Master Thesis

Pre-Design of a Household Scale Power-to-Gas Conversion System

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Hamburg, 25th February 2015
Statutory Declaration

I (Paavo Hilber) declare that I have authored this thesis independently, that I have not used other than the declared sources / resources, and that I have explicitly marked all material which has been quoted either literally or by content from the used sources.

Hamburg, 25.02.2015  _____________________
                      (signature)
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# Abbreviations

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>AEL</td>
<td>Alkaline Electrolyser</td>
</tr>
<tr>
<td>CAPEX</td>
<td>Capital Expenditures</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>CNG</td>
<td>Compressed Natural Gas</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>H₂O</td>
<td>German synthetic standard load profile</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HHV</td>
<td>Higher Heating Value</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium Hydroxide</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower Heating Value</td>
</tr>
<tr>
<td>LR</td>
<td>Learning Rate</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane-Electrode-Assembly</td>
</tr>
<tr>
<td>MPPT</td>
<td>Maximum-Power-Point Tracker</td>
</tr>
<tr>
<td>OPEX</td>
<td>Operational Expenditures</td>
</tr>
<tr>
<td>PEMEL</td>
<td>Polymer Electrolyte Membrane Electrolyser</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure Swing Adsorption</td>
</tr>
<tr>
<td>PtG</td>
<td>Power-to-Gas</td>
</tr>
<tr>
<td>PtSNG</td>
<td>Power-to-SNG</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>RE</td>
<td>Renewable Energy</td>
</tr>
<tr>
<td>SNG</td>
<td>Substitute/Synthetic Natural Gas</td>
</tr>
<tr>
<td>TRL</td>
<td>Technology Readiness Level</td>
</tr>
<tr>
<td>% mol.</td>
<td>Molar Percentage</td>
</tr>
<tr>
<td>% vol.</td>
<td>Volumetric Percentage</td>
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symbol directory

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\alpha_{a,c}$</td>
<td>-</td>
<td>Charge transfer coefficients of electrodes</td>
</tr>
<tr>
<td>$c_i$</td>
<td>J/kg·K</td>
<td>Specific heat capacity</td>
</tr>
<tr>
<td>$\delta_m$</td>
<td>$\mu$m</td>
<td>Membrane thickness</td>
</tr>
<tr>
<td>$d_i$</td>
<td>mm</td>
<td>Diameter of element $i$</td>
</tr>
<tr>
<td>$E_i$</td>
<td>V</td>
<td>Reversible cell voltage of element $i$</td>
</tr>
<tr>
<td>$\eta_i$</td>
<td>-</td>
<td>Efficiency of element $i$</td>
</tr>
<tr>
<td>$F$</td>
<td>C/mol</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>$f_i$</td>
<td>m$^3$/h</td>
<td>Gas flow rate of element $i$</td>
</tr>
<tr>
<td>GHSV</td>
<td>1/l</td>
<td>Gas Hourly Space Velocity</td>
</tr>
<tr>
<td>$H(i)$</td>
<td>kJ/mol</td>
<td>Enthalpy of element $i$</td>
</tr>
<tr>
<td>$i$</td>
<td>A/cm$^2$</td>
<td>Current density</td>
</tr>
<tr>
<td>$I$</td>
<td>A</td>
<td>Current</td>
</tr>
<tr>
<td>$i_{0,a,c}$</td>
<td>A/cm$^2$</td>
<td>Exchange current densities of electrodes</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>-</td>
<td>Membrane humidification</td>
</tr>
<tr>
<td>$L_{\text{reactor}}$</td>
<td>mm</td>
<td>Length of reactor</td>
</tr>
<tr>
<td>$m_i$</td>
<td>kg</td>
<td>Mass of element $i$</td>
</tr>
<tr>
<td>$n$</td>
<td>-</td>
<td>Number of transferred electrons</td>
</tr>
<tr>
<td>$n_b$</td>
<td>-</td>
<td>Number of gas bottles</td>
</tr>
<tr>
<td>$N_{\text{cell}}$</td>
<td>-</td>
<td>Number of electrolyser cells</td>
</tr>
<tr>
<td>$(n_{\text{H}<em>2}:n</em>{\text{CO}_2})$</td>
<td>-</td>
<td>Reaction stoichiometry</td>
</tr>
<tr>
<td>$p$</td>
<td>bar</td>
<td>Relative pressure</td>
</tr>
<tr>
<td>$\phi_i$</td>
<td>% vol.</td>
<td>Gas volume fraction of element $i$</td>
</tr>
<tr>
<td>$\phi_V$</td>
<td>-</td>
<td>Empty space share</td>
</tr>
<tr>
<td>$P_i$</td>
<td>W</td>
<td>Power of element $i$</td>
</tr>
<tr>
<td>$Q_{m,\text{excess}}$</td>
<td>J/mol</td>
<td>Molar excess heat flow</td>
</tr>
<tr>
<td>$Q_{v,\text{excess}}$</td>
<td>J/m$^3$</td>
<td>Volumetric excess heat flow</td>
</tr>
<tr>
<td>$R$</td>
<td>J/mol·K</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$\rho_i$</td>
<td>kg/m$^3$</td>
<td>Mass density of element $i$</td>
</tr>
<tr>
<td>$RR$</td>
<td>-</td>
<td>Recirculation Rate</td>
</tr>
<tr>
<td>$\sigma_m$</td>
<td>-</td>
<td>Ohmic resistance</td>
</tr>
<tr>
<td>$T$</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>h</td>
<td>Time</td>
</tr>
<tr>
<td>$V_i$</td>
<td>V</td>
<td>Voltage of element $i$</td>
</tr>
<tr>
<td>$V_M$</td>
<td>m$^3$/mol</td>
<td>Molar volume of ideal gas</td>
</tr>
<tr>
<td>$V_{\text{reactor}}$</td>
<td>m$^3$</td>
<td>Volume of reactor</td>
</tr>
<tr>
<td>$\xi$</td>
<td>-</td>
<td>Parasitic power ratio</td>
</tr>
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1 Introduction

In consideration of climate destructive future scenarios by an unlimited exploitation of fossil resources, supranational organizations such as the European Union (EU) advocate internationally valid agreements on how the dependency on fossil fuels can be diminished. Europe plays a leading role in avoiding serious and irreversible damaging effects on nature and is therefore ambitioned to reduce greenhouse gas emissions like carbon dioxide (CO$_2$) by increasing the share of Renewable Energy (RE) in energy consumption.

At the end of April 2009 the European Council published the revised version of the European Directive 2009/28/EC [1] for the promotion of the use of energy from renewable sources. The members of the EU are requested to develop a national roadmap in order to fulfil their specific obligations to raise the percentage of RE in gross final energy consumption until 2020. Based on the natural conditions, the country-specific targets vary from 10 % (Malta) to 49 % (Sweden). The national overall target for Germany is 18 % and it is 38 % for Finland. At the present time Germanys contribution of RE is 12.4 % and 34.3 % for Finland. Directive 2009/28/EC requires an ambitioned implementation of RE in the three energy sectors electricity generation, energy for heating or cooling and transport energy consumption. To meet their obligation each Member State has to release appropriate national regulations.

The main issues arising with a significantly high share of RE affect the electricity sector. The increasing share of electricity feed, in particular Photovoltaic (PV) and wind power plants, define new challenges which have to be faced in many countries of the EU. The effects of a high share of volatile REs can presently be seen in Germany. Due to the fact that the generation and consumption of electricity has to be in balance, a volatile feed implies grid imbalances which have to be compensated. A lower demand for base load and a limited operational flexibility of conventional coal and nuclear driven power plants make it essential to look for alternative solutions. Beside natural gas power plants which meet the flexibility challenges, three further options are being discussed [2].

An electricity grid expansion is able to match volatile generation and consumption that come up simultaneously. Decentralized RE from PV and wind power plants can be transmitted from regions with an overproduction to regions with a demand of energy if electricity links on
all voltage levels are built. But high costs and a lack of public acceptance lead to a delay in
the national grid expansion plans in Germany. Furthermore this option reaches its limit if vol-
atile generation and consumption arise at different times.

The second option is called **generation and consumption management**. On the one hand
mismatches of demand and supply side can be balanced by a flexible generation of RE. It has
to be kept in mind that the path of flexible RE generation is limited. Biomass can buffer mar-
ginal imbalances without notable energy losses. PV and wind generated electricity differ in
that point. A reduction of RE feed by PV and wind plants is possible at any times but in fact
\( \text{CO}_2 \)-neutral and free energy is wasted.

On the other hand energy consumption could be synchronized with the variable generation.
An intelligent network, a so called smart grid, could align the consuming behaviour of house-
holds by measuring the grid condition and vary the load switching electrical consumers on or
off. If many smart grid systems are installed, intraday volatility could be balanced. Though,
seasonal energy imbalances cannot be avoided.

The third alternative to face the mismatch of energy supply and demand is the **storage of RE**.
Both short and long term storages are necessary to balance the RE input. A short-term storage
covers hourly and daily mismatches and the long-term storage assures seasonal compensation.
The chart in Figure 1 visualizes the RE storage options which are currently in the centre of
attention [3]. The options are classified according to their stored energy amount and the abi-
ility to perform as a short- or long-term storage. A short-term storage is able to store energy up
to a maximum period of a few days. Long-term storages are operated in periods up to one
year to provide seasonal storage of RE which is basically the main challenge for a renewable
energy system.

Flywheels belong to the ultrashort-term category of energy storage options. Electric energy is
stored in the form of rotational energy of a spinning mass. Via integration of additional rotat-
ing masses to the electricity grid small frequency deviations can be diminished. Flywheels are
characterized by high power performances but very low energy storage capacities. Thus they
are not applicable for storing large amounts of RE.

In the recent past a huge number of battery storage options were investigated. Large invest-
ments in research fields are made to promote the battery in different energy systems and in-
dustries. Electric energy is stored electrochemically in terms of charge carriers, which are
absorbed or emitted in a redox reaction.
From the perspective of the conversion performance batteries enable the charge and discharge of energy with a relatively high efficiency rate of 60 – 98 % depending on the technology [4]. Main disadvantages are the high self-discharge rate up to 20 % per month and a limited lifetime. Certain battery applications like domestic PV-island systems have their right to exist and can have a significant contribution to prevent an expensive grid expansion. If major obstacles like the low energy density and high costs can be overcome, the mobility sector will certainly make a commercial use of batteries in electric vehicles. However, these barriers are still existing and comprehensive studies showed that even if all 42 million German cars are supplied with an application-oriented battery storage system, which are to 50 % accessible for storing RE, the total amount of stored energy is ten times bigger than the capacity of all hydro power plants in Germany but by far too less to provide a practical storage solution [2].

