

# **Power-to-Gas – A technical review**

## (El-till-Gas – System, ekonomi och teknik)

Gunnar Benjaminsson, Johan Benjaminsson, Robert Boogh Rudberg

"Catalyzing energygas development for sustainable solutions"



Power to Gas – a Technical Review

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Malmö 2013

Martin Ragnar Verkställande direktör

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Martin Ragnar Chief Executive Officer

### Authors' Foreword

The project has been carried out by Gasefuels AB in collaboration with a reference group. Data were mainly collected through literature studies and field trips. The study has been going on from January to June 2013.

A reference group has been linked to the project consisting of the following persons;

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## Summary

This report investigates the possibilities of producing methane from hydrogen and carbon dioxide. The source of carbon dioxide can be an upgrading unit for biogas or the biogas itself. The hydrogen is produced by electrolysis of water, in which water is cleaved by electricity. Electricity of renewable origin therefore makes the methane produced renewable. The methanation can undergo two different paths: catalytic and biological methanation.

For production of hydrogen by electrolysis there are two commercial technologies, alkaline and PEM electrolysis, both with efficiencies of about 65 %. They differ primarily by the material used as electrolyte, that is, the medium which transfers charges between the electrodes. The production cost for hydrogen is 0.8-0.9 SEK/kWh.

The efficiency of both catalytic and biological methanation processes are limited by the Sabatier reaction to a maximum of 80 %. Each of the techniques can, besides pure carbon dioxide, also be fed with biogas and can then serve as an upgrading technique.

Catalytic methanation occurs in fixed bed reactors packed with catalysts that lower the energy of activation for the Sabatier reaction. A minimum of 20 % of the incoming energy is released as heat. Therefore, the reactor is in need of cooling to maintain the right temperature. The temperature of the refrigerant in the catalytic methanation depends on the reactor type but ranges from 350-700 °C.

Biological methanation takes place in reactors filled with archea-culture that extracts some of the energy released from the Sabatier reaction and use it for growth and reproduction. The rest of the energy is released as heat and the biological process may therefore be in need of cooling to maintain a temperature of 60 °C. The production rate for biological methanation is up to 140 m<sup>3</sup>/day per m<sup>3</sup> of reactor volume.

With an electrolysis efficiency of 65 % and a methanation efficiency of 80 % the overall system efficiency from electricity to methane is 52 %. Hence, a low price of electricity is of great importance to obtain low production costs.

Based on the electricity prices in 2012 the production costs for catalytic methanation is 1.4-1.7 SEK/kWh and for biological methanation 1.3 SEK/kWh. If the Power-to-Gas facility is credited for waste heat recovery and for the upgrading service, the production costs can be lowered to 1.1-1.3 SEK/kWh for catalytic methanation and 1.0 SEK/kWh for biological methanation. If the electricity grid cost can be avoided the production cost can be lowered with another 0.2 SEK/kWh.

The capital cost is, besides the cost for electricity, the most important cost bearing parameter. This study thus shows that Power-to-Gas primarily is a technique for the production of renewable methane for use in, for example, vehicles. To balance the electricity market, where the produced methane is subsequently used for production of electricity at high electricity prices, the technology does not appear to be competitive for Swedish conditions.

Keywords: biogas upgrading, methanation, Power-to-Gas

## Sammanfattning

I denna rapport studeras möjligheterna att producera metan av vätgas och koldioxid. Vätgasen produceras med elektrolys där vatten sönderdelas av elektricitet. Om elen har förnybart ursprung blir därför även metanen förnybar. Koldioxidflöden om 100 till 600 Nm<sup>3</sup>/h studeras i rapporten. För att metanisera ett sådant koldioxidflöde behövs ett vätgasflöde på motsvarande 400 till 2400 Nm<sup>3</sup>/h. Koldioxiden kan tas som ett rent koldioxidflöde från en uppgraderingsanläggning för biogas eller från ett biogasflöde som innehåller både koldioxid och metan.

Koldioxiden och vätgasen kan genom en katalytisk eller biologisk process omvandlas till metan. De översta formlerna nedan visar Sabatier-reaktionen där koldioxiden är i gasfas respektive löst i vatten. De nedre reaktionerna visar hur mikroorganismer bildar metan med ättiksyra som mellansteg. Det bildas lika stor mängd metan som processen tillförs koldioxid.

$4 H_2 + CO_2 \leftrightarrow CH_4 + 2 H_2O$	katalytisk metanisering, Sabatierreaktionen
$4 \operatorname{H}_2 + \operatorname{HCO}_3^- + \operatorname{H}^+ \to \operatorname{CH}_4 + 3 \operatorname{H}_2 \operatorname{O}$	biologisk metanisering i vatten
$4 \text{ H}_2 + 2 \text{ CO}_2 \rightarrow \text{CH}_3\text{COOH} + 2 \text{ H}_2\text{O}$	biologisk metanisering via ättiksyra
$CH_3COOH \rightarrow CH_4 + CO_2$	biologisk metanisering via ättiksyra

Temperaturen i en katalytisk process varierar mellan 300 och 700°C. Den lägsta temperaturen är den för vilken katalysatorerna aktiveras och den högsta temperaturen ges av den temperatur då reaktionen inte längre är termodynamiskt gynnsam. Nickelbaserade katalysatorer är den vanligaste typen av katalysator för metanisering. I den biologiska processen sker reaktionen vid mikrobernas tillväxtoptimum på ca 65°C.

För framställning av vätgas genom elektrolys finns två kommersiella tekniker. De skiljer sig främst åt genom vilket material som används som elektrolyt, det vill säga det medium som överför laddningen mellan elektroderna. Alkalisk elektrolys är vanligast där elektrolyten utgörs av kaliumhydroxid löst i vatten. Den andra tekniken för elektrolys är PEM (Proton Exchange Membrane) som använder sig av en fast elektrolyt bestående av ett polymermembran. Verkningsgraden från el till vätgas ligger i nuläget kring 65 % men genom förbättrad teknik kan verkningsgraden stiga. Med en verkningsgrad på 80 % från vätgas till metan i katalytiska och biologiska processer blir verkningsgraden från el till metan cirka 52 %.

En lovande teknik för elektrolys är SOEC (Solid Oxide Electrolysis Cell) som använder sig av en keramisk elektrolyt som tål höga temperaturer. Haldor Topsøe arbetar idag med att bygga en 40 kW SOEC integrerad med en katalytisk metanisering för demonstration av tekniken i Foulum. Höga temperaturer underlättar sönderdelning av vatten vilket kan ge verkningsgrader från el till vätgas på över 95 % under förutsättning att spillvärme från metaniseringsreaktorn används för att värma processen. Haldor Topsøe uppger att SOEC-teknik kan bli kommersiellt tillgänglig inom 4-5 år. Högre verkningsgrad på elektrolysen ger lägre kostnader för vätgasframställning vilket bidrar till minskade produktionskostnader för metan.

Leverantörer som idag kan leverera integrerade system för vätgasproduktion och katalytisk metanisering är ETOGAS och Sunfire. ETOGAS använder sig av en alkalisk elektrolys och en isoterm metaniseringsreaktor som ger spillvärme på 350 °C. Den isoterma fastbäddsreaktorn kyls effektivt vilket gör att endast en katalysreaktor behövs vilket ger lägre investeringskostnader än om två eller flera katalysreaktorer hade använts. ETOGAS har anläggningar i Bad Hersfeldt och Stuttgart. I Bad Hersfeldt drivs en pilotanläggning med rå biogas som koldioxidkälla och vätgas från en elektrolysanläggning om 25 kW<sub>el</sub> medan en större demonstrationsanläggning i Stuttgart på 250 kW<sub>el</sub> till elektrolysen metaniserar koldioxid från luften. Dessutom byggs under 2013 en anläggning på 6 MW<sub>el</sub> i Werlte för metanisering av koldioxid från en uppgraderingsanläggning. ETOGAS uppger att processen inte blir mindre effektiv om koldioxidflödet innehåller metan. Det gör att katalytisk metanisering kan användas som uppgraderingsteknik som ersättning för vattenskrubber, PSA eller kemisk absorption.

Företaget Sunfire tillverkar idag bränsleceller och förväntar sig kunna utnyttja den kunskapen för att producera en SOEC elektrolys. Idag erbjudet företaget dock en alkalisk elektrolys för vätgasproduktionen i processen. Sunfire har ingen anläggning i drift men har tagit fram ett koncept för en katalytisk metaniseringsprocess. Processen består av en adiabatisk katalysprocess följt av en isoterm reaktor. Fördelen med att först ha en adiabatisk reaktor är att temperaturen på spillvärmen kan bli upp till 700°C. Genom att utnyttja den höga temperaturen från den adiabatiska reaktorn hoppas man kunna integrera detta värmeflöde med en SOEC elektrolys. Den högvärdiga ångan kan även användas för elproduktion.

I den biologiska processen utnyttjar metanogena arkéer energin som frigörs då vätgas och koldioxid blir till metan och vatten. Då mikroorganismernas optimala tillväxttemperatur är betydligt lägre än för en katalytisk process blir temperaturen på kylvattnet cirka 60 °C. Värmeflödet kan exempelvis användas för att värma en biogasreaktor. Den biologiska metaniseringen begränsas av vätgasens löslighet i vatten. För att öka lösligheten för vätgas kan reaktorer för biologisk metanisering förses med omrörare eller hålfibermembran som ökar masstransporten från gas till vätska.

Leverantörer till biologiska metaniseringsprocesser som studerats i rapporten är MicrobEnergy, Krajete och Electrochaea. MicrobEnergy erbjuder två processtekniker för metanframställning. Företaget har dels en teknik för biologisk metanisering av koldioxid och vätgas i en separat extern reaktor och dels en teknik för vätgastillsats till en befintlig biogasanläggning som även matas med organiska material. Vid metanisering i en separat reaktor uppger företaget att metanproduktionen per m<sup>3</sup> reaktorvolym är cirka 6 Nm<sup>3</sup>/h, det vill säga 140 Nm<sup>3</sup> metan per m<sup>3</sup> reaktorvolym och dygn. MicrobEnergys använder sig av omrörare och testar parallellt även med ett hålfibermembran för att öka lösligheten av vätgas i reaktorn. På sin anläggning i Schwandorf har företaget en reaktor på en kubikmeter för biologisk metanisering av koldioxid och vätgas. För att underhålla processen behöver tanken tillföras ett tillväxtmedium som företaget själv producerar, preparatet innehåller både näring och mikroorganismer. Vätgasen kan även tillföras en befintlig biogasanläggning vilket medför att metanhalten i produktgasen ökar. I företagets egen pilotanläggning har metanhalten ökat från 50 till 75 % genom vätgastillsats men högre metanhalter har uppnåtts i laboratorium.

Krajete erbjuder en biologisk process för metanisering av koldioxid och vätgas. De har således inte en teknik för vätgastillsats till en befintlig biogasanläggning. Företaget har en testanläggning i Linz varifrån verksamheten sköts. Reaktorn som



Krajete har för den biologiska metaniseringen är försedd med en omrörare för att öka lösligheten. Även Electrochaea erbjuder en lösning för biologisk metanisering av koldioxid och vätgas. Företaget använder sig av en demonstrationsanläggning på 250 kW<sub>el</sub> i Foulum för tester av metanisering av koldioxid och vätgas.

I rapporten har möjligheterna att biologiskt omvandla syntesgas till metan undersökts. Syntesgas består utöver metan, koldioxid och vätgas även av kolmonoxid. Den biologiska omvandlingen av kolmonoxid har visat sig fungera i labb men ingen tillverkare av ett sådant system har identifierats.

Investeringskostnaden för ett vätgasflöde på 400 Nm<sup>3</sup>/h är mellan 11-26 miljoner kronor. Leverantörerna uppger att det inte finns skalfördelar för flöden mellan 400-2400Nm<sup>3</sup>/h. Produktionskostnaden för vätgas är ca 0,8-0,9 kr/kWh beräknat på genomsnittligt elpris för 2012. Den totala investeringskostnaden för integrerade system med både elektrolys och efterföljande biologiska eller katalytiska metanisering redovisas i tabellen nedan.

