# DNV·GL

TECHNICAL ASSUMPTIONS, TECHNOLOGY DEMONSTRATION AND RESULTS P2G PROJECT

# **Power-to-Gas project in Rozenburg, The Netherlands**

**TKI Gas – TKI 01015** 

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#### Objective:

An overview of the technical assumptions and results of the Power-to-Gas demonstration project in Rozenburg, The Neherlands

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## **EXECUTIVE SUMMARY**

In the future our energy system will see a transition to a system that is based on sustainable and renewable energy sources. Renewable energy sources are different from conventional fossil energy sources because of their low life-cycle carbon emissions and their intermittent nature. The intermittent nature of solar and wind energy means that matching the supply and demand of sustainably generated electricity will become more of a challenge. There will be a greater need for energy storage and flexibility of the energy infrastructure. When more intermittent sustainable sources are used, supply and demand is no longer easy to balance. In order to facilitate sustainable electricity production in the best possible way it is needed to look for opportunities to use and/or store the excess of sustainable electricity production. Power-to-Gas (P2G) is a technology that enables flexible operation and buffering of electricity excesses in the short and long term by storing electricity in the gas grid.

Due to the innovative technological nature of P2G, Stedin, DNV GL, TKI Gas, Community of Rotterdam and Ressort Wonen carried out a demonstration project that investigated the use and applicability of this technology. Prior to its realisation, the technical design guidelines, process criteria and principles were determined. They formed the basis for demonstrating P2G technology in a realistic environment that considered every element of the value chain - from production to end use. Sustainable electricity that was generated with solar panels was converted into synthetic gas of natural gas quality, via hydrogen and methane and is applied in a gas-fired boiler of nearby flat buildings.

During the term of the demonstration project the system proved that it is possible to deploy Power-to-Gas on a continuous basis for the application of peaks of sustainably generated electricity. The produced synthetic gas complied with all the specifications that apply to injection into the Dutch gas grid.

During the implementation of the project practical information was obtained about the technical feasibility of the complete system and the individual system components. For example, the conversion of electricity into hydrogen and oxygen was performed with an energetic efficiency of 47%. The remainder of the energy - in the form of heat - could not be used locally. Heat is also released during the catalytic conversion of hydrogen and carbon dioxide, and this could not be used either. The energetic efficiency of this methanation process was set at 73%. The energy balance of the complete Power-to-Gas system demonstrated an energetic efficiency of 35%. Besides optimising the energetic efficiency, it is important that the outgoing gas complies with the specifications that apply to injection into the gas grid. The Dutch distribution network requires gas to contain no more than 0.1 mole% hydrogen. The optimum settings of the methanation process are therefore a compromise between the highest achievable energetic efficiency and the outgoing hydrogen concentration. Maximising the energetic efficiency requires increasing the hydrogen specification of the gas grid.

The entire Power-to-Gas system can be started up from standstill to maximum capacity in approximately 40 minutes. This means that approximately 4 minutes are required to start up the electrolyser and approximately 35 minutes for methanation. The electricity consumption of methanation is low in relation to the electricity consumption of the electrolyser. The amount of electricity that is used by the Power-to-Gas system therefore largely depends on the electricity demand of the electrolyser. This means there is a control speed for electricity consumption within approximately 4 minutes.

The completed process releases several product flows that are not used economically yet. Future study could focus on expanding the system with other technologies to close cycles for those product flows (process water, heat and oxygen). From a sustainability point of view it is recommended to perform further studies into the possibility of recovering water and carbon dioxide from the flue gases of the gas-fired systems in order to close the carbon cycle.

# LIST OF ABBREVIATIONS

Abbreviation	Description
ATEX	ATmosphères EXplosibles, the European Directive for explosion hazards under
	atmospheric conditions
CH <sub>4</sub>	Methane
CO <sub>2</sub>	Carbon dioxide
Ср	Specific heat capacity
DCMR	Environmental Department Rijnmond and competent authority in Rozenburg for safety
	and environment
GC	Gas chromatograph
Hazop	Hazard and Operability Study, i.e. a fault analysis
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
kWh	Kilowatt hour
N <sub>2</sub>	Nitrogen
Ni	Nickel
0 <sub>2</sub>	Oxygen
P2G	Power-to-Gas
PED	Pressure Equipment Directive
PEM	Proton-Exchange Membrane
PV cell	Photovoltaic cell
RVS	Stainless steel
SEM-EDX	Scanning Electron Microscope - Energy Dispersive X-Ray (raster electron microscope
	and x-ray defraction)
SNG	Synthetic Natural Gas, i.e. a natural-gas substitute of synthetic origin
THT	Tetrahydrothiophene, an odorous substance that is added to natural gas for odour
	recognition
TRA	Task Risk Analysis
ΔΗ	Heat of generation or enthalpy

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# **1 INTRODUCTION**

In the future our energy system will see a transition to a system that is based on sustainable and renewable energy sources. Renewable energy sources are different from conventional fossil energy sources because of their low life-cycle carbon emissions and their intermittent nature. Sustainable electricity production is highly dependent on weather conditions. The intermittent nature of solar and wind energy means that matching the supply and demand of sustainably generated electricity will become more of a challenge and there will be a greater need for energy storage and flexibility of the energy infrastructure. Energy carriers will have to be available at all times. During the winter season, the demand for energy is many times larger than in the summer. The purchase profile also fluctuates strongly over a 24-hour period. In order to be able to meet this constantly changing energy demand in future, other energy carriers will have to be available at all times.

When more intermittent sustainable sources are used, supply and demand is no longer easy to balance. In order to facilitate sustainable energy production, electricity production in particular, in the best possible way, we are looking for opportunities to use and/or store the excess of sustainable electricity production. There are several technologies available for storing electricity that can be used in function of the amount of available electricity, duration of the storage, and geographical circumstances. Some examples include a flywheels, batteries, compressed air energy storage and hydro-power. Each of those specific storage technologies has its own specific advantages and disadvantages that depend on the storage location, capacity and duration.

# 1.1 **TKI Gas System flexibility**

Besides the technologies that are available for storing in the form of electricity, the flexibility of the gas system can also be used. Innovations are required in order to use the system function of gas in the best possible way in the future. These innovations are in the areas of technology, ecology, business models, trade, regulations, social and system aspects. The policy theme 'System function of gas' of TKI Gas is centred on the question as to which innovations are possible to ensure the gas system makes an optimum contribution to the transition to a sustainable energy economy.

TKI Gas serves to achieve a substantial contribution of green gas to the sustainable energy economy and to provide the Netherlands with a strong competitive and export position in the area of knowledge, technology, innovation and trade. Within the policy theme 'System function of gas' of TKI Gas the central question is which innovations are possible to ensure the gas system makes an optimum contribution to the transition to a sustainable energy system.

# 1.2 Role of Power-to-Gas

As an alternative to conventional storage methods, Power-to-Gas (P2G) can play a role by converting electricity into gaseous hydrogen (see Figure 1). P2G uses electrolysis, which uses electricity to decompose water molecules into hydrogen and oxygen. The hydrogen that is released during electrolysis can be used in different ways, such as direct use in an incineration plant or injection in the public gas grid. The amount of hydrogen that can be injected into the gas grid is limited by the gas quality that is supplied in the relevant grid and the type of users who are supplied by the grid. Partly because the existing Dutch gas infrastructure is set up for using gas that mainly consists of methane, the direct application of hydrogen is not always immediately possible. For situations where the use of hydrogen is limited, hydrogen can be converted into methane with carbon dioxide.

This principle is called methanation and was discovered by Paul Sabatier around 1910. Hydrogen and carbon dioxide are converted using a catalyst, where they are converted into methane and water (see Figure 2).



Even though the sub-processes and processes of the Power-to-Gas concept are available, the P2G concept has a new application in controllable load. That makes Power-to-Gas an intelligent technology that facilitates flexible operation and buffering of energy surpluses in the short and long term. Consequently Power-to-Gas can fulfil a key function in the entire energy system in the near future, by linking up the world of electricity and the world of gas. Part of the economic benefits that are offered by Power-to-Gas to the integration of renewable electricity sources can be attributed to this technology. However, the application of Power-to-Gas as controllable load and the corresponding economic interests fall outside the scope of this project.

### 1.3 **Objective of the demonstration project**

The objective of the project was to develop and demonstrate technical design guidelines, process criteria and principles. By implementing the project in a realistic environment, all the elements of the value chain can be considered - from production to end use. The study included preparing the design guidelines and determining the process criteria, and they were used to construct an actual system. During the demonstration of the system, the relevant performance characteristics were determined that may serve as the basis for future P2G systems.

### 1.4 **Partners**

To achieve the objective following partners concluded a cooperation agreement on 19 April 2013. The parties expressed the intention to use a P2G system to turn sustainable electricity into sustainable gas in Rozenburg (Rotterdam Council). The partners undertook different roles and had different objectives.

### 1.4.1 Stedin

Stedin Netbeheer is linked to the P2G project as the most important project partner and external financier and consequently contributed to the sustainability objectives that it pursues as grid operator without developing additional activities or incurring costs outside the statutory duties of a grid operator. Stedin provided the construction of the required infrastructure on site. Stedin also secured the supply of synthetic natural gas to Ressort Wonen and supervised the safety of the P2G system.

