

# METHANATION

## Technical Fundamentals and Market Overview



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gasunite  
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GasTerra

DNV·GL

## METHANATION – Technical Fundamentals and Market Overview

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*GasTerra is a wholesaler. It buys gas from domestic and foreign producers and in the open gas market. Its customer base consists of energy companies, industry and other large customers.*

*Gasunie is an energy network operator. It manages and maintains the infrastructure for large-scale transport and storage of gas in the Netherlands and the north of Germany.*

*Both companies are active in the field of energy transition, specifically supporting the shift from natural gas to renewable gases.*

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## FOREWORD

We hold the view that gas produced from sustainable sources has an important role to play in decarbonising the energy system in the lead-up to the middle of the century. Whether it is biomethane produced from biomass gasification, hydrogen produced by electrolysing renewable power or biomethane from anaerobic digestion, the gas infrastructure is ready for it. However, meeting our sustainability goals will require more gas input if we are to deliver this to households and industries in large volumes.

Methanation is a crucial technology as the last step in the value chain from renewable sources to grid-injected biomethane. With Europe as frontrunner in introducing renewable gases into the market, there have been recent significant advances in developing almost market-ready or market-ready methanation systems. Several experimental and demonstration gasification installations are already in operation today. New opportunities also arise from developments in Power-to-Hydrogen and from initiatives to improve the biomethane production of anaerobic digestion plants.

We believe that it is important for biomethane to become available as quickly as possible in a reliable, affordable and socially responsible manner. Consequently, cooperation, sharing knowledge and starting up joint innovation projects are fundamental to the ambition to produce and supply biomethane more economically and on a large scale. Supporting technology development in renewable gas production by sharing valuable market and technological knowledge has been the driver underpinning Gasunie and GasTerra's request to DNV GL to produce this report on methanation technologies.

The aim of this document is to provide project developers, technological innovators and operators of anaerobic digestion and gasification plants with theoretical, operational and commercial information on methanation technology and systems. This document provides an overview of basic methanation principles and discusses the relevant technical aspects of methanation systems. We trust that this document, together with the manufacturer-specific fact sheets, proves valuable to many industry players.

The study is based on available public sources and detailed feedback from project owners and technology suppliers and is specifically focused on the production of grid-injected biomethane. Other possible applications of biogas, such as cogeneration or combined heat and power (CHP), are outside the scope of this project.

Our aspirations for this report are to provide the insights and knowledge that will enable you to accelerate the energy transition. We hope that you will enjoy reading our report.

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## LIST OF ABBREVIATIONS

Abbreviation	Description
Al <sub>2</sub> O <sub>3</sub>	Aluminium oxide
C	Carbon
CeO <sub>2</sub>	Cerium (IV) oxide
CH <sub>4</sub>	Methane
CO	Carbon monoxide
Co	Cobalt
CO <sub>2</sub>	Carbon dioxide
COS	Carbonyl sulphide
CO <sub>x</sub>	Carbon oxides
C <sub>p</sub>	Specific heat capacity
C <sub>x</sub> H <sub>N</sub>	Hydrocarbons
Fe	Iron
GJ	Gigajoule (10 <sup>9</sup> Joule)
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
H <sub>2</sub> S	Hydrogen sulphide
Ir	Iridium
kWh	Kilowatt hour
MJ	Megajoule (10 <sup>6</sup> Joule)
N <sub>2</sub>	Nitrogen
NH <sub>3</sub>	Ammonia
Ni	Nickel
O <sub>2</sub>	Oxygen
P2G	Power-to-Gas
Pd	Palladium
Pt	Platinum
Rh	Rhodium
Ru	Ruthenium
SiO <sub>2</sub>	Silicon dioxide
SNG	Synthetic Natural Gas, i.e. a natural-gas substitute of synthetic origin
TiO <sub>2</sub>	Titanium oxide
TRL	Technology Readiness Level
ZrO <sub>2</sub>	Zirconium oxide
ΔH	Heat of generation or enthalpy

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# 1 INTRODUCTION

Over the next three decades, our energy system will undergo a transition towards a less carbon-intensive and more sustainable system with a rapid growth of renewable energy resources. These renewable sources, which differ from fossil energy sources because of their low cyclic carbon emissions, can be divided roughly into the following categories:

- Wind, solar and hydro energy sources, to be converted into electric power with electrolysis;
- Dry biomass, from which syngas, mainly consisting of hydrogen, carbon monoxide and carbon dioxide, can be produced with gasification;
- Wet biomass, from which biomethane can be produced with a fermentation process or syngas with gasification.

One of the greatest challenges of the future sustainable energy system is to match supply and demand. Wind and solar power production in particular are subject to strong natural fluctuations in their availability. Due to the intermittent character of sustainable power production, excess electricity produced at some point must be stored to ensure an uninterrupted power supply at another other time. Many countries, rather than storing electricity, consider converting power into hydrogen a promising option due to the availability of an extensive natural-gas infrastructure with a large storage capability

The physical properties of syngas and hydrogen differ from those of natural gas to such an extent that direct injection into the public-gas grid or use in gas appliances is not permitted. Consequently, conversion into methane has to be considered. The process of converting hydrogen or syngas into gas-grid quality methane is called methanation.

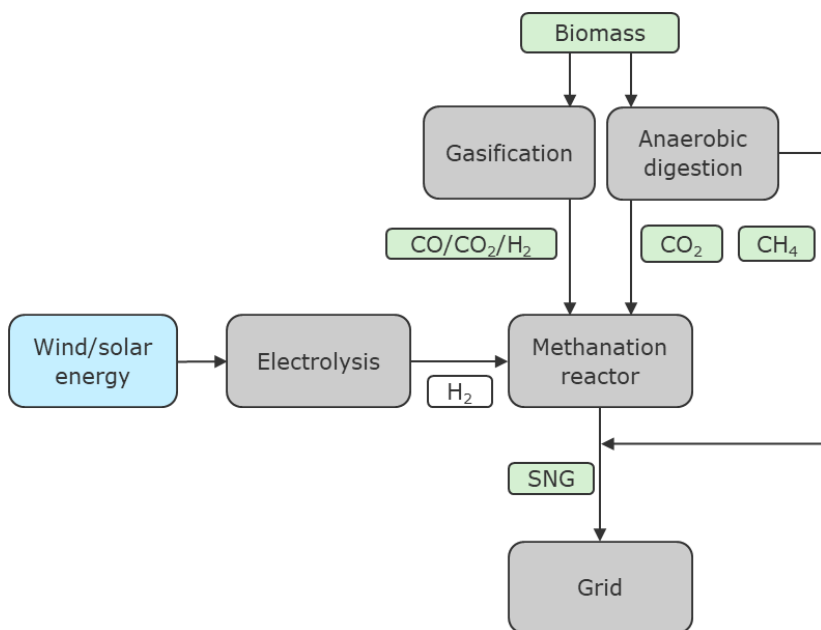
Methane production from syngas draws on more than 100 years of research and process development. Recently, there has been a great deal of progress in developing various gasification and methanation technologies. Biomethane can make an important contribution to the success of the energy transition in the future. Technology developers have arrived at a point where a number of suitable methanation techniques is more or less market ready.

## 1.1 Report structure

Chapter 2 provides a brief description of the production processes that deliver feed gas to the methanation systems. Exit specifications for feeding gas into the grid are also discussed. Chapter 3 discusses the various methanation techniques in more detail. Chapter 4 contains additional, more detailed information from project operators and technology suppliers that were added to the shortlist. Finally, Chapter 5 summarises the findings and relevant topics that must be addressed when selecting suitable methanation techniques.

## 2 UNDERSTANDING THE RENEWABLE GAS VALUE CHAIN

Figure 1 shows a schematic representation of methanation's place in the sustainable value chain. Inputs are the different renewable sources, e.g. biomass, wind or solar. The output is biomethane that can be fed into the gas grid.



**Figure 1: Methanation in the sustainable gas value chain**

In order to understand the applicability of the various methanation techniques in specific situations, it is key to have detailed insight into the different biogas or syngas production processes. This Chapter describes those processes, as well as process conditions and output gas quality (feed gas for the methanation processes). As this study focused on biomethane introduction into the Dutch gas transmission and distribution systems, the gas-quality specifications for feeding biomethane into the Dutch gas grid are provided.

### 2.1 Gasification

Gasification of biomass is a process that converts biomass into syngas, which mainly contains carbon monoxide, hydrogen and carbon dioxide. This is achieved by having the biomass react at high temperatures (typically >700 °C), with steam, carbon dioxide or oxygen (partial combustion). The resulting gas mixture is called syngas, which is also known as synthesis gas.

## 2.1.1 Reaction process steps

Several equilibrium reactions occur in the gasification process and are listed below.

<b>1.Primary devolatilization (pyrolysis)</b>			
Primary tar (CH <sub>x</sub> O <sub>y</sub> ) (vapor)			
Biomass → CO, H <sub>2</sub> , CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , H <sub>2</sub> O (gas)		[eq.1]	
char (solid)			
<b>2.Tar cracking and reforming</b>			
Secondary tar			
Primary tar → CO, CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , H <sub>2</sub>		[eq. 2]	
<b>3.Homogenous gas-phase-reactions    ΔH</b>			
Secondary tars → C, CO, H <sub>2</sub>		[eq. 3]	
H <sub>2</sub> + 0,5 O <sub>2</sub> → H <sub>2</sub> O	-242 kJ/mol	[eq. 4]	H <sub>2</sub> – Combustion (oxidation)
CO + 0,5 O <sub>2</sub> → CO <sub>2</sub>	-283 kJ/mol	[eq. 5]	CO - Combustion (oxidation)
CH <sub>4</sub> + 0,5 O <sub>2</sub> → CO + 2 H <sub>2</sub>	-110 kJ/mol	[eq. 6]	CH <sub>4</sub> - Combustion (oxidation)
CH <sub>4</sub> + CO <sub>2</sub> → 2 CO + 2 H <sub>2</sub>	+247 kJ/mol	[eq. 7]	Dry reforming methanation
CH <sub>4</sub> + H <sub>2</sub> O → CO + 3 H <sub>2</sub>	+206 kJ/mol	[eq. 8]	Steam reforming methanation
CO + H <sub>2</sub> O → CO <sub>2</sub> + H <sub>2</sub>	-40,9 kJ/mol	[eq. 9]	Water-gas-shift reaction
<b>4.Heterogenous reactions</b>			
C(s) + O <sub>2</sub> → CO <sub>2</sub>	-393,5 kJ/mol	[eq. 10]	Oxidation of carbon
C(s) + 0,5 O <sub>2</sub> → CO	-123,1 kJ/mol	[eq. 11]	Partial oxidation
C(s) + CO <sub>2</sub> → 2 CO	+159,9 kJ/mol	[eq. 12]	Boudouard reaction
C(s) + H <sub>2</sub> O → CO + H <sub>2</sub>	+118,5 kJ/mol	[eq. 13]	Water-gas reaction (steam reforming)
C(s) + 2 H <sub>2</sub> → CH <sub>4</sub>	-87,5 kJ/mol	[eq. 14]	Methane production reaction

### Process parameters and their effect on the composition of the syngas mixture

Gasification temperature increment leads to an increase in reaction rates. In general, high temperatures promote endothermic reactions, such as eq. 7, 8, 12 and 13. This results in higher hydrogen concentrations and lower methane concentrations. Furthermore, higher temperatures increase the conversion efficiency and reduce the production of tar. Tars are viscous organic compounds, which condense at a broad temperature range, that can cause serious contamination in the downstream equipment. In essence, if a syngas contains methane it will also have various tar (C<sub>x</sub>H<sub>y</sub>) components.

Higher gasification pressure produces a shift in equilibrium reactions to the side with a lower gas volume (Le Chatelier's principle). This means that eq. 6, 7 and 8 will shift to the left, thus increasing the methane yield in the syngas production.

Possible gasification agents are air, steam or pure oxygen. If air is used as gasification agent, the gas mixture will contain a significant fraction of nitrogen gas, which dilutes the gas and consequently reduces its heating value. The use of pure oxygen generates syngas with a high heating value and allows for smaller reactor sizes. However, this requires the availability of pure oxygen, generated by an air-separation unit or stemming from an electrolysis unit that converts water into hydrogen and oxygen. If steam is used in the gasification reaction, eq. 8, 9 and 13 will shift to the right, thus increasing the hydrogen yield. By varying the steam/oxygen ratio, the final hydrogen/carbon monoxide ratio can be controlled.

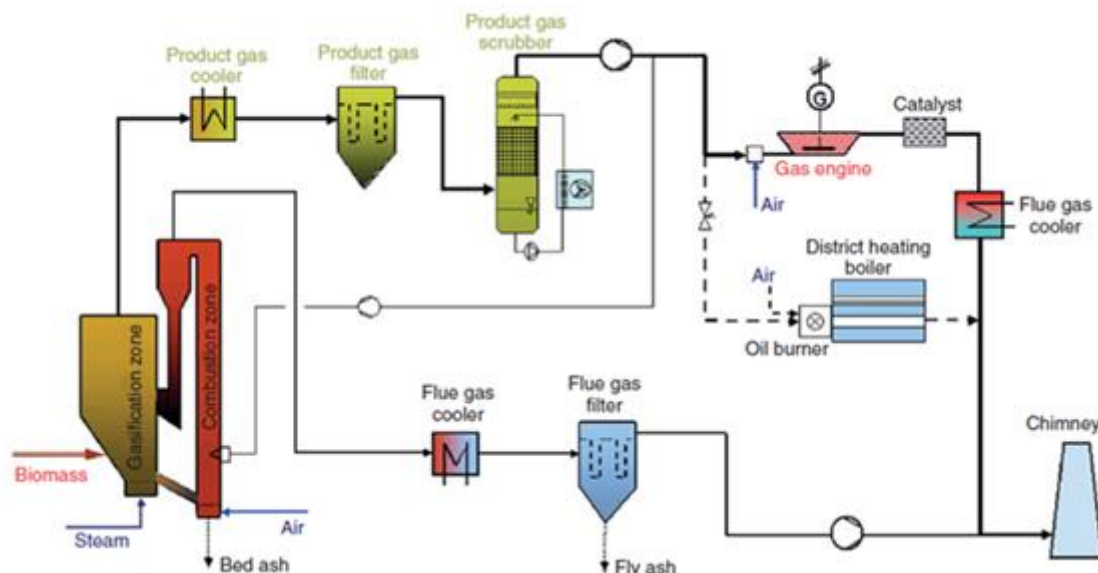
Gasification at a higher pressure enhances methane formation in the gasification process and reduces equipment size but will require narrower feedstock specifications and more complex biomass-dosing systems. It will also require equipment in the downstream process to be pressure resistant.