Compressed air energy storage systems are designed to store electrical energy in form of pressurized air in underground gastight salt cavern formations. The basic equipping includes a compressor, a turbine and a heating or cooling management system. If a surplus of generated RE in the national grid occurs, the system provides negative balancing power and the compressor starts to fill the storage with pressurized air. If positive balancing power is required the pressure is released through a turbine and generates electricity. Two variations of that storage technology are in the center of attention. They differ in terms of their heat management. The diabatic system inserts a gas heater to compensate the required heat during the re-

Figure 1: Short and long term options for RE storage [3]
lease of air. The adiabatic system is 100 % renewable by using a temporarily heat storage. The maximum efficiency of the entire system is between 40-55 %. The storage duration is limited by the intermediate heat storage, which allows a period of a few days. The caverns used in compressed air systems are strongly competing with natural gas storage technology. It is counted among the main disadvantages that the energy density of compressed air is significantly lower than hydrogen or methane.

The mostly established option of energy storage is hydro energy. If negative balancing power is required water can be pumped in higher level reservoirs and converting the potential energy into electricity by turbines when power is required. For medium-term storage purposes hydro power storages are technologically and economically more efficient than the options mentioned above. Their conversion efficiency of the entire system ranges between 75 – 83 % and provides an attractive short-term power balancing. The available storage capacity is more relevant to assess the potential of hydro power. In Germany almost all geographical capabilities for hydro reservoirs are exhausted. Summed up, the energy capacity accounts far less than 1 % of the required quantity for a RE dominated electricity sector. The exploitation of hydro potentials in Scandinavian countries like Norway or Sweden result in transport losses of up to 20 % absolute percentage [2]. Additionally, an increasing international demand for long-term energy storage capacities cannot be completely covered by Scandinavians hydro potential.

For the time being, converting fluctuating RE in a gaseous fuel is the most promising method for achieving long-term energy storage. The chemical process, well known as Power-to-Gas (PtG) technology, is accomplished in one or optional two conversion steps. The first step includes the production of hydrogen, which is the desired product in a water-split reaction of water electrolysis. Efficiencies of 82 % are achievable [5], but for some load conditions, lower performances can be considered. Hydrogen can be e.g. utilized for fuel cell applications in the transportation sector or can be stored in the national natural gas grid up to a certain limited concentration. This limit defines the capacity of a hydrogen based PtG storage system. A significant higher capacity can be reached by implementing the second conversion step. In a methanation synthetic natural gas (SNG) can be generated. The entire system (PtSNG) includes a pre-conversion of electricity to hydrogen in a water-electrolysis and a subsequent reaction of hydrogen with carbon-dioxide (CO₂) to SNG. An entire system SNG conversion efficiency of 60 % referred to the lower heating value (LHV) of SNG can be reached [6]. Chemically the generated methane is completely compatible with natural gas and can be used in the same applications and distribution grid like fossil methane. In Germany natural gas grid
allows a storage capacity of 220 TWh which is equal to a 120 TWh electricity-storage, assuming an efficiency of 55% for the re-conversion to electricity. This capacity exceeds the aspirated amount of 40 TWh by far [2]. From a purely exergetic point of view the losses of PtSNG technology combined with a re-conversion to electricity are comparatively high and therefore the cost effectiveness is low but it has to be kept in mind that storage gas is currently and in the near future the only option to face a high share of RE in electricity sector. Furthermore the share of RE in transportation sector can be affected by expanding the SNG production. Nowadays the combustion of compressed natural gas (CNG) is state of the art and vehicles engines can easily be replaced to be fuelled with SNG instead of gasoline.

Additionally, excess heat, which occurs along the entire SNG conversion process, may partially cover the heat demand for nearby industries or households. Consequently the degree of utilization of the PtG system increases.

1.1 Abstract

In this work a technical pre-feasibility study is carried out for a small-scale Power-to-Gas device. Small-scale is meant here by a nominal power range up to 20 kW electrical input. The objective is to pre-design a small-scale device for solar energy based SNG production for transportation in short to medium term (2020->2030) when the majority of the road transportation fleet will definitely be based on internal combustion engines. Optionally the storage can be offered to the storage market for storing wind energy, too.

If volatile PV- and wind-generated energies fed in large proportion into an electricity grid, it is inevitable that in large part of the year there is surplus of electricity in the grid, and also long periods when solar and wind energy are not sufficient to cover the consumption. Long- and short-term PtG-based storage solutions could be implemented to stabilize the electricity grid. If feasible compact PtG devices could be established in households and provide decentralized storage systems as an alternative for feeding into the grid. It may well be an incentive to produce a RE fuel for a vehicle as fossil fuels are expensive for a consumer to purchase.

As referred to above, one of the most promising large-scale and long-term energy storage option for solar and wind power is the production of hydrogen which is then used in synthesis with CO₂ to form hydrocarbons such as SNG. The PtSNG technology provides most probably a feasible large-scale seasonal energy storage option, but in this work it will be assessed if there is a feasible concept to provide also household level producers with such technology that enables a decentralized production of SNG from a household’s rooftop PV plant.
A PtSNG system will be modelled that consists of two main components. Firstly an electrolyser has to be chosen that meet the challenges of a volatile energy input best. Secondly an appropriate methanation reactor will be suggested. The operational performances will be examined by static models or evaluated by literature reviews. Further essential system elements like an intermediate storage and power electronics will be taken into considerations as well.

The SNG yield will be calculated by applying the developed PtSNG model to the real PV data of a reference site in Germany. The potential for excess heat integration in the domestic heating system will be determined.

Finally, cost estimation is made for a single PtSNG unit and further in the context of learning rates for mass-produced units.

1.2 Approach

Section 2: After an overall view about the concept, each main component of the PtSNG-system is introduced. Beginning with a description of a state-of-the-art PV rooftop system, this section focuses on the conversion process technology of water-electrolysis and methanation, which includes the fundamental thermodynamics and chemical equations, implementable efficiencies and applicable types of reactors for a small-scale conversion system. Section 2 is mainly targeting the static model development of the components electrolyser and methanation reactor. The system model is carried out with Matlab®. Furthermore an intermediate storage option within the process chain is presented and the essential interconnectors between all components are described. In the end the SNG use options will be assessed according to German gas standards.

Section 3 presents the results of the model calculations. Each component calculation will be explained step by step and the important results will be shown graphically. For the calculations, the data input originates from electricity generation measurements over a two-year period of a real rooftop PV plant at a site in Lütjensee (Germany) and the yearly electricity consumption of a German three-person household. The SNG yield of the reference site will be calculated, as well as the potential of excess heat to cover the domestic heating demand.

Section 4: A sensitivity analysis is supposed to pinpoint the measures for optimization of the PtSNG system regarding dimensioning and the operational mode. Rough financial calculations are carried out to assess the range of system-related costs and the expected revenues. In the context of the intended small-scale PtSNG device, the technical feasibility, the potential of
system optimization, cost related aspects and outstanding issues of the previous section are summarized and discussed.

**Section 5:** The relevant results and findings of the designed small-scale energy conversion system are summarized and a future prospect is given. Finally, recommendations for further research work are given.
2 Power-to-SNG Concept

As referred to section 1, from the electricity sector’s point of view it can be valuable to integrate RE storage options via conversion to a gaseous storage medium called SNG. According to temporal fluctuations of RE input, the grid frequency variation can be diminished and a long-term storage can be provided. Therefore, a system which enables the transformation from electricity to SNG has to be designed.

In this thesis the focus will be on a compact PtSNG-plant, which may be installed in the garage or the basement of a one-family house. The concept will be designed to maximize the gas output in a technological feasible environment but heat integration can also be applied. The system is intended to be composed of the main components:

- Rooftop PV-plant (installed Power < 20 kWp)
- Water electrolyser
- Intermediate hydrogen storage
- Methanation reactor

Figure 2 visualizes the functional design of the PtSNG plant, which is partially based on a previous scientific work from Thilo Bocklisch et al. [4]. During the day a standard type rooftop PV panel (a) converts solar irradiation to electricity in accordance to its efficiency performance. The generated energy is optimized due its maximum power by a Maximum-Power-Point-Tracker (MPPT) and is being customized for household electricity alternating current (AC) bus by an inverter (b). An intelligent energy management system (c) measures the generated electricity and determines the difference between generation and consumption. The components a, b and c are state-of-the-art technology and installed in large numbers in conventional rooftop PV plants to cover the proprietary requirements of the house. In case the current demand cannot be covered, the energy has to be supplied from the grid. In case there is a surplus of energy, the PtSNG system can be patched in and act like an unidirectional storage. If the surplus power exceeds the installed nominal power of the PtSNG device, the peak energy has to be “dumped” into the grid. Theoretically, the PtSNG system can be supplied by electricity from the grid, if there is a surplus of RE in the grid.
Figure 2: Proposed Power-to-SNG Conversion System
The electrical set-up for the PtSNG unit, which is modelled in this work, comprises an AC-DC inverter (d). The inverter is supposed to provide a constant voltage to the electrolyser (e). Within the electrolyser, water is split to oxygen, which is released to the atmosphere, and to hydrogen, at the operational pressure of the electrolyser. The electrolyser excess heat could be integrated in the domestic heating system. Hydrogen (H\textsubscript{2}) will be stored in H\textsubscript{2}-pressure bottles (f). The carbon dioxide is stored in pressurized bottles at 250 bar (g). A small-scale SNG methanation reactor (h) can be fed with the reactants to work in steady-state operation. A moderate temperature and a pressure level of about 8 bar assure the synthesis of Methane (CH\textsubscript{4}) from the gaseous educts H\textsubscript{2} and CO\textsubscript{2}. The dried product gas SNG mainly contains methane and a reduced share of hydrogen and carbon dioxide. The SNG can be compressed, stored and provided as a combustible fuel for car engines (i). In order to maximize the efficiency an integration of methanation excess heat can be performed as well.