# 1.4.2 DNV GL

The P2G project is led by DNV GL (KEMA Nederland B.V.), which operates worldwide as an independent technical adviser in the oil and gas industry amongst others. DNV GL supported the P2G project from a technological point of view by defining the technical design and control guidelines, validating the chosen technology and safeguarding the safety, system and gas-quality requirements. Consequently DNV GL contributes to making the gas supply sustainable in a safe and effective manner.

# 1.4.3 TKI Gas

The project is also financed by TKI Gas. Within TKI Gas, the P2G project is known as TKI01015 and comes under the TKI theme "System function of Gas".

# 1.4.4 Rotterdam Council

Rotterdam/Rozenburg Council made a site of 625 m<sup>2</sup> available for implementing this project and provided support during the permit process.

# 1.4.5 Ressort Wonen

Ressort Wonen represents the end users by purchasing the produced gas in the flat buildings at Bosseplaat in Rozenburg. Ressort Wonen made room available for installing measuring equipment for this project.

# 1.5 More information

More information about this P2G project is available on <u>www.powertogas.nl</u> and on the website of TKI Gas, <u>www.tki-gas.nl</u>. The TKI Gas website also contains information about other projects within this programme. One of those projects is "Exploring the role of Power-to-Gas in the Dutch energy system", which studies the role P2G could play at system level within the future Dutch energy supply.

There is also major interest in this topic at international level. For example the North Sea Power to Gas Platform was founded; this alliance has the objective to explore the feasibility and viability of Power-to-Gas in countries around the North Sea. More information about the platform and the studies that are carried out within this platform is available on <u>www.northseapowertogas.com</u>.

# **2 THEORETICAL BACKGROUND AND DESIGN CRITERIA**

This chapter deals with the production chain of the Power-to-Gas process and describes the impact of the various parameters. The described information was partly obtained from literature and partly from simulations and calculations performed by DNV GL as part of this project. The design criteria that the system must comply with were determined on this basis.

# 2.1 **Production chain**

The Power-to-Gas production chain consists of two technologies, being 'electrolysis' and 'methanation'. Electrolysis refers to converting electricity into hydrogen. Methanation is the synthetic conversion of hydrogen and carbon dioxide into methane.

From an exergetic and economic point of view it is always preferable to use sustainably generated electricity locally as electricity or to sell it to the grid. However, when supply outstrips demand and there are problems in the electricity sector, such as congestion, negative electricity prices or physical damage, the electricity can be converted into hydrogen. The sale of hydrogen is limited by economic and/or technical limits and thresholds and may be converted into methane that can be upgraded to natural-gas quality to ensure it is fully exchangeable with natural gas. The 'merit order' for Power-to-Gas is as follows:

(1) Convert electricity into hydrogen and inject it into the gas grid;

(2) Methanise hydrogen and carbon dioxide and upgrade the synthetic gas to natural-gas quality ('Synthetic Natural Gas, SNG) and inject it into the gas grid.



Every step of the Power-to-Gas production chain is set out in Figure 3.

Figure 3: Power-to-Gas production chain

To provide more insight into the product flows of the Power-to-Gas concept, Figure 4 contains a flow diagram that describes the flows on a proportional basis. It visualises the material flows and the mass efficiency of the process can be estimated. The flow diagram demonstrates that only part of the electricity is converted into hydrogen and only part of the hydrogen is converted into methane. Methane is then mixed with a small flow of carbon dioxide in order to comply with the gas-quality parameters before it can be injected into the gas grid. Electrolysis and methanation release heat that cannot be applied usefully in the current concept.



#### Figure 4: Product flows in the Power-to-Gas concept

### 2.2 Electrolysis

The first step of the Power-to-Gas production chain uses electrolysis. Electricity is used to decompose water molecules into hydrogen and oxygen. This project used Proton-Exchange Membrane (PEM) electrolysis. The electrolysis cell consists of a (positive) anode, where oxygen production takes place, and a (negative) cathode, where hydrogen is formed. The two gaseous components are separated by a proton exchange membrane (PEM), see Figure 5. Due to the charge of both electrons, water decomposes into (negative) oxygen and (positive) hydrogen ions. The electrodes are in direct contact with the membrane, which means the ions diffuse through the membrane to the opposite charged electrode [2].





# 2.2.1 Reaction mechanisms and reaction kinetics

The chemical part reactions of the conversion of electricity into hydrogen and oxygen are set out in formulas (R.1).

 $H_2O(I) \rightarrow 2H^+(aq) + O^2^-(aq)$ kathode:  $2H^+(aq) + 2e^- \rightarrow H_2(g)$ anode:  $O^2^-(aq) \rightarrow O_2(g) + 2e^-$ 

(R.1)

The net or overall reaction of the electrolysis process is:

 $2H_2O \rightarrow 2H_2 + O_2$   $\Delta H^0 = -286 \text{ kJ/mol}$  (R.2)

Reaction R.2 demonstrates that this is an exothermal process that releases 286 kJ/mol as heat.

# 2.3 Methanation

The second step in the Power-to-Gas production chain is methanation where hydrogen is converted into methane and water by adding carbon dioxide. The principle is based on the Sabatier reaction and a catalyst is required for the conversion into methane. Methanation is a developed technology that is commercially available in the market. However, the technology is only applied in various large-scale industrial applications.

### 2.3.1 Reaction

The methanation reaction is an equation, as following:

$$CO_2 + 4H_2 \xleftarrow{kat} CH_4 + 2H_2O$$
  $\Delta H^0 = -165 \text{ kJ/mol}$  (R.3)

Several steps are required to achieve full conversion into methane. After every step the formed water is removed to prevent the equation shift to the left. The conversion into methane produces 165 kJ/mol of heat.

Besides the ideal reaction (R.3), side reactions may also take place, such as the formation of carbon monoxide (R.4). However, the formed carbon monoxide can also be used for conversion into methane, as set out in reaction R.5.

$$CO_{2} + H_{2} \xleftarrow{kat} CO + H_{2}O \qquad \Delta H^{0} = +42 \text{ kJ/mol} \qquad (R.4)$$

$$CO + 3H_{2} \xleftarrow{kat} CH_{4} + H_{2}O \qquad \Delta H^{0} = -206 \text{ kJ/mol} \qquad (R.5)$$

It is assumed that the heterogenic, catalytic reactions R.3 to R.5 take place in accordance with the Langmuir-Hinshelwood (HS) principle, where reactions take place between adsorbed active particles [3]. The reaction mechanism for this gas reaction is described in the reaction equations R.6 to R.10. S is the catalyst surface.

$CO_2 + S \leftrightarrow CO_2 \bullet S$	(Adsorption)	(R.6)
$4H_2 + 4S \leftrightarrow 4H_2 \bullet S$	(Adsorption)	(R.7)

$CO_2 \bullet S_{(ads)} + 4H_2 \bullet S \leftrightarrow CH_4 \bullet S + 2H_2O \bullet S + 2S$	(Surface reaction)	(R.8)
$CH_{\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!}\bulletS\leftrightarrowCH_{\!$	(Desorption)	(R.9)
$2H_2O \bullet S \leftrightarrow 2H_2O + 2S$	(Desorption)	(R.10)

Figure 6 is a schematic representation of reactions R.6 to R.10.

Active surface of the catalyst Non-active surface of the catalyst 2.6 CO<sub>2</sub> 2.8 CO 2.7 2.9 CH₄ 2 H<sub>2</sub> 2 H<sub>2</sub> 1 D  $\overline{Z}$ 2.10 H<sub>2</sub>C H<sub>2</sub>O 777

Figure 6: Schematic representation of the Langmuir-Hinshelwood principle [12]

The reactants carbon dioxide and hydrogen will adsorb to the catalyst surface (reactions R.6 and R.7). 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 achieved (reaction R.8). The affinity of the formed reaction products with the catalyst material is less than that of the reactants, which means they will desorb [1], as represented in reactions R.9 and R.10).

At the start the equilibrium formula R.8 will move from left to right due to the absence of methane and water, in other words the reactants carbon dioxide 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 part of the formed methane and water will react back to hydrogen and carbon dioxide. This reverse reaction will take place until a balance situation has been achieved.

In a balance situation a full conversion of reactants does not take place. 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 dioxide. This is achieved by cooling the gas mixture after every reactor, which means the formed water will condensate and that makes it easy to discharge.

# 2.3.2 Catalyst

A certain amount of activation energy is required for the reaction to take place. The activation energy is the smallest amount of energy that is required to activate atoms or molecules into a state where they can undergo a chemical reaction [7]. During the methanation process, a catalyst is used to increase the reaction speed and to reduce the activation energy.

In the case of an exothermal reaction, such as the Sabatier process, the reaction will continue after the reaction has been activated because this is more favourable from an energetic point of view and more energy is supplied than required for the reaction. An external heat source is no longer required.

### 2.3.2.1 Choosing the catalyst

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 because of its large specific surface. A carrier with a large specific surface (m<sup>2</sup>/kg) generally promotes the effectiveness of the catalyst as large amounts of catalyst are present per volume-unit of material. The carrier material also determines the stability of the catalyst. Nickel is generally used for the methanation of carbon dioxide, carbon monoxide and hydrogen. It is also possible to use ruthenium (Ru), rhodium (Rh), platinum (Pt), iridium (Ir), cobalt (Co), iron (Fe) or palladium (Pd). On the basis of the information in literature, the following order of selection is used for the methanation of is where the catalyst with the highest specific activity is listed first (Ross, 2006).

