxidation. The one for steam reforming is shown in figure 5.3 on the next page.
Figure 5.3: Base large scale methanol production concept based on steam reforming.

It must be kept in mind, that the presented concept is only one out of several possible production schemes and therefore only serves as a basis scheme. Especially for the steam reformer burner several configurations exist. These configurations will be further investigated after the core process modeling has been established.

One of the major incentives for using partial oxidation is the reason for high recovery of annual expenditures by district heating sales. It is assumed that the amount of surplus heat is higher for a scheme based on partial oxidation than for steam reforming, why a larger cost recovery is possible. The last scheme proposed is shown in figure 5.4.

Figure 5.4: Base large scale methanol production concept based on partial oxidation reforming.
As a continuation of the pre-investigation of biogas reforming, this chapter deals with the basic modeling assumptions of the core components presented in the three novel production concepts from the previous chapter. First the different types of reactors and their general reactor modeling will be presented. In depth information about reaction kinetics and modeling of minor components is described in Appendix A on page 101. Secondly the electrolysis unit will be outlined.

6.1 Reactor Types and General Reactor Modeling

The three different reactors; steam reformer, POX reactor and methanol reactor will all be modeled as tubular plug flow reactors. With the plug-flow assumption no radial variations will be assigned to the flow, and mixing issues are ignored. Additionally, all reactors are modeled with a packed catalyst bed, for which the generalized mole balance of specie, i, can be given as in equation 6.1 for the reaction rate of the j reaction [Fogler, 2010].

\[
\frac{dh_i}{dW} = \sum r_{ij} \left[ \frac{\text{moles}}{\text{kg} \cdot \text{s}} \right]
\] (6.1)

It has been decided to ignore reactor pressure losses due to software optimization complications. However, a fixed pressure loss has been assigned to each reactor. The pressure losses are given in Appendix D on page 119.

6.1.1 Steam Reformer

It was mentioned in Chapter 4 on page 17 that the steam reforming mechanisms are endothermic, why heat must be supplied to maintain reactivity. Steam reforming of CH\(_4\) is governed by the three following reactions.

\[
\begin{align*}
CH_4 + H_2O &\rightarrow 3H_2 + CO & \Delta H = 206169 \\
CH_4 + 2H_2O &\rightarrow 4H_2 + CO_2 & \Delta H = 165012 \\
CO + H_2O &\rightarrow CO_2 + H_2 & \Delta H = -41157
\end{align*}
\] (6.2) (6.3) (6.4)

The steam reforming is carried out in the radiant part of the reactor, where a single or multiple tubular pipes filled with catalytic material are stacked. To provide reaction heat some of the feed or purge gas is burned externally the tubes. Two different configurations of the burner placement to the reaction tubes will be discussed; the top fired and the side fired reactor. For a top fired reactor, multiple parallel tubes are often utilized. Typically tube dimensions are: diameter = 70-130 mm, length = 7-12 m and wall thickness = 10-20 mm [Lögdberg and Jakobsen, 2010]. For the side fired reactor only a single tube is used. This means that the diameter of the
single side fired tube is larger than for the top fired. The different burner placement and tube diameter, means that the heat flux through the tube differs between the two reactor configurations. This can be illustrated from figure [6.1].

The side fired reactor yields a higher average heat flux, a lower tube wall peak temperature and higher exit temperature, which benefits the \( \text{CH}_4 \) conversion. Using a side fired tube in large scale, heat transfer issues may arise due to large dimensions. These observations lead to the assumption, that a top fired reactor is used.

The presented heat flux curves are only valid for a certain reactor configuration and operation, since the heat transfer is dependent on temperature gradients, convection and conduction resistances and radiative temperature etc. Nevertheless, the presented heat flux curve for top fired steam reforming will be assumed representative within the range of operational conditions and reactor geometry.

Typically, 50 % of the heat produced by the burners is transferred to the reacting flow in the radiant reactor section and the second half is available in the flue gas in the convection part. This heat is generally utilized for preheating of feed gas and steam generation. If no surplus steam generation is desirable, the percentage leaving the convection section can be significantly reduced [Dybkjær, 1994].

### 6.1.2 POX Reactor

The partial oxidation is an exothermic reaction, which produces heat. Contrary steam reforming, there is no need for heat transfer through the reactor walls, and so there is no need for bypassing and combusting some of the feed gas. The partial oxidation reaction mechanism is based on reaction [6.5] to [6.8] on the facing page.
\[ CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \quad \Delta H = -803000 \quad [kJ/mole] \quad (6.5) \]

\[ CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H = 247000 \quad [kJ/mole] \quad (6.6) \]

\[ CH_4 + H_2O \rightarrow 3H_2 + CO \quad \Delta H = 206169 \quad [kJ/mole] \quad (6.7) \]

\[ CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = -41157 \quad [kJ/mole] \quad (6.8) \]

Since there is no need for heat exchanging in the POX reactor it could operate adiabatically or be cooled if necessary. This in fact make the POX reactor very simple compared to the steam reformer as pointed out in table 4.2 on page 20. In this study the POX reactor will be modeled adiabatically, for which the energy equation is calculated by equation 6.9 [Fogler, 2010].

\[ \frac{dT}{dW} = \frac{\sum r_{ij} \cdot H_{ij}}{\sum \dot{n}_j \cdot c_{p,j}} \quad [K/kg] \quad (6.9) \]

The high operational temperature of POX results in very fast kinetics, why the size of the reactor can be reduced significantly. On the other hand, the high temperatures may introduce the need for exotic alloys for the reactor tubes. Good mixing is required prior the reactor to reduce hot spots inside the reactor, which in worst case can cause a melt down.

### 6.1.3 Methanol Reactor

The methanol synthesis is an exothermic process, which requires a significant cooling duty to maintain reaction temperatures in a feasible temperature window. The synthesis is governed by two exothermic hydrogenation reactions and the shift reaction.

\[ CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H = -49316 \quad [kJ/mole] \quad (6.10) \]

\[ CO + 2H_2 \rightarrow CH_3OH \quad \Delta H = -91000 \quad [kJ/mole] \quad (6.11) \]

\[ CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H = 41157 \quad [kJ/mole] \quad (6.12) \]

For methanol synthesis, generally three different fixed bed reactors are used:

- Quench reactor
- Adiabatic reactors in series
- Boiling water reactor

The quench reactor is an adiabatic catalytic bed, where a fraction of the feed syngas stream is split and injected into the reactor along its length to provide cooling. By synthesis through a quench reactor no secondary cooling medium is used.

6. Core Process Component Modeling
Instead of injection of syngas into the adiabatic reactor, several adiabatic reactors placed in series with interstage cooling can be used. The interstage cooling can be used to preheat the recycled syngas or the feed gas from the reforming process. Contrary the quench type interstage cooling can also be used to preheat high pressure feed water or generate medium pressure steam. The adiabatic reactor system features good economy of scale and mechanical simplicity contributes to low investment cost [Aasberg-Petersen et al., 2009].

The boiling water reactor is in principle a shell and tube heat exchanger. Cooling of the reactor is provided by controlling the pressure of boiling water on the shell side. The pressure level can be visualized from figure 6.3 where the saturation pressure of H\textsubscript{2}O is plotted for the operation temperature window of methanol synthesis. Using a boiling water reactor the high pressure outlet steam can be used as feed for steam reforming or high pressure electrolysis.

Especially the boiling water reactor has an isothermal behavior [Aasberg-Petersen et al., 2009], but due to the relatively narrow temperature window of synthesis and the need for a temperature management to obtain a high
methanol yield, all synthesis reactor types will be assumed to behave isothermally. Hence, equation 6.13 is applied.

\[
\frac{dT}{dW} = 0 \quad [\frac{K}{kg}] (6.13)
\]

The narrow temperature window is caused by low catalyst activity below 500 K and accelerated copper recrystallization above 550 K [supermethanol.eu 2012].

### 6.2 Electrolysis

Described in Chapter 4 a high utilization of the available CO\(_2\) from the biogas can be achieved, if additional H\(_2\) is added to the methanol synthesis. In the case of steam reforming co-adding CO will increase the utilization even more. By the use of co-electrolysis, H\(_2\), CO and O\(_2\) can be produced from the dissociation of H\(_2\)O and CO\(_2\) by the following reactions.

\[
\begin{align*}
2H_2O & \rightarrow 2H_2 + O_2 \quad \Delta H = 241811 \\
2CO_2 & \rightarrow 2CO + O_2 \quad \Delta H = 282958
\end{align*}
\]

The dissociation of H\(_2\)O and CO\(_2\) is an energy demanding process both in terms of work and heat. The theoretical minimum amount of energy needed can be calculated by the change in enthalpy between the products and the reactants, which sums the change in Gibbs energy and entropy. The theoretical energy demand for steam and CO\(_2\) dissociation is visualized in figure 6.4 and 6.5. By increasing the operational temperature increases the heat demand but at the same time decreases the electricity demand.

![Figure 6.4: Energy demand for dissociation of H\(_2\)O at standard pressure for increasing temperatures.](image)

![Figure 6.5: Energy demand for dissociation of CO\(_2\) at standard pressure for increasing temperatures.](image)

The actual energy demand dependents on the system efficiency, which may differ considerable between different electrolysis technologies. In order to estimate the actual energy consumption the thermo-neutral voltage in
equation 6.16 and the current according to Faraday’s law as in equation 6.17 will be calculated.

\[ E_{in}(T) = \frac{\Delta H(T)}{z \cdot F} \quad [V] \] (6.16)

\[ I = (\dot{n}_{H_2O} + \dot{n}_{CO_2}) \cdot z \cdot F \quad [A] \] (6.17)

By applying the thermo-neutral voltage, the generated Joule effect balances out the heat consumption for the endothermic reactions, and the electrolyser operates thermo-neutrally [Jensen et al., 2008]. Evidently, this also means that more electricity is consumed, than when heat is supplied by other means, since the stack is operating at lower voltage. However, lower operating voltage leads to a lower current density and larger cell surface area, \( A_{surface} \), is needed. This increases in turn the capital cost according to equation 6.18.

\[ A_{surface} = \frac{I}{i} \quad [m^2] \] (6.18)

[Fu et al., 2010] investigated the cost of syngas production from high temperature co-electrolysis, and showed the counteracting effect of lowering stack voltage. The result was a maximum cost reduction of only 1.5%, and therefore a thermo-neutral voltage operation is recommended to simplify system design. To calculate the active surface area from equation 6.18 a current density, \( i \), of 2 A/cm\(^2\) will be used.

Due to existing over-potentials such as electrochemical and ohmic polarizations, the actual electrical consumption is calculated by equation 6.19.

\[ P_{el}(T) = \left( E_{th}(T) + \frac{ASR(T)}{A_{stack}} \right) \cdot I \]

\[ = \Delta H(T)_{H_2O} \cdot \dot{n}_{H_2O} + \Delta H(T)_{CO_2} \cdot \dot{n}_{CO_2} + I \cdot ASR(T) \cdot i \quad [W] \] (6.19)

Here all the over-potentials are compressed into one single parameter, ASR (Area Specific Resistance). As mentioned, the change in reaction enthalpy is a function of operational conditions and so is the over-potential.

To estimate the energy consumption it will be assumed that the electrolysis unit operates at constant temperature and pressure and that part load energy consumptions can be calculated based on polarization curves for calculating the ASR. Since specific curves for commercial units are rarely available, typical polarization curves from the literature are used. Polarization curves behave non-linearly, but at common loads the curves are linear, why the ASR can be treated as constant at common loads. The ASR then present the slopes in the linear region of the polarization curves. [Fu et al., 2010] reports that state-of-the-art H\(_2\) SOFCs perform at ASRs is the range of 0.2-0.3 \( \Omega \) cm\(^2\) in the temperature window of 973-1073 K. Therefore, a base value of ASR = 0.2 is used at 1073 K, and its sensitivity to the methanol price will be discussed.

For the SOEC co-electrolysis will be performed, why the ASR may vary according to the inlet gas composition. However, since the purpose of this study is to estimate methanol production prices from a process scheme level and not to validate highly detailed models, the base ASR value will be assumed constant for all inlet compositions.
Further assumptions include a utilization factor of 100% will be assumed and only the stoichiometric equations presented above are considered. Even though this may introduce real life complication like coke formation. [Das 2011] investigated the coke formation lines shown in figure 6.6, where coke formation is an issue above the border lines. It can been seen, that at low pressures and high temperature the assumption is almost valid.

![Figure 6.6: Coke formation borders as a function of temperature and pressure. Inlet composition: 45 mol% H₂O - 45 mol% CO₂ - 5 mol% H₂ - 5 mol% CO](image)

Only mass transport of charge carriers through the membrane will accounted for, i.e. H₂O management is neglected.
In this chapter a sensitivity analysis will be carried out to investigate different process parameters. The purpose for this is to identify feasible design spaces for the scheme operation and identify sensitive optimization parameters for a later cost minimization. The sensitivity analysis will be performed on each of the described reactors in Chapter 6 on page 35. All the figures in this chapter are presented on a wet basis.

7.1 Steam Reforming Analysis

The focus on the identification of a feasible design space for the steam reforming process will be based on the conversion of CH\textsubscript{4}. The reason for this is the inert behavior of CH\textsubscript{4} in the methanol synthesis reactor [Ausberg-Petersen et al., 2009]. This means, that if CH\textsubscript{4} is not fully converted in the reformer, it will accumulate in the synthesis loop if not separated from the reformer outlet stream. By considering the equilibrium composition in the steam reformer the influence of temperature and pressure can be stated as shown in the figure 7.1 and 7.2 on the next page.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure71.png}
\caption{Steam reforming equilibrium composition of CH\textsubscript{4} at 1 bar and S/C = 2.5.}
\end{figure}

It is seen, that CH\textsubscript{4} conversion is favored at high temperatures, with a full conversion in the interval of 1000 - 1100 K at standard pressure. As mentioned in section 6.1 on page 35 a specific temperature profile for the steam reformer will be applied as given in figure 6.1 on page 36 with an outlet temperature of around 1150 K. For this reason the temperature in the steam reformer will not be considered an optimization parameter since it is fixed. By applying this temperature profile, it is evident that the outlet temperature is sufficient to achieved a full CH\textsubscript{4} conversion at standard pressure.
When the pressure is increased the steam reforming reactions will shift the equilibrium to the right, which means that a full conversion is not reached at the applied temperature profile. For this reason elevated pressures are not favorable, and the pressure should be kept as low as possible to obtain full CH$_4$ conversion. Elevated pressure leads to less tendency of carbon formation, why a lower S/C-ratio can to tolerated. Additionally, since the pressure eventually must be raised for the synthesis, elevating the pressure before the steam reformer, allows for liquid compression rather than the more energy consuming vapor compression. Therefore, from a cost perspective pressure could be a sensitive parameter and will be considered as an optimization parameter. A lower pressure limit will be applied to avoid levels, at which carbon formation could be an issue.

7.2 Partial Oxidation Analysis

Since the partial oxidation mechanism is strongly dominated by equilibrium, the sensitivity analysis is based on equilibrium considerations [Lögdberg and Jakobsen 2010]. As for the steam reformer the influence of temperature and pressure variations on the outlet composition will be outlined. The inlet conditions are similar to those described in Chapter 4 on page 17, with $\lambda = 0.5$.

