

Implementation of electrofuel production at a biogas plant

Case study at Borås Energi & Miljö

Master's Thesis within the Sustainable Energy Systems programme

TOBIAS JOHANNESSON

MASTER'S THESIS

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Cover:
Schematic picture over a simplified biogas process with an implemented Sabatier reactor.

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Abstract

One way to decrease the emissions of greenhouse gases is to use a renewable vehicle fuel, such as biogas. By separating methane from carbon dioxide in raw gas in a gas upgrading system, biogas is produced. This study focuses on how to increase the production of biogas by implementing a Sabatier reactor at a biogas plant. The implementation was simulated in Aspen Plus. The simulation was later used together with Aspen Process Economic Analyzer to evaluate the economic performance of the proposed process, including also sensitivity analysis of market changes in e.g. electricity price and biogas price. A future scenario analysis was also performed using Energy Price and Carbon Balance Scenarios (ENPAC) tool. Retrofitting a gas upgrading system which uses a water scrubber was found not to be economically feasible, mainly due to high costs for desorbing CO₂. A process where raw gas is fed to the Sabatier reactor directly was found to be a cheaper alternative, however only profitable for low electricity prices together with high biogas prices or where the investment pay back time was set to its assumed technological life time instead of the assumed economic life time. The case of building a new upgrading system with an amine scrubber was not simulated but investigated using data from literature. The economic performance of this process option was similar to raw gas methanation process. For future studies, it would be important to focus more on the operation of the Sabatier reactor (e.g. controlling the temperature profile) and also look further into optimally utilising the heat from the strong exothermic reaction.

Key words: electrofuels, power-to-gas, Sabatier reactor, biogas, upgrading, ENPAC, Aspen Plus, Aspen Process Economic Analyzer, synthetic hydro-carbons, carbon recycling

Implementering av elektrobränsleproduktion vid en biogasanläggning
Fallstudie vid Borås Energi & Miljö
Examensarbete inom masterprogrammet Hållbara Energisystem
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Sammanfattning

Ett sätt att minska utsläppen av växthusgaser är att ersätta fossila fordonsbränslen med biobränslen, t.ex. biogas. Biogas tillverkas idag bland annat vid Borås Energi & Miljö's anläggning vid Sobacken. Rågasen de producerar uppgraderas genom att koldioxid och metan separeras i en vattenscrubber. Denna studie syftar till att undersöka de ekonomiska utsikterna för en implementering av en Sabatier-reaktor som använder koldioxiden och vätgas som råmaterial för att tillverka mer biogas. Processen simulerades i Aspen Plus och en utvärdering av kostnaderna för processen gjordes med hjälp av Aspen Process Economic Analyzer. För att utvärdera en framtida implementering användes också verktyget Energy Price and Carbon Balance Scenarios för att ta fram fyra olika framtida energipris-scenarion. Resultaten visade att det inte var ekonomiskt lönsamt att bygga om vattenscrubberanläggningen genom att tillsätta en återkokare till stripperkolonnen. Däremot visade sig det vara ekonomiskt försvarbart att införa en Sabatier-reaktor som använde rågasen direkt för att producera biogas, men då endast om man antog att återbetalningstiden för investeringskostnaden var den teknologiska livstiden och inte den ekonomiska livstiden. Det jämfördes även med kostnaden för att bygga en ny uppgraderingsanläggning, tagna från litteraturen, där en amin-scrubber istället användes. Kostnaderna för amin-scrubbersystemet liknade kostnaderna för rågas-metaneringen. I fortsatta studier bör det undersökas hur kylningen av Sabatier-reaktorn mer noggrant ska konstrueras för att den ska fungera väl, samt även undersöka hur värmen från den exoterma reaktionen kan återanvändas i processen ännu mer.

Nyckelord: elektrobränslen, biogas, uppgradering, Aspen Plus, Aspen Process Economic Analyzer, Sabatier-reaktor, ENPAC, syntetiska kolväten, koldioxidåtervinning

Contents

ABSTRACT	I
SAMMANFATTNING	II
PREFACE	V
NOTATIONS & ABBREVIATIONS	VI
1 Introduction	1
1.1 Background	1
1.2 Purpose	2
2 Theoretic background	2
2.1 Gas upgrading system	2
2.2 Sabatier process	4
2.2.1 Catalyst	5
2.2.2 Sabatier reactor	7
2.3 Hydrogen production	7
2.3.1 On-site production	8
2.3.2 Off-site production	11
2.4 Criteria for a sustainable biofuel production	12
2.5 Aspen Plus and Aspen Process Economics Analyzer	13
2.6 Energy Price and Carbon Balance Scenarios tool	13
3 Methodology	15
3.1 Locating off-site hydrogen production	15
3.2 Process simulations	15
3.2.1 Simulation of separation of CO ₂	16
3.2.2 Simulation of methanation	17
3.2.3 Simulation of heat recovery	20
3.2.4 Simulation of plant without CO ₂ separation	20
3.2.5 Estimation of economic performance	21
3.2.6 Sensitivity analysis	24
3.3 Economic assessment	26
4 Results	28
4.1 Mapping of H ₂ sources	28
4.2 Validation of vapor/liquid property method	30
4.3 Results from process simulations	31
4.3.1 CO ₂ separation simulation results	31
4.3.2 Methanation simulation results	32
4.3.3 Results from sensitivity analysis	33
4.3.4 Heat recovery simulation results	37
4.3.5 Simulation results for raw gas methanation process	38
4.4 Results from the economic assessment	39
4.4.1 Results from ENPAC	39

4.4.2	Dependence on electricity and biogas price	39
4.4.3	Dependence on hydrogen price	42
4.4.4	Cost analysis	42
5	Discussion	45
5.1	Interpretation of results	45
5.2	Sources of error	47
5.3	Suggestions for future work	48
6	Conclusion	49
	References	50
	Appendix A	I
	Appendix B	III
	Appendix C	VI
	Appendix D	VII
	Appendix E	VIII
	Appendix F	XIII
	Appendix G	XVI
	Appendix H	XVII

Preface

This study focused on the economic performance of an implementation of a Sabatier reactor at Borås Energi & Miljö's biogas plant in Sobacken. Simulations were made for two types of processes; one where raw gas is first upgraded in a water scrubber and the resulting stream of CO₂ is fed to the Sabatier reactor, and another where the raw gas is fed to the Sabatier reactor directly. The project was carried out at the department of Energy and Environment at Chalmers University of Technology, at both the division for Physical Resources Theory and Industrial Energy Systems and Technologies, in close collaboration with Borås Energi & Miljö.

I am very grateful to my supervisors Stavros Papadokonstantakis and Camilla Ölander and my examiner Maria Grahn for their help with everything. I also want to show my gratitude towards Alexander Orton Sørensen for the great collaboration on mapping the hydrogen sources and the many discussions in the office; David Malm at Borås Energi & Miljö for answering my many questions; Joao Patricio for assisting with the mapping of hydrogen sources; Elin Svensson who introduced ENPAC to me and the authors of "*Electrofuels for the transport sector: a review of production costs*" who showed me their article before it was published. Last but not least I would also like to thank the people at the many companies I have contacted for their help with providing me with information.

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Tobias Johannesson

Notations & Abbreviations

APEA	Aspen process economics analyzer
$C_{distr,x}$	Distribution cost for a fuel, where x is either d (diesel) or m (biogas)
C_{el}	Electricity price
$C_{eqi,vac}$	Equipment cost for vacuum pump
C_{rawgas}	Potential profit lost by instead burning raw gas
$C_{upgrade}$	Cost for upgrading raw gas
$C_{uti,vac}$	Utility cost for vacuum pump
CEPCI	Chemical engineering plant cost index
CHP	Combined heat and power plant
CH ₄	Methane
Cl ₂	Chlorine gas
CO ₂	Carbon dioxide
CRF	Capital recovery factor
CRG	Catalytic rich gas
ΔH°	Enthalpy of reaction
$\eta_{electrolysis}$	Electrolysis LHV efficiency
$E_{electricity}$	Electricity demand for electrolyser
ENPAC	Energy price and carbon balance scenarios tool
f_x	The fuel economy for different fuels, where x is either d (diesel) or m (biogas)
G&A	General and Administration
GHG	Greenhouse gases
H ₂	Hydrogen gas
H ₂ S	Hydrogen disulfide
HCl	Hydrogen chloride
i	Interest rate
I_{gas}	Loss of income due to less upgraded raw gas
IEA	International energy agency
K_{eq}	Equilibrium constant
K_i	Adsorption constant, where i is H ₂ , OH or <i>mix</i>
k_{sab}	Kinetic factor for the sabatier reaction rate
LHHW	Langmuir-Hinshelwood Hougen-Watson

LHV _{<i>i</i>}	Lower heating value for component <i>i</i>
N ₂	Nitrogen gas
Ni	Nickel
O ₂	Oxygen gas
$P_{cons,x}$	Consumer price per driven km, where <i>x</i> is either d (diesel) or m (biogas)
$P_{gate,x}$	Gate price for production of a fuel, where <i>x</i> is either d (diesel) or m (biogas)
P_i	Partial pressure for component <i>i</i>
PEC	Photoelectrocatalytic
PEM	Polymer electrolyte membrane
ppm	Parts per million
ppb	Parts per billion
PSA	Pressure swing adsorption
r	Reaction rate
rWGS	Reverse water gas shift
Ru	Ruthenium
S	Driving power of vacuum pump [kW]
SF	Size factor
SNG	Synthetic natural gas
SNI	Standard för svensk näringsindelning
SOEC	Solid oxide electrolyser cell
T	Investment pay back time
VAT	Value added tax
WEO	World energy outlook

1 Introduction

The emissions of greenhouse gases (GHG) in the world increased from 30 to 50 Gton/year between 1970 and 2010, and today 60 vol-% of the world's emissions of GHG comes from burning of fossil fuels in power plants or vehicles such as cars and trucks [Victor et al., 2014; Burkett et al., 2014]. One way to decrease the emissions from vehicles is to use a fuel which is produced from a more renewable raw material instead of using a fossil based fuel. Biogas produced from municipal organic waste is one of the more renewable fuels that can replace the fossil based fuel, and it is produced in many municipalities around Sweden today. One of the production sites is placed in Borås (Sobacken) where Borås Energi & Miljö is handling the production.

1.1 Background

Borås Energi & Miljö is producing 800 Nm³/h of biogas from their two biogas facilities at Sobacken and Gässlösa. The biogas is produced by anaerobic digestion of organic waste at Sobacken and sewage sludge at Gässlösa. During the anaerobic digestion, both methane (CH₄) and carbon dioxide (CO₂) is formed. To be able to utilise the biogas as a fuel in cars and buses, the CO₂ is today separated from the raw gas via an upgrading process. The upgrading process at Sobacken includes a water scrubber, a flash and a stripper column which separate CO₂ and hydrogen sulfide (H₂S) from CH₄, and then emits the separated gases to the atmosphere. Today the gas upgrading system is not effective enough, which results in too high emissions of CH₄ into the atmosphere.

There is research being done focusing on utilising CO₂ together with hydrogen gas (H₂) and let the gases react in a Sabatier reactor for production of methane, according to Equation 1 [Jürgensen et al., 2015]. Placing a Sabatier reactor after the upgrading system would solve the problem with CH₄ emissions to the atmosphere, and at the same time increase the production of biogas.



An arising problem with an implementation of a Sabatier reactor is how H₂ should be supplied to the plant. Borås Energi & Miljö must, as all Swedish biogas producers, fulfill specific criteria for sustainability to get a tax exemption. This implies that H₂ produced via steam reforming of fossil fuels is not a viable choice. Instead, H₂ could be produced by water splitting via electrolysis or other hydrogen production options, for example a photoelectrocatalytic (PEC) process [Ranney, 2011]. There is also the possibility of an already existing process within reasonable distance from Sobacken, where H₂ is produced as a byproduct, which then could be utilised at Sobacken. Mapping and finding ways of utilising different H₂ sources like this may be an interesting exercise in order to find possibilities for realising the process.

1.2 Purpose

The purpose of the project is to assess the economical viability through the implementation of a Sabatier reactor at Sobacken. Two cases are to be investigated; one where the existing upgrading system at Sobacken is retrofitted to make it possible for an implementation of a Sabatier reactor, and one where the raw gas from anaerobic digestion is fed to a Sabatier reactor directly. The influence of different options for retrofit and reactor configurations are also included in the investigation, together with how the supply of H₂ is to be realised. The economic viability will be assessed according to four predicted future scenarios.

2 Theoretic background

2.1 Gas upgrading system

The raw gas produced from the digester consists mainly of CH₄ and CO₂, but there are also often traces of O₂, N₂ and H₂S. The CH₄ content at Sobacken is about 60 vol-%. The biogas produced needs to fulfill a certain standard according to Swedish standard SS 15 54 38 [Persson, 2006]. The standard depends on the type of vehicle that will use the fuel. Regular cars and the majority of new heavy vehicles uses biogas of type B, while older heavy vehicles uses biogas of type A. Some of the standard properties are listed in Table 2. The lower Wobbe index is defined as the lower heating value (LHV) divided by the relative density. The standard does not state anything about hydrogen concentration, but there are regulations set by both The United Nations Economic Commission for Europe (UNECE) regulation 110 and International Organization for Standardization (ISO) standard 11439 for the gas cylinder tank in the vehicle, stating a maximum content of 2 vol% of hydrogen in the tank [Schiebahn et al., 2015; Altfeld and Pinchbeck, 2013]. To achieve this standard, the gas is run through a gas upgrading system. There are many different kinds of upgrading systems used for biogas production, for example absorption, adsorption and membrane separation [Bailón Allegue and Hinge, 2012].

Table 2: The standard properties of biogas according to Swedish standard SS 15 54 38 [Persson, 2006].

Property	Unit	Biogas - Type A	Biogas - Type B
Lower Wobbe index	MJ/Nm ³	44.7-46.4	43.9-47.3
Water content (max)	mg/Nm ³	32	32
CH ₄	vol-%	97 ± 1	97 ± 2
CO ₂ + N ₂ + O ₂ (max)	vol-%	4	5
O ₂ (max)	vol-%	1	1

The absorption method involves using a scrubber where the raw gas is meeting a liquid flow. CO_2 is soluble in the liquid and therefore separated from the raw gas. The liquid is most often water or an organic solvent such as mono-ethanol-amine (MEA), and the method is therefore either called water scrubbing or physicochemical absorption respectively. The solvent can be regenerated by using a stripper column and a stripping agent where the CO_2 is removed and the solvent is then recirculated. Figure 1 shows a schematic picture of the absorption process, excluding the gas dryer.

A water scrubbing technique is used at Sobacken, where the CO_2 is absorbed to water and then separated by using air as the stripping agent. There are also the possibilities to use heat, steam or an inert gas as a stripping agent [Kaparaaju et al., 2013]. Another way of regenerating the water is by using a vacuum pump instead of an air flow to remove the CO_2 , with the advantage that the effluent stream will consist of mainly CO_2 which may be utilised [Läntelä et al., 2012; Petersson and Wellinger, 2009]. However, the study by Läntelä et al. [2012] shows that there might be problems with air leaking into the effluent stream. After the CO_2 has been separated from the methane, the water in the biogas must be removed to fulfill the standard of maximum 32 mg/Nm^3 . At Sobacken this is done by a gas dryer system with two columns containing an adsorption material that removes water. As the gas is flown through one of the columns, the other is regenerated using heated dry gas.

At Gässlösa, the chemical absorption method is used with an amine solution as the solvent. The main advantage with this method is that the methane losses through the effluent stream from the stripper are low due to the selectivity of the amine solution. There is also the advantage that the CO_2 in the effluent stream can be easily separated and captured, because the stripping agent is heat which causes some steam to follow with the effluent stream, and it can simply be condensed. If the raw gas contains H_2S the regeneration must be performed at a higher temperature though, since H_2S absorbs stronger to the amine solution than CO_2 . [Petersson and Wellinger, 2009]

Upgrading by adsorption means that CO_2 is separated from the raw gas by being adsorbed to a solid's surface at high pressure and then desorbed at lower pressure. The adsorption material can consist of e.g. active carbon or zeolites. A problem with this technique is that H_2S deactivates the adsorption material by adsorbing irreversibly. Upgrading by membrane separation means that CO_2 (and H_2S and H_2O) is transported through a membrane while CH_4 , which does only pass the membrane to very low extent, is accumulated on the other side of the membrane. [Bailón Allegue and Hinge, 2012; Petersson and Wellinger, 2009]

Out of the different upgrading methods, there is not one single best option due to the local conditions being very different for each process. A study concerning capacity, product quality and start up/shutdown performance has to be performed to evaluate which is the best choice. The start up/shutdown performance is important since the digestion is a batch process, which causes the upgrading process to start up/shutdown often. The CO_2 content in the effluent stream might also be something

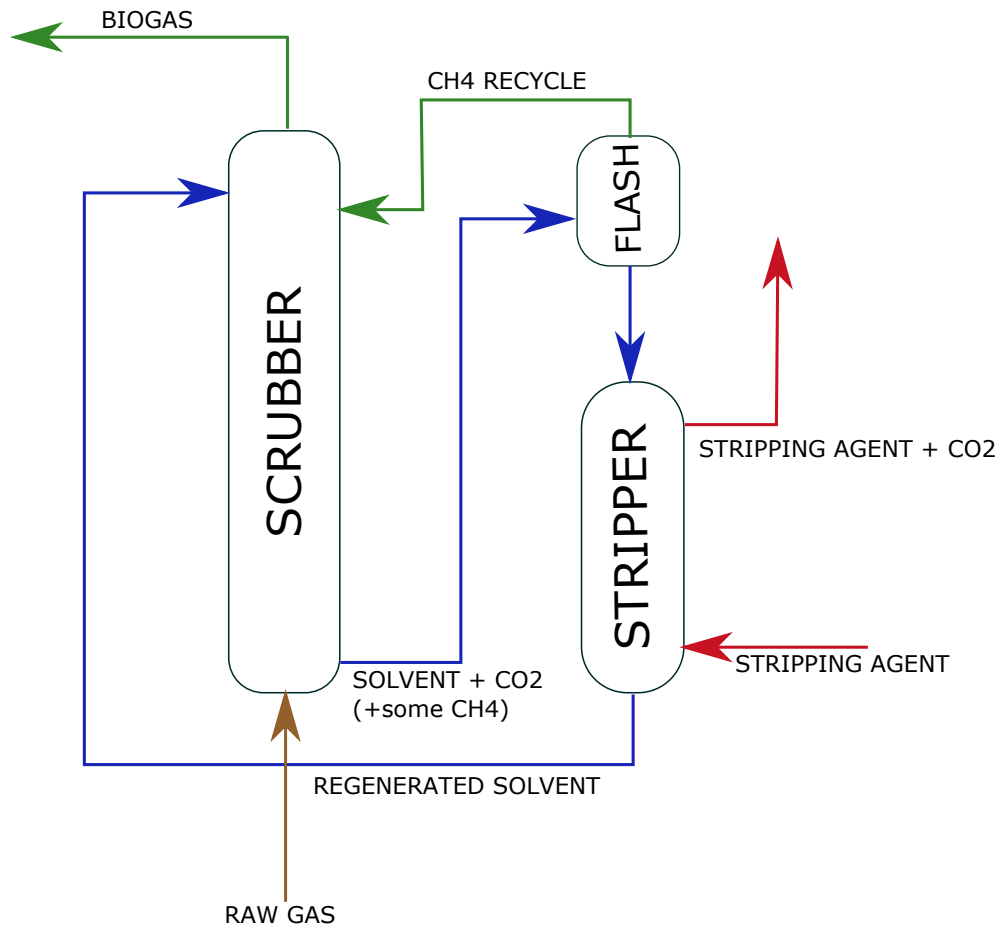
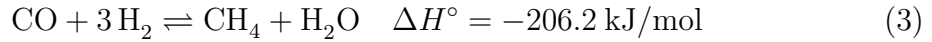
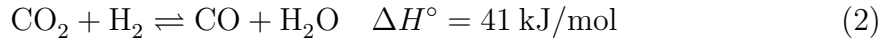


Figure 1: Schematic picture of the absorption process. It is in the effluent stream from the stripper where the too high emissions of CH_4 occur at Sobacken.

to evaluate if it is to be used as feedstock in a Sabatier reactor. The most common method used in Sweden is the water scrubbing technique, while an adsorption technique called pressure swing adsorption (PSA) is the most common in Germany [Bailón Allegue and Hinge, 2012]. The price for each technique is between 1.2-2.5 €/kWh of produced gas, depending on the capacity of the plant, and there is not a process which is cheaper than any other [Petersson and Wellinger, 2009].

2.2 Sabatier process

The Sabatier process is based on the Sabatier reaction, shown in Equation 1. It consists of two reaction steps; the first step being the reversed water gas shift (rWGS) reaction in which carbon dioxide together with hydrogen is forming water and carbon monoxide, and the second step being methanation of CO in which methane and water is formed from carbon monoxide and hydrogen. Both reactions are illustrated in Equation 2 and 3 respectively.