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

However, literature study also demonstrates that the situation is slightly different for the methanation of carbon dioxide. It should be noted that different orders are given. The selectivity does not only depend on the catalyst material, but is also strongly affected by the carrier material. This may explain the discrepancies in the various literature sources. A recent literature review [14] demonstrated that the highest methane production is expected from the following catalysts:

 $Ru > Rh > Pt > Ir \sim Pd$ 

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

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 means that nickel is the optimum catalyst. This project and many other commercial processes use nickel as a catalyst. Oxygen adsorbs easily to 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:

$$2Ni-KAT+O_2 \leftrightarrow 2Nf^+O^{2-}$$
(R.11)

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 a low-oxygen gas, such as nitrogen or hydrogen.

$$2(KAT-H)+N^{2+}\leftrightarrow(KAT)_{2}N^{2+}+2H^{-}$$
(R.12)

During the methanation reaction carbon dioxide and hydrogen will adsorb to the catalyst surface (reactions R.6 and R.7). Here there is a reaction between the adsorbed reactants, which means the products methane and water are formed (reaction R.8) until the situation is in balance. It could be said that desorption of the products takes place, because they adsorb less strongly to the catalyst surface in relation to the reactants [1] hydrogen and carbon dioxide.

#### 2.3.2.2 Catalyst degeneration

A decrease in the catalytic activity and selectivity over time is a process that 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 the loss of activated ions. However, for as long as this process occurs in a controlled manner it is a slow process and engineering and investment decisions can be taken accordingly. Although normal degradation is inevitable, unintentional immediate poisoning or deactivation must be prevented. Table 1 represents the mechanisms for degeneration and deactivation.

Mechanisms	Туре	Description
Poisoning	Chemical	Chemical adsorption of molecules to the catalyst which reduces the reaction surface of the catalyst.
Contamination	Mechanical	Deposit of reaction fluids and/or solid substances on the reaction surface and the pores of the catalyst.
Thermal degradation	Thermal	Losses of reaction surface, ion activity or impacting the support material to which the catalyst material is applied due to high temperatures.
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) of the catalyst and/or carrier material.

 Table 1: Degeneration and deactivation mechanisms of catalysts

### 2.3.3 Hydrogen conversion

In the Power-to-Gas concept achieving a balance situation is not important, as forming as much methane as possible is the ultimate aim. The balance constant cannot be used as a measure for methane formation. Therefore a conversion factor is used as a measure for the conversion rate of reactants into products. In this report, conversion on the basis of hydrogen is the determining factor and we do not deal with conversion on the basis of carbon dioxide, as hydrogen is part of the main flow of Power-to-Gas. The conversion is calculated as follows:

$$X_{H2} = \frac{H_{2,in} - H_{2,out}}{H_{2,in}} *100\%$$

(F.1)

#### Whereby:

XH2conversion rate (%)H2,inincoming hydrogen concentration (mol%)H2,outoutgoing hydrogen concentration (mol%)

# 2.3.4 Reaction kinetics and thermodynamics

The reaction kinetics were studied as input for the system design. An equilibrium was assumed, as set out in equation R.3. The balance constant for the reaction is:

$$K_{p} = \frac{X^{2}_{H2O} \cdot X_{CH4}}{X_{CO2} \cdot X^{4}_{H2}} \cdot \left(\frac{P}{P_{0}}\right)^{-2}$$
(F.2)

Whereby:

- K<sub>p</sub> balance constant (-)
- $X_n$  concentration of individual components (mol%)
- *P* operating pressure (kPa)
- $P_0$  atmospheric pressure (101.325 kPa)

It is not possible to deduce the balance constant immediately, since this depends on reaction temperature. However, literature study has demonstrated that the process temperature most certainly affects the reaction kinetics. We know from literature that undesirable side reactions may occur at temperatures of <150°C and >700°C [8]. In the low temperature range the toxic nickel tetracarbonyl may be formed, whilst at temperatures above 700°C tar is formed as methane decomposes. The formed tar can contaminate the catalyst material, which reduces the efficiency of the catalyst [6].

On the basis of the balance reaction, which is given in equation R.3, it is possible to determine the theoretical energetic efficiency of the methanation:

$$\eta = \frac{\Delta H_r}{\Delta H_p} = \frac{4 \cdot \Delta H_{r,H2} + \Delta H_{r,CO2}}{\Delta H_{p,CH4} + 2 \cdot \Delta H_{p,H2O}}$$
(F.3)

Whereby:

- η energetic efficiency
- $H_r$  heat of formation of the reactants (at 298K and 101.325 kPa: Δ $H_{r,H2}$ =-0 KJ/mol and Δ $H_{r,CO2}$ =- 393.5 KJ/mol)
- $H_r$  heat of formation of the products (at 298K and 101.325 kPa: Δ $H_{p,CH4}$ =-74.87 KJ/mol and Δ $H_{p,H20}$ -241.82 KJ/mol)

Under standard conditions (101.325 KPa and 298 K) and on the basis of a chemical balance, this means that the maximum theoretical efficiency of methanation is 70%. The maximum theoretical efficiency of methanation depends on the Cp specific heat capacity (Cp) of the products, in accordance with:

$$\Delta H_{p,298K} = \int C p \cdot dT$$

(F.4)

The formula means that the specific heat capacity of methane and water changes in function of the temperature of the products. This is represented graphically in Figure 7.



Figure 7: Theoretical efficiency and conversion plotted against temperature

The theoretical energetic efficiency of the balance reaction may rise from 73% at 200°C to 81.5% at 700°C as the temperature of the products methane and water increases. However, the conversion decreases with a rising temperature. The so-called 'Break Even Point' between both factors is at a system temperature of 377°C. This temperature is the optimum temperature that achieves the highest energetic efficiency and the highest conversion.

#### 2.3.4.1 Temperature influence

The reaction kinetics strongly depend on temperature, and the methane concentration decreases with a higher temperature. The relationship between hydrogen conversion and temperature for an adiabatic reactor, without heat exchange with the environment, is represented in Table 2. Here the conversion of hydrogen and carbon dioxide is influenced by the increase in the reaction products methane and water, with a rising temperature. This is caused by an increase in the specific heat capacity of methane and water, which means the conversion rate decreases with a rising temperature [10]. Table 2 gives some examples of this temperature dependence.

temperatures			
Component	Cp at 400 K	Cp at 800 K	
Methane	40	63	
Water	34	39	

Table 2: Specific heat capacity (Cp, in KJ.kmol<sup>-1</sup>.K<sup>-1</sup>) of the reaction products at different temperatures

Besides insight into the progress of the equilibrium under the influence of temperature, Figure 8 also provides insight into the formation of any side products and any deposits on the catalyst. It is relevant to consider this, because it can be used to affect the efficiency of the process and the quality and effectiveness of the catalyst material. The figure visualises that the carbon monoxide concentration in the product gas increases with a rising temperature. This is an indication of an incomplete conversion and may be an indicator of deposits of tar (carbon) on the catalyst, due to dissociation of carbon and oxygen at high temperatures. The performed reaction kinetics simulation for the various scenarios demonstrated that the optimum temperature range is 200-250°C, when the highest possible conversion can be achieved. It must be noted that the energetic efficiency was not taken into consideration.



Figure 8: Concentration ratio of the outgoing gas in function of the temperature

#### 2.3.4.2 Pressure influence

Theoretically speaking the balance of reaction R.3 shifts right with an increasing pressure, which means more products (methane and water) are formed. This also follows from formula F.2, where the pressure dependence of the reaction is described in the term ( $P/P_0$ ). The performed reaction kinetics simulation for the various scenarios also demonstrated that a higher conversion is achieved when the pressure is increased. This pressure dependence is represented in Figure 9, which shows graphically that under unchanged circumstances the methane concentration increases and the concentrations of reactants decrease when the pressure is increased. The pressure is limited by the material specifications.



Figure 9: Concentration ratio in function of pressure

#### 2.3.4.3 Influence of hydrogen/carbon dioxide ratio

The theoretical mol ratio between hydrogen and carbon dioxide is 4:1 (or 4). With a smaller ratio (<4) there is an excess of carbon dioxide and with a higher ratio (>4) there is an excess of hydrogen.

Formula F.3 allows us to deduce that with an excess of carbon dioxide the reaction temperature decreases whilst an excess of hydrogen increases the reaction temperature. If the calculated conversion does not take account of incoming and outgoing concentrations of hydrogen, the conversion will be determined too low, particularly for an excess of hydrogen. An excess of carbon dioxide means that the conversion is calculated too high. Figure 9 represents the conversion, not taking account of dilution of the incoming and outgoing gas flows due to the component available in excess.



Figure 10: Influence of hydrogen/carbon dioxide ratio

### 2.3.4.4 Sensitivity analysis on the reaction kinetics

The previous sub-paragraphs have demonstrated that various parameters affect the balance reaction and therefore the methane production. However, the influence of these parameters varies. On the basis of certain influences a sensitivity analysis has been performed that helps to determine the extent to which a certain parameter contributes. The reference situation assumes a reactor temperature of 350°C, a pressure of 1 bara and a mol ratio between hydrogen and carbon dioxide of 4:1. This sensitivity analysis is represented in Figure 11, where all the parameters were varied 20%.

The analysis demonstrated that a reduction of the reactor temperature had the most positive effect in relation to the reference situation. Increasing the hydrogen level - whilst the carbon dioxide level stays the same - and increasing the reactor temperature has a negative impact on hydrogen conversion.