Figure 7.3 and 7.4 on the next page show the temperature dependency of the equilibrium composition at a pressure of 1 and 20 bar, respectively. From the figures it is seen, that the conversion of CH$_4$ is favored at high temperatures, why the temperature should be kept as high as possible. It is assumed that there will be a surplus of heat from the process scheme why preheating of reactants is not an issue. The inlet temperature of the POX reactor will therefore be fixed at a level, for which the reactor peak temperature does not exceed the material temperature limit. Therefore, the POX temperature is not involved in the optimization.
Figure 7.3: Equilibrium composition of CH₄ for POX, 1 bar and varying temperatures.

Figure 7.4: Equilibrium composition of CH₄ for POX, 20 bar and varying temperatures.

Furthermore, higher pressures are not desirable in a conversion perspective and should be kept as low as possible. Contrary the steam reformer, no significant beneficial effect of pressuring prior the reformer can be obtained, since there is no liquid phase present. Hence, pressure will not be an optimization parameter, and the POX reactor will operate at fixed pressure.

Identical for both the steam and POX reformer is the presence of a catalyst in the reformer bed. Since the rate expressions are functions of the catalyst weight in the reformer, the kinetics are strongly dependent on the amount of catalyst present. Both reformers have been fixed with a bed voidage of 0.5 and a particle density of 2355 kg/m³ and 1870 kg/m³ for the steam reformer and pox reformer, respectively. When the bed voidage is constant, varying the length of the reactor will vary the amount of catalyst present linearly. In figure 7.5 on

7. Sensitivity Analysis
7.3 Methanol Synthesis Analysis

The following page the conversions of CH$_4$ and H$_2$ throughout both reactors are shown as a function of reactor length. The inlet stream composition for the reactors is based on the large scale case, with a S/C-ratio of 2.5 for the steam reformer and a $\lambda$ of 0.5 for POX. The steam reformer operates under isothermal conditions with a temperature of 1173 K and the POX reactor is operated adiabatically with an inlet temperature of 1000 K at standard pressure.

![Graph showing the conversions of CH$_4$ and H$_2$ throughout both reactors as a function of reactor length.](image)

Figure 7.5: Steam and POX reforming of CH$_4$.

The figure gives an indication of the reaction rates in the two reactors. It is seen that the reaction kinetics in the POX reactor are faster than in the steam reformer. If a maximum molar fraction of 5 % CH$_4$ is allowed in the outlet composition, the POX will have a length of 0.75 m whereas the steam reformer length should be around 3.5 m. This observation leads to the fact that the POX reactor can be made more compact than the steam reformer. But due to the fast exothermic reactions of the partial oxidation, the POX reactor is sized more from a mixing perspective to avoid hot spot formation than from a conversion perspective. Since the reactor models are based on a plug flow assumption, mixing mechanisms are not considered, and a minimum length of the POX reactor will be assumed. Hence, length is not an optimization parameter for the POX reactor. For the steam reformer, length will be an optimization parameter.

7.3 Methanol Synthesis Analysis

A sensitivity analysis for the synthesis reactor is carried out in the same manner as the two previous reactors. The main objective of the methanol reactor is to convert the syngas into methanol, why the sensitivity analysis is based on the methanol molar fraction in the outlet stream of the reactor. The reactor inlet conditions and the reactor sizing is based on the numbers from [Vanden Bussche and Froment, 1996].

First the sensitivity of the temperature in the reactor is investigated. Figure 7.6 on the next page shows the output yield of methanol from the reactor at different temperatures. The pressure is kept constant at 50 bar and the temperature is assumed constant throughout the reactor.

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7. Sensitivity Analysis
The figure indicates, that methanol conversion is highly sensitive to temperature with a very narrow operational interval. The tendency of the curve can be explained by the nature of the equilibrium constants and reaction rates. The equilibrium is favored at low temperatures. However, lowering the temperature in the reactor, will result in a great reduction in the reaction rates, which is kinetically undesirable [Lee et al., 2007].

Next the sensitive to operational pressure is investigated. Methanol yield at varying pressures and constant temperature of 520 K is shown in figure 7.7.

The figure shows a large increase as the pressure increases at low pressures, however at larger pressures the increase is less significant. Therefore, pressure is a trade off between methanol yield and operational costs as-
sociated with higher pressures. Due to the sensitivity of methanol production to both temperature and pressure both parameters will be included in the optimization.

In Chapter 4 on page 17 is was stated, that the optimum syngas composition is at a stoichiometric number of 2. For this reason a SOEC is present in the production scheme to be able to optimize the syngas by bypassing some of the CO₂ and by adding H₂. The sensitivity for the methanol yield to the syngas composition is next investigated by varying molar fractions of CO₂ and H₂ in the syngas prior the methanol reactor. These results are visualized in figure 7.8 and 7.9 were the fraction of the varying component is expressed as a fraction to the sum of the remaining components.

**Figure 7.8:** Methanol yield at varying CO₂ compositions.

**Figure 7.9:** Methanol yield at varying H₂ compositions.
It is clear, that the methanol yield is sensitive to the inlet gas composition, at least for the two investigated parameters. This fact justifies the need for a SOEC for syngas optimization. To adjust the CO₂/CO ratio of the gas composition, the bypass fraction can be altered. The amount of H₂ can be changed by adding more H₂O to the SOEC. Since the methanol yield is sensitive to both the CO₂ and H₂ concentrations, the bypass fraction and the H₂O flow to the SOEC are also optimization parameters.

7.4 Summary

Based on the above observations, the optimization parameters for each reactor will be summarized.

For the POX reactor the sensitivity analysis showed, that the CH₄ conversion temperature should be increased and pressure decreased. Since there are no intuitively reasons for not doing so, temperature and pressure will be fixed numbers. Length is mainly based on good mixing prior reaction to avoid hot spots, but since mixing is not considered in this study, length is also a fixed figure. This means, that no optimization parameters will be assigned to the POX reactor.

For the steam reformer a fixed temperature profile is applied, which is independent of all the other operation parameters. Though low pressures favor CH₄ conversion, pressure will still be an optimization parameter. The reason is, that liquid compression prior the steam reformer could be more economically beneficial than when operating at low pressure, with a subsequent high gas compression. It is assumed, that mixing is not an issue in the steam reformer, why the length of the reactor is only related to reactant conversion. Contrary the POX reactor, length will be optimized for the steam reformer.

The methanol reactor is modeled isothermal, why only the inlet temperature is of importance. The sensitivity of this parameter is very significant and will therefore be optimized. The methanol reactor is not governed by fast kinetics like the POX reactor and length will together with pressure be added to the optimization parameters.
In this section a description of the optimization problem will be outlined. Since the optimization will be performed by a in-built optimization routine in Aspen Plus®, a short introduction to the available algorithms will be given. Afterwards the cost function and the optimization parameters will be presented with the corresponding bounds. The primary reason for the optimization is to minimize methanol production cost. The secondary reason is a prior case study for the determination of several possible plant configuration feasibilities.

Aspen Plus® have two optimization algorithms available; the COMPLEX method and the Sequential Quadric Programming (SQP) algorithm.

The SQP method is a quasi-newton method, using the derivatives of the cost and constraint functions to perform the optimization. This means, that for nicely behaved systems, this method may be very efficient, since a search direction is approximated. For complex systems, obtaining gradient and Hessian information can be cumbersome, leading to an inefficient solution method.

The COMPLEX method is a pattern search method capable of handling inequality constraints and bounds on the optimization variables. It is a semi-random method, and it does not require any gradient nor Hessian information. A number of pseudo-randomly determined design points are generated and checked for feasibility. If constraints are violated or an unfeasible function value is obtained for the pseudo-random design point, the design point is altered until its function value does not yield the least feasible value of the generated design points. This type of method generally requires more function evaluations but yield a high robustness due to its simplicity.

The optimization problem in this present report is fairly sensitive to the design parameters, due to highly non-linear model equations and the fact that a loop is presented in the production scheme, which can complicate model convergence. Therefore, the COMPLEX method is chosen over the SQP method due to its robustness.

**8.1 Cost Function**

The cost function is based on the economics associated with the plant. It expresses the yearly based methanol production price concerning operational expenditures for compressors, pumps, SOEC, H₂O and O₂ addition. Furthermore the investment costs of reactors, SOEC and biogas plant are included, since they are assumed to be the main investments considering methanol production from biogas. In general the objective function is expressed by equation 8.1 on the following page. A more thoroughly description of the cost function is found in Appendix E on page 121.
8.2 Design Variables

\[
\text{minimize } f(x_i) = \frac{\text{costs}(x_i)}{\text{methanol produced}(x_i)} \quad \begin{bmatrix} \text{DKK} \\ \text{kg} \end{bmatrix} \quad (8.1)
\]

From the equation it can be seen that the production price can be reduced either by reducing operational and investment costs or by increasing the methanol produced.

### 8.2 Design Variables

In table 8.1 the optimization variables are presented together with the respective bounds.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit of measure</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol reactor temperature</td>
<td>K</td>
<td>500</td>
<td>550</td>
</tr>
<tr>
<td>Methanol reactor pressure</td>
<td>Bar</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>Methanol reactor length</td>
<td>m</td>
<td>1/50</td>
<td>7/100</td>
</tr>
<tr>
<td>Steam reformer pressure</td>
<td>Bar</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Steam reformer length</td>
<td>m</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Split fraction of CO\textsubscript{2} to the SOEC</td>
<td>%</td>
<td>50 - 70</td>
<td>99</td>
</tr>
<tr>
<td>Split fraction of purge gas to recirculation</td>
<td>%</td>
<td>0.1</td>
<td>10</td>
</tr>
</tbody>
</table>

*Table 8.1: Table of design variables for farm / large scale.*

Regarding the H\textsubscript{2}O mass flow into the SOEC the lower bounds are set to ensure a feasible inlet composition to the synthesis reactor.

### 8.3 Constraints

For the endothermic reactions in the steam reformer heat must be added to obtain a high CH\textsubscript{4} conversion. For the purpose it is argued, that the steam reformer is heated by combustion of purge gas, see Appendix B on page 113. The burner feed is balanced by matching the heat absorbed by the endothermic reactions in the reformer, with the heat released in the burner. The oxidant feed to the burner is based on stoichiometric combustion of every combustible component and based on a Gibbs energy minimization routine at 1273 K at standard pressure. Therefore, the constraint will be expressed by equation 8.2.

\[
\dot{Q}_{\text{combustion}} = \dot{Q}_{SR} \quad \begin{bmatrix} \text{W} \end{bmatrix} \quad (8.2)
\]

In the production scheme several equality constraints are imposed upon system pressures. The steam reformer inlet pressure is determined from the two feed pressures, i.e. the pump and compressor outlet pressures, \(P_{\text{out,H}_2\text{O}}\) and \(P_{\text{out,CH}_4}\). These two pressures need to be identical. After the steam reformer the wet syngas is flashed to remove excess H\textsubscript{2}O. The pressure of the flash tank is set equal to the outlet pressure of the steam reformer. The
dry gas is then mixed with the H₂ and CO from the electrolysis unit and the remaining CO₂ from the biogas tank. A compressor is needed to raise the additional syngas from the electrolysis unit to the same pressure as the steam reformer outlet. Thus, the equality constraint will be:

\[ P_{\text{out},H2O} = P_{\text{out},CH4} = P_{\text{flash,SR}} + \Delta P_{SR} = P_{\text{add,syngas}} + \Delta P_{SR} \] [bar] (8.3)

### 8.4 Global Optimum Search

In the search for a minimum cost from the optimization, some issues arise. The problem in question can not be guarantied convex, why several candidate points may exist from an optimality criteria perspective.

![Illustration of a one dimensional convex and non-convex problem.](image)

\textbf{Figure 8.1:} Illustration of a one dimensional convex and non-convex problem.

The COMPLEX method used for the optimization is only a local optimization method, meaning that the optimum found can not guarantied a global one. Therefore, the optimum found is indeed dependent on initial guesses. To increase the possibility of finding the global minimum, an exhaustive search will done by varying the initial guess on every design parameter in the whole design space. The minimum function value obtained from the trial will be assumed to be the global one.
In this chapter a heat integration analysis will be carried out for the three concepts presented. The main purpose for this is to estimate external heating and cooling duties to be supplied by utilities. For farm scale in particular high heat recovery is essential, as mentioned in Chapter 5 on page 29, since excess heat can not be sold. For large scale on the other hand, heat recovery analysis enables estimations on, how much heat that can be sold as district heating.

The heat integration followed by heat exchanger network design and utility selection should be an integrated part of the whole process optimization for cost minimization. In this study only the heat integration is investigated as a sequential analysis to the core process analysis. The heat exchanger network design is disregarded, since the network is priced based on the core components as explained in Chapter 10 on page 61.

---

**Figure 9.1:** Left: Total system optimization, Right: Methodology used in this study [Pagh, 2011].

For the heat integration, pinch analysis will be used. It is a systematic methodology to investigate heat recovery within the process scheme. One of the targets is to find heating and cooling duties, which are not recovered, since these must be supplied by the external utility. The methodology is based on first and second law analysis.

Pinch is a linear analysis, for which heating and cooling duties are expressed by equation (9.1)

\[
\dot{Q} = \dot{m} \cdot c_p \cdot \Delta T = CP \cdot \Delta T \quad [W] \tag{9.1}
\]

Since the specific heat is a function of temperature, an effective specific heat averaged, over the temperature interval, must be stated. Alternatively, the specific heat must be segmented into several fractions, when significant changes occur. Since vaporization and super heating of steam occurs in the process scheme, for which the specific heat can not be assumed constant, segmentation will be used. The mean \( \bar{c}_p \) is expressed by equation (9.2)

\[
\bar{c}_p = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} c_p(T) \, dT \quad \left[ \frac{J}{kg \cdot K} \right] \tag{9.2}
\]
The impact on segmentation is illustrated in figure 9.2 and its importance will later become clear when a minimum forcing temperature difference is introduced.

![Figure 9.2: Different \( C_p \) representations.](image)

First target of the heat integration is to state a minimum temperature difference, \( DT_{\text{min}} \), between two heat transferring fluids. According to [Sahdev, 2012], experienced temperature differences for chemical processes are in the range of 10-20 K. It is evident, that a lower temperature difference allows a higher heat recovery, hence less need for external utilities and lower heat exchanger costs. For this reason a minimum temperature difference of 20 K is used to prevent an underestimation.

Next task is to identify the stream population including all heating and cooling duties within the process scheme. All streams will be temperature shifted; hot streams are decreased by half the \( DT_{\text{min}} \) and cold streams are increased by half the \( DT_{\text{min}} \). A heat balance is then calculated in each shifted temperature interval according to equation 9.3. Shifting the temperatures ensures feasible temperature differences in each temperature interval.

\[
\Delta \dot{Q} = \left[ \sum CP_C - \sum CP_H \right] \Delta T \quad \text{[W]} \quad (9.3)
\]

Recall from section 6 on page 35 that the synthesis reactor is modeled isothermal. To take into account the heat duty hereof due to the exothermic reactions, attention will once again be drawn to the different synthesis reactor types.

Using a boiling water reactor will generate pressurized steam in the range of 25-50 bar according to figure 6.3 on page 38. To utilize steam at this pressure level properly, a steam cycle has to be present. However, steam cycles are not taking into consideration in is project, and due to this fact, the boiling water reactor is not an option. Therefore, all external cooling duties are assumed to be supplied by cooling water.