For the application of downstream methane production from the produced syngas, gasification in (nearly) pure oxygen has significant advantages with regards to the amount of syngas that must be produced and handled and in the downstream purification steps that must be performed to meet feed-in specifications. Possible gasification reactors are fixed bed, fluidised bed and entrained flow reactors. As each type of reactor requires its own specific reaction conditions, the choice of gasifier has an impact on the syngas mixture. Fixed and fluidised bed systems are usually medium-temperature systems, whereas entrained flow gasifiers are high-temperature systems. The operational temperature is a trade-off between the applied fuel, gasification medium, fuel conversion and cold gas efficiency. Biomass can either be wet or dry, which determines the initial amount of water in the system. An excess of water may shift the equilibrium reactions 8, 9 and 13 to the right, thus increasing the hydrogen yield. Depending on the process lay-out, the biomass may require additional pre-treatment, such as drying, milling, and/or pressurisation.

Biomass feedstock will always contain impurities such as nitrogen, sulphur, chlorine, trace elements and ash. These elements will remain in the gas mixture e.g. as hydrogen sulphide (H<sub>2</sub>S), carbonyl sulphide (COS), hydrogen chloride (HCl), dust, ammonia (NH<sub>3</sub>), etc. Suitable gas-cleaning systems must be used in function of the concentrations of such impurities and the feed-in specifications of the downstream methanation process.

### 2.1.2 Process chain

As an example, figure 2 shows the layout of the Güssing gasification plant, where biomass is gasified with steam. After purification, the syngas is combusted in a gas engine. [1]



**Figure 2: Layout of Güssing gasification plant, where biomass is gasified with steam, producing syngas, which is cleaned and then used in a gas engine. [1]**

Figure 3 shows the process chain of biomass gasification and cleaning of syngas. Each of the steps in the gasification process chain will be discussed below.



**Figure 3: Process chain of the overall gasification of biomass and cleaning of syngas.**

### **Biomass preparation**

In order to prepare the biomass for the gasification process, the biomass feedstock generally needs to be dried (typically to 10-15 vol% of water content) and granulated into particle sizes that fit the requirements of the gasifier dosing equipment. Impurities, such as stones or metal particles, should be removed. Removal technologies are cyclones, electrostatic or barrier filters, and scrubbers. Each type of biomass feedstock or subsequent gasification process may require specific pretreatment steps, enabling storage of the biomass and dosing it into the gasification system.

### **Biomass gasification**

Gasification is the full thermal breakdown of biomass into combustible gas, volatiles, tar and ash in an enclosed reactor (gasifier) in the presence of any externally supplied oxidising agent, such as air, oxygen, steam hydrogen, carbon oxides, etc.

Gasification is carried out in several steps. During the first pyrolysis step, 70-80% of the biomass weight is vaporised at temperatures below 600 °C without the assistance of oxidising agents. Tar and ash are non-volatile by-products of the pyrolysis process.

During the next step, the reaction products of the previous steps are gasified in a reaction with oxidising agents, such as air, pure oxygen, steam, hydrogen, carbon dioxide, etc. at high temperatures. When syngas is used for methanation, pure oxygen is the preferred gasification agent.

### **Syngas production**

The main syngas components are carbon monoxide, hydrogen and carbon dioxide. However, during a number of complex equilibrium reactions other products, such as methane and light hydrocarbons, are also produced. Depending on the process conditions and the quality of the biomass, the syngas mixture may also contain inert gases, such as nitrogen and water, and impurities, such as ash, tar, dust, bed material, alkali salts, sulphur (e.g. COS, H<sub>2</sub>S), nitrogen (e.g. NH<sub>3</sub>, HCN) and halogen compounds. In general, methane is considered to be an inert gas in syngas. However, if the syngas is used in the methanation process, the concentration of methane is beneficial to the overall methane yield but might enhance tar issue formation.

### **Cleaning syngas**

Syngas should always be cleaned to prevent corrosion, erosion and deposits in the system. Furthermore, it is important to prevent poisoning of downstream processes, such as the methanation catalyst. After leaving the gasifier, hot syngas is cooled first - usually to temperatures around 200 to 400 °C. The released heat can be captured in a heat exchanger and can be used for one of the heating steps to improve overall energy efficiency or for other purposes. Subsequently, dust can be removed with a filter. Sulphur and nitrogen compounds may also cause poisoning of the downstream methanation catalyst and are usually removed in wet scrubbing processes. Tar must be removed, as it can condense on the surface of heat exchangers or it may block filters. It is possible to scrub tar from syngas with organic liquids for instance.

Tar is usually removed by cooling down the gas and performing a gas wash or through condensation in a wet electro-filter.

If the cleaned syngas is to be used in the downstream methanation process, it must meet the specifications determined by the applied catalyst and other downstream equipment; see Chapter 3.1.

## 2.2 Digestion

Biomethane can be produced from wet biomass - e.g. manure, energy crops and domestic organic waste - with anaerobic digestion. Depending on the type of biomass and operating conditions, the produced biogas contains 40-50% carbon dioxide, 0.1-1% hydrogen sulphide and several trace components [2]. To meet the grid code specifications as described in table 1, the carbon dioxide content should be reduced to concentrations below 10.3%. This takes place in a so-called upgrading plant where - depending on the gas quality and the used upgrading process - trace components are also removed. In most of the current situations, there is no use for the excess carbon dioxide and therefore it is vented into the air. If that carbon dioxide is to be used as a source of carbon in the methanation process, it has to be checked for other components that could affect the methanation process. Currently, there are six upgrading techniques are in use. [3]:

- **Pressure swing adsorption (PSA)** With this technique, carbon dioxide is separated from biogas with adsorption under elevated pressure. The adsorbing material, usually activated carbon or zeolites, is regenerated by a stepwise pressure-drop before the column is reloaded again. If hydrogen sulphide or halogens are present in the biogas, these components will be adsorbed irreversibly on the adsorbing material. Therefore, hydrogen sulphide and halogens must be removed before the gas enters the PSA column.
- **Membranes** Dry membranes for biogas upgrading are made of materials that are permeable to carbon dioxide, water and ammonia. Hydrogen sulphide and oxygen permeate through the membrane to some extent, while nitrogen and methane hardly pass at all. Membranes are usually bundled into hollow fibres. The process is often performed in two stages. Before entering the hollow fibres, the gas passes through a filter that retains water and oil droplets and aerosols, which would otherwise have a negative impact on membrane performance. Usually and in addition, hydrogen sulphide is removed before entering the membrane section.
- **Chemical scrubbing** Chemical scrubbers use amine solutions. Carbon dioxide is not only absorbed into the liquid, but it also reacts chemically with the amine in the liquid. As the chemical reaction is highly selective, the methane loss might be as low as <0.1%. However, part of the liquid is lost due to evaporation and must be replaced. The liquid to which carbon dioxide is chemically bound is regenerated by heating. If hydrogen sulphide is present in the raw gas, it will be absorbed in the amine scrubber solution and higher temperatures will be required for the regeneration. Therefore, it is removed before absorption in the amine scrubber.
- **Water scrubbing** Carbon dioxide has a higher solubility in water than methane. Therefore, carbon dioxide will dissolve to a higher extent than methane, particularly at lower temperatures. In the scrubber column, carbon dioxide is dissolved in water, while the methane concentration in the gas phase increases. Consequently, the gas leaving the scrubber has an increased methane concentration. The water leaving the absorption column is transferred into a flash tank where the dissolved gas, which contains some methane but mainly carbon dioxide, is released and transferred back to the gas inlet. If the water is to be recycled, it is transferred to a desorption column filled with plastic packing, where it meets a counter flow of air, into which carbon dioxide will be released. Other components that are soluble in water may be present in the carbon dioxide. In most cases, a bio trickling filter is used to avoid emission of these components into the air.

- **Organic physical scrubbing** Organic physical scrubbing is very similar to water scrubbing, with the important difference that the carbon dioxide is absorbed in an organic solvent, such as polyethylene glycol. Carbon dioxide is more soluble in polyethylene glycol than in water and with the same upgrading capacity it is possible to reduce the flow of the liquid phase and limit plant size at the same time. The polyethylene glycol solution is regenerated by heating and/or depressurisation. Hydrogen sulphide, water, oxygen and nitrogen may be removed together with carbon dioxide. However, more often such components are removed prior to upgrading.
- **Cryogenic separation** Cryogenic upgrading relies on low temperatures to perform a physical separation of the carbon dioxide from the biogas. Carbon dioxide is frosted or liquefied as the gas passes through a heat exchanger at temperatures between  $-90\text{ }^{\circ}\text{C}$  and  $-120\text{ }^{\circ}\text{C}$ . This makes it possible to reach the methane purity level required for liquefaction for example. The process is based on the physical properties of the gas components, and consequently achieves extremely pure carbon dioxide and further purification is not necessary.

As described before, trace components are only removed to a certain level by using the various technologies. Whether this would suffice is something that should be tested. Therefore, it is necessary to consider gas quality in more detail to determine whether additional purification would be required.

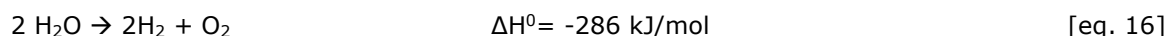
## 2.3 Electrolysis

When more intermittent sustainable sources of energy are used, balancing supply and demand will become increasingly difficult. Power-to-Gas (P2G) is a technology that allows flexible operation and buffering of an electricity surplus in the short and long term by storing electricity indirectly in the gas grid.


Renewable electricity is used to split water molecules into hydrogen and oxygen. The electrolysis cell consists of a (positive) anode, where oxygen production takes place, and a (negative) cathode, where hydrogen is formed. The chemical partial reactions of the conversion of electricity into hydrogen and oxygen are set out in equation 15.



The net or overall reaction of the electrolysis process is an exothermic process that releases 286 kJ/mol of heat:



Hydrogen production with electrolysis is carried out with an alkaline, proton exchange membrane and solid oxide methodologies. The materials used and the advantages and disadvantages of each methodology are discussed in [4]. After leaving the electrolyser stack, the hydrogen is dried by using a pressure swing adsorber (PSA). Depending on the design of the stack and dryer, the hydrogen discharge pressure ranges between 8 and 30 bar. The obtained hydrogen quality exceeds 99.99 mole% pure. Gas composition measurements carried out by DNV GL demonstrated that, apart from hydrogen, only water and oxygen



were present at sub-ppmV levels<sup>1</sup>. Occasionally some ppmVs of carbon dioxide were also measured, which is most probably caused by carbon dioxide dissolved in water. Generally, it can be concluded that the detected contaminations (water, oxygen and carbon dioxide) in the produced hydrogen will not lead to problems in the further process.

## 2.4 Grid feed-in specifications

Carbon oxides are used to make biomethane from syngas or hydrogen. To be able to feed this biomethane into the public gas grid, it must comply with the feed-in specifications of the grid. The gas quality specifications for the Dutch gas grid are described in the "Regeling Gaskwaliteit (2018)". [5] This document distinguishes between entry and exit point gas specifications, and between low calorific gas (G-Gas, W= 43.5-44.4 MJ/m<sup>3</sup>(n)) and high calorific gas (H-Gas, W=49.9-55.7 MJ/m<sup>3</sup>(n)). The specifications are summarised in Appendix A.

Meeting the specifications, as described in the table, requires defining a set of preconditions that must be considered when engineering the methanation system and the gas-production plant. The most important aspects are:

- The maximum permissible hydrogen and carbon monoxide concentrations are low. Compliance requires the chemical efficiency of the methanation process to be close to 100%. Syngas from gasification systems generally contains excess carbon monoxide and carbon dioxide, making it necessary to remove all or part of these components following methanation.
- Nitrogen is not involved in the methanation process. As nitrogen cannot be removed from the gas without removing methane, it is important that nitrogen levels of the feed gas for the methanation process are not too high, so that the produced gas stays below the lower limit of the G-gas Wobbe-index. Consequently, the use of air, which contains approximately 80% nitrogen, is restricted in the gasification process. Meeting H-gas specifications requires the use of only pure oxygen or steam in the gasification process.
- Depending on the chosen methanation technique, trace components such as sulphur, chlorine and fluorine may have a negative effect on the process and should be removed from the gas before entering the methanation process; see Chapter 3. Therefore, meeting the entry specifications for these components is not expected to lead to major modifications of the plant.

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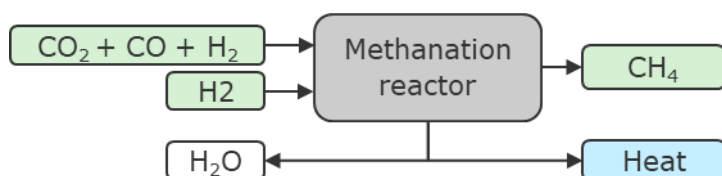
<sup>1</sup> These measurements were carried out for third parties. Therefore, no references are mentioned.

## 3 BASICS OF METHANATION TECHNOLOGIES

This Chapter provides a more detailed explanation of chemical and biological methanation technologies.

### 3.1 Chemical methanation

Chemical methanation is the thermochemical conversion of carbon monoxide and/or carbon dioxide with hydrogen into methane with the aid of a catalyst. It is a mature technology that is available in the market commercially. The main challenge is handling the enormous heat release. This imposes high requirements on the design of the catalyst, the reactor system and the degree of heat integration.



**Figure 4: Schematic representation of a methanation process where syngas is converted into methane.**

#### 3.1.1 Reaction kinetics

Starting with syngas, the reactants consist of carbon monoxide and carbon dioxide. The reactions are given below. In this mixture, methanation of carbon monoxide is found to surpass that of carbon dioxide.

**1. Methanation of carbon monoxide (cat=catalyst):**

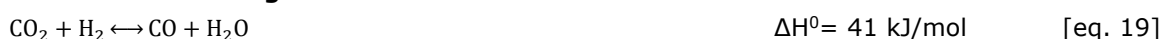


**2. Methanation of carbon dioxide:**



These two reactions are closely related to the reverse water-gas shift reaction.