	MicrobEnergy	Krajete	Sunfire ETOGAS				
Nm³/h CH₄	100	300	300	600	125	250	625
Mkr	37	84	156	214	71	107	226

Produktionskostnaderna för biologisk metanisering utan kreditering för avsättning av värme eller biogasuppgradering blir ca 1,3 kr/kWh. Vid försäljning av både värme och uppgraderingstjänst blir produktionskostnaden cirka 1,0 kr/kWh för biologisk metanisering. Detta gäller för samtliga studerade koldioxidflöden om 100 till 600 Nm<sup>3</sup>/h.

Både Sunfire och ETOGAS har vissa men inte betydande skalfördelar. Produktionskostnaden varierar mellan 1,4 till 1,7 kr/kWh för en metanproduktion mellan 100 till 625 Nm<sup>3</sup>/h. Genom reducerade kostnader till följd av värmeavsättning och uppgraderingstjänst minskar produktionskostnaderna till mellan 1,1-1,3 kr/kWh. Utöver kapitalkostnaden utgör kostnaden för el den största utgiftsposten. Om nätavgiften kan undvikas minskar produktionskostnaden för metanen med ca 0,2 kr/kWh. Det gör metanisering särskilt intressant på de platser där el kan levereras direkt från exempelvis ett vindkraftverk eller kraftvärmeanläggning.

De nuvarande kapitalkostnaderna medför att produktionskostnaderna minskar upp till de 8600 billigaste elpristimmarna varefter de ökar. Anledningen till att anläggningen behöver många drifttimmar är främst på grund av att kapitalkostnaden stiger med minskat antal drifttimmar, samtidigt som den försålda mängden metan minskar. Det är inte sannolikt att framtidens perioder med lågt elpris skulle vara tillräckligt långa för att kompensera för den höga kapitalkostnad och låga produktionsvolym av metan som blir följd av en kortvarig drift vid låga elpriser. Utredningen har således visat att Power-to-Gas främst är en teknik för framställning av förnybar metan för användning till exempelvis fordonsbränsle. För balansering av elmarknaden där den producerade metanen senare används till produktion av el vid höga elpriser, ser inte tekniken ut att vara konkurrenskraftig.



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#### 1 Introduction

#### 1.1 Background

An increased demand for biogas has contributed to development focused on finding new substrates and technologies for biogas production. Today, biogas is mainly produced by sludge, food waste and slaughterhouse waste but preprocessing techniques for e.g. straw have also been developed. Gasification plants are also being built where wood is gasified into a synthesis gas which is then methanized in catalysis reactors to methane. New substrate sources could also be hydrogen and carbon dioxide. If hydrogen is produced from renewable electricity in an electrolysis process, the hydrogen will be renewable. By combining hydrogen with a flow of carbon dioxide, methane may be produced in biological or catalytic processes.

An increased expansion of renewable electricity from e.g. wind and solar power could generate large variations in electricity prices. Electricity is expensive to store and therefore the conversion of electricity into methane could be used as a mean for balancing the power market. This concept is called "Power to Gas" and is demonstrated at several sites in Germany. In Sweden biogas is mainly used as vehicle fuel and the concept thus offers a way to convert electricity into vehicle fuel.

Biogas contains up to 50% carbon dioxide and by transforming the carbon dioxide into methane in catalytic or biological processes, the production in existing plants can be doubled. This could be particularly important for installations where the biogas production today is too small to be upgraded.

#### 1.2 Purpose

This report aims to evaluate the technical, economic, environmental and commercial status of catalytic and biological methanation of hydrogen and carbon dioxide. An analysis of hydrogen and synthesis gas integration with existing biogas plants in order to achieve increased biogas production and reduced upgrading costs will be carried out.

#### 1.3 Methodology

The report was written by Gunnar Benjaminsson, Johan Benjaminsson and Robert Boogh Rudberg. The project has been guided by Tobias Persson (SGC), Niels Bjarne Rasmussen (DGC), Liisa Fransson (Lunds Energi), Fredrik Andrén Sandberg (Lunds Energi), Irene Bohn (NSR), Per Karlsson (Borås Energi och Miljö) and John Bøgild Hansen (Haldor Topsøe). Avfall Sverige has participated through partial funding of the investigation.

The study was conducted through literature studies and manufacturer contacts. Three visits were carried out at the following German plants:

- MicrobEnergy in Schwandorf, biological methanation
- Sunfire in Dresden, catalytic methanation
- ETOGAS in Bad Hersfeldt, catalytic methanation

The report begins with a theoretical and technical background for electrolysis as well as catalytic and biological methanation, see Chapter 2. To quickly get an overview of the technology the reader is referred to directly start reading Chapter 3 and Chapter 4 with information about manufacturers and case studies.

#### 2 Theoretical and Technical Background

This chapter provides a theoretical background for electrolysis as well as catalytic and biological methanation.

#### 2.1 Electrolysis

Lysis means decomposition in Greek and analogous electrolysis means decomposition using electricity. Electrolysis occurs when current and voltage are applied to a substance, dividing it into smaller components. Hydrogen and oxygen are formed when current and voltage are applied in water. The process is called electrolysis of water. Decomposition of water into hydrogen and oxygen using electrolysis is normally only called electrolysis.

The electricity used to produce hydrogen by electrolysis of water can have a fossil as well as a renewable origin. Renewable electricity provides renewable hydrogen. The production system Power-to-Gas uses hydrogen and carbon dioxide to produce methane in a catalytic or biological process. Production of methane from hydrogen and carbon dioxide is shown in Figure 1.



Figure 1. Hydrogen production to a methanation process.

A general view of an electrolytic cell is shown in Figure 2 with the components anode, cathode, electrolyte and the membrane. The anode and cathode are commonly called electrodes. There are three different techniques of electrolytic cells. The techniques have the same basic components such as electrodes, electrolyte, and a type of membrane. The simplest type of electrolysis is the alkaline electrolysis. The basic principles of the alkaline electrolysis have been further developed and have resulted in the development of PEM and SOEC electrolysis. All these electrolysis techniques will be illustrated in this chapter.

It is important to note that Figure 2 shows a liquid alkaline electrolyte. The electrolyte in PEM and SOEC electrolysis works as an ion-conducting electrolyte, as a membrane that provides mechanical stability and as a gas barrier between hydrogen and oxygen.



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Figure 2. Components of an electrolytic cell.

Electrons are led from a power source to the cathode in the electrolytic cell, where water molecules are adsorbed and decomposed to hydrogen and ions at the active sites on the cathode surface (Lyklema, 1991). The ions formed are then transferred through the electrolyte to the anode where oxygen is formed, and electrons are transferred to the anode, so that the electric circuit is closed. For a balanced reaction formula twice as much hydrogen as oxygen is produced according to the reaction Formula 1.

#### Formula 1 $2 H_2 O(l) \rightarrow O_2(g) + 2 H_2(g)$

The efficiency of the transition from electricity to hydrogen is mainly determined by the total current resistance of the electrolytic cell. The resistance of the electrolytic cell is mainly built up by the resistance of the electrodes, electrolyte, membrane and the so-called three-phase transition. The three-phase transition is the boundary layer where the water, gas and electrodes meet. High temperatures also facilitate the decomposition of the water, so that higher temperatures give higher efficiency.

A high temperature facilitates the decomposition of water since the bonding strength between oxygen and hydrogen atoms in the water molecules decreases with increasing temperature (Lessing, 2007) (Mazloomi S.K., 2012). A high temperature means that less electricity is needed for the decomposition of water but also means that the product gases will contain a greater amount of steam. Alkaline electrolysis is normally executed at 70 ° C, since higher temperatures will increase the risk of steam, which leads to lower conductivity and increased resistance of the electrolytic cell. Vaporization also causes water to be condensed from the produced hydrogen.

Hydrogen production at high temperature is called "High Temperature Electrolysis of Steam" (HTES) and occurs at temperatures up to 800 °C. Electrolysis at these temperatures requires heat resistant materials, such as for example SOEC (Solid Oxide Electrolysis Cell) that makes use of ceramic materials with a high heat resistance in the electrolyte. High temperatures may cause materials in the electrodes or the electrolyte to react and form compounds that reduce the conductivity and increase the resistance so that the efficiency decreases (Mazloomi S.K., 2012).

#### 2.1.1 Electrodes

The reaction rate of formation of hydrogen and oxygen at the electrodes at a given electric current is determined by several factors such as the conductivity and the number of active sites (Beller M., 2012). The electrolyte and the electrodes must have good conductive properties to transport electrons. The electrodes must also have many active sites to facilitate the transfer of electrons to the water molecules and electrons from the ions.

Normally metals have good conductive properties when made of tightly packed atoms with one or more electrons that are relatively loosely bounded. Transition metals have good conductive properties by forming a stable layer of substance oxide on the surface of the substance (Chang, 2008). Examples of common substances used in electrodes for electrolysis is nickel (Ni) and cobalt (Co). The material most suited depends on the electrolyte used, for example, if the electrolyte is acidic or basic.

To facilitate the donation of electrons at the cathode, and the absorption of them at the anode, a catalytic material is fastened around the electrodes which aim to increase the number of active sites. For example, a porous surface provides better transmission capacity than a smooth surface (Mazloomi S.K., 2012).

In order not to inhibit the process, gas generated at the electrodes must quickly leave the electrodes in order to make room for new molecules. The electrodes must therefore bind water molecules strongly, but not be inclined to bind to the produced gas. The gas bubble must be small and quickly disappear so that it does not prevent new water molecules to be adsorbed.

Inefficient desorption of gas and water adsorption are some of the factors that cause voltage spikes. Voltage spikes, corrosion and thermal stress causes the electrodes to degrade so that they eventually need to be replaced (Lessing, 2007). The electrodes are exposed to different types of wear depending on the technology used.

#### 2.1.2 Electrolyte

The electrolyte in the electrolytic cell acts to facilitate the transfer of ions between the anode and cathode. A low resistance in the electrolyte is desirable because it gives a higher efficiency. The resistance of the electrolyte is generally described by Formula 2 and depends on the resistivity ( $\rho$ ) of the material used, the length between the electrodes (I), and the cross-sectional area (A) of the electrolyte.

Formula 2 
$$R = \frac{\rho * l}{A}$$

It appears from the formula that the resistance of the electrolyte may be reduced by choice of electrolyte, a shorter distance between the electrodes and by designing the electrolyte with a larger cross sectional area.



Several solutions, polymers or ceramic materials can be used as electrolytes in an electrolytic cell. Different electrolysis techniques are usually distinguished by the electrolyte medium. Dissolved ions such as potassium hydroxide (KOH) are used in alkaline electrolysis, polymers are used in PEM electrolysis and ceramic materials are used in SOEC electrolysis. The various electrolysis technologies have different conductive properties and temperature resistance. This constitutes the fundamental differences between the different techniques.

In order to reduce the resistance in the electrolyte, the distance between the anode and cathode is reduced. However, the distance must be sufficiently long so that hydrogen and oxygen may be separated since the mixture between them is explosive. A separation between hydrogen and oxygen to obtain pure hydrogen is also difficult and costly. The gases are separated by a membrane but the membrane itself causes an increased resistance in the electrolytic cell. The distance between the anode and cathode is also restricted by the gas. A short distance provides a low resistance which causes high voltage and large current, which gives a rapid gas formation. The gas bubbles cause a void fraction of gas around the electrodes. To send a charge through the gas requires a very high voltage and void fractions therefore affect the efficiency negatively (Mazloomi S.K., 2012).

#### 2.1.3 Membrane

The membrane between the anode and cathode separates the product gases but also causes increased resistivity, which reduces the efficiency of the process. The membrane makes it more difficult for ions to pass through and gas bubbles are formed as a layer around the membrane, a so-called void fraction, resulting in increased resistance (Mazloomi S.K., 2012).

#### 2.2 Electrolysis Techniques

#### 2.2.1 Alkaline Electrolysis

Alkaline electrolysis is the simplest and most common technique for electrolysis of water into hydrogen. A schematic sketch of how alkaline electrolysis works is shown in Figure 3.