Figure 11: Sensitivity analysis reaction kinetics

# 2.4 Gas grid injection and end use

Safeguarding and monitoring gas quality are essential to safe, sustainable and reliable gas transport, distribution and utilisation. Safety can be guaranteed by imposing strict quality requirements on the gas that may be injected into the gas grid. The injection conditions include that injecting gas must be stopped automatically when the gas does not comply with the imposed requirements. This means that only on-spec gas ends up in the grid and the safety of the grid and the end users is guaranteed. The requirements for injected gas are set out in the Ministerial Scheme for Gas Composition (MR Gassamenstelling), as addition to the Gas Act of the Ministry of Economic Affairs [11]. The applicable requirements from this Scheme for the Power-to-Gas project are set out in Table 3.

Parameter	Value	Unit
Wobbe number*	44.10 - 44.41	MJ/m <sup>3</sup> (n)
Oxygen	≤ 0.5	mol%
Carbon dioxide	≤ 10.3	mol%
Hydrogen	≤ 0.1	mol%
Carbon monoxide	≤ 0.23	mol%
Water dew point	≤ -10	°C (at 8 barg)

Table 3: Requirements for gas composition

\* The lower limit of the Wobbe is limited, because the carbon dioxide content exceeds 8%.

### 2.5 Health, safety and the environment

A successful implementation of Power-to-Gas requires the technical aspects and the corresponding risks of such a system to be under control and the system to comply with all the requirements in relation to health, safety and the environment.

# 2.5.1 Risk identification

The risks mainly originate in process conditions (temperature and pressure), the presence of flammable gases (hydrogen and methane), possibly asphyxiating gases (carbon dioxide and carbon monoxide), nickel-containing catalyst material and the presence of high electricity voltages. The gas to be injected must also comply with all the specifications (gas quality and pressure) that are imposed by the grid manager. Figure 12 is a schematic representation of all the risks. This paragraph deals with the most important process risks for every process element.



Figure 12: Identified system risks

To mitigate the risks, the system components are considered individually, but the influence of the system components on each other is also taken into account. All risks may be identified during the design phase with a fault analysis ("Hazard and Operability" or Hazop) and/or a Task Risk Analysis (TRA). The next step is to determine the effect for every risk and the chance of it occurring. This information is used to determine whether control measures must be taken.

They may consist of:

- Hardware modifications to prevent an undesirable situation from occurring;
- Measuring the relevant parameter, following which a software check is performed as to whether predefined threshold values were exceeded or not. If the threshold values are exceeded, a so-called safety procedure must be put into motion whereby the system is switched off under controlled conditions.

It was ascertained that the Power-to-Gas system, either as a whole or its components - the pressure vessels, pipes or systems - does not come under the Pressure Equipment Directive (PED) 97/23/EC, as the internal volume in combination with the pressure is sufficiently low. NEN1010 (low-voltage system installation), NEN3140 (operating low-voltage systems) and ATEX (explosion safety) standards do apply.

#### 2.5.1.1 Electrolyser

The electrolyser is operated at high capacity and must be connected in accordance with the NEN-1010 guidelines During electrolysis, hydrogen and oxygen are formed under high pressure (approx. 10-15 barg). Hydrogen is a flammable gas and oxygen is highly corrosive and fire intensifying. The system must be classified in accordance with the ATEX guidelines. During assembly this classification must be taken into account by using elements that comply with this class or that are positioned at an adequate distance from the electrolyser. The room must also be fitted with the required gas-detection equipment.

#### 2.5.1.2 Methanation

The risks of methanation are more diverse than those of the electrolyser. For example, the pressure and temperature may become higher than those for which the system is specified and certified. There is also a chance methane, hydrogen and carbon dioxide leaks that are flammable or asphyxiating. The process also contains heavy metals (catalyst).

The methanation process is operated in the temperature range of 200–500°C, whereby the temperature in the catalyst may run up locally to 700°C. The ignition temperature of hydrogen lies within this temperature range, which means the presence of oxygen in the process produces an increased risk of self-combustion. Adding oxygen must be prevented.

When the Sabatier reaction does not run stoichiometrically or is not operated within the correct temperature range, there is a chance of side products being formed, such as carbon monoxide, higher hydrocarbons and nickel carbonyl. The formation of those components may lead to blockage of the reactors and hazardous situations during exposure.

The water that is formed during the reaction may contain traces of nickel. The concentration of this heavy metal may not exceed the standard for discharge into the sewer. The temperature of the discharge water must also comply with the requirements for discharging into the sewers.

The system must be classified in accordance with the ATEX guidelines. During assembly this classification must be taken into account by using elements that comply with this class or that are positioned at an adequate distance from the electrolyser. The room must also be fitted with the required gas-detection equipment.

The methanation is operated at high electrical power and must be connected in accordance with the NEN-1010 guidelines

### 2.5.1.3 Injection into the gas grid

In order to guarantee the safety of gas transport and distribution, the outgoing gas must comply with the specifications as set out in Table 4. Therefore the specified parameters of the gas composition must be measured or calculated continuously. The system must be equipped with a provision that makes it possible to stop the injection immediately if one or more parameters are outside the threshold values. The system must be fitted with pressure monitoring in order to prevent exceeding the maximum pressure of the pipe network.

### 2.5.2 Waste management and emissions

During normal operation of the P2G system, emissions to air are not expected. During emergencies the gas that is present in the system must be vented briefly. Water that is formed during the reaction (process water) is discharged as wastewater to the sewer. This water may contain traces of heavy metals. The temperature of the discharge water is limited to 25°C. Process water quality and temperature must be monitored in order to control any risks and to comply with the requirements for the discharge. There are no emissions to soil and the noise level is below 40 dB.

The catalyst material that is present in the reactors contains the heavy metal nickel and must be collected by a specialist company.

# 2.6 Design criteria methanation

To guarantee successful implementation, the design criteria for methanation and injection were determined on the basis of the reported theoretical background and safety criteria. They are summarised in Table 4.

Parameter	Value	Unit
Temperature range	150 - 700	°C
Optimum temperature	377	°C
Temperature range catalyst	150 - 700	°C
Mol ratio H <sub>2</sub> :CO <sub>2</sub>	4:1	mol/mol
Wobbe index	44.10 - 44.41	MJ/m <sup>3</sup> (n)
Oxygen content	≤ 0,5	mol%
Carbon dioxide content	≤ 10,3	mol%
Hydrogen content	≤ 0,1	mol%
Carbon monoxide content	≤ 0.23	mol%
Water dew point temperature	≤ -10	°C (at 8 barg)

#### Table 4: Design and process criteria methanation and injection

There are four solid-bed reactors in order to achieve the highest possible methane production. Figure 13 plots the methane concentration against the temperature, whereby the rising methane concentration occurs in one reactor until the balance has been achieved. The gas is then cooled to ambient temperature, heated again and introduced into the next reactor.



Figure 13: Methane formation process in relation to system temperature in the methanation system at a system pressure of 1 bara, whereby the incoming methane concentration in the first reactor is 0 mol%.

# **3 EXPERIMENTAL PROCESS IMPLEMENTATION**

This chapter describes the system that was built and deals with the various system components. The description of the system components has been divided into four paragraphs, as set out in Figure 14. Risk-mitigating measures have also been detailed further.



Figure 14: Schematic representation of system components

The entire system consists of three containers. The first container contains the electrolysis, the second container is where methanation takes place and where the gas is upgraded to the correct specifications. The third container contains two storage tanks that are filled with carbon dioxide.



Figure 15: Overview of the entire system

# 3.1 Electricity supply

The electrolyser is partly supplied with electricity that is generated with photovoltaic cells (solar panels) that are positioned on the roof of the containers. As the generated electrical capacity is not sufficient to meet the complete electrical demand, green power is obtained from the electricity grid.

# 3.2 Electrolysis

The project used a commercially available electrolyser that had been used earlier by Stedin for a project in Ameland [5].

The Hogen® S-40, series II electrolyser is able to generate hydrogen with a theoretical purity of 99.9995%, <5 ppm water and < 1 ppm oxygen. The electrolysis is based on PEM technology, whereby a membrane polymer ensures the split of hydrogen and oxygen in the stack (Figure 17). The net hydrogen production capacity is 1.05 Nm<sup>3</sup>/hour or 2.27 kg/day. Water consumption is 9.93 kg water/kg hydrogen. The theoretical gas-energetic efficiency of the electrolyser is 46.7%. The electricity consumption is 8.3 kWh/Nm<sup>3</sup> hydrogen.

Parameter electrolyser	Value
Electrical capacity	8.3 kWe
Maximum output gas flow	1.1 Nm <sup>3</sup> /hour
Maximum output gas flow	2.27 kg/24 hour
Nominal output gas pressure	13.8 barg
Electricity consumption	$8.3 \text{ kWh/Nm}^3 \text{H}_2$
Water input flow	0.94 L/hour
Hydrogen purity	99.9995%
Heat generation	4.3 kW
Energetic efficiency	46.7 %

Table 5: Characteristics Hogen® S40 electrolyser [4]

Electrolysis imposes requirements on the conductivity of the incoming water. The conductivity is affected by the presence of the number of ions and salts and determines the efficiency of the electrolyser. In order to meet the water-quality requirements on a continuous basis, a separate water deionisation system was included in the system (Figure 18). According to the technical specifications of the PEM electrolyser, the required conductivity (EC) is <1  $\mu$ S/cm. However, the manufacturer advises an EC <0.1  $\mu$ S/cm in order to achieve greater efficiency and to guarantee a longer lifespan of the PEM components.