The reaction rate for the Sabatier reaction can be described in many ways, for example as a power law or a Langmuir-Hinshelwood Hougen-Watson (LHHW) expression (Equation 4), where the adsorption to the catalyst and driving force of the reaction also is considered together with the kinetic factor. It can also be expressed as either one rate expression for the whole Sabatier reaction, or one reaction rate for each reaction (rWGS and methanation) [Schlereth, 2015; Kopyscinski, 2010]. Schlereth [2015] presented a reaction rate expressed as a LHHW equation, which is presented further in Appendix A.

$$r = \text{Kinetic factor} \cdot \frac{\text{Driving force}}{\text{Adsorption}} \quad (4)$$

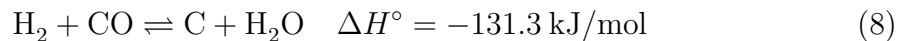
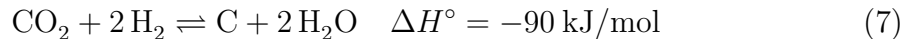
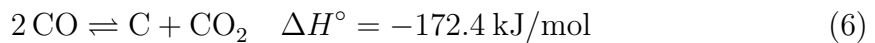
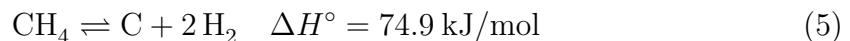
2.2.1 Catalyst

Due to kinetic limitations at lower temperatures in the reactor, a catalyst is needed to keep the Sabatier reaction going [Kiewidt and Thöming, 2015]. Ruthenium (Ru) and nickel (Ni) based catalysts are commonly used because they have a selectivity and conversion efficiency of about 90 %. Ni is the most common since it is the cheaper alternative of the two [Müller et al., 2013; Katoufa et al., 2015]. Using a bimetallic catalyst with both Ni and Ru has been shown to improve the CH₄ yield at low temperatures [Katoufa et al., 2015].

Deactivation of the catalyst is to be avoided as much as possible to reduce the need to replace the catalyst. Deactivation can occur because of poisoning by sulfur compounds (H₂S, hydrogen chloride (HCl), mercury (Hg) or arsenic (As) in the gas, which adsorb to the active sites of the catalyst and therefore hinder the reactants from being catalysed [Mills and Steffgen, 1974; Forzatti and Lietti, 1999]. Compounds containing sulfur are especially difficult to handle, because they affect the activity of the catalyst already at ppb level [Bartholomew, 2001]. To remove compounds containing sulfur, a filter containing active carbon is commonly used. This is also the case at Sobacken. The filter must however be regenerated by blowing steam through it which is energy demanding. Hydrogen chloride is removed by using a guard catalyst bed made of activated alumina before the reactor, and it is necessary to change the guard catalyst when it has been saturated [Twigg, 1989]. Zhou Junbo et al. [2010] proposed a system with a series of columns to purify hydrogen gas from chlorine production. Both adsorption and chemical reactions were used to remove the impurities present. The resulting H₂ gas after purification had a purity of 99.999 vol-% and it contained non-detectable amounts of Cl₂ and H₂O, while O₂ and N₂ were reduced to 0.6 and 5 ppm respectively [Junbo et al., 2010].

The recommended temperature range for a Ni catalyst on alumina substrate is 190-450 °C [Hoekman et al., 2010]. The upper limit is because an increase in temperature can also cause deactivation of the catalyst through sintering. Sintering is a general expression for a decrease in active surface area due to structural modifications of the catalyst. There are two mechanisms behind sintering in supported catalysts; atomic or crystallite migration, which both involve crystallites forming, agglomerating and reducing the active surface [Forzatti and Lietti, 1999]. Sintering is an irreversible, kinetically slow process enhanced at higher temperatures. The thermal stability is affected by which metal-support being used, where alumina has higher thermal stability compared to silicon dioxide and carbon [Bartholomew, 2001]. Since the methanation reaction is an exothermic reaction, sintering might become a problem unless the reactor is properly cooled [Kopyscinski, 2010]. Twigg [1989] however states that sintering is not the important cause of deactivation for methanation catalysts and overheating up to 650 °C is not affecting the activity as much as poisoning. The lifetime of the catalyst will depend on the deactivation of the catalyst. For methanation processes using Ni-based catalysts, the lifetime of the catalyst could vary between 3-10 years¹, depending on the operating conditions and amount of deactivating substances in the gas feed.

During the Sabatier reaction, formation of solid carbon might occur according to Equations 5-8. Carbon formation and deposition on the catalyst could also result in deactivation of the catalyst. Jürgensen et al [2015] simulated the carbon formation at equilibrium for different conditions. They concluded that at elevated pressures, carbon formation occurs at higher temperatures. Therefore, to avoid carbon formation they suggest that the reactor should operate at an elevated pressure, and the peak temperature in the reactor should not exceed the temperature where solid carbon starts to form, e.g. a reactor operating at 10 bar should not exceed 500 °C.



¹It is unsure whether this period includes regeneration of the catalyst or not.

2.2.2 Sabatier reactor

The need for synthetic natural gas (SNG)² first occurred in the early 1970's, when a future shortage of natural gas was recognised. This led to the development of the first SNG process: "Catalytic rich gas" (CRG) which used oil as feedstock. The CRG process used three methanation reactors in series with intercooling in between to handle the strong exothermic behaviour of the Sabatier reaction. There were also developed different kinds of processes which used coal as feedstock, for example the Lurgi coal process, consisting of two methanation reactors with both product recirculation and interstage cooling. [Twigg, 1989]

Today there are two types of reactors that can be used for methanation; the fixed bed reactor and the fluidised bed reactor [Götz et al., 2014]. The fixed bed reactor can be cooled by diluting the inlet stream with either an inert gas or by recirculating the gas stream and thereby reducing the temperature rise. It is also possible to operate it at isothermal conditions with external cooling, which however may be difficult to control. For a more efficient control, two reactors or more can be connected in series with either interstage cooling or product gas recirculation [Schaaf et al., 2014]. Fluidised bed reactors are better at keeping the temperature stable because of the mixing between the gas and the catalyst particles, but there are problems with entrainment of the catalyst in the gas flow [Schaaf et al., 2014]. Today there are a few methanation plants in operation, e.g. in North Dakota, USA using the Lurgi coal process and the first power-to-gas plant in Werlte, Germany where an isothermal approach with a multitubular reactor is used [Götz et al., 2014].

2.3 Hydrogen production

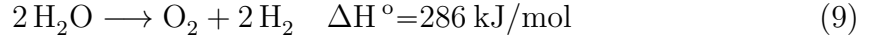
To produce biogas from the Sabatier process both H₂ and CO₂ is needed. Since CO₂ already is produced at Sobacken, the remaining issue is how to acquire H₂. H₂ can be produced in many different ways. There are both processes where hydrogen is the desired product e.g. steam reforming of natural gas, and those processes where it is produced as a byproduct, e.g. chlorine electrolysis. To use hydrogen produced from natural gas to produce synthetic natural gas would however be counterproductive. There are also technical solutions in development which try to utilise renewable energy sources such as solar and wind for large scale hydrogen production, e.g. electrolysis or PEC methods. Biological methods using for example algae, where the sun is used as energy source, are also under investigation. Neither the biological methods or the PEC will however be further analysed in this project as they are both rather immature technologies. [Schüwer et al., 2015]

²Biogas is SNG produced by biogenic feedstock, which is why SNG production is of interest in this study.

2.3.1 On-site production

One way to produce H_2 on-site is to use electrolysis where water is the feedstock. There are three main catalytic methods for electrolysis of water; alkaline electrolysis, solid oxide electrolyser cell (SOEC) and polymer electrolyte membrane (PEM). The alkaline electrolysis and PEM are the methods commercially available today, while SOEC is not expected to be available until earliest 2020-2025 [Mathiesen et al., 2013].

The chemical reaction behind electrolysis of water (Equation 9) is a redox reaction driven by electricity. The redox reaction is divided into two separate electrochemical reactions, one anodic and one cathodic reaction which are different for the three different types of electrolytic methods [Benjaminsson et al., 2013; Graves et al., 2011]. The type of electrolyte and electrode are also different for the three methods.



The costs, efficiencies, lifetimes³ and properties of the hydrogen produced from electrolysis is presented in Table 3. The efficiency of the respective electrolysis method is defined as electricity to fuel efficiency, based on LHV according to Equation 10, where $\eta_{electrolysis}$ is the efficiency, LHV_{H_2} is the LHV for H_2 and $E_{electricity}$ is the electricity demand for the electrolyser.

$$\eta_{electrolysis} = \frac{LHV_{H_2}}{E_{electricity}} \quad (10)$$

Table 3: Costs and efficiencies of different electrolysis methods [Mathiesen et al., 2013; Benjaminsson et al., 2013; Brynolf et al., 2016].

Method	Operating cost	Investment cost	Efficiency (LHV)	Lifetime	Pressure and Temperature
<i>Unit</i>	<i>% of inv.cost/year</i>	<i>M€/MW</i>	<i>%</i>	<i>years</i>	<i>bar/ °C</i>
Alkaline	4	1.07	40-70	25 ^a	<30/60-80
PEM	4	2.55	48-72	20	<30/50-80
SOEC ^b	2-3	0.7	77	10-20	40/800

^aAssuming major services on electrodes every 6 years [Benjaminsson et al., 2013].

^bCosts and lifetime estimated for 2030.

The enthalpy of reaction for the dissociation of water corresponds to a voltage, referred to as the thermoneutral voltage. If the cell is operating at this voltage, referred to as isothermal operation, the efficiency would be 100 %, and no losses in form of heat dispersion would occur. A high hydrogen production rate for the cell is desired and it corresponds to a high current density. The problem is that

³Assuming a operating time of 8000 h/year.

since voltage and current is related through Ohm's law, a decreasing voltage means a decreasing current.

Graves et al. [2011] states four things to keep the total cost down for an electrolysis cell. Operating the cell at low voltage, lower the production cost, increasing the current density under which the cell is operated and increasing the lifetime and durability of the cell. The different operating points for the different electrolysis methods are illustrated in Figure 2. It can be seen that for SOEC, the area of operation can be below the thermoneutral point, meaning that the efficiency can be over 100 %. The reason for this is that both heat and electricity supplies energy to the electrolytic reaction, making it possible for the efficiency in Equation 10 to surpass 100 %.

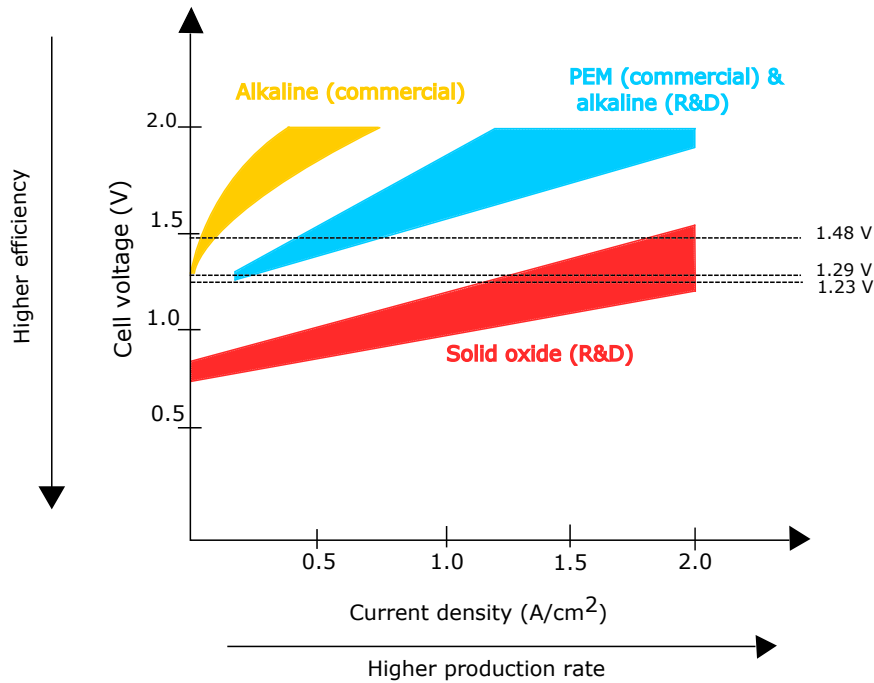


Figure 2: Diagram showing the voltages and current densities at which the different methods are operating. The dotted lines are the thermoneutral voltages for water dissociation (1.48 V), for steam dissociation (1.29 V) and for reverse water electrolysis at 25 °C (1.23 V). [Graves et al., 2011]

2.3.1.1 Alkaline

The electrolyte used in an alkaline electrolyser is often a solution of potassium hydroxide (KOH). An aqueous solution of an acid or a base is needed as the electrolyte, because water is not contributing with a high enough conductivity from ionising itself which is needed for the transfer of charges [Benjaminsson et al., 2013; Graves et al., 2011]. However the basic properties of the electrolyte causes the electrodes (often Ni or cobalt (Co) electrodes) to degrade due to corrosion, and thus they

need to be changed every 5-6 years [Mathiesen et al., 2013; Benjaminsson et al., 2013].

As can be seen in Table 3, alkaline electrolysis is the cheapest method that is available on the market today. The cost is however increasing significantly when being operated intermittently, even though it has been shown to not affect the durability of the cell [Graves et al., 2011]. Another disadvantage is that the cell is not operated at maximum efficiency, due to the fact that the operating costs would be increased. This is because the operating voltage would have to be lowered to increase energy efficiency (reach thermoneutral voltage) which in turn would mean lowering the current density and therefore increasing the costs significantly [Mathiesen et al., 2013].

2.3.1.2 PEM

PEM electrolysis uses, as the name suggests, a polymer membrane as electrolyte which increases the conductivity of the cell and therefore the efficiency. The lifetime of a PEM electrolysis cell is however shorter than for an alkaline cell, due to the solid nature of the electrolyte. The solid polymer membrane is being degraded by thermal and mechanical stress and this can in some cases lead to membrane perforation [Mathiesen et al., 2013; Benjaminsson et al., 2013].

Another disadvantage is that the electrodes typically contain expensive materials as electrocatalysts (noble metals, for example platinum), which increases the investment cost [Graves et al., 2011]. The current production rate of H_2 is also lower than for alkaline (maximum $30 \text{ Nm}^3/\text{h}$ for PEM, compared to $760 \text{ Nm}^3/\text{h}$ for alkaline). An important advantage for PEM compared to the commercial alkaline electrolyzers is that the start up is quicker, and therefore works better for intermittent energy sources [Mathiesen et al., 2013]. The feature that it could operate at a somewhat higher efficiency but keep a lower investment cost according to Figure 2 is also important to consider.

2.3.1.3 Solid oxide electrolysis cell

The solid oxide electrolysis cell uses a ceramic material as electrolyte. The ceramic material has a better thermal resistance which makes it possible to operate the cell at higher temperatures (around $800 \text{ }^\circ\text{C}$), which is why SOEC is often referred to as high temperature electrolysis [Benjaminsson et al., 2013]. If operated at these high temperatures, the heat supplies a part of the energy needed for the electrolysis to occur, meaning the amount of power needed is reduced and thus reducing the cost. The heat can be supplied either from an external source or from the heat created in the cell due to internal electric resistance [Graves et al., 2011]. The higher temperature also decreases the need for expensive catalytic materials [Graves et al., 2011].

The possibility to operate at a higher temperature is the reason that SOEC can be operated close to the thermoneutral voltage (1.29 V) and at a high current density at the same time, see Figure 2. This could potentially lead to a lower production cost. There are uncertainties however of how current densities at such a high level might actually degrade the components, which would lead to an increase in production cost instead [Graves et al., 2011]. SOEC has, similar to PEM electrolyzers, a good regulation ability as long as the temperature is kept at operating conditions. Starting the cell when it is cold will however take several hours, meaning there must be a system to keep the temperature for the cell to operate well with intermittent energy sources [Mathiesen et al., 2013].

2.3.2 Off-site production

Apart from producing hydrogen on-site there is the option to get hydrogen from off-site production, for instance by certain industries, where hydrogen is produced as a byproduct. In some cases the surplus of hydrogen is burnt to recover heat, a usage of hydrogen that has far lower value than commodity hydrogen [Junbo et al., 2010]. Such sources of hydrogen would be preferable over electrolysis of water since it would be both more sustainable to utilise a byproduct rather than producing new material. The lower pricing for the hydrogen would probably be set to cover the cost for buying another heat source, such as biomass or natural gas for example.

The possibility of finding a local source of hydrogen depends on the type of industry located nearby the biogas production site. A good source would be a production site where the hydrogen is considered as a byproduct which is not utilised on-site (maybe only as a heat or energy source) [Schüwer et al., 2015]. Schüwer et al. [2015] also points out that the possibilities for finding local hydrogen sources depends a lot on the specific industrial structure locally and therefore it is of importance to investigate the possibilities in areas close to the biogas production facility.

Typical industries with surplus of hydrogen that are present in Sweden are listed in Table 4 [Schüwer et al., 2015]. The problem with finding a well suited source is that today most of the H_2 is already utilised as much as possible in the different processes as a chemical. For example, the hydrogen is often fully used for desulphurisation in the refining industry, and in the chlorine industry it is often used as a chemical reagent in other processes [Schüwer et al., 2015; Euro Chlor, 2015].

To be able to use hydrogen from industries, impurities may need to be removed. The more important impurities to consider are H_2S and HCl because they deactivate the catalyst used in the Sabatier reactor (see Chapter 2.2.1) [Forzatti and Lietti, 1999; Bartholomew, 2001]. Another problem with using H_2 from a local source is how to store it. The most common way to store it today is by using pressurised tanks, because it is a relative simple storage method proved to be both time and energy efficient [Mazloomi and Gomes, 2012; Churchard et al., 2011]. There are limitations to the storage capability though, because of a phenomenon known as hydrogen embrittlement [Mazloomi and Gomes, 2012]. The diffusion of single hydrogen atoms into minuscule spaces in the metal of a pressurised tank causes a pressure build up as the

Table 4: Listing different processes where H₂ is produced as a byproduct, the raw materials used during the process and the purity of the produced H₂.

Process	Raw material	Purity
Chlor/chlorate alkali electrolysis	Water and NaCl	Up to 99.99 vol-% ^a
Steam cracking and refineries	Fossil fuels and steam	Often in different mixtures with CH ₄
Steel industry	Coke, steel scraps, lime	Up to 66 vol-% ^b

^aImpurities consisting of Cl₂, HCl, O₂, H₂O and N₂ [Junbo et al., 2010; Schüwer et al., 2015]

^bImpurities consisting of CO, CH₄, C₂H₆, CO₂ and N₂ [Lundgren et al., 2013]

single atoms start to form molecules. The increasing pressure may eventually cause the metal to crack. There are however guidelines and recommended maintenance procedures to prevent this from occurring. Another possible storage alternative is liquefying the hydrogen. This will however add 30 % to the energy used during production and demand more expensive production material, which makes the cost 4-5 times larger and thus a less economically viable option [Mazloomi and Gomes, 2012; Churchard et al., 2011].

2.4 Criteria for a sustainable biofuel production

In 2009, the directive to promote the usage of energy from renewable resources was introduced to all member states of the EU. The directive includes targets of having 10 % renewable resources in the transport sector and 20 % in total. It also states that for biofuels and bioliquids to be accounted for as renewable resources, certain criteria for sustainability has to be fulfilled. Among the criteria is the need of reducing GHG emissions by at least 35 %, compared to the emissions from instead using fossil fuels (83.8 g CO₂ equivalent/MJ), and the prohibition to produce biofuels or bioliquids from raw material produced on land with high biodiversity. The need for reduction of GHG emissions is to be increased to 50 % by 2017 and 60 % by 2018. The biogas produced in Sweden today reduces the emissions by about 65 %. [European Parliament, Council of the European Union, 2009; Energimyndigheten, 2015a]

In Sweden, the criteria was implemented in 2010 by the law "Hållbarhetslagen". Since 2011, all companies in Sweden which are liable of taxation for biofuels, or use biofuels in their profession, can get a tax exemption, electricity certificates or count their emissions from bioliquids as zero in the emission trading system, if the criteria is fulfilled. The control of the criteria is made by the company itself and this is every year reported to an administrative authority (Energimyndigheten). The company checks the emissions and land use of the raw material production by tracing it upstreams in the production chain. For Borås Energi & Miljö to fulfill the criteria in the future, it is important for this study to take the production method and feedstock used for H₂ production into consideration when investigating different options. [Energimyndigheten, 2015a; Energimyndigheten, 2015b]

2.5 Aspen Plus and Aspen Process Economics Analyzer

Aspen Plus is the leading flowsheeting tool used for modeling, optimising and analyzing chemical processes, which is used by polymer, bulk, fine, special and biochemical industries. It gives the user the possibility to choose from many different property methods and pieces of equipment to handle both gas, liquid and solid phase processes. It is possible to simulate steady state processes, as well as dynamic batch processes and continuous processes.[Aspen Technology, Inc., 2016b]

Aspen Process Economics Analysis (APEA) is a tool used for estimating capital and operating costs of processes. It is integrated into Aspen Plus and estimates both capital and utility costs for each equipment as well as installation costs by including parameters such as isolation, paint, instrumentation among others. The installation cost for each piece of equipment is calculated by using a calculation model, referred to as mapping by the tool. There are many different mappings depending on the type and purpose of the equipment. The results from the mapping is then used for sizing and evaluate the equipment. The sizing and evaluation is performed with data from the Aspen Plus simulation. Both Aspen Plus and APEA have default settings based on the American market. [Aspen Technology, Inc., 2016a]

2.6 Energy Price and Carbon Balance Scenarios tool

It is important for an investment to be robust and profitable both in short- and mid-term future terms, it is however difficult to predict the future energy prices due to many different parameters that interact with each other, e.g. the price of CO₂ emissions and fuel prices. One way to estimate the development of the energy prices is to construct different scenarios depending on which regulatory decisions are made and see how they affect the parameters. The Energy Price and Carbon Balance Scenarios (ENPAC) tool was made for this purpose by the IEST division at Chalmers University of Technology, and it covers four different scenarios; three scenarios stated by the International Energy Agency (IEA) in their report World Energy Outlook (WEO) 2013, and an average scenario of the current policy scenario and the WEO-450 scenario. The descriptions of the scenarios are listed in Table 5. The ENPAC tool calculates prices on the electricity market, fossil fuel market, bioenergy market and heat market for the different scenarios. The prices are mainly calculated for European conditions and it is using 2012 as the reference year when it calculates prices for the years 2020, 2030, 2040 and 2050 [Harvey and Axelsson, 2010].