Figure 3. Schematic sketch of the alkaline electrolytic cell with potassium hydroxide ions in the electrolyte. The transfer of charges in the alkaline electrolysis takes place by means of ions. The ability of the water to ionize itself only contributes to very small conductive capacity. Therefore ions are added, often as acids or bases. High concentrations of acids and bases cause a wear on the electrodes which leads to shorter service life. A controversy exists, therefore, between a high conductivity in the electrolyte and a long electrode service life (Mazloomi S.K., 2012). The service life of the electrolyte for alkaline electrolysis is normally around 5 years. The most common electrolyte in alkaline electrolysis is a saline solution with potassium hydroxide (KOH).

The ion that transfers the charge affects the reactions that occur and the intermediates that are formed. In the alkaline electrolysis, the hydroxide ion transfers charge between the electrodes. The reaction formulas at the anode and cathode in alkaline electrolysis are shown in Formula 3 and Formula 4.

Formula 3	$4 \ 0 H^{-}(aq) \rightarrow 2 \ H_2 O(l) + O_2 (aq) + 4 \ e^{-}$	Anode reaction
Formula 4	$4 H_2 O(l) + 4 e^- \rightarrow 2 H_2(g) + 4 OH^-(aq)$	Cathode reaction

The formation of hydrogen and oxygen at the electrodes means that there will be a high concentration of hydrogen ions at the anode and hydroxide ions at the cathode. This means that the pH is low at the anode and high at the cathode compared to the surrounding electrolyte. The efficiency of the electrodes decreases as the reaction has to work against a concentration gradient, which also contributes to a lower efficiency of the process. Nickel (Ni) and cobalt (Co) are often used to meet requirements for electrodes, in particular concerning resistance to acid and base attacks and conductive ability.

Alkaline electrolysis uses a less complex electrolyte in comparison with the other techniques PEM and SOEC electrolysis. The disadvantage is however that the efficiency of this technique is about 50-70%, which is lower than PEM electrolysis and significantly lower than SOEC electrolysis. Alkaline electrolysis cannot be driven in the opposite direction, i.e. produce electricity from hydrogen and oxygen which is possible for the other two types of electrolysis.

#### 2.2.2 PEM Electrolysis

In a PEM electrolysis (PEM stands for Proton Exchange Membrane or Polymer Electrolyte Membrane) the electrolyte consists of a polymer which is intended to increase the conductivity and thereby obtaining a higher efficiency. A schematic sketch of a PEM electrolysis is shown in Figure 4.



Figure 4. Schematic sketch of the PEM electrolysis.



In a PEM electrolysis charges are transferred by the movement of hydrogen ions from the anode to the cathode, see Formula 5 and Formula 6 (Lessing, 2007).

Formula 5  $2 H_2 O(l) \rightarrow O_2(g) + 4 H^+(aq) + 4 e^-$ Anode reaction

Formula 6 
$$4 H^+(aq) + 4 e^- \rightarrow 2 H_2(g)$$

Cathode reaction

The polymer used as the electrolyte in PEM electrolysis can have multiple chemical structural formulas. A sulfonate polymer, such as Nafion ®, is often used as electrolyte. Polymers used as electrolytes have a good conductive ability at the intended temperature range. The conductive ability in specific temperature ranges differ between different polymers (Agrawal R.C., 2008).

The polymer degrades over time, which means that both the electrodes and the electrolyte require replacement. The decomposition of the electrolyte occurs in the three-phase area at the electrodes and at the polymer. The three-phase area is the layer where the material meets the liquid and gas. The electrodes are degraded by thermal and mechanical stress, although they are not degraded in the same way by acids and bases as in an alkaline electrolysis. The service life of the electrodes and electrolyte is between 5-10 years (Newton, 2013).

PEM electrolysis can serve as both an electrolyzer and a fuel cell to produce electricity. A PEM electrolysis cell can theoretically produce electricity from hydrogen and oxygen at high electricity prices and hydrogen and oxygen at low electricity prices (Lessing, 2007).

#### 2.2.3 SOEC Electrolysis

A SOEC electrolysis (Solide Oxide Electrolysis Cell) has a ceramic electrolyte that is intended to provide good conductivity and thermal resistance. SOEC can thus be operated at higher temperatures than alkaline and PEM electrolysis and therefore achieve higher efficiencies. A schematic sketch of SOEC electrolysis is shown in Figure 5.



Figure 5. Schematic sketch of SOEC electrolysis.

Oxygen ions are transported through the electrolyte from cathode to anode at SOEC electrolysis. The ceramic material contains vacancies in the atomic structure that enables the transport of oxygen ions. The reaction formula at SOEC electrolysis differs from alkaline and PEM electrolysis, as it is the oxygen ion that transfers the charge, see Formula 7 and Formula 8.

Formula 7  $2 0^{2-} \rightarrow 0_2 + 4e^-$ 

Anode reaction

Formula 8  $2 H_2 0 + 4 e^- \rightarrow 2 H_2 + 2 0^{2-}$ 

Cathode reaction

Materials commonly used in electrolytes at SOEC electrolysis are yttrium (Y) and zirconium (Zr). The term YSZ, yttrium-stabilized zirconia, is used to denote the electrolyte in a SOEC (Lessing, 2007). Yttrium can transmit ions with good stability even though Scandium has been shown to have better ability but also a higher price. The electrolyte must be thin to hold a low resistance (Sohal M. S., 2010).

The anode in an SOEC often consists of a porous ceramic metal made of nickel and YSZ. The cathode uses LSM-YSZ where LSM stands for strontium doped lanthanum manganite (Sohal M. S., 2010). In order to obtain a pure hydrogen flow, the water vapor has to be separated. This can be accomplished by condensation or hydrogen conductive membranes (Lessing, 2007).

SOEC electrolysis takes place at temperatures around 800 °C. The heat is used to reduce the amount of electricity required to decompose water. SOEC electrolysis takes place in a thermally insulated module in order to reduce heat losses. Inside the module, there are one or more cells similar to the cell in Figure 6 (Becker, 2013).



Figure 6. Schematic sketch of a SOEC cell

An advantage of SOEC electrolysis compared to alkaline and PEM electrolysis are possibilities to operate the electrolysis at higher temperatures. The power demand decreases if heat is added to the electrolysis, which helps to reduce the costs for electricity. When producing hydrogen from electricity the efficiency can be over 90% for a SOEC electrolysis (Sohal M. S., 2010). However, the system requires access to high grade heat, such as waste heat from adiabatic catalytic methanation reactors.

#### 2.3 Catalytic Methanation

The definition of a catalyst is that it accelerates a chemical process without being consumed in the process. Catalysts speed up chemical reactions by bringing the



reacting molecules together and holding them in such a way that the reaction is favored.

A catalysis process that occurs with reactants and catalysts in various phases is called heterogeneous while a reaction with the catalyst and the reactants in the same phase is called homogeneous. The reactants are the elements undergoing reaction, which is carbon dioxide and hydrogen at methanation. The methanation process to be studied is a heterogeneous catalysis with reactants in the gas phase and the catalyst in the solid phase (Lyklema, 1991).

#### 2.3.1 Catalyst Properties

The suitability of a material as a catalyst is determined by its electron configuration. Four properties will generally determine whether a substance is a good catalyst:

- Valence electrons in the d-shells
- The ability to adopt different oxidation states
- Ability to form intermediates with the reactants
- Defects in the crystal structure

The four properties of the catalysts are discussed below.

#### 2.3.1.1 Valence electrons in the d-shells

The various material properties depend on several factors; the size of the atom, compliance with the octet rule and electron positions in the shells. The outermost electron shell around the nucleus is called the valence shell. A common feature of catalysts is that they have valence electrons in the d-shells. (Cotton A., Advanced inorganic chemistry 5th edition, 1988). By donating and accepting electrons, substances with one or more electrons in the valence shell get the outermost electron shell filled.

Table 1 shows a part of the periodic system of materials having the valence electrons in the d-shells. Substances which are particularly suitable for methanation is nickel (Ni), ruthenium (Ru), rhodium (Rh), platinum (Pt), iron (Fe) and cobalt (Co) (Kopyscinski J., 2010).

Group 8	Group 9	Group 10
Fe	Со	Ni
Ru	Rh	Pd
Os	lr	Pt

#### 2.3.1.2 The ability to adopt different oxidation states

The oxidation state shows the charge of the ion. The sum of the oxidation states in a compound is 0 but the oxidation state of each atom varies. For example, oxygen in a water compound has oxidation state -2 and each hydrogen atom has oxidation state +1.

The electrons in the d-shells are loosely bound and have low ionization energy. Ionization energy is the energy required to remove electrons from a material in

order to form an ion. Table 2 shows that the transition metals can donate varying numbers of electrons which gives them different oxidation states. All materials in Table 1 may adopt different oxidation states. Table 2 provides examples of how oxidation states can vary for the materials in the top row of Table 1.

Oxidation state	Fe	Со	Ni
+1			
+2	Х	Х	Х
+3	Х	Х	Х
+4	Х	Х	
+5			
+6	Х		
+7			

Table 2. Various oxidation states of transition metals

#### 2.3.1.3 Ability to form intermediates with reactants

An illustration of intermediate formation is shown in Figure 7. The hydrogen is bound to the catalyst which in the figure is an atom of palladium (Pd). The catalyst splits hydrogen into ions and the promoter, which in this case consists of magnesium oxide (MgO), binds the carbon dioxide. The promoter binds to carbon dioxide and then to hydrogen ions in several steps in the formation of water and finally methane. The various molecules in the outer shell of the figure are methane intermediates.



Figure 7. Methanation of  $CO_2$  and  $H_2$  using a Pd catalyst with MgO promoter.

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#### 2.3.1.4 Defects in the crystal structure

The catalyst has active sites which consist of defects in the crystal structure (Lyklema, 1991). The reactants bind to these active sites and undergo reaction. Many active sites provide low activation energy. A catalyst can be produced so that it has a porous structure which provides many active sites.

#### 2.3.2 Reaction Processes in the Catalyst

In Figure 8,  $G_{reactants}$  corresponds to the energy of the reactants and  $G_{products}$  to the energy of the products. If the energy of the product is lower than the energy of the reactants, the difference  $\Delta G$  between them will be negative. A negative  $\Delta G$  indicates that the reaction is thermodynamically favorable. A catalyst can only speed up a reaction that has a negative  $\Delta G$ . Activation energy is required for the process to start. As seen from the figure, the activation energy is higher when the reaction occurs in absence of a catalyst as shown by the black curve in the figure. The presence of a catalyst decreases the activation energy which is indicated by the blue reaction pathway in Figure 8. A sufficiently high temperature makes reactions take place until all reactants are consumed.



Figure 8. Activation energy with and without catalyst.

The reactions illustrated in the catalyst in Figure 7 are shown in Formula 9. The reaction is called the Sabatier reaction. A negative sign in front of  $\Delta H$  indicates that energy is released when the reaction goes from left to right and the process is then called exothermal. The opposite of an exothermal reaction is an endothermal reaction, which means that the reaction goes from right to left so that heat is consumed.

Formula 9  $4 H_2 + CO_2 \leftrightarrow CH_4 + 2 H_2O$   $\Delta H_R = -189 (kJ/mol) (T = 523 K)$ 

At temperatures above 300 °C, the catalysts have sufficient activity to catalyze the process (Watson, 1980) (Brandin J., 2011). The temperature range for methana-

tion therefore lies between the activation temperature and the temperature at which the Sabatier reaction is no longer thermodynamically favorable. Depending on the pressure, the temperature varies when the Sabatier reaction ceases to be thermodynamically favorable.  $\Delta G$  become positive at a certain temperature and the reaction thus ceases to be thermodynamically favorable, see Figur 9. At a pressure of 2 bar the reaction ceases at 500 °C (Barbarossa V., 2011) but may proceed up to 800 °C at increased pressure (Gao J., 2011). Thus, the catalytic methanation processes proceed in the temperature range between 300 and 800 °C in a pressure range up to 20 bar.