For the implementation of a PtSNG conversion system, it is essential to examine the central performance characteristics of all components which are connected to a volatile power input. In the next section, the basics and state of the art of PV electricity generation are roughly explained and the term residual load is introduced. The main focus of the next section is the introduction of the thermodynamics of the electrolyser and methanation unit, whose equations provide the basis for a static model of the entire SNG conversion system.

2.1 Photovoltaic Electricity Generation

A PV cell consists of a semi-conductor material. All suitable elements for solar energy conversion belong to the IV main group of the periodic table. The most common used material is Silicon (Si) as semi-conductor material. Si is, compared to other group IV elements, relatively cheap and next to oxygen the second most occurring element on earth but the basic principle of converting solar energy to electricity is the same for all group IV elements.

The ability of Si to convert solar energy into electricity is explained by the band model of semi-conductors, extensively described in [7]. Si is usually doped with high- and low order elements to form p-n depletion region. The material specific electrical potential difference between the conduction band and valence band defines the maximum cell voltage of a semi-conductor configuration and the wavelength range of the solar spectrum that could be absorbed. The intensity of irradiation is proportional to the cell current. The internal photoelectric effects within a solar cell are visualized in Figure 3. Incident solar radiation generates a separation of charges, so called electron-hole pair. When the negatively charged electron is
able to migrate to the front contact and the corresponding positive hole reaches the back contact without the recombination within the p-n fields, an electrical current can be detected.

Figure 3: Effects of irradiation within a solar cell [7]

### 2.1.1 Photovoltaic Rooftop System

Fifty to hundred single cells are electrically connected to about 100 x 160 cm solar modules to be more physically resistant and protected against weather. For achieving structural rigidity, solar cells are embedded in an arrangement of different layers (Figure 4).

Figure 4: Standard PV module system [7]

The transparent Ethylen-Vinylacetat (EVA) foil protects the cells against cracks. The PV cell active wavelengths of solar radiation are able to transmit the polymer foil as well as the glass pane, which stabilizes the module and prevents moisture penetration. The back cover is supported by polymeric foil or a second glass pane. The maximum module efficiencies of Si
based cells vary with the type of used cell technology from 12 % (amorphous silicon) up to 20 % (crystalline silicon), measured under standard conditions [7].

Depending on the desired installed power of a rooftop PV system and the level of current and voltage, a few modules can be connected in series or in parallel. The PV system is completed by power electronics consisting of a MPPT, which assures pinpointing the maximum product of voltage and current for high efficiencies of approximately 99 % [8], and a DC-AC inverter for supplying the household with alternating current.

Generally there are two common types of PV systems in use. Remote areas are predestined for PV island systems which are not connected to the grid and supposed to supply the energy demand of small households. Highly relevant is the dimensioning of the PV plant to assure a maximum of supply security but avoiding an unnecessary over-dimensioning. In the past a practical usage of island systems were demonstrated in remote areas in Africa for example. In the industrial countries most installed PV plants are directly connected to the national electricity grid. The surplus generated electricity is fed into the grid and a lack of energy can be provided by the grid. Due to grid imbalances caused by volatilities, efforts were intensified to combine both types of PV systems [9].

A typical rooftop PV plant is installed decentralized connected to the low voltage distribution grid in a power range up to 20 kWp (kilowatt peak) according to the limited roof area per house. In the following section the electricity generation of a 10.8 kWp PV rooftop plant is discussed.

### 2.1.2 Electricity Generation & Consumption – Residual Load Curve

The daily and annual fluctuations of the residual load are plotted and discussed in this subsection. The residual load is the difference between rooftop PV electricity generation and household electricity consumption. The residual energy is the maximum potential of energy, which can be fed into the PtSNG conversion system.

The PV electricity generation $P_{PV,Load}$ data was measured at a 10.8 kWp PV plant and is available for nearly two years at a reference site in Lütjensee, Germany (53° 39’ N, 10° 22’ E). The plant is commissioned at 26 March 2013 and the average electricity generation rate is about 828.0 kWh/kWp. Calculating the entire yearly energy conversion, the data from 01 January - 25 March 2013 is added from measured data of the following year 2014.
The common way to predict the energy consumption is to consider the German $H_0$ synthetic standard load profile, which was developed over the past 20 years to display a normalized 1000 kWh/a load curve depending on daytime and the season, represented through a dynamic polynomial [10]. The annual standard energy consumption (equation 1) is adjusted by a factor $F_H$ to compare it with the load profile of an average three- to four-person household, which is considered in this work. For each quarter of an hour the **consumed power of the household** $P_H$ can be calculated:

$$P_{H_{i,j,d,s}} = P_{H0} \cdot \beta_{d,s} \cdot F_H$$  \hspace{1cm} (1)

where $P_{H0}$ is the quarter-hourly required power, normalized to 1000 kWh/a, changing due every quarter $(i)$ of an hour per day, in weekly intervals $(j)$. $\beta_{d,s}$ represents the dynamic polynomial, which changes every day $(d)$ in seasonal intervals $(s)$. The fitting parameter $F_H$ adjusts the dimension of the household, which is done here by a value $F_H = 3.939$, according to real data measured at a smart metering device for a three-person household.

Finally, the **residual load curve** can be defined. As defined above, the residual load is calculated by the subtraction of PV-generated electricity and the consumed electricity of the household at the same time. The difference can either be positive for a surplus of generated energy, or negative for a lack of electricity and zero for a match of generation and consumption. The positive residual load curve of the year 2013 is depicted in figure 5.

![Figure 5: Positive residual load curve of the reference site in Lütjensee](image)
It is obvious that the residual load curve corresponds to the seasonal solar elevation which is the greatest during the summer months and the smallest during wintertime. The power volatility is explained by the day and night rhythm and by the rapid change of irradiation due to clouds. Figure 6 is an exemplary quarter-hourly plot of a cloudy day in summertime at the reference site. The sunshine hours at that day were reported as 4 hours.

Figure 6: Residual load on a cloudy day on 11. August 2013

Clouds cause load volatilities over a power range of 6 kW during the day. A higher resolution of measured data would certainly reflect the reality more accurately. However, the characteristic changes of irradiation need to be taken into account when a SNG conversion plant is connected to that variable energy flow. Facing those challenges, one of the two electrolyser technologies, which are introduced in the following section, meets the volatile energy supply best.


2.2 Hydrogen Generation

Considering a RE source, a technologically feasible way to generate a fuel is the water electrolysis. If a direct current (DC) is applied to water, the molecule is dissociated into the gaseous products oxygen and the storable gas hydrogen. This chapter gives an overview of the basic electrochemical reaction of splitting water into hydrogen and oxygen, equations for modelling the performance of an electrolyser cell and the system efficiency. In the next step two commercially available technologies, the alkaline electrolyser (AEL), and the polymer electrolyte membrane electrolyser (PEMEL), are presented. Finally the suitability of both devices to convert volatile RE to hydrogen efficiently is discussed. For this purpose both systems are compared due to their characteristic operational behaviours to get the maximum output of hydrogen in a small-scale RE electrolyser connected to a PV plant.

2.2.1 Thermodynamics of Water Electrolysis

Applying a direct current to water the molecule is split into the gaseous elements hydrogen and oxygen.

$$H_2O (l) \rightarrow \frac{1}{2} O_2 (g) + H_2 (g) \quad (R1)$$

For isothermal conditions, reaction (R1) takes place when the enthalpy change $\Delta H$ (2) is reached. $\Delta H$ represents the total amount of energy which contains the Gibbs free energy $\Delta G$ for the reversible part, and the entropy change $\Delta S(T)$, representing the irreversible part of the electrolysis reaction.

$$\Delta H(T) = \Delta G(T) + T\Delta S(T) \quad (2)$$

The free Gibbs energy can be described as the amount of electrical energy and $T\Delta S$ represents the heat energy which has to be delivered for starting the electrolysis. It can be seen, that the enthalpy change is temperature dependent. At standard conditions (at 298 K and 1 bar pressure) the total required energy per mol hydrogen is $\Delta H = 285.84 \text{ kJ/mol}$ [11]. The value for $\Delta G$ is 237.22 kJ/mol and positive as well. It is appropriate to describe the fundamental energy equation (2) as electrical values. The transformation of enthalpy, reversible and irreversible energy to the thermoneutral voltage $V_{th}$ is realized by factor $nF$ ($n$, number of transferred electrons; $F$, Faraday constant) in equation (3):
The minimum cell potential for splitting water by electrolysis is called the reversible cell voltage and is calculated by the Gibbs free energy $\Delta G$. The \textit{reversible voltage} $V_{rev}$ can be expressed by the general \textbf{Nernst equation} (4) \cite{11}.

\begin{equation}
V_{rev} = \frac{\Delta G(T)}{nF} = E^0 + \frac{RT}{nF} \ln \frac{p_{O_2} p_{H_2}}{a_{H_2O}}
\end{equation}

Accordingly, $V_{rev}$ is a function of temperature and pressure. $E^0$ represents the reversible cell voltage at standard conditions ($T = 289$ K, $p = 1$ bar), $R$ is the absolute gas constant in \textit{J/mol/K}, $p_i$ are the partial pressures of oxygen and hydrogen and the activity of water $a_{H_2O}$ can be assumed to be close to unity. The influence of pressure on the reversible voltage is significantly smaller than the temperature impact. If the product gas pressure increases by a factor of $X$, the reversible voltage increases by the amount of $(RT/2F) \cdot \ln(1/\sqrt{X})$. Although a higher pressure level affects the reversible voltage adversely, it is common practice to operate an electrolyser as an electrochemical compressor to avoid a subsequent compression of hydrogen for pressurized storage \cite{12}.

For water electrolysis the transferred number of electrons is two resulting in a thermo-neutral voltage of 1.48 V at standard conditions. The share of the energy-representing voltage levels depending on the electrolysis temperature is visualized in figure 7.

![Figure 7: Temperature dependency of thermodynamics and cell voltage \cite{13}](image)
For a temperature less than 100 °C the thermo-neutral voltage is approximately constant. It changes abruptly when water is evaporated and then remains constant. If an ideal electrolyser cell is applied with an operating cell voltage of $V_{\text{cell}}$, three cases can be considered [13]:

1) $V_{\text{cell}} < V_{\text{rev}}$: The electrolysis reaction cannot take place, because too less energy is applied to the cell.