Harvey and Axelsson [2010] clearly states that the tool is not an energy market forecast tool, but should be used for predicting plausible cornerstones of the future energy market. The basic assumptions made in the tool are that all prices are based on production cost minimisation and that the energy markets responds quickly to price signals and adapt immediately to variations of climate targets. More specific assumptions are made for each energy market.

The electricity price is given as the generation cost for a new base load plant in the build margin, namely coal plants for all the scenarios except WEO 450, where natural gas combined cycle (NGCC) plants are at the build margin. It is calculated using the fuel prices, policy instruments and option of carbon capture and storage (CCS) set by the different scenarios. The starting point of the calculations is the fossil fuel prices in 2012, and then the prices calculated for the different markets are used as inputs in the next energy market, like a cascade; the market cascade being fossil fuels, electricity, bioenergy and heat. The heat price is calculated for a newcomer industry selling excess heat to the district heating system, depending on both the local heat market and the local heat production mix. The price ranges between the price of producing heat via a local gas boiler and the price of producing heat at a combined heat and power (CHP) plant. [Harvey and Axelsson, 2010]

Table 5: The four different scenarios used in ENPAC as described in WEO [OECD/IEA, 2016].

Scenario	Description
Current policies	Current Policies Scenario assumes no changes in policies from the mid-point of the year of publication.
New policies	New Policies Scenario takes account of broad policy commitments and plans that have been announced by countries, including national pledges to reduce greenhouse-gas emissions and plans to phase out fossil-energy subsidies, even if the measures to implement these commitments have yet to be identified or announced.
WEO-450	450 Scenario sets out an energy pathway consistent with the goal of limiting the global increase in temperature to 2°C by limiting concentration of greenhouse gases in the atmosphere to around 450 parts per million of CO ₂ .
Average	An average scenario for the current policy scenario and the WEO 450 scenario

3 Methodology

3.1 Locating off-site hydrogen production

To locate possible sources for off-site hydrogen production, the SNI (Standard för svensk NäringsIndelning) codes for the different industries listed in Table 4 were established. The SNI code system is the Swedish version of the EU recommended standard NACE (nomenclature statistique des activités économiques dans la Communauté européenne) codes, which is the European standard method to classify industries. The SNI codes were used to sort out the companies likely to produce excess hydrogen among all companies in the Västra Götaland region, according to a methodology proposed by the Urban Metabolism Group⁴. These companies were contacted by phone and email and asked whether they have any excess production of hydrogen, and if they did, at what amount and purity it is produced. The search was mostly restricted to the region of Västra Götaland since the hydrogen should preferably be placed close to the biogas production facility, but for certain promising cases, searches were made for the whole of Sweden as well.

3.2 Process simulations

The process simulations were performed by using Aspen Plus for flowsheeting together with APEA to do the cost estimation of the plant. Three simulations were constructed; one simulation of the existing plant, a second simulation of a plant with both separation of CO₂ and methanation, and finally a plant where the raw gas was fed directly to the methanation. Both capital costs and operating costs were calculated partly by APEA and partly by hand using cost data for electrolysis and other equipment for the different plants. This was due to the electrolysis and vacuum pump not being modeled by Aspen.

Using "Guidelines for Choosing a Property Method", two property methods were used to simulate different parts of the process [Aspen technology, Inc., 2013b]. ELECNRTL was used to simulate the vapor/liquid equilibrium that occurs in the scrubber, flash, condensers and stripper because it considers the solubility of CO₂ and the impact of the electrolytes formed (HCO₃⁻ and CO₃²⁻). To confirm that ELECNRTL was correctly estimating the vapor/liquid equilibrium, simulated data on the solubility of CO₂ in water was compared with experimental data at the different pressures and temperatures in the process. The other parts of the process were simulated using Soave-Redlich-Kwong (SRK) as the property method due to its confirmed performance for the type of substances, temperatures and pressures of the process [Aspen technology, Inc., 2013a].

The assumptions made and input data used for the simulations are presented in Table B.1, E.1 and F.1 in Appendix B, E and F. The first simulation was made for the gas upgrading system that exists in the plant today. This was done to verify

⁴<https://www.chalmers.se/en/staff/Pages/yuliya-kalmykova.aspx>

that Aspen Plus could successfully simulate the different processes involved and size the equipment in a way that resembled the real plant. The generated simulation is illustrated in Figure 3.

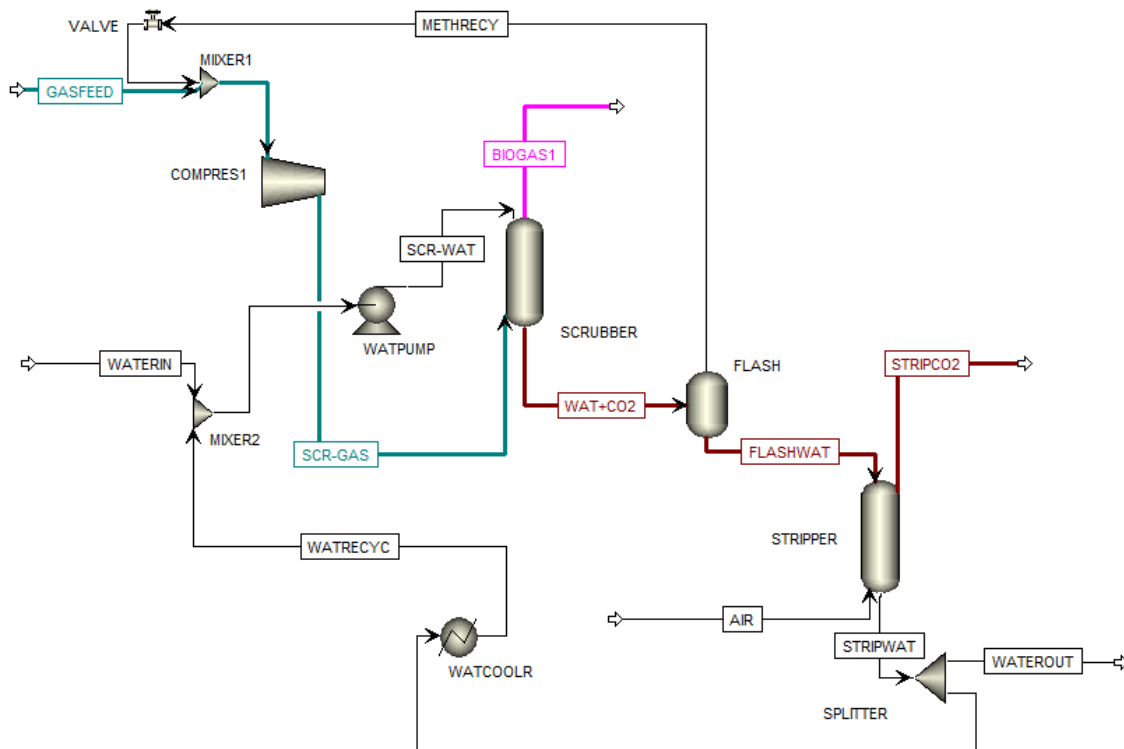


Figure 3: The flowsheet for the simulation of the plant as it works today. The blue lines are the streams containing both CH_4 and CO_2 , while the pink contains mainly CH_4 and the brown contains mainly CO_2 . The descriptions of the acronyms used in the flowsheet is listed in Table E.4 in Appendix E.

3.2.1 Simulation of separation of CO_2

Currently the CO_2 is mixed with air in the effluent stream (about 30 vol-% CO_2). The air would make it impossible to create biogas of the demanded quality (see Table 2), and also increase the needed reactor volume. This creates the need for changing the desorbing method of the stripper column to a method where the effluent stream instead would consist of almost pure CO_2 . To minimise the process changes that need to be done at the plant, the method which was investigated further was using a reboiler at the bottom of the stripper to recirculate some of the process water as steam and desorb the CO_2 . The effluent stream consisting of steam and CO_2 would then need to be cooled in a condenser to remove the water, as illustrated in Figure 4a.

The difficulty with using this method is that the reboiler will demand heat at temperatures over $100\text{ }^\circ\text{C}$ to evaporate the water. This heat would have to be supplied by steam from a boiler at the plant, which could either be fueled by the produced gas or bought fuel. Since steam production is expensive, the case of cheaper industrial

excess heat was investigated, assumed to be available at below 100 °C, which could be utilised in the reboiler if the stripper is operated at subatmospheric pressure. This would however increase the pumping cost due to a vacuum pump.

To reduce the costs for the CO₂ separation, it was investigated which operating pressure in the stripper would be the most economically feasible. This was done by reducing the reboiler duty as much as possible at the different operational pressures, and compare the annualised production cost for the different cases. For more details about the cost calculations, see Chapter 3.2.5.

3.2.2 Simulation of methanation

The methanation was simulated by first pressurising the CO₂ rich stream from the separation. This was done in two stages with an intercooler in between to remove more steam from the flow and thus avoiding condensation in the compressor and also lowering the power usage. H₂ was assumed to be produced by alkaline electrolysis and it was mixed with the CO₂ rich stream after the intercooler, see Figure 4b. The gas was preheated before the reactor for the reaction to start. The reactor was simulated as a multitubular fixed bed reactor using an RPlug block as suggested by Jürgensen et al. [2015]. The kinetic model presented by Schlereth [2015] (see Appendix A) was used to describe the reaction. When the simulated conversion of CO₂ was compared to experimental data presented by Schlereth [2015], a deviation was noticed (see Figure 5). This was likely due to the kinetics not being well represented in the model suggested by Jürgensen et al. [2015]. The activation energy was therefore adjusted to 86.5 kJ/mol at which the simulated conversion fitted the experimental data better. The reactor outlet gas was then run through a condenser to remove the produced water and then dried in a gas dryer (modeled with a Sep unit in Aspen Plus according to ideal drying). A small amount of the gas had to be purged to lower the hydrogen fraction in the produced gas for a sufficient quality (Table 2) to be achieved.

Because of the reaction being strongly exothermic, some different cooling methods of the reactor were studied. Both a constant and varying cooling flow were tested, where the constant cooling flow was modeled as boiling water as the thermal fluid, and where the varying cooling flow was simulated by setting different temperature profiles in the reactor, which are illustrated in Figure 6. The temperature profiles were chosen to be around temperatures corresponding to the maximum CO₂ conversion according to Figure 5, and because the isothermal temperature profile is difficult to control according to previous studies. The non-isothermal profiles are therefore interesting to investigate since they might be easier to control. A refrigerated brine was used as the cooling medium in the reactor when investigating the temperature profiles.

The evaluation of the different reactor settings was made by verifying that the produced gas was fulfilling the fuel gas specifications from Table 2 and also the hydrogen specification, comparing the operating and annualised capital cost of the plant, and to some extent the possibility of energy recovery from the outlet stream of the reactor. The operational properties might be important parts to consider for the cooling method, but it is out of the scope of this project.

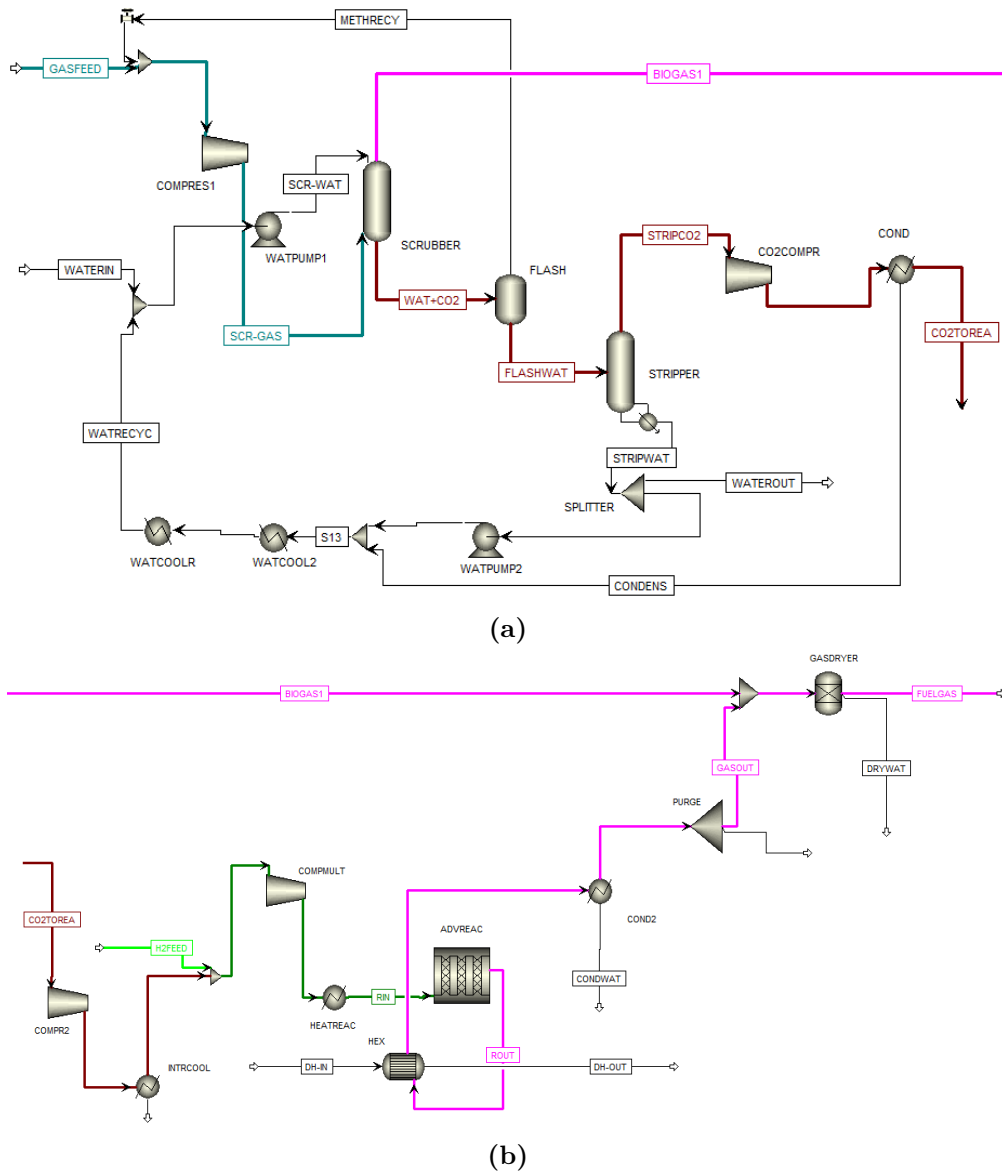


Figure 4: Figure a) shows the flowsheet for the separation of CO₂ (excluding the vacuum pump which was not simulated in Aspen), while Figure b) shows the flowsheet for the methanation. The descriptions of the acronyms used in the flowsheet is listed in Table E.4 in Appendix E. The blue lines are the streams containing both CH₄ and CO₂, the pink contains mainly CH₄, the brown contains mainly CO₂, the light green contains H₂ and the dark green contains a mix of CO₂ and H₂.

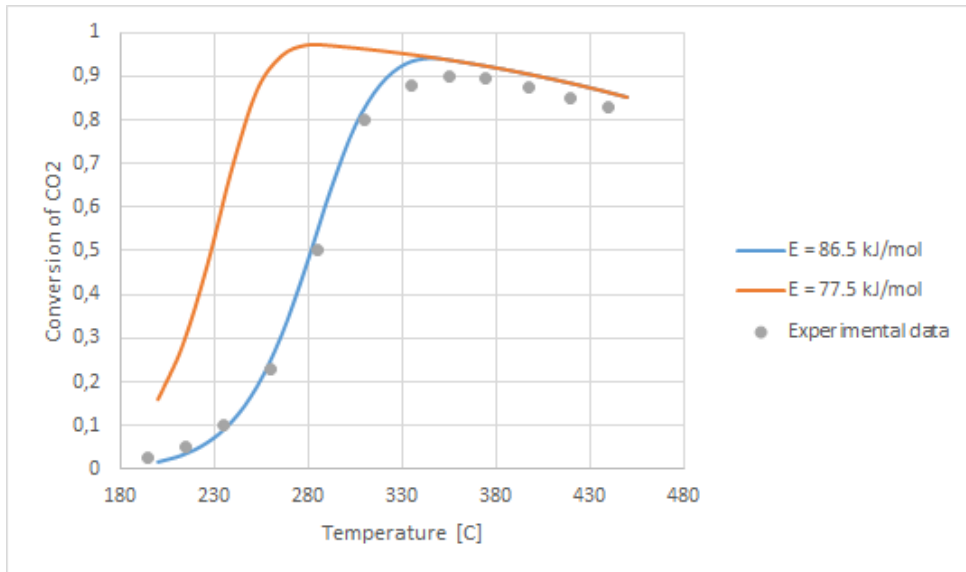


Figure 5: The figure is illustrating how the original kinetic model with an activation energy of 77.5 kJ/mol did not fit the experimental data well. The kinetic model with an activation energy of 86.5 kJ/mol did fit the experimental data better and therefore it was used to model the reaction further on. It can be noticed that the conversion of CO₂ has a maximum value at about 330-350 °C.

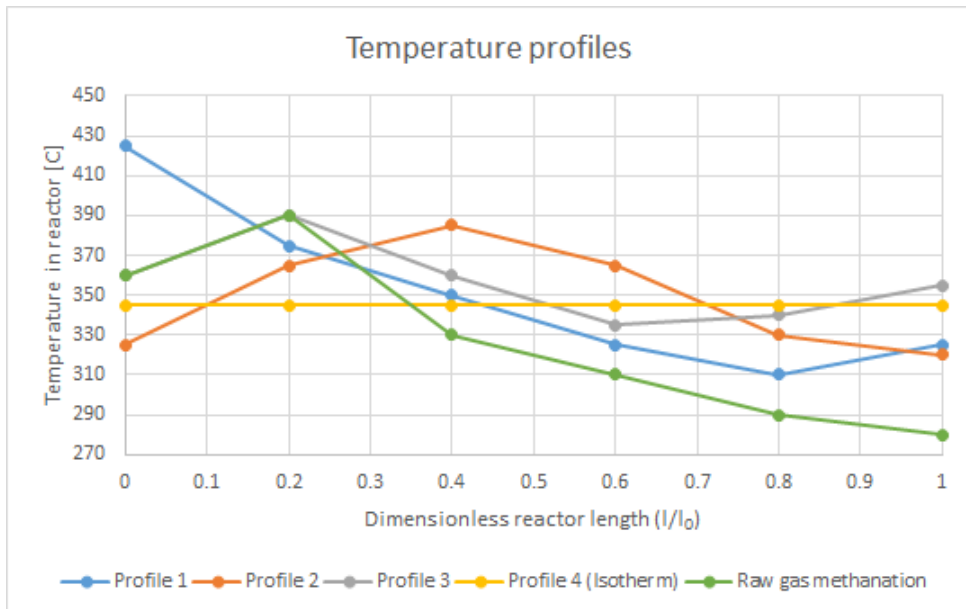


Figure 6: The first four temperature profiles (Profile 1-4) are the ones investigated for the process including CO₂ separation and methanation. Raw gas methanation is the temperature profile used for evaluating the process without any separation of CO₂.

3.2.3 Simulation of heat recovery

Since the Sabatier reaction is exothermic, a lot of heat is created which can be utilised. The heat created is transferred to the cooling medium of the reactor or left in the product gas flowing out of the reactor. The heat left in the product gas stream could either be used to heat up the incoming gas to the reactor or be connected to a district heating network. The options of utilising the heat from cooling the the reactor is not investigated in this project. The set up for the two different cases is illustrated in Figure 7a and Figure 7b.

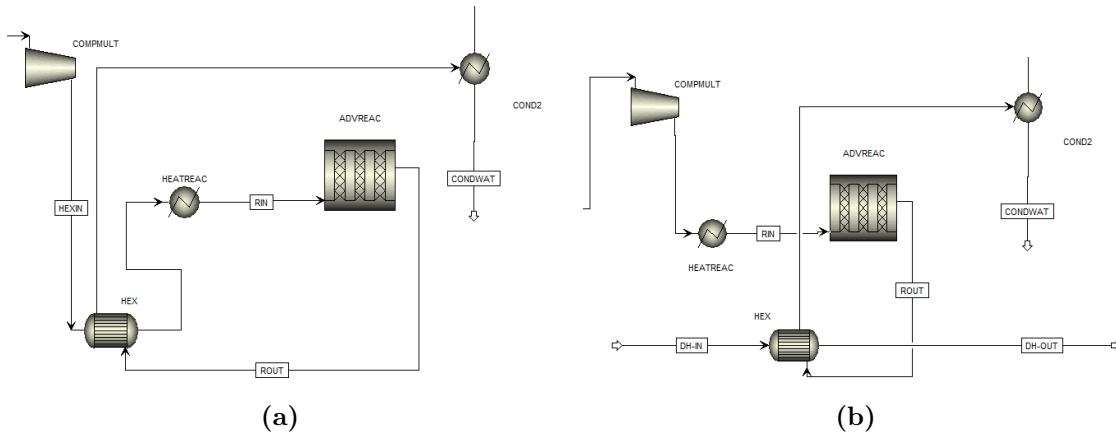


Figure 7: The flowsheet for recirculating the heat from the reactor outlet stream to heat the feed gas to the reactor is shown in a), and the flowsheet for selling the heat from the reactor outlet stream to the district heating network is illustrated in b). The descriptions of the acronyms used in the flowsheet is listed in Table E.4 in Appendix E.