Figur 9. Diagram showing the temperature dependence of the Sabatier reaction at a given pressure (Barbarossa V., 2011)

Since heat is released when the reaction in Formula 9 goes from left to right, several adjustments can be made to control the reaction and temperature. By taking the product gas that consists of methane and mix it with the reactant, a less favorable and hence slower reaction is achieved. A slow reaction results in lower methane production and lower temperature. An admixture of water in the reactant gas can be used in the same way as methane in order to reduce the reaction rate and thereby reduce the temperature. There are thus various techniques to obtain a stable catalysis temperature.

One advantage of allowing the reactors to operate at a high pressure is the high production of heat per unit volume in comparison with processes at lower pressure. (Kopyscinski J., 2010). A concentrated source of heat makes it easier to utilize high grade waste heat for steam production or gives the possibility to heat a SOEC. Since the temperature in an adiabatic reactor can be up to 800 °C, high grade steam may be obtained from the process. Higher pressure also enables more methane according to Le Chatelier's principle, which states that the reaction is favorable in the direction with the least number of moles, see Formula 9.

On a molecular level, the pathway of the reactant molecules towards a finished product is illustrated by Figure 10. When the reactants are in the particle boundary



layer of the catalyst(1) they diffuse (2) into the catalyst because the amount of reactants inside the catalyst is lower than outside. Reactants are adsorbed on an active site (3) directly with strong bonds, or via weaker bonds followed by strong bonds. Binding with strong bonds is called chemisorption and binding with weak bonds is called physorption. When four hydrogen molecules and one carbon dioxide molecule have been adsorbed (4) they undergo the Sabatier reaction and desorb (5) from the catalyst surface as methane molecules and then diffuse out (6) to the boundary layer (7) and leave the catalyst.



Figure 10. Catalysis process where reactant gases diffuse into active sites where the Sabatier reaction occurs

#### 2.3.3 Inactivation of the Catalyst

If the active sites of the catalyst are covered by any material, they will be inhibited and the reaction cannot be catalysed. The sensitivity of the catalysts varies and *Table 3* shows six types of deactivation of a catalyst (Bartholomew, 2001).

Inactivation	Wear	Explanation
Poisoning	Chemical	Chemisorption on active sites.
		Sulfur binds to the active sites.
Impurities	Mechanical	Contamination on the catalytic sites and
		pores.
		Carbon deposits that prevent adsorption
		on active sites.
Thermal degradation	Thermal	Thermal wear of the catalyst material.
Gas formation	Chemical	Formation of volatile compounds from
		catalyst and reactant gases.
		Catalytic material is removed with the
		product gas containing volatile com-
		pounds.
Gas-Solid/Solid-Solid	Chemical	Reaction of catalytic materials with gas or
reactions		other catalytic materials. Formation of an
		inactive phase on the catalyst surface
		without catalytic properties.
Abrasion	Mechanical	Loss of catalytic material and surface.

Table 3. Physical parameters influencing the catalyst stability

Poisoning of the catalysts can occur if reactant gases contain contaminants like sulfur. Poisoning makes the catalyst lose its ability to catalyze. Sulfur is the compound that mainly affects the properties of the catalyst (Bartholomew, 2001) and especially nickel catalysts are extremely sensitive to sulfur. Therefore there is a requirement for gas purification before the methanation. Both raw biogas and synthesis gas contain sulfur.

Thermodynamically, the formation of carbon monoxide is possible above about 370 °C (Lunde P. J.) which can cause problems with carbon deposits because carbon monoxide then can react according to Formula 10. Methane can also provide deposits of carbon as shown in Formula 11.

Formula 10 2  $CO \leftrightarrow +CO_2 + C$  $\Delta H^\circ = -173 \text{ kJ/mol}$ Formula 11  $CH_4 \leftrightarrow C + 2 H_2$  $\Delta H^\circ = -41 \text{ kJ/mol}$ 

Carbon deposits cause catalysts to lose active sites which contributes to a reduced ability to convert reactants to methane (Bartholomew, 2001). Carbon can bind with weak and strong bonds like the reactants but can also fully enclose a catalyst particle with complete inactivation as a result. The inactivated sites can regenerate and regain their active sites. There are several ways to regenerate deactivated catalysts. Pure carbon dioxide can be added to drive the reaction back or the catalysts can be washed by steam (Bartholomew, 2001).

#### 2.3.4 Catalysis Reactors

The reactants are supplied in the bottom of the reactor and rises through the catalyst bed. In a fixed bed reactor, the gas passes up between the catalyst particles, but the gas does not make catalysts swirl around in the reactor. If the flow of reactant gas increases in proportion to the catalyst volume, bubbles are formed in the



catalyst bed; a so called bubbling fluidized bed. If further flow is applied channel formation is obtained in the reactor bed, which is called a turbulent fluidized bed. At high flows catalysts begin to be evenly distributed in the reactor and then risk falling out; a fast fluidized bed. Figure 11 shows how the catalysts are distributed in a reactor depending on the speed of the incoming gas.



*Figure 11. Appearence of reactors depending on space velocity* (Kopyscinski, 2010).

The advantage of a fixed bed reactor is that it is easy to cool and it is the most frequently used reactor. The advantage of bubbling, turbulent and fast fluidized beds are that the transfer surface between catalysts and reactant gases then becomes larger than in a fixed bed reactor.

#### 2.3.4.1 Adiabatic fixed bed reactor

An adiabatic reactor is thermally insulated and no heat is exchanged with the surroundings. A high concentration of reactant gases gives a high temperature in the reactor. A schematic sketch of the adiabatic reactors in series is shown in Figure 12. In the first reactor, the concentration of the reactants is the highest. A high concentration of reactants generates a high temperature in the reactor. A too high temperature prevents methanation although there are still remaining reactants. The concentration of carbon dioxide and hydrogen decreases at each step, while the content of methane increases. Before the gas is supplied to the next reactor the gas is cooled down so that water can be separated. The purpose of the cooling of the product gas is also a lower inlet temperature to the next reactor which favors methane formation thermodynamically. The input gas to the second reactor has a lower proportion of reactants, and a higher proportion of methane in comparison with the incoming gas to the first reactor. This process is repeated and effluent product gas from the last reactor has a high content of methane. Heat in the methane gas coming from the last reactor is often used to heat the reactant gas supplied to the first reactor.





An advantage of the adiabatic reactors is that superheated steam can be obtained from the cooling circuit. The steam can then be used for district heating or a steam turbine. The amount of heat also corresponds to the heat needed for a SOEC electrolysis, making it appropriate to integrate the two processes in the future. Only a small amount of external heating would have to be added to a SOEC electrolysis in addition to the heat obtained by cooling the adiabatic reactor.

#### 2.3.4.2 Isothermal fixed bed reactor

An isothermal reactor has a relatively constant temperature since the process is cooled continuously, see Figure 13. The homogeneous temperature in the reactor requires efficient cooling. A disadvantage of an isothermal reactor is that less high grade steam may be obtained than from an adiabatic reactor, since the temperature is lower than in an adiabatic reactor. The Sabatier reaction is favored by the efficient cooling of an isothermal reactor so that it only takes one reactor for the formation of methane.



Figure 13. Isothermal reactor with heat exchange.

There are several different types of isothermal reactors. The refrigerant can pass through helical or straight tubes. Plate heat exchangers are also available as a cooling method. A schematic sketch of how the catalysts and the refrigerant are located in relation to each other in an isothermal reactor tube is shown in Figure 14.





Figure 14. Isothermal fixed bed reactor with a refrigerant flow that cools the tube containing catalysts.

#### 2.4 Biological Methanation

The biomethanation is a limited part of the biogas process. The biogas process is shown in Figure 15 and consists of all reactions in the figure. The degradation of the substrate proceeds in several steps where methanation consists of reactions 4-7 in the figure. Formation of methane is performed by methanogenic archaea that convert carbon dioxide and hydrogen or acetic acid (CH3COOH) to methane.



Figure 15. Decomposition of organic matter to methane.

Various steps are carried out with organisms that use energy released when longer carbon chains are cleaved into shorter. The different steps are shown in Figure 15.

- 1) Hydrolysis
- 2) Fermentation
- 3) Anaerobic oxidation
- 4) Syntrophic acetate oxidation
- 5) Hydrogen oxidation
- 6) Acetotrophic methanogenesis (methanogenic archea)
- 7) Hydrogenotrophic methanogenesis (methanogenic archea)

Biological methanation is supplied only with carbon dioxide and hydrogen. Step 1 and step 2 in Figure 15 will therefore not be described in the report. The addition of hydrogen to an existing reactor affects the biogas process in step 3. Several compounds are decomposed by the anaerobic oxidation to carbon dioxide, hydrogen and acetic acid. If the concentration of hydrogen becomes too high, this reaction would be thermodynamically unfavorable. Under normal conditions, the concentration of hydrogen is low because it is consumed by the methane-producing Archaea. Figure 16 shows an example of the importance of the hydrogen for the anaerobic oxidation of propionate. Propionate is a molecule that forms acetate (ion form of acetic acid) by oxidation. Only in the small triangle in the middle both propionate oxidizing bacteria and methanogenic archaea get enough energy to grow. Propionate oxidizing organisms prefer a low pressure of hydrogen while methano-



gens want a high pressure of hydrogen. This means that if hydrogen is added to an existing biogas plant, it must be done in such a way that no significant effect on the anaerobic oxidation occurs.



Figure 16. Hydrogen content when anaerobic oxidation and methane formation can occur.

The products of the anaerobic oxidation are used by methane-producing organisms. As seen in Figure 15, acetate may either be decomposed directly into carbon dioxide and methane (6) or to carbon dioxide and hydrogen (4) which may then be methanized (7). The path illustrated with number 4 followed by number 7 can undergo reactions in two stages in accordance with Formula 12 and Formula 13. Hydrogen formation by syntrophic acetate oxidation is not thermodynamically favorable, but it is by combining the reactions that methane formation is thermodynamically favorable.

Formula 12 $CH_3COO^- + 4 H_2O \rightarrow 2 HCO_3^- + 4 H_2 + H^+$	$\Delta G$ = 104,6 kJ/mol
Formula 13 4 $H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3 H_2O$	$\Delta G$ = -135,6 kJ/mol

The addition of hydrogen to an existing biogas plant complicates the metabolic pathway for methane production by syntrophic acetate oxidation. A high partial pressure of hydrogen gives a concentration gradient that is hard to overcome for the microbes performing the reaction in Formula 12. Thus, microorganisms that perform Formula 13 must have time to grow in number as more hydrogen is added. Reaction 4 in Figure 15 can also take place in the opposite direction corresponding to number 5 in the figure. Hydrogen oxidation means that bacteria produce acetic acid from hydrogen and carbon dioxide as shown in Formula 14. Ace-

tic acid may then be cleaved into carbon dioxide and methane according to the reaction of Formula 15, see number 6 in the Figure 15.

Formula 14 4  $H_2$  + 2  $CO_2 \rightarrow CH_3COOH$  + 2  $H_2O$ 

Formula 15  $CH_3COOH \rightarrow CH_4 + CO_2$ 

Acetic acid may also be produced directly by fermentation and anaerobic oxidation. The acetate cleaving methanogens normally contributes to approximately 70% of all methane in a biogas process (Schnürer A., 2009). Hydrogen and carbon dioxide can also form methane directly, see number 7 in Figure 15. Methane formation by reduction of carbon dioxide (Ferry, 2010) takes place according to the reaction in Formula 16 (Stams). The carbon dioxide is dissolved in water as a bicarbonate ion. The only difference between Formula 16 and Formula 9 is therefore a water molecule.

Formula 16 4  $H_2$  +  $HCO_3^-$  +  $H^+ \rightarrow CH_4$  + 3  $H_2O$ 

#### 2.4.1 Reactor Design for Biological Methanation

The hydrogenotrophic methanogens are dependent on high hydrogen concentrations. Since hydrogen has a very low solubility in water, hydrogenotrophic methanogens requires a reactor design that increases the solubility of hydrogen (Ako O., 2007). Figure 17 shows the solubility of hydrogen in water and Figure 18 the solubility of carbon dioxide in water at atmospheric pressure. The figures show that the solubility at 0 °C is 1500 times higher for carbon dioxide than hydrogen. It is apparent that the solubility decreases with increasing temperature.



Figure 17. Solubility of hydrogen in water.