Figure 16: Electrolyser

Figure 17: PEM stack in electrolyser

Figure 18: Water deionisation system

The produced hydrogen is saturated with water and is therefore dried internally by using a pressure swing adsorber (PSA). The level of drying depends on the pressure in the system. Therefore the pressure in the electrolyser is kept at a level of approximately 13.8 bar.

The hydrogen output is subject to fluctuations in pressure and volume that are mainly caused by switching the PSA driers. In order to minimise pressure and flow variations two buffer vessels, with a water volume of 6.7 litres, were placed after the electrolyser.

# 3.3 Methanation and gas-quality conversion

Chemical methanation is a conglomerate of various system components with the four solid-bed reactors at the heart of the system. The reactors are heated electrically by means of heating tape. The process water that is formed during the reaction is separated from the gas phase with counter flow water/gas plate heat exchangers that are positioned down flow from the reactors. The condensed process water is then discharged by means of steam traps. Cooling in the heat exchangers reduces the temperature of the gas. The acidity (pH) and conductivity (EC) of the outgoing liquid flow (process water) is measured to detect any links between the degradation of the catalyst material and the reaction water.

After the reactors the gas is dried to the specifications of the public gas grid and the gas flow and composition are measured. The amount of carbon dioxide that is to be added to comply with the Wobbe criteria is calculated on the basis of the gas composition and flow. Finally, tetrahydrothiophene (THT) is added to the gas in order to give it the same characteristic smell as natural gas. Figure 19 is a schematic representation of the entire process.



#### Figure 19: Schematic representation of methanation and gas quality conversion

ICCy.			
FT	Flow transmitter	Р	Pressure sensor
Т	Temperature sensor	pН	Acidity measurement
EC	Electric conductivity measurement	Wdp	Water dew point sensor (humidity)
GC	Gas chromatograph	THT	Odorisation

Kov

Table 6:	Characteristics	of methanation
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Parameter methanation	Value
Number of reactors	4
Electric capacity reactor heating	2 kW/reactor
Maximum material temperature	750 <sup>0</sup> C
Maximum system pressure	15 bar
Reactor volume	1.06 L
Total reactor volume of 4 reactors	4.2 L





Figure 20: Reactors of methanation

Figure 21: Methanation system

The gas supply is controlled with mass-flow meters that are controlled with the flow signal of the hydrogen that is released during the electrolysis. The gas supply of carbon dioxide is controlled on the basis of the hydrogen signal and the required hydrogen/carbon dioxide ratio.

Each reactor is built up of three tubes that contain the finely ground catalyst material in the inner tube (Figure 22, white). The internal (Figure 22, red) and external sleeve (Figure 22, yellow) are intended to cool the catalyst material if necessary. The reactor is heated by using 4 heating tapes that are positioned in the sleeve tubes so they cannot come into contact with the flammable gas mixture. The incoming gas (Figure 22, blue) enters the inner tube in the reactor, where the gas is already preheated. The temperature gradient of the catalyst material is measured at 20%, 40%, 60% en 80% of the tube length. Each reactor has a pressure sensor in order to monitor any pressure build-up due to blockages.





The reactors are made of stainless steel 316L, because this material is highly resistant to high temperatures and corrosion by water. The specifications of the reactors are given in Table 7.

Description		
Height	580	mm
External diameter 1	60.3	mm
Wall thickness 1	1.7	mm
External diameter 2	33.4	mm
Reactor volume	1.06	L
Total reactor volume	4.22	L

#### Table 7: Reactor characteristics

The four reactors are filled with different types of commercially available catalyst material. As the temperature of the reaction increases with increasing hydrogen and carbon dioxide concentrations, we opted for catalyst material with different nickel oxide (NiO) contents. The choice was a compromise between the conversion rate and the temperature, so the reactors could be operated within the limits of the material specifications.

The nickel content in the first reactor is the lowest, in order to avoid exceeding the temperature requirements due to the temperature increase in the first reactor. As the hydrogen and carbon dioxide concentrations are highest in the first reactor, this is where most exothermal heat is generated. The chosen NiO contents in the reactor are a compromise between the maximum exothermal reaction temperature and the material specifications of the reactors.

#### **Table 8: Characteristics of catalyst materials**

	CAT-A*	CAT-B*	CAT-C*
	Reactors 1+2	Reactor 3	Reactor 4
Active components	Nickel oxide (11%)	Nickel oxide (33-39%)	Nickel oxide (54%)
Density (g/cm <sup>3</sup> )	1.0	1.2	1.05
Regular temperature range ( <sup>0</sup> C)	Max 850	180 - 550	230 - 650
Regular pressure range (bar)	Max 40	20 - 300	20 - 60
Space velocity hour <sup>-1</sup>	2,000	3,000 - 20,000	

\* Specific client or type information for the catalyst materials has not been given, because this is competitionsensitive information and DNV GL is duty bound to comply with its duty of confidentiality in respect of the supplier(s).

To safeguard the gas quality and to monitor the performance of the methanation, the gas quality is measured continuously. This is done with a gas chromatograph that determines the concentrations of the following components:

- methane (CH<sub>4</sub>);
- carbon dioxide (CO<sub>2</sub>);
- carbon monoxide (CO);
- hydrogen (H<sub>2</sub>);
- nitrogen (N<sub>2</sub>);
- oxygen  $(O_2)$ .

The water dew point is measured with a water dew point sensor.

The produced gas is injected into a 30 mbarg pipe that was laid especially for this purpose between the P2G site and nearby flat buildings where the gas was used to heat the buildings. The pipe is managed by Stedin. This is not a public grid, but in order to guarantee a safe application of the supplied gas, the specifications of the public distribution grid were applied. By testing against these specifications, the outcomes also prove useful for future injections into the public grid.

Table 4 demonstrates that the hydrogen content of the injectable gas must be <0.1 mol%, which means it is essential - for this project - to work with a hydrogen/carbon dioxide ratio that is less than 4 (see paragraph 2.6). In order to comply with the Wobbe specification, - assuming 100% methane in the outgoing mixture - 10.0-10.3 mol% carbon dioxide must be added. Therefore, we chose a ratio of approximately 3.8 with an excess of approximately 5 mol% carbon dioxide in the incoming gas mixture. Then the gas quality after the reactors was measured and another approximately 5 mol% carbon dioxide was added.

### 3.4 Safety and risk-mitigating measures

The following paragraphs detail the matters that related to the safety of and around the system. There is a distinction between matters that apply to the entire system and matters that apply to specific system components.

# 3.4.1 General

#### Programmable Logic Computer

The Programmable Logic Computer (PLC) is central to managing the system. The PLC reads data from the sensors and the measuring instruments in the process system. Threshold values are recorded in the PLC on the basis of which the PLC generates an alarm. In the event of shortage or excess, the safety procedure is put in motion automatically and a possibly unsafe situation is turned into a safe situation.

#### Safety procedure

During the safety procedure, the hydrogen and carbon dioxide supply are stopped immediately and the heating of the reactors is switched off. The gas discharge is also stopped. The methanation system is then flushed with nitrogen to flush away any hydrogen in the reactors safely by means of a blow-down pipe. The system is fitted with so-called 'normally open' valves for this purpose.

#### Start-up procedure

In order to start up the system safely, a start-up and release procedure has been prepared. The start-up procedure describes in detail which actions must be performed in order to start up the hydrogen generator and methanation. The release procedure contains a checklist and when all the conditions have been met, the produced gas is injected. The start-up procedure is carried out partly manually and partly automatically, because it is linked to the sensors and measuring systems in the process.

#### Inspection

The safety aspects of the entire system have been inspected by an independent third party. This considered whether the process elements comply with the zoning class of their position.

#### Pressure

All gas-carrying parts, e.g. reactors and pipes, are tested for compliance with the Pressure Equipment Directive (PED) 97/23/EC. All gas-carrying parts are supplied or tested to at least 5/3 times the maximum operational pressure.

The outgoing pipe of the electrolysers and the methanation unit are fitted with overpressure safety. The pressure in the gas grid is secured by fitting a so-called HAS cabinet (high pressure connection set), where the maximum pressure is set at 32 mbar.

#### **Explosion safety**

Equipment that is set up near the gas-carrying process elements is suitable for use in this zone and has the correct ATEX (explosion safe/source of ignition free) certification. All non-ATEX equipment is applied at sufficient distance from the gas-carrying parts, whilst multiple room ventilation is also applied.

#### Gas leaks

The LEL meters for the benefit of detecting general gas leaks are set at 0.4% gas in air, which matches 10% of the LEL value. Separate sensors have been fitted for detecting hydrogen leaks, and they are set at 250 ppm.

Carbon dioxide is heavier than air and has an asphyxiating effect. Therefore the container with the carbon dioxide storage may only be entered with a carbon dioxide sensor that acts as personal protective equipment.