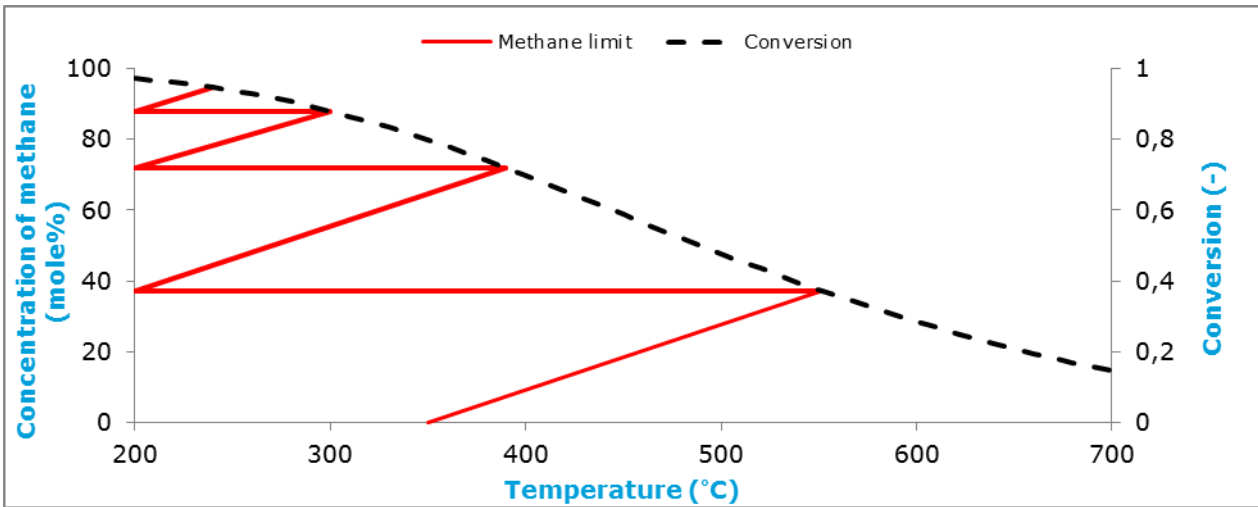
**3. Reverse water-gas-shift reaction:**



The reaction kinetics are highly dependent on temperature and pressure. In general, methanation takes place between 250-550°C and is enhanced at higher pressures.

As the formation of methane is based on equilibrium reactions, several steps are required to achieve full conversion into methane. It is preferable for the formed water to be removed after every step to prevent the equations shifting (back) to the left.

At low temperatures (200-300 °C), the product stream contains mostly methane and water. With rising temperatures, the product stream contains more carbon oxides and hydrogen. When the temperature exceeds 600 °C, methane conversion decreases and more tar is produced. [7] As methanation reactions are exothermic, good temperature control is required in the reactor to prevent thermodynamic limitations and catalyst sintering (compacting and forming a solid mass of material by heat or pressure without melting it to the point of liquefaction). The released heat can be re-used in one of the other process steps, increasing the overall energy efficiency.



**Figure 5: Example of the methane concentration as a function of temperature**



It is assumed that the heterogeneous, catalytic reactions (eq. 17-18) take place in accordance with the Langmuir-Hinshelwood (HS) principle, where the reactions take place between adsorbed active particles [8]. The reaction mechanism for this gas reaction is described in the reaction equations 20-24, where CAT is the catalyst surface.

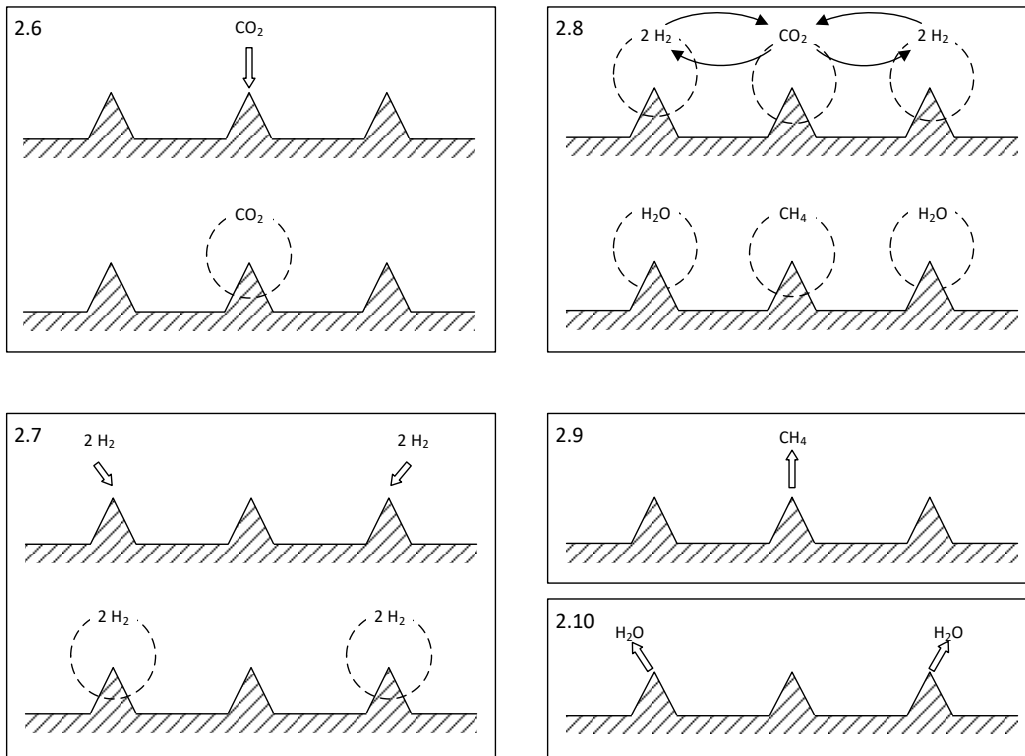
$\text{CO}_x + \rightleftharpoons \text{CAT} \leftrightarrow \text{CO}_x \cdot \text{CAT}$	<b>(Adsorption)</b>	[eq. 20]
$4\text{H}_2 + 4\text{CAT} \leftrightarrow 4\text{H}_2 \cdot \text{CAT}$	<b>(Adsorption)</b>	[eq. 21]
$\text{CO}_x \cdot \text{CAT}_{(\text{ads})} + 4\text{H}_2 \cdot \text{CAT} \leftrightarrow \text{CH}_4 \cdot \text{CAT} + x\text{H}_2\text{O} \cdot \text{CAT} + 2\text{CAT}$	<b>(Surface reaction)</b>	[eq. 22]
$\text{CH}_4 \cdot \text{CAT} \leftrightarrow \text{CH}_4 + \text{CAT}$	<b>(Desorption)</b>	[eq. 23]
$2\text{H}_2\text{O} \cdot \text{CAT} \leftrightarrow 2\text{H}_2\text{O} + 2\text{CAT}$	<b>(Desorption)</b>	[eq. 24]

The reactants (carbon oxides and hydrogen) will adsorb to the catalyst surface (eq. 20-21). This is where the reaction takes place between the adsorbed reactants, which means the reaction products (methane and water) are formed until a balance has been reached (eq. 22). The affinity of the formed reaction products with the catalyst material is less than that of the reactants, which means that they will desorb, as represented in eq. 23-24. [9]

At the start the equilibrium eq. 22 will shift from left to right due to the absence of methane and water, in other words the reactants (carbon oxides and hydrogen) react to methane and water. As the concentrations of methane and water increase, the reverse reactions will also take place more frequently, which means that part of the formed methane and water will react back to hydrogen and carbon oxides. This reverse reaction will take place until a balanced situation has been achieved.

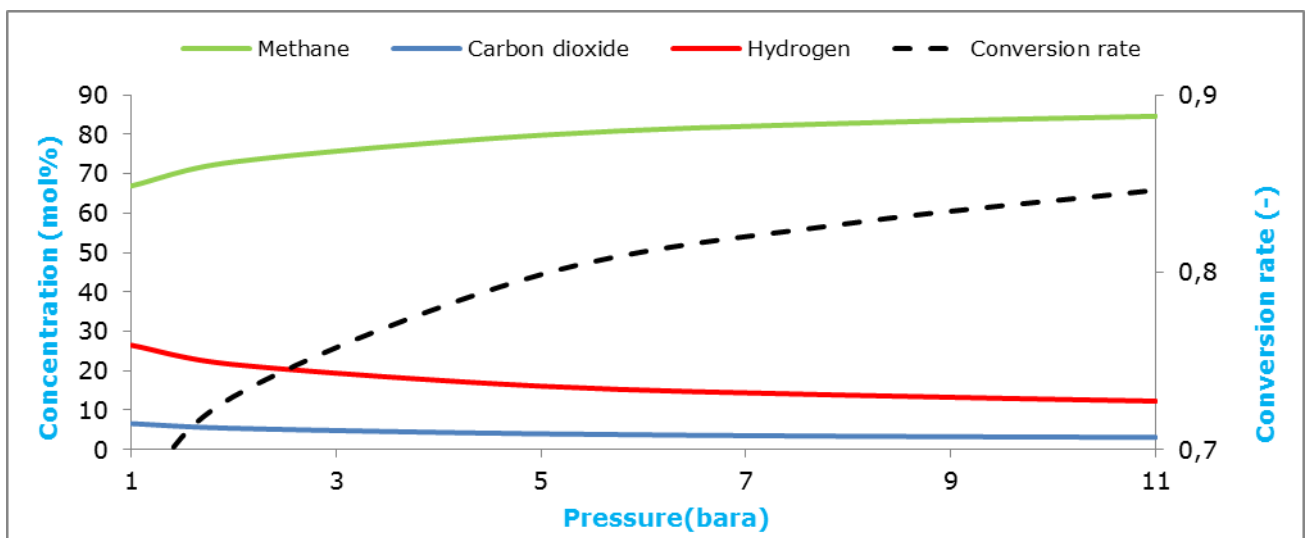
In the equilibrium situation, there is no full conversion of reactants. However, it is possible to affect the position of the balance to encourage the formation of the required products. Water is removed from the gas to prevent the formation of hydrogen and carbon oxides. This is achieved by cooling the gas mixture after every reactor, which means the formed water will condensate and can be discharged easily.

 Active surface of the catalyst  
 Non-active surface of the catalyst



**Figure 6: Schematic representation of reactions eq. 20-24 [10]**

Methanation can take place at pressures between 1-100 bar [11]. It is thermodynamically preferable to perform methanation at a high pressure, as both methanation reactions (eq. 17-18) are volume decreasing. That is because the molar number of products is less than the number of reactants, leading to higher methane yields at the same temperature. An example is given in figure 7. The pressure is limited by the material specifications.



**Figure 7: Example of the influence of pressure on carbon dioxide methanation [12]**

As mentioned before, methanation of carbon monoxide is preferred over methanation of carbon dioxide as it yields the highest fraction of methane. Therefore, the preferred hydrogen/carbon dioxide ratio for methanation is 3. This is adjusted by the reverse water-gas-shift reaction where carbon dioxide and hydrogen are converted into carbon monoxide and water. The heat required for this endothermic reaction comes from the methanation of carbon monoxide, thus increasing the carbon monoxide concentration and suppressing the carbon dioxide methanation.

### 3.1.2 Catalysts

Even though the methanation reactions are exothermic, a catalyst is required to activate them. The suitability and effectiveness of a catalyst is determined by the catalyst and the carrier material. The carrier material often consists of a metal oxide, such as TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and ZrO<sub>2</sub>, because of its large specific surface. A carrier with a large specific surface (m<sup>2</sup>/kg) generally benefits the effectiveness of the catalyst, as large amounts of catalyst are present per volume-unit of material. The carrier material also determines the thermal stability of the catalyst. Generally, it can be said that most catalysts have sufficient mechanical strength, so that pressure is not an issue.

Nickel (Ni) is generally used for the methanation of carbon oxides and hydrogen. It is also possible to use ruthenium (Ru), rhodium (Rh), platinum (Pt), iridium (Ir), cobalt (Co), iron (Fe) or palladium (Pd). Based on the information in literature, the following order of selectivity is used for the methanation of hydrogen and carbon dioxide, where the catalyst with the highest specific activity is listed first. [13]

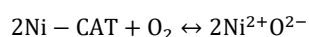
Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir

The selectivity depends on the catalyst material and it strongly affected by the carrier material. This may explain the discrepancies in the various literature sources. [14]

Nickel must be mentioned separately, because the above overview is based on precious metals. Nickel is less selective for hydrogen/carbon oxides than ruthenium or rhodium, but it is much cheaper. An adverse property of nickel is that carbon deposits (from syngas) occur sooner at low temperatures (< 250 °C) than with precious metals and that reduces the effective surface. Ruthenium causes carbon deposits to a lesser extent but produces more heavier hydrocarbons that are not required for the efficiency of the catalyst. [13]

In summary, it is possible to say that the listed precious metals are generally more effective than nickel but weighing up the effectiveness and the costs generally makes nickel the optimum catalyst.

The presence of nitrogen as an inert gas has an impact on the heat balance of the process, because of its heat absorption capacity. This effect can be positive as it contributes to cooling the reaction mixture and negative when it requires additional heating energy and further downstream purification steps. Oxygen adsorbs easily into the catalyst surface, which reduces the effectiveness. On contact with oxygen, the active (positively charged) nickel is given a neutral charge (oxidation), which reduces the reactive ability:



[eq. 25]

In order to improve the effectiveness of the reaction, the adsorbed oxygen atoms (oxides) must be removed from the catalyst surface. This chemical reduction is carried out by flushing the catalyst with low-oxygen gas, such as nitrogen or hydrogen. After activating the catalyst, any oxygen leakage should be avoided in order to prevent high temperatures and explosive situations inside the reactor, caused by uncontrolled exothermic reactions.



A decrease in catalytic activity and selectivity over time is a continuous risk in catalytic processes and this risk should be taken into account during methanation. It is inevitable that catalysts lose their activity over time due to a loss of activated ions. However, as long as this process occurs in a controlled manner it is a slow process. Although normal degradation is inevitable, unintentional immediate poisoning or deactivation must be prevented. Table 1 represents the mechanisms for degeneration and deactivation.

Most catalysts, but especially nickel, are sensitive to sulphur poisoning. The area of the reactive surface can also be decreased by mechanical grinding or by reactions between the catalyst and other species. Thermal degradation can also deactivate the catalyst, for example nickel is converted into inactive nickel carbonyl at temperatures below 200°C and nickel is prone to sintering or carbide and tar formation above 550°C [7].

**Table 1: Degeneration and deactivation mechanisms of catalysts**

Mechanisms	Type	Description
Poisoning	Chemical	Chemical adsorption of molecules to the catalyst, which reduces the reaction surface of the catalyst.
Contamination	Mechanical	Deposits of reaction fluids and/or solid substances on the reaction surface and the pores of the catalyst.
Thermal degradation (sintering)	Thermal	High temperatures causing losses of reaction surface, ion activity, or impacting the support material to which the catalyst material.
Vapour formation	Chemical	The production of volatile components due to a reaction between catalyst material and gas and a consequent loss of active material.
Phase transition reactions	Chemical	Chemical reaction between gases, liquids that are produced or volatile components and catalyst or support material.
Grinding	Mechanical	Loss of catalytic activity due to mechanical damage (grinding) to the catalyst and/or carrier material.