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Figure 18. Solubility of carbon dioxide in water.

Carbon dioxide and hydrogen must be dissolved in the liquid so that methanogens can absorb gases as substrates. An efficient process that increases the availability of the reactant gases means less reactor volume in relation to the incoming flow of gas in comparison to an inefficient process. A smaller reactor gives a lower investment cost. Temperature, difference in concentration, pressure, time, transfer surface area and mechanical mixing are some factors that can be used to influence the solubility of gases in liquids. A reactor for the methanation of carbon dioxide and hydrogen can be designed so that one or more of these factors are optimized for enhanced gas-liquid mass transfer. Microbial and thermodynamically there is a contradiction regarding the methanation of carbon dioxide and hydrogen. Rising temperatures mean lower solubility but at the optimum temperature for growth of cells, about 65 °C, this is compensated by the fact that the levels of available gases in the liquid are kept low by the methanogens. The difference in concentration between the gas and liquid increases if the microorganisms continuously consume hydrogen which provides increased mass transfer and increased methane production. The optimum temperature for growth of the microbes prevents the reaction to occur at low temperatures. Temperature is therefore no parameter that can be adjusted to optimize the hydrogen solubility. The temperature of the reactor will therefore be the same as the optimal temperature for growth of methanogenic organisms. Other factors such as pressure and time can be optimized to enhance the mass transport of gas-liquid. A high pressure results in more gas dissolved in the liquid but a high pressure also causes a favored methane production according to Le Chatelier's principle, since there are more moles of reactant gas than product gas (Klasson K. T., 1991). A pressure that is applied during a long time in a liquid also enhances the solubility.

One way to increase mass transport of gas to liquid is by allowing the reactor to be designed as a high vertical column. If gas is supplied at the bottom of the reactor a gas bubble will have a long time to reach equilibrium with the surrounding fluid which leads to higher solubility (Klasson K. T., 1991).

By increasing the pressure, the size of the bubbles is reduced. Small bubbles rise more slowly and have larger contact area between gas and liquid in comparison with large bubbles (M.I Breedwell, 1999). Really small bubbles have both a larger contact area and a higher partial pressure by the so-called Young-Laplace effect. One way to obtain small bubbles is to decompose them into an aqueous solution before the gas is supplied to the reactor. The challenge is to do this in an efficient manner at high flow rates (Morikawa, 2013). Gas may also be mechanically forced into the liquid by vigorous stirring in the reactor. This way of increasing the solubility is at expense of efficiency since energy is used to stir the reactor.

#### 2.4.2 Reactor Types

#### 2.4.2.1 CSTR

A Continuously Stirred Tank Reactor (CSTR) is a reactor with continuous stirring. It is used to mechanically force gas down in liquid and thereby increasing the solubility (Klasson K. T., 1991). The gas is compressed before it is supplied to the reactor to prevent that liquid falls out. A CSTR with an agitator that has a gas inlet at the bottom is shown in Figure 19.



Figure 19. Schematic sketch of a CSTR.



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#### 2.4.2.2 Trickle-bed reactor

A trickle-bed reactor is a column reactor with a fixed bed with microbes on the bed material. The liquid is pumped up and trickles down through the bed beside the gas that is also supplied from above and collected at the bottom (Marshall Breedwell, 1999) see Figure 20. One advantage of the technique is that energy-intensive stirring is avoided. The column height as well as the flow of liquid and gas can be adjusted to increase the time for transmission of gas to liquid.



Figure 20. Schematic sketch of a trickle-bed reactor.

#### 2.4.2.3 Reactor with hollow fiber membranes

The reactant gas is supplied to a reactor with permeable pipes that allow carbon dioxide and hydrogen to blend into the liquid. The liquid cannot penetrate into the pipes, because the pressure is higher in the separate gas flow than in the reactor. The gas only needs to be pressurized and recirculated. The advantage of this technology is that the stirring that consumes energy can be avoided. A reactor with hollow fiber membranes can both act as a reactor and as a complement to another reactor. A schematic sketch of a hollow fiber membrane reactor is shown in Figure 21. In Chapter 3, Figure 28 shows how a separate column of hollow fiber membranes can be integrated into a reactor where methane is produced.





Figure 21. Methanation reactor with hollow fiber membranes.

2.5 Biological Conversion of Synthesis Gas

Gasification is a process that thermally decomposes a solid or a liquid biomass into a gas consisting mainly of carbon monoxide, hydrogen, carbon dioxide and methane. Intervals for the different gas components are shown in Table 4. Synthesis gas is often used as a name for mixtures of carbon monoxide and hydrogen. Moreover, even solid fractions in the form of ash and tar remain after gasification.

Table 4.	Range	for the	most	common	gases	in .	synthesis	gas
					0			<u> </u>

	CO	CO <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O	$CH_4$	N <sub>2</sub>	$H_2S$
Vol-%	10-40	10-40	5-40	0-40	5-20	0-60	0-1

The proportion of the different gases in the synthesis gas varies with the choice of process, media added, pressure and temperature. This report refers to the methanation of synthesis gas that does not contain nitrogen, i.e. gasification without addition of air.

In this chapter biological processes to convert carbon dioxide and carbon monoxide to methane are investigated with and without addition of hydrogen. The hydrogen produced by the gasification is not sufficient for a stoichiometric conversion of all the carbon in the synthesis gas (in the form of carbon monoxide and carbon dioxide) to methane.

The conversion of carbon dioxide and hydrogen to methane have been addressed earlier in this report and therefore only methanation of carbon monoxide via acetate to methane or carbon monoxide conversion to carbon dioxide and hydrogen will be studied.



#### 2.5.1 Biological Conversion of Carbon Monoxide

Carbon monoxide may be converted to methane in different pathways and Figure 22 shows examples of these. Generally, one way is through acetic acid, and the other through carbon dioxide and hydrogen.

Just as in the biogas process, carbon dioxide and hydrogen is converted to acetic acid, and just like in the biogas process acetic acid can decompose back into carbon dioxide and hydrogen. The carbon monoxide is harmful to the organisms that do not have any enzyme capable of converting carbon monoxide to other compounds. Thus, the involved microbes differ from microbes in a biogas process.



Figure 22. Metabolic pathways for the conversion of carbon monoxide to methane.

The bacteria convert carbon monoxide to carbon dioxide and hydrogen by a reaction that is called the water-gas shift reaction when water turns into gas. The reaction corresponds to number 8 in Figure 22. From the water-gas shift reaction, carbon dioxide and hydrogen is obtained in a 1:1 ratio, which reduces the need for hydrogen from electrolysis.

Formula 17  $CO + H_2O \rightarrow CO_2 + H_2$ 

There are several species of bacteria that are proven to be able to implement the water-gas shift reaction (Mohammadi M., 2011) (Klasson K. T., 1991) (Amos, 2004) . In experiments, some of them have been able to produce carbon dioxide and hydrogen in a CSTR as well as in a trickle-bed reactor (Amos, 2004). Carbon dioxide and hydrogen can then be methanated as previously described.

Conversion of carbon monoxide to acetic acid by the reaction of Formula 18 corresponds to number 9 in Figure 22. Methanation of acetic acid then proceeds by Formula 19, which corresponds to number 6 in Figure 22.

Formula 18 4 CO + 2 $H_2O$   $\rightarrow$   $CH_3COOH$  + 2 $CO_2$ 

Formula 19  $CH_3COOH \rightarrow CH_4 + CO_2$ 

The conversion of carbon monoxide to acetic acid and methanation of acetic acid may proceed in a co-culture in the same reactor (Barik S., 1988). Table 5 shows

the different paths for methane formation as illustrated in Figure 22. The table shows the relationship between the various reactants in the production of one mole of methane. For each component of a reactant or a product, the number of moles consumed and produced in the formation of one mole of methane is shown.

Table 5. The ratio between the various reactants and products of the three paths for methane production in Figure 22

Metabolic	Reactant-	Reactant-	Reactant-	Product-	Product-
pathway	CO	H <sub>2</sub> O	H <sub>2</sub>	$CH_4$	CO <sub>2</sub>
9+6	4	2	0	1	3
8+7	1	1	3	1	0
8+5+6	2	2	2	1	1

The table shows that pathway 9+6 does not need any extra hydrogen. The table also shows that three of four carbon atoms are unused when only one mole of methane is formed of four moles of carbon monoxide molecules. Theoretically, electrolysis is not necessary for hydrogen production when hydrogen is extracted from water. This could result in reduced costs for methane by this process. Lack of actual experiments, however, makes this process uncertain.

Pathway 8+7 starts with the water-gas shift conversion of carbon monoxide to hydrogen and carbon dioxide prior to methanation. This pathway requires a relatively large amount of hydrogen, and by designing and controlling indirect gasification, it would be possible to obtain a synthesis gas consisting of three times more hydrogen than carbon monoxide. Unlike pathway 9+6 all carbon atoms in the carbon monoxide is converted to methane.

The pathway 8+5+6, where hydrogen and carbon dioxide are methanized via acetic acid formation, consumes equal amounts of carbon monoxide and hydrogen. If the synthesis gas has a content of equal parts of carbon monoxide and hydrogen, this pathway occurs without extra addition of hydrogen.

Hydrogen and carbon monoxide have a low solubility in water (Mohammadi M., 2011). As shown in Figure 23, the solubility of carbon monoxide in water is about 75 times higher than for hydrogen but 20 times lower than the solubility of carbon dioxide in water.





Figure 23. The solubility of carbon monoxide in water.

#### 3 Manufacturers

#### 3.1 Electrolysis

Table 6 shows examples of manufacturers working with electrolysis who have commercial products that enable production of hydrogen by the electrolysis of water with a capacity of 150 Nm<sup>3</sup> hydrogen per hour. Hydrogenics also manufactures electrolysis units but they are not included in the table since they mostly work with customized installations in a smaller scale.

Table C	Commilation	of monoral for otherworks	of all calling a			
i able 6.	Compliation	of manufacturers	of alkaline e	Hectrolysis	and PEIN e	iectrolysis

	NEL	Erredue	Proton-Onsite
Production rate Nm <sup>3</sup> /h	≤ 500	≤200	≤400 <sup>1</sup>
Efficiency	0,69-0,73	0,6	<sub>~</sub> 0,65
Technique	Alkaline	Alkaline	PEM
Gas pressure (bar) H <sub>2</sub>	15	5	
Service life	≤87 600 <sup>2</sup>	≤48 000 <sup>3</sup>	≤70 000

Among the manufacturers that are presented in the table, the alkaline electrolysis is more common and can be considered to be commercialized to a greater extent than PEM electrolysis. In addition, it should also be mentioned that a large number of manufacturers of alkaline electrolysis are delivering smaller applications with lower capacities. In the table no supplier of SOEC electrolysis is represented, since there are not yet any participants in the market offering such a commercial product.

For the various suppliers of electrolysis for hydrogen production the efficiency when producing hydrogen from electricity is generally around 0.6 to 0.7 depending on suppliers and technology used. Often, the efficiency is not given directly by the manufacturer but is given in quantity of electricity required to produce one cubic meter of hydrogen, where 1 Nm<sup>3</sup> of hydrogen contains about 3 kWh. The service life of the electrolysis cells varies from 50,000 to 100,000 hours.

#### 3.2 Catalytic Methanation

#### 3.2.1 ETOGAS

ETOGAS has three plants in Germany. A 25 kW pilot plant was built in Bad Hersfeldt for testing of biogas upgrading. There is also a 250 kW installation in Stuttgart. In collaboration with Audi, ETOGAS has built a 6 MW plant in Werlte. The powers given refer to the incoming electricity at each facility. The 6 MW plant in Werlte consists of three 2 MW units.

ETOGAS designs and manages the construction of plant facilities and purchases components from subcontractors. Electrolysis units and catalytic reactors are shipped in containers. A methanation reactor has a capacity to produce 300 Nm<sup>3</sup> methane per hour. In order to exceed a 300 Nm<sup>3</sup>/h production an additional methanation reactor has to be built or an expansion of the first reactor is required.