3.2.4 Simulation of plant without CO₂ separation

The simulation of the plant without any separation of CO₂ was performed by using a 2-stage compressor with an intercooler to pressurise the raw gas, where the hydrogen then was inserted after the intercooler. The gas was preheated with a fired heater before entering the reactor, with raw gas used as fuel for the fired heater. The temperature profile in the reactor was decided by trial and error to achieve a sufficient quality of the biogas. The profile is presented in Figure 6. The produced gas was then run through a condenser and dried in the gas dryer to remove all produced water. The whole process is illustrated in Figure 8.

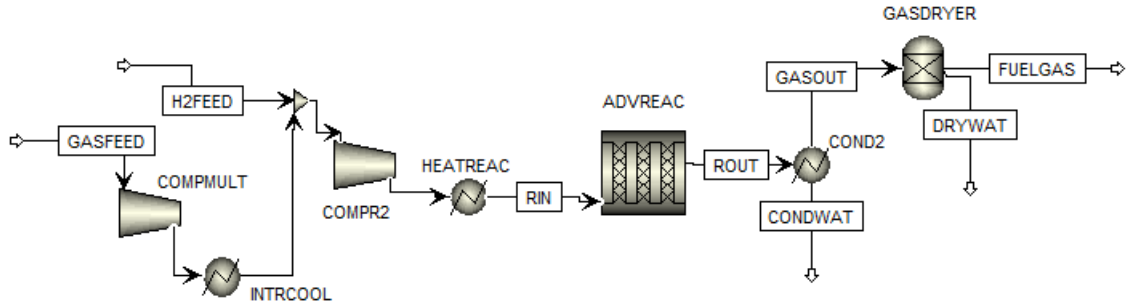


Figure 8: The flowsheet for the simulation of the methanation by the Sabatier reactor without separating the CO₂ from the raw gas. The descriptions of the acronyms used in the flowsheet is listed in Table E.4 in Appendix E.

3.2.5 Estimation of economic performance

The estimation of the different costs of the process was mainly performed by APEA, but some additional cost calculations were performed for the vacuum pump and electrolysis. The prices and assumptions made for the estimation are presented in Table 8 and Table B.2 in Appendix B. The different costs that APEA calculates are presented in Table 6. The capital costs considered in this project were the equipment and installation cost, adding up to the installed equipment cost. To evaluate the economic feasibility of the different processes, the installed equipment cost was annualised using the capital recovery factor (CRF), see Equation 11, assuming the investment payback time (T) is 5 years and the interest rate (i) is 5 %. The economic feasibility was then evaluated using this annualised cost together with the utility and raw material costs.

Table 6: The different costs that are calculated by APEA is divided into two parts; the capital costs and the operating costs. The costs marked in bold text are the ones that are used for comparison in this project. The sum of the capital costs marked in bold are hereon referred to as the installed cost. G&A means general and administration.

TOTAL COST	
<i>Capital cost</i>	<i>Operating cost</i>
Equipment , Equipment setting, Piping , Civil, Steel, Instrumentation, Electrical , Insulation, Paint, Other, Subcontracts, G&A overheads, Contract fee, Escalation, Contingencies	Raw material , Utilities , Labor & Maintenance, Operating charges, Plant overhead, G&A costs

$$CRF = \frac{i(1+i)^T}{(1+i)^T - 1} \quad (11)$$

Not all equipment costs in the process chart were included due to the fact that some equipment units already exist at Sobacken or that the cost was assumed to be minor. The excluded minor costs were costs for valves, splitters and mixers. The other equipment units were divided into three categories, depending on if they already exist at the plant and can be reused (group 1), already exist at the plant but it is unsure whether they can be reused or not (group 2) and new equipment (group 3). The equipment are listed in Table 7.

Table 7: The table lists all equipment according to their naming in the flowsheet (see Figure 4a and 4b), separated into three groups depending on if they already exist at the plant and can be reused (group 1), already exist at the plant but it is unsure whether they can be reused or not (group 2) and new equipment (group 3).

Group 1	Group 2	Group 3
COMPRES1	WATCOOLR	ADVREAC
FLASH	STRIPPER	CO2COMPR
GASDRYER		COMPR2
SCRUBBER		COMPMULT
WATPUMP1		COND2
HEX(DH)		COND
		HEATREAC
		HEX
		INTRCOOL
		WATCOOL2
		WATPUMP2

The equipment in group 1 was excluded from total equipment cost since they already exist at Sobacken. The water cooler which cools down the process water using brine (named WATCOOLR in the flowsheet) is in group 2 due to the difficulty in determining if the existing water cooler would be able to operate well at a higher temperature difference for the new process or not. It is however assumed that it can be used without any modifications needed and the equipment cost is set to zero for further calculations. The water cooler which cools down the process water using river water (WATCOOL2) is considered to be in group 3 since it uses another cooling utility (river water). The stripper is placed in group 2 because it might be possible to use the stripper column that exists today, but with a few modifications on the tower and an additional reboiler. The cost for the stripper is therefore calculated as the difference between the estimated costs from the simulation of the proposed plant and the existing plant. The heat exchanger to the district heating system (HEX(DH)) was placed in group 1 due to it being part of the district heating

company's equipment, while the heat exchanger used for heating the reactor inlet gas (HEX) was in group 3

APEA calculates equipment cost by first mapping the equipment, then sizing the equipment and last the program evaluates the cost. The mapping was performed by choosing a type of model to use for sizing and evaluating the cost for each piece of equipment. The different equipment models used are listed in Table B.2 in Appendix B. The equipment cost for the vacuum pump was not estimated by APEA, but estimated according to Equations 16 and 17 in Appendix C.

The operating costs used for comparison in this project were the raw material and utility costs. The raw material cost consisted of the cost of process water for the scrubber and the catalyst cost for the reactor. The utility costs consisted of costs for electricity, cooling utility and heating utility. The properties and prices of the different utilities are listed in Table 8. The price for industrial heating is assumed to be as if it is sold from a CHP plant, which is a reasonable assumption because a CHP plant is being built at Sobacken. The price of electricity was the price in Sweden during the second half of 2015 for industries utilising between 70 - 150 GWh/year (Borås Energi & Miljö is utilising ~ 96 GWh/year [Borås Energi & Miljö AB, 2014])

The cooling utility is assumed to be either a refrigerated brine or river water depending on the cooling need. The cost of the refrigerated brine was calculated according to the method proposed by Towler and Sinnott [2012], where it is assumed to only consist of the cost of the electricity demand for the cooling system. The river water price was quite similar to the price for brine (see Table 8) which can be explained by the price reported by Rerat et al. [2013] being for the European market, based on a European electricity price. This was however not taken into consideration when calculating the costs and the price was kept as it was presented by Rerat et al. [2013].

The production income from selling gas today is based on 30 % of the fuel gas being sold to private consumers and 70 % being sold to the local bus company. The price to the private consumers includes Value Added Tax (VAT) of 20 % and both prices include a distribution cost. The gate price was set according to the diesel price to be competitive, which is the case at Borås Energi & Miljö today.

The fired heater used for preheating the reactor feed was fueled by either purged gas or raw gas. The cost of using purged gas as fuel was assumed to be zero. The possibility of burning it in a gas boiler to produce steam was only considered for the heat recovery simulations⁵, and not included in the cost estimations due to the small steam production possible. The cost of using raw gas as fuel (C_{rawgas}) was assumed to be the potential profit lost by burning it. It was calculated according to Equation 12, where I_{gas} is the loss of income due to less upgraded raw gas and C_{upgrade} is the cost that would be for upgrading the combusted raw gas instead. The price for raw gas was different for the different processes since it depended on the cost for

⁵The difference in purged gas used as fuel for preheating between the case without heat recovery and the case with heat recirculation, was assumed to be sold at 0.0332 US\$/kWh.

Table 8: The utilities used in the simulation and their respective prices and properties. The heat from a fired heater is using the purged biogas as fuel, which is why the cost is assumed to be 0. The price for low pressure steam was given by Rerat et al. [2013] for 6 bar and 160 °C, which was assumed to be the same for steam at 2 bar and 120 °C.

Utility	Price	Inlet T	Outlet T	Pressure
	US\$/kWh	°C	°C	bar
Electricity [Statistics Sweden, 2016a]	0.0396	-	-	-
Cooling water (brine)	0.014	-3	10	1
Cooling water (river) [Rerat et al., 2013]	0.013	15	25	1
Process water [Lari et al., 2016]	1 ^a	7	63	1
Low pressure steam [Rerat et al., 2013]	0.04	120	120	2
Industrial heat [Harvey and Axelsson, 2010]	0.0036	80	75	1
Heat from fired heater fueled by purged gas	0	>400 °C	-	-

^aThe process water is given in US\$/ton

upgrading gas. The cost for electrolysis was calculated by using the data from Table 3 and assuming it was produced by alkaline electrolysis. Stack replacement costs were excluded from the cost estimation because the pay back time was 5 years, and the stack did not need to be replaced during that time.

$$C_{rawgas} = I_{gas} - C_{upgrade} \quad (12)$$

3.2.6 Sensitivity analysis

The sensitivity analysis was performed in two steps. First an analysis were performed to find a well performing set of parameters so that the production cost was decreased. Second, an analysis were performed to see how robust the process is, concerning the varying properties of the raw gas.

The first analysis was performed to see how the production cost⁶ could be decreased by varying parameters such as the H₂/CO₂ ratio, catalyst amount, reactor operating pressure and purge amount. The effect on the amount of gas produced, the Wobbe index, CO₂ fraction and H₂ fraction was also monitored to ensure the quality of the produced gas. Each parameter was first varied while the other ones were kept constant at the values in Table 9. The initial value of the H₂/CO₂ ratio was chosen because it was the equimolar ratio. The reactor pressure was initially set as 10 bar

⁶Due to the calculator block in Aspen Plus being incompatible with APEA and only the relative costings were important, the capital cost used in the sensitivity analysis consisted of the equipment costs for only the major pieces of equipment (compressors, heat exchangers, stripper and electrolyser), calculated by using equations presented by Towler & Sinnott [2012] and Biegler et al. [1997].

according to Jürgensen et al. (2015), but since the required hydrogen fraction was not achieved at this pressure, the initial value was increased to 40 bar. The initial catalyst amount was chosen for the reactor to reach equilibrium, while the initial purge fraction was set to fulfill the quality standard of hydrogen fraction. After finding a set of parameter values giving the lowest cost and highest gas production, they were all combined to confirm that the gas quality still was in the standard range.

Table 9: The initial values before trying to decrease the production cost.

Property	H ₂ /CO ₂ ratio	Reactor operating pressure	Catalyst loading	Purge fraction
Initial values	4	40 bar	36 kg	0.2

The second analysis was made due to the variations in the raw gas flow, composition, pressure and temperature. The process must be able to handle variations of these parameters and still produce biogas of the standard quality. For this reason it is important to analyse how the varying raw gas properties affected the produced gas. The analysis was performed for the process with both separation of CO₂ and methanation without any heat recovery. The ranges for the different parameters were taken from process data from Sobacken which are presented in Table 10.

Table 10: The ranges for the raw gas properties that were analyzed. The value for the methane slip is the fraction of CH₄ in the outlet of the stripper.

Property	Flow	O ₂ fraction	N ₂ fraction	CH ₄ fraction
Varying range	110-190 Nm ³ /h	0-0.1 vol-%	0-0.3 vol-%	50-73 vol-%
Property	Pressure	Temperature	Methane slip	
Varying range	1.01-1.3 bar	5-11 °C	0.9-3.5 vol-%	

3.3 Economic assessment

To study the future economic feasibility of the process, the ENPAC tool was used to estimate future electricity prices and the correlated biogas prices for the four different scenarios given in Table 5. The tool was set to calculate diesel prices using energy and CO₂ tax as in Sweden. ENPAC only calculates the European electricity price and therefore a Swedish price was estimated using a constant factor based on the ratio between the Swedish and European average price for industries in the third quarter of 2015. The prices were 0.063 and 0.12 €/kWh respectively, making the ratio 0.525 [Eurostat Statistics Explained, 2016].

The biogas price is not calculated in the ENPAC tool, but the diesel price is. Since the biogas price follows the diesel price, a respective correlation was used to calculate the biogas price. The diesel price given by ENPAC excludes energy taxes and VAT. Assuming the consumer price per driven km (P_{cons}) was the same for both fuels it was possible to calculate the biogas gate price (P_{gate}) using Equation 13 and 14, where the indexes d and m refer to diesel and biogas respectively. Since biogas is considered as a renewable fuel, there are no CO₂ or energy tax added to the consumer price. The factors f_d and f_m is the fuel economy of the cars, expressed as amount of energy required per driven km. The ratio $\frac{f_d}{f_m}$ was set to 1.1668, based on the fuel economy for a diesel car being about 10 % higher and one diesel gallon equivalent (DGE) being equal to 105.5 MJ of compressed natural gas [Florida city gas, 2016]. The data used for the calculations can be found in Table B.2 in Appendix B

$$P_{\text{cons},m} = f_m(P_{\text{gate},m} + C_{\text{distr.},m} + \text{VAT}) \quad (13)$$

$$P_{\text{cons},d} = f_d(P_{\text{gate},d} + C_{\text{distr.},d} + \text{VAT} + \text{CO}_2 \text{ tax} + \text{Energy tax}) \quad (14)$$

It was assessed how the profit of biogas production was dependent on the electricity and biogas prices. The dependence on the electricity and biogas price was also studied for a future case where SOEC was assumed to be developed according the the predictions in Table 3. The total cost was divided into costs of the three main processes; separation of CO₂, methanation and hydrogen production. How the investment pay back time affected the profit was also considered in the analysis of the partial costs.

It was also investigated what the cost would be if the hydrogen instead was supplied by another company, which already produces it as a byproduct. It was assumed for this study, that the hydrogen was previously used by the producer as a fuel for internal heating and the same amount of heat had to be given by combusting another fuel instead. The hydrogen price was therefore dependent on the price of the fuel used to replace the hydrogen (e.g. wood pellets or natural gas), but also the distribution method from the source of H₂ to the Sobacken plant. The distribution could either be via pipeline or by trucks carrying tanks containing either gas or liquefied hydrogen. The hydrogen price was lowest if wood pellets were used to

produce heat and pipeline was the distribution method, and highest if natural gas was used to produce heat and the distribution method was trucks carrying liquefied hydrogen in tanks.

All assessments, with the initial values and ranges investigated, are listed in Table 11. The initial values for the electricity and biogas price were the prices of today, and the ranges investigated were taken from the ENPAC scenarios. Alkaline electrolysis was assumed to be the hydrogen production method because it is one of the most commonly used methods at a relatively low price. SOEC is said to be available in 2030 and thus it was included in the range investigated. The initial value of the investment payback time was set to five years due to it being a common economic life time for process industries. The higher pay back time was included in the investigated range because it is a common technological life time often used in research. The assessments were all made for two processes; the process using the set of parameters that the sensitivity analysis resulted in, that included separation of CO₂, methanation and heat recovery via the district heating network (which is hereon referred to as the base case), and the process with methanation of raw gas directly.

Table 11: Listing all the assessments performed. The assessments were performed for the base case process and the raw gas methanation process. There are no initial value for the hydrogen price due to assumption that the hydrogen production method is electrolysis initially.

Parameter	Electricity price	Biogas price	H ₂ price
Initial value	0.0396	1.72	-
Range investigated	0.01-0.1 US\$/kWh	1.72-2.36 US\$/kg	2.12-3-98 US\$/kg
Parameter	Type of electrolysis	Investment pay back time	
Initial value	Alkaline	5 years	
Range investigated	Alkaline & SOEC	5 & 25 years	

4 Results

4.1 Mapping of H₂ sources

The possible H₂ sources that were found during this study are presented in Table 12. The main focus was put on finding sources in Västra Götaland since the biogas production plant is placed in that area. However a hydrogen source in Sundsvall was also included because of promising characteristics. It must be kept in mind though, that the sources listed might not be the only sources in the investigated region. This is because it was not possible to make contact with all companies that plausibly was producing H₂ in excess.

The H₂ produced at ST1 and Preem is already used as feedstock in the desulphurisation process at the industries. At Preem, they even have a deficit of H₂ and need to buy more to cover their need for the desulphurisation process. This, together with the fact that it is non-renewable H₂, causes the two refineries to not be considered as viable sources further on.

The amount of H₂ produced during Borealis ethylene production is actually about 24 000 ton/year, but it is mixed with methane which is also formed during the steam cracking process. The hydrogen separated from methane with a PSA unit is only 5600 ton/year, out of which an unknown part is used internally for hydrogenation. The H₂ gas produced has a purity of minimum 99.9 vol-% with maximum 0.1 vol-% CH₄ and CO on ppm level. Borealis uses hydrocarbons from oil and gas industry as raw material, which makes the H₂ a product from fossil fuels. This might cause the criteria of sustainability not to be fulfilled, and thus Borealis was not considered a viable source.

The electricity needed for electrolysis for both Inovyn and Akzo Nobel is considered to be a fossil free energy source, since it can be based on the Swedish electricity mix consisting of mostly hydroelectric and nuclear power. Because Sundsvall is located far from Sobacken, it is not considered as a viable source for this study; however it may be interesting to produce biogas from this hydrogen if a CO₂ source is located near Sundsvall⁷. This makes the H₂ produced at Inovyn the only viable source for off-site H₂ production in this study. The H₂ produced by electrolytic processes at Inovyn is today mostly used internally as a source of energy or chemical reagent, and the remaining share of about 10 % is sold. It is however important to consider the impurities of the gas, presented in Table 13. The catalyst is known to be deactivated by H₂S and HCl, and the sulphur and chlorine concentrations in the gas might be high enough to cause deactivation of the catalyst and forcing the catalyst bed to be exchanged more often. The hydrogen from Inovyn was therefore further on partly considered as a viable source.

⁷Especially since there is a low content of catalyst deactivating impurities.

Table 12: Listing productions sites where H₂ is produced as a byproduct and might be used as hydrogen source for biogas production. The yearly production assumes an operating time of 8000 h/year. The viability of utilising the hydrogen from the different processes depends on the amount of hydrogen, location of production and the raw material used for production. ✓ means that the hydrogen would be viable, while X means the opposite.

Company	Process	Location	Amount [ton/year]	Viable [✓/X]
Inovyn	Chlor alkali electrolysis	Stenungsund	3 120	✓
Akzo Nobel	Sodium chlorate alkali electrolysis	Sundsvall	2 800	X
Borealis	Ethylene production ^a	Stenungsund	5 600 ^b	X
ST1	Refinery	Göteborg	14 600	X
Preem	Refinery	Lysekil	52 000	X

^aVia steam cracking

^bUnknown part of it is used internally

Table 13: The impurities of the hydrogen produced from the two mapped electrolysis processes at Inovyn and Akzo Nobel. The impurities are all given as the maximum value in molppm.

Company	Cl ₂	Hg	S	CO and CO ₂	O ₂	HC	N ₂
Inovyn	0.3	6 · 10 ⁻⁴	0.7	1	30	-	-
Akzo Nobel	<0.05	0	-	20	2000	20	7000

4.2 Validation of vapor/liquid property method

By comparing experimental data with simulated data from Aspen Plus for the amount of CO_2 dissolved in water, the use of ELECNRTL to describe the vapor/liquid equilibrium in the gas upgrading system could be validated for different pressures and temperatures that were present in the processes. The result for a subatmospheric pressure of 0.168 bar is presented in Figure 9. The results for the other studied pressures (atmospheric and higher pressure at 9.9 bar) are presented in Figures D.1 and D.2 in Appendix D. It is clear that ELECNRTL is a valid property method at the different pressures, since the simulated data is following the curve of the experimental results well. The experimental data was given by three different studies, the low pressure data are presented by Novák et al. [1961], the atmospheric pressure data are presented by Li and Tsui [1971] and the high pressure data are presented by Matouš et al. [1969].

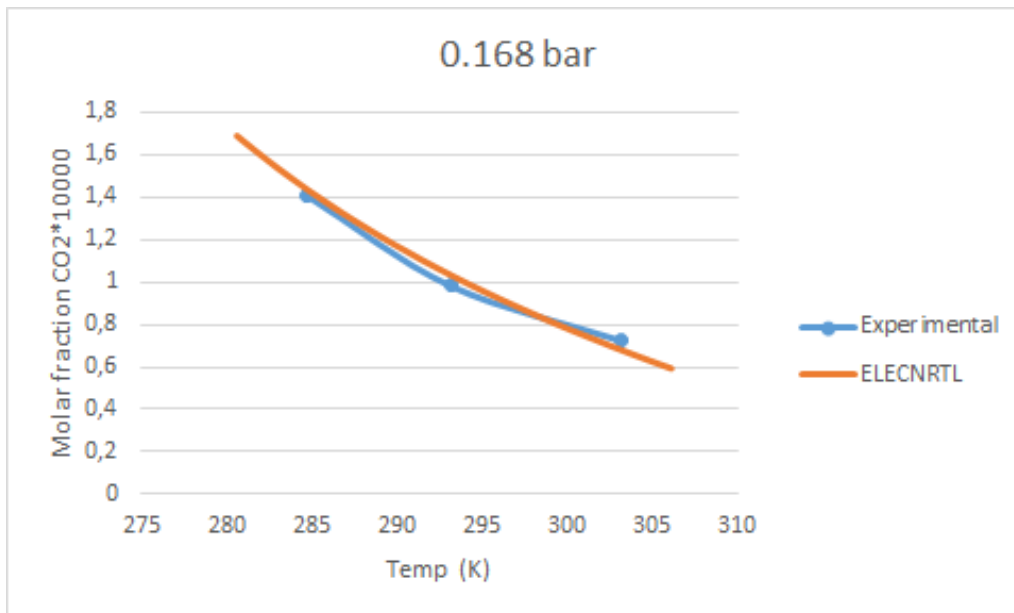


Figure 9: Graph showing both experimental and simulated data of the solubility of CO_2 in water at 0.168 bar for temperatures ranging from 280-305 K [Novák et al., 1961]. It can be seen that the simulated data using ELECNRTL is following the trend of the experimental data well.