2) $V_{\text{rev}} < V_{\text{cell}} < V_{\text{th}}$: The electrolysis reaction takes place, but heat has to be provided from the environment.

3) $V_{\text{th}} < V_{\text{cell}}$: The electrolysis reaction is exothermic and heat is released to the environment.

Usually an electrolyser is operated above the thermo-neutral voltage and the system has to be cooled. In the following section the real cell voltage is introduced to define both the cell efficiency and the system efficiency.

### 2.2.2 Efficiency Losses

In reality, different energy losses cause that the real cell voltage is higher than the thermo-neutral cell voltage. Hence the minimum cell voltage to be applied for splitting of water is higher than the reversible cell voltage or in practice, the thermo-neutral cell voltage. The required cell voltage $V_{\text{cell}}$ is the sum of several overvoltages occurring due to electrolyser specific properties [13]:

$$V_{\text{cell}} = V_{\text{rev}} + V_{\text{act}} + V_{\text{ohm}} + V_{\text{conc}}$$

(5)

As mentioned in the previous subsection, the reversible voltage is related to the temperature and the pressure level of the electrolyser cell and varies with the current density applied to a cell. It represents the ideal behaviour of a reversible water splitting reaction, in the proper sense it is no overvoltage.

Activation losses occur due to limited electrode reaction in an electrolyser cell. Both, losses at the anode $V_{\text{act,a}}$ and the cathode $V_{\text{act,c}}$ can be summed up and cause an activation overvoltage $V_{\text{act}}$:

$$V_{\text{act}} = V_{\text{act,a}} + V_{\text{act,c}}$$

(6)

The overvoltages of both electrodes can be described by the Tafel equation [14]:

$$V_{\text{act}} = \frac{E_{\text{rev}}}{2.303RT} \ln \frac{J}{J_0}$$

Where $J$ is the current density, $J_0$ the exchange current density, $R$ the gas constant, and $T$ the temperature.
\[ V_{\text{act}}^{a,c} = \frac{RT}{F \alpha a/c} \arcsinh \left( \frac{i}{n \cdot i_0 a,c} \right) \]  \hspace{1cm} (7)

where \( i \) is the current density (A/cm\(^2\)), which is applied to the cell and \( i_0 \) is the exchange current density of the cathode and anode, strongly dependent on the electrodes material, roughness and geometry. For platinum-coated electrodes the values for the charge-transfer coefficients \( \alpha_a, \alpha_c \) vary between 0-1, depending on the cell temperature. Biaku did a comprehensive analysis of temperature dependency on the electrodes charge transfer coefficients and the exchange current densities [14]. Except \( \alpha_a \), which is slightly increasing with temperature, almost all parameters are approximately in the same range for temperatures up to 60°C.

According to its name, ohmic losses result from electric resistances within the electrolyser cell. The membrane resistivity is described as the dominating resistance of a PEM electrolyser by Awasthi [15]. Hence it is reasonable to consider the influence of membrane resistivity for **ohmic overvoltage** \( V_{\text{ohm}} \) exclusively:

\[ V_{\text{ohm}} = \frac{\delta_m}{\sigma_m} \cdot i \]  \hspace{1cm} (8)

\( \delta_m \) represents the thickness of the PEMEL membrane, which in practice is within the range between 100–200 \( \mu \)m [11]. The ratio between \( \delta_m \) and \( \sigma_m \) is known as the ohmic resistance.

The **conductivity of the membrane** \( \sigma_m \) can be described by (6a):

\[ \sigma_m = (0.005139 \lambda - 0.00326) e^{1268(\frac{1}{303} - \frac{1}{T})} \]  \hspace{1cm} (9)

As can be seen, the conductivity depends on the temperature \( T \) of the electrolysis and the degree of humidification of the membrane \( \lambda \), which ranges from 14-21 mol\(_{\text{H}_2\text{O}}\)/mol\(_{\text{SO}_3}\) [15].

Concentration losses relate to the mass transport limitations of the product gases in the gas channel. An optimized flow management of the gaseous products minimizes the **concentration overvoltage** \( V_{\text{conc}} \) which can be expressed by [16]:

\[ V_{\text{conc}} = \frac{RT}{nF} \ln \left( 1 - \frac{i}{i_L} \right) \]  \hspace{1cm} (10)

where \( i_L \) is the limiting current density (A/cm\(^2\)) of the specific electrolyser. It is the maximum current, which can be applied to the electrolyser cell. Concentration losses can be neglected...
for low currents, but must be considered at high current densities. For a PEMEL $i_L$ can be assumed as 2 A/cm$^2$ [13].

Figure 8 displays the polarization curve of a single electrolyser cell with a varying current density, which should be interpreted as a mathematical approximation to a real operating electrolyser cell. The model was developed in Matlab® at a constant pressure of 30 bar and constant temperature of 60°C.

The polarisation curve can be divided into three sections along increasing the current density. The lowest cell potential is defined by the reversible cell voltage at the point of contact with the vertical axis. Within the first section up to 0.2 A/cm$^2$ the influence of the activation overvoltage is dominating all losses. At first the cell voltage is rapidly ascending but then flattens to the second section, a linear behaviour for a current density range between 0.2 – 1.9 A/cm$^2$, which is mainly affected by activation and ohmic overvoltage. The third section is dominated by the concentration overvoltage which starts around 1.9 A/cm$^2$ and diverges when close to the limiting current density $i_L$, which is assumed to be 2 A/cm$^2$ [13]. In order to run the electrolysis at either high efficiencies or a higher hydrogen production rate, it is essential to select a constant operating cell voltage accordingly. Barbir estimates the operating cell voltage from 1.6 V to 2.0 V [17]. The first value is used for optimized efficiencies and the latter for a higher hydrogen production rate.

![Figure 8: Polarization curve of a single PEM electrolyser cell](image-url)
2.2.3 Electrolyser Efficiency

In the previous subsection the losses of a real electrolyser cell are illustrated in detail. This section focuses on the definitions of cell and system efficiency.

There are different definitions of efficiencies described in the literature. Millet is introducing a \textit{thermo-neutral efficiency} $\eta_{TN}$ which is the rate of free Gibbs energy $\Delta G$ to the reaction enthalpy $\Delta H$ or of reversible and thermo-neutral voltage [11]:

$$\eta_{TN} = \frac{\Delta G(T)}{\Delta H(T)} = \frac{V_{rev}(T)}{V_{th}(T)}$$

(11)

Lehner is defining a cell voltage efficiency $\eta_V$ as a ratio of the ideal thermo-neutral voltage and the cell voltage $V_{cell}$ applied to the real cell, that are both related to the temperature [13]. He also suggested relating the cell voltage to the \textit{higher heating value corresponding voltage} $V_{HHV}$, which is dependent on the temperature in degree Celsius [18]:

$$V_{HHV} = 1.4754 + 2.252 \cdot 10^{-4} T + 1.52 \cdot 10^{-8} T^2$$

(12)

Barbir simplified the model for the narrow the temperature ranges of commercially available electrolyser, assuming the minimum ideal operating voltage at 1.482 V as constant [14]. The simplified \textit{cell efficiency} $\eta_{cell}$ is therefore:

$$\eta_{cell} = \frac{1.482 \text{ V}}{V_{cell}(T, p)}$$

(13)

Figure 9 illustrates the Matlab\textsuperscript{®} plot of the HHV cell efficiency distribution of a PEM electrolyser for a current density of 1 A/cm\textsuperscript{2} dependent upon temperature and pressure. The selected model parameters are summarized in annex 1. Figure 9 shows, that the efficiency rises with increasing cell temperature, whereas it declines with increasing pressure. The isolines expand significantly for temperatures above 50°C. The range of cell efficiency which can be reached in the illustrated field is in the range between 77 to 80%. Considering the cell efficiency exclusively it appears that high temperatures and low pressures are the optimal choice for an efficient conversion of electricity to gas, but one thing has to be kept in mind when including the worth of a pressurized hydrogen product gas for storage purposes.
Noting that the decrease of efficiency by increasing the pressure is comparatively low, a high pressure level could avoid a subsequent energy intensive compression of hydrogen, in order for a medium-term storage.

Shapiro is highlighting the benefits of running a PEMEL as an electrochemical gas compressor [12]. Hence research laboratories aim at increasing pressure levels. Considering the start-up of an electrolyser, the cell efficiency is dominated by the transient heating of the stack. The start-up time depends on the material volumes, heat capacities and the internal heat source of the water split reaction. However, the cell efficiency ranges between a narrow band from 77 to 79 % and can be neglected for a simple pre-design of a PtG system.

Considering the entire electrolyser system, Barbir introduces module inefficiency due to hydrogen permeation losses via the polymer membrane of a PEMEL. Görgün quantifies the general hydrogen losses, represented through $i_{\text{loss}}$, at a very low level less than 1 % of the operating current density [19]. Finally there is some auxiliary equipment needed for electrolyser regulation during operation (pumps, fans, solenoid valves, instrumentation and controls), represented in the ratio $\xi$ between parasitic power of auxiliaries and the net power consumed by the electrolyser [17], which can be assessed as 5 % of the actual load [20].

![Figure 9: Cell efficiency at 1 A/cm² depending on pressure and temperature level](image)
An electrolyser requires a nearly constant voltage at a specific level. An AC-DC coupler assures the supply of steady voltage but also causes energy losses due to electrical switching. According to Barbir the actual system efficiency $\eta_{sys0}$ of a PEMEL can be calculated by equation 14. Index 0 describes here the adjusted data for neglected long term cell efficiency degradation. The coupler efficiency $\eta_{DC}$ is considered in section 2.2.9 in this work.

$$\eta_{sys0} = \frac{1.482}{V_{cell}} \frac{i - i_{loss}}{i} \frac{\eta_{DC}}{1 + \xi}$$  \hspace{1cm} (14)

Simulating the operating conditions of a PV connected electrolyser, it is essential to assess the partial load performance, which is from great importance dealing with a volatile energy supply. The system efficiency and the corresponding specific energy demand for the production of hydrogen was plotted in Matlab® (figure 10). All assumptions for the PEMEL system model parameters are summarized in annex 2.