<sup>&</sup>lt;sup>3</sup> (Pucci, 2013)



<sup>&</sup>lt;sup>1</sup> Under utveckling (Shiller, 2013)

<sup>&</sup>lt;sup>2</sup> (Taalesen, 2013)

In case of increased production, more containers of electrolysis units are connected to the plant. ETOGAS can guarantee a methane content of over 96% in the product gas.

ETOGAS supplies the gas to the methanation reactors with a relatively low space velocity. A low flow gives less mechanical wear on the catalysts. The catalysts consist mainly of nickel which is the same material used in the electrodes of the electrolysis. The advantage of having the same material in electrolysis and catalysis is that material costs potentially can be reduced through coordinated purchasing (Rieke, 2013).

ETOGAS's reactor in Bad Hersfeldt is an adiabatic reactor with catalysts placed in tubes. When the catalysts are worn out they are drained from the bottom of the reactor and subsequently new catalysts are filled from the top of the reactor.

Since the catalysts as mentioned earlier become polluted with time, cleaning will be required. Regeneration of catalysts is expected to take two days a year to complete. The degradation of the electrodes results in a need of replacement and is estimated to take 10 days a year to complete. Maintenance costs are estimated to be around 40 €/kW power input. ETOGAS Gmbh currently delivers plants with electrolysis units produced by H2Nitidor in Italy. The methanation reactor is a so-called flat isothermal fixed bed and provides high methane content with just one reactor due to the efficient heat exchange. A schematic representation of the process is shown in Figure 24.



Figure 24. ETOGAS's process for catalytic methanation.

ETOGAS has through its three plants shown that carbon dioxide from both air and biogas can be catalytically converted to methane by the addition of hydrogen from electrolysis. A comparison of ETOGAS's three plants is summarized in Table 7. All of the plants upgrade carbon of different origins to at least 96% methane content.

	Bad Hersfeldt	Stuttgart	Werlte
Power Input	25 kW <sub>el</sub>	250 kW <sub>el</sub>	6 MW <sub>el</sub>
Production rate	Not in continuous operation	No data available	25 GWh/year
Commissioning Year	2009	2012	2013
Source of Hydro-	Electrolysis	Electrolysis	Electrolysis
gen			
Source of Carbon	Non-upgraded	Air	Separated from up-

Table 7. ETOGAS's pile	ot and demonstration	plants
------------------------	----------------------	--------

Dioxide	biogas		grading plant
Methane Content	>96 %	>96 %	>96 %

#### 3.2.2 Sunfire

Sunfire has not yet delivered any facility for catalytic methanation. The company has a technical expertise in Solid Oxide Fuel Cells (SOFC) and has begun the development of SOEC. Just as ETOGAS, Sunfire has developed a conceptual solution where all components are purchased from other suppliers. 2016 Sunfire expects to offer a SOEC which will have a higher efficiency than alkaline electrolysis. According to their own estimates the expected efficiency of electrolysis will be 90%.

The company gets support by Bilfinger which accounts for construction and maintenance of the facilities that Sunfire produces. Sunfire is expected to offer a facility in 2014. Until Sunfire's SOEC is developed, these facilities will use alkaline electrolysis. Sunfire finds SOEC suitable for sites with access to an unused heat flow, for example, the cooling circuit from catalytic methanation.

The first reactor is an adiabatic fixed bed reactor followed by an isothermal reactor. The heat of methanation can be supplied to the electrolysis unit through a heat pump, but also an additional heat source, such as heating equipment, will be needed. Sunfire estimates that an amount of energy corresponding to 3.5-4 % of the energy in the hydrogen must be supplied to the electrolysis in the form of heat via an external heater (Aldag, 2013).



Figure 25. Schematic representation of Sunfire's process.

Sunfire states that its SOEC technology can achieve an overall efficiency of the system from electricity to methane of 80%. This means that the efficiency from electricity to hydrogen is very high, which is possible when the electrolysis also is supplied with high grade heat of over 700 °C.

#### 3.2.3 Haldor Topsøe

Haldor Topsøe manufactures both catalysts and fuel cells. In 2004 the department Topsoe Fuel Cell was founded and through its expertise in SOFC, Haldor Topsøe hopes to deliver a finished SOEC electrolysis within the next few years. Haldor Topsoe is currently working at constructing a 40 kW SOEC for demonstrating the technology in Foulum within a EUDP project.



Haldor Topsøe has a patented process for methanation of synthesis gas called TREMP (Topsøe Recycle Methanation Process). The process consists of three adiabatic fixed bed reactors. The TREMP process uses steam recovery for heating the incoming reactant gases and the process comprises the extraction of super-heated steam. Haldor Topsøe uses home developed catalysts in the process (Kopinsky, 2009). The catalysts in the first reactor must be more thermally stable in comparison with the catalysts in the latter two reactors, which do not need to withstand as high temperatures.

A schematic outline of Haldor Topsøe's integrated adiabatic catalytic reactor and SOEC technology is shown in Figure 26. One advantage of using non-upgraded biogas as carbon source is that the methane content is already up to about 65%. It allows the use of only one adiabatic catalytic reactor to reach a methane content of 96 to 98%. In the case that pure carbon dioxide becomes methanized with hydrogen several adiabatic catalytic reactors in series are necessary due to the vast heat generation in the process. Only a small heat flow needs to be added to the electrolysis in addition to the steam obtained by cooling the outgoing methane from the catalytic reactor.



Figure 26. Haldor Topsøe's combined SOEC and methanation system.

#### 3.3 Biological Methanation

#### 3.3.1 MicrobEnergy

Viessmann Group has through its company MicrobEnergy two plants for Power-to-Gas in Schwandorf; one reactor for increased production of methane by hydrogen addition to an existing biogas reactor and one separate reactor for methanation of pure carbon dioxide and hydrogen. The power of electrolysis to the existing biogas plant is 120 kW, which corresponds to a 70 kW hydrogen flow. The biogas reactor is also supplied with organic substrates in the form of maize and grass. The biogas plant has the shape of a lying container. At the plant in Schwandorf, the company also has a biological reactor for methanation of carbon dioxide and hydrogen with a 55 kW electrolysis unit. MicrobEnergy plans for additional facilities and in 2014 the company intends to deliver a biological methanation plant with a 1 MW electrolysis unit. However, MicrobEnergy is still in the start-up phase where the current and the next coming plants are primarily designed to increase the knowledge about the technology.

The pilot plant with the addition of hydrogen to an existing biogas plant is schematically shown in Figure 27. Hydrogen is supplied and seeps out through holes in the pipes in the bottom of the reactor. During the time that the hydrogen rises to the surface of the liquid, the gas is consumed by methanogenic bacteria. Due to high content of dry matter the liquid in the reactor becomes viscous causing bubbles to rise slowly which facilitates gas-liquid mass transfer since the bubbles have more time to transfer the gas to the liquid.



Figure 27. MicrobEnergy's biogas reactor with addition of hydrogen.

The stirrer affects the rise of the bubbles. The design of the stirrer must be such that the residence time of the bubbles is slow and poor design can have the opposite effect. The horizontal design of the stirrer drives the material from left to right. This means that high levels of dry matter can be managed with this type of reactor.

MicrobEnergy controls the hydrogen addition so that the biogas process is stable. If the hydrogen content in the product gas increases, the supply of hydrogen to the reactor is reduced. Hydrogen in the product gas indicates in this type of digestion not necessarily problems in the process. MicrobEnergy states that addition of hydrogen at the test facility does not affect the pH by acid formation in the reactor (Reuter M. , 2013). Hydrogen in the product gas is in this case rather indicating that microbes have not had time to transform the supplied hydrogen.

In MicrobEnergy's facility for addition of hydrogen to the existing biogas reactor the methane content has been raised from 50 to 75%. However, MicrobEnergy expects the number to grow through improved technology for gas-liquid mass transfer. In the laboratory, higher levels of methane in the product gas have been obtained.



MicrobEnergy delivers an integrated system with electrolysis and a reactor for biological methanation. In addition to the cost of the reactor and electrolysis, costs for handling the material, installation, compressors and other equipment are required.

MicrobEnergy also offers a solution for biological methanation of carbon dioxide and hydrogen in a separate reactor where addition of organic substrates such as maize and grass does not take place. Formation of methane takes place through the addition of hydrogenotrophic methanogens and nutrients. Since no acentrophic methanogens are added, methanation via the acetate formation route will not take place in a separate reactor.

Biological methanation in a separate reactor of carbon dioxide and hydrogen with MicrobEnergy's technology can be designed in two different ways, see Figure 28 and Figure 29. In both types of reactors, the gas is supplied in the bottom of the reactor and both reactors are provided with an axial agitator.



Figure 28. MicrobEnergy's methanation reactor with supply of hydrogen in a separate membrane column.



Figure 29. MicrobEnergy's reactor for biological methanation of hydrogen by stirring.

In Figure 28 gas is supplied through a hollow fiber membrane to a flow of fluid in the opposite direction. The fluid is then returned to the reactor where methane formation occurs. In this way, less electrical energy must be supplied to the agitator for the gas-liquid mass transfer in comparison with the transfer in Figure 29.

In the reactor in Figure 29, the reactant gas is supplied in the bottom by pipes with similar appearance as the reactor in Figure 27. For the reactor in Figure 27 the only possibility to stir the reactor is via the slow agitator. More rapidly stirring as seen in Figure 29 leads to higher methane yield but requires additional energy in the form of electrical power for the agitator.

At the 55 kW pilot plant it has been demonstrated that the reactor can handle a flow of gas per hour which is 30 times the size of the reactor volume at a stirring rate of hundreds of rotations per minute. A one cubic meter reactor can thus handle an incoming gas flow of carbon dioxide and hydrogen of 30  $\text{Nm}^3/\text{h}$ .

At biological methanation both heat and biomass will also be produced. The proportion of heat and biomass is not yet known to MicrobEnergy (Reuter M. , 2013). The temperature in the reactor is between 40-65 °C and the pressure is atmospheric. The 55 kW pilot plant must be supplied with heat in order to reach the right temperature.

#### 3.3.2 Krajete

Krajete was founded in Linz in Austria in 2012 and currently has three full-time employees. The business idea came up in 2007 and the process was developed as a part of work within the field of waste-to-energy. Krajete owns two bioreactors, of which one is a pilot plant with a production capacity of 0.2 Nm<sup>3</sup> per hour.

Krajete offers reactors for biological methanation and upgrading of biogas. The reactor has the same principal appearance as the reactor in Figure 29, with the hydrogen supplied in the bottom. Krajete estimates that the ratio of gas flow and reactor volume will be about 20/h with current technology. It is estimated that approximately 10-30 % of the released energy from methane formation becomes heat and the remainder becomes cell mass. The cell density in the reactor is esti-



mated to be about 5 g/l and the temperature in the reactor is around 65°C. A reactor with an incoming carbon dioxide flow of 600 Nm<sup>3</sup>/h would generate 38 tons of biomass per year. Krajete is currently investigating how to make use of the biomass formed during biological methanation (Krajete, 2013).

In order to increase the solubility of hydrogen, the reactor is provided with an axial agitator. The stirring is estimated to have an electricity consumption of 0.5 kW/m<sup>3</sup> reactor volume. According to Krajete the microbes are able to utilize the energy of both hydrogen sulfide (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>).

#### 3.3.3 Electrochaea

Electrochaea was founded in 2010 as a spinoff from the University of Chicago, USA. The business idea is based on a protected strain of methanogenic archaea used for biological methanation. The company currently has a 250 kW plant at the Power-to-Gas demo facility at the University of Aarhus in Foulum, Denmark. The project is partly financed by EON, Erdgas Zurich, EWZ and NEAS.

Electrochaea plans to build a 1 MW plant in 2014 and will receive funding from the Danish grid operator Energinet.dk for a feasibility study. The company has five employees and operates in both the U.S. and Denmark. Electrochaea does not want to disclose any prices or technical details concerning the bioreactor. Estimates of production of methane via Electrochaea's technology will therefore not be presented in this report. Electrochaea acknowledges that the reactor in Figure 29 is similar to the one the company uses but also points out that the current pilot plant is built for conventional biogas production and not optimized for biological methanation (Hofstetter, 2013).