Regarding the quench reactor and a series of adiabatic reactors, the choice of reactor type will be based on the magnitude of feed preheat and the cooling duty associated with the synthesis reactor, see figure 9.3 on the next page.

If \( Q_{\text{preheat}} > Q_{\text{reactor}} \) the synthesis cooling can be handled by a quench reactor or sequential reactors. It has been chosen to use a quench reactor. In this case the cooling duty of the quench reactor equals a decrease in the preheat duty of the synthesis feed stream, see figure 9.4 on the facing page.
If $Q_{\text{preheat}} < Q_{\text{reactor}}$, a quench reactor is not ideal, because other means of cooling need to be supplied as well. In this case sequential reactors are used.

The heat duty of the steam reformer and the heat from purge gas combustion will not be included in the heat integration, due to the optimization constraint shown below for reference.

$$\dot{Q}_{\text{combustion}} = \dot{Q}_{\text{SR}}$$  \[W\] (9.4)

The distributed water, for district heating purposes, is assumed to be delivered with a supply temperature of 358 K and returns with a temperature of 328 K.

### 9.1 Distillation

So far distillation has not been drawing any attention, though it may affect the utility and amount of heat suitable for district heating. Therefore, a short investigation of the impact by the distillation train will be outlined in this section.

According to [Douglas and Hoadley, 2005], the condensate flashed from the synthesis loop is generally purified in a conventional two column distillation train as in figure 9.5 on the next page.
9.1 Distillation

The topping column is commonly associated with 20% of the total heat demand, while the remainder is associated with the refining column for methanol-water separation. In Figure 9.6, a grand composite curve of a topping and refining column is shown for a world scale methanol plant [Douglas and Hoadley 2005].

To calculate the heat duty associated with the reboilers, the heat duty from Figure 9.6 will be scaled linearly to the respective production capacities given in this project.

From Figure A.6 on page 111, it can be seen that the VLE-curve (vapor-liquid-equilibrium) increases the gap to
the x=y line as pressure decreases, and so does the theoretical number of distillation trays. Hence, traditional methanol-water distillation is operating at pressures slightly above atmospheric pressure [Douglas and Hoadley 2005]. For this reason, no further attention will be given to electricity consumption in the distillation train, since it is assumed to be neglectable compared to gas compression and electrolysis.
In this chapter an economic assessment will be carried out. For the completion of this task, the economic assessment will be divided into two different parts; one for capital costs and one for operational costs. The aim of the assessment is, beside estimating capital and operational cost, to address sensitive and non-sensitive parameters prior the statement of a cost function for cost optimization.

The starting point for this task, will be the cost distribution evaluated by [Hansen et al., 2011] for a large scale methanol production plant with a SOEC installed as presented in figure 10.1. To be able to compare methanol production based on wood gasification with biogas, the same operating horizon and interest rate for all components has been set equally, namely 20 years and 10 % respectively. Moreover, it is assumed that the plant is operating 8000 hours a year. It is expected, that all components but the electrolyser will last for 20 years. The electrolyser life time is set to 5 years. Additional, the payback time on the investment is set to 20 years, why the annualized investment cost will be calculated by equation (10.1).

\[
I_{\text{annual}} = I_{\text{total}} \cdot \frac{IR}{1 - 1/(1+IR)^t}
\]

\[\text{DKK/year}\] (10.1)

**Figure 10.1:** Cost distribution. Left: Annual capital expenditures, Right: Operating expenditures

One of the major differences between methanol production from wood pellets and biogas is the operational costs. For the wood pellet case, the biomass cost has a high share of the annual cost, which is not current in the case using biogas. Especially on farm scale, slurry is already available, why biomass costs are neglectable. Therefore, in this study no costs will be assigned to the biomass on farm scale. On large scale the biomass has to be supplied by numerous farmers. From [Henrik et al., 2006] there are economic incentives for farmers when joining a centralized biogas plant, if the degassed slurry is returned and used as fertilizer. The economic incentives are mainly related to slurry storage and redistribution in the fields. For these reasons biomass costs on a large scale are entirely associated with transportation and separation costs, and are therefore dependent
10.1 Capital Costs

on transportation distance and the degree of separation. This also means, that if biomass costs are significantly reduced the sensitivity of capital costs and electricity price on the methanol production price will be higher for a production scheme based on biogas.

It is evident from figure 10.1 on the previous page, that the main capital costs are shared among the electrolyser, reactors and the biomass preparation with a summed share of almost 50 % of the total investment. For a biogas plant, however, acid-gas removal, tar reformer and the shift reactor are not to be found in the process scheme. These costs are substituted by an expensive biogas processing plant. The summed share of the electrolyser, reactors and the biomass processing plant will then almost constitute the whole investment. For this reason it is reasonable only to price estimate core components, since their sum will have the highest weight on the investment. Minor investment contributors will be based on the core components.

10.1 Capital Costs

When pricing individual system components, true capital cost can only be found, if already commercial components are used for the scheme design. Often a desirable component capacity, \( Q_C \), differs from that available, why estimates on off-capacity costs are useful. These estimates will be based on a power expression, where the capacity cost, \( C_C \), is calculated from a known base cost, \( C_B \), and base capacity, \( Q_B \), and scaled by a component specific exponent as shown in equation 10.2.

\[
C_C = C_B \cdot \left( \frac{Q_C}{Q_B} \right)^M \cdot f_M \cdot f_P \cdot f_T \quad [DKK] \quad (10.2)
\]

Since the material of construction and operational conditions have a great influence on the capital cost, correction factors are applied to the expression. The factor, \( f_M \), is called the material of construction capital cost factor and accounts for material considerations. \( f_P \) is the pressure correction factor and \( f_T \) is the temperature correction factor. The base cost, capacity, scale exponents and correction factors can be found in [Smith, 2005].

10.1.1 Reactors

The capital cost estimation of the POX reactor, steam reformer and methanol reactor is priced as an Inconel pressure vessel. In table 10.1, the base cost, capacities and correction factors are presented together with the typical operational conditions for the vessels. The base cost is based on values from [Smith, 2005] and inflated by 2 % to a 2012 level. The exponent, \( M \), is 0.82 for all reactors.

<table>
<thead>
<tr>
<th></th>
<th>Design pressure [bar]</th>
<th>Design temperature [K]</th>
<th>Base cost [DKK]</th>
<th>Base capacity [ton]</th>
<th>( f_M )</th>
<th>( f_P )</th>
<th>( f_T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>POX reactor</td>
<td>1</td>
<td>1473.15</td>
<td>697,150</td>
<td>6</td>
<td>3.9</td>
<td>1</td>
<td>4.1</td>
</tr>
<tr>
<td>Methanol reactor</td>
<td>50-100</td>
<td>473.15-573.15</td>
<td>697,150</td>
<td>6</td>
<td>3.9</td>
<td>1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Steam reformer</td>
<td>20-50</td>
<td>1073.15-1273.15</td>
<td>697,150</td>
<td>6</td>
<td>3.9</td>
<td>1.3</td>
<td>3.3</td>
</tr>
</tbody>
</table>

*Table 10.1: Reactor base costs, capacities, operation conditions and correction factors [Smith, 2005].*
Since the limit of the temperature factor in \cite{Smith:2005} is 773.15 K a linear extrapolation has been made to obtain a reasonable temperature factor for both the POX reactor and steam reformer. The maximum temperature in the POX reactor is limited to 1473.15 K, why the reactor is priced after this value. The other correction coefficients are based on average values within the operational intervals.

The cost value calculated from equation 10.2 on the facing page only expresses raw material purchase price of the pressure vessel, which in fact only comprises a subcomponent of the complete reactor system. For realistic cost estimation several other factors have to be considered: Equipment erection, piping, instrumentation and control, electrical, utilities etc. To account with these extra costs, the capital cost, \( C_C \), is multiplied with a factor of 2.3 \cite{Smith:2005}.

The capital cost associated with the desulphurizer, will be ascribed to the reforming reactor capital cost. According to \cite{NREL:2006}, the capital price of a hydrodesulphurizer is approximately one fifth of the reforming reactor cost. Therefore, the capital cost of the reforming reactor will be multiplied by a factor of 1.20 to handle this extra cost.

The capacity of the reactors is based on the weight of the pressure vessel in tonnes with a reference capacity of 6 tonnes. The weight of the tubular reactors are calculated according equation 10.3.

\[
    w = (r_1^2 - r_2^2) \cdot \pi \cdot L \cdot \rho
\]

\[\text{[kg]} \quad (10.3)\]

\textbf{Figure 10.2:} Tubular reactor size parameters.

It is observed, that the reactor weight scales only linearly with reactor length but squared to the tube thickness. The inner diameter and the tube length are both sensitive parameters to the reactor yield and cost, but the outer diameter and thereby the thickness does only affect the reactor cost. The reason for this relies on the reactor modeling assumption, that heat flux etc. is not a function of wall thickness. Wall thickness is therefore not an optimization parameter, and a base line value is fixed to 15 mm. Additionally, the weight is also a linear function of density, which must be specified. For this purpose the Inconel 625, a high temperature alloy, is used with a density of 8440 kg/m\(^3\) and a melting point of 1623 K.

The reactor capital cost model has been validated by scaling the steam reformer capital cost given in \cite{NREL:2006} to the capacity presented in this project. It was found, that the two capital costs on the steam reformer deviated by less than 30\%.
10.1 Capital Costs

10.1.2 Electrolyser

In [Hansen et al., 2011] it was found, that the SOE technology is preferable over the AE technology, due to a higher efficiency and a projected lower investment cost. Since SOE is not yet fully commercial, price estimates must be done in order to calculate the investment cost. Such estimates can be found in [Jensen et al., 2008], where the price is estimated to 4000 $/m$^2$ of cell area with a life time of 5 years. The surface area is calculated based on an assumed current density of 2 A/cm$^2$ according to equation 6.18 on page 40. Since a long life time is always preferable from a production price perspective, the life time is not an optimization parameter. For this reason an average life time of 5 years will be used as a base line.

10.1.3 Biogas Plant

To estimate the investment cost of the biogas processing plant the data presented in [Henrik et al., 2006] for three central biogas plants (300, 550 and 800 tonnes/day) will be extrapolated linearly for the farm and large plant sizes used in this work. The investment costs for the different plant components found by the extrapolation are shown in table 10.3. Kept in mind, that the large scale cases process more than 25 times the amount of biomass than the farm scale case, it is clear from the table, that all components beside the tanks benefit from economy of scale.

<table>
<thead>
<tr>
<th>Component</th>
<th>Farm scale Cost (1000 DKK)</th>
<th>Large scale Cost (1000 DKK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Land</td>
<td>800</td>
<td>1850</td>
</tr>
<tr>
<td>Excavation</td>
<td>800</td>
<td>1850</td>
</tr>
<tr>
<td>Fence</td>
<td>-</td>
<td>2250</td>
</tr>
<tr>
<td>Road</td>
<td>-</td>
<td>1450</td>
</tr>
<tr>
<td>Buildings</td>
<td>2500</td>
<td>5100</td>
</tr>
<tr>
<td>Tanks</td>
<td>1150</td>
<td>28500</td>
</tr>
<tr>
<td>Filters</td>
<td>1400</td>
<td>3000</td>
</tr>
<tr>
<td>Pump system</td>
<td>1250</td>
<td>2550</td>
</tr>
<tr>
<td>Gas system</td>
<td>275</td>
<td>400</td>
</tr>
<tr>
<td>Electrical installations</td>
<td>1750</td>
<td>3000</td>
</tr>
<tr>
<td>Mounting and counselling</td>
<td>5000</td>
<td>20000</td>
</tr>
<tr>
<td>Total investment</td>
<td>14925</td>
<td>69950</td>
</tr>
</tbody>
</table>

*Figure 10.3:* Cost distribution for farm and large scale biogas plants.

The validity of the extrapolation, the estimated investment costs are compared to investment costs of several existing Danish biogas plants. Though the extrapolation was done linearly, especially the farm scale plant estimation seems to be consistent with similar sized plants. Regarding the large scale plant it is assumed, that the found investment cost is valid, though it follows more a logarithmic function than a linear one, when compared to real plant data, see figure 10.4 on the facing page.
10.1.4 Miscellaneous Component Investment Costs

Besides the major scheme components mentioned above, all remaining BOP components like heat exchangers, compressors, pipe lines etc. will not be price estimated through scheme operation. It will thus be assumed that all minor components and utilities will constitute the same percentage of the total capital costs on syngas preparation and synthesis as in figure 4.17 on page 27.

### 10.2 Operation Costs

Next the operation costs will be described. As already mentioned the raw biomass will not be assigned any costs. However, on large scale estimates on the biomass transport will be given. Forecast electricity prices are given to calculate operation power consumption, and prices for different upgrading technologies are presented.

#### 10.2.1 Biogas Upgrading

The upgrading of biogas into a CH$_4$ and CO$_2$ fraction, makes it possible to direct some of the CO$_2$ to the electrolysis unit to optimize the syngas composition. Also, at large scale the upgrading enables the opportunity of periodic hold up of CH$_4$ in the natural gas network. The economics of upgrading for three different existing upgrading plants are shown in table 10.2.

<table>
<thead>
<tr>
<th>CarboTech (PSA)</th>
<th>Malmberg Water (Water Scrubber)</th>
<th>Ammongas (Chemical Absorption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production price</td>
<td>0.88 [DKK/m$^3$] (650 m$^3$/hr.)</td>
<td>0.85 [DKK/m$^3$] (650 m$^3$/hr.)</td>
</tr>
<tr>
<td></td>
<td>0.51 [DKK/m$^3$] (1100 m$^3$/hr.)</td>
<td>0.49 [DKK/m$^3$] (1600 m$^3$/hr.)</td>
</tr>
</tbody>
</table>

*Table 10.2: Upgrading costs incl. investment and operational costs. The prices are per cubic meter of CH$_4$.*
10.2 Operation Costs

It can be seen, that the chemical absorption technology yields the lowest upgrading price, though it does not have the lowest energy input as was shown in figure 3.4 on page 14. It has been chosen to use the chemical scrubbing technology mainly due to its superiority in price against the other presented technologies. Also both from an economical and environmental point of view a CH4 slip as low as possible is desirable, which is neglectable for chemical scrubbing, see table 3.2 on page 14. Also, if the separated CO2 is to be injected for the methanol synthesis, low concentrations of CH4 are desirable [Hansen et al., 2011]. Due to the low CH4 slip it is also reasonable to assume a pure CH4 and CO2 fraction out of the scrubber.

The upgrading price will be linearly extrapolated from the data presented in table 10.2 on the previous page for the respective sizes of the farm and large scale plants. This means, that the upgrading price for the farm scale and large scale plant is 0.58 and 0.45 DKK/m3, respectively. Additional, power and heat consumption of the scrubber shown in figure 3.4 on page 14 will be assumed included in the presented prices.

10.2.2 Electricity Price

As shown in figure 10.1 on page 61 the electricity price represent almost a third of the total OPEX in the work done by [Hansen et al., 2011]. Electricity is used to operate pumps, compressors and other components in the system with the electrolyser as the largest electricity consumer. With an increasing amount of renewable energy sources a larger variation in electricity production and prices will be present. When the electricity production exceeds the demand the price of electricity will be low for the consumers. With a large penetration of e.g. windpower the risk of overproduction will have an influence on the electricity price. An estimate of the power spot prices with increasing amount of renewables are shown in figure 10.5 [Hansen et al., 2011].