### 3.1.3 Reactors

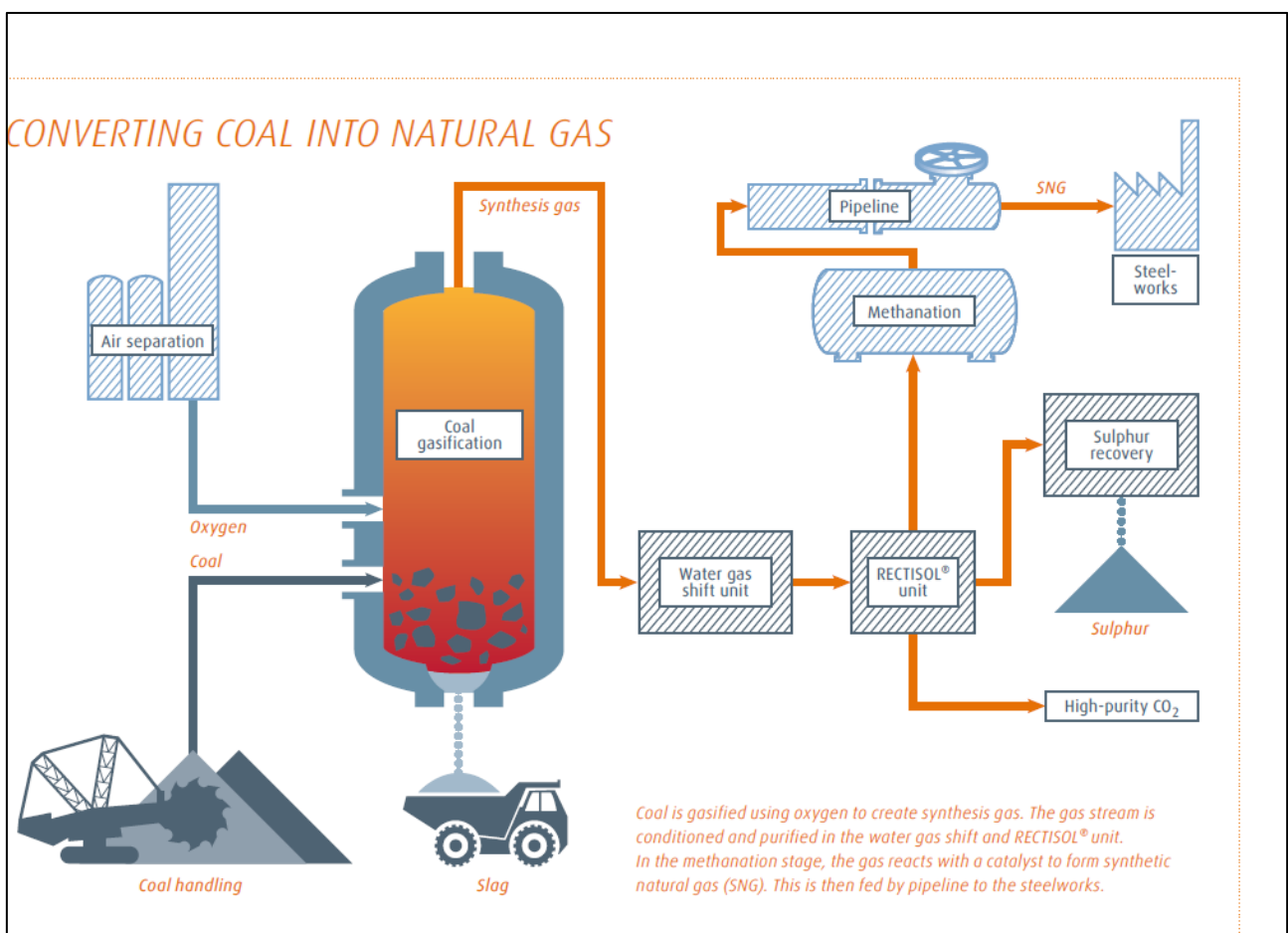
Fixed bed, fluidised bed and three-phase reactors ('slurry') are commonly used for methanation [15,16]. A fixed-bed reactor is packed with small catalyst particles. As there is no heat exchange, methanation develops under adiabatic conditions. The generated heat should be removed by intermediate gas-cooling steps (intercooling). Above 500 °C, contamination of the catalyst by deposition of tar or carbide is likely to occur. [16] The first demonstration plant in the Netherlands, Rozenburg, consists of four fixed-bed reactors in series. [12]

A fluidised bed reactor contains small catalyst particles, which are mixed with the gas mixture and led into the reactor with a special flux. Methanation takes place under isothermal conditions, as the fluidisation of gas and catalyst particles enables sufficient heat transfer. In a fluidised bed reactor, the catalyst particles are vulnerable to degradation. Catalyst and reactor walls of fluidised-bed reactors can be damaged due to a mechanical load resulting from fluidisation. [16]

In a three-phase reactor the catalyst powder is suspended in an inert liquid medium that enables heat transfer. However, the conversion rate is limited due to limited mass transfer by the liquid phase. Multiple reactors in series enable intermediate cooling of reactants and water removal by condensation and in turn that increases the overall conversion rates.

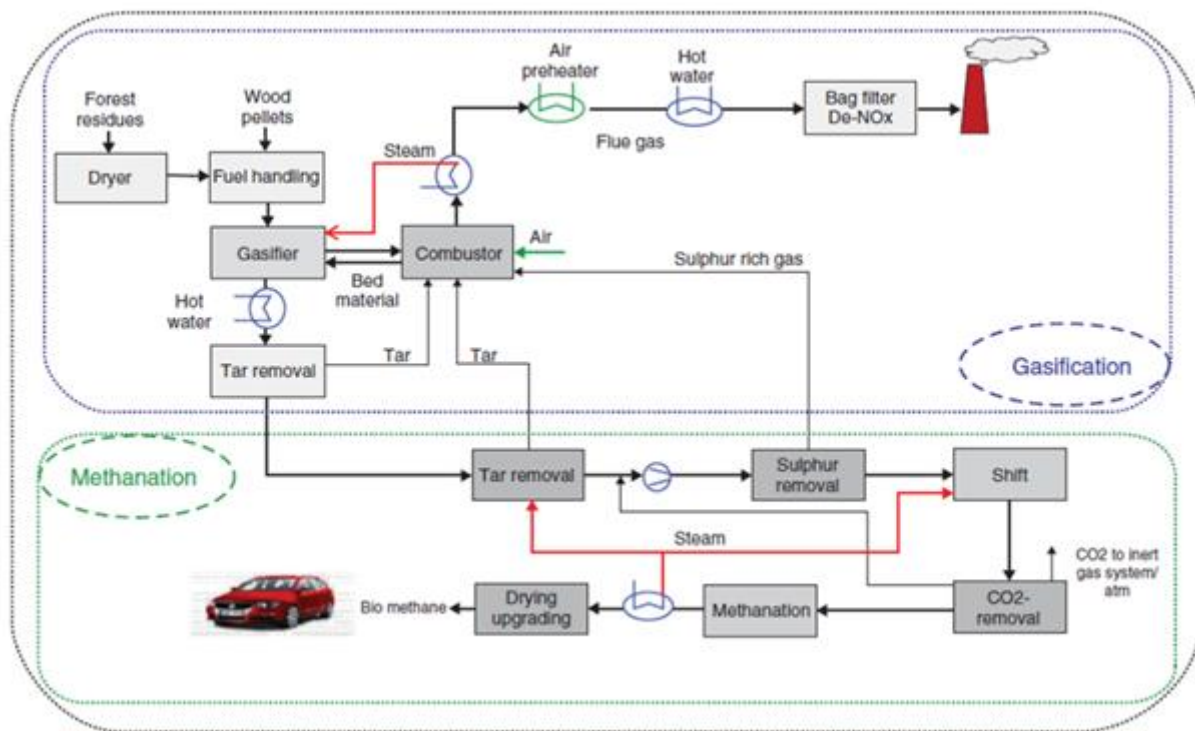
### 3.1.4 Process diagram

Figure 8 shows the process diagram of gasification and methanation from Linde Technology. [17] In this process coal is gasified with oxygen. Syngas is upgraded in a water-gas-shift unit to adjust the hydrogen-carbon monoxide ratio. The syngas is purified in a Linde Rectisol unit, which removes carbon dioxide and hydrogen sulphide from the syngas. Subsequently, the syngas enters a methanation reactor where carbon monoxide, carbon dioxide and hydrogen are catalytically converted into methane.



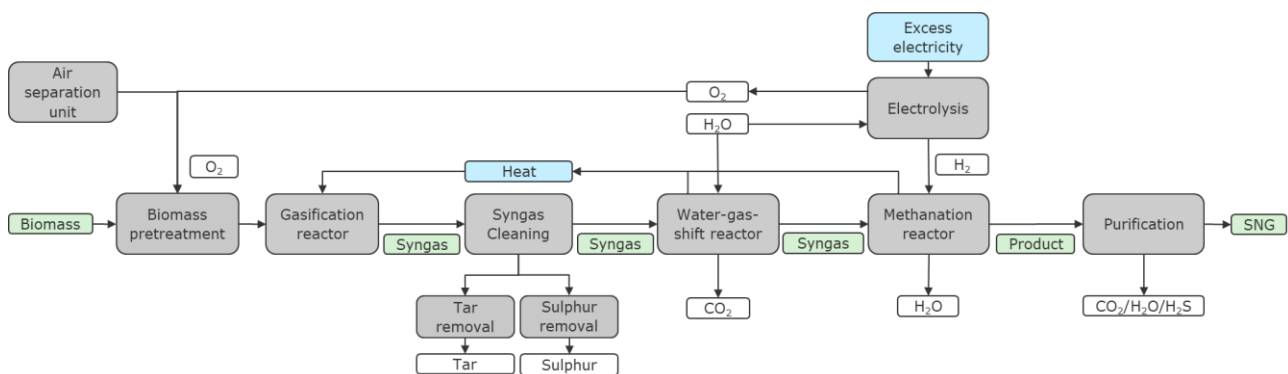
**Figure 8: Process diagram of gasification and methanation by Linde Technology [17]**

Figure 9 shows the flow chart of the GoBioGas project where forest residues are gasified with steam. [19] The produced syngas is cleaned, i.e. it passes two tar removal steps and a sulphur removal step. Then the hydrogen-carbon monoxide ratio is adjusted in a water-gas-shift unit and a carbon dioxide removal unit. Subsequently, the remaining syngas enters a methanation reactor. The produced methane is dried and upgraded for use as bio transportation fuel. The flow chart also shows the recycling possibilities for material and energy. For example, heat produced during methanation is used for steam production which can be applied in the tar removal or water-gas-shift units. Similarly, tar removed during tar removal can be used in a combustor that provides heat for the gasifier.



**Figure 9: Flow chart of the GoBioGas project of gasification and methanation [19]**

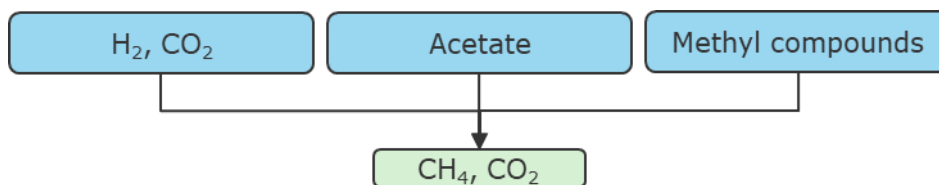
On the basis of desktop research, the indicative process flow chain, as shown in figure 10, is proposed for (bio)gasification and chemical methanation. Syngas from the gasifier should be cleaned to make it suitable for the methanation process, and therefore tar and sulphur must be removed. The hydrogen-carbon monoxide ratio can be adjusted in a water-gas-shift reactor. The cleaned syngas enters a methanation reactor, where methanation takes place with the aid of a nickel catalyst. It is possible to add additional hydrogen from electrolysis, for example. The oxygen that also is formed during the electrolysis process may be used for the gasification reaction. The methanation takes place in multiple reactors with intermediate cooling steps to ensure the generated water condensates and can be removed. The produced methane must pass several purification steps (carbon monoxide and carbon dioxide removal, drying) before feeding into the gas grid; see Chapter 2.4.



**Figure 10: Indicative process flow chain for gasification and chemical methanation of biogas**

### 3.2 Biological methanation

Biological methane production is performed with the help of so-called methanogens, a number of species of single celled micro-organisms from the domain of the archaea. These archaea are a distinct group, different from bacteria. Methanogens can convert carbon dioxide, acetate or methyl compounds into methane (figure 11).




**Figure 11: Routes of methanogenesis**

Biological methane production is best performed at neutral pH (~7) and at mesophilic (37 °C) or thermophilic (>55 °C) temperatures. Although thermophilic conditions have the potential of higher reaction speeds, the process is more sensitive to disruptions. Most methanogens prefer mesophilic temperatures, as only a fraction of the species can survive at higher temperatures. Methanogens can survive extremely high pressures, even up to 1200 bars [23]. However, biological methane production is generally carried out at around atmospheric pressure, because of economic considerations. At high pressures, acidity - due to the dissolved carbon dioxide - is a point of attention.

All the micro-organisms that are used for biological methane production occur in nature as well. Ideal conditions for methane-producing organisms are created in a biological reactor, ensuring these organisms will flourish there and facilitate the process. Optimum conditions for methanogens lead to optimum methane production.

If the conditions change for the micro-organisms that facilitate conversion, this will influence the efficiency of the reactor. Changes to operating conditions should be made slowly to enable the microbial community inside a reactor to adjust. Methanogens are slow growing, and it can take days to weeks for a reactor to recover if changes are made too quickly. Making too many adjustments too fast is unfavourable from a biological perspective, because the micro-organisms will be constantly trying to catch up and this will decrease methane production.



Nutrients are essential to the proper operation of a reactor. Micro-organisms need nutrients to build their cells (genetic material, enzymes, cell membrane, etc.) and without them they will not grow. Nutrients can be divided into two groups - macronutrients and micronutrients, sometimes known as trace elements. Micronutrients are needed in much lower quantities than macronutrients, but both are essential to good growth and activity of micro-organisms. The most important macronutrients are bound oxygen, carbon, nitrogen, phosphor and sulphur. The most important micronutrients are iron, cobalt, molybdenum, nickel, manganese, copper and zinc.

### **Pure carbon dioxide conversion**

Biological methanation of pure carbon dioxide uses hydrogen as the electron donor, and only uses hydrogen and carbon dioxide and only creates methane and water. This metabolism is highly exothermic. [21] The heat production of these specific methanogens is advantageous because they prefer thermophilic (~65 °C) temperatures [24], in contrast to methanogens that use carbon sources other than carbon dioxide.