#### **Room ventilation**

The capacity of room ventilation in gas-carrying rooms is designed and set in such a manner that a specific leak flow can be ventilated away adequately, which means the leak load cannot produce an atmosphere that exceeds the LEL threshold value. The ventilation rate is determined on the basis of the leak load and a capacity calculation in accordance with NEN-EN-IEC 60079-10-1. On the basis of a hypothetical leak flow of 0.35 g/s and safety value of 50% LEL, the room ventilation for the hydrogen container has been set at a minimum of 1,800 m<sup>3</sup>/hour, which equals a refreshing rate of 126 times the room volume per hour. For the methanation container, the minimum refreshing rate is calculated at 132. After detection of a gas outflow, the gas flows are blocked but the ventilators run for another 30 minutes before they are switched off by the software. This prevents rooms from having to be entered whilst they are still full of gas.

#### **Room heating**

In order to prevent freezing, a room heating system has been fitted. This is suitable for use in a gascarrying room and starts working when the room temperature falls below 5°C. The electricity supply of the system is connected to a separate circuit to prevent the heating system from decommissioned when the system is switched off and freezing could occur.

#### Location

The site around the system is protected with a fence. The risk profile for the system has been calculated. The distance between the actual system and the fence is such that all risk contours fall within the site.

### 3.4.2 Electrolysis

The electrolyser was purchased commercially and complies with all the criteria for being used in a gascarrying zone. However, attention was paid to the practical implementation of the this system component in the full set-up. For example, the outgoing process pressure of the electrolyser is 13.8 bar and flow variations are minimised by including two buffer vessels in the system with a water volume of 6.7 litres. The outgoing pipe is fitted with overpressure safety that is set at 8 barg to prevent the pressure in the system exceeding the maximum desirable system pressure.

# 3.4.3 Methanation

The risks of the methanation process are mainly produced by the presence of a combination of flammable and possibly asphyxiating gases, high temperatures and increased pressures. The process also contains heavy metals and is based on chemical reactions.

#### Temperature

The methanation process is operated in the temperature range of 200-500°C, whereby the catalyst temperature in the first reactor in particular may run up locally to 700°C. The ignition temperature of hydrogen lies within this temperature range. This means that if oxygen is present in the reactors there is an increased risk of self-combustion or self-explosion. The presence of oxygen in the process is therefore to be avoided. Therefore the reactors should be flushed with hydrogen and/or carbon dioxide before heating until there is no more oxygen present in the system.

If the catalyst temperature is below 150°C there is risk of nickel carbonyl forming. If catalyst temperatures exceed 700°C tar may be formed which may cause blockages of the reactors. In order to ensure that the temperature of the reactors is neither too low nor too high, it is monitored continuously. At the same time, the pressure in the separate reactors and the entire system is monitored continuously.

#### **Catalyst material**

The nickel-based catalyst material must be treated as chemical waste at all times.

During the reaction process water is formed that is discharged to the sewers. This process water may contain traces of nickel but may be discharged because the maximum load of metals amounts to 25 kg per year and this cannot be exceeded. The conductivity of the process water to be discharged is monitored continuously. A change in conductivity is used as an indication for the discharge of catalyst material and/or hydrocarbons, but does not provide insight into the cause or nature of the contamination.

#### Gas quality

To prevent gas from being injected that could produce risks for the end user, the composition is measured with a gas chromatograph at a measuring frequency of 2 minutes. When the threshold values, as included in the Ministerial Scheme (Table 4), are exceeded or not met injection is ceased automatically.

#### Discharge process water

To check the quality of the discharge water, its conductivity and acidity are measured continuously. The temperature of the water is also monitored.

# 3.5 **Process criteria methanation**

On the basis of the conditions described in paragraphs 2.6 and 3.4, a list of process criteria has been prepared that are checked continuously. If the threshold values are exceeded or not met, a so-called safety procedure must be put into motion whereby the system is switched off under controlled conditions. The relevant process criteria are given in Table 9.

Parameter	Operating condition	Unit			
Electrolyser					
Gas detection, lowest explosion limit (LEL)	<u>&lt;</u> 0.4	% gas/air			
Gas detection, hydrogen	<u>&lt;</u> 250	ppmV			
Electrolyser fault	0 *				
Methanation and gas co	onditioning				
Gas detection, lowest explosion limit (LEL)	<u>&lt;</u> 0.4	% gas/air			
Gas detection, hydrogen	<u>&lt;</u> 250	ppmV			
Incoming hydrogen flow	0.5-2.5	m³(n)/h			
Incoming carbon dioxide flow	<u>&gt;</u> 0.1	m³(n)/h			
Hydrogen/carbon dioxide ratio	3-5				
Incoming pressure	<9	bara			
Pressure reactors	<u>&lt;</u> 8	barg			
Temperature reactors	200-550	°C			
Temperature heat exchangers	<u>&lt;2</u> 5	°C			
Hydrogen concentration (after methanation)	<u>&lt;</u> 0.5	mol%			
Carbon dioxide concentration (after methanation		mol%			
and before adding)	<u>&lt;</u> 8				
Methane concentration (after methanation)	<u>&gt;</u> 90	mol%			
Carbon monoxide concentration (after		mol%			
methanation)	<u>&lt;</u> 0.23				
Oxygen concentration (after methanation)	<u>&lt;</u> 0.1	mol%			
Nitrogen concentration (after methanation)	<u>&lt;</u> 0.5	mol%			
Status gas chromatograph	95-105 **	mol%			
Wobbe (after methanation)	<u>&gt;</u> 47.0	MJ/m <sup>3</sup> (n)			
Wobbe (after adding carbon dioxide)	44.10-44.41	MJ/m <sup>3</sup> (n)			
Status THT	0 *				
Status gas drier	0 *				
Water dew point	-10	°C @ 8 bara			

Table 9: Operating conditions within which the process must operate

\*) 0=release/in operation, 1=fault

\*\*) on the basis of the non-standardised sum of the components

# **4 RESULTS PRACTICAL IMPLEMENTATION**

This chapter includes the results and the calculations based upon those results. To represent the results, we have made a distinction between the electrolyser, the methanation and the entire power-to-gas system, which are described in different paragraphs of this chapter.

# 4.1 Electrolyser

# 4.1.1 Mass balance

The electrolyser decomposes water into hydrogen and oxygen by means of an electrochemical reaction that uses electricity. Not all the water is converted and part of the water is recirculated for reuse. The mass balance is prepared on the basis of operational data that is obtained during constant, maximum operation of the electrolyser. The data demonstrates that the ratio of hydrogen/ingoing water is 1:10 and that 8.7% of the water is not used in the electrolyser. The mass balance of the electrolyser is given in Figure 23.

Water 944 g/b	→	Water 82 g/h
унт <u>у</u> /п	Elektrolyser	Hydrogen 99 g/h
		Oxygen 763 g/h

Figure 23: Mass balance electrolyser<sup>1</sup>

# 4.1.2 Energetic efficiency and energy balance

The energy balance is prepared on the basis of operational data that is obtained during constant, maximum operation. For 8.3 kWh of electricity 3.9 kWh pure hydrogen is formed. This demonstrates an energetic efficiency of the electrolyser of 47%. The operational energetic efficiency in practice is virtually the same as the efficiency in the manufacturer's statement, see paragraph 3.2.



Figure 24: Energy balance electrolyser (on the basis of calorific upper value, Hs)

<sup>&</sup>lt;sup>1</sup> Determined theoretically on the basis of Hogen Installation/Operation instructions S40 II series

## 4.1.3 Contaminations

In order to mitigate the negative impact of contamination in the hydrogen that is used as input for methanation, the contamination level has been determined. The measured oxygen content is <5 ppm. The water content is <50 ppm. These concentrations are sufficiently low, which means we do not anticipate any negative impact on the methanation process.

# 4.1.4 Start-up time

In order to determine how quickly the electrolyser can be used as a flexible energy-conversion system, the start-up time of the electrolyser was monitored. The start-up procedure consists of three phases:

- 1. Internal release. After starting up, various safety checks are performed in order to guarantee proper and safe operation of the equipment. Moving through these checks takes 2.5 minutes and the electricity consumption is virtually nil;
- Start-up PEM. After completing the internal checks, the PEM cell is started up and electricity consumption moves up to 8.3 kW. During this phase there is a pressure build-up in the system. This pressure is required to guarantee the proper operation of the PSA drier. At this time there is no production of hydrogen that can be used for methanation. Completing this phase takes approximately 1.3 minutes;
- 3. Normal operation. After the internal pressure has moved up to the required value, the hydrogen supply is started. The maximum hydrogen flow is reached within a few seconds. Electricity consumption during normal operation is 8.3 kW.

Roughly speaking, the electrolyser produces hydrogen within 4 minutes of starting up. However, the maximum electricity consumption is reached after 2.5 minutes. This enables us to conclude that the electrolyser that was used can be used within 2.5 minutes to consume electricity of maximum 8.3 kW.



Figure 25: Start-up time electrolyser

# 4.2 Methanation

# 4.2.1 Mass balance

Methanation synthesises hydrogen and carbon dioxide into methane and water. In practice conditions it was demonstrated that the synthesis is not complete in the four reactors and that there are fractions of hydrogen and carbon dioxide in the product gas. The mass balance for stoichiometric conditions (hydrogen:carbon dioxide=4:1) for methanation is represented in Figure 26.

Hydrogen		Methane 198,2 g/h
Carbon dioxide	Methanation	Hydrogen <0,1 g/h
	included in	Carbon dioxide <0,1 g/h
		Water 444,8 g/h

#### Figure 26: Mass balance of methanation under stoichiometric conditions

This mass balance is prepared on the basis of operational data that is obtained during constant, maximum operation of methanation.