<table>
<thead>
<tr>
<th>Wind penetration:</th>
<th>20 % VE</th>
<th>50 % VE</th>
<th>100 % VE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wind penetration:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2025</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2025</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hours per year:</td>
<td>1000</td>
<td>2000</td>
<td>3000</td>
</tr>
<tr>
<td></td>
<td>2025</td>
<td>2025</td>
<td>2025</td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>2025</td>
<td>2025</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3000</td>
<td>4000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5000</td>
<td>6000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7000</td>
<td>8000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8760</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>186</td>
<td>267</td>
</tr>
<tr>
<td></td>
<td></td>
<td>305</td>
<td>327</td>
</tr>
<tr>
<td></td>
<td></td>
<td>334</td>
<td>349</td>
</tr>
<tr>
<td></td>
<td></td>
<td>372</td>
<td>394</td>
</tr>
<tr>
<td></td>
<td></td>
<td>394</td>
<td>461</td>
</tr>
<tr>
<td></td>
<td></td>
<td>453</td>
<td>528</td>
</tr>
<tr>
<td></td>
<td></td>
<td>453</td>
<td>609</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 10.5: Minimum average power price in DKK/MWh.

It is important to note, that these prices are a parameterization of the spot marked price structure in 2006, and it does not account for future changes in power infrastructure, wind power penetration in neighboring countries, fuel prices etc. [Jørgensen and Ropenus, 2008]. These accumulated electricity price per hour during a year is used in this present report.
10.2.3 Transportation

The OPEX in transportation is linked to large scale plants, since it is assumed, that transportation costs on farm scale plant is neglectable. According to [Henrik et al., 2006] transportation of manure will be on a semitrailer with a loading of 31 m$^3$. The pricing for the investment and operational costs are listed in table 10.3.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Truck</td>
<td>700,000 DKK.</td>
</tr>
<tr>
<td>Semitrailer</td>
<td>900,000 DKK.</td>
</tr>
<tr>
<td>Average speed</td>
<td>40 km/h</td>
</tr>
<tr>
<td>Load size</td>
<td>31 m$^3$</td>
</tr>
<tr>
<td>Time spend at process plant</td>
<td>15 min/trip</td>
</tr>
<tr>
<td>Time spend at farms</td>
<td>15 min/trip</td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>1.5 km/liter</td>
</tr>
<tr>
<td>Diesel price</td>
<td>9.5 DKK/liter [OK, 2012]</td>
</tr>
<tr>
<td>Driver salary</td>
<td>140 DKK/h</td>
</tr>
<tr>
<td>Taxes and insurance</td>
<td>26,000 DKK/year</td>
</tr>
<tr>
<td>Repair and maintenance</td>
<td>4 DKK/m$^4$ processed biomass</td>
</tr>
</tbody>
</table>

*Table 10.3: Costs regarding transportation*

Since the liquid fraction of slurry is rich in nutrients, which is used as a fertilizer in the fields, it can be separated from the manure, leaving only the fiber fraction for the biogas plant. This will increase the biogas yield per mass while lowering the transportation cost. It is assumed, that after the biomass is degassed, it will be returned to the farms. [Henrik et al., 2006] calculated an average transportation distance from three different sized biogas plants, and with a extrapolation from these data the average driving distance is calculated to be 21.8 km. In table 10.4 the costs regarding transportation of manure are shown.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Trips, [trips/day]</td>
<td>40</td>
</tr>
<tr>
<td>Average trip time, [hr]</td>
<td>1.045</td>
</tr>
<tr>
<td>Salary, [DKK/day]</td>
<td>5861</td>
</tr>
<tr>
<td>Fuel costs, [DKK/day]</td>
<td>5531</td>
</tr>
<tr>
<td>Repair and maintenance, [DKK/day]</td>
<td>4968</td>
</tr>
<tr>
<td>Number of trucks, [-]</td>
<td>2</td>
</tr>
<tr>
<td>Number of semitrailers, [-]</td>
<td>2</td>
</tr>
<tr>
<td>Payback time, [year]</td>
<td>10</td>
</tr>
<tr>
<td>OPEX, [DKK/year]</td>
<td>5,453,209</td>
</tr>
<tr>
<td>CAPEX, [DKK/year]</td>
<td>520,785</td>
</tr>
</tbody>
</table>

*Table 10.4: Cost of transportation*

10.2.4 Miscellaneous Operatinoal Costs and Earnings

Besides the already mentioned operational costs some additional economic flows exist. It was pointed out in Chapter 5 on page 29 the SOEC has to be fed with demineralized water. Furthermore, by-products like excess O$_2$ and heat may be valuables, which can be sold. These flows will also be evaluated in the economic

10. Economic Assessment

67
10.2 Operation Costs

assessment according to the table presented below.

<table>
<thead>
<tr>
<th></th>
<th>Cost</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demineralized water</td>
<td>12.5 DKK/Ton</td>
<td>Jensen et al. 2008</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.5 DKK/Nm³</td>
<td>Hansen et al. 2011</td>
</tr>
<tr>
<td>Excess heat</td>
<td>236 DKK/MWh</td>
<td>Hansen et al. 2011</td>
</tr>
<tr>
<td>Cooling water</td>
<td>4.3 DKK/MWh</td>
<td>AspenTechnology.Inc 2009</td>
</tr>
</tbody>
</table>

*Table 10.5: Miscellaneous operational costs and earnings*
Results

In this chapter the results obtained will be presented. First, the optimized parameters from the cost optimizations for each of the three different schemes will be presented and analyzed. Next, the heat integration results derived from the optimized solutions are outlined. These results are the basis for calculating costs of external utilities and earnings from district heating sales. Hereafter, the cost distribution of each scheme is presented. A comparison on the methanol price will be estimated and compared to the prices in figure 4.2 on page 18. The prices are calculated from the assumptions made in Chapter 10 on page 61 with the electricity price corresponding to the 2010 rate. Finally, a short discussion on the optimized solutions will be given.

11.1 Optimization Results

In this section the optimized results will be presented. The section is split into subsections with the results from the different process schemes.

11.1.1 Farm Scale Plant

In table 11.1 the optimized parameters, with their corresponding bounds are presented. Regarding the CO\(_2\) and H\(_2\)O flows to the electrolysis unit the bounds are set to maintain a reasonable syngas composition. The tendency is, however, to minimize the flow to the SOEC and thereby reduce the costs involved in the electrolysis. The methanol reactor temperature is rather high compared to the temperature found in the sensitivity analysis. This is mainly due to a different composition in the feed gas to the reactor. The pressure of the methanol reactor is maximized. The purge fraction is found to be 0.15 % ensuring a high utilization of biogas.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lower bound</th>
<th>Upper bound</th>
<th>Optimized value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Split fraction of CO(_2) to SOEC, [-]</td>
<td>0.5</td>
<td>0.99</td>
<td>0.5</td>
</tr>
<tr>
<td>Split fraction of purge gas, [-]</td>
<td>0.001</td>
<td>0.1</td>
<td>0.00477159</td>
</tr>
<tr>
<td>Water mole flow into the SOEC, [kmol/s]</td>
<td>0.00075</td>
<td>0.002</td>
<td>0.00075</td>
</tr>
<tr>
<td>Methanol reactor temperature, [K]</td>
<td>500</td>
<td>550</td>
<td>538.635</td>
</tr>
<tr>
<td>Methanol reactor length, [m]</td>
<td>1</td>
<td>7</td>
<td>2.764</td>
</tr>
<tr>
<td>Methanol reactor pressure, [bar]</td>
<td>30</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Module, [-]</td>
<td></td>
<td></td>
<td>1.38</td>
</tr>
</tbody>
</table>

Table 11.1: Farm scale optimized parameters.

In figure 11.1 on the next page a mass balance diagram of the farm scale plant is shown. It is evident, that only a very small fraction of the input biomass is actually converted to methanol. For the partial oxidation based plant this fraction corresponds to around 5.5 %. Also, due to the equilibrium limits of methanol synthesis, the recycled mass flow is relative large compared to the syngas feed. As it will be shown later, such a large loop also leads to the accumulation of large concentrations of inert gases.
11.1 Optimization Results

Figure 11.1: Sankey diagram of flows in the farm scale plant.

11.1.2 Large Scale Plant, Partial Oxidation

The optimized parameters for the large scale plant based on partial oxidation are shown in table 11.2. The tendency is similar to that of the farm scale plant, where the flows to the electrolysis unit are settling at the lower bounds. This also means, that the tendency of the mass distribution is similar to that of the farm scale, and will therefore not be shown here. The mass distribution can be found in Appendix C on page 117.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lower bound</th>
<th>Upper bound</th>
<th>Optimized value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Split fraction of CO(_2) to SOEC, [-]</td>
<td>0.5</td>
<td>0.99</td>
<td>0.5</td>
</tr>
<tr>
<td>Split fraction of purge gas, [-]</td>
<td>0.001</td>
<td>0.1</td>
<td>0.004184</td>
</tr>
<tr>
<td>Water mole flow into the SOEC, [kmol/s]</td>
<td>0.017</td>
<td>0.02</td>
<td>0.017</td>
</tr>
<tr>
<td>Methanol reactor temperature, [K]</td>
<td>500</td>
<td>550</td>
<td>547.231</td>
</tr>
<tr>
<td>Methanol reactor length, [m]</td>
<td>50</td>
<td>100</td>
<td>88.6317</td>
</tr>
<tr>
<td>Methanol reactor pressure, [bar]</td>
<td>30</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Module, [-]</td>
<td></td>
<td></td>
<td>1.73</td>
</tr>
</tbody>
</table>

Table 11.2: Partial oxidation based large scale optimized parameters.
11.1.3 Large Scale Plant, Steam Reforming

In table 11.3 the optimized variables are shown with their bounds. The bounds are slightly different from the plants based on partial oxidation. The lower bound of the CO$_2$ purge fraction is raised due to a higher CO$_2$ concentration in the steam reformer outlet stream. The lower bound of H$_2$O flow into the SOEC is lowered to 0, due to a higher molar fraction of H$_2$ out of the steam reformer. However, the same tendencies as for the other plants occur, where the work of the SOEC is minimized. The synthesis loop purge fraction is not an optimization parameter, since it is assumed that the purge gas is burned to provide heat for the endothermic reactions in the steam reformer.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lower bound</th>
<th>Upper bound</th>
<th>Optimized value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Split fraction of CO$_2$ to SOEC, [-]</td>
<td>0.7</td>
<td>0.99</td>
<td>0.7</td>
</tr>
<tr>
<td>Water mole flow into the SOEC, [kmol/s]</td>
<td>0</td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td>Methanol reactor temperature, [K]</td>
<td>500</td>
<td>550</td>
<td>522.434</td>
</tr>
<tr>
<td>Methanol reactor length, [m]</td>
<td>50</td>
<td>100</td>
<td>90.1778</td>
</tr>
<tr>
<td>Methanol reactor pressure, [bar]</td>
<td>30</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Steam reformer length, [m]</td>
<td>20</td>
<td>100</td>
<td>48.32</td>
</tr>
<tr>
<td>Steam reformer pressure, [bar]</td>
<td>10</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>Module, [-]</td>
<td></td>
<td></td>
<td>1.82</td>
</tr>
</tbody>
</table>

Table 11.3: Steam reforming based large scale optimized parameters.

In figure 11.2 the Sankey diagram of flows in the large scale plant based on steam reforming is shown. Like for partial oxidation, the CO$_2$ purge fraction is optimized.

11. Results
oxidation, the steam reforming based scheme also experience a weak biomass to methanol conversion. Due to a large fraction of purge gas the conversion efficiency is less than 3%. The increased purge gas fraction compared to partial oxidation also results in a less significant recycle loop.

## 11.2 Heat Integration Results

In this section the heat integration results will be outlined. The results will be subdivided for the three different schemes.

### 11.2.1 Farm Scale Heat Integration Results

For the heat integration analysis it is important to distinguish between a mesophil and a thermophil operation of the biomass processing tank. The main reason for this is the high liquid fraction of the biomass supply, which demands a high heating duty. To calculate the heat duty it is assumed, that the entire liquid fraction of the biomass consists of H$_2$O, which must be heated to the respective temperatures given in section 2.2.1 on page 10. The grand composite curves for both operation modes can be shown in figure 11.3 and 11.4 on the facing page. Since the biogas yield from the two operation modes are almost equal, their grand composite curves only differ by their different heating duties corresponding to the biomass heating.

![Grand composite curve for mesophil operation of the farm scale plant.](image)

*Figure 11.3: Grand composite curve for mesophil operation of the farm scale plant.*

For both mesophil and thermophil operation it was found, that there is only a deficit of cold utilities. This is also expected, since the production scheme is highly dominated by exothermic processes. The amount of minimum cold utilities for the two operation modes corresponds to approximately 170 and 140 kW of cooling for mesophil and thermophil operation, respectively. Thereby, it can be concluded that the thermophil operation requires the least amount of external utilities of the two different cases. Add that to the fact, that the thermophil
operation produces slightly more biogas, the thermophil operation is preferable for the farm scale case.

![Grand composite curve for thermophil operation of the farm scale plant.](image)

*Figure 11.4:* Grand composite curve for thermophil operation of the farm scale plant.

The distillation heat duty is represented by a blue box, showing the heat demand by its length and the operational temperature interval by its height. For farm scale the distillation heat duty corresponds to approximately 115 kW, which is less than the needed cold utility. It is therefore assumed that the distillation can be integrated without the need for extra utilities.

### 11.2.2 Large Scale (POX) Heat Integration Results

For the large scale plants it is also important to distinguish between mesophil and thermophil. It is observed that the mesophil operation produces almost 15 % more biogas than at thermophil conditions. Another reason for the distinction is the difference between minimum utilities. For farm scale the difference between the two operations represent an expense. For large scale it represents an earning, since excess heat can be sold.

For the large scale plant based on partial oxidation it is found, that the amount of minimum cooling utility corresponds to approximately 3000 and 2100 kW for mesophil and thermophil operation respectively, see figure 11.5 and 11.6 on the next page.

Not only does mesophil condition produce more biogas, it also produces more excess heat, which represents an income. The conclusion is, that mesophil operation is preferable for large plants based on partial oxidation.

### 11. Results
For the large scale plant based on partial oxidation, distillation heat duties are estimated to approximately 2300 kW. It is observed, that due to the heat duty and temperature interval of distillation in combination with the temperature interval of district heating water, integrating the distillation train could introduce the need for extra utilities.
11.2.3 Large Scale (SR) Integration Results

The grand composite curve for the steam reformer based plant is shown in figure 11.7. Here, the same conclusion can be drawn, that mesophil conditions are preferable, due to the higher biogas yield and the greater surplus of heat. The need for external utilities amounts to around 1400 kW.

In the steam reforming case, the distillation heating duty was estimated to approximately 1500 kW. The lower heating duty compared to the partial oxidation based scheme, is caused by the lower methanol output.

![Grand composite curve for mesophil operation of the large scale plant based on steam reforming.](r:en):

Figure 11.7: Grand composite curve for mesophil operation of the large scale plant based on steam reforming.

Figure 11.7 shows, the integrating the distillation train with the remaining plant in this case, could also lead to a deficit of external utilities.

Though it has been addressed, that several heat integration issues could arise if the distillation train was included in the pinch analysis, no further attention will be given. It will thus be assumed, that all surplus heat can be sold as district heating.