The system efficiency reaches its maximum value of 75 % at 10 % of the PEM electrolyser`s nominal load. The efficiency below 5 % electrolyser load is strongly decreasing. This characteristic drop is caused by the ac-dc rectifier performance, which is further explained section 2.2.9. In the load range between 10 % and 100 % the PEMEL cell performance is dominating the efficiency behaviour. Ohmic losses cause a nearly steady decline from 75 % efficiency to 62 %. The narrow efficiency drop at 98 % is caused by activation losses within the electrolyser cells. The system efficiency directly affects the volumetric energy demand for hydrogen production.

Figure 10: PEMEL system efficiency and specific energy demand for hydrogen production
production. The red curve is depicted as the inverse of the blue curve. Referring to the **higher heating value** $HHV_{H2}$, the volumetric energy of hydrogen is 3.54 kWh/Nm$^3$. Due to efficiency losses, the minimum energy demand for the electrolyser amounts 4.7 kWh/Nm$^3$. Except for low loads the range is between 5.0 to 6.0 kWh/Nm$^3$. The difference between the higher heating value energy demand and the required energy for the electrolysis appears as excess heat, which is removed by a fan, but could also be integrated in the domestic heating system.

The current **hydrogen flow rate** $f_{H2}$ in Nm$^3$/h (standard cubic meters per hour) for an electrolyser stack with N cells can be calculated considering the higher heating value of hydrogen, the electrolyser load and the system efficiency:

$$f_{H2} = \eta_{sys0} \frac{N_{cell}V_{cell}I_{cell}}{HHV_{H2} \cdot \Delta t \cdot 1000 \frac{W}{kW}}$$  \hspace{1cm} (15)

$N_{cell}$ is the number of cells in the electrolyser module. Multiplying the number of cells with each cell voltage $V_{cell}$, assuming all cells are connected in series, results in the total voltage applied to the stack. The fraction denominator designates the electrolyser load, $\Delta t$ is 1 hour.

### 2.2.4 Electrolyser Lifetime

When dimensioning an electrolyser the decay of efficiency over time has to be taken into account. The aging process relates to the cell voltage increase caused by degradation of the catalyst, electrolyte and membrane. Barbir explains the increasing resistance of the cell components by oxidation processes of catalysts and metallic component and the equilibration of water in the membrane [17]. Barbir also analysed the lifetime performance of a HOGEN® PEM electrolyser [21] for 14 000 operating hours and concludes to an average cell degradation of 5 $\mu$V/h and mentioned a high initial voltage increase and medium voltage decay after 2 000 h in operation. These results are approximately consistent with manufacturer information about degradation rates. Lehner estimates the maximum degradation rate of a PEMEL up to 10 $\mu$V/h. Both exemplify the degradation process as nearly constant, hence the initial system efficiency $\eta_{sys0}$ has to be adjusted by a **lifetime efficiency** $\eta_{time}$ for long term hydrogen production calculation.

$$\eta_{sys} = \eta_{time} \eta_{sys0}$$  \hspace{1cm} (16)

The effect of a dynamic electrolyser operation on the lifetime of a cell has not been investigated sufficiently to obtain meaningful results [22].
2.2.5 Polymer Electrolyte Membrane Electrolyser

A polymer electrolyte membrane electrolyser (PEMEL) is characterized by a solid polymer proton exchange membrane (PEM), whereas the alkaline electrolyser (AEL) uses a liquid electrolyte for ionic transportation, as described in the next section.

The operating principle and the main components of a PEMEL cell are depicted in Figure 11 [5,23].

![Figure 11: Cross-section of a polymer electrolyte membrane electrolyser [5,23]](image)

The core element of a PEMEL is the solid polymer membrane (1). The most common material for the PEM is Nafion®, a polymer membrane based on perfluorosulfonic acid, which benefits high proton conductivity and adequate mechanical and electrochemical stability. Due to polymer material the operating temperature is limited to 80 °C. Elevated temperature levels result in a significantly higher thermal degradation of the polymer membrane. A major chal-
lenge is to protect all cell components against corrosion due to acidity of Nafion®. Furthermore
the costs for Nafion® are comparatively high [13].

Both surfaces of the PEM are pressed with catalytic electrode layers and form the membrane
electrode assembly (MEA). Materials for catalysts must meet the requirements that come
along with the harsh conditions of high acidity. The thin-film electrode design is characterized
by carbon supported catalyst particles, as the reactive surface is large and the porosity allows
gas to escape. Platinum group elements are resistant against corrosion and assure high catalytic
activity. However, platinum, iridium and others are scarce and therefore expensive, as they
are commonly used in PEMELs and fuel cell applications. Ito describes a widely used cell
thin-film electrode configuration which contains an iridium oxide (IrO₂) catalyst for the anode
side (2a) and a platinum catalyst for the cathode side (2b) [24].

The current collectors (3) serve two purposes. Firstly they assure a low resistant electric connec-
tion to the catalyst layers, and secondly they supposed to remove the generated gas prod-
ucts from the active catalyst quickly. The current collectors are also called gas diffusion layers
of flow fields. These porous layers are made of titanium and are often modified by protective
coatings like gold or platinum to avoid negative influences caused by oxide precipitation on
the collector surfaces.

The last main components of the PEMEL cell configuration are the bipolar plates (4). Similar
to the current collectors/ gas diffusion layers, bipolar plates are usually made of coated titani-
um. The plates serve two purposes. They should optimize the electrical contact to the current
collectors by minimizing the electrical losses, and promote the efficient removal of product
gases from the diffusion layer to the gas outlets of the cell via engraved flow fields. Ito inves-
tigated the influence of flow field arrangements and concludes that the parallel dimension,
which is aligned to the natural gas flow, is the most energy efficient arrangement.

A gasket on head and foot side, which is stressed by the pressure level of the cells inner life, is
supposed to avoid leakage of process water (5). The inlet for ionized water (6) is on the anode
side at the bottom and the outlets for hydrogen (7a) and oxygen (7b) are located at the top of
the cell. If direct current applies to the cell, the partial reactions at each electrode take place:

\[
\begin{align*}
\text{Anode} & \quad \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \\
\text{Cathode} & \quad 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2
\end{align*}
\]  

(R2)  

(R3)
Deionized water is fed by a circulation pump into the cell, but only on the anode side, where the oxidation reaction takes place. It flows through the engraved channels of the positive bipolar plate and diffuses through the porous current collector to the anode catalyst layer. When a DC current is applied to the cell, two electrons of the water molecule are released and the molecule then splits into gaseous oxygen and two protons (R2). The solvated protons are able to migrate through the permeable membrane Nafion® to the cathode electrode. Each proton is accompanied by a couple of water molecules, assuring that the cathode side is also soaked with water, although the water is fed to the anode side exclusively. Nafion® guarantees that no gaseous elements can pass the membrane and therefore avoids the dangerous mixture to explosive oxyhydrogen. Two electrons are required to reduce the two protons to molecular and gaseous hydrogen at the cathode side (R3). On both sides of the cell the product gases migrate through the gas diffusion layer to the flow channels of the bipolar plates and escape the cell at the particular gas outlets. It is common to remove the liquid water in hydrogen product gas by an accumulator. The removed water can recirculate the electrolysis process and the dried gas can escape the PEMEL [24]. Usually the cells of a PEMEL are electrically connected in series (bipolar stack configuration).
2.2.6 Alkaline Electrolyser

The alkaline electrolyser (AEL) is the most developed technology for electro-chemical splitting of water. Currently it is the only technology, which is used in large-scale industrial applications and is therefore discussed in short. The cell structure is visualized in Figure 12.

All cell components are installed within a steel container (1). It contains the two electrodes anode (2a) and cathode (2b), current distributors and a separator membrane (3) which allows a migration of hydroxyl ions from the cathode to the anode side. The porous separator membrane is supposed to avoid an exchange of product gases between both sides of the electrolyser cell. The thickness of the membrane defines the ohmic losses. Hence the separator layer has to be dimensioned also for a minimum increase of the cell resistance. Typically the separator material is based on sulfonated polymers, polyphenylene sulfides, polybenzimidides and composite materials [13].

Figure 12: Cross-section of an alkaline electrolyser [5,23]
All electro conductive components, electrodes included, are made of low resistive and non-corrosive nickel (Ni) or Ni-coated steel, which meet the requirements for basic milieu. Cathode and anode are fully immersed in a solution of water and the aqueous potassium hydroxide (KOH) electrolyte with a concentration up to 40 wt%. The surface of the electrodes can be optimized by increasing the catalytic active areas mechanically and chemically. Established modifications are etching, sintering, sandblasting and additional coatings of the anode and cathode. In order to overcome the problem of deactivation of nickel catalysts, several stabilizing coatings can be applied to enlarge the lifetime of the electrolyser cell.

The AEL cell is fed with water at both electrodes (4). Theoretically the electrolyte KOH is not consumed in the cell, but has to be refilled in practice due to physical leakages. If a direct current is applied to the electrolyser cell the following cell reactions take place:

\[
\begin{align*}
\text{Cathode} & & 2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{H}_2 + 2\text{OH}^- & \quad (R4) \\
\text{Anode} & & 2\text{OH}^- & \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- & \quad (R5)
\end{align*}
\]

On the cathode side two water molecules are reduced to gaseous hydrogen (R4), which can escape through the hydrogen outlet (5a) on the top. Two hydroxide ions are released simultaneously and migrate through the porous separator membrane to the anode side. The second half reaction takes place on the surface of the anode, where both ions are oxidized to liquid water and stoichiometrically to a half molecular of gaseous oxygen (R5), which escapes through the oxygen outlet (5b).

Millet describes the general electrode membrane configurations in an AEL cell. In the gap-cell configuration the massive electrodes are installed very close to the separator, but do not contact the membrane. This gap is only a few millimetres in size and the product gases can escape in between to the top. Due to very high resistances of closed gaseous films on the active surfaces, this set up limits the maximum current density to 100 mA/cm$^2$.

The second more efficient configuration is called zero-gap configuration. Similar to the MEA of the PEMEL, both electrodes are pressed and laminated to the separator membrane. The electrodes are porous, the product gas can escape through the pores of their matrix and minimal ohmic losses due to a zero-gap zone are assured. Thereby the maximum current density can be significantly increased [11].
Single alkaline cells can be connected in series (bipolar stack configuration) or in parallel (unipolar stack configuration) but the latter is losing its importance according to relatively high ohmic losses. In a large-scale AEL up to 200 cells are connected in series [13].