The data demonstrate that the mass ratio of the hydrogen consumption in relation to methane production is 1:2.0. The largest part of the ingoing mass is converted into water. Approximately 30% of the outgoing mass is methane. Approximately 70% of the total outgoing mass is water. This outgoing mass flow is 47% of the water consumption of the electrolyser, which means reuse is possible.

As described in paragraphs 2.4 and 3.3, methanation comprises four reactors. In order to obtain insight into the performance of the separate reactors, a mass balance was prepared for each reactor. They are represented in Table 10.

Table 10: Hass balance per react	VI			
Reactors	1	2	3*	4*
Hydrogen, in [g/hour]	99.0	6.5	0.3	0.4
Carbon dioxide, in [g/hour]	544.1	35.7	1.4	2.3
Methane, in [g/hour]	0.0	185.1	198.4	197.4
Water, in [g/hour]	0.0	3.9	4.0	5.1
Hydrogen, out [g/hour]	6.5	0.4	0.1	0.1
Carbon dioxide, out [g/hour]	35.7	2.3	0.3	0.0
Methane, out [g/hour]	185.2	197.4	198.3	198.2
Water, out [g/hour]	415.6	31.2	5.4	6.9

#### Table 10: Mass balance per reactor

\* The results for reactors 3 and 4 are obtained by using the outgoing gas flow of reactor 2.

\*\* After heat exchanger of the previous reactor

The hydrogen conversion rate is also calculated per reactor (see formula F.1).

#### Table 11: Conversion rate per reactor under stoichiometric conditions

Parameter	1	1+2	1+2+3	1+2+4
Hydrogen conversion [%]	89.5	99.3	99.9	100.0
Incoming mol ratio H <sub>2</sub> :CO <sub>2</sub>	4.0:1	4.0:1	4.0:1	4.0:1

The formation of methane means the hydrogen/carbon dioxide load in the next reactor decreases, which increases the conversion rate. The nickel content on the catalyst is also higher in the last two reactors, because the lower load means the maximum reactor temperature does not exceed the material specifications.

# 4.2.2 Energy balance

To prepare the energy balance, the energy flows of methanation measured under practice conditions and they are represented in Figure 27.

The overall energetic efficiency is defined as the percentage of the total energy that enters the system and is applied usefully for the conversion into methane. The energy balance demonstrates that the overall energetic efficiency amounts to 73% and that there is an energy loss of 27% in the form of heat.



#### Figure 27: Energy balance methanation (on the basis of calorific upper value, Hs)

The gas-energetic efficiency is defined as the percentage of the energy that enters the system as gas and leaves as methane. The gas-energetic efficiency amounts to 79%, which demonstrates that approximately 21% of the gas is converted into heat.

The specific electricity consumption was also determined on the basis of the energy balance. The specific electricity consumption is defined as the number of kWh electricity required to produce  $1 \text{ Nm}^3$  of methane. The specific electricity consumption for methanation amounts to  $1.1 \text{ kWh/Nm}^3$  methane.

Table 12: Results energy balanc
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Parameter	Value
Specific electricity consumption [kWh/Nm <sup>3</sup> methane]	1.1
Overall energetic efficiency [%]	73
Gas-energetic efficiency [%]	79
Energy consumption start-up [kWh]	1.6
Energy consumption CO <sub>2</sub> addition [kWh]	0.2
Energy consumption normal operation [kWh]	0.3

### 4.2.2.1 Energetic efficiency per reactor

In order to obtain insight into the performance of the individual reactors, the working method of paragraph 4.2.2. The results are given in Table 13. The gas-energetic efficiency is defined as the percentage of energy that enters the reactor as gas and leaves the reactor in the form of methane and hydrogen.

Parameter	Reactor 1	Reactor 2	Reactor 3	Reactor 4 <sup>*</sup>
Hydrogen, incoming [MJ/hour]	14.0	0.9	0.0	0.1
Methane, incoming [MJ/hour]	0.0	10.3	11.0	11.0
Hydrogen, outgoing [MJ/hour]	0.9	0.1	0.0	0.0
Methane, outgoing [MJ/hour]	10.3	11.0	11.0	11.0
Gas-energetic efficiency [%]	79.8	98.3	99.7	99.9

Table 13: Energy balance overview (on the basis of calorific upper value, Hs)

\* The results for reactors 3 and 4 are obtained by using the outgoing gas flow of reactor 2.

### 4.2.3 Heat distribution reactors

As described earlier in paragraph 3.3, the heat distribution in the reactors is measured at four different heights. This provides insight into the areas of the reactor where heat development is greater in relation to other places and whether so-called hot spots occur in the catalyst material. As this concerns an exothermal reaction it is likely that areas with the highest temperatures have the highest conversion of hydrogen and carbon dioxide into methane and water.

The diversity in the temperature movement in the different reactors, during start-up and under normal operating conditions, is represented for reactor 1 in Figure 28 and for reactor 3 in Figure 29. The figures also chart the total electricity consumption for methanation against time.

The results for reactor 2 are comparable with those of reactor 1 and those of reactor 4 with reactor 3 and therefore they are not represented in a graph.



Figure 28: Temperature movement in reactor 1 and electricity consumption (of entire system) for an average system pressure of 2.26 bara and the set points for preheating  $T=350^{\circ}C$  and after the start of adding  $CO_2$  T=300°C.

The figure demonstrates that a major temperature gradient could be observed in the reactor, whereby the highest temperature was measured by temperature sensor 3 in a place where 75% of the catalyst material was used for the reaction. At this point the temperature increases from approximately 300°C (due to heating) to approximately 490°C. Other temperatures drop after heating to lower values. This allows us to conclude that the conversion reaction only occurs near temperature sensor 3.

Electric heating of the reactor occurs because the catalyst at the first measuring point cools down too much, possibly caused by the contact with the relatively cold incoming gas.

Electricity consumption in a stable situation is approximately 25% of peak consumption at start-up, which allows us to conclude that the reactor has additional heating in only one of the four places. Any hot spots were not proven.



Figure 29: Temperature movement in reactor 3 and electricity consumption (of entire system) for an average system pressure of 2.26 bara and the set points for preheating  $T=250^{\circ}C$  and after the start of adding  $CO_2$  T=200°C.

The picture for reactor 3 does not compare with reactor 1, because the amount of hydrogen and carbon dioxide is limited which means the temperature runs up very little during the reaction. In order to prevent the formation of nickel carbonyl, the minimum temperature is set at 150°C, which means the reactor requires additional heating continuously.

The results of Figure 28 and Figure 29 can be matched with the infra-red images that were made of the reactors in continuous operation. The warmest places have the lightest colours and are visible in the middle of the reactors.



Figure 30: Heat imaging of the reactors

# 4.2.4 Sensitivity of the conversion rate

In order to obtain more insight into methanation, a total of 27 experiments were performed with varying system pressure, hydrogen/carbon dioxide ratio and the used reactor combinations (and therefore the nickel content). The results are given in Table 14.

Unit	Varied settings			
Pressure (bara)	1.5	3.0	4.5	
Mol ratio $H_2:CO_2$	3.6:1	4:1	4.4:1	
Used reactors (Nickel	1+2	1+2+3	1+2+4	
content of the catalyst)	(11%+33-39%)	(11% + 2x 33-39%)	(2x11%+54%)	

#### Table 14: Varied parameters

Figure 31 presents the conversion in function of the pressure and the reactors used with a hydrogen/carbon dioxide ratio of 4:1. This shows that as the pressure increases conversion also increases. Conversion also increases with an increase of the nickel content.

During the performance of the experiments it became clear that a hydrogen/carbon dioxide ratio of 4.4:1 is not usable in practice, as the concentration of hydrogen after the reaction is too high (>0,5 mol%). Figure 32 represents the conversion in function of the system pressure and the nickel content with a hydrogen/carbon dioxide ratio of 3.6:1. As can be seen in Figure 32, compared to a hydrogen/carbon dioxide ratio of 4:1 (Figure 31) the variation in the determined conversions is greater. It is possible to conclude from the graph that increased pressure combined with a higher nickel content produces a higher conversion.



Figure 31: Overall hydrogen conversion in function of pressure and in different reactors with a ratio of 4:1



Figure 32: Overall hydrogen conversion in function of pressure and in different reactors with a ratio of 3.6:1

# 4.2.5 Variation in gas composition

To determine the stability of the outgoing gas composition, we performed an endurance test. During 5040 minutes (84 hours) 1008 measurements were performed. The stability of the gas composition is given in Figure 33. It is possible to deduce from the figure that the gas composition is relatively constant over the measuring period. The analysis of the measuring details, as represented in Table 15, demonstrates that the relative spread in the  $CO_2$  concentration is the greatest. The variation on Wobbe is determined at 0.04 MJ/m<sup>3</sup>(n) with a 95% reliability interval.

Parameter			*	Wobbe
	CH <sub>4</sub> (mol%)	CO <sub>2</sub> (mol%)	H <sub>2</sub> (mol%)	(MJ/m <sup>3</sup> (n)
Average measuring value	97.840	2.039	0.108	51.44
Standard deviation	0.010	0.102	0.009	0.02
95% reliability interval	0.020	0.203	0.018	0.04

Table 15: Results variation (hydrogen/carbon dioxide ratio=3.9
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Figure 33: Variation in the outgoing gas composition

# 4.2.6 Effects of varying hydrogen supply

The effect of the varying hydrogen flows on the gas-energetic efficiency and the conversion was studied. To determine the effects, experiments were performed by varying the hydrogen flow between 0.5 and  $2.5 \text{ m}^3(n)/h$ .