11.3 Cost Distribution and Sensitivity

In this section the economic assessments from the plants are presented. The economic assessments are based on the optimization results and the heat integration. Likewise, this section is divided in to subsections containing the representative plants.
11.3 Cost Distribution and Sensitivity

11.3.1 Farm Scale Plant

The optimized parameters can be used to find the investment and operational costs. The annualized investment cost is slightly higher than the operational costs as indicated in figure 11.8. Furthermore, it can be seen, that the income regarding O₂ sale only recovers a small fraction of the costs.

![Annual expenditures of the farm scale plant](image)

Figure 11.8: Annual expenditures of the farm scale plant

In figure 11.9 and 11.10 the CAPEX and OPEX distribution for the plant is shown. The CAPEX is strongly dominated by the price of the biogas plant with 84 % of the total investment. By observing the figures it is clear, that the major expense regarding methanol production on farm scale is the investment price of the biogas processing plant.

![CAPEX distribution for the farm scale plant](image)

Figure 11.9: CAPEX distribution for the farm scale plant.

![OPEX distribution for the farm scale plant](image)

Figure 11.10: OPEX distribution for the farm scale plant.

11.3.2 Large Scale Plant, Partial Oxidation

Similar, the capital and operational expenditures are shown in figure 11.11 on the facing page. In this case the tendency of the costs are very different from the farm scale plant. Only 22 % of the annual expenditures are caused by the investment cost. Furthermore, the excess heat is now sold to a price corresponding to almost 50 % of the annualized capital cost.
The CAPEX and OPEX distribution for the large scale plant based on partial oxidation is shown in figure 11.12 and 11.13. From the figures it is evident, that the economy of scale have a large impact on the cost distributions. This is in evidence especially on the biogas plant reducing its influence significantly.

The OPEX distribution is highly dominated by the operation price of the SOEC. Since the operation price scales linearly for the electrolysis unit, and the other components involving the operation is affected by the economy of scale the influence of the SOEC becomes more significant for the large scale plant compared to the farm scale plant.

11.3.3 Large Scale Plant, Steam Reforming

The investment price is much similar to the large scale POX plant. However, the operational prices are significantly lower due to less SOEC work. Also the sales in terms of heat is lower because of the endothermic nature of the steam reformer.
11.3 Cost Distribution and Sensitivity

**Figure 11.14:** Annual expenditures for the large scale plant based on steam reforming.

The CAPEX distribution for the steam reforming plant is shown in figure [11.15](#). It can be seen, that the CAPEX distribution is much similar to the large scale plant based on partial oxidation. From the OPEX distribution in figure [11.16](#) it can be seen, that the annual CAPEX cost have become the dominating cost, due to a significant reduction in electrolysis work.

**Figure 11.15:** CAPEX distribution for the large scale plant based on steam reforming.

**Figure 11.16:** OPEX distribution for the large scale plant based on steam reforming.

### 11.3.4 Methanol Production Price

The methanol price is calculated from the results presented above and the annual production of methanol presented in table [11.4](#). Even though the large scale plant based on steam reforming has the lowest annual expenditures, the production of methanol is lower as well. The low production of methanol is caused by the large amount of gas purged, in order to heat the steam reformer. The purge fraction is 30 % in the steam reforming configuration compared to only 0.2 % in the plant based on partial oxidation, hence a better conversion to methanol can be achieved in the POX configuration.

<table>
<thead>
<tr>
<th></th>
<th>Farm scale POX</th>
<th>Large scale POX</th>
<th>Large scale SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total annual expenditures, [DKK/year]</td>
<td>4,002,215</td>
<td>50,712,302</td>
<td>34,327,131</td>
</tr>
<tr>
<td>Annual methanol production, [kg/year]</td>
<td>1,040,240</td>
<td>21,635,711</td>
<td>13,544,472</td>
</tr>
<tr>
<td>Methanol price, [DKK/kg]</td>
<td>3.85</td>
<td>2.34</td>
<td>2.53</td>
</tr>
<tr>
<td>Methanol price, [USD/ton]</td>
<td>687.03</td>
<td>418.56</td>
<td>452.57</td>
</tr>
</tbody>
</table>

**Table 11.4:** Total expenditures and production of the plants.
By comparing the methanol production price it is clear, that the farm scale plant suffers from the economy of scale with the most expensive production price. The cheapest production price is achieved by the large scale plant based on partial oxidation. Even though is has the largest annual expenditures, the larger throughput of methanol outweighs this disadvantage.

![Figure 11.17: Methanol prices compared to MNDRP and Hansen et al., 2011.](image-url)

**11.3.5 Cost Sensitivity**

In order to find those parameters, which affect the methanol price the most in the three cases, a sensitivity analysis have been made. The parameters of interest are the interest rate, electricity price, heat price and the costs involved in upgrading of biogas. The analysis is carried out by evaluating the methanol price by changing the parameters ± 10 %. The results are presented in normalized values around the base numbers presented in table 11.4 on the facing page.

The sensitivity of the parameters on farm scale is presented in figure [11.18](image-url). From the figure is can be seen, that the interest rate and electricity price are the most sensitive parameters. Even though the interest rate has an influence on all expenditures involving the investment, corresponding to 51 % of the total annual costs, it all most have the same influence as the electricity price, which only has a 35 % share of the costs. This is due to the nonlinear development in equation [10.1 on page 61](equation-url) As previously stated the heat sales is not included on farm scale.

![Figure 11.18: Sensitivity analysis of the farm scale plant.](image-url)
11.4 Discussion of Optimization Results

The influence of the sensitivity parameters for the large scale POX plant is shown in figure 11.19. As expected the electricity price is the most sensitive parameter involved, due to the high share of OPEX. By decreasing the electricity price by 10%, the methanol production price can be reduced by 6%. Comparing 11.18 and 11.19 it is shown, that the interest rate is now less dominant and the influence of upgrading costs is almost unchanged.

![Figure 11.19: Sensitivity analysis of the large scale plant based on partial oxidation.](image1)

The last figure in the sensitivity analysis is the large scale plant based on steam reforming. Again the electricity is the most sensitive parameter. However, it is now less significant, compared to the partial oxidation plant, due to a lower electricity consumption regarding the electrolysis unit. It follows, that by lowering the electricity price, only a 3% reduction in methanol production price can be achieved. Furthermore the figure indicates, that the sensitivity of both interest rate and upgrading price is almost the same.

![Figure 11.20: Sensitivity analysis of the large scale plant based on steam reforming.](image2)

For both large scale plants it is evident, that the heat price is the less sensitive parameter.

11.4 Discussion of Optimization Results

In this section a brief discussion on the optimization results will be carried out. The discussion will be based on composition plots through the reactors and the observations derived from these. The tendencies of the POX based plants are the same, why only the farm scale plant will be described.
11.4.1 Farm Scale

The reactor plots in the farm scale case are presented in figure [11.21] and [11.22]. Since the length of the partial oxidation reactor is not an optimization parameter the figure is only presented to see the outlet composition. It is observed, that the POX reactor reaches equilibrium after 1/3 of the reactor length. Worth noticing is the molar fraction of both CH\(_4\) and O\(_2\) of 0.539 % and 0.047 % respectively, since they acts as inerts in the proceeding processes.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{farm_scale_po.png}
\caption{Gas composition throughout the farm scale POX reactor.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{farm_scale_syn.png}
\caption{Gas composition throughout the farm scale synthesis reactor.}
\end{figure}

In figure [11.22] the composition throughout the synthesis reactor is shown. From the figure it can be seen, that recirculation loop accumulation of inerts is present. This build-up results in a outlet molar fraction of 11 %
and 1 % for CH\textsubscript{4} and O\textsubscript{2}, respectively. This large accumulation have some unwanted effects in the system. It causes increased cooling duties, compressor work and have a significant influence on the synthesis reactor kinetics. According to Appendix A on page 101 the reaction rates are based on partial pressures. Since the partial pressures of the main component in the synthesis decreases with increasing accumulation of inerts, this will have a negative influence on the reaction rates. As mentioned in Chapter 7 on page 43, equilibrium is favored at low temperatures and kinetics at high temperatures. Due to the high amount of inerts present in the syngas, it is kinetically desired to have a higher reactor temperature. Therefore, the obtainable methanol yield is lowered due to equilibrium. Furthermore, the optimized length of the reactor seems to be around the point it reaches equilibrium.

11.4.2 Large Scale, Steam Reformer

In figure 11.23 the composition through the steam reformer is shown. It is evident, that a slightly higher molar fraction of CH\textsubscript{4} (1.1 %) is present in the outlet stream of the reformer compared to the POX reformer. The steam reformer reaches equilibrium at around 22.5 m, but the optimized reactor length is found to be 48.32 m. This gives the indication, that a local minimum has been reached. However, by changing the initial guess values, it was not possible to achieve a more realistic optimum for the steam reformer length, hence a global optimum is not found.

Since a larger amount of inert gas is present in the syngas from the steam reformer, it is expected that the methanol synthesis will perform more inefficiently. But due to the large synthesis loop purge fraction, a smaller amount of inert gases is recirculated to the reactor. Therefore, the accumulation of inert gases in the synthesis loop is less dominant in this case. In figure 11.24 on the facing page it is seen, that the inert gases, consisting of CH\textsubscript{4} and H\textsubscript{2}O, only have molar fractions of 3 % and 2 %, respectively. The lower amount of inerts in the synthesis loop favors the reaction kinetics, allowing a lower reactor temperature, hence a higher methanol conversion can be achieved. A methanol molar fraction of 13 % is present in the outlet composition compared
to 9.5% in the farm scale plant. Again it is observed, that the optimized length of the methanol reactor seems to be around the point, it reaches equilibrium.

**Figure 11.24:** Gas composition throughout the methanol synthesis in the large scale plant based on steam reforming.

### 11.5 Summary

The heat integration and economic assessment have been evaluated from the results obtained by the cost optimization. It was found, that the biomass processing plant has a high share of the CAPEX for all three schemes. Due to economy of scale the biomass processing plant investment has a less significant share on the total annualized costs when increasing the capacity from farm scale to large scale. The SOEC operation is overall a main contributor to operational costs, why it was found the SOEC work should be minimized to minimize methanol production costs.

The O$_2$ sales price in this project has been adapted from [Hansen et al. 2011](#). It is not known whether this price is based on pressurized O$_2$ or not. The pressurization of O$_2$ has not been included in the assessment, which poses an extra expense. However, it is expected that this fact does not have any impact on the results, since the cost recovery from O$_2$ sales is low.

It must be emphasized, that the optimized values obtained for operational and size parameters are based on nominal load. Hence, the optimum solution obtained is not necessary valid, if part load operation is included in the optimization.
During the project period methanol production schemes have been identified and subjected to a cost-optimization to minimize the methanol production price. The results showed, that methanol produced from renewable and intermittent power sources, could potentially become a cost-effective method for producing biofuels. Several issues still remain unanswered to fully address the production potential though. These issues will be discussed in this chapter.

### 12.1 Future Electricity Prices

All scenarios presented have been based on a 2010 level regarding the electricity price. As it has been shown, especially the large scale plant based on partial oxidation is sensitive to the electricity price. Future production prices have been estimated by changing the electricity price from the 2010 level, to the projected prices presented for the two 2050 levels from table 10.5 on page 66. The results are shown in table 12.1. The production price of the farm scale plant increases by approximately 12 %. Due to the increase and the higher sensitivity on the electricity price for the large scale POX based schemes, the production price increases by more than 20 %. It is now evident, that at 2050 levels the production price is almost identical for the two large scale plants.

<table>
<thead>
<tr>
<th>Methanol production price</th>
<th>2010, 20 % VE</th>
<th>2025, 50 % VE</th>
<th>2025, 100 % VE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farm scale POX, [USD/ton]</td>
<td>687.03</td>
<td>768.58</td>
<td>772.90</td>
</tr>
<tr>
<td>Large scale POX, [USD/ton]</td>
<td>418.56</td>
<td>504.11</td>
<td>509.33</td>
</tr>
<tr>
<td>Large scale SR, [USD/ton]</td>
<td>452.57</td>
<td>501.87</td>
<td>504.43</td>
</tr>
</tbody>
</table>

*Table 12.1: Methanol production price for different electricity price scenarios.*

As already been discussed in Chapter 5 on page 29, the high sensitivity to the electricity price leads to speculation on operation strategies to decrease the operational costs. Discussed previously, the natural gas network connection on large scale schemes enables several options in terms of operation. A few of these options will be discussed in the succeeding.

### 12.2 Large Scale Steam Reformer using Natural Gas

The major drawback of using steam reforming is the large purge fraction needed to supply the reformer burner with enough combustible matter. Since the purge gas consists mostly of H\(_2\), having a low volumetric energy density, a rather large amount of purge gas is needed in the burner. Since the plant is connected to the natural gas network, it might be more feasible to use natural gas for the burner, hence having a smaller purge fraction in the synthesis loop. In figure 12.1 and 12.2 on the following page, the CAPEX and OPEX of such plant are shown.
12.3 Co-production of Methanol and Biogas

The natural gas is priced to 2.59 DKK/m³ according to [Jensen, 2009] and is assumed to be supplied to the burner to provide the same amount of heating needed in the steam reformer, introducing the constraint in equation 8.2 on page 52. From the figures it can be seen, that the CAPEX distribution is much similar to the original steam reforming plant. On the contrary, the OPEX cost is now dominated by the CAPEX and the cost of natural gas. Since the purge fraction is reduced significantly, the plant now produces 20,067,186 kg/year. The large increase in methanol production outweighs the extra cost of using natural gas, and a production price of 433.81 USD/ton can be achieved. A reduction of approximately 4 %.

Since the OPEX now is dominated by the CAPEX, this configuration could be interesting due to a more relaxed sensitivity to the electricity prices. The feasibility of this configuration will be dependent on the future development of both electricity and natural gas prices.

12.3 Co-production of Methanol and Biogas

A second option enabled, is a co-production scenario, where methanol is produced, whenever electricity prices are low. When electricity prices are high, biogas is upgraded and sold. To meet the vision of a fossil free Denmark by 2050, [CEESA, 2011] made a proposal to the energy supply for various renewable sources and the energy consumption by various fuel types have been given. The proposal is shown in figure 12.3 on the facing page for reference. From this proposal it appears, that both biogas from manure and methanol produced from biomass and synthesis play a significant role by 2050.

As a consequence of this double effect, it will be investigated, if co-production of methanol and upgraded biogas is feasible. Upgraded biogas for the natural gas network is now considered an income like sales of district heating and O₂. The methanol price for both large scale schemes are shown in figure 12.4 on the next page for different methanol production hours per year.
Figure 12.3: CEESA proposal for the energy supply for various renewable sources.

Figure 12.4: Methanol price for different methanol production hours per year.

According the figure the methanol price decreases for the partial oxidation based plant, when methanol production hours decrease. Actually, if the methanol production hours are halved, the production price can be decreased by around 15%. The production price decrease is caused by the sensitivity and high share of OPEX.

Regarding the steam reforming based plant, first the production price slightly decreases but then increases as methanol production hours decreases. The increase is caused by the reduced methanol production and the high share of CAPEX.

12. Discussion
12.4 Contribution to a Future Energy System

From figure 12.4 on the preceding page it also appears, that from the recommendable scenario with a medium increase in energy consumption, the need for syn-DME/methanol and bio-DME/methanol is in the order of 100 PJ/year. If the energy content of the methanol produced in this project is based on a heating value, the contribution to the 100 PJ/year target can be shown in table 12.2.