The main challenge in biological methanation of pure carbon dioxide is ensuring the availability of hydrogen for the methanogens, as it dissolves poorly in water. Rigorous stirring is a commonly used method for mixing hydrogen in the reactor solution, but this uses a significant amount of energy and reduces the overall efficiency. Stirring is further limited by the sheer forces that micro-organisms are able to handle, as stirring too fast will tear them apart. Different reactor designs are currently being tested to increase the availability of hydrogen and to increase methane production without having to spend considerable energy on stirring. Bioclear Earth achieved conversion rates of >99% with their trickle-bed reactors without a significant energy input for stirring.<sup>2</sup> Increasing pressure is another way of improving hydrogen availability that can increase the methane-evolution rate. However, higher pressure is an economical trade-off, as stricter safety and material margins are required.

### **Upgrading biogas**

Biogas that comes directly from a digester can have a high carbon dioxide content, which limits its uses, and ideally this carbon dioxide is also converted to methane. In addition, biogas may contain hydrogen sulphide because of sulphate-reducing bacteria. Hydrogen sulphide is malodorous and in high concentrations it can become corrosive and toxic. Both of these problems can be solved by micro-organisms.

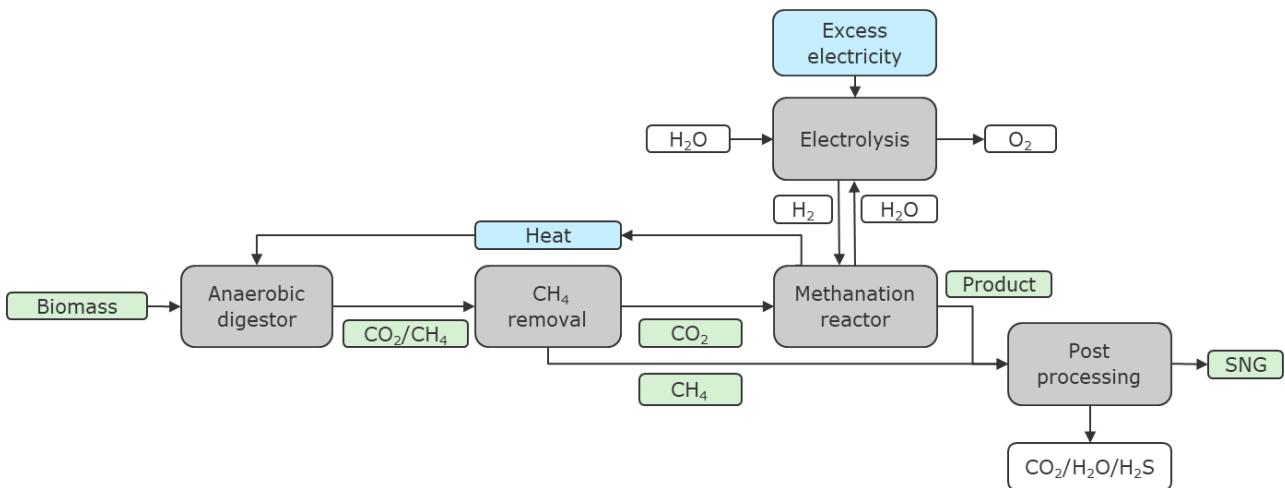
Conversion of residual carbon dioxide to methane is possible by injecting hydrogen into the anaerobic digester, which stimulates the hydrogen-carbon dioxide metabolism. However, if done incorrectly, hydrogen injection can slow down steps in the anaerobic digestion that take place before methane formation, effectively lowering methane production. In the worst cases it can shut down the reactor entirely. Furthermore, buffer capacity will be removed when the carbon dioxide content in the reactor is lowered. In-situ upgrading has the advantage of a lower footprint and energy cost, as the same reactor can be used. The downside of in situ treatment - if not performed correctly - is lower stability of the digester.

Ex-situ treatment is an alternative that mixes hydrogen and biogas in a second reactor, where hydrogen/carbon dioxide utilising methanogens can create an optimum community for these specific conditions. A conversion rate of >99% can be reached with ex-situ treatment. In essence, the ex-situ treatment is the same as pure carbon dioxide conversion, and it needs the same operational conditions.

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<sup>2</sup> More information at [bioclearearth.nl](http://bioclearearth.nl)

Methanogens are relatively resistant to hydrogen sulphide and they are generally able to deal with the contaminations in biogas. Biological treatment of hydrogen sulphide is a well-developed technology that can be used to remove hydrogen sulphide from biogas with efficiencies of >95%. Biological oxidation of hydrogen sulphide is an aerobic process. Air will have to be added to the biogas in function of the hydrogen-sulphide content.

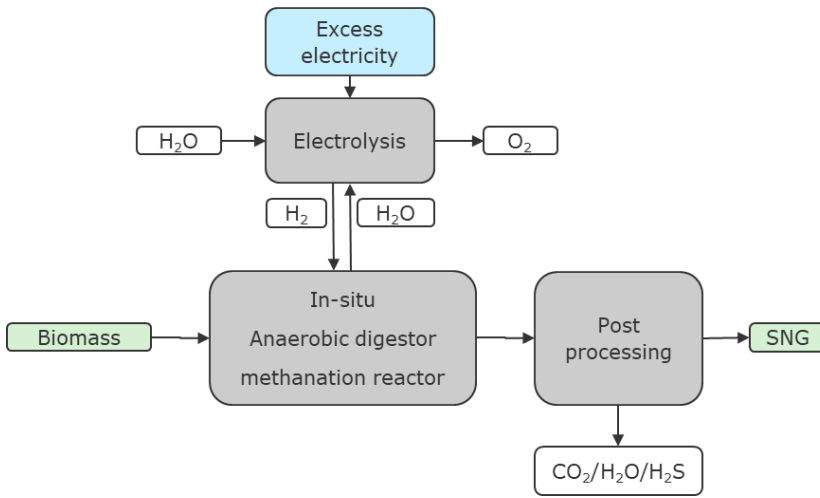


**Figure 12: Ex-situ biological upgrading of biogas**

### Syngas conversion

Syngas contains carbon monoxide, hydrogen and carbon dioxide, as well as possible contaminations, such as hydrogen sulphide and halogens. Some methanogens are able to oxidise carbon monoxide to methane directly. However, carbon monoxide seems to slow down methanogenesis; under syngas conditions methanogens prefer acetate and formate formation. [6,22] A major challenge with syngas is that hydrogen and carbon monoxide are poorly soluble in water, leading to a mass transfer limitation for both components. One possibility is to add syngas in situ to an anaerobic digester, as this creates co-digestion of syngas and biomass (figure 13). In an anaerobic digester there is a robust community of methanogens that are able to form acetate from carbon monoxide and methane from this acetate. Depending on the composition of the syngas, it is important not to disturb the anaerobic digestions process when using this in-situ method.

Depending on the concentrations, contaminations in syngas should not constitute major problems, as biogas contains traces of hydrogen sulphides and halogens as well. However, in higher concentrations halogens can inhibit methane production and hydrogen sulphide can lead to corrosion. [20]. Depending on its composition, tar is not necessarily toxic to methanogens and in some cases it can even be used as a substrate for growth. However, clogging of the reactor and toxicity are possible problems.



**Figure 13: In-situ syngas treatment**

## 4 PRACTICAL INFORMATION ON PROJECTS AND SUPPLIERS

This Chapter provides an overview of projects that are currently operational or almost operational. A list of technology suppliers is also included. The aim is to help future project developers to get into contact with such parties in order to make the best choices for their specific situations.

Table 2 provides an overview of catalyst suppliers. Table 3 provides an overview of projects where methanation is applied. The information has been obtained from public sources. The table shows the applied methanation technology (chemical/biological) and relevant process conditions. Contact information has also been added. More information on projects and suppliers is summarised in a list, that is made available free of charge at the websites of the partners, Groen Gas Nederland and TKI Nieuw Gas.

**Table 2: Overview of suppliers of catalysts and methanation systems**

Supplier	Loc.	Technology	Website
AMEC Foster Wheeler	UK	Chemical	<a href="mailto:www.valentina.depetri@woodplc.com">www.valentina.depetri@woodplc.com</a>
Atmostat-Alcen	FR	Chemical	<a href="http://www.atmostat-alcen.com/en/contact-us">www.atmostat-alcen.com/en/contact-us</a>
BASF Catalysts Germany GmbH	DE	Chemical	<a href="https://catalysts.basf.com/about-us/contact">https://catalysts.basf.com/about-us/contact</a>
Clariant	DE	Chemical	<a href="http://www.clariant.com/en/Corporate/News/2016/07/VESTA-Oncethrough-Methanation-New-Technology-with-Wide-H2CO-Flexibility-Successfully-Passes-Pilot-Te">www.clariant.com/en/Corporate/News/2016/07/VESTA-Oncethrough-Methanation-New-Technology-with-Wide-H2CO-Flexibility-Successfully-Passes-Pilot-Te</a>
DWE MAN ES	BE	Chemical	<a href="mailto:dwe-info@man.eu">dwe-info@man.eu</a>
Electrochaea GmbH	DE	Biological	<a href="mailto:info@electrochaea.com">info@electrochaea.com</a>
Euro Support Headquarters	NL	Chemical	<a href="mailto:info@eurosupport.com">info@eurosupport.com</a>
Haldor Topsøe	DK	Chemical	<a href="mailto:roc@topsoe.dk">roc@topsoe.dk</a>
Hitachi Zosen Inova (HZI)	CH	Chemical	<a href="mailto:info@hz-inova.com">info@hz-inova.com</a>
Ineratec	DE	Chemical	<a href="mailto:info@ineratec.de">info@ineratec.de</a>
Johnson Matthey (Katalco)	NL	Chemical	<a href="mailto:group.info@matthey.com">group.info@matthey.com</a>
MicrobEnergy (Viessman)	DE	Biological	<a href="mailto:info@microbenergy.com">info@microbenergy.com</a>
NIAP	RU	Chemical	<a href="mailto:sekretar-aup@niap-kt.ru">sekretar-aup@niap-kt.ru</a>
Sunfire	DE	Chemical	<a href="mailto:info@sunfire.de">info@sunfire.de</a>
Umicore AG & Co.	DE	Chemical	<a href="mailto:chemistry@umicore.com">chemistry@umicore.com</a>
Unicat Catalyst Technologie	BE	Chemical	<a href="https://www.unicatcatalyst.com/contact/technical-support/">https://www.unicatcatalyst.com/contact/technical-support/</a>

**Table 3: Overview of relevant projects (1 of 3): Chemical methanation**

Owner/Project	Loc.	Capacity	Catalyst	Operating conditions		Supplier/Partners
				Temp.	Press.	
AMEC - Foster Wheeler (VESTA)	CN	100 m3/h	*	230-700 °C	*	AMEC-Foster Wheeler/Clariant International AG/Wison Engineering
Atmostat	FR	Modular	powder	*	*	Metamod
Bioengineering Group, NRC Energy, Mining & Environment Portfolio	CA	*	*	*	*	Bioengineering Group, NRC Energy, Mining & Environment Portfolio
Biogas Zurich (COSYMA)	CH	1-2 m3/h	Ni-based	350-365 °C	7 bar	PSI/TCP Group/Energie360°/FOGA/Swiss federal office of Energy/Swiss Competence Center of
CEA Tech (Jupiter 1000)	FR	25 m3/h	*	*	*	GRTgaz/Atmostat/McPhy
Conocophillips/British gas company/HiCom	US	*	Ni-based	*	*	ConocoPhillips/Peabody Energy Site
Dekotagas/Lurgi (Air Liquide)	US	*	Ni-based	*	*	Dekotagas/Lurgi (Air Liquide)
DNV GL/Stedin Pilot plant	NL	0.5 m3/h	Ni-based	377 °C	≤8 bar	DNV GL/Stedin/TKI Gas/Rotterdam Council and Resort Wonen/NIAP
ECN/TNO (ESME)	NL	*	Ni-based	340 °C	6 bar	ECN/TNO
ENGIE, GAYA	FR	*	*	*	*	Engie/Cirad/CTP/FCBA/CEA and others
Gobigas	SE	20 MW	Ni-based	*	*	Göteborg Energi/Chalmers University of Technology/CFB technology (HT catalyst and
Gogreengas (CADENT)	UK	0.05 MW	AMEC Foster Wheeler	*	*	National Grid Gas Distribution/Advanced Plasma Power (APP)/Progressive Energy/ Carbotech (a
Güssing gasifier (PSI)	AT	1 MW	Ni-based	350 °C	*	PSI, Vienna University of technology
Haldor Topsøe (Foulum)	DK	10 m3/h	Ni-based	280 °C	*	Haldor Topsøe
Haldor Topsøe (TREMPE) Qinghua	CN	160 m3/h	Ni-based	*	*	Haldor Topsøe
Haldor topsøe/Linde (POSCOs) (TREMPE)	KR	80 m3/h	Ni-based	*	*	Haldor Topsøe
Helmeth	DE	6 m3/h	Ni/Ru-based	≥250 °C	10-30 bar	KIT, POLITO, SUNFIRE, ERIC, EEI, NTUA, DVGW

**Table 3: Overview of relevant projects (2 of 3): Chemical methanation**

Owner/Project	Loc.	Capacity	Catalyst	Operating conditions		Supplier/Partners
				Temp.	Press.	
HZI Etogas (Werite)	DE	500 m3/h	*	250-550 °C	8 bar	HZI ETOGAS/Audi/Fraunhofer/IWES/ZSW/EWE/DWE
IET/ HEPP (High Efficiency Power-to-Methane Pilot)	CH	1,2 m3/h	Ni/zeol./other	250-300 °C	5-9 bar	<a href="https://www.iet.hsr.ch/index.php?id=16924&amp;L=4">https://www.iet.hsr.ch/index.php?id=16924&amp;L=4</a>
INERATEC GmbH	SP	4 m3/h modular	*	*	*	<a href="http://www.flexchx.eu/workshop2019/INERATEC_FLEXCHX%20Workshop%20Presentation%2003">http://www.flexchx.eu/workshop2019/INERATEC_FLEXCHX%20Workshop%20Presentation%2003</a>
Inpex	JP	Not Started	*	*	*	Inpex
Johnson Matthey Process technologies (Baotou)	CN	*	*	*	*	Johnson Matthey Process technologies (Baotou)
MeGa-store	DK	Modular up to 874 m3/h per	*	*	*	DTU Makenic
MeGa-store (Heden,Funen)	DK	9 m3/h	*	*	*	DTU Makenic
MeGa-store (Lemvig)	DK	1 m3/h	*	260-310 °C	8 bar	DTU Makenik/Aarhus University in Herning/Lemvig biogas/Green Hydrogen/Elplatek
Renovagas	ES	15 kW	Ru-based	275-325 °C	≥25 bar	<a href="https://www.etip-snet.eu/wp-content/uploads/2017/06/5-The-Renovagas-">https://www.etip-snet.eu/wp-content/uploads/2017/06/5-The-Renovagas-</a>
SCW	NL	*	*		100	N.V. Nederlandse Gasunie/Gasterra
SoCalGas@ P2G/University of California	US	*	*	*	*	SoCalGas@ P2G/University of California
STORE&GO (Falkenhagen)	DE	58 m3/h	*	*	*	<a href="https://www.storeandgo.info/partners/">https://www.storeandgo.info/partners/</a>
STORE&GO (Troia)	IT	7.2 kg LNG/h	Atmostat	280 °C	4 bar	<a href="https://www.storeandgo.info/partners/">https://www.storeandgo.info/partners/</a>
Tauron	PL	4.4 m3/h	Atmostat	*	*	<a href="https://media.tauron.pl/en/pr/302932/the-innovative-project-on-co2-management-already-">https://media.tauron.pl/en/pr/302932/the-innovative-project-on-co2-management-already-</a>
ZBT Hydrogen Technologies	DE	1 m3/h	*	550 °C	16 bar	ZBT Hydrogen Technologies