The process of Electrochaea indicates that 18% of the incoming energy turns into heat, and only 1.6% of the carbon dioxide turns into biomass. The majority of the energy released turns into heat which is a big contrast to Krajete's biological methanation where most of the energy released turns into biomass, but no further analysis of these contradicting data have been performed in the present investigation. The biomass produced in the reactor can be brought to a biogas reactor without pretreatment. The process requires the addition of microorganisms and nutrients.

Like the other processes for biological methanation of MicrobEnergy and Krajete, methanation occurs at 65°C. Electrochaea indicates, however, that the heat of the reaction can be used for heating purposes via a heat exchanger.. The company estimates that the biological methanation process requires service and maintenance costs of about 2 % of the investment cost.

#### 3.3.4 Biological Conversion of Synthesis Gas

No company has been found to offer a system capable of converting carbon monoxide into methane or hydrogen and carbon dioxide.

Lanza Tech, Coskata and INEOS Bio produce ethanol from synthesis gas but none of these companies could offer a system for the conversion of carbon monoxide to carbon dioxide and hydrogen or acetate for further methanation.

#### 4 Case Studies and System Analysis

Below is a description of the studied systems for methanation with figures showing flows of energy that are converted in electrolysis, digestion and methanation. Only the input substrate flow and the outgoing flow of gas, without distinction of incoming electricity or outgoing waste heat and digestate, are shown for the biogas production and upgrading units. A compilation of the conditions for calculations is presented after a review of the various systems. Cost estimates with sensitivity analyses are carried out for catalytic and biological methanation of either raw biogas or pure carbon dioxide flows from an upgrading facility. No schematic diagram of a system for biological conversion of synthesis gas is represented as no company in the current situation offers such a system.

#### 4.1 Catalytic Methanation and Upgrading

For the catalytic methanation, two cases have been studied with different choice of reactors for each of the cases. A system with one or more adiabatic reactors together with an isothermal reactor is reported separately as the heat from the process generates a more high grade flow of heat compared to an isothermal reactor.

Figure 30 corresponds to Sunfire's system for catalytic methanation with an adiabatic and an isothermal reactor. The flow of heat from the methanation process is of high temperature since the temperature of the effluent gas from the adiabatic reactor is high. As seen in the figure, the carbon dioxide in the process originates from an upgrading facility.



Figure 30. Technology from Sunfire.

ETOGAS's technique is shown in Figure 31. Since the methanation takes place in an isothermal reactor, the temperature of the outgoing flow of steam will be lower than for the methanation process presented in Figure 30. The temperature of the isothermal reactor is estimated to be 350 °C (Rieke, 2013).



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Figure 31. ETOGAS's technology for methanation.

The system in Figure 32 differs from the systems presented in Figure 30 and Figure 31 as no separation of carbon dioxide is performed before the biogas is supplied to the reactor. Upgrading of biogas can proceed in both adiabatic and isothermal reactors. Both Sunfire, Haldor Topsøe and ETOGAS have pointed out that they can use their technology for upgrading of biogas directly.



Figure 32. ETOGAS's system for upgrading.

The energy in the flow of biogas consists of methane which means that carbon dioxide does not add any energy. All the carbon dioxide added to the process of methanation is assumed to undergo complete methanation. The manufacturers state that the cost of methanation of a flow of pure carbon dioxide is similar to the cost of catalytic upgrading of a flow of biogas. No impact on investment costs and efficiency have therefore been used in the comparison of the systems. Thus, the catalytic methanation serve as a method for biogas upgrading.

#### 4.2 Biological Methanation and Upgrading

MicrobEnergy's and Krajete's technologies show no differences from a system perspective, both techniques are presented in Figure 33. The efficiency of biological methanation is the same as for catalytic methanation, since both methanation processes undergo, and are limited by, the Sabatier reaction. Unlike the catalytic processes, no steam from cooling is obtained from biological methanation since the temperature in the reactor is around 65 °C.

The archaea that catalyze the reaction obtain energy through methane formation which they use to grow at the same time as heat is emitted into the environment. Data from Krajete states that only 18 % of the constituted hydrogen in the biological methanation reactor is transformed to heat in the process. The conversion of

microbes of carbon dioxide to biomass is thus estimated to occupy 2 % of the energy in the hydrogen.

The amount of substrate supplied to the biogas reactor generates a flow of methane and carbon dioxide equivalent to full utilization of the hydrogen supplied to the methanation reactor. As can be seen in Figure 33 the process generates, in addition to methane, heat and biomass. At biological conversion of hydrogen and carbon dioxide, heat of about 60 °C is obtained. This waste heat can be used for heating a biogas reactor or premises. The methanation reactor in Figure 33 is only supplied with substrates in form of carbon dioxide and hydrogen.



Figure 33. Methanation reactor from MicrobEnergy and Krajete.

The biological methanation may like the catalytic methanation processes be used to upgrade biogas. None of the manufacturers have indicated any problems having the reactor for biological methanation supplied directly with biogas. As shown in Figure 34, the methane production is twice as high if the biogas has 50 percent methane content.





MicrobEnergy states that the content of methane from a biogas reactor can increase from about 50% to 75% upon the addition of hydrogen. A schematic sketch



of how such a system may look like is shown in Figure 35. Hydrogen is supplied in the bottom of the reactor and in addition to methane digestate is also obtained.

Normally, 5% of the energy in the outgoing flow of methane needs to be added to the biogas reactor in the form of heat to maintain the right temperature. To be consistent with previous figures, the flow of hydrogen into the biogas reactor in Figure 34 is the same as in previous examples, which means that the amount of substrate must increase to 1.6 MW for the gas to contain 75% methane. Methanation of hydrogen and carbon dioxide provides 0.13 MW of heat and hence 0.06 MW is used for the internal heating. This means that the biogas plant must be cooled by about 0.07 MW. If the amount of substrate to the reactor is increased to 3.2 MW, the waste heat from the Sabatier reaction corresponds to the heat demand of the biogas reactor. The addition of 3.2 MW substrate reduces the methane content in the effluent gas flow to 63 %.



Figure 35. Schematic sketch of a biogas reactor with hydrogen addition.

#### 4.3 Electricity Prices

The raw material used besides water for electrolysis is electricity. The cost of electricity is more than 100 times higher than the cost of water for hydrogen production. The single largest variable cost of hydrogen production by electrolysis is thus electricity.

The price of electricity is composed of three parts. Approximately 40% of the price of electricity goes to the electricity supplier. Most of this is compensation to the electricity producers. 20 % goes to the electric grid operator and can be seen as a cost for distribution of the electricity. The remaining 40 % is taxes and fees. Since plants for energy production are exempted from energy, carbon dioxide and sulfur taxes, the price of electricity to produce hydrogen and methane primarily consists of electricity grid cost, certificates and energy cost. The cost of an energy certificate was about 0.03 SEK/kWh in 2012.

Electricity trading in the Nordic countries occurs at the market Nord Pool. The prices prevailing at the Nord Pool govern what the end consumer of electricity ultimately pays. Electricity prices vary depending on where in the country you are. Figure 36 shows the areas with different electricity prices that are within Nord Pool's trading area. The price paid at Nord Pool corresponds to the energy cost.



Figure 36. Areas in the Nordic countries with different electricity prices.

In area SE1 corresponding to the northernmost part of Sweden, see Figure 7, the average electricity price in 2012 was more than 7 % lower compared to area SE4, see Table 8. Best conditions for hydrogen production by electrolysis from an electricity cost perspective, therefore, are in the northernmost area SE1.

Hours with the lowest electricity price	1000	2000	3000	4000	5000	6000	7000	8000	8760
SE3, % cheaper than SE4	1,09	2,79	3,33	3,30	3,36	3,56	4,19	5,46	5,55
SE2, % cheaper than SE4	1,09	2,79	3,33	3,32	3,43	3,69	4,44	6,12	7,14
SE1, % cheaper than SE4	0,96	2,73	3,31	3,42	3,57	3,87	4,62	6,32	7,32

Table 8. Electricity price levels in relation to SE4

The average price of electricity in 2012 is shown in Table 9.

#### Table 9. Average electricity prices in 2012

Area	SEK/MWh
SE1	276,7
SE2	277,2
SE3	282,0
SE4	298,5



Figure 37 shows how the hourly price of electricity relates if hourly rates for SE4 are sorted from lowest to highest. The electricity price was below 500 SEK/MWh for the 8000 hours with the lowest price.



Figure 37. Distribution of hourly electricity prices in 2012.

In addition to dependence of regional prices the electricity prices varies during the year. In Figure 38 the hourly electricity prices in 2012 are shown and it shows that the highest electricity prices occur during the winter. A suitable time for maintenance, service and replacement of electrodes was between December and January in 2012.



Figure 38. Variation of electricity prices in 2012.

#### 4.4 Production Costs

This chapter presents the production cost of both hydrogen and methane. The production cost of hydrogen has a big impact on the cost of methane production. The specific hydrogen production cost is therefore first shown in a separate part of this chapter, thereafter the total cost of methanation is calculated. Parameters for calculation of the production costs are presented in Table 10.

Table 1	0. Parameters	used for calculatio	n of the	production	costs
TUDIC I	o. i ulumotoro			production	00010

Parameter	Quantity	Unit
Hours of operation	8600	h
Low-grade heat from the electrolysis,	32	% of input electricity for
70 °C		electrolysis
High-quality heat from the catalysis	12	% of input electricity for
processes, 300 °C		electrolysis
Water price	13,5	SEK/m <sup>3</sup>
Heat price, 70 °C	250	SEK/MWh
Heat price, 300 °C	250	SEK/MWh
Electrolysis efficiency	64,8	%
Efficiency of catalytic and biological	81	%
methanation		
Overall efficiency of electricity to me-	52	%
thane		
Electricity grid price	0,1	SEK/kWh
Electricity price	0,299	SEK/kWh
Electricity certificate	0,031	SEK/kWh
Economic lifetime	15	Year
Cost of capital	5	%
Project costs	10	% of investment cost



Construction costs	10	% of investment cost
Unforeseen costs	10	% of investment cost
Electricity consumption, compressors	0,01	kWh <sub>el</sub> /kWh <sub>methane</sub>
Maintenance and service	3	% of investment cost
Rate of utilization, CO <sub>2</sub>	100	%
Rate of utilization, $H_2$	100	%
Price, CO <sub>2</sub>	0	SEK
Value, O <sub>2</sub>	0	SEK
CO <sub>2</sub> -content in biogas	50	%
Biogas upgrading costs		
200 Nm <sup>3</sup> /h	0,242	SEK/kWh
600 Nm <sup>3</sup> /h	0,126	SEK/kWh
1200 Nm <sup>3</sup> /h	0,09	SEK/kWh
Exchange rate	9	SEK/EUR
	6,5	SEK/USD

#### 4.4.1 Investment Costs

The investment costs when producing hydrogen by electrolysis are shown in Table 11. The cost includes both the cost of connection and design of the facility. Under each manufacturer the production volume is stated. The manufacturers have indicated that electrolysis does not have any major economies of scale in hydrogen production between 400 - 2400 Nm<sup>3</sup>/h. Investment costs for a flow of hydrogen that is twice as large as those given in the table are thus twice as high. For an input flow of carbon dioxide at 100 Nm<sup>3</sup>/h, 400 Nm<sup>3</sup>/h of hydrogen is consumed. Erredue's technology may reach a high hydrogen production but increased operating costs and wear is then needed. This means that the electrolysis can produce flows of hydrogen in the range of 200 to 600 Nm<sup>3</sup>/h.

	Proton-Onsite	NEL	ErreDue
Technique	PEM	Alkaline	Alkaline
Hydrogen flow Nm <sup>3</sup> /h	400	400	200-600
Investment MSEK	26	18	11

The investment costs for a methanation plant, consisting both of electrolysis and methanation, are reported in Table 12. Total costs include construction, connections and design for both electrolysis and methanation. The techniques are compared on the basis of outgoing product gas.