<table>
<thead>
<tr>
<th>Energy content</th>
<th>Farm scale POX</th>
<th>Large scale POX</th>
<th>Large scale SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV</td>
<td>$2.4 \cdot 10^{-2}$ PJ/year</td>
<td>$5 \cdot 10^{-1}$ PJ/year</td>
<td>$3.1 \cdot 10^{-1}$ PJ/year</td>
</tr>
<tr>
<td>LHV</td>
<td>$2.1 \cdot 10^{-2}$ PJ/year</td>
<td>$4.3 \cdot 10^{-1}$ PJ/year</td>
<td>$2.7 \cdot 10^{-1}$ PJ/year</td>
</tr>
</tbody>
</table>

*Table 12.2: Energy content of yearly produced methanol.*

It is clear from the three figures, that even the large scale plants yield low contributions to an overall target of 100 PJ/year. Considering the HHVs the contributions are in the order of 0.24‰, 5‰ and 3.1 ‰. Hence, in order to meet the requirements roughly 200 large scale plants based on partial oxidation are needed for a 2050 scenario.

Due to the low contributions, the purpose of such plant configurations lead to yet another discussion: Should these plants be considered as contributors to the energy carrier supply in a future energy system, or should they act as alternatives to biogas combustion, and thereby increase the incentives to even more biogas production? In the last case, the plants enables another slurry management technology, with the positive side effects of reducing GHG emissions and produce a valuable product in the form of methanol.

12.5 Biogas Yield and Composition

The biomass feed composition and thereby the biogas yield for this project, was adopted from [Pedesen et al., 2010], and therefore not subjected to any considerations.

The results of the biogas yield, obtained from [Pedesen et al., 2010] are based on a biomass retention time of 90 days in the tanks. Figure 12.5 on the facing page illustrates the biogas yield over varying retention times.

According [Jørgensen, 2009] a typical retention time is around 20 days, on which the costs of the biogas plants are based. From the figure it can be seen, that there is a large difference in the biogas yield comparing a retention time of 20 day to a retention time of 90 days for some resources of biomass. Therefore, the biogas yield of the plants might be slightly overpredicted in this report. If a retention time of 90 days should be obtained, significant larger reactor tanks are necessary, which increases the investment cost of the biogas plant.
It followed from the economic assessment, that the biogas plant constitutes a significant fraction of the total investment. Especially on a large scale, the most expensive components are the processing tanks, which must store the large amount of biomass.

From table 2.5 on page 9, the manure fibers only make up 15% of the total feed on a mass basis, but over 50% of the biogas is derived from these fibers. Increasing the share of manure fibers will introduce a rearrangement of the production costs and earnings. Increasing the fiber share will increase the biogas yield, decrease transportation and the processing tank expenditures. At the same time, the heating duty of biomass heating will decrease and lead to even more excess heat. Thereof, the earnings from district heating sales increases, if it is still assumed, that all excess heat can be sold. On the other, more slurry must be separated, which poses an expense. Due to the many benefits of a higher manure fiber share compared to the extra expense of separation, it is expected that methanol production will become cheaper by increasing this share.

12.6 Subsidies

According to the energy settlement of 2012, it is a political target to enhance the production of biogas, and to extend its end utilization beyond co-generation of heat and power purposes. Until recently, governmental subsidies were only attributed to biogas used for heat and power production. Through the new energy settlement, it has been decided to introduce an equality between biogas grants attributed for co-generation and upgraded biogas for the natural gas network. Likewise, the subsidies for plant initiation has been increased. Since the CAPEX annualized costs amount to 22%, 34% and 51% of the total annualized costs for the three different plants, subsidies for plant initiation will significantly reduce the cost of methanol production. In figure 12.6 on the following page, the investment and the subsidies attributed for several existing Danish biogas plants are shown. With an average percentage of 26%, subsidies at this level will have a major impact, and could be a crucial promoting element for the enhancement of biogas produced especially on a farm scale.
In fact, if 26% of the CAPEX on a farm scale plant is covered by governmental subsidies, methanol production price can reach a level below 600 USD/ton. This price is still above current methanol prices, but during financial booms, this price could be competitive as indicated by figure 11.17 on page 79. To fully address the feasibility of the presented concepts, future work should include elements like subsidies.

### 12.7 SOEC

In this present report the feed gas composition to the SOEC is not under consideration. The feed gas composition will have a direct influence on the unit lifetime due to the risk of carbon deposition. The assumption, that the SOEC is fed with pure CO$_2$, can be an issue on the large scale plant based on steam reforming. Therefore, it might be necessary to add H$_2$O to obtain a feasible inlet composition to the electrolysis unit, hence a larger operational cost will be introduced.

Furthermore, the current density is assumed constant at 2 A/cm$^2$. From equation 6.19 on page 40, it can be seen that the current density influences the losses occurring in the cell. By lowering $i$, the SOEC operational cost decreases as well. Decreasing $i$ will, on the other hand, result in an increase in cell area according to equation 6.18 on page 40. Hence, an optimized value of $i$ could be found to account for the trade-off of lowering the operational costs and increasing the investment cost. Likewise, a constant ASR of 0.2 has been assumed. Altering this value will change the losses occurring.

The SOEC investment cost is based on numbers from [Hansen et al., 2011]. These numbers are on a 2025 level as indicated by figure 5.1 on page 31, why these probably are underestimated for a work investigated on a 2010 level. A significant price drop occur in the interval from 2010 to 2025, hence the price of the electrolysis unit on a 2010 level can be 6 times higher than the projected investments.

Likewise, availability of especially the electrolysis unit has not been subjected to any discussion. As it appears from table 5.1 on page 31, the maximum demonstrated SOEC system is 15 kW. The electrolysis unit size in
this project is around 300 kW and 7 MW for the small and large scale plant, respectively. Due to the non-commercialized technology of SOEC, availability could be an issue.

12.7.1 Production without SOEC

Consistently throughout the optimization the electrolysis work is minimized. The bounds are maintained to obtain a feasible synthesis gas composition and get full carbon utilization. If CO\textsubscript{2} from the biogas is allowed to be purged from the system the electrolysis unit may not be necessary, and the optimization bounds regarding the SOEC could be set lower. Therefore, an optimization routine has been investigated without the presence of a SOEC. The results can be seen in table 12.3.

<table>
<thead>
<tr>
<th></th>
<th>Farm scale</th>
<th>Large scale POX</th>
<th>Large scale SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total annual expenditures, [DKK/year]</td>
<td>2,908,977</td>
<td>27,198,580</td>
<td>28,276,238</td>
</tr>
<tr>
<td>Annual methanol production, [kg/year]</td>
<td>706,495</td>
<td>14,368,320</td>
<td>11,825,317</td>
</tr>
<tr>
<td>Methanol price, [DKK/kg]</td>
<td>4.12</td>
<td>1.89</td>
<td>2.39</td>
</tr>
<tr>
<td>Methanol price, [USD/ton]</td>
<td>735.26</td>
<td>338.02</td>
<td>426.99</td>
</tr>
<tr>
<td>CO\textsubscript{2} purge, [%]</td>
<td>80</td>
<td>80</td>
<td>72</td>
</tr>
</tbody>
</table>

*Table 12.3: Optimization results without SOEC.*

Consequently, the annual expenditures are lower than the basic process schemes, since there is no electrolysis unit. Since a rather large fraction of the CO\textsubscript{2} is purged and the absence of added H\textsubscript{2} from electrolysis, less matter is added to the recirculation loop, leading to a decrease in production of methanol. It is seen, that a reduction potential of 80 USD/ton methanol is present for the large scale plant based on partial oxidation and 25 USD/ton for the plant based on steam reforming.

Contrarily to the large scale plants, the farm scale plant experiences an increase of 48 USD/ton in methanol production price. The result for the farm scale plant indicates that an optimum is present between the two cases investigated. This could be the case for the large scale plants as well; hence an even cheaper methanol production price might be possible with the opportunity of both purging and utilizing a SOEC. By allowing a full elimination of the SOEC in the process scheme the technology will only be considered as a way to utilize the biogas potential, rather than intermittency friendly energy storage.

Though an electrolysis unit is incorporated within the process scheme, its ability to act as a power peak shaver is not clarified, since averaged power spot prices are used. To fully address this feature, fluctuated electricity prices etc. should be included the process schemes evaluation.

12.8 Global Optimization

It has already been pointed out, that the optimization method used in this project only guaranties a local optimum. It was experienced, that the optimum solution obtained from this method was highly sensitive to initial guesses on the optimization parameters. Hence, applying some evolutionary algorithm or any other global optimization method, production prices could potentially be even lower than pronounced.
Conclusion

The aim of this thesis was to contribute with knowledge about alternative utilization of biogas from agricultural biowaste, in the sense of pig and cattle manure. This should be in contrast to the direct combustion for co-generation of electricity and district heating. Thereby, increase the incentives of biogas utilization and enabling a wind power peak shaving mechanism by a ETL-process.

Consequently, the main focus of this work was to investigate the feasibility of methanol production from animal manure combined with co-generation by utilization of a SOEC. Two cases were chosen: A farm scale plant processing 18,500 ton/year and a large scale plant processing 500,000 ton/year.

Different process schemes were investigated on the large scale plant using either a steam reformer or catalytic partial oxidation reactor to convert biogas into a more desirable synthesis gas, which could be synthesized into methanol. On farm scale, only partial oxidation was considered due to the fast kinetics and therefore a more compact and simple system. For all plants the possibility of using a SOEC to add H\(_2\) and CO was present.

Overall process models were developed in the software Aspen Plus\textsuperscript{®}. An initial sensitivity analysis was performed on core components in the process scheme, to identify the sensitivity of the operational conditions. From equilibrium considerations of the steam reformer it was found, that CH\(_4\) conversion was favored at high temperatures and low pressures, but due to the risk of carbon deposition a minimum pressure of 10 bar was applied. The same tendencies were found for the POX reactor. For the methanol synthesis reactor it was found, that the methanol conversion was sensitive to temperature and the synthesis should be operated in a narrow temperature window. Since the possibility of adding H\(_2\) and CO from a SOEC was present, a sensitivity study of the feed gas composition to the methanol synthesis was carried out. The methanol yield of the reactor was found to be sensitive to the feed composition as well.

After the identification of the most sensitive parameters, an objective function was developed to calculate the methanol production price. The optimization parameters were chosen from the sensitivity analysis and the economic assessment of the process components. The systems were optimized using a build-in optimization algorithm. The key results involving the methanol production are presented in table 13.1.

<table>
<thead>
<tr>
<th></th>
<th>Farm scale</th>
<th>Large scale POX</th>
<th>Large scale SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total annual expenditures, [DKK/year]</td>
<td>4,002,215</td>
<td>50,712,302</td>
<td>34,327,131</td>
</tr>
<tr>
<td>Annual methanol production, [kg/year]</td>
<td>1,040,240</td>
<td>21,635,711</td>
<td>13,544,472</td>
</tr>
<tr>
<td>Methanol price, [DKK/kg]</td>
<td>3.85</td>
<td>2.34</td>
<td>2.53</td>
</tr>
<tr>
<td>Methanol price, [USD/ton]</td>
<td>687.03</td>
<td>418.56</td>
<td>452.57</td>
</tr>
</tbody>
</table>

*Table 13.1: The key results from the optimizations.*
The general tendency of the optimizations was, that the work of the SOEC was minimized. Even though the feed composition of the methanol synthesis reactor was a sensitive parameter, the extra costs associated with SOEC work were not profitable. The optimization routine also showed, that the investment costs of the biogas plant had the highest share of the annual expenditures on farm scale. For the large scale unit based on partial oxidation it was the expenditures regarding SOEC operation. The large scale plant based on steam reforming was dominated by the investment costs in general.

Though, additional operation costs are present for large scale production in the sense of biomass separation and transportation, the economy of scale benefits for large scale production clearly exceed the extra costs.

It has also been projected, that due to the high cost sensitivity to the electricity price, methanol production will be more expensive in the future as a result of higher average electricity prices.

A proposal for a future energy demand and supply for various types of fuels was given in [CEESA, 2011]. The projection showed that the need for syn-DME/methanol and bio-DME/methanol was in the order of 100 PJ/year. Results showed that the large scale plant based on partial oxidation yielded the highest methanol production. However, this annual methanol production corresponds only to 0.5 ‰ of the recommended production in 2050. The large quantity of plants needed to meet the requirements, leads to the conclusion that a Danish methanol infrastructure based entirely on synthesis of biogas is unlikely. Instead this technology should act as a way to increase the incentives of utilization of slurry with a valuable production of methanol.

It can be concluded from the work done that methanol production, as an alternative to co-generation, from biogas can become a feasible technology for the enhancement of biogas production and utilization. To fully address the potential, the discussion pointed out several perspectives to be investigated in a future work.
In the discussion several things have already been mentioned, which need to be further investigated in order to address the potential of the proposed methanol plants. Towards the achievement of a full potential addressing, the project group has pointed out the most important tasks to be done in a future work:

- Only a few production schemes have been proposed in this project. Therefore, topology investigation and optimization among various production schemes is recommended.

- The large scale plants have the ability for poly-generation, where power, heat, cooling and fuels are produced on site. To investigate this potential the schemes have to be evaluated in a real case study.

- Future work has to be done considering integration in the existing energy system.

- A thorough economic assessment should be carried out, in which utilities and general balance of plant components are included.

- Operational conditions regarding biomass processing and biomass feed should be included in a whole system analysis.

- Future work should include elements like subsidies and electricity overproduction allocation for intermittent energy storage.

- If high carbon utilization has to be achieved, solid oxide electrolysis must be commercialized on a large scale. Therefore, future development within this research area is needed.

- A global optimization should be carried out to ensure, that the production price obtained is indeed a global minimum. Additionally, an efforts should be made towards a total system optimization, in which heat integration is incorporated.
Bibliography


A.1 Steam Methane Reforming and Methanol Synthesis Kinetics

First the stoichiometric reactions for both the steam reforming and the methanol synthesis reactor will be introduced, followed by the modeling procedure in Aspen Plus. Finally the rate expressions and parameters will be presented for the reactions involved.