**Table 3: Overview of relevant projects (3 of 3): Biological methanation**

Owner/Project	Loc.	Capacity	Catalyst	Operating conditions		Supplier/Partners
				Temp.	Press.	
Bareau	NL	1 m3/h	Archaea	50 °C	20 bar	Bareau
Electrochaea (Audi, Hydrogenics)	DK	60 m3/h	Archaea	63 °C	9 bar	Electrochaea/Audi/Hydrogenics/NEAS energy/HMN Naturgas/Biofos/Insero
Krajete GmbH	AU	above 30 NL L-1 h-1	Archaea	*	6-15 bar	Krajete GmbH
MicrobEnergy (Viesmann Group)/ Audi	DE	15 m3/h	Archaea	40 °C	5 bar	MicrobEnergy/Audi
MicroPyros GmbH	DE	2-10 m3/h	Archaea	59-67 °C	3-7 bar	MicroPyros GmbH
NREL	US	*	*	49 °C	17 bar	NREL and Southern California Gas Company
STORE&GO (Solothurn)	CH	30 m3/h	*	62 °C	10 bar	

## 4.1 Project/Supplier fact sheets

Approximately twenty projects have been selected from the longlist, representing the widest possible variation in projects and technologies. The project owners and technology suppliers involved were approached and invited to provide more detailed information. Six project owners and technology suppliers were kind enough to reply to our request. Their feedback is summarised in fact sheets, which are provided in this paragraph. The fact sheets contain technical and commercial information.

The chemical efficiency, as mentioned in the sheets, is based on the restraining gas component. An example:

*A gas mixture contains 60 moles of hydrogen and 40 moles of carbon dioxide. The maximum methane content that can be produced from that is 15 moles, leaving 25 moles of carbon dioxide in the outlet gas (see eq. 18).*

*Supposing the gas mixture contains 4 moles of hydrogen, 26 moles of carbon dioxide and 14 moles of methane, the chemical efficiency will be 93% ( $=100\% \cdot (14/15)$ ).*

The electric efficiency is not taken into consideration because it is highly dependent on the feed-gas composition flow.

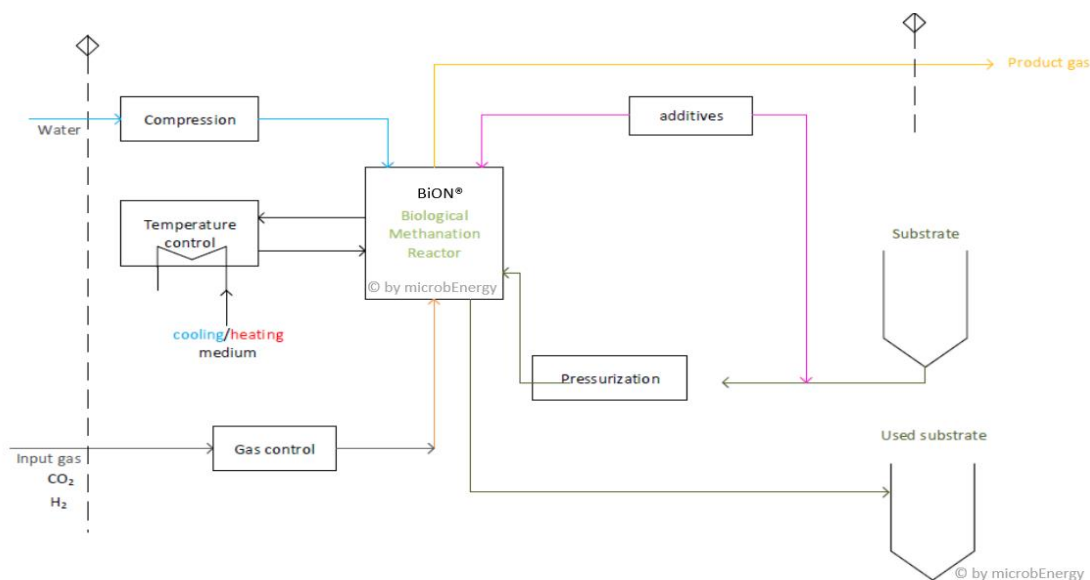
## 4.1.1 MicrobEnergy (supplier)

### 1. GENERAL INFORMATION

MicrobEnergy is a development and engineering company for Power-to-Gas and biological methanation concepts. In support of Power-to-Gas projects, MicrobEnergy offers feasibility studies. MicrobEnergy's sister company Schmack Biogas is a supplier of Power-to-Gas turnkey plants, based on biological methanation technology (BiON<sup>®</sup>-process). MicrobEnergy is located in southern Germany and is part of the Viessman Group.

Furthermore, MicrobEnergy operates a laboratory for bench tests and a technical centre for anaerobic digestion applications and methanation. MicrobEnergy operates the world's first methanation plant from which biomethane is injected into a gas grid. BiON<sup>®</sup> uses a broad and robust consortium of archaea micro-organisms.

### 2. PROCESS FLOW DIAGRAM



### 3. OPERATING CONDITIONS

Operating principle	Biological (anaerobic)
Catalyst type	Archaea microbes
Reactor principle	Continuous process
Number of reactors	1 reactor
Residence time (Reactor volume/flow rate ratio)	Scalable, 2-16 h <sup>-1</sup>
Scale range (MW)	Scale up and down possible
Process pressure	5-10 bar(g)
Process temperature	60-70 °C
Process acidity (pH)	6-8
Temperature control	Heat-exchanger system

### 4. INPUT SPECIFICATIONS & CONSTRAINTS

FEED GAS COMPOSITION		GAS CONTAMINATIONS		PROCESS INPUT	
Component	Range	Component	Limit	Parameter	Range
CO	< 0.5 vol%	Halogens	Not specified	Pressure	5-10 bar(g)
CO <sub>2</sub>	Not limited	Sulphur	None	Temperature	60-70 °C
H <sub>2</sub>	Not limited	Tar	None	Flow rate	15 m <sup>3</sup> (n)/h
CH <sub>4</sub>	Not limited	O <sub>2</sub>	< 0.3 vol%		

#### Additional comments from the supplier

- Syngas can be used as an input gas.
- CO is converted partially, generally CO should be shifted into CO<sub>2</sub>. If required, an additional water-gas-shift reactor has to be installed.

### 5. PRODUCTS & EFFICIENCY

- Chemical efficiency: :98% CH<sub>4</sub>
- Process pressure drop: approx. 0.5 bar
- Process side reactions (conversion of other trace components): not specified

## 6. MAINTENANCE & FINANCE

- MTBM (mean time between maintenance): Not specified Depending on location, operator, operator model, full-load hours.
- Micro-organisms are not affected during a stop for maintenance. There are no major issues to be expected at start-up.

FINANCE		
Plant size (thermal energy of H <sub>2</sub> input)	CAPEX (m €)	OPEX (m €)
5 MW	5.6	Not specified
10 MW	9.5	Not specified
20 MW	15.4	Not specified

## 7. ADDITIONAL REMARKS SUPPLIER

- Experience from ongoing operating of demonstration plant since 2013.
- Fully equipped technical centre with several bioreactors.

## 8. REFERENCES & CONTACT

- A production plant Allendorf, Germany for the production of egas for Audi, finalised in 2016.
- A 300kW demonstration plant is operated by MicrobEnergy. ([www.biopower2gas.de](http://www.biopower2gas.de))
- A 2.5 MW plant in Dietikon (Switzerland) is under construction.

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E-mail [Thomas.Heller@microbenergy.com](mailto:Thomas.Heller@microbenergy.com)

## 4.1.2 Hitachi Zosen Inova (supplier)

### 1. GENERAL INFORMATION

Hitachi Zosen Inova is part of the Japanese multinational Hitachi Zosen Corporation. HZI has more than 80 years of worldwide experience in plant construction and more than 600 reference projects, making HZI one of the leading providers of complete turnkey energy-from-waste plants.

By acquiring the business of the German company Etogas GmbH in 2016, HZI is now also in business in Power-to Hydrogen, Hydrogen-to-SNG and Power-to-SNG projects.

### 2. PROCESS FLOW DIAGRAM

### 3. OPERATING CONDITIONS

Operating principle	Chemical methanation
Catalyst type	Nickel based, specific catalyst is based on project requirements
Reactor principle	Fixed-bed reactor
Number of reactors	One reactor
Residence time	1300 h <sup>-1</sup> (Reactor volume/flow rate)
Scale range (MW)	The minimum scale is 160kW, there is no maximum limit
Process pressure	6 – 8 bar(g)
Process temperature	220 - 260 °C
Process acidity (pH)	Not relevant
Temperature control	The reactor is cooled by water/steam

### 4. INPUT SPECIFICATIONS & CONSTRAINTS

FEED GAS COMPOSITION	
Component	Range
CO	<25 vol%
CO <sub>2</sub>	<20 vol%
H <sub>2</sub>	16-80 vol%
CH <sub>4</sub>	<80 vol%

GAS CONTAMINATIONS	
Component	Limit
Halogens	<0.1 volppm
Sulphur	<0.1 volppm
Tar	<5 mg/m <sup>3</sup> (n)
O <sub>2</sub>	<10 volppm

PROCESS INPUT	
Parameter	Range
Pressure	6-8 bar(g)
Temperature	220-260 °C
Flow rate	Not specified

#### Additional comments from the supplier

- Syngas is possible as a feedstock
- H<sub>2</sub>/CO feed ratio will be 3
- H<sub>2</sub>/CO<sub>2</sub> feed ratio will be 4
- Gas contaminations reduce the catalyst lifetime and must be removed upstream. HZI-Etogas has a broad knowledge of gas-purification processes. These systems are engineered to the specific site requirement

## 5. PRODUCTS & EFFICIENCY

- Chemical efficiency: 96% CH<sub>4</sub> (combined with a membrane gas-upgrading system)
- Process pressure drop: 0.5 bar max.
- Process side reactions (conversion of other trace components): no side reactions will take place

## 6. MAINTENANCE & FINANCE

- MTBM (mean time between maintenance): Not specified No special maintenance required.
- It is estimated that the catalyst will be operational for 3 - 10 years depending on feed-gas quality

FINANCE		
Plant size (thermal energy of H <sub>2</sub> input)	CAPEX (m €)	OPEX (m €)
5 MW	Not specified	Not specified
10 MW	Not specified	Not specified
20 MW	Not specified	Not specified

## 7. ADDITIONAL REMARKS SUPPLIER

- HZI's technology differs from other methanation technologies in that reactor cooling is performed by water/steam in natural circulation. High pressure/temperature steam ( $\geq 25$  barg) is produced for downstream applications.
- Due to the natural circulation for reactor cooling, and therefore the absence of rotating equipment, the plant OPEX and maintenance are very low.
- HZI has broad experience in energy-from-waste with chemical and biological processes.

## 8. REFERENCES & CONTACT

- 160kW P2G demonstration plant, Nagaoka, Japan
- 6 MW Audi e-gas plant, Werlte, Germany

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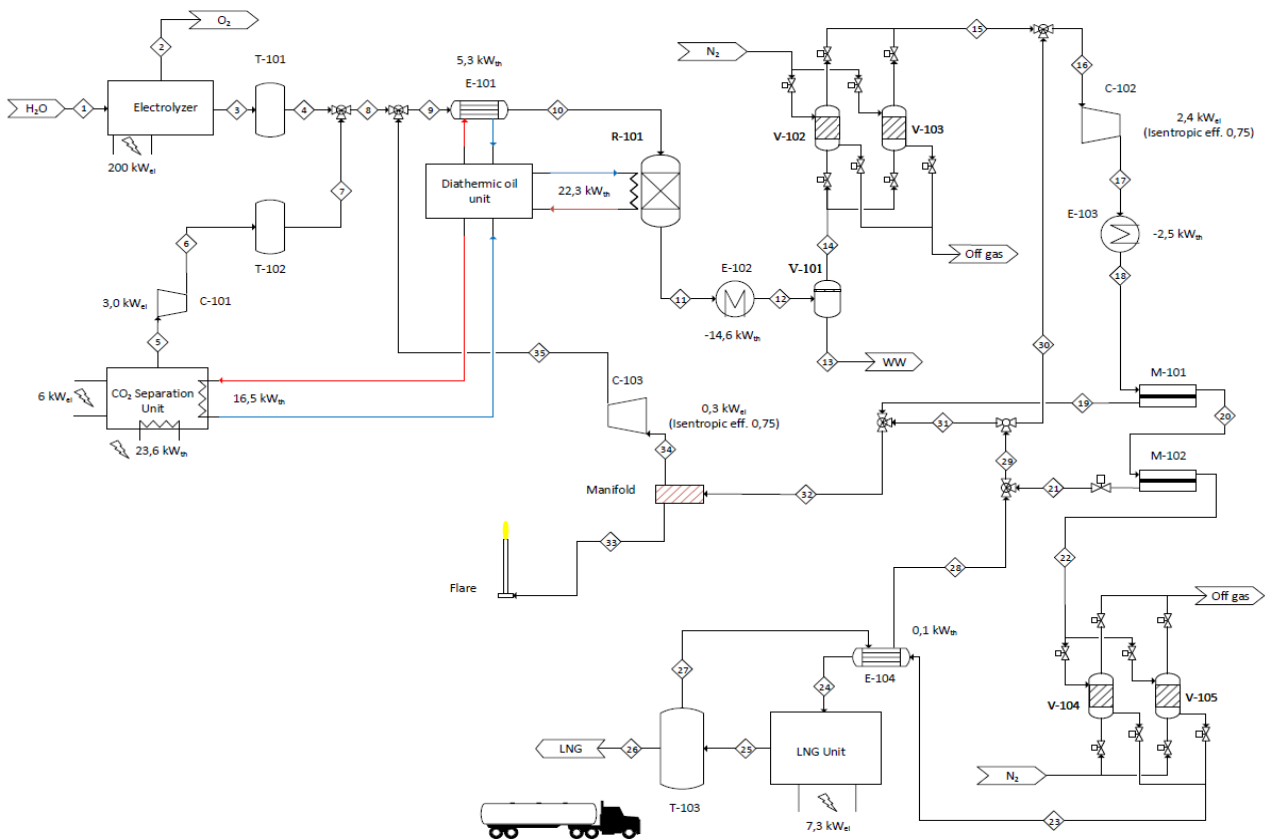
### 4.1.3 Store & Go TROIA (project)



## 1. GENERAL INFORMATION

The plant in Troia, Italy, is a demonstration site of the Store and Go consortium. This consortium received funding from the European Union's Horizon 2020 research and innovation program. The plant produces liquefied methane by using renewable electricity. The process consists of an alkaline electrolyzer to produce hydrogen that is combined with carbon dioxide (directly captured from air) to produce methane through the methanation process. The liquefaction is achieved with a Stirling cycle. Quality specifications for liquefied gas are more stringent than the gas-grid injection-quality requirements. Therefore, the product gas can be also injected in the natural-gas grid. The plant was built as joint effort between three industrial partners of the consortium: Atmosat Alcen (methanation unit), Climeworks (direct CO<sub>2</sub> capturing unit from air) and Hysytech (membrane separation unit and liquefaction unit). The plant has been in operation since Q1-2019.