4.3 Results from process simulations

The model of the existing plant at Sobacken showed properties similar to the real plant, except for a higher pressure in the flash (100 % higher), a larger flow of recirculated gas (545 % larger) and a smaller stripper diameter (50 % lower). All the results from the simulation of the existing plant are presented in Table H.1 in Appendix H, where they are compared to values from the existing plant. The equilibrium model used for the columns might have caused some of the dissimilarities between the simulation and the plant at Sobacken, and using a rate-based model instead could have improved the simulation. Using Aspen Plus as the simulation tool was because of this deemed sufficient to describe the processes further investigated.

4.3.1 CO₂ separation simulation results

The results of varying the pressure in the stripper column is displayed in Table 14. The costs of the equipment and utilities were calculated by APEA, except for the vacuum pump where the equipment and utility costs were calculated according to the method described in Appendix C. The 1 bar case has a lower installed cost due to no vacuum pump needed, but it also had a much higher utility cost due to the high price of steam needed to heat the reboiler. The reboiler temperature for 0.3 bar is above the temperature limit (for a $\Delta T_{min} = 10^\circ C$), making excess heat at 80 °C insufficient. For the evaluation of the cost however, the heat was assumed to be available at 86 °C with a return temperature of 81 °C at the same price. Comparing the annual costs it can be noticed that 0.3 bar pressure is the lowest cost, but it is not a viable option due to the assumption of excess heat only available at 80 °C. The optimal pressure was therefore set to 0.2 bar.

Table 14: The reboiler temperature and costs for separation processes using different pressures in the stripper. For 0.05-0.2 bar, the reboiler is heated with industrial excess heat in the form of hot water at 80 °C, and at 86 °C for 0.3 bar, while steam at 120 °C is used for 1 bar.

Pressure [bar]	0.05	0.1	0.2	0.3	1
Reboiler temperature [°C]	40.9	50.6	62.8	71.1	102.3
Installed cost [US\$]	2 600 000	2 300 000	2 000 000	1 800 000	1 300 000
Utilities & raw material cost [US\$/year]	338 000	336 000	351 000	383 000	1 496 000
Annualised cost [US\$/year]	940 000	870 000	808 000	798 000	1 615 000

4.3.2 Methanation simulation results

When evaluating the case where the Sabatier reactor was cooled with a constant flow of cooling medium, it was noticed that it resulted in a high temperature peak in the reactor, see Figure G.1 in Appendix G. The high temperature peak in the reactor is a result of the reaction being strongly exothermic and the cooling not being sufficient because of the global transfer coefficient being low for heat transfer between gas and boiling water. The temperature becomes as high as 800 °C, at which sintering of the catalyst would occur. The Wobbe index of the resulting gas is also out of range (42.73), because when the reaction starts to slow down the temperature lowers so quickly that the reaction actually stops completely before the CO₂ conversion is high enough to get a Wobbe index in range. This alternative was not evaluated further due to these results.

The result of the evaluation of the four different temperature profiles is presented in Table 15. Profile 4 failed to produce gas of sufficient quality (hydrogen content over 2 vol-%), which is why it was not evaluated further on. Out of the remaining profiles, temperature profile 3 had the highest profit, but the profits were similar for all three profiles. The potential of heat recovery was therefore an important parameter to consider when deciding which temperature profile to investigate further. Since this study only considers the possibility for energy recovery from the outlet stream, the outlet stream temperature is the important factor for the heat recovery potential. Taking both profit and heat recovery potential in consideration makes profile 3 the best profile. It must be noticed that for all profiles, the annualised profit was negative which means that no profit is made and the production cost is too high relative to the income generated by selling the biogas produced.

Table 15: Listed below are the reactor outlet temperature and production costs for the different temperature profiles. The costs are for the whole process, including the separation of CO₂. The reactor outlet temperature is considered to evaluate the possibility of heat recovery. ✓ means that the quality of the produced gas is sufficient, while X means the opposite.

Profile	1	2	3	4
Reactor outlet temp [°C]	325	320	355	345
Installed cost [US\$]	4 300 000	4 270 000	4 260 000	4 320 000
Utility & raw material cost [US\$/year]	755 000	751 000	752 000	751 000
Production income [US\$/year]	612 000	613 000	613 000	614 000
Annualised profit ^a [US\$/kg]	-3.186	-3.147	-3.141	-3.173
Gas quality [✓/X]	✓	✓	✓	X

^aIncluding utility cost, raw material cost and annualised installed cost

4.3.3 Results from sensitivity analysis

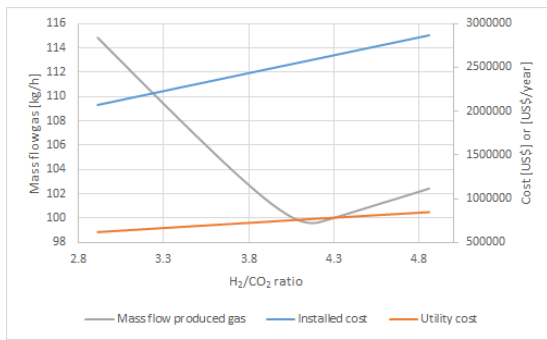
The production cost was decreased by analyzing how the costs and biogas production were affected when varying the H_2/CO_2 ratio, reactor operating pressure, catalyst amount and purge amount. The biogas production was monitored in kg/h due to biogas having a flat price per kg of gas. The results are presented in Figure 10. A lower cost is achieved for a lower H_2/CO_2 ratio, while the mass flow shows a minimum at a ratio of 4.1. The mass flow has a minimum because CO_2 has a higher molar mass than CH_4 , meaning that the conversion of CO_2 is highest at the minimum. Increasing the ratio even more would just add H_2 to the flow that would not react due to the shortage of CO_2 . Looking at Figure 10b, it can be noticed how there are a region between 3.7-3-9 where all constraints are met. Comparing this to Figure 10a it is clear how a lower ratio would be most profitable.

The result from varying the reactor operating pressure is illustrated in Figures 10c and 10d for the effect on cost and quality respectively. It is clear how the installed cost increases for a higher pressure due to the higher compressor work and the need for more pressure resilient equipment. The reactor is designed so that the reaction reaches equilibrium, which is illustrated in Figure G.2 in Appendix G. At equilibrium, a higher pressure pushes the Sabatier reaction towards producing more CH_4 and H_2O according to Le Chatelier's principle, and thus the mass flow decreases due to the differences in molar mass between the reactants and products. The pressure must however be above 37 bar due to the limitation of H_2 content in the produced gas, as can be seen in Figure 10d.

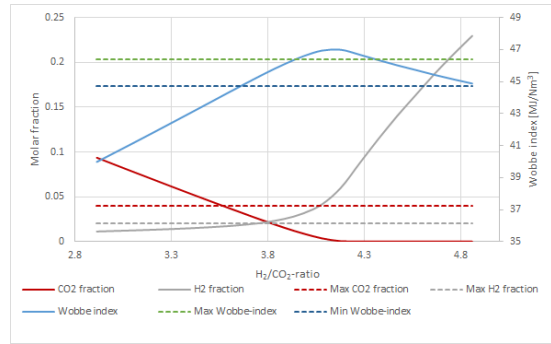
Figures 10e and 10f illustrates the effect on production cost and gas quality respectively when the amount of catalyst in the reactor is varied. The utility cost decreases with a lower catalyst amount while the mass flow increases, which implies that a lower catalyst amount is preferred. A lower catalyst amount than 34 kg would make the H_2 fraction exceed 2 mole-% though, see Figure 10f, and therefore the minimum catalyst amount is 34 kg.

The amount of purged gas is preferably reduced as much as possible since it can be considered as a loss of product, even though it can be used as fuel for the preheating before the Sabatier reactor. The increase in mass flow of produced gas when changing the purge is illustrated in Figure 10g, where it is also clear that the installed cost is not affected by the purge. The factor limiting the reduction of purge is the H_2 content in the produced gas as is illustrated in Figure 10h.

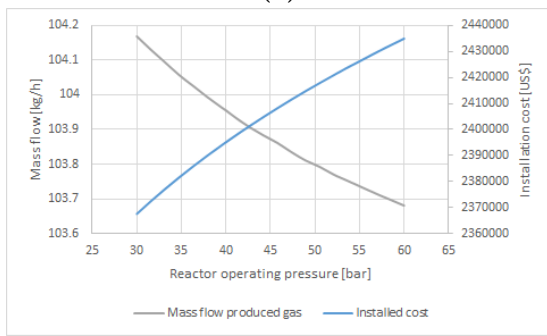
The optimal values found for the H_2/CO_2 ratio, reactor operating pressure, catalyst amount and purge were all combined to confirm that the gas was still of satisfactory quality. This was however not the case because the H_2 fraction became too high. To solve this, the catalyst amount and reactor pressure were instead set to 36 kg and 40 bar respectively. The production cost was most sensitive to the H_2/CO_2 ratio, while the mass flow was most sensitive to both the H_2/CO_2 ratio and the purge. This is why those parameters were kept at their optimal values while the reactor operating pressure and catalyst amount were increased to achieve a satisfactory quality of the produced gas (see Table 16). Due to the strict standard quality of the gas, the



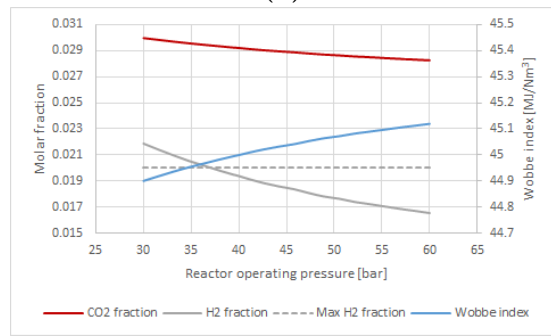
(a)



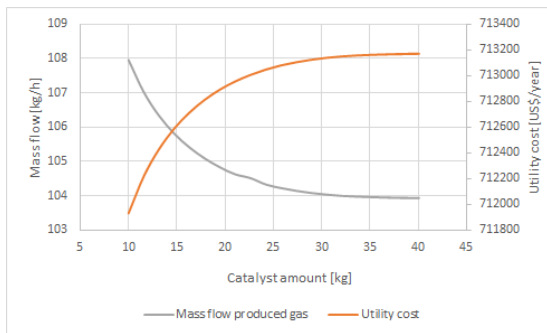
(b)



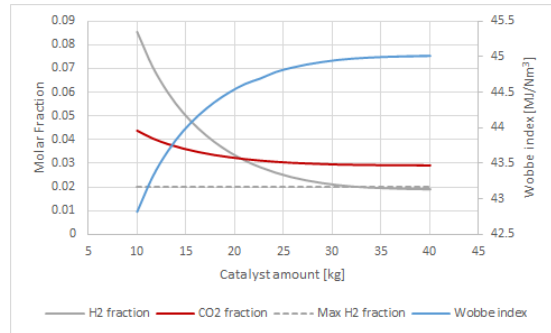
(c)



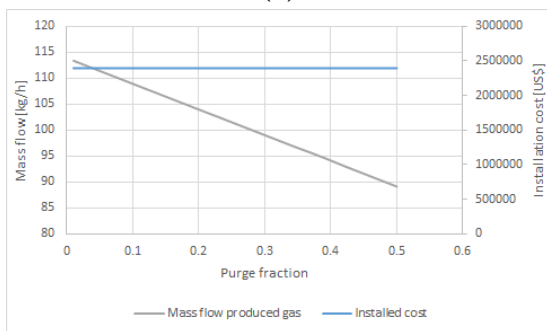
(d)



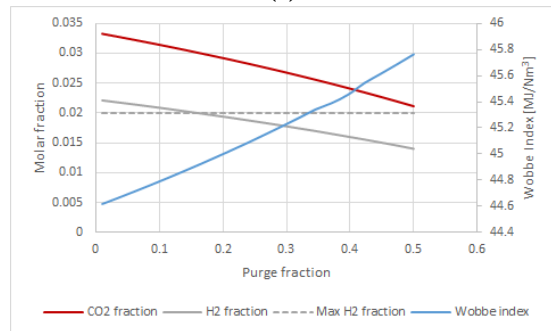
(e)



(f)



(g)



(h)

Figure 10: Investigating the effect of parameters to decrease the production cost of the process. The H_2/CO_2 ratio is varied in a) and b), reactor operating pressure in c) and d), catalyst amount in e) and f), and purge fraction in g) and h).

increase in profit was only small. The profit was -3.141 US\$/kg before the cost reduction and -3.110 US\$/kg after. A higher profit might be realised if a rigorous optimisation would have been performed, this was however outside the scope of this project.

Table 16: The set of parameters after decreasing the production cost.

Property	H ₂ /CO ₂ ratio	Reactor operating pressure	Catalyst loading	Purge fraction
Initial values	4	40 bar	36 kg	0.2
Optimal values	3.7	40 bar	36 kg	0.165

The sensitivity analysis of the effect from variations in raw gas parameters and methane slip was performed for the process with both separation of CO₂ and methanation, using the cost optimal parameter settings derived above. The results of the analysis are presented in Figure 11. From Figures 11a and 11b it is clear that the variations in temperature and pressure of the raw gas does not affect the process. Figures 11c and 11d shows how the small fractions of O₂ and N₂ in the raw gas affect the produced gas. One can see that the quality of the gas is sufficient for the ranges investigated, because the Wobbe index never gets below the lower limit and the combined fraction of CO₂, O₂ and N₂ never exceeds the higher limit of 4 vol-%.

The flow of the raw gas affects the quality of the produced gas according to Figure 11e. The lower flows show a good quality of the produced gas, while the quality worsens rapidly for higher flows. There are problems at lower flows as well, not visible in the figure, due to condensation occurring in the raw gas compressor. The condensation in the compressor would most likely not occur if the compressor was a multistage compressor with intercooler that removed some of the water coming from the recirculating gas. This is however not investigated closer in this study. The problems at higher flows also suggest that the process should be somewhat redesigned to withstand a larger variation of flows.

The results of varying the methane content of the raw gas are illustrated in Figures 11f and 11g. Figure 11f shows how the Wobbe index is affected while Figure 11g shows how the fraction of H₂ changes with the CH₄ content. There was condensation in the raw gas compressor at higher CH₄ content, which might be possible to avoid if a multistage compressor with an intercooler instead was used, the same as for the lower raw gas flow. A higher methane content resulted in the Wobbe index and H₂ content at sufficient levels though. The lowest CH₄ content is on the contrary making the process to not reach the standard conditions; the Wobbe index is below the limit for the whole range of flow rates, and the H₂ content is above the limit for the smaller flows. These results mean the same as for varying the flow rate only, the process has to be somewhat redesigned to withstand variations both in raw gas flow and CH₄ content.

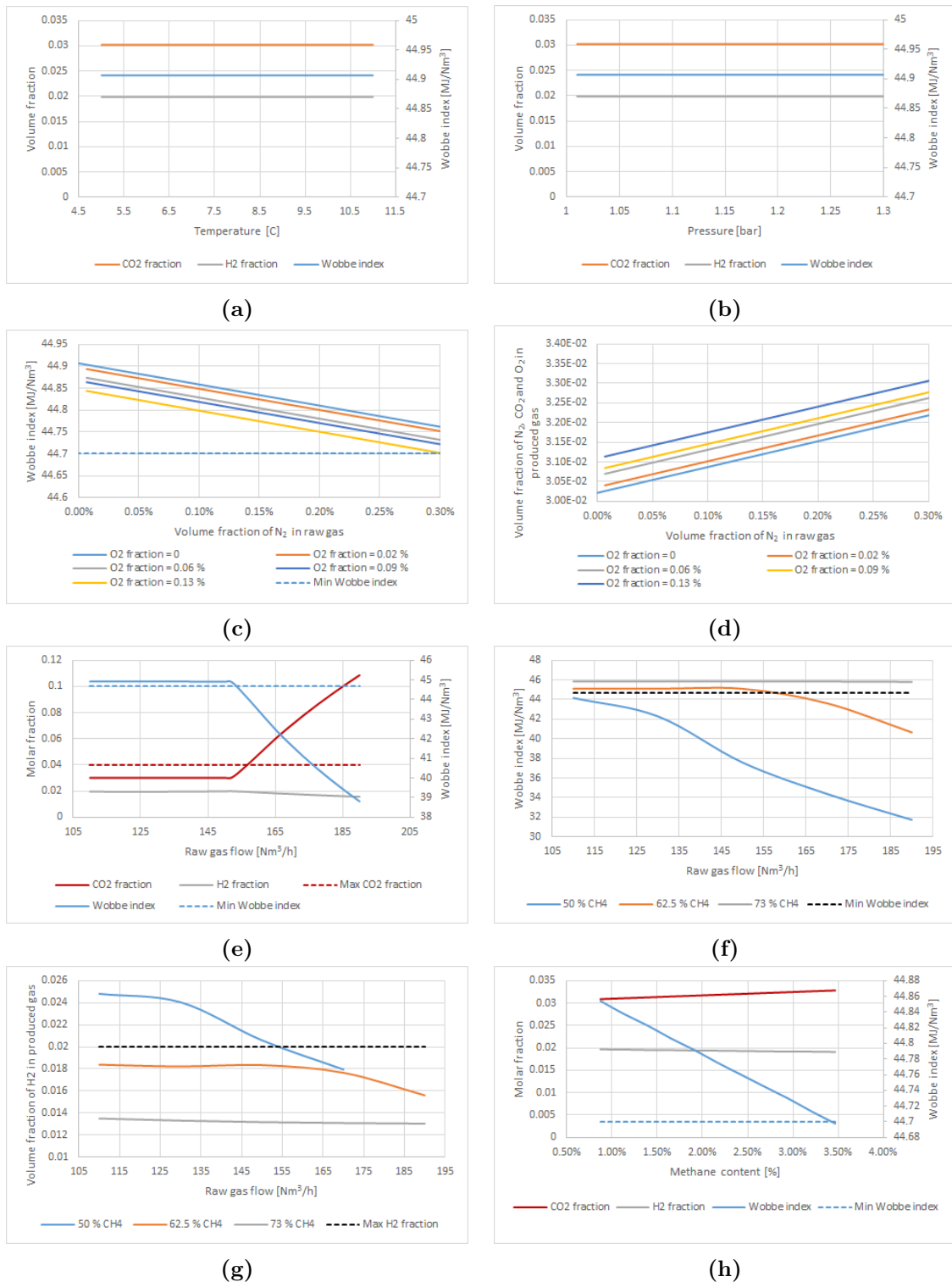


Figure 11: Investigating the effect of varying properties of the raw gas. The effect from temperature and pressure variations are illustrated in a) and b) respectively, the effect from O₂ and N₂ variations are illustrated in c) and d), the effect from varying raw gas flow and CH₄ fraction is illustrated in e), f) and g). The effect of a varying methane slip from the stripper is illustrated in h).

The analysis of the effect of methane fraction in the feed gas to the Sabatier reactor is presented in Figure 11h. There it can be seen that the fractions of CO₂ and H₂ are sufficient for the investigated range, but the Wobbe index would be below the limit for a higher slip, making it important to measure the slip. The reason behind the lower Wobbe index for a higher methane slip is that the Sabatier reaction operates at chemical equilibrium and it is shifted towards the reverse reaction to CO₂ when methane is present in the feedstock according to Le Chatelier’s principle. This effect can also be noted for the CO₂ fraction, which increases slightly.

4.3.4 Heat recovery simulation results

The comparison between the two heat recovery methods (recirculating the heat to the reactor feed gas or selling it to the district heating network) was performed for the process including both separation of CO₂ and methanation. The results of the three cases are displayed in Table 17. The profit for the heat recirculation is the lowest, meaning that using the heat for partly heating up the reactor feed would be more expensive than only using a fired heater to heat the feed. This is because the cost for the heat exchanger becomes higher compared to the gain from producing steam from the purged gas instead of burning it. The profit for the case where the heat is sold to the district heating network gives the highest total profit out of the three compared cases and it is henceforth referred to as the base case. Complete tables of the set variables, resulting properties and installed costs for the base case is presented in Table E.1, E.2, E.3 and E.5 in Appendix E.

Table 17: The costs for the process without any heat recovery and the processes with two different ways of recovering heat. The profit is highest for the case with district heating and lowest for the case with heat recirculation, due to a high investment cost.

Costs	Without heat integration	With district heating	With heat recirculation
Installed cost [US\$]	4 360 000	4 320 000	4 650 000
Utility & raw material cost [US\$/year]	750 000	745 000	748 000
Production income [US\$/year]	625 000	639 000	625 000
Annualised profit [US\$/kg]	-3.110	-3.030	-3.282

4.3.5 Simulation results for raw gas methanation process

The simulation of the process with methanation of raw gas was performed with different parameter settings due to the difference in the reactor feed gas. The high methane content in the flow pushes the equilibrium reaction towards the reactant side and to get a sufficient biogas quality, some modifications had to be done. By increasing the pressure to 60 bar in the second compressor stage, the H_2/CO_2 ratio to 3.75 and the catalyst loading to 50 kg, the quality of the produced gas was according to the standard given in Table 2. A complete table of the set variables, resulting properties and installed costs for the raw gas methanation is presented in Table F.1, F.2, F.3 and F.4 in Appendix F. The results of the cost estimation are presented in Table 18. It is clear that the annualised profit is higher than for the base case, but still negative. However it must be noted that the operating cost consisting of utility and raw material cost is lower than the income from selling the gas, which makes the process profitable when the capital cost has been payed off after 5 years.