### 2.2.7 Comparison of Characteristics

This section contrasts the alkaline and the proton exchange membrane electrolyser for a decision making, which technology meets the PtG requirements of a volatile energy input best. Therefore key performance indicators, representing main characteristics of both systems, are listed in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>AEL</th>
<th>PEMEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature</td>
<td>60 - 80°C</td>
<td>50 - 80°C</td>
</tr>
<tr>
<td>Pressure level</td>
<td>&lt; 30 bar</td>
<td>&lt; 50 bar</td>
</tr>
<tr>
<td>Cell current density [A/cm²]</td>
<td>0.2 - 0.4</td>
<td>0.6 - 2.0</td>
</tr>
<tr>
<td>Cell voltage [V]</td>
<td>1.8 - 2.4</td>
<td>1.8 - 2.2</td>
</tr>
<tr>
<td>Cell area [m²]</td>
<td>&lt; 4</td>
<td>&lt; 0.03</td>
</tr>
<tr>
<td>System efficiency (HHV)</td>
<td>62 - 82 %</td>
<td>67 - 82 %</td>
</tr>
<tr>
<td>Operating range [% of P_{Nominal}</td>
<td>30 - 100</td>
<td>5 - 100</td>
</tr>
<tr>
<td>H₂ purity</td>
<td>&gt; 99.5 %</td>
<td>&gt; 99.9 %</td>
</tr>
<tr>
<td>Specific energy demand [kWh_{el}/Nm³]</td>
<td>Stack: 4.2 - 5.9</td>
<td>Stack: 4.2 - 5.6</td>
</tr>
<tr>
<td></td>
<td>System: 4.5 - 7.0</td>
<td>System: 4.5 - 7.5</td>
</tr>
<tr>
<td>Lifetime</td>
<td>Stack: &lt; 90 000 h</td>
<td>Stack: &lt; 20 000 h</td>
</tr>
<tr>
<td></td>
<td>System: 20 - 30 a</td>
<td>System: 10 - 20 a</td>
</tr>
<tr>
<td>Degradation rate [μV/h]</td>
<td>&lt; 3</td>
<td>&lt; 14</td>
</tr>
<tr>
<td>Specific investment costs €/kW (MW-scale)</td>
<td>1000 - 2000</td>
<td>1900 - 2300</td>
</tr>
</tbody>
</table>

As mentioned above and in contrast to the PEMEL, the AEL is both, the more mature technology and the more often installed electrolyser technology in MW-scale industry plants. To find a common basis to compare two technologies with fundamentally different maturity levels is quite challenging. Especially investment cost estimations are affected by cost reducing consequences of the economy of scale. Even though, a technical comparison can provide a rough impression of pros and cons. Future trend assessments, carried out by Bertuccioli [22] may be helpful to align both maturity levels for a more even comparison.
As presented in table 1 the operating pressure level of the AEL is generally lower than the PEMEL. A pressurized hydrogen product gas is from great importance according to store volatile RE effectively. Even small-scale PEMEL are available for operating at a pressure which exceeds 30 bar. Using the PEMEL as an electrochemical compressor is widely practiced on lab-scale plants and can avoid an energy-intense subsequent compression of hydrogen [13].

Another major difference of both technologies is the operating cell current density which directly influences the hydrogen production rate and the system size. Especially the latter is a design requirement for compact, domestic applications. Due to the fact that the operating cell voltages are approximately on the same level, the power density, as the product of cell current density and cell voltage, is up to five times higher in a PEMEL cell which results in a higher hydrogen production rate per cell area and therefore a more compact design.

To consider the maximum system efficiency, both technologies provide a gas conversion up to 82%. The essential differences in electrolyser performances can be observed at partial load operation. The minimum load of an AEL is between 20 and 40% of the nominal load, whereas the PEMEL can operate almost to the entire load range. Serious disadvantages arise for an AEL at low loads, but they are typical for intermittent power supply of a PV generator. The lowest operating condition of an AEL is defined by the hydrogen gas crossover rate to the anode side. A low current density implies a diffusion of gases to the undesired electrode, which represents a security risk, if the explosion threshold of hydrogen exceeds 40 mol % in the oxygen gas. Hence the AEL has to be shut down if a certain gas crossover rate is reached [5]. The thin proton conducting membrane Nafion® is highly selective and avoids an undesired gas crossover over the whole load range. The lower load limit is rather defined by switching losses of the AC-DC coupler [17]. Furthermore the greater dimension of an AEL stack results in a big thermal inertia which prevents an immediate tracking of energy fluctuations and longer cold start times.

At the present time, the lifetime of the AEL stack is significantly higher than the PEMEL stack, which is one of the great benefits of AEL technology. The lifetime is directly linked to the cell voltage degradation which results in an increase of resistivity over time. For domestic plants, it has to be assessed if a replacement of the stack is boosting the system efficiency so that it becomes economic, or the level of additional costs for a second stack is improvident. It is reported that the PEM stack lifetime will noticeably increase in the next decades due to advances in material technology [22].
The increased use of noble metals reflects the high costs of a PEMEL compared to AEL. The investment costs depicted in table 1 include system control and gas drying [22]. Today, the average investment cost of a PEMEL is about twice as high as an AEL but is expecting to decrease significantly in the next decades. Carmo identifies the biggest PEMEL costs as the stack material, which is responsible for 53 % of the entire costs [5]. 75 % of the stack costs are accounted for current collectors, separator plates and the MEA, which consist noble metals like iridium and platinum.

Moreover the handling of liquid chemicals is an important issue, designing a PtSNG system for households. Due to safety aspects the solid electrolyte of the PEMEL is to be preferred to the liquid KOH electrolyte of the AEL, which has to be replenished manually from time to time.

Furthermore specialist literature agrees on the better dynamic behaviour of the PEMEL. The dynamic properties of electrolyser are measured by the so called step response time. It is defined as a period of time, which the electrolyser follows an electrical input step signal. Lehner reports a step response time of 100 ms and Andersen even states 50 ms, which is significantly higher than AEL technology [13,25]. Bocklisch appreciates the low start-up times for PEM technology [4].

**2.2.8 Components of an Electrolyser Device**

Besides the cell stack, which is the central component of an electrolyser, some technical auxiliary equipment is necessary to run the electrolyser almost automatically. Every electrolyser comprises of the following components:

- Power supply and electric conditioning
- Water conditioning and supply management
- Water circulation pump
- Ventilation fan
- Control system
- Gas drying unit

Focusing on the PEM technology it has to be taken into account that the dynamic performance of an electrolyser and finally the system response time to track a volatile power input is mainly depending on the dynamics of the auxiliary components [20].
In figure 13 several components of the technical inlet from a fully automated PEMEL HOGEN® S40 are depicted [26]. The electrolyser unit is manufactured by Proton OnSite for hydrogen production rates up to 1 Nm³/h [21]. The dimensions of the HOGEN® S Series are 79 x 97 x 107 cm (W x D x H). In order to enhance the lifetime of the cells, the tap water is deionized to the minimum required conductivity of 1 µS/cm. A water circulation pump is feeding the anode side with deionized water and assures a certain water level at the anode and cathode side of all cells. The excess heat, which is generated within the stack, is removed by a ventilation fan. Phase separators on both gas outlets accumulate the liquid phase of the product gas streams and let it recirculate to the anode.

Figure 13: System components of a HOGEN® S40 PEM electrolyser [26]

A gas detector measures dangerous gas impurities that can lead to explosive oxyhydrogen. Optionally a desiccant dryer can upgrade the hydrogen gas stream up to 99.9995% in purity.

Rough calculations for auxiliary equipment power demand

As mentioned above, the parasitic power of all auxiliary equipment can be estimated of approximately 5% of the actual load of a PEMEL. The largest consumer is the ventilation fan which is requires 250 W at nominal load of a 7 kW electrolyser [26]. The power demand for heating up the tap water is comparably low. Assuming a constant water consumption of 0.5 l/h and a temperature spread of 60°C, the required power for heating is far below 50 W, which is provided by the excess heat itself.

The power supply and electric conditioning are of great importance, as they affect the electrolyser system significantly. Therefore a brief overview of the power converters and efficiency curves is given in the next section.
2.2.9 Electric Conditioning & Converter Efficiency

A power electronic system enables the exchange of energy between two electric systems with different characteristics by conditioning and controlling the energy flow [27]. The connection of an electrolyser to an energy source like PV electricity set demands in regards to high power volatility and an operation over the whole load range. The latter is of great relevance, being aware of the present power distribution of the residual load, which is significantly high for loads small loads, if the RE source is solar energy.

Due to mostly existing alternating current domestic mains supply, this thesis focuses on the AC-DC power topology and efficiency considerations. Other topologies like a DC-DC coupling [27] or a direct coupling of a certain type of connection of PV modules, matched to the electrolyser polarization curve, are also technically possible [17]. All systems have in common, that the power output for an electrolyser must be a DC power on a nearly constant voltage level, which fits to the polarization curve of the electrolyser stack. For the 5 kW electrolyser model, which consists 20 cells in series at 1.8 V, a DC voltage of 36 V is required. The general scheme of power conditioning is shown in figure 14.

![Figure 14: Control scheme for power conditioning [27]](image)

The DC-power output of the AC/DC rectifier is controlled to the reference value of the required DC-voltage. Supposing a switching without losses the current must take a value so that the product of constant voltage and volatile current is equal to the volatile AC-power input.

In order to maximize the performance, power converters main switching component is a semiconductor, which either can be commuted naturally or forced by a controlled switching sequence. Passive energy storages like inductors and capacitors filter the output voltage and homogenize the DC-voltage against ripples. The losses occur mainly when switching the semiconductor on and off. Moreover losses are caused by internal resistances of the inductors and capacitors [27].
For power conversions up to 5 kW a single-phase converter can be used. The PV connected alternating current domestic mains is typically a 50–60 Hz source, which represents the power input. A low frequent transformer can be patched in, if a pre-conditioning of the voltage is required to reduce the grid voltage to an adequate value.

In general there are two categories of AC-DC converters available, which perform different functions.