## 2. PROCESS FLOW DIAGRAM



### 3. OPERATING CONDITIONS

Operating principle	Chemical methanation
Catalyst type	Nickel based, millimetre-scale
Reactor principle	Fixed-bed reactor with millimetric reaction channels
Number of reactors	4 reactors running parallel
Residence time	Not specified
Scale range (MW)	Not specified
Process pressure	< 10 bar(g)
Process temperature	280-340 °C
Process acidity (pH)	Not relevant
Temperature control	The reactor is cooled by thermal oil, part of the oil preheats the inlet gas

### 4. INPUT SPECIFICATIONS & CONSTRAINTS

FEED GAS COMPOSITION		GAS CONTAMINATIONS		PROCESS INPUT	
Component	Range	Component	Limit	Parameter	Range
CO	Not specified	Halogens	Not specified	Pressure	<10 bar(g)
CO <sub>2</sub>	Not specified	Sulphur	Not specified	Temperature	280-340 °C
H <sub>2</sub>	Not specified	Tar	Not specified	Flow rate	10 m <sup>3</sup> n/h
CH <sub>4</sub>	<6 vol%	O <sub>2</sub>	Not specified		(4 reactors)

#### Additional comments from the supplier

- H<sub>2</sub>/CO<sub>2</sub> feed ratio will be 4
- The system separates and recycles unreacted gas, enabling it to achieve higher overall conversion rates.
- The installation draws CO<sub>2</sub> from air, therefore N<sub>2</sub> and O<sub>2</sub> are the only contaminant that can be present in the CO<sub>2</sub> feed stream.

### 5. PRODUCTS & EFFICIENCY

- Chemical efficiency: >99% CH<sub>4</sub> (with separation and recycling of unreacted CO<sub>2</sub> and H<sub>2</sub>). The methanation unit reaches a CO<sub>2</sub> conversion of >95% per pass in only one reaction stage.
- Process output pressure: LNG is stocked between 1 and 2 bar (for direct production of SNG, the output pressure would be 13 bar (after the membrane separation unit))
- Process side reactions (conversion of other trace components): no side reactions

## 6. MAINTENANCE & FINANCE

- MTBM (mean time between maintenance): Not specified MTBM cannot be specified due to the installation being 6 months in operation.

FINANCE		
Plant size (thermal energy of H <sub>2</sub> input)	CAPEX (m €)	OPEX (m €)
5 MW	Not specified	Not specified
10 MW	Not specified	Not specified
20 MW	Not specified	Not specified

## 7. ADDITIONAL REMARKS SUPPLIER

- The milli-structured methanation reactors make it possible to obtain an intensification of heat and mass transfer. Furthermore, it is a compact and modular design that allows easy maintenance and thermal management to avoid deactivation of the catalyst and to obtain a high conversion in a single reaction stage.
- The produced gas is liquefied and can be used immediately as bunker fuel or in heavy truck freight transportation.

## 8. REFERENCES & CONTACT

WWW	<a href="http://www.dvgw-ebi.de">www.dvgw-ebi.de</a> <a href="https://www.storeandgo.info">https://www.storeandgo.info</a>
CONTACT PERSON	Simon Verleger
PHONE	+49 (0)721 608-41281
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#### 4.1.4 Electrochaea (Supplier)



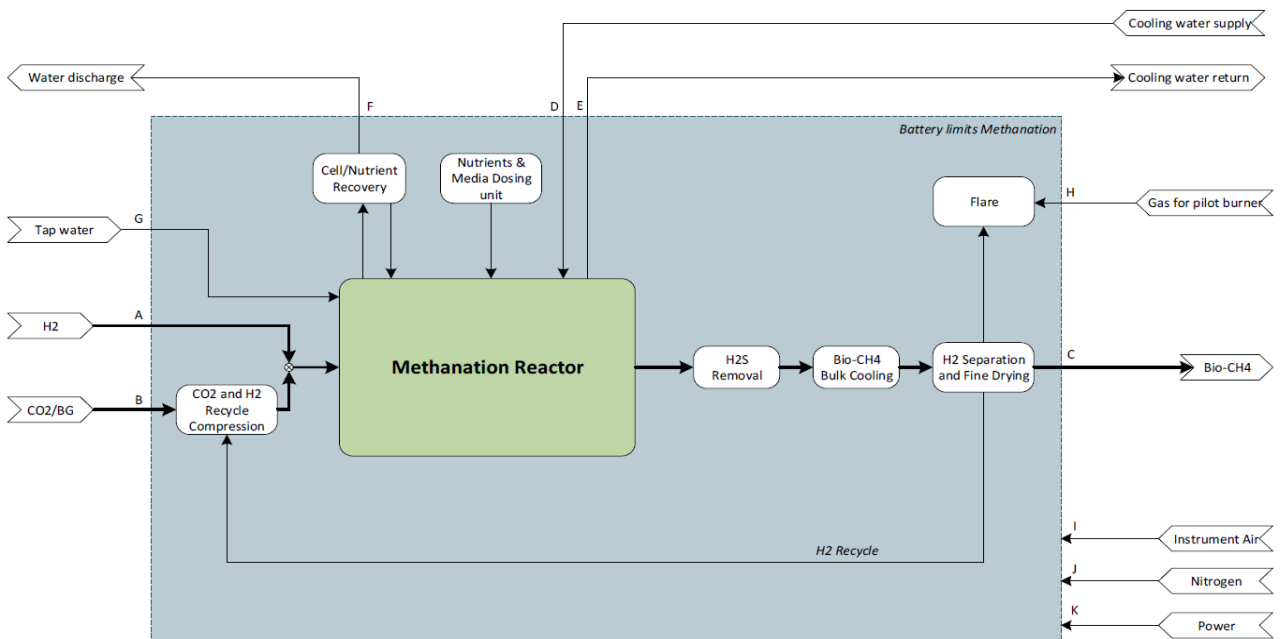
### 1. GENERAL INFORMATION

Electrochaea GmbH is a supplier of Power-to-Methane technology, using a biological methanation process. Electrochaea's patented strain of archaea, when fed CO<sub>2</sub> and H<sub>2</sub>, produces biomethane that is ready to be injected into the gas grid. Their headquarters are located in Planegg, Munich, Germany, where engineering and development take place.

Electrochaea has developed its product from the laboratory to industrial scale and currently has three industrial demonstration plants. In 2016, Electrochaea deployed the largest biological methanation plant in the world with an installed electrolyser capacity of 1 MW at a wastewater-treatment plant in Avedøre, near Copenhagen, Denmark, as part of the BioCat project. Additional demonstration plants are operating in Solothurn, Switzerland, as part of the STORE&GO Project funded by Horizon2020, where renewable methane is being injected into the Swiss gas grid, and at NREL in Golden, Colorado, USA.

Electrochaea's biological methanation plants can be built in a capacity range from 1 to more than 100 MWe. When integrated into wastewater-treatment plants, biogas plants or landfill sites, biomethane output is doubled. CO<sub>2</sub> from industrial sources, such as fermentation, cement or steel plants can also be used to produce methane with Electrochaea's technology.

### 2. PROCESS FLOW DIAGRAM



### 3. OPERATING CONDITIONS

Operating principle	Biological
Catalyst type	Archaea: patented single strain ECH0100
Reactor principle	CSTR
Number of reactors	Currently 1 reactor
Residence time	Reactor volume/inlet flow rate: 0.02-0.1 h *)
Scale range (MW)	No limits
Process pressure	1-10 bar(g)
Process temperature	62-65 °C is optimum
Process acidity (pH)	Neutral
Temperature control	Standard technology

\*) at 8 bar; inlet flow rate in Nm<sup>3</sup>/h

### 4. INPUT SPECIFICATIONS & CONSTRAINTS

FEED GAS COMPOSITION	
Component	Range
CO	20%
CO <sub>2</sub>	35-100%
H <sub>2</sub>	100%
CH <sub>4</sub>	0-65%

GAS CONTAMINATIONS	
Component	Limit
Halogens	n.d.
Sulphur	n.d.
Tar	n.d.
O <sub>2</sub>	100 volppm

PROCESS INPUT	
Parameter	Range
Pressure	1-10
Temperature	62-65
Flow rate	

n.d.=not determined

#### Additional comments from the supplier

- Flow rate depends on reactor size
- Electrochaea's archaea can use different CO<sub>2</sub> sources and are robust against many contaminants commonly found in industrial environments, including oxygen, hydrogen sulphide, carbon monoxide, ammonia, particulates, and biological contaminants.

### 5. PRODUCTS & EFFICIENCY

- Chemical efficiency: >99%
- Process output pressure: pressure of the reactor followed by pressure of the gas grid
- Process side reactions (conversion of other trace components): H<sub>2</sub>S content will be lowered due to being metabolised.

## 6. MAINTENANCE & FINANCE

- MTBM (mean time between maintenance): yearly maintenance on mechanical parts.
- CAPEX cost for the plants depend on local conditions and requirements (e.g. input quality of gas, required gas quality, local utilities, access to hydrogen among others).

FINANCE		
Plant size (thermal energy of H <sub>2</sub> input)	CAPEX (m €)	OPEX (m €)
5 MW	Not specified	Not specified
10 MW	Not specified	Not specified
20 MW	Not specified	Not specified

## 7. ADDITIONAL REMARKS SUPPLIER

Applications of Electrochaea's biomethanation technology:

- Increasing biomethane output from wastewater treatment, biogas plants and landfill sites
- Processing geothermal gases that contain CO<sub>2</sub> or biomass gasification upstream gases
- Use of carbon dioxide from industrial sources (e.g. fermentation, cement and steel plants)

## 8. REFERENCES & CONTACT

- 1 MW plant for the BioCat project. <https://biocat-project.com/>
- 700 kW equivalent Store & Go plant in Solothurn Switzerland. <https://www.storeandgo.info/>
- Demonstration plant at NREL, Golden, Colorado. <https://www.nrel.gov/news/program/2019/nrel-marks-partner-forum-with-dedication-of-bioreactor.html>

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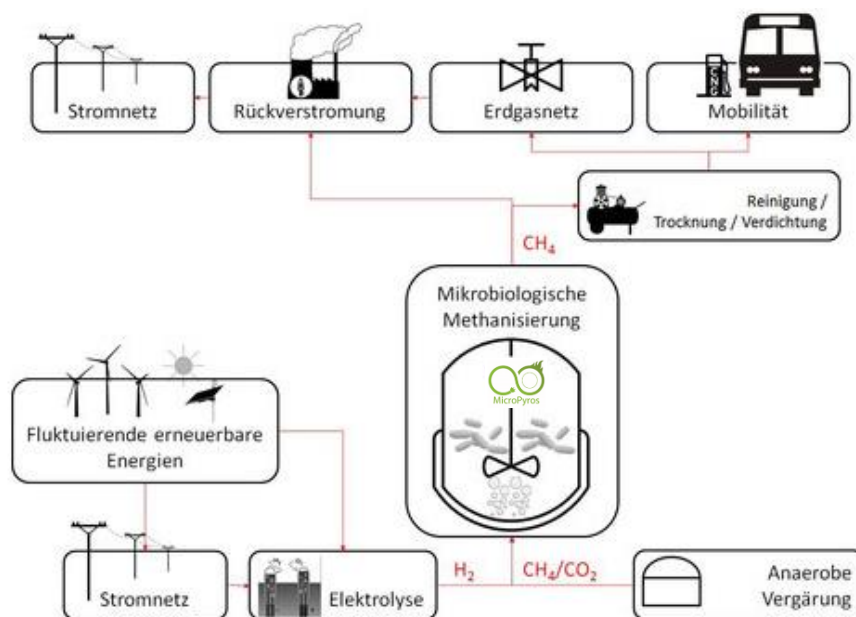
## 4.1.5 MicroPyros GmbH (Supplier)

### 1. GENERAL INFORMATION

MicroPyros GmbH is a German company founded in 2012. Their aim is to develop, engineer and coordinate Power-to-Gas plants. In order to achieve this, MicroPyros has developed a biological methanation concept. The methanation technology of MicroPyros can be applied to achieve a higher degree of methane in biogas, sewage and landfill gases. Another option is to use other CO<sub>2</sub> and/or H<sub>2</sub> sources, such as gases from thermochemical conversion of organic residuals and waste materials, in order to produce biomethane with micro-organisms as a biological catalyst.

MicroPyros offers its clients various assessments in order to find the best way to build a methanation plant. These assessments are based on aspects, such as available feedstock gases, technical and economically feasibility. After evaluation, MicroPyros plans and builds methanation plants together with partner companies, supports the operation of the plant and provides service, maintenance and repair as required.