Table 12. Investment co.	st for methanatior	and electrolysis
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	MicrobEnergy	Krajete	Sunfire			ETOGAS		
Nm³/h CH₄	100	300	100	300	600	125	250	625
Investment MSEK	37	84	94	156	214	71	107	226

In this report the total system costs for alkaline electrolysis and methanation for MicrobEnergy, Krajete, Sunfire and ETOGAS are calculated. For the methanation technology Linde has also estimated investment costs for their technique. Linde has submitted a cost estimate for a methanation process consisting of either multiple adiabatic reactors in sequence or alternatively a single isothermal reactor (Stiller, 2013). With the increment for connections and planning, the cost of methanation excluding electrolysis is about 50 million SEK for a flow of 250 Nm<sup>3</sup>/h methane. Linde states no economies of scale for catalysis reactors and a half as large flow may thus mean half the investment cost. A hydrogen production rate of 1,000 Nm<sup>3</sup>/h can be expected to have an investment cost of about 45 million SEK, resulting in a total system cost of 95 million SEK for catalysis reactors and electrolysis units of Linde. It is comparable to ETOGAS's system for 250 Nm<sup>3</sup>/h methane production, which costs about 107 million SEK.

#### 4.4.2 Hydrogen Production

Figure 39 shows the costs of production for 400 Nm<sup>3</sup>/h of hydrogen based on data from manufacturers. From the figure it can be seen that the largest cost for hydrogen production by electrolysis is electricity. The variations in electricity price have a significant impact on the cost of production of hydrogen. The studied manufacturers have production costs between 0.8-0.9 SEK/kWh hydrogen.



Figure 39. Compilation of production costs of hydrogen by electrolysis.

#### 4.4.3 Methane

Production costs are estimated for two different usage areas. First Power-to-Gas is described as a process for methane production of a flow of carbon dioxide from biogas upgrading or another carbon dioxide source. The cost bearing energy is therefore the produced methane from carbon dioxide.

Power-to-Gas can also be used as an upgrading technology for biogas. The carbon dioxide in the biogas is converted to methane, and the methane that is already in the biogas is upgraded to natural gas quality. The cost bearing energy is still the



new methane produced in the methanation process but the production cost can be reduced through the biogas upgrading costs which in any case had charged the biogas.

The production costs in Figure 40 are the actual production costs and do not take sales of the heat generated in electrolysis and through Sabatier reaction into account. The costs have not been reduced with the performed biogas upgrading service.



Figure 40. Production costs of methane without crediting for waste heat recovery and biogas upgrading services.

MicrobEnergy has indicated that their technique does not have any economies of scale so that the production cost is more or less the same regardless of the carbon dioxide flow. Thus MicrobEnergy can be compared to any of the other technologies, regardless of their capacity. The production cost of MicrobEnergy is basically as high for the methanation of carbon dioxide and hydrogen in a separate reactor as for methanation via hydrogen addition to an existing biogas plant. The methanation in a separate reactor results in somewhat higher capital costs that give rise to a difference in the production cost of 0.03 SEK/kWh. The cost presented for MicrobEnergy is the higher cost for methanation of carbon dioxide and hydrogen in a separate reactor.

For other techniques cost calculations have been done for flows of carbon dioxide in the range of 100 to 625 Nm<sup>3</sup>/h, generating a methane flow of the same size. Krajete has reported a price for a flow of carbon dioxide of 300 Nm<sup>3</sup>/h and the production costs of their technology should be seen as relevant only for this production volume.

Furthermore, in the case study analysis Sunfire 100 will not be taken into account since the technology is not considered relevant for small flows of carbon dioxide. As a result of economies of scale the production costs for Sunfire are decreasing with increasing production flows. ETOGAS expects no major economies of scale since the plant is delivered in containers that are added together to give the desired capacity.

If the waste heat from the electrolysis and catalysis reactions is utilized and sold it provides a benefit that reduces the production cost. The effect of crediting sale of heat on the production costs is shown in Figure 41. Since Sunfire uses both an adiabatic and an isothermal methanation reactor, the temperature of the steam from the methanation process is higher than from ETOGAS's isothermal catalytic reactor. The willingness to pay for the steam affects the production cost. The willingness to pay for heat is estimated to be the same regardless of the temperature. A higher willingness to pay for high quality steam would give an advantage to Sunfire's production cost because the steam produced by Sunfire's technology has a temperature around 500 °C compared to steam from ETOGAS's isothermal reactor that has a temperature of 350 °C.



Figure 41. Production costs of methane with credit for waste heat recovery.

If methanation of carbon dioxide is seen as an upgrading technique for biogas, the upgrading of methane gives a reduced production cost corresponding to the willingness to pay for upgrading services. The willingness to pay will depend on the magnitude of the biogas flow and decreases with higher production due to economies of scale in conventional upgrading. A compilation of the various production costs with and without the sale of heat and upgrading services is shown in Figure 42. The reduced upgrading cost is based on biogas containing 50 % methane and 50 % carbon dioxide.



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Figure 42. Production costs of methane with credit for waste heat recovery and upgrading services.

#### 4.4.4 Sensitivity Analyses

Sensitivity analyses are based on a basic assumption that the production cost can be credited for sale of heat and upgrading services. The production costs of methane are thus in the range of 1.0 to 1.3 SEK/kWh as a starting point. In the following charts, the default values from Table 10 are marked with a dashed line.

Figure 43 shows how the production cost of methanation depends on operation time and electricity price. The electricity price has been arranged in the same manner as in Figure 37, that is, methanation is running from the cheapest to the most expensive hours during the year. This means that at the time of 8760 hours the process operates all hours of the year while 8500 means that the 260 most expensive hours are avoided. As seen in the figure, the costs decline for all techniques until about 8500 hours. The fact that the production costs decrease even while the electricity price increases is due to the high capital costs. Less hours of operation produces less energy, which in turn leads to increased capital costs per unit of energy. The catalytic processes have higher capital costs than the biological processes allowing optimum operating at around 8600 hours for catalytic processes.



Figure 43. Impact of operating hours on methane production costs.

Crediting sales of heat and its effect on production costs is shown in Figure 44. A higher willingness to pay for the heat results in lower production costs.



Figure 44. Production costs and their dependence of price of heat.

Figure 45 shows a sensitivity analysis of the impact of investment costs on production costs. The catalytic processes have higher capital costs, so they are more affected by changes in capital costs compared to the biological processes. Today the investment costs are high due to the fact that methanation yet only is demonstrated on a few sites. With increased demand, technical maturity and competition, the investment costs are expected to fall in the future.



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Figure 45. Impact of investment costs on the production costs of methane.

Production costs depending on prices on energy and electricity certificates are shown in Figure 46. Production costs of methane are all calculated with 65 % electrolysis efficiency, which means that all providers are affected by higher electricity prices in the same way.



Figure 46. Impact of electricity price on the production costs of methane.

Figure 47 shows how the efficiency of the electrolysis affects production costs for methane. An improved electrolysis with higher efficiency results in lower production costs.



Figure 47. Impact of electrolysis efficiency on the production costs of methane.

Figure 48 shows how the cost of methanation decreases if credit is given for upgrading services, which nevertheless had been needed for the removal of carbon dioxide. A high alternative cost for biogas upgrading provides lower cost for methanation.



Figure 48. Impact of willingness to pay for upgrading services on production costs of methane.

Figure 49 shows the impact of the cost for the electrical grid on production costs. If electricity generated by own power can be used so that the electrical grid cost is zero, the cost of methane production is reduced by about 0.2 SEK/kWh.



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Figure 49. Impact of electricity grid price on the cost of production of methane.

#### 5 Discussion and Conclusions

The efficiency of the entire system for methanation of carbon dioxide and hydrogen to methane depends on the efficiency of the electrolysis cells and the methanation reactor. Since the efficiency of the Sabatier reaction cannot be affected, only the efficiency of the electrolysis may affect the total overall efficiency. For alkaline and PEM electrolysis, the efficiency can be expected to increase by future improvements of the technologies. An increased efficiency in the production of hydrogen by use of SOEC could increase the efficiency up to 90%. The overall efficiency would then increase from 50 to 70%. If a SOEC is used instead of a PEM or alkaline electrolysis, the high grade heat from the methanation process will be consumed in the degradation of water. Therefore high grade heat cannot be disposed if a SOEC is used. The heat balance for methanation combined with a SOEC is not investigated in this report. In order to compare heating costs and heat revenue for a system with alkaline or PEM electrolysis, this issue requires to be further investigated.

Catalytic methanation processes could be integrated with power plants in two ways. First, the high grade steam obtained by cooling the gas and the reactors can be integrated with the existing steam system of a power plant. It would also be possible to use electricity directly from the power plant without intermediate electricity grid costs. If the cost of the electricity grid can be avoided, the production cost of methane will decrease with 0.2 SEK/kWh.

A system based on biological methanation can be integrated to heat a biogas reactor. The heat from the cooling of the electrolysis and the separate methanation reactor can be used to heat the biogas reactor. A biogas plant that currently heats the digester with the methane produced can then increase the production of methane by using waste heat from the process. If hydrogen is added to an existing reactor, the increased production of methane partially can be attributed to the Sabatier reaction that releases heat (it is also possible to go through acetate formation). Addition of hydrogen to existing reactors therefore seems to be a way to heat biogas plants.

If the electrolysis process can be adapted in such a way that production of hydrogen temporarily increases at low electricity prices, production costs may decrease as the average price of electricity is lower. However, an additional cost for storage of hydrogen will be necessary. The investment cost for production of hydrogen can also be reduced if larger plants are developed with greater economies of scale than today.

Improvements in catalysis reactors can also result in lower costs. By improving and developing cooling of isothermal reactors, smaller catalytic reactors can be used generating lower costs.

The biological methanation reactors produced today use mechanical agitation to increase the solubility of hydrogen. There seems to be a potential for development of the design of reactors so that mechanical agitation is not needed to the same extent as today. By having vertical reactors or by supplying the gas into smaller bubbles, a higher contact surface per volume unit would be reached. Another way is if the archaea can operate under higher pressures. Higher pressures increase the solubility of hydrogen and are also thermodynamically favorable in the formation of methane.



During the electrolysis half as much oxygen as hydrogen is formed, based on volume. This oxygen can be sold for industrial use but can also be used in water treatment plants, which today normally use air to bring oxygen into their treatment basins. By replacing the air with oxygen, the cost for the work of the compressor can be reduced. A supplier of electrolysis has proposed that investments in electrolysis can be partly financed by a company that sells oxygen. The Swedish gas supplier AGA has stated that one can contact the company for discussion about oxygen sales when designing a Power-to-Gas facility.

Crediting of biogas upgrading services reduces the production costs and biogas would have been upgraded in any case. Since upgrading has large economies of scale, low biogas flows will be most credited. Sewage treatment plants with too small biogas production for feasible upgrading of biogas with conventional technique can with Power-to-Gas double its production of methane. As the conventional upgrading technologies have a high cost for small plants Power-to-Gas technology would also be interesting for smaller plants.

If more Power-to-Gas plants become operational, investment costs may decrease. That would make the cost of capital as a share of the total production cost decrease in relation to the impact of the electricity price. With the calculation parameters used in this study, the optimal operating time is 8500-8600 hours per year. In the future, a lower investment cost and more volatile electricity prices could reduce the optimal operating time. The assumption is based on the fact that the plant is operating at the hours with the cheapest electricity prices during the year. Investment costs of electrolysis and methanation reactors and electricity prices today do not make it economically feasible to use the Power-to-Gas technique to balance the electricity market, since the produced methane will be too expensive to be able to compete with other alternatives such as natural gas. In order to use the system to balance the electricity market, a grant to compensate for the high cost of production would be needed. The reason that the plant requires many hours is mainly due to the fact that the cost of capital rises with reduced number of hours, while the sold amount of methane decreases. It is not probable that future periods of low electricity prices would be long enough to compensate for the high capital costs and low production volume of methane, which is a result of a temporary operation at low electricity prices. This conclusion is also supported in the Danish study ForskNG 2011 Project no. 10677 which concludes that a combined SOEC and catalytic methanation has an optimal operational time of over 7000 hours.

This study thus shows that Power-to-Gas primarily is a technique for the production of renewable methane for use in, for example, vehicles. To balance the electricity market, where the produced methane is subsequently used for the production of electricity at high electricity prices, the technology does not appear to be competitive for Swedish conditions.

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