The steam reformer is used to convert the biogas consisting of CH\(_4\) and CO\(_2\) into a syngas consisting mainly of H\(_2\) and CO using a nickel based catalyst. In the reformer, steam and CH\(_4\) is reacted through the two steam reactions, shown in equations A.1 and A.2, and the water gas shift reaction in equation A.3 [Xu and Froment, 1989a].

\[
\begin{align*}
CH_4 + H_2O & \rightarrow 3H_2 + CO \quad \Delta H = 206169 \text{ [kJ/kmole]} \\
CH_4 + 2H_2O & \rightarrow 4H_2 + CO_2 \quad \Delta H = 165012 \text{ [kJ/kmole]} \\
CO + H_2O & \rightarrow CO_2 + H_2 \quad \Delta H = -41157 \text{ [kJ/kmole]}
\end{align*}
\] (A.1, A.2, A.3)

In the synthesis reactor syngas is converted into methanol. The main stoichiometric reactions involved in the methanol synthesis are described by the hydrogenation of CO\(_2\) and CO in reaction A.4 and A.5 and the reverse water gas shift reaction in equation A.6 [Vanden Bussche and Froment, 1996].

\[
\begin{align*}
CO_2 + 3H_2 & \rightarrow CH_3OH + H_2O \quad \Delta H = -49316 \text{ [kJ/kmole]} \\
CO + 2H_2 & \rightarrow CH_3OH \quad \Delta H = -91000 \text{ [kJ/kmole]} \\
CO_2 + H_2 & \rightarrow CO + H_2O \quad \Delta H = 41157 \text{ [kJ/kmole]}
\end{align*}
\] (A.4, A.5, A.6)

The steam reformer and methanol reactor is modeled in Aspen Plus as plug flow reactors. The Langmuir-Hinshelwood Hougen-Watson (LHHW) kinetic formulation is used to express the rate of reaction. The general LHHW expression is shown in equation A.7 [Aspen Technology Inc., 2000].
A.1 Steam Methane Reforming and Methanol Synthesis Kinetics

\[
\text{rate} = \text{kinetic factor} \cdot \frac{\text{driving force}}{\text{adsorption term}} \quad (A.7)
\]

Where

\[
\text{kinetic factor} = A \cdot e^{\frac{E_A}{RT}} \quad (A.8)
\]

\[
\text{driving force} = k_1 \prod_{i=1}^{N} C_i^{C_i} - k_2 \prod_{j=1}^{N} C_j^{C_j} \quad (A.9)
\]

\[
\text{adsorption term} = \left[ \sum_{i=1}^{N} K_i \left( \prod_{j=1}^{N} C_j^{C_j} \right)^m \right] \quad (A.10)
\]

The rate expressions for the catalytic surface kinetics of the steam reformer can be represented by equation \[\text{A.11, A.12 and A.13} [Xu and Froment, 1989a].\]

\[
r_{I} = k_1 \frac{p_{H_2}^{2.5} p_{CH_4} p_{H_2O} - \frac{1}{K_{CO} p_{CO}}}{\left(1 + K_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O} \right)^{2}} \quad \left[ \frac{\text{k mole}}{\text{kg catalyst s}} \right] \quad (A.11)
\]

\[
r_{II} = k_2 \frac{p_{H_2}^{3.5} p_{CH_4} p_{H_2O} - \frac{1}{K_{CO} p_{CO}}}{\left(1 + K_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O} \right)^{2}} \quad \left[ \frac{\text{k mole}}{\text{kg catalyst s}} \right] \quad (A.12)
\]

\[
r_{III} = k_3 \frac{p_{CO} p_{H_2O} - \frac{1}{K_{CO} p_{CO}}}{\left(1 + K_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O} \right)^{2}} \quad \left[ \frac{\text{k mole}}{\text{kg catalyst s}} \right] \quad (A.13)
\]

The rate constants can be calculated using the Arrhenius correlation with the data shown in table \[\text{A.1}].

<table>
<thead>
<tr>
<th>(k)</th>
<th>(A)</th>
<th>(E_A) [kJ/kmole]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1) [(\text{k mole} - \text{bar}^{0.5} - \text{kg}^{-1} - \text{s}^{-1})]</td>
<td>1.1736E12</td>
<td>240.1E3</td>
</tr>
<tr>
<td>(k_2) [(\text{k mole} - \text{bar}^{0.5} - \text{kg}^{-1} - \text{s}^{-1})]</td>
<td>2.8333E11</td>
<td>243.9E3</td>
</tr>
<tr>
<td>(k_3) [(\text{k mole} - \text{bar}^{-1} - \text{kg}^{-1} - \text{s}^{-1})]</td>
<td>543.055</td>
<td>67.13E3</td>
</tr>
</tbody>
</table>

\[\text{Table A.1: Pre-exponential factor and activation energy for the rate constants}\]

The adsorption constants can be calculated using the Van’t Hoff equation with the parameters given in table \[\text{A.2}\].

<table>
<thead>
<tr>
<th>(K)</th>
<th>(A)</th>
<th>(\Delta H) [kJ/kmole]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{CO}) [(\text{bar}^{-1})]</td>
<td>8.23E-5</td>
<td>-70650</td>
</tr>
<tr>
<td>(K_{H_2}) [(\text{bar}^{-1})]</td>
<td>6.12E-9</td>
<td>-82900</td>
</tr>
<tr>
<td>(K_{CH_4}) [(\text{bar}^{-1})]</td>
<td>6.65E-4</td>
<td>-38280</td>
</tr>
<tr>
<td>(K_{H_2O}) [-]</td>
<td>1.77E5</td>
<td>88680</td>
</tr>
</tbody>
</table>

\[\text{Table A.2: Parameters for calculating the adsorption constants}\]

The equilibrium parameters are listed in table according to \[\text{A.3}\].
Table A.3: Parameters for calculating the equilibrium constants.

<table>
<thead>
<tr>
<th>$K_{eq.1}$ [bar]</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.707E12</td>
<td>223064.62</td>
<td></td>
</tr>
<tr>
<td>$K_{eq.2}$ [bar]</td>
<td>5.375E10</td>
<td>186483.02</td>
</tr>
<tr>
<td>$K_{eq.3}$ [-]</td>
<td>1.142E-2</td>
<td>-36581.6</td>
</tr>
</tbody>
</table>

During a catalytic reaction over a solid porous pellet, the reaction undergoes a sequence of mechanisms which are influential on the reaction rates. Firstly, in order for the reactants to react on the pellet surface the reactants must first diffuse from the bulk flow to the pores. Secondly, the reactants then adsorb at the solid surface prior reaction. The products then desorb and diffuse back to the bulk flow. The reaction rate is thus determined by the slowest of the involved mechanisms. For porous catalysts diffusion of the species ends up being the rate limiting mechanism, why the reaction rates determined by the LHHW kinetics alone do not represent the actual rates. In the estimation of the actual rates [Xu and Froment, 1989b] calculated rate effectiveness coefficients, by solving the concentration profiles within the catalyst. The effectiveness coefficients, however, are not constants but depending on several process parameters and catalyst structure etc, see figure [A.1].

Figure A.1: Effectiveness coefficients calculated by [Xu and Froment 1989b].

The effectiveness coefficients used in this model will though be assumed constant. For both steam reforming reactions the effectiveness coefficients will be set equal to 0.02. Regarding the effectiveness coefficient for the shift reaction is was found through a parametric study that the reactor outlet composition was non-sensitive to the effectiveness coefficient. For this reason it will also be set equal to 0.02.

Since only two of the three reaction equations in the methanol synthesis are stoichiometric independent, only two expressions are needed for the reaction rates. The corresponding reaction rates for the hydrogenation of CO$_2$ and the reverse water gas shift is shown in equation [A.14] and [A.15] [Vanden Bussche and Froment, 1996].

\[
\begin{align*}
    r_{CH_3OH} &= k_d \frac{p_{CO_2}p_{H_2}^4 p_{H_2O} p_{CH_3OH}}{(p_{H_2} + k_c p_{H_2O} + k_a p_{H_2}^{1.5} + k_b p_{H_2} p_{H_2O})^3} \\
    r_{H_2O} &= k_e \frac{p_{CO_2}p_{H_2} p_{H_2O} p_{CO}}{p_{H_2} + k_c p_{H_2O} + k_a p_{H_2}^{1.5} + k_b p_{H_2} p_{H_2O}}
\end{align*}
\]
According to [Grue, 2005] the equilibrium constant for equation (A.14) can be expressed by equation (A.16). The equilibrium constant for the water gas shift reaction is the same as in the steam reformer.

\[ K_{eq}^1 = \left( \frac{p_{CH_3OH}p_{H_2O}}{p_{CO}p_{H_2}} \right) = 10^{-10.592 + \frac{306}{T}} \approx \exp \left( -24.389 + \frac{7059.726}{T} \right) \]  

The parameters for the rate expressions are given in table A.4.

Table A.4: Parameters for the reaction rates in the methanol synthesis.

<table>
<thead>
<tr>
<th>( k )</th>
<th>( A )</th>
<th>( B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_a \ [bar^{-0.5}] )</td>
<td>0.499</td>
<td>17197</td>
</tr>
<tr>
<td>( k_b \ [bar^{-1}] )</td>
<td>6.62E-11</td>
<td>124119</td>
</tr>
<tr>
<td>( k_c \ [-] )</td>
<td>3453.38</td>
<td>0</td>
</tr>
<tr>
<td>( k_d \ [mole/(kg - s - bar^2)] )</td>
<td>1.07</td>
<td>36696</td>
</tr>
<tr>
<td>( k_e \ [mole/(kg - s - bar)] )</td>
<td>1.22E10</td>
<td>-94765</td>
</tr>
</tbody>
</table>

Both models are validated through a molar and mass balance check for the individual species. Furthermore the results obtained from the steam reformer is compared with results from [Xu and Froment, 1989b] with good agreement. The results from the methanol reformer is in agreement with results from [Vanden Bussche and Froment, 1996] at a temperature of 523.15 K and 50 bar. However [Mignard and Pritchard, 2008] did a more comprehensive validation of the model and compared the results with experimental results from [Klier et al., 1982]. Figure A.2(a) shows the conversion of carbon to methanol as a function of CO\(_2\) concentration for both the model and experiment.

From figure A.2(a) it is clear that the model has a lack of sensitivity to temperatures. The tendency of the curves is consistent with the experimental data, however a over prediction is present for temperatures lower that 523.15 K. [Mignard and Pritchard, 2008] suggested that the lack of sensitivity to temperatures is caused by too low activation energies of the reactions. The activation energies in \( k_d \) and \( k_e \) (table A.4) was increased to 40,000 J/mol – K and 98,084 J/mol – K respectively, still being within the 95 % confidence interval of [Vanden Bussche and Froment, 1996]. The results obtained with the modified parameters are shown in figure A.2(b). It can be seen that the model with the adjusted parameters gives a better match with the experimental results, why these activation energies will be used in the present report.
A.2 Partial Oxidation Kinetics

In this section the kinetic modeling of the partial oxidizer (POX) unit will be described. All the information presented has been obtained by [Pagh, 2011]. The reaction mechanism for the POX will be formulated by the four reactions expressed below.

\[
\begin{align*}
CH_4 + 2O_2 &\rightarrow 2H_2O + CO_2 \quad \Delta H = -803000 \quad [kJ \text{ kmole}] \quad (A.17) \\
CH_4 + CO_2 &\rightarrow 2CO + 2H_2 \quad \Delta H = 247000 \quad [kJ \text{ kmole}] \quad (A.18) \\
CH_4 + H_2O &\rightarrow 3H_2 + CO \quad \Delta H = 206169 \quad [kJ \text{ kmole}] \quad (A.19) \\
CO + H_2O &\rightarrow CO_2 + H_2 \quad \Delta H = -41157 \quad [kJ \text{ kmole}] \quad (A.20)
\end{align*}
\]

Though, the following model is based on a catalytic partial oxidation, the reaction kinetics for these given four reactions will not be expressed by the LHHW-kinetics like the previous reactors but by a power law formulation with the general description as in equation (A.21).

\[
r = k \prod_{n=1}^{m} [C_n]^{n_e} \quad [k \text{ mole}] \quad \text{kmole} \text{ kg catalyst} \text{ hr} \quad (A.21)
\]

For the reversible reactions the net production of the respective species is determined by their forward and reversed reactions.

\[
r_{i,\text{net}} = r_{i,\text{forward}} - r_{i,\text{reverse}} \quad [k \text{ mole}] \quad \text{kmole} \text{ kg catalyst} \text{ hr} \quad (A.22)
\]

The net production rates based on the given formulation for the given four reactions are presented below.

\[
\begin{align*}
 r_1 &= 0.288 \cdot e^{-8.7929E+4 \cdot 81.94109972 \cdot T} \cdot C_{CH_4} \cdot C_{O_2} \quad [k \text{ mole}] \quad \text{kmole} \text{ kg catalyst} \text{ hr} \quad (A.23) \\
r_2 &= 0.1836 \cdot e^{-3.8529E+3 \cdot 81.94109972 \cdot T} \cdot \frac{1}{k_2} (C_{CH_4} \cdot C_{CO_2} \cdot k_2 - C_{CO}^2 \cdot CH_2^2) \quad [k \text{ mole}] \quad \text{kmole} \text{ kg catalyst} \text{ hr} \quad (A.24) \\
r_3 &= 0.4608 \cdot e^{-2.0027E+3 \cdot 81.94109972 \cdot T} \cdot \frac{1}{k_3} (C_{CH_4} \cdot C_{H_2O} \cdot k_3 - C_{CO} \cdot CH_2^3) \quad [k \text{ mole}] \quad \text{kmole} \text{ kg catalyst} \text{ hr} \quad (A.25) \\
r_4 &= 0.2628 \cdot e^{-1.5959E+4 \cdot 81.94109972 \cdot T} \cdot \frac{1}{k_4} (C_{CO} \cdot C_{H_2O} \cdot k_4 - C_{CO_2} \cdot CH_2) \quad [k \text{ mole}] \quad \text{kmole} \text{ kg catalyst} \text{ hr} \quad (A.26)
\end{align*}
\]

The three driving force coefficients are expressed in equation (A.27) and (A.28) and (A.29)

\[
k_2 = e^{2014} \quad (A.27)
\]

\[
k_3 = e^{18106} \quad (A.28)
\]
For the multiple reaction mechanism the total production for the individual represented six species is thus given by the sum of reactions in which the species are produced or consumed.

The presented reaction rates have been obtained by experiments, why there is no need to introduce further effectiveness factors as for the case of the steam reformer. For the catalyst properties a bed density of 1870 [kg/m$^3$] and a void fraction of 0.5 is used.

### A.3 Flash Tank

After the methanol reactor, the produced methanol must be flashed from the effluent gas mixture and the remaining matter must be recycled to the methanol reactor. To separate the different species a flash tank can be utilized from which the entering mixture will exit in a liquid fraction and a vapor fraction. The composition of the two fractions will be determined by the thermo dynamic equilibrium. Since the Gibbs function for each component in each phases must equalize at equilibrium as shown in equation (A.30), the calculation of phase equilibrium is often done by an ideal behavior assumption or by somewhat empirical relations for non-ideal mixtures like the UNIQUAC model.

\[
g_i,\text{gas} = g_i,\text{liquid} = g_i,\text{solid} \tag{A.30}
\]

Consequently, further on the liquid fraction and a vapor fraction will be determined entirely upon the specified vessel temperature and pressure by the UNIQUAC model. The vessel is assumed adiabatic and there is no pressure loss through the vessel. Hence, equation (A.31) and (A.32) are valid.

\[
T_{\text{inlet}} = T_{\text{out}} \tag{K} \quad \text{(A.31)}
\]

\[
P_{\text{total},\text{inlet}} = P_{\text{total},\text{vapor}} = P_{\text{total},\text{liquid}} \tag{bar} \quad \text{(A.32)}
\]

### A.4 Compressor

Several compressors are present in the process scheme, mainly to compress the syngas from the steam reformer before it enters the methanol reformer. The isentropic compressor work, needed to compress the gas, can be expressed by equation (A.33).

\[
w_{\text{comp}} = \frac{1}{\eta_i} \frac{kP_{1}v}{k-1} \left[ \left( \frac{P_{2}}{P_{1}} \right)^{(k-1)/k} - 1 \right] \tag{W} \quad \text{(A.33)}
\]

For a well-designed compressor the isentropic efficiency, $\eta_i$, ranges from 80-90 % [Cengel and Boles, 2007]. From the equation it is evident that in order to minimize the compressor work the specific volume of the gas should be kept as low as possible. Since the specific volume is proportional to the temperature, a way to lower the specific volume is to lower the temperature. However since the compression will introduce an increase in temperature it is sometimes preferable to divide the compression into multiple stages with cooling between
the stages in order to keep the compressor work at an acceptable value and at the same time lower energy consumption. The number of compressor stages is a tradeoff between capital costs and compressor work. Figure A.2 shows the influence on the compressor work of adding extra compressor stages.