The results demonstrate that the dimension of the reactors is sufficient to convert 2.5 m<sup>3</sup>(n)/h of hydrogen into methane. However, this does exceed the maximum temperature (550 °C) in reactor 1 as a result of the increasing hydrogen capacity. For continuous operation with this flow, the first reactor should be cooled to prevent tar formation

The overall energetic efficiency decreases when several reactors are used. This is the result of the decreasing hydrogen and carbon dioxide concentration in reactors 2, 3 and 4, which means the heat development due to the exothermal process is less and additional heating is required to prevent the formation of nickel carbonyl.

With an increasing hydrogen flow the temperature in the reactors increases and the conversion decreases as a result.

# 4.2.7 Start-up time

In order to determine how quickly the methanation process can be used as a flexible energy-conversion system, the start-up time of the electrolyser was monitored. The start-up procedure consists of three phases:

- 1. Start-up. To start up the reaction, the reactors are heated to approximately 300°C. Heating up takes approximately 27 minutes and the electricity demand is 1.5 kW during that period;
- Carbon-dioxide supply. After the reactors have been heated up properly, the carbon-dioxide supply is opened and methane production will start up slowly. This process is stable after 10 minutes and the electricity consumption is approximately 0.2 kW;
- 3. Normal operation. The process runs under stable conditions. The average electricity consumption is 0.3 kW.



Figure 34 is a representation of the entire process.

Figure 34: Start-up time methanation

### 4.2.8 Ageing catalyst material

Several methods were used to determine the ageing of the catalyst material. For example the acidity and conductivity of the condensed reaction water were measured. During the period the system operated there was no significant change in either the acidity or the conductivity.

The catalyst material from reactors 1 and 2 was also analysed on element basis with a raster electron microscope (SEM). The mass fractions of the different metals were determined with x-ray defraction (EDX).

Used and unused catalyst material was measured. The used catalyst material was used approximately 250 hours in the process and had a total hydrogen throughput of 260 Nm<sup>3</sup>. During these measurements the maximum temperatures were exceeded several times.





The results demonstrate that significant differences were not observed on the catalyst material for carbon and aluminium content. The fact that the carbon content is the same for the unused and used catalyst material allows us to conclude that there was no carbon deposit or tar deposit in the reactor. The aluminium is the carrier material for the catalyst and was not affected by use. The use of the catalyst material did produce a decrease in the nickel content. The nickel content reduced through use by an average of 45%. This is most probably the result of changes in the material form after the first heating. It is not expected that the nickel content will decrease in the same way over time which would suggest a limited lifespan for the catalyst material. This is substantiated by the results of the project. Figures 37 and 38 give the SEM imaging as illustration.



Figure 36: SEM images of unused (left) and used (right) material



Figure 37: SEM images of unused (left) and used (right) material

The SEM-EDX images as given in Figure 37, are made with a 'Secondary Electron' detector and a 'Backscattered Electron' detector. The images that are made with the 'Secondary Electron' detector largely provide an image of the three-dimensional structure of the material. The images that are made with the 'Backscattered Electron' detector largely highlight the differences in chemical composition, whereby the darker areas contain relatively many light elements and the lighter areas largely heavy elements. The images show that the metallic sheen of the unused material has disappeared from the used material. This confirms the results of the SEM-EDX that the nickel contents on the used material have decreased.

# 4.3 Entire Power-to-Gas system

By combining the results in 5.1 and 5.2 we obtain information about the characteristics of the integrated Power-to-Gas system that consists of the electrolysis system and the methanation system.

# 4.3.1 Mass balance

The mass balance of the integrated power-to-gas system is represented in Figure 38. This mass balance was prepared for normal operation.



#### Figure 38: Mass balance Power-to-Gas system under stoichiometric conditions

The results demonstrate that 13% of the ingoing mass is converted into methane. Some 51% of the outgoing mass is oxygen that is not used. The carbon dioxide required for the conversion is approximately 2.7 times the mass of the formed methane.

# 4.3.2 Energy balance

The energy balance of the total system is represented in Figure 39.



#### Figure 39: Energy balance Power-to-Gas system

The represented energy balance of the entire Power-to-Gas system demonstrates an overall energetic efficiency of 35%. The specific electricity consumption for the system amounts to 31.2 kWh/Nm<sup>3</sup> methane.

Parameter	Value
Specific electricity consumption [kWh/Nm <sup>3</sup> methane]	31.2
Energetic efficiency electrolyser [%]	47
Energetic efficiency methanation [%]	73
Overall energetic efficiency [%]	35

The energy balance is visualised in the following Figure 40 and the flows are represented proportionately on the basis of the energy flows. This demonstrates that the energy loss largely occurs in the form of heat.



#### Figure 40: Energy balance Power-to-Gas system

### 4.3.3 Start-up time

The start-up time and energy consumption of the entire Power-to-Gas system was determined on the basis of information from paragraphs 4.1.4 and 4.2.7. The results are summarised in Table 17 and visualised in Figure 41.

The figure demonstrates that the entire system is operational within 41 minutes. The electricity consumption of the methanation is low in relation to the electricity consumption of the electrolyser. The electricity demand of methanation is briefly high because of heating the reactors. The amount of electricity that is used by the Power-to-Gas system therefore only depends on the electricity demand of the electrolyser.

Table 17: Start up times and electricity consumption						
Parameter	Electricity consumption (kWh)	Time per phase (minutes)	Start-up time (minutes)			
Electrolyser						
Internal release	0	3	0			
Start-up PEM	8.3	1	3			
Normal operation	8.3		4			
Methanation						
Start-up	1.6	27	4			
CO <sub>2</sub> addition	0.2	10	31			
Normal operation	0.3		41			

 Table 17: Start-up times and electricity consumption



Figure 41: Start-up time of the entire Power-to-Gas system

# **5 CONCLUSION**

The project partners conducted the first Dutch Power-to-Gas project. Electricity that was partly generated with solar panels was converted into hydrogen in first instance, which was then converted into methane with carbon dioxide. The produced methane was upgraded to Dutch natural-gas quality and used in a gas-fired boiler in a nearby flat building.

Prior to building the system, the influence of the various process parameters on the conversion from hydrogen into methane and the energetic efficiency was studied. The safety risks, requirements for the outgoing gas mixture and environmental aspects were also charted.

The design and process criteria that the system must comply with were determined on this basis. The various safety provisions were also implemented on the system. The required process and gas-quality measurements were also included. Risk mitigation took place by means of continuous monitoring of the threshold values of the measured parameters and by switching off the system in a controlled manner when they were not met or exceeded.

During the implementation of the project practical information was obtained about the technical feasibility of the complete system and the individual system components. For example, the conversion of electricity to hydrogen and oxygen was performed with an energetic efficiency of 47%. The remainder of the energy - in the form of heat - could not be used locally. Heat is also released during the catalytic conversion of hydrogen and carbon dioxide, and this could not be used either. The energetic efficiency of this methanation process was set at 73%. The energy balance of the entire Power-to-Gas system demonstrated an energetic efficiency of 35%, as represented in Figure 42.



#### Figure 42: Energy balance of the Power-to-Gas system

Besides optimising the energetic efficiency, it is important that the outgoing gas complies with the specifications that apply to injection into the gas grid. The Dutch distribution network requires gas to contain no more than 0.1 mol% hydrogen. The optimum temperature of the methanation process is therefore a compromise between the highest achievable energetic efficiency and the outgoing hydrogen concentration.

Theoretical calculations have demonstrated that the energetic efficiency of methanation is maximum 70-78%. The determined energetic efficiency of this methanation process was set at 73%. For a system temperature of 377°C, the theoretically calculated optimum, with due regard to the hydrogen specification, is as represented in Figure 43. Maximising the energetic efficiency requires easing the hydrogen specification of the public gas grid.



Figure 43: Temperature dependent system configuration for methanation

The entire Power-to-Gas system can be started up from standstill to maximum capacity in approximately 40 minutes. This means that approximately 4 minutes are required to start up the electrolyser and approximately 35 minutes for methanation. The electricity consumption of methanation is low in relation to the electricity consumption of the electrolyser. The amount of electricity that is used by the Power-to-Gas system therefore largely depends on the electricity demand of the electrolyser. This means there is a control speed for electricity consumption within approximately 4 minutes.

During the term of the demonstration project the system proved that it is possible to deploy Power-to-Gas on a continuous basis for the application of peaks of sustainably generated electricity. The produced synthetic gas complied with all the specifications that apply to injection into the Dutch gas grid.

# **6 RECOMMENDATIONS FOR POSSIBLE FOLLOW-UP STUDIES**

This study has demonstrated that Power-to-Gas, with adequate security of supply, can be used for energy storage in the gas grid.

The completed process releases several product flows that are not used usefully as yet. Future study could focus on expanding the system with other technologies to obtain cycles for those product flows (process water, heat and oxygen).

From a sustainability point of view it is recommended to perform further studies into the options to recover water and carbon dioxide from the flue gases of the gas-fired systems in order to close the carbon cycle, as represented in Figure 44.



Figure 44: Potential future system configuration

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