Table 18: The costs for the raw gas methanation process. The costs are lower compared to the process with separation of CO_2 .

Costs	Process without separation of CO_2
Installed cost [US\$]	2 800 000
Utility & raw material cost [US\$/year]	451 000
Production income [US\$/year]	668 000
Annualised profit [US\$/kg]	-1.112

4.4 Results from the economic assessment

4.4.1 Results from ENPAC

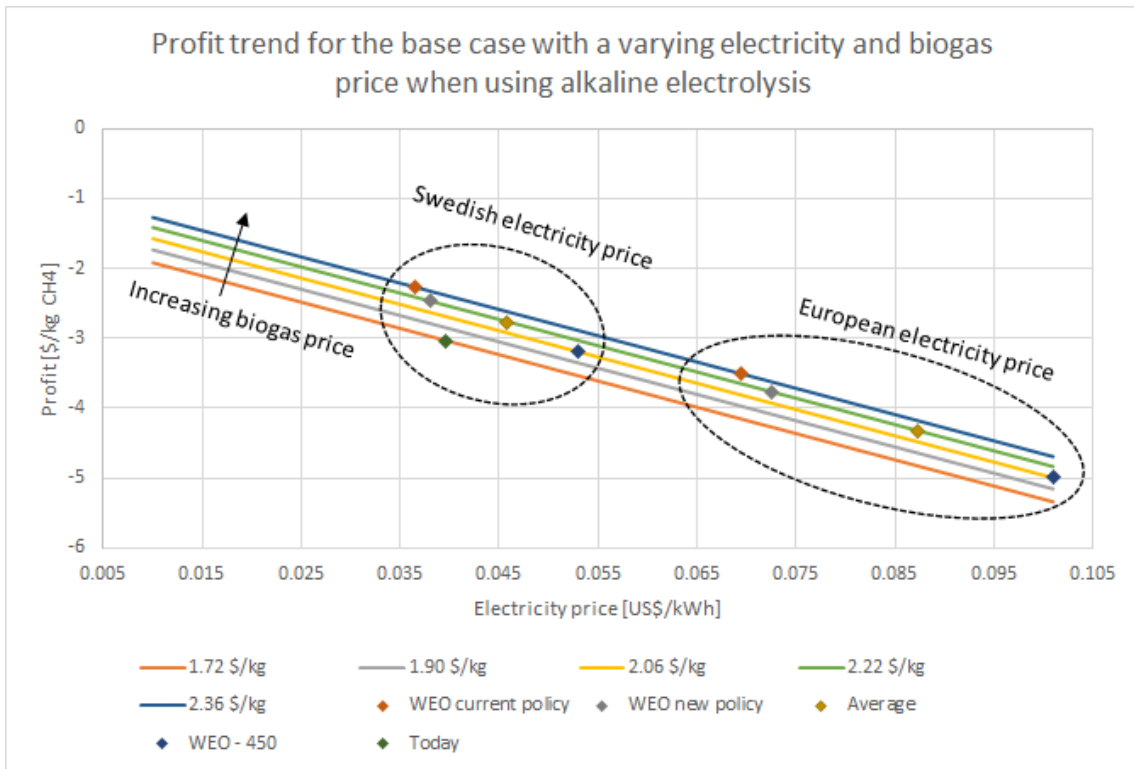
An economic assessment was made for two processes; the base case and the process with only methanation. The assessment covered a variation of electricity, biogas and hydrogen prices, where four future scenarios calculated by the ENPAC tool were studied specifically to evaluate the future economic feasibility of the Sabatier reactor implementation. The results from the ENPAC tool are given in Table 19, where the Swedish electricity price is calculated on the basis of the EU average price (see Chapter 3.3) and the biogas prices are recalculated on the basis of the diesel prices (see Chapter 3.3).

Table 19: The prices for electricity and diesel in 2030 for the different scenarios as calculated by the ENPAC tool. The Swedish electricity price and biogas price were calculated using the EU electricity price and diesel price respectively. The reference scenario shows the prices from 2012 upon which the scenarios are based.

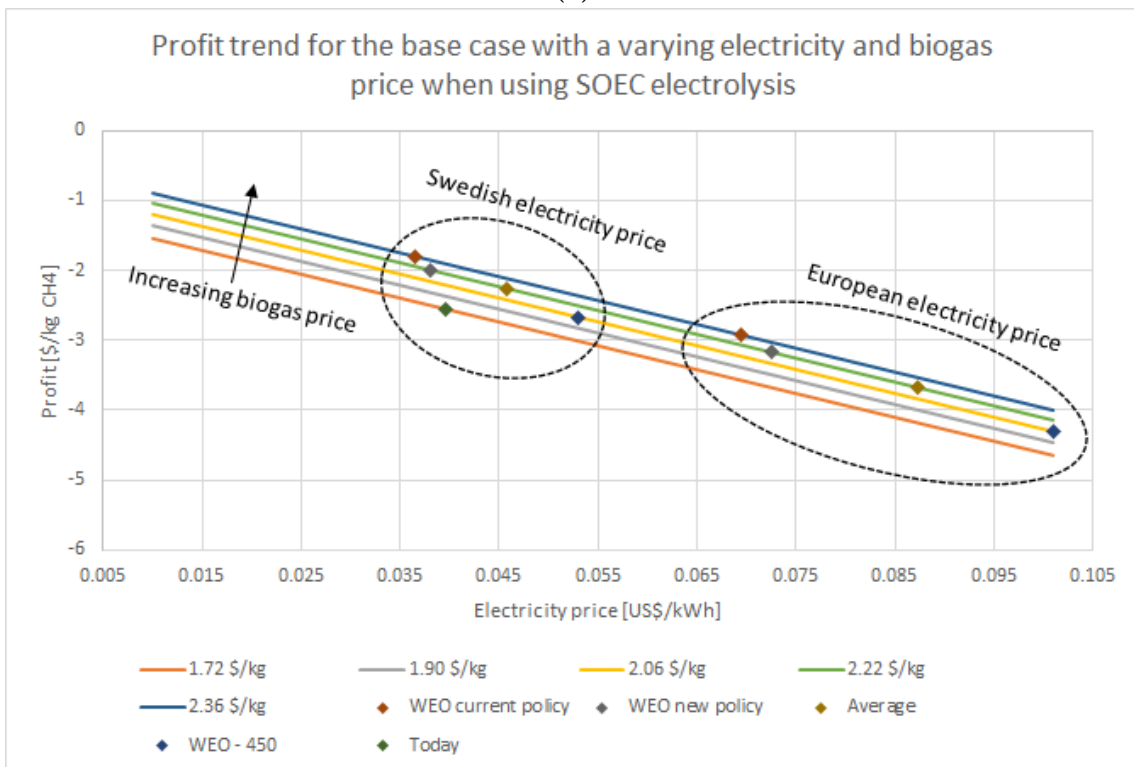
Scenario	Reference	Current policies	New policies	WEO-450	Average
Electricity price (EU) [US\$/kWh]	0.064	0.069	0.073	0.101	0.087
Electricity price (Sweden) [US\$/kWh]	0.034	0.036	0.038	0.053	0.046
Diesel consumer price (excl. energy tax and VAT) [US\$/MWh]	122	136	127	117	126
Biogas gate price [US\$/kg]	2.19	2.36	2.22	2.06	2.21

4.4.2 Dependence on electricity and biogas price

The resulting profit when varying the price of electricity and biogas is illustrated in Figure 12 - 13. The profit shows the same trend for all four process configurations, where the profit is decreasing with an increasing electricity price and decreasing biogas price. Figures 12a and 12b show the profit for the base case with today's alkaline electrolysis and a predicted future SOEC electrolysis respectively. The profit is negative at all electricity and biogas prices for both types of electrolysis, even though the future SOEC electrolysis has a higher efficiency and lower cost. This is however not the case for the raw gas methanation process, as can be seen in Figures 13a and 13b, where a low electricity price and a high biogas price gives a positive profit which makes the investment feasible at those conditions. The four scenarios showed the same trend for all cases, where the Current policies scenario gave the highest profit while the WEO-450 scenario gave the lowest, making Current policies the most preferable scenario from an investor's point of view. Out of the four scenarios, Current policies was the only scenario to show profitability, but only for raw gas methanation when the electrolysis method was SOEC.

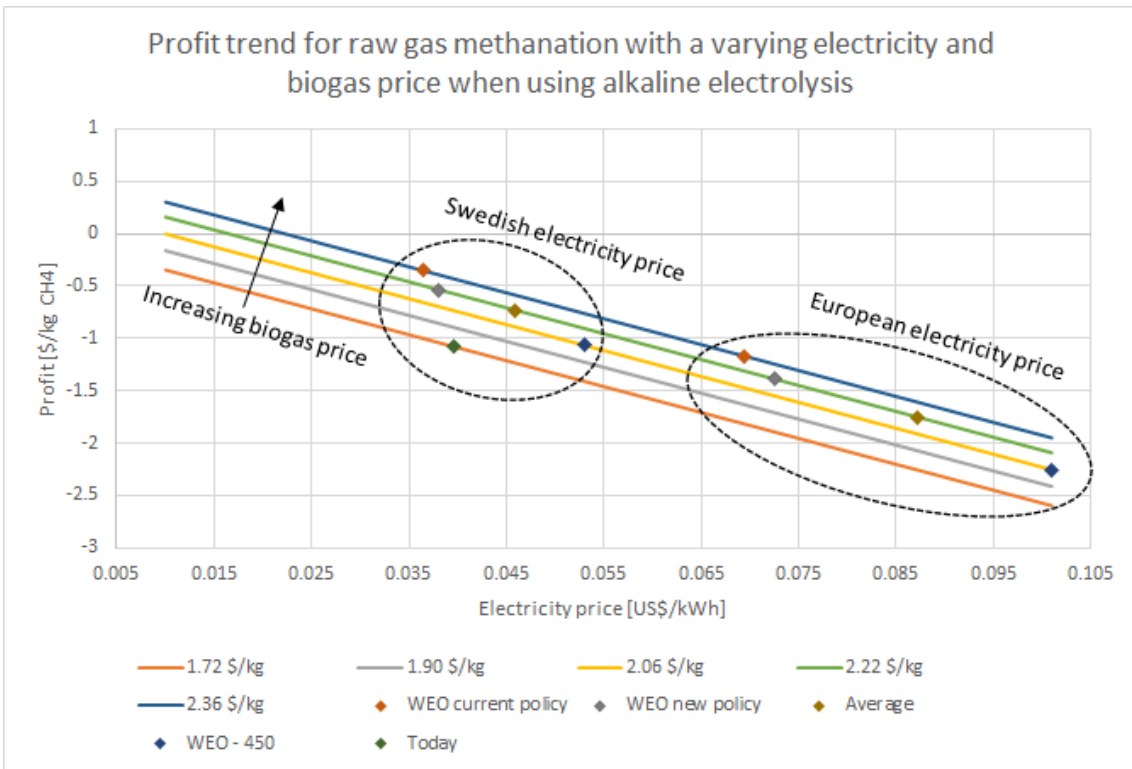


(a)

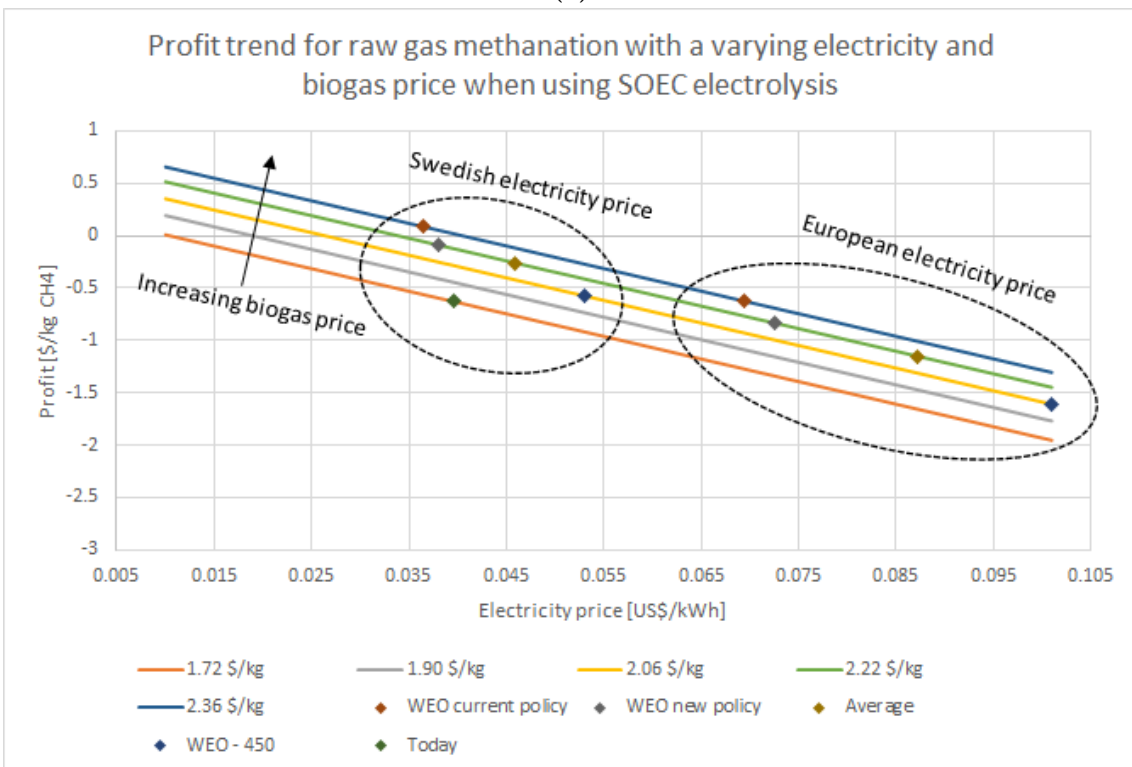


(b)

Figure 12: Impact of the prices of electricity and biogas price on the profit of the base case, considering either alkaline (a) or SOEC electrolysis (b). Each line indicates a different biogas price. Today's situation and four future scenarios for energy price development are also pointed out.



(a)



(b)

Figure 13: Impact of the prices of electricity and biogas price on the profit of the raw gas methanation, considering either alkaline (a) or SOEC electrolysis (b). Each line indicates a different biogas price. Today's situation and four future scenarios for energy price development are also pointed out.

4.4.3 Dependence on hydrogen price

The case of buying off-site produced hydrogen was studied for the four future scenarios and today's conditions. The hydrogen demand for the process was calculated to be 20 kg/h, while the production of hydrogen at Inovyn is 390 kg/h. It could therefore be assumed that all hydrogen could be supplied by Inovyn at a price in the range of 2.12-3.98 US\$/kg. The effect of the hydrogen price on the profitability is illustrated in Figures 14a and 14b for the base case and raw gas methanation respectively.

Similar to the results of varying the electricity and biogas price, the profit was negative at all hydrogen prices for the base case process. The raw gas methanation process however showed positive profits for three future scenarios at a low hydrogen price. "Current policies", "New policies" and "Average" would all be profitable at a lower hydrogen price.

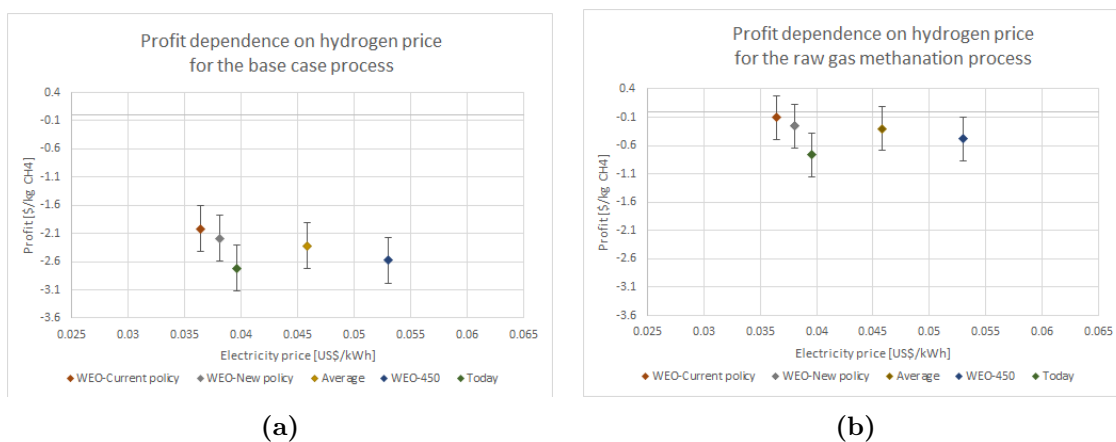


Figure 14: The profit for the base case (a) and raw gas methanation (b), and how it changes with the hydrogen price, is illustrated for the four future scenarios and today's conditions. The bars show the profit if the hydrogen price is either 2.12 US\$/kg (the top bar) or 3.98 US\$/kg (the low bar). For the base case, no scenarios would be profitable for any hydrogen price. For raw gas methanation, three scenarios would be profitable if the hydrogen price is low; "Current policies", "New policies" and "Average".

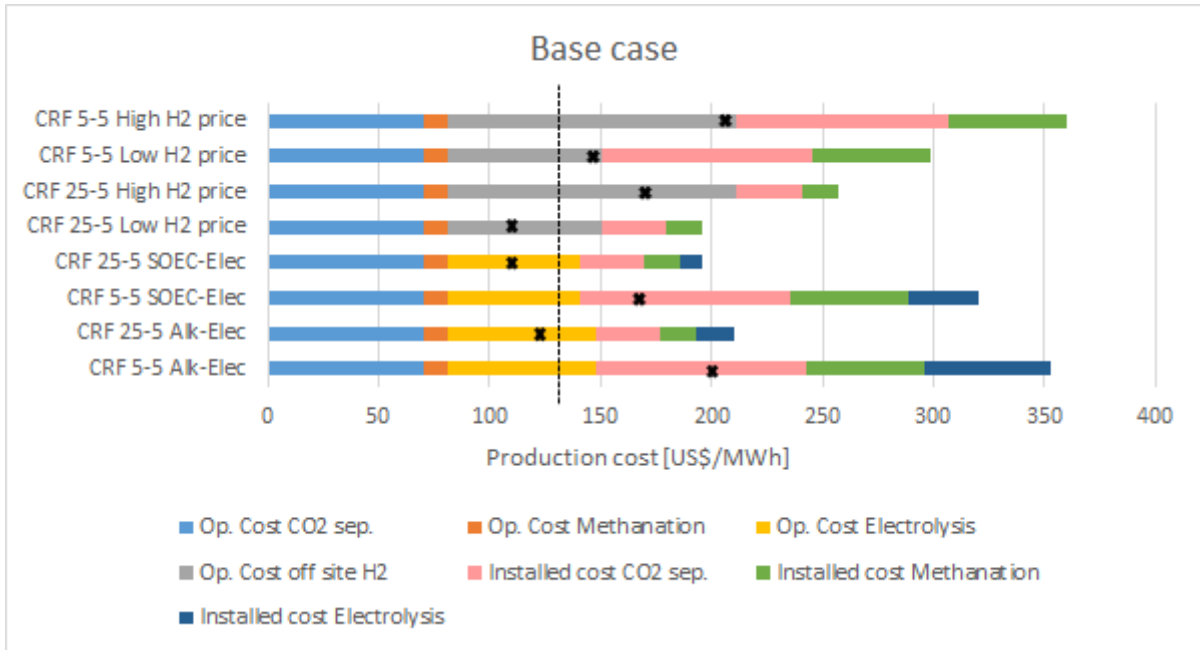
4.4.4 Cost analysis

A cost analysis was performed to see which parts of the process were contributing most to the total production cost. The results are presented in Figure 15 for both the base case (15a) and raw gas methanation (15b). There it can be seen that the raw gas methanation process has a significantly lower cost than the base case for any investment payback times between 5-25 years and for either of the hydrogen production methods (alkaline, SOEC or off-site). The large difference in total cost was mainly due to the cost for separation of CO₂.

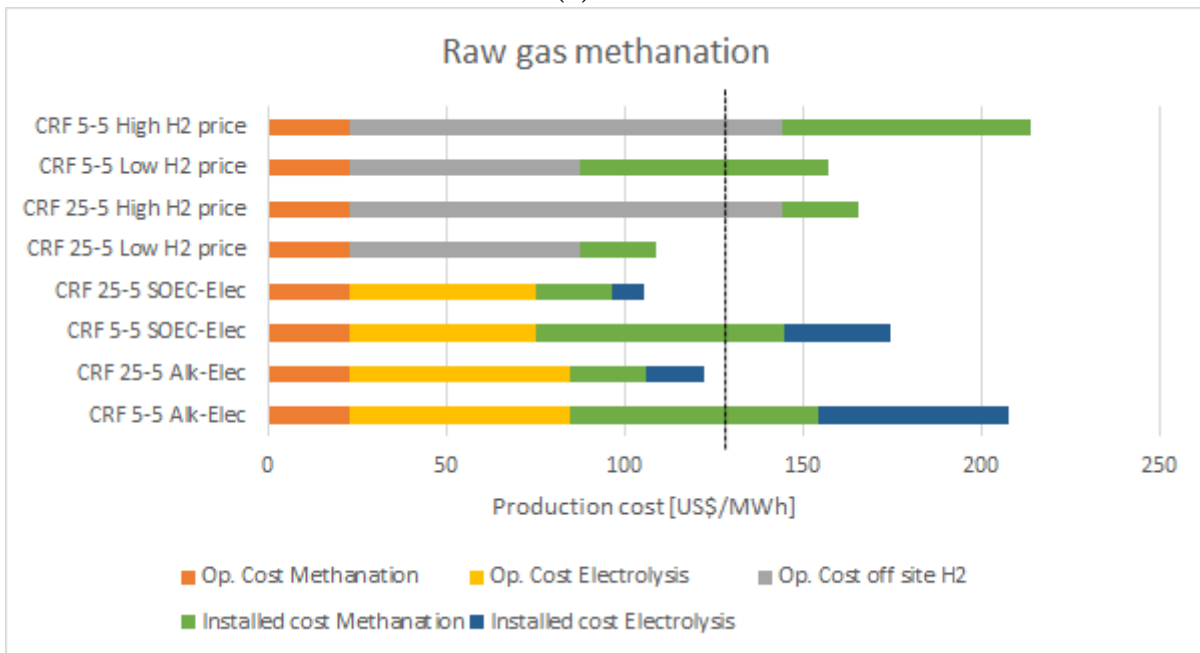
Focusing on the CRF 5-5 Alk-Elec case for the base case process, see Figure 15a, one can see that almost all the costs for the different parts of the process are similar. The operating cost for methanation is clearly the lowest cost, while the largest cost is marginally the installed cost for the separation of CO₂. Adding both operating and installed cost it results in methanation having the smallest share of the total cost, and the separation of CO₂ having the largest share. Although the cost decrease significantly for the cases where the investment pay back time is 25 years, it is still not enough to be a competitive cost. When SOEC is assumed to be the hydrogen production method, the cost decreases substantially when the investment pay back time is 5 years, however it only decreases marginally for longer pay back periods. The most profitable case, as seen in Figure 15a, would be the case where the investment pay back time was 25 years and either SOEC electrolysis or off-site produced hydrogen at low price was the method for supplying hydrogen. However, even the most profitable case would not be profitable for the base case process.