- **Uncontrolled natural commutation converters** belong to the first category. Rectifiers like that only use diodes, which cannot be controlled externally. It is not possible to reverse the power flow, which is in fact not necessary for the unidirectional operation of the electrolyser. A negative aspect of the diode-type rectifier is the comparably high riffle of the voltage output that has to be filtered.

- The second category is the **controlled natural commutation converter**, which consists of a thyristor. A thyristor can be switched on and this allows a controlled dc voltage output and a reverse of power flow as well.

Ursua describes the latter rectifier technology as best fitted for a small-scale AC-DC rectifier [27]. Thyristors can withstand the high current output up to 200 A, and require less passive components which would result in higher costs, weight and efficiency losses, whereas high harmonic distortion lowers the efficiency.

The topology of a commercially used set-up is depicted in figure 15 [27].

![Figure 15: Half controlled three-phase rectifier set-up of a transformer and a thyristor-diode configuration [27]](image-url)
Ursua mentions leading electrolyser manufacturers, such as Hydrogenics, NEL Hydrogen, Industrie Haute Technologie and Assa-Gen., using the three-phase half controlled bridge configuration for the electric conditioning, especially for small-scale electrolysers [27].

In order to display a realistic PEM electrolyser system performance a simple converter model could be synthesized according to suppliers measuring data of a certain 6 kW AC-DC converter DELTA ELECTRONICS PCL [28] and performance analysis of AC-DC rectifiers in general [29].

The efficiency curve $\eta_{DC}$ in % can be approached by the following equation:

$$\eta_{DC} = 100 \cdot \frac{0.95}{1 + \frac{1}{I_{out}}} \quad (17)$$

The output current $I_{out}$ ranges from 0 A, which is equal to 0 % load to the maximum operating current of 140 A at 100 % electrolyser load. The efficiency curve is visualized in figure 16:

![Figure 16: AC-DC converter efficiency curve](image)

The general characteristics of the curve can be displayed but it has to be noted, that this graph is based on assumptions and has to be considered as a rough estimation in order to approximate the converter performance. The partial load efficiency also depends on the input and output voltage levels. Over a broad region from 15 % to 100 % of PEMEL load, the efficiency of the rectifier is above 90 % and 93 % in average. For smaller loads the efficiency is signifi-
significantly declining due to switching losses and internal resistances of filtering components. The losses in electronic resistors generate heat, which has to be removed by an internal cooling.

Especially the partial load behaviour has to be taken into account modelling electrolyser system efficiency. The converter efficiency is comparably low for low residual loads, which occurs the most.

The above mentioned efficiency estimation $\eta_{DC}$ of an AC-DC converter is also included in the Matlab model for the system efficiency $\eta_{sys}$, in section 2.2.3.

### 2.3 Hydrogen Intermediate Storage

An intermittent hydrogen feed affects the methanation process adversely in regards to the reaction stability and heat management. Neither the required gas flow rates, nor the SNG yield in the product gas can be guaranteed. Hence a steady-state methanation process is aimed [13].

To ensure a constant feed gas flow in a volatile environment a hydrogen buffer can be applied. The intermediate hydrogen storage is connected in series between the electrolyser and the methanation reactor. It is charged with volatile generated hydrogen during the daytime, and is discharged if the maximum storage capacity is reached.

Two hydrogen storage principles are being reported as state of the art [30]:

- Cryogenic hydrogen storage
- Pressurized hydrogen storage

The thermodynamics of hydrogen need to be taken into consideration to store a sufficient amount of gas in a small tank.

For a cryogenic temperature below -253 ºC the hydrogen can be stored in liquid phase. Due to high technological challenges and cost issues, the cryogenic storage path can be neglected for a small-scale PtG plant.

The easiest solution to store the daily generated hydrogen is the pressurized storage principle. The intermediate storage is supposed to provide a daily storage of the generated hydrogen in a few 50 l gas bottles. The compressed hydrogen storage option takes advantage of the already pressurized PEMEL gas output. Avoiding an additional gas compressor, no intermediate storage losses come up, as the PEMEL delivers a maximum operating pressure of 30 bar. If the storage capacity is reached, the hydrogen can steadily be released to the subsequent methana-
tion process. The discharge of hydrogen finishes if the pressure level of the methanation reactor is reached.

Assuming hydrogen as an ideal gas, a constant gas temperature for charge and discharge and an atmospheric pressure $p_{amb}$, the dischargeable hydrogen volume $V_{H2}$ in Nm$^3$ can be calculated:

$$V_{H2} = n_b \cdot V_b \cdot \frac{(p_i - p_u)}{p_{amb}}$$

(18)

where $V_b$ is the gas bottle volume, $n_b$ is the number of gas bottles, $p_i$ is the initial pressure before gas discharge and $p_u$ is the ultimate pressure level, which is set by the operational pressure of the methanation reactor.

According to the requirements of a domestic conversion plant, the storage size has to be taken into account. The intermediate storage is dimensioned in section 3.3 in compliance with the maximum hydrogen volume produced by the PEMEL at a certain day in 2013 and the conversion flow rates of the methanation unit.
2.4 Methanation

The reduction of carbon dioxide (CO$_2$) by H$_2$ to methane (CH$_4$) can be achieved in a methanation process over a catalyst. In 1902 Sabatier reported about the conversion of hydrogen and carbon dioxide to methane which is now well known as synthetic natural gas (SNG). Thus the idea of the gas conversion is about 100 years old and methanation processes were mainly applied to produce SNG from solid biomass or coal. In the last decade, increasing research efforts has been made to promote the gaseous methanation process for RE storage options. In this work it will be rather looked at the catalytic methanation than on biologic conversion processes. As mentioned in the introduction, the SNG conversion step is optional for a PtG system, as gaseous hydrogen could be used as a fuel as well. Though drawbacks like further efficiency losses and higher investment costs for a subsequent methanation, CH$_4$ as a product gas offers a broader field of applications, especially when feeding SNG into the existing natural gas grid or running established combustion engines with compressed natural gas (CNG).

This section presents the basic reactions and thermodynamics appearing within a methanation device. Suitable steady-state reaction conditions will be found out for a small-scale methanation reactor. A pre-design of a system set up will be carried out to provide both, a product gas with a sufficient quality, and excess heat integration. Finally a static model is developed to calculate the gas product flow rates and to manage the excess heat production.

2.4.1 Basics of Catalytic Methanation

The methanation describes a heterogeneous, catalytic reaction of CO$_2$ reduced by H$_2$ over a catalyst to CH$_4$ and H$_2$O. The global reaction which was found in 1902 by Sabatier is reversible and exothermic [13]:

\[
CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O_{(g)} \quad \Delta H^0_R = -160.0 \frac{kJ}{mol}
\]  

(R6)

under standard conditions (T = 298 K; p = 1 atm). The oxidation number of carbon changes from +IV to −IV, so eight electrons will be transferred during the methanation. Oftentimes the methanation reaction is described as partial reactions, which are formulated as follows:

\[
CO + 3H_2 \rightleftharpoons CH_4 + H_2O_{(g)} \quad \Delta H^0_R = -206.2 \frac{kJ}{mol}
\]  

(R7)

\[
CO_2 + H_2 \rightleftharpoons CO + H_2O_{(g)} \quad \Delta H^0_R = 41.2 \frac{kJ}{mol}
\]  

(R8)
The CO-methanation (R7) and the water-gas shift reaction (R8) can be formulated as intermediate states of the global Sabatier reaction (R6). Considering a methanation reactor, the partial reactions (R7, R8) and their chemical compounds CO₂, CO, H₂O and H₂ have to be taken into account.

To avoid generating undesired compounds in the product gas, favourable operating conditions within the reactor have to be chosen. The product gas composition can mainly be influenced by an appropriate choice of:

- Temperature level
- Pressure level
- Catalysts
- Gas residence time/ feed gas flow velocity

Schollenberger performs a calculation in Aspen PLUS® of the thermodynamic equilibrium of all reactions taking part, depending on the pressure and temperature level [31]. The results of a stoichiometric educt feed of 20 % vol CO₂ and 80 % vol H₂ are visualized in figure 17.

![Figure 17: Methanation product gas composition dependent of the thermodynamic equilibrium [31]](image-url)
Temperature level
Reflecting the meaning of the principle of Le Chatelier, the thermodynamic equilibrium of an exothermic reaction moves to the product side for lower temperatures. Therefore it is important to guarantee an effective removal of heat. But weak kinetics of methanation reaction at low temperatures have to be taken in consideration [32]. Moreover the operating temperature level is restricted by the formation of toxic substances of CO and nickel, which is widely used as a catalyst. To assure safety and health, the temperature should be above 200°C [31].

Brooks defines a suitable temperature level around 350°C and Schollenberger selects a range between 200 and 475°C [31,32]. Thermodynamically the water-gas shift reaction tends to dominate at higher temperatures and causes undesired impurities. Xingxing outlines that thermal stress is a significant drawback for nickel based catalyst, so a constant operating temperature should be aspirated [33].

Due to the strong exothermic reaction, a proper heat management has to be provided to avoid built-up of hot spots. A local hot spot appears, if there is an imbalance of exchanged and generated heat. Xingxing proposes a product gas recirculation which is implemented next to the regular reactor wall cooling [33]. Chemically, the product gases behave inert. This procedure delivers a considerable advantage, so next to the prevention of hot spots, the fresh feed gas is preheated and therefore the gas quality can be boosted. The occurrence and management of hot spots is a dynamic process, which requires an appropriate control strategy for an efficient running of the methanation, which is investigated by Xingxing, but is negligible for the system pre design in this work.

Pressure level
As can be seen from the global Sabatier reaction (R6), the number of molecules is reduced from five at the reactant side to three at the product side. Hence a higher pressure boosts the conversion rate of CO₂ and influences the methane yield of product gas stream positively, as also depicted in figure 17. Due to the desired system set up without an additional compression, the operating pressure level has to be adjusted to the boundary conditions of pressurized hydrogen bottle storage.

Catalysts
The hydrogenation of CO₂ implies an eight-electron process with kinetic limitations. To overcome a low reactivity at moderate temperatures around 300°C, a catalyst is required to achieve an acceptable methane yield, besides finding a suitable carrier material for the catalyst.
Some vital requirements of catalysts are listed below [34]:

- Activity at the desired operating condition.
- Selectivity towards methane.
- Stability for long-term use.
- Low material costs.
- Health and safety issues.