![Figure A.2: Influence of adding stage compression on the compressor work $\int_{P_1}^{P_2} Vdp$](image)

[Biegler et al., 1997] have presented a guideline to determine the number of stages in a compression. The guideline states that the compression ratio of each stage should not exceed 2.5, ($P_i/P_{i-1} \leq 2.5$).

### A.5 Pumps

The pump work is modeled using the pump equation in [A.34]

$$w_{pump} = \frac{\Delta PV}{\eta} \quad [W] \quad (A.34)$$

The pump is used to raise the pressure of H$_2$O before entering the steam reformer.

### A.6 Distillation

The distillation columns are used to separate the methanol-water mixture exiting the flash tank from the methanol reformer. During the distillation process the liquid is partially vaporized, creating a vapor with a high content of volatile components leaving the liquid with less volatile components. The distribution of the components in each phase can be described by vapor-liquid equilibrium considerations, if it is assumed that the mixture has reached equilibrium in each stage. From the initial stage the vapor flows up to a new stage.
where it will reach a new equilibrium and the liquid will flow down to a new stage. Typically in crude methanol purification a 2 or 3 column distillation unit is used. The first column separates the light end components, such as DME, methyl formate, acetone and other dissolved gases from the flash tank. In a two column configuration, the second column is the purification column and operates at nearly standard pressure. If a third column is present, the second column operates at elevated pressure, and uses the overheads to reboil the second purification column which works at lower pressures [Douglas and Hoadley 2005],[LurgiGmbH 2010].

A measurement of how well the liquid mixture separate is the relative volatility. It is given by equation A.35

\[
\alpha_{LH} = \frac{y_L/x_L}{y_H/x_H}
\]

A high relative volatility (\(\alpha_{LH} > 1.5\)) indicates a easier and less energy consuming distillation. An indication of which specie is the volatile component is the vapor pressure. The vapor pressure gives an indication of the rate of evaporation at a given temperature. Figure A.3 show the vapor pressure curves for methanol and H\textsubscript{2}O [Luyben 2006].

From the figure is can be seen that the vapor pressure increases with increasing temperature. Furthermore it is evident that methanol in general has a higher vapor pressure than H\textsubscript{2}O, hence methanol is the lighter component in the mixture (Indicated with subscript L in equation A.35). In figure A.4 the Txy diagram for the methanol water mixture is shown. The figure shows the liquid and vapor fraction of methanol with varying temperatures and different pressures.
At the left most point of the figure, where the liquid and vapor fraction of methanol is zero, the boiling temperature of H₂O is shown. Likewise at the right most point of the graph the boiling temperature of methanol is shown. The difference in boiling temperatures of the components is in the order of 40-50 K and it is seen that the boiling temperature increases with increasing pressure for both components.

When designing the distillation column some parameters like the molar flow rate and composition in and out of the column, minimum number of trays and minimum reflux ratio need to be known.

By knowing the feed molar flow rates and the purity of the distillate, the flow rates for both the distillate and bottom can be found using equations A.36 to A.38 [Luyben, 2006].

\[
F = D + B \quad \left[ \frac{kmol}{s} \right] \quad (A.36)
\]

\[
zF = D x_D + B x_B \quad \left[ \frac{kmol}{s} \right] \quad (A.37)
\]

\[
D = F \left( \frac{z - x_B}{x_D - x_B} \right) \quad \left[ \frac{kmol}{s} \right] \quad (A.38)
\]

By knowing the reflux ratio and the purities of the products the minimum number of stages in the distillation column can be visualized using the McCabe Thiele method. This method uses a VLE curve as shown on figure A.5(a) and the minimum number of stages is determined through several interpretations on the graph. These steps are illustrated on A.5(b). At first vertical lines is drawn from the purities of both the top and bottom streams of the distillate (\(x_D\) and \(x_B\)) to the 45° line.

Figure A.4: Txy diagram of the methanol water mixture
A.6 Distillation

Afterwards the two operating lines can be drawn. The rectifying operation line (ROL) and the stripping operation line (SOL) are both straight lines intersecting with $x_D$ and $x_B$ respectively. The slope of the ROL can be determined from the reflux ratio as given in equation A.39, [Luyben, 2006].

$$\text{ROL}_{\text{slope}} = \frac{R}{R + D} = \frac{RR}{1 + RR} \quad [-] \quad (A.39)$$

The third operation line is called the $q$ line. This line gives a relationship of the feed composition ($z$) and the intersection of the two other operation lines. The line is generated by offsetting the feed composition to the $45^\circ$ line and creating a straight line from this point to the intersection of the other operation lines. The slope of the $q$ line is defined as:

$$q_{-\text{line}}_{\text{slope}} = \frac{-q}{1 - q} \quad [-] \quad (A.40)$$

$q$ is a function of the thermal conditions of the feed stream and varies from 1 (vertical line) at saturated liquid to 0 (horizontal line) for saturated vapor. When the $q$ line and the ROL is known, the SOL can be illustrated going from $x_B$ to the intersection. After identifying the operation lines the number of trays in the distillation column can be determined. The procedure is to draw a vertical line from $x_B$ to the VLE curve. From the VLE curve a horizontal line is drawn back to the operation line. This is repeated until $x_D$ is crossed and the minimum number of trays corresponds to the number of steps generated. The step where the operation lines crosses is the feed tray. The stepping is shown in figure A.5 [Luyben, 2006].
**Figure A.5:** McCabe Thiele stepping.

**Figure A.6:** VLE of methanol and water at varying pressures.
From the graph it is evident that the fatter the VLE curve the less stages is necessary. This relates to that a high relative volatility will give a fat curve and a easy separation, hence less stages. A small relative volatility will give a thin curve and more stages will be needed to separate the components. To see how the pressure of the distillation column affects the relative volatility of the methanol water mixture, the VLE graph is shown at different pressures on figure A.6.

The graph shows that by operating the column at higher pressure, the separation of the components will be harder and consequently require more stages in the column to achieve the same purities of the distillate [Luyben, 2006].
Burner Feed Configurations

In Chapter 5 on page 29 three basis schemes were presented. Regarding the large scale concept based on steam reforming some questions still remain unanswered. For the combustion in the steam reformer burner two options for the oxidant feed exist: Feed the burner with atmospheric air or use produced $O_2$ from the electrolyser. It is evident, that by using pure $O_2$ the adiabatic flame temperature increases, due to the absence of diluting inerts, why less fuel is needed. However, a precondition for using pure $O_2$ is, that enough $O_2$ is produced from the electrolysis. Otherwise an air separation unit is needed to supply any deficit, which is unacceptable due to its high investment cost.

Also, for the fuel two options exist: Feed the burner with purge gas or bypass input $CH_4$. This leads to four different combinations for the burner configuration. Which combination to be used will be investigated by maximizing the methanol yield for each combination and thereafter examine mass flows for feasibility. The optimization is based on the parameters listed in table 8.1 on page 52. The burner feed is balanced by matching the heat absorbed by the endothermic reactions in the reformer, with the heat released in the burner. The oxidant feed to the burner is based on stoichiometric combustion of every combustible component and based on a Gibbs energy minimization routine at 1273 K. The results can be viewed in the following figures.

For the optimization only a local algorithm is used, and since the whole design space has not been investigated for these cases only a local optimum is guarantied. However, it is assumed that the same tendencies hold for global optimums. It was observed, that using the synthesis loop purge gas instead of bypassing feed $CH_4$, slightly more methanol is produced. It was also observed, that by the utilization of produced $O_2$ for the steam reformer burner, less fuel is used, which also leads to an increased methanol production. Yet another important observation is that, for the scheme with purge gas as burner fuel, there is actually a minor surplus of $O_2$. It must though be kept in mind, that the production of $O_2$ relies on the assumption, that there is a 100 % conversion in the electrolysis unit. This means that the surplus $O_2$ is a figure of maximum production. Additionally, the numbers are based on a methanol yield maximization, why this in fact could lead a potential $O_2$ deficit, when the stategy is turned towards a cost minimization. For this reason it is argued that the scheme using purge and atmospheric air for burner feed is the better of the four different configurations. For this scheme the surplus of $O_2$ is then considered as a valuable by-product.
Figure B.1: Large scale plant based on burner feed of purge gas and atmospheric air.

Figure B.2: Large scale plant based on burner feed of purge gas and O₂.
Figure B.3: Large scale plant based on burner feed of input CH\textsubscript{4} and atmospheric air.

Figure B.4: Large scale plant based on burner feed of input CH\textsubscript{4} and O\textsubscript{2}.
Figure C.1: Sankey diagram of farm scale plant.
Figure C.2: Mass balance diagram of large scale plant based on partial oxidation.

Figure C.3: Sankey diagram of large scale plant based on steam reforming.
Assumptions

Biogas
Composition: 65% methane and 35% CO₂
Mesophil operation: 310.15 K
Thermophil operation: 325.15 K

Compressor, multistage
η = 0.72
Pressure ratio for each stage aimed for 2.5
No heat loss

Compressor, single stage
η = 0.72
No heat loss

Currencies
1 USD = 5.6 DKK (1/5-2012)
1 EUR = 7.43 (1/5-2012)

Economics
Electrolyser life time: 5 years
Interest rate: 10%
Operation hours: 8000 hours/year
Pay back time: 20 years
Plant life time: 20 years
Oxygen price: 0.5 DKK/Nm³
Natural gas price: 2.59 DKK/Nm³

Electrolyser
Deionized water is used as water supply
Operating in thermo-neutral state
Utilization factor of 1
Operating at 1073.15 K
ASR = 0.2 Ωcm²
i = 2 A/cm²

Equation of State
Peng-Robinson

Flash drum
Adiabatic
No pressure loss

Heat exchanger
Δp/p = 2%
Minimum ΔT = 293.15 K
No heat loss

Phase Equilibrium

UNIQUAC

Pump

$\eta = 0.2956$

No heat loss

Reactor, general

Plug-Flow reactor

Bed voidage = 0.5

Reactor, Steam-methane reformer

50% of burner heat exists with flue gas

Oxygen supplied at stoichiometry for burner

Burner modeled as an stoichiometric reactor with outlet temperature of 1173.15 K

Stoichiometric combustion of $\text{H}_2$, $\text{CO}$ and $\text{CH}_4$

$\Delta p/p = 2\%$

Tap water is used as water supply

Top fired reactor tube

Reactor temperature given by figure 6.1 on page 36

Catalyst density = 2355 kg/m$^3$

Reactor, Partial oxidation reformer

Adiabatic reactor

$\Delta p/p = 2\%$

Catalyst density = 1870 kg/m$^3$

Reactor, Methanol reactor

Isothermal reactor

$\Delta p/p = 2\%$

Purge gas match for burner requirement

Catalyst density = 1775 kg/m$^3$

Separation

Correspond to 5 % of the net electricity production, provided that all biogas is combusted with an electrical efficiency of 40 % and a heat efficiency of 46 %.

Upgrading, Chemical Scrubber

No methane slip
In this appendix the objective function used for the optimization routines will be presented. The objective function expresses the yearly based methanol production price based on operational expenditures for compressors, pumps, SOEC, H₂O and O₂ addition. Furthermore the investment costs of reactors, SOEC and biogas plant are included, since they are assumed to be the main investments considering methanol production from biogas. In general the objective function is expressed by equation E.1.

\[ f(x_i) = \frac{\text{costs}(x_i)}{\text{methanol produced}} \left[ \frac{\text{DKK}}{\text{kg}} \right] \]  

(E.1)

From the equation it can be seen that the production price can be reduced either by reducing operational and investment costs or by increasing the methanol produced. The nominator of equation E.1 is presented in the equation E.2.
\[
\text{Investment of biogas plant} = \frac{C_{\text{biogas plant}}[\text{DKK}]}{1 - 1/(1+IR)^t} \left[ \frac{1}{\text{yr}} \right]
\]

\[
\text{Investment of SOEC} = \left( \frac{n_{H_2 O} [\text{kmol/s}] + n_{CO_2} [\text{kmol/s}]}{z[-]} \cdot F \left[ \frac{C_{\text{kmol}}}{\text{kmol}} \right] \cdot \frac{1}{\text{cm}^2} \cdot C_{\text{SOEC}} [\text{DKK/cm}^2] \right) \cdot \frac{IR}{1 - 1/(1+IR)^t} \left[ \frac{1}{\text{yr}} \right]
\]

\[
\Sigma C_B [\text{DKK}] \cdot \left( \left( \frac{D_{\text{reactor}} [\text{m}]}{2} + t_w [\text{m}] \right)^2 - \left( \frac{D_{\text{reactor}} - 2} {2} \right)^2 \right) \cdot \frac{\pi \cdot L_{\text{reactor}} [\text{m}] \cdot \rho_{\text{inconel}} [\text{kg/m}^3]}{Q_C [\text{kg}]} \right)^{0.82} \cdot f_M [-] \cdot f_T [-] \cdot f_P [-] \cdot \frac{IR}{1 - 1/(1+IR)^t} \left[ \frac{1}{\text{yr}} \right]
\]

\[
\text{Compressors and pumps} = w_{\text{compression}} \cdot \frac{\text{OP}_{\text{hr}} [\text{hr/year}]}{\text{DKK/MWhr}} \cdot \frac{\text{C}_{\text{electricity}} [\text{DKK/MWhr}]}{10^{-6} [\text{MW/W}]} \cdot \text{Electricity}
\]

\[
\text{Thermo-neutral power} = \left( \frac{n_{H_2 O} [\text{kmol/s}] + n_{CO_2} [\text{kmol/s}]}{z[-]} \cdot F \left[ \frac{KC_{\text{kmol}}}{\text{kmol}} \right] \cdot ASR \left[ \frac{\Omega \text{cm}^2}{\text{A} \text{cm}^2} \right] \cdot \frac{\text{OP}_{\text{hr}} [\text{hr/year}]}{\text{DKK/MWhr}} \cdot \frac{\text{C}_{\text{electricity}} [\text{DKK/MWhr}]}{10^{-6} [\text{MW/W}]} \cdot \text{Electricity}
\]

\[
\text{SOEC losses} = \left( \frac{m_{\text{water}} [\text{kg/s}]}{\rho_{\text{water}} [\text{kg/cm}^3]} \cdot 28800000 \left[ \frac{s}{\text{yr}} \right] \right)
\]

\[
\text{Water costs} = \left( \frac{m_{\text{O}_2,\text{in}} [\text{kg/s}] - m_{\text{O}_2,\text{out}} [\text{kg/s}]}{\rho_{\text{O}_2} [\text{kg/m}^3]} \cdot 28800000 \left[ \frac{s}{\text{yr}} \right] \cdot \frac{C_{\text{O}_2} [\text{DKK/m}^3]}{\text{OP}_{\text{hr}}} \cdot \frac{\text{OP}_{\text{hr}} [\text{hr/year}]}{\text{DKK/MWhr}} \right)
\]