The raw gas methanation gave similar results as the base case concerning both electrolysis method and pay back time. For the CRF 5-5 Alk-Elec case, the methanation operational cost was still clearly the smallest cost, while the largest cost however was the installed cost for methanation. Compared to the base case, the total cost for methanation is higher due to the higher pressure and higher flow rates, but the difference is only 29 US\$/MWh and the decrease in cost due to no separation of CO₂ makes the total cost for the whole process lower. The cost is low enough for three cases to be profitable; CRF 25-5 Alk-Elec, CRF 25-5 SOEC-Elec and CRF 25-5 Low H₂ price.

The costs for methanation and electrolysis are in the same range as Brynolf et al. [2016] presents, which increases the credibility of the methodology used in this study. The cost for separation of CO₂ for the base case is much higher compared to the same study though. The cost was calculated to 618 US\$/ton captured CO₂, for an annualised installed cost using an investment payback time of 20 years. This is an order of magnitude higher value compared to the cost for a power plant to implement a chemical absorption method to capture the CO₂ from the exhaust gases, which is approximately 15-65 US\$/ton CO₂ [Brynolf et al., 2016; Rubin et al., 2015]. The black crosses in Figure 15a illustrate the total production cost if the separation of CO₂ instead was performed by implementing the chemical absorption method at a cost of 65 US\$/ton, which is hereon referred to as the amine process. It is clear that the total cost of building a new separation system, instead of retrofitting the upgrading system used today, would be lower, and for three cases the process would be profitable. The cost is even lower than the cost for raw gas methanation for some cases.



(a)



(b)

Figure 15: Decomposition of the total cost is divided into costs of different parts of the process, where the black dotted line marks the production income in US\$/MWh. The cost for the base case is illustrated in a), while the costs for raw gas methanation is illustrated in b). The black crosses in a) are marking the process cost if the separation of CO₂ instead would occur by chemical absorption, according to the price given by Rubin et al. (2015). The naming of the bars follows the pattern: CRF T-5, where T is the investment pay back time and i is the interest rate, and then the way of supplying hydrogen, where Alk-Elec is alkaline electrolysis, SOEC-Elec is SOEC electrolysis, High H2 price is off-site produced hydrogen at 3.98 US\$/kg and Low H2 price is off-site produced hydrogen at 2.12 US\$/kg.

5 Discussion

5.1 Interpretation of results

One of the main assumptions for the base case simulation is that there would be industrial excess heat available which can be utilised in the process. This was considered as a strong assumption due to the fact that a CHP plant is being built next to the biogas plant at Sobacken, which likely will have excess heat available for utilisation. The temperatures of industrial excess heat in Gävleborg county in Sweden is reported to be between 50-100 °C at different amounts, which makes a temperature at 80 °C a good assumption if it is further assumed that the temperature range is the same in the Västra Götaland region [Viklund and Johansson, 2014]. Another temperature of the excess heat could change the result though. A higher temperature would make it possible to have a higher pressure in the stripper which probably would decrease the costs (since the vacuum pump costs are lowered), while a lower temperature would mean the opposite. However, since the cost for separation of CO₂ is considerably higher than an amine based separation of CO₂, this would most likely not change the conclusion that separating CO₂ thermally in the present systems are clearly not profitable under any scenarios tested, despite the relatively low investment needed to modify the existing equipment.

The results from the ENPAC tool show how the electricity price and diesel price could be for different future scenarios. The electricity price would be more expensive compared to the reference for all scenarios; most expensive for the WEO-450 scenario and least expensive for the Current policies scenario. This is explained by the future cost for emitting CO₂, which would increase a lot for WEO-450 but not much for the Current policies scenario, making it expensive to produce electricity from fossil resources for WEO-450. The opposite trend for the diesel price, with WEO-450 as the least expensive and Current policies as the most expensive, can be explained by the concept of supply and demand. The demand on fossil fuels would decrease if the taxes on emissions become high (e.g., in WEO-450) and, assuming a rather inelastic change in supply, the prices would also drop. Since diesel is an oil based fuel, the price for it would follow the oil price and decrease. This however contradicts the purpose of the 450 case, because for the customer to stop using fossil fuels, it must become more expensive to buy it. Due to this contradiction, it should be further studied how the diesel price could change for the different scenarios.

The prices calculated by the ENPAC tool were used to calculate the Swedish electricity price and methane price. Adjusting the electricity price to the Swedish electricity market by only using a factor based on a constant ratio between the electricity prices can be justified for the reference case, since the calculated electricity price for Sweden was similar to the real price. It is however uncertain how the ratio between the electricity prices will be in 2030. For the methane price calculated from the diesel price given by ENPAC, one can see that for the reference year it was overestimated compared to the gate price for Borås Energi & Miljö today (1.716 US\$/kg). This could mean that the calculated prices for the four scenarios are overestimated as

well. The results concerning the future scenarios in Figure 12a - 14b should be considered as preliminary predictions.

The hydrogen produced off-site is assumed to be fed to the process at the same temperature and pressure as hydrogen produced by electrolysis. This might not be the case but it is unlikely to have a large impact on the process, similar to the impact on temperature and pressure variations for the feed of raw gas. The impurities reported by Inovyn are also not considered in this study. The impurities of importance is the sulfur and chloride which both deactivate the catalyst. Neither the cost for removal of the impurities nor an increased catalyst cost due to deactivation has been included in the cost estimation, thus making it an underestimation. It is however not sure that this makes the off-site produced hydrogen less competitive compared to the hydrogen produced by electrolysis since the stack exchange has been excluded from the installed cost of the electrolysis in this study, which made the electrolysis cost an underestimation as well.

By comparing the cost for the processes using either electrolysis or off-site produced H_2 , it was possible to see when each case was the most profitable. For both the base case and raw gas methanation, the cost for alkaline and SOEC electrolysis was in between the cost range for the off-site H_2 . If the price on hydrogen from off-site production would be low, using it would be the cheapest alternative out of all the hydrogen production techniques investigated. A low hydrogen price assuming distribution via pipeline is rather unlikely though, since the mapped possible source is located in Stenungsund from where distribution via pipeline is not plausible for such a small quantity of hydrogen. This means that if SOEC would be available with the efficiency assumed in this study, it would probably be the cheapest alternative. For alkaline electrolysis to be cheaper than off-site produced hydrogen, the hydrogen price from off-site production must be almost 4 US\$/kg.

The results from the cost estimation point out that the base case would not be profitable for any case, and thus not a feasible investment for Borås Energi & Miljö to retrofit the existing water scrubber gas upgrading unit to produce more biogas from a Sabatier reactor. The raw gas methanation did show profitability for some cases when the investment pay back time was 25 years or if the electricity prices would be low and biogas prices high at the same time. This was however not the case for any of the future scenarios of ENPAC. If hydrogen was available from either SOEC or at low price from another industry, it would also be profitable to implement raw gas methanation for some cases. The likelihood of the different cases is difficult to predict though. A low electricity price is plausible if more intermittent electricity production were implemented, such as solar or wind power plants, which then might increase the amount of excess electricity and thus lowering the price. The effect on profitability from varying the investment pay back time is large since the installed cost is more than half of the cost, but for Borås Energi & Miljö the pay back time of interest is 5 years, which is also a reasonable time for today's process industries considering the volatile market conditions. The uncertainties about the future prices and the fact that upgrading raw gas to biogas by a Sabatier reactor is not yet a mature technology, makes it a rather doubtful investment.

The total cost for the amine process is in the same range as the raw gas methanation process cost, but the cost estimation was performed assuming the cost for separating and capturing CO₂ from raw gas is the same as from flue gas from a power plant. Since the flue gas has a lower amount of CO₂ (about 30 vol-%), different gas composition in general (contains mainly N₂ and O₂) and the amount of flue gas processed is much larger, the cost for upgrading raw gas is likely to be different. This makes the cost estimation somewhat uncertain. It is however unlikely that the cost would be more than doubled since it is still a similar process, which means that the amine process still would be the cheaper alternative compared to the base case. This means that for a new biogas plant, installing an amine-based raw gas upgrading system would be a viable option which simultaneously increase the flexibility with respect to a future implementation of electrofuel production. This is because the only extra equipment needed, except for the methanation process equipment, would be a condenser to remove a small amount of water from the effluent CO₂ rich stream.

5.2 Sources of error

The installed equipment costs calculated by APEA was used for the cost estimations for the majority of the equipment. However, based on a comparison between the installed cost of the raw gas compressor given by APEA and the installed cost given by Borås, a big discrepancy has been observed (470 000 compared to 40 000 US\$). The costs for any other pieces of equipment were not available from Borås Energi & Miljö and could therefore not be compared to the costs given by APEA, but since the compressors were such a large part of the total installed cost (33 % of the installed cost for the base case, and 45 % for the raw gas methanation), it is probable that the total installed cost was overestimated. This error is especially important since the installed cost is a significant part of the total cost. For further work, a more comprehensive analysis on the methods to calculate the installed cost should be performed.

The costs compared consisted of the installed cost, the utility cost and the raw material cost. This means that costs such as labor, maintenance, general & administration and plant overhead were disregarded for the total operating cost. For the total capital cost, subcontracts, contract fees, civil, steel and general & administrative costs were disregarded. The cost for storing hydrogen on the site has also been disregarded in this study. Neglecting all these costs may affect the potential profitability of the processes, but not so much the relative comparison between the different process options.

5.3 Suggestions for future work

The upgrading system at Sobacken is functioning as a continuous process when the raw gas is being supplied, but due to the digestion process being a batch process it is only supplied to the upgrading system about 8 hours/day. This implies that the system must cope with many start ups and shut downs. The effect it has on the produced gas quality has not been investigated in this study and therefore it should be looked further into. The previous studies performed on a Sabatier reactor also suggests that the cooling is difficult to operate in a good way, making it important to study that more as well.

The results from the sensitivity analysis also suggests that the process design should be further investigated to operate well at higher flows and lower CH₄ fractions. This investigation should also consider the potential for having a raw gas storage unit at Sobacken to be able to control the flow and composition better, and thereby make it simpler to operate the process in the stable range. A study should also be made on how the Sabatier process could be integrated with the power plant that is to be built at Sobacken. For example it could be possible to design the power plant in a flexible way in respect to making the integration of a future implementation easier.

By investigating heat recovery possibilities even further, the costs could probably be reduced. It would for example be possible to use the heat transferred from the exothermic Sabatier reaction to the reactor cooling medium. There are 123.5 kW of heat available from the base case reactor (producing 106 kg biogas/h) and 138.2 kW available from the raw gas methanation reactor (producing 113 kg biogas/h) which definitely could be re-utilised. The heat from the base case could for example be used to heat the stripper, be sold to the district heating network or used to produce steam. In addition to burning the purged gas to produce either steam or electricity, there is also the possibility to sell the gas to be mixed with natural gas and then used as fuel gas. This is however not within the scope of this project because it promotes the usage of fossil fuels. For the raw gas methanation, no heat recovery scenario was investigated. There is definitely potential for heat recovery though, both from the biogas out of the reactor and the reactor cooling medium as for the base case.

The cost analysis for the amine-based upgrade of the CO₂ stream should be further investigated. This can be done by either developing a model for the actual raw gas composition and flow, or by a thorough screening of literature for similar upgrading systems. As mentioned above, the cost is likely to end up in the same range as for the power plant, since the lower flow of raw gas should make the cost higher while the higher CO₂ concentration in the raw gas should make the separation easier and lower the cost.

6 Conclusion

This study shows how adding a reboiler to the stripper column of a water scrubber gas upgrading system is not an economically viable method to get a pure stream of CO₂, where the CO₂ was supposed to be used for an implementation of a Sabatier reactor. The best way to implement a Sabatier reactor at a biogas plant would more likely be to either invest in a chemical absorption method to get clean CO₂ and then perform the methanation, or perform the methanation directly on the raw gas. The implementation is most promising for the Current policies scenario as indicated by ENPAC.

The hydrogen could be provided by either electrolysis or maybe be bought from a promising source in Stenungsund, although transportation and logistic issues are still to be resolved. The best alternative is difficult to pinpoint, and it depends on the technology available for electrolysis and the price of the hydrogen from the off-site production. To implement a Sabatier reactor further investigation is required. This is because the operation of the reactor has not been studied enough yet and experimental validation of the reactor performance for raw gas methanation is needed.

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Appendix A

Schlereth [2015] presented a rate equation for the Sabatier reaction which was based on experimental results from using a co-precipitated Ni-alumina (Al_2O_3) catalyst in a fixed bed reactor. The rate equation was developed by following the Langmuir-Hinshelwood approach. The rate equation was modeled by assuming the formation of the functional group formyl (HCO-X) being the rate limiting step, resulting in an expression for the reaction rate for the Sabatier reaction, r_{sab} , according to Equation 15. k_{sab} is the kinetic factor for the Sabatier reaction; P_i is the partial pressure for the reactant/product; K_{OH} , K_{H_2} and K_{mix} are the adsorption constants for OH, H_2 and a mix of them respectively and K_{eq} is the equilibrium constant for the Sabatier reaction. Schlereth (2015) confirmed the accuracy of the rate by comparing with more experimental results for temperature ranges between 190 - 450 °C. The constants in the rate expression are presented in Table A.1 (a) and (b) [Schlereth, 2015].

$$r_{\text{sab}} = k_{\text{sab}} \cdot \frac{P_{\text{CO}_2}^{0.5} P_{\text{H}_2}^{0.5} \cdot \left(1 - \frac{P_{\text{CH}_4} P_{\text{H}_2\text{O}}^2}{P_{\text{CO}_2} P_{\text{H}_2}^4 K_{\text{eq}}} \right)}{\left(1 + K_{\text{OH}} \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}^{0.5}} + K_{\text{H}_2} P_{\text{H}_2}^{0.5} + K_{\text{mix}} P_{\text{CO}_2}^{0.5} \right)^2} \quad (15)$$

The temperature dependence of the reaction rate can be seen in Figure 5, where the conversion of CO_2 is plotted against temperature. The rapid increase in conversion between 230 - 330 °C is because the equilibrium constant for reaction 3 is high at temperatures below 330 °C (see Figure A.1), meaning that the reverse reaction is almost not occurring at all, and the carbon monoxide created from the rWGS reaction is almost immediately converted into methane by the methanation reaction. At higher temperatures however, the backwards reaction of the methanation starts to occur and therefore the slow decrease in CO_2 conversion can be seen. There is also a dependence on pressure, due to the reaction not being equimolar, where the forward reaction is favoured when the pressure increases according to le Chatelier's principle [Gao et al., 2012].

Table A.1: Adsorption and equilibrium constants given in Table (a) and kinetic factors given in Table (b) [Schlereth, 2015].

(a) Expressions for the equilibrium and adsorption constants K_i given as $\ln K_i = A + BT^{-1} + C \ln T$ with their respective units.

Constant	A	B	C	Unit
$\ln K_{OH}$	-1.595	-2694	-	Pa ^{-0.5}
$\ln K_{H_2}$	-7.921	746	-	Pa ^{-0.5}
$\ln K_{mix}$	-8.051	1203	-	Pa ^{-0.5}
$\ln K_{eq}$	-18.106	19087	-3.998	Pa ⁻²

(b) The kinetic factor k is expressed with a pre-exponential factor κ and an activation energy E , according to $k = \kappa \cdot \exp(\frac{-E}{RT})$.

κ	E
$68.0710 \cdot 10^{-3} \frac{kmol}{Pa \cdot kg_{cat} \cdot s}$	$77.5 \frac{kJ}{mol}$

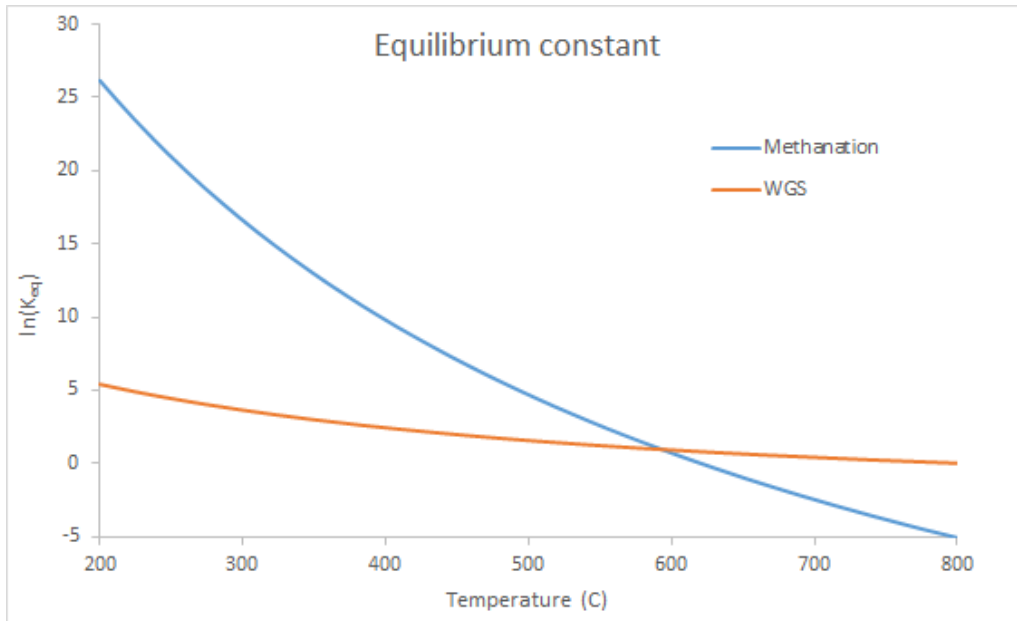


Figure A.1: The equilibrium constant for the methanation and WGS reaction for different temperatures.

Appendix B

Table B.1: The assumptions made for the process simulations.

<u>Variable</u>	<u>Assumption</u>
Property method	ELECNRTL for equipment with vapor/liquid equilibrium SRK for equipment with only vapor [Aspen technology, Inc., 2013b]
Column model	Equilibrium model
Packing material	Hackettes Tripacks [Billet, 1995]
Column pressure drop	0.1 psi/stage [William L. Luyben, 2006]
Compressor type	Isentropic, efficiency 72 %
Industrial excess heat	Available at temperatures 80 °C inlet & 75 °C outlet [Viklund and Johansson, 2014]
ΔT_{min}	10 °C
Steam for reboiler	Low pressure steam at 120 °C
Hydrogen properties from SOEC	Cooling before feeding to process assumed
Reactor model	Multitubular, fixed bed reactor using RPlug model [Jürgensen et al., 2015]
Catalyst	Ni catalyst with a particle density of 1700 kg/m ³ [Jürgensen et al., 2015]
Kinetic model	$r_{sab} = k_{sab} \cdot \frac{P_{CO_2}^{0.5} P_{H_2}^{0.5} \left(1 - \frac{P_{CH_4} P_{H_2O}^2}{P_{CO_2} P_{H_2}^4 K_{eq}}\right)}{\left(1 + K_{OH} \frac{P_{H_2O}}{P_{H_2}^{0.5}} + K_{H_2} P_{H_2}^{0.5} + K_{mix} P_{CO_2}^{0.5}\right)^2}$ [Schlereth, 2015]
Activation Energy	86.5 kJ/mol
Reactions with O ₂ and N ₂	Neglected due to low fraction
Global heat transfer coefficients	50 W/m ² K (gas/gas), 150 W/m ² K (condensing gas/gas), 200 W/m ² K (gas/liq), 600 W/m ² K (liq/liq) and 750 W/m ² K (condensing gas/liq) [Towler and Sinnott, 2012]
Reactor cooling medium properties when constant flow	102.5 °C, 1 atm
District heating water properties	1 bar, 70 °inlet temperature, 90 °outlet
Gas dryer model	Component separator, removing all water

Table B.2: The assumptions made for the cost estimations.