### 2. PROCESS FLOW DIAGRAM



### 3. PROCESS

Operating principle	Biological methanation
Archaea type	Typically 2-4 out of 70 types of archaea
Reactor type(s)	Not specified
Number of reactors	1-4 or more depending on scope
Residence time	Aimed at >3 h <sup>-1</sup>
Scale range (MW)	10 kW to 100 kW for technical scope
Process pressure	1MW to 20 MW for technical scope 5-7 bar(g)
Process temperature	40 °C to 90 °C, depending on the used types of archaea; typically 60 °C-70 °C
Process acidity (pH)	more extreme values in alkaline or acid milieu possible, typically 6-8
Temperature control	Ability to heat and cool (allowing heat extraction)

### 4. INPUT SPECIFICATIONS & CONSTRAINTS

FEED GAS COMPOSITION		GAS CONTAMINATIONS		PROCESS INPUT	
Component	Range	Component	Limit	Parameter	Range
CO	<25 vol%	Halogens	Not specified	Pressure	5-12 bar(g)
CO <sub>2</sub>	<20 vol%	Sulphur	Not limited	Temperature	40-90 °C
H <sub>2</sub>	Not limited	Tar	Not specified	Flow rate	Not specified
CH <sub>4</sub>	Not limited	O <sub>2</sub>	<5000 volppm		

#### Additional comments from the supplier

- Sulphur Up to now limitation has not been observed
- Tar: small concentrations possible, but not specified up to now
- Archaea that convert CO into CO<sub>2</sub> are available

### 5. PRODUCTS & EFFICIENCY

- Chemical efficiency: >96%
- Pressure drop: not specified.
- Process side reactions (conversion of other trace components): H<sub>2</sub>S is reduced in the process, but it has not been specified up to now.

### 6. MAINTENANCE & FINANCE

- Maintenance depends on used feedstock; an example is a component exposed to hydrogen.

FINANCE		
Plant size (thermal energy of H <sub>2</sub> input)	CAPEX (m €)	OPEX (m €)
5 MW	A Request for quotation is necessary	A Request for quotation is necessary
10 MW		
20 MW		

## 7. ADDITIONAL REMARKS SUPPLIER

MicroPyros' technology differs from other methanation technologies in the following:

- Large range of educt gases due to different types of archaea
- Robust and flexible process
- Robust fumigation technology
- High methanation production rate due flexible process technology

## 8. REFERENCES & CONTACT

- 5 kW in-house technical pilot plant.
- 100 kW in-house industrial technical plant.

WWW	<a href="http://www.micropyros.de">www.micropyros.de</a>	
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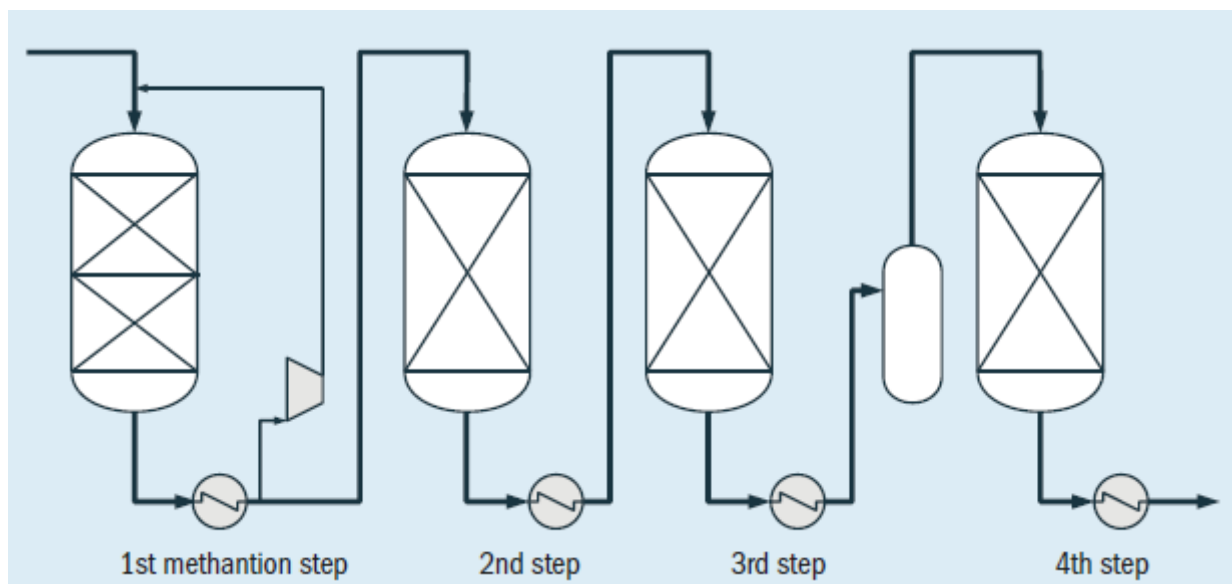
## 1. GENERAL INFORMATION

Haldor Topsoe is a Danish company specialised in catalysis and process technology. These days Haldor Topsoe is a renowned multinational, responsible for some of the largest SNG production plants in the world with their TREMP process.

This process is based on gasification and catalytical methanation, including secondary processes, such as tar reforming, gas cleaning and water-gas-shift. The TREMP process can also be used to convert biomass to bio-SNG.

The methanation installation depicted below is an isothermal fixed-bed reactor that uses steam production to control the exothermic energy from the Sabatier reaction.

## 2. PROCESS FLOW DIAGRAM



### 3. PROCESS

PROCESS FACTS	
Operating principle	Chemical methanation
Catalyst type	2 types of Ni-based cats. depending on operational T.
Reactor type(s)	Either adiabatic or isothermal (cooling by steam production) fixed-bed reactor
Number of reactors	Either 1 isothermal reactor or 5 intercooled adiabatic reactors for bigger units
Residence time	Not specified
Scale range (MW)	Up to 1900 MW
Process pressure	5-50 bar(g), typically 20-30 bar(g)
Process temperature	200-700 °C
Process acidity (pH)	Not specified
Temperature control	Product gas recycling for adiabatic or pressure control for isothermal reactors

### 4. INPUT SPECIFICATIONS & CONSTRAINTS

FEED GAS COMPOSITION		GAS CONTAMINATIONS		PROCESS INPUT	
Component	Range (v/v%)	Component	Limit (ppm)	Parameter	Range
CO	<25 vol%	Halogens	Not specified	Pressure (barg)	5-50
CO <sub>2</sub>	<20 vol%	Sulphides	Not specified	Temperature (°C)	200-700
H <sub>2</sub>	16-80 vol%	Tar	Not specified	Flow rate (Nm <sup>3</sup> /h)	Not specified
CH <sub>4</sub>	<80 vol%	O <sub>2</sub>	Not specified		

#### Additional comments from the supplier

- Syngas should be scrubbed in order to be free of dust, chloride and heavy metals.

### 5. PRODUCTS & EFFICIENCY

- Chemical efficiency: 96% CH<sub>4</sub>
- Process pressure drop: not specified
- Process side reactions: not specified

### 6. MAINTENANCE & FINANCE

- MTBM (mean time between maintenance) 2 years
- Maximum operation time of catalyst 3-10 years

FINANCE		
Plant size (thermal energy of H <sub>2</sub> input)	CAPEX (m €)	OPEX (m €)
5 MW	2	Not specified
10 MW	3	Not specified
20 MW	4,5	Not specified

## 7. ADDITIONAL REMARKS SUPPLIER

- Haldor Topsoe has produced an alternative to the intercooled adiabatic fixed-bed reactors as an improvement on the cost-effectiveness of the bio-SNG production process.
- Turning heat to steam facilitates more demanding processes, such as driving steam turbines.

## 8. REFERENCES & CONTACT

- GoBiGas in Gothenburg, Sweden, capacity of 2,200 Nm<sup>3</sup>/h from biomass, started up in 2014.
- Hengli Petroleum in Dalian, China, capacity of 130,000 Nm<sup>3</sup>/h from coal, started up in 2019.
- Wulan in Inner Mongolia, China, capacity of 78,800 from coal to LNG, started up in 2020.

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## 5 CONCLUDING REMARKS

This report considered the process chain from biogas or syngas production processes to methanation, because it is key to have detailed insight into the various biogas or syngas production and cleaning processes in relation to the applicability of the different methanation techniques in specific situations. The report contains a wealth of practical tips and information.

There are two main methanation areas, being chemical and biological methanation. Chemical methanation is the thermochemical conversion of carbon monoxide and/or carbon dioxide with hydrogen into methane with the aid of a catalyst. Biological methane production is performed with the help of so-called methanogens, a number of species of single celled micro-organisms from the domain of the archaea.


Chemical methanation has been applied for many decades, particularly with regard to coal gasification, which implies that the technology in this application field is fully developed. However, in other application fields and on a much smaller scale that suits biomethane production projects it is relatively new and unknown. This is more or less confirmed by the limited feedback on the request for information, which suggests that market readiness is not that high.

Biological methanation is relatively new in the market, but the development has accelerated in recent years and biological methanation may prove to be a good alternative to chemical methanation.

The methanation projects found in public sources are all located in Europe, Asia and North America. Most projects (approximately 75%) have been realised in Europe.

Differences between chemical and biological methanation technologies in particular occur in the integration of processes, such as the recovery of heat flows and the incoming gas composition. In addition, it is possible to identify a number of other differences:

- The residence time of gas in a chemical catalyst is factors lower than in a biological system. As a result, a chemical system has a more compact construction, resulting in a smaller physical footprint;
- Biological methanation can be performed at low temperatures and pressures, in contrast to chemical methanation, which requires elevated temperatures (250-550 °C). Both chemical and biological methanation can be used at high pressures, although the biological systems are used at 10 bars maximum in practice;
- Chemical catalysts are very sensitive to sulphur compounds and tar. As a result, the use of catalysts in the methanation of syngas is not easily performed; pre-cleaning must take place. Biological systems are expected to be more resistant to these trace components. Some suppliers mentioned that sulphur compounds could be converted into elementary sulphur;
- In a catalyst, both carbon monoxide and carbon dioxide can be converted. Not all micro-organisms are capable of converting carbon monoxide, so pre-conversion of carbon monoxide into carbon dioxide may be required;
- High and quick fluctuations in the incoming gas quality may have an adverse effect on the performance of biological methanation and consequently they should be prevented;
- High and quick fluctuations in the incoming gas quality can affect the temperature of the chemical methanation and have an adverse impact on the lifetime of the catalyst and therefore they are not desired.




Generally, it is possible to conclude that all technologies can be used for methanation of hydrogen and carbon dioxide. Methanation of syngas is more complex, due to the presence of carbon dioxide and trace components, mainly sulphur and tar.

Specific regulations for feeding the biomethane into the gas grid may lead to restrictions for components, such as oxygen and sulphur compounds, especially hydrogen sulphide.

In the Netherlands there are two gas qualities, being low calorific gas (G-Gas,  $W = 43.5-44.4 \text{ MJ/m}^3(\text{n})$ ) and high calorific gas (H-Gas,  $W = 49.9-55.7 \text{ MJ/m}^3(\text{n})$ ). As nitrogen is not converted in or removed from the methanation process, the maximum permissible concentration of this component is limited. Even the G-gas specification cannot be met using an air-operated gasifier. As a result, the gasifier placed before the methanation plant must be operated with pure oxygen or steam.

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## APPENDIX A: DUTCH FEED-IN SPECIFICATIONS

### Table: Entry specifications for the Dutch gas grid.

- 1) Distribution grid ( $\leq 9$  bar(a))
- 2) Regional transport grid (16-40 bar(a))
- 3) High pressure transport grid ( $\geq 40$  bar(a))
- 4) Hourly average. Deviations are specified
- 5) For gas mixtures that contain over 99 mol% CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>, the maximum CO<sub>2</sub> content is limited to:  
[CO<sub>2</sub>max]=10,32-0,72[N<sub>2</sub>]-0,87[O<sub>2</sub>]
- 6) Annual average. Peak value:  $\leq 20$  mg/m<sup>3</sup>(n)
- 7) Annual average. Peak value:  $\leq 31$  mg/m<sup>3</sup>(n)
- 8) Non-odorized grids: 0 mg THT/m<sup>3</sup>(n)

**Table: Entry specifications for the Dutch gas grid (cont'd)**

	G-Gas			H-Gas		
	RNB <sup>1)</sup>	RTL <sup>2)</sup>	HTL <sup>3)</sup>	RNB <sup>1)</sup>	RTL <sup>2)</sup>	HTL <sup>3)</sup>
Wobbe-Index (MJ/m <sup>3</sup> (n))	43,46-44,41 <sup>4)</sup>	43,46-44,41 <sup>4)</sup>	43,46-44,41 <sup>4)</sup>	49,9-55,7	49,9-55,7	49,9-55,7
Water dewpoint (°C @ bar(a))	≤-10 @ 8	≤-8 @ 70	≤-8 @ 70	≤-8 @ 70	≤-8 @ 70	≤-8 @ 70
Propane equivalent (mole%)	≤5	≤5	≤5			
Gas condensate (mg/m <sup>3</sup> (n) @ -3°C)	≤80	≤80	≤80	≤5	≤5	≤5
Temperature (°C)	5-20	5-30	5-30	5-30	5-30	5-30
Oxygen (mole%)	≤0,5	≤0,5	≤0,0005	≤0,5	≤0,5	≤0,0005
Carbon dioxide (mol%)	≤10,3 <sup>5)</sup>	≤10,3 <sup>5)</sup>	≤3	≤2,5	≤2,5	≤2,5
Carbon monoxide (mg/m <sup>3</sup> (n))	≤2900	≤2900	≤2900	≤2900	≤2900	≤2900
Organic chlorine (mg Cl/m <sup>3</sup> (n))	≤5	≤5	≤5	≤5	≤5	≤5
Organic Fluoride (mg F/m <sup>3</sup> (n))	≤5	≤5	≤5	≤5	≤5	≤5
Hydrogen (mole%)	≤0,5	≤0,5	≤0,02	≤0,02	≤0,02	≤0,02
Particulates (mg/m <sup>3</sup> (n))	≤100	≤100	≤100	≤100	≤100	≤100
Pathogene microbes (number/m <sup>3</sup> (n))	≤500	≤500	≤500	≤500	≤500	≤500
Anorganic sulphur components (H <sub>2</sub> S+CO <sub>2</sub> , (mg S/m <sup>3</sup> (n))	≤5	≤5	≤5	≤5	≤5	≤5
Alkylthioles (mg S/m <sup>3</sup> (n))	≤6	≤6	≤6	≤6	≤6	≤6
Total sulphur, before odorization (mg S/m <sup>3</sup> (n))	≤5,5 <sup>6)</sup>	≤5,5 <sup>6)</sup>	≤5,5 <sup>6)</sup>	≤30	≤30	≤30
Total Sulphur, after odorization (mg S/m <sup>3</sup> (n))	≤16,5 <sup>7)</sup>	≤16,5 <sup>7)</sup>	≤16,5 <sup>7)</sup>	≤41	≤41	≤41
Tetra hydro thiophene (odorant, mg THT/m <sup>3</sup> (n))	10-40	10-40	10-40 <sup>8)</sup>	10-40	10-40 <sup>8)</sup>	0
Sillicium (mg Si/m <sup>3</sup> (n))	≤0,1	≤0,1	≤0,1	≤0,1	≤0,1	≤0,1