Wang reports that the research mainly takes interest in catalysts of Group VIII metals, which are supported on oxides [35]. Ni-based and noble metal-based (Rh, Ru, Pd, Pt, Ir) catalysts promise both, high reaction kinetics and a low degradation, affecting the stability. Nickel is the most studied and applied catalyst, due to promising performances and low costs. Various catalyst support materials can be used, which are all oxides like Al₂O₃, SiO₂, TiO₂, ZrO₂ and CeO₂. The supporting material provides a high specific surface (above 100 m²/g) to gain in high catalytic active areas. Figure 18 shows the reaction scheme of the catalytic CO₂ methanation.

![Reaction scheme of catalytic CO₂ methanation](image)

The gaseous carbon dioxide dissociates to the surface of the catalyst support and is intermediary adsorbed. Gaseous hydrogen dissociates to the metal and two elements form water together with the first oxygen element of CO₂. The remaining CO is still absorbed and bounded either at the metal support interface or at the support matrix. CO then is transferred to the metal catalyst for the final methanation. Six further hydrogen elements are involved for a complete hydrogenation of metal dissociated CO to the gaseous products CH₄ and H₂O.
2.4.2 Carbon Dioxide Sources

The PtSNG conversion requires a carbon source to perform the methanation. Carbon is bounded in CO$_2$, which is theoretically unlimited available on earth. However the availability of different CO$_2$ sources differs in the necessary process technology to capture the gas. Therefore, the processes of making CO$_2$ available for a hydrogenation to methane have to be assessed in particular, regarding efficiencies, economic and environmental aspects. The latter is of particular importance as only a renewable CO$_2$ source enables a 100 % renewable SNG product gas.

Basically there is a distinction between biogenic and industrial CO$_2$ sources [36]. Zuberbuehler is reporting the relevant CO$_2$ potentials in Germany for the production of SNG (table 2).

<table>
<thead>
<tr>
<th>Carbon Source</th>
<th>CO$_2$ Potential</th>
<th>SNG Production Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biogenic Sources</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biogas Plants</td>
<td>5.1 x $10^6$ [t/a]</td>
<td>27 [TWh$_{SNG}$/a]</td>
</tr>
<tr>
<td>Energetic Utilisation of Other Biomass</td>
<td>73</td>
<td>385</td>
</tr>
<tr>
<td>CO$_2$ from Air</td>
<td>unlimited</td>
<td>unlimited</td>
</tr>
<tr>
<td><strong>Industrial Sources</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement/ Limestone Production</td>
<td>17</td>
<td>92</td>
</tr>
<tr>
<td>Non-renewable Trash</td>
<td>25</td>
<td>130</td>
</tr>
<tr>
<td>Fossile Power Plants</td>
<td>309</td>
<td>1 618</td>
</tr>
</tbody>
</table>

The reported quantities of CO$_2$ exceed the required amounts by far [2]. Biogas plants by itself can deliver climate neutral CO$_2$ for a couple of millions of domestic PtSNG plants in Germany. Combining all CO$_2$ sources from biomass, no shortages in the gas delivery for competing future SNG industries can be assumed. In order to design a 100 % renewable energy source, the focus of CO$_2$ supply is on the biogenic sources biomass and CO$_2$ from air.

In all cases CO$_2$ has to be extracted from a gas mixture, either an exhaust gas or the ambient air. Principally there are four process technologies for an extraction of carbon-dioxide [6]:

- Absorption - in different solutions
- Adsorption - on solid sorbents like mol sieves
- Condensation - in cryogenic distillation processes
- Membrane separation
The three latter processes are energy intense due to a strong cooling for a condensation of CO$_2$ or a high pressure for the adsorption and membrane separation. Though, the adsorption of CO$_2$ is common practice for the purification of biogas to biomethane.

A standard technology for gas cleaning is the so called pressure-swing adsorption (PSA). The PSA plant utilized the different adsorption behaviour of CH$_4$ and CO$_2$. The dry and pressurized gas flow enters the adsorption unit which contains the adsorbent, a carbon molecular sieve. A defined pressure level allows a faster adsorption of CO$_2$ than CH$_4$ to the sieve surface. If the sieve is saturated, the biogas stream is rerouted to a second adsorption unit where the purification can be continued. The saturated sieve is then desorbed by releasing the pressure and its adsorbate CO$_2$. So far the CO$_2$ has been released to the environment since there is no utility of it. Implementing a PtSNG industry, CO$_2$ can be utilized as a 100 % renewable reactant for methanation processes. Because the carbon molecular sieve is highly sensitive to fine dust this technology is unsuitable for CO$_2$ extraction of flue gas from combustions [6].

The company Climeworks, which is based in Zurich developed in collaboration with ETH Zurich and the Swiss Federal Laboratories for Materials Science and Technology (Empa) a CO$_2$-from-air capture plant using adsorption [37]. The size of the laboratory plant provides 4 kg CO$_2$/day. An upscale to a commercial demonstration plant for 20 kg CO$_2$/h is planned for 2015.

The adsorption process is based on a similar cyclic process like the PSA technology, using thermal energy instead of pressure-swings to run a cycle. The working principle of the plant is depicted in figure 19 [37]. Ambient air enters the adsorption unit, which contains a filter sieve with a CO$_2$ selective absorbent. The adsorption of CO$_2$ takes place at ambient temperature and pressure level. Once the absorbent is saturated, the air flow is interrupted and the desorption can be performed. In order to obtain pure CO$_2$ and to regenerate the unit, the capturing unit is heated with low temperature heat (T ~ 95°C).

A benefit of combining this technology with PtSNG systems is the low temperature level of heat, which could be provided by the excess heat of the electrolyser and methanation reactor. Nevertheless a subsequent compression of CO$_2$ is required to be fed in the pressurized methanation reactor.

Schmid delineates the CO$_2$ from air capture of a 25 kW$_{el}$ PtSNG plant at ZSW in Stuttgart [6]. The extraction principle is carried out by absorption of the gas in a scrubbing solution.
CO₂ can be recovered by adding sulphuric acid, which together with the scrubber solution can be regenerated in a second stage. The energy demand for capturing and regenerating the chemicals is about 2.3 kWh/kg CO₂ and 2 300 m³ air have to be processed.

Due to a significant low concentration of carbon dioxide in the air, it is more efficient to capture concentrated renewable CO₂ from biomass. Nevertheless, certain applications like energy island systems require a secure provision of CO₂ from air, if the other alternatives are technically or economically not feasible.

Hereinafter CO₂ as a reactant for the proposed small-scale methanation reactor is provided in 13.4 l gas bottles at a pressure level of 250 bar.
2.4.3 Small-Scale Reactor Concepts

Methanation reactors can be subdivided in two general principles, the two-phase and three-phase system [38]. In a two-phase system the educts are in a gaseous state and the catalyst is solid, whereas in a three-phase system the gaseous educts and solid catalysts are surrounded by a liquid heat transfer fluid.

In the scope of this thesis, a two-phase reactor is considered to be integrated in the domestic PtSNG system. Basically there are three possible approaches for a two-phase methanation reactor:

- Fixed-bed reactor
- Fluidized-bed reactor
- Metal comb reactor

The fixed-bed reactor is the most widely used as methanation reactor. Solid particles contain the Ni-catalysts, which form the active fixed-bed catalyst. The powdery catalyst can simply be filled in a reactor tube which then is almost completed to be applied with the reactants. Once the bulk is packed, the catalyst particles rest on-the-spot during methanation. Hence, there is no threat of catalyst degradation via mechanical abrasion.

Negative aspects of fixed-bed reactors are relatively high pressure losses, possible mass transport limitations and the risk of hot-spots due to ineffective heat removal [38].

The fluidized-bed reactor enables the hydrogenation of CO$_2$ in a fluidized bed. A certain gas stream swirls up the catalyst particles within a defined reaction zone. The temperature level inside the fluidized bed can be assumed to be constant and the high turbulences improve the mass transport properties. Negative aspects of the fluidized-bed principle are the high mechanical forces on the catalyst particles and the limited ability to convert a variable gas stream. Inflexibility, a high maintenance demand and the undesirable noises occurring with a fluidized-bed of particles make this methanation principle uninteresting for domestic applications.

An advanced system for a two-phase methanation reactor is represented through the metal comb reactor, which are under investigation for different designs. The metal combs are loaded with a catalyst-support washcoat dispersion, which has to be calcinated for 3 h at 450°C afterwards [32]. Compared to the fixed-bed reactor, the gas flow through the comb channels causes no significant pressure loss and due to the high thermal conductivity of the metal comb structure the excess heat can be removed effectively. Furthermore the reactor inside can be
considered as isothermal. So the danger of hot-spots is diminished or can be avoided by a
proper external heat management. Moreover, the metal combs provide a slightly better flexi-
bility property for varying gas flows and pressure levels respectively. However, the reduced
proportion of volume regarding the metal comb structure and the inside volume of the reactor,
causes a fast cooling if the methanation reaction is interrupted.

In conclusion the metal comb reactor has to ensure both, an effective cooling system for the
operational mode and a sufficient heat provision for transients when starting the methanation
[38]. The characteristics and performances of different metal comb reactor designs are being
discussed in the following section. Combining the different reactor concept benefits should
result in a plant set-up, which is the basis for a subsequent reactor modelling in terms of heat
transfer flows.

2.4.4 Metal Comb Reactor Designs

The metal comb methanation reactor seems to meet the purposes of a small-scale methanation
device best, due to a radially isothermal inlet and a feasible heat management. The methane
yield in the product gas will also be discussed in this section.

Typically in a metal comb reactor, the reactor inlet is coated with the catalyst and the support
material. Figure 20 shows three reactor designs:

   a) Metal honeycomb reactor inlet design from Karlsruhe Institute of Technology (KIT) in
      Germany [31].
   b) A related concept like the micro-channel reactor [32].
   c) The plate-type reactor (c) from ETOGAS, which differs in the channel shape and cool-
ing mechanism [39].

The latter is the closest to commercialize a large-scale methanation reactor for PtSNG purpos-
eses.

The metal comb reactor is operated in a temperature range between 220-300°C at 8 bar but
designed for pressures up to 40 bar. The reactor consists of a double-walled pipe. In the inner
pipe the metal honeycombs are installed, whereas in the outer double containment pipe the
heat transfer medium is