<u>Variable</u>	<u>Assumption</u>
Investment pay back time	5 years
Interest rate	5 %
Compressor model	Reciprocating compressors
Column model	Packed tower with Pall rings in stainless steel
Reactor, condenser, heat exchanger and water cooler model	TEMA (Tubular Exchanger Manufacturers Association) heat exchanger
Flash and gasdryer model	Vertical vessel
Heater model	Box furnace
Pump model	Centrifugal pumps
Biogas gate price	1.716 US\$/kg
Distribution cost biogas	0.104 US\$/kg [Consumers Energy, 2016]
LHV raw gas	20 MJ/kg
LHV purged gas	44 MJ/kg
LHV H ₂	120 MJ/kg
LHV wood pellets	17.5 MJ/kg [VIDA Energi AB, 2016]
LHV natural gas	48 MJ/kg [Persson, 2006]
Thermal efficiency gas boiler	83 % [Cleaver-Brooks Inc., 2010]
Thermal efficiency fired heater	70 % [CETAC-West, 2009]
Catalyst price	941.5 US\$/kg [Sigma-Aldrich, 2016]
Catalyst life time	5 years [Twigg, 1989]
Alkaline electrolysis efficiency	65 %
Alkaline electrolysis investment cost	1.07 M€/MW
Alkaline electrolysis operational cost	4 % of inv.cost/year
SOEC electrolysis efficiency	77 %
SOEC electrolysis investment cost	0.7 M€/MW
SOEC electrolysis operational cost	2.5 % of inv.cost/year
Electrolysis stack replacement cost	Disregarded in this study
Wood pellets price	0.17 US\$/kg [Energimyndigheten, 2016]
Natural gas price	0.62 US\$/kg [Statistics Sweden, 2016b]
Hydrogen distribution cost	0.96-2.42 US\$/kg H ₂ [NRC and NAE, 2004]
Hydrogen price	2.12-3.98 US\$/kg H ₂
Hydrogen storage cost	Disregarded in this study
CEPCI 1968	115

Continuation of Table B.2

<u>Variable</u>	<u>Assumption</u>
CEPCI 2014	576.1
VAT	20 %
Energy tax	14 €/MWh
Ratio between Swedish and European electricity price 2015	0.525 [Eurostat Statistics Explained, 2016]

Appendix C

The vacuum pump could not be modeled in Aspen, which is why the cost was calculated manually using the following correlations. The utility cost for the vacuum pump ($C_{uti,vac}$) was calculated using equation 16, where C_{el} is the electricity price and SF is called the size factor and is dependent on the evacuated systems pressure (P) and an air equivalent flow (m) according to $SF = \frac{m}{P}$ [Cheresources.com, 2016; Tuthill Vacuum & Blower System, 2016]. SF should lie in the range of 0.02 - 16 . For the process with 0.05 bar in the stripper the value of SF was 19.8 but the correlations were used anyway. The equipment cost ($C_{eqi,vac}$) was calculated using equation 17 assuming it is a reciprocating compressor, where S is the driving power in kW [Towler and Sinnott, 2012]. To calculate the installation cost, the equipment cost was then multiplied by an installation factor for compressors of 2.5 proposed by Hand in 1958 [Towler and Sinnott, 2012].

$$C_{uti,vac} = C_{el} \cdot 13.5 \cdot SF^{1.088} \quad [$/h] \quad (16)$$

$$C_{eqi,vac} = 260000 + 2700 \cdot S^{0.75} \quad [\$] \quad (17)$$

Appendix D

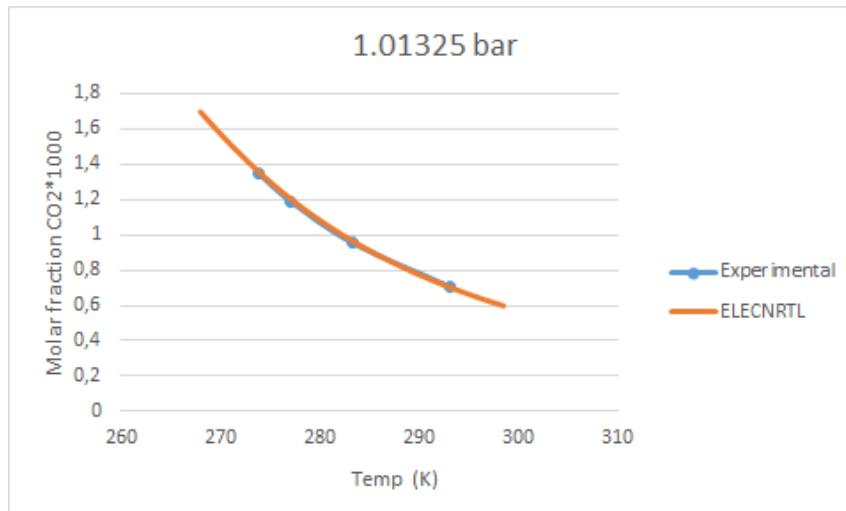


Figure D.1: Graph showing both experimental and simulated data of the solubility of CO₂ in water at 1.01325 bar for temperatures ranging from 270-300 K [Li and Tsui, 1971]. It can be seen that the simulated data using ELECNRTL is following the trend of the experimental data well.

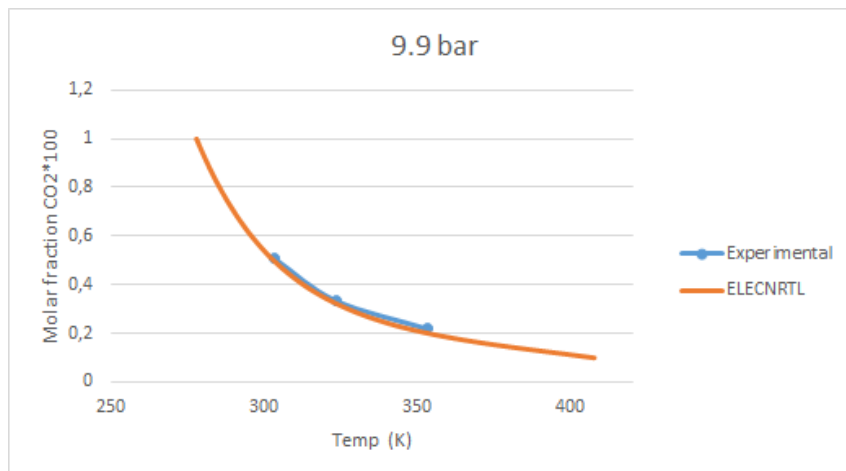


Figure D.2: Graph showing both experimental and simulated data of the solubility of CO₂ in water at 9.9 bar for temperatures ranging from 280-410 K [Matouš et al., 1969]. It can be seen that the simulated data using ELECNRTL is following the trend of the experimental data well.

Appendix E

Table E.1: The set variables in the process simulation of the base case. The names of the equipment are referring to the naming in the flowsheet in Figure E.1.

Set variable upgrading system	Value	Set variable methanation	Value
GASFEED flow [Nm ³ /h]	150	COMPR2 outlet pressure [bar]	10
GASFEED CH ₄ content [mol %]	59.8	INTRCOOL outlet temperature [°C]	50
GASFEED CO ₂ content [mol %]	39.8	H2FEED flow [kg/h]	19.86
GASFEED O ₂ content [mol %]	0.1	H2FEED pressure [bar]	10
GASFEED N ₂ content [mol %]	0.3	H2FEED temperature [°C]	70
GASFEED pressure [bar]	1.1	COMPMULT outlet pressure [bar]	40
GASFEED temperature [°C]	10	HEATREAC outlet temperature [°C]	360
WATERIN flow [l/min]	4.7	ADVREAC length [m]	1
S4 temperature [°C]	7	ADVREAC tubediameter [cm]	3
Pressure in scrubber top stage [bar]	9	ADVREAC number of tubes	60
Pressure drop in scrubber [psi/stage]	0.1	ADVREAC catalyst loading [kg]	36
Number of stages in scrubber	10	HEX cold stream outlet temperature [°C]	90
Pressure in flash [bar]	2	DH-IN temperature [°C]	70
Flash duty [kW]	0	COND2 outlet temperature [°C]	20
Pressure in stripper top stage [bar]	0.2	PURGE split fraction	0.165
Pressure drop in stripper [psi/stage]	0.1		
Number of stages in stripper	5		
Boilup ratio stripper	0.09		
CO2COMPR outlet pressure [bar]	2		
COND temperature [°C]	20		
SPLITTER water purge fraction	0.011		
WATPUMP2 outlet pressure [bar]	1		
WATCOOL2 outlet temperature [°C]	25		
WATCOOLR outlet temperature [°C]	7		

Table E.2: The resulting values for the process simulation of the base case. The names of the equipment are referring to the naming in the flowsheet in Figure E.1.

Resulting values upgrading system	Value	Resulting values methanation	Value
COMPRES1 net work [kW]	25.15	COMPR2 net work [kW]	4.88
WATPUMP1 net work [kW]	10.31	INTRCOOL duty [kW]	4.21
Scrubber diameter [m]	0.40	COMPMULT net work [kW]	22.94
Flash temperature [°C]	8.71	HEATREAC heat duty [kW]	10.72
Stripper diameter [m]	0.95	ADVREAC heat duty [kW]	123.45
Reboil temperature [°C]	62.84	HEX heat duty [kW]	80.81
Reboil duty [kW]	1621.45	COND2 heat duty [kW]	5.52
CO2COMPR net work [kW]	7.68		
COND heat duty [kW]	8.92		
WATRECYC flow [m ³ /h]	25.25		
WATPUMP2 net work [kW]	1.00		
WATCOOL2 heat duty [kW]	1109.62		
WATCOOLR heat duty [kW]	528.33		

Table E.3: The installation costs of each equipment for the base case. The installation costs for all equipment except the vacuum pump and electrolyser were calculated by APEA. The names of the equipment are referring to the naming in the flowsheet in Figure E.1.

<u>CO2 sep. Equipment</u>	<u>Installed Cost [US\$]</u>	<u>Methanation Equipment</u>	<u>Installed Cost [US\$]</u>
CO2COMPR	583400	ADVREAC	73700
COMPRES1	472300	COMPMULT	444600
COND	48400	COMPR2	344400
FLASH	120200	COND2	55100
SCRUBBER	136700	GASDRYER	99200
STRIPPER	316700	HEATREAC	106200
Vacuum pump	1106114	HEX	107300
WATCOOL2	86600	INTRCOOL	99900
WATCOOLR	91000	<u>Electrolysis Equipment</u>	<u>Installed Cost [US\$]</u>
WATPUMP1	38400	Electrolyser	1198492
WATPUMP2	39100		

Table E.4: The descriptions of the acronyms used for equipment and streams in the flowsheet for all processes

Equipment acronym	Description	Stream acronym	Description
ADVREAC	Sabatier reactor	GASFEED	Raw gas feed
COMPMULT	Compressor	METHRECY	Recycling stream of methane
COMPR2	Compressor	SCR-WAT	Water stream to scrubber
COND2	Condenser	WATERIN	Make-up process water
GASDRYER	Gas dryer	WATRECYC	Recycling stream of process water
HEATREAC	Heater	SCR-GAS	Gas stream to scrubber
HEX	Heat exchanger	WAT+CO2	Water stream with CO ₂ dissolved
INTRCOOL	Intercooler	FLASHWAT	Water stream out of flash with CO ₂ dissolved
CO2COMPR	Compressor	STRIPWAT	Water stream out of stripper
COMPRES1	Compressor	STRIPCO2	Gas stream out of stripper
COND	Condenser	WATEROUT	Purged water
FLASH	Flash vessel	CONDENS	Condensed steam recycled to process
SCRUBBER	Scrubber column	BIOGAS1	Produced biogas from upgrading system
STRIPPER	Stripper column	CO2TOREA	Pure CO ₂ stream from upgrading system
WATCOOL2	Cooler	H2FEED	Feed of hydrogen
WATCOOLR	Cooler	RIN	Reactor inlet stream
WATPUMP1	Pump	ROUT	Reactor outlet stream
WATPUMP2	Pump	DH-IN	District heating inlet water
		DH-OUT	District heating outlet water
		CONDWAT	Condensed steam
		GASOUT	The biogas produced from the Sabatier reactor
		DRYWAT	Water removed in dryer
		FUELGAS	The biogas produced from both upgrading and methanation system

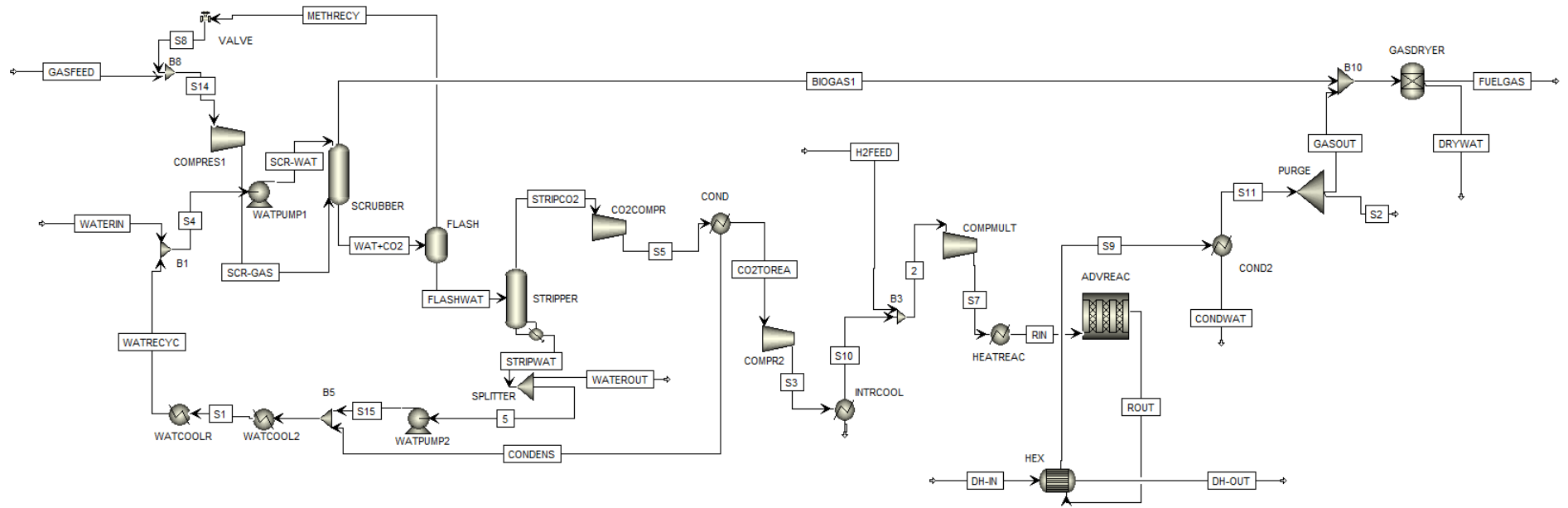


Figure E.1: Flowsheet for the base case process.

Appendix F

Table F.1: The set variables in the process simulation of the raw gas methanation. The names of the equipment are referring to the naming in the flowsheet in Figure F.1.

Set variable methanation	Value
GASFEED flow [Nm ³ /h]	150
GASFEED CH ₄ content [mol %]	59.8
GASFEED CO ₂ content [mol %]	39.8
GASFEED O ₂ content [mol %]	0.1
GASFEED N ₂ content [mol %]	0.3
GASFEED pressure [bar]	1.1
GASFEED temperature [°C]	10
COMPMULT outlet pressure [bar]	20
INTRCOOL outlet temperature [°C]	50
H2FEED flow [kg/h]	20.14
H2FEED pressure [bar]	20
H2FEED temperature [°C]	70
COMPR2 outlet pressure [bar]	60
HEATREAC outlet temperature [°C]	360
ADVREAC length [m]	1
ADVREAC tubediameter [cm]	3
ADVREAC number of tubes	60
ADVREAC catalyst loading [kg]	50
COND2 outlet temperature [°C]	20
GASDRYER pressure [bar]	8

Table F.2: The resulting values for the process simulation of the raw gas methanation. The names of the equipment are referring to the naming in the flowsheet in Figure F.1.

Resulting values methanation	Value
COMPMULT net work [kW]	24.37
INTRCOOL duty [kW]	22.42
COMPR2 net work [kW]	22.64
HEATREAC heat duty [kW]	27.56
ADVREAC heat duty [kW]	138.16
COND2 heat duty [kW]	92.44

Table F.3: The installation costs of each equipment for the raw gas methanation. The installation costs for all equipment except the electrolyser were calculated by APEA. The names of the equipment are referring to the naming in the flowsheet in Figure F.1.

Methanation Equipment	Installed Cost [US\$]
ADVREAC	74500
COMPMULT	609700
COMPR2	712400
COND2	49100
GASDRYER	104900
HEATREAC	123600
INTRCOOL	68800
Electrolysis Equipment	Installed Cost [US\$]
Electrolyser	1214897

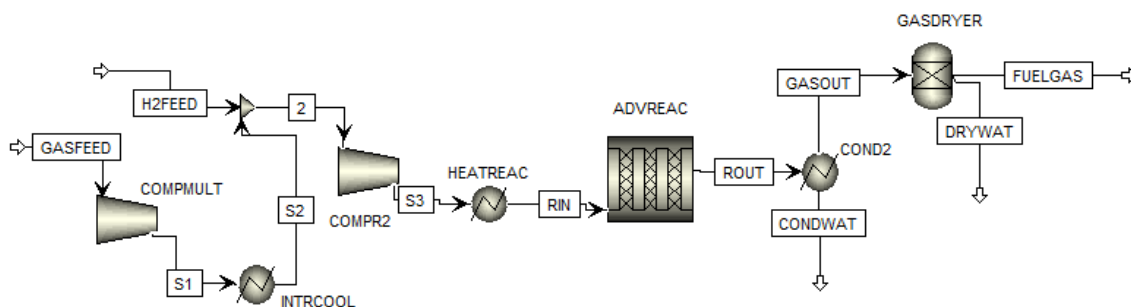


Figure F.1: Flowsheet for the raw gas methanation.

Appendix G

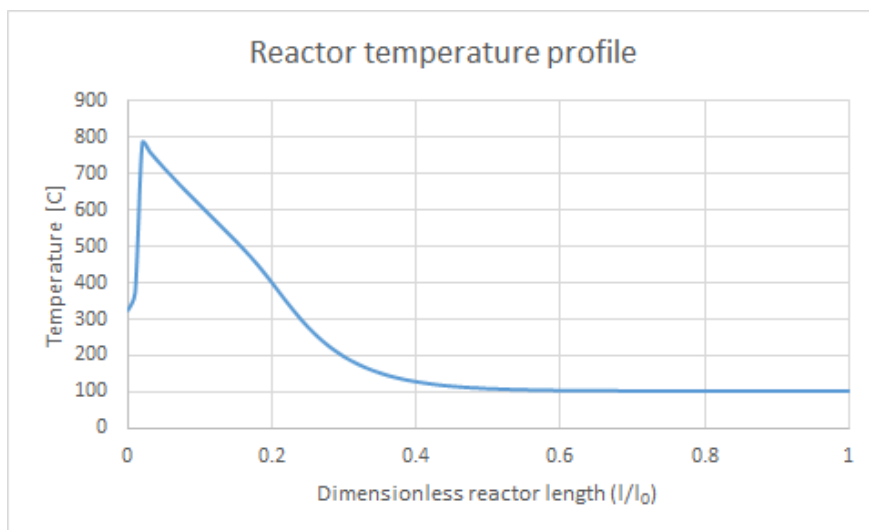


Figure G.1: The temperature profile of the reactor with a constant flow of the cooling medium. l is the distance in the reactor, while l_0 is the total length of the reactor.

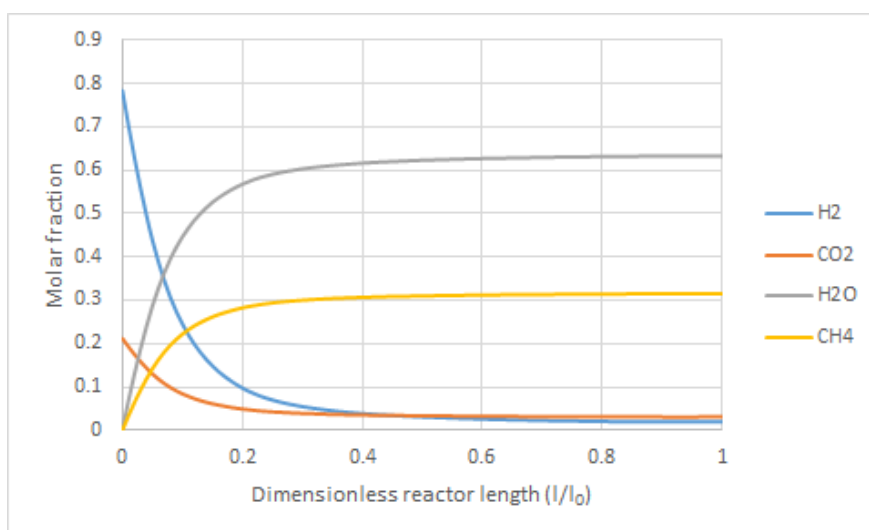


Figure G.2: The molar fraction profile of the reactor. The reaction reaches equilibrium as the fractions level out. l is the distance in the reactor, while l_0 is the total length of the reactor.

Appendix H

Table H.1: The results of the simulation of the existing plant compared to the values from the site.

Variable	Simulation results	Real value
Raw gas feed	150 Nm ³ /h	150 Nm ³ /h
Methane recycling flow rate	96.0 Nm ³ /h	17.6 Nm ³ /h
Scrubber liquid flow rate	393.3 l/min	423.1 l/min
Biogas flow rate	95.2 Nm ³ /h	98.6 Nm ³ /h
Flash liquid flow rate	389.6 l/min	422.4 l/min
Flash pressure	2 bar	1 bar
Air inlet flow rate	130 Nm ³ /h	132 Nm ³ /h
Stripper gas outlet flow rate	187.0 Nm ³ /h	187.4 Nm ³ /h
Scrubber diameter	0.4 m	0.6 m
Stripper diameter	0.3 m	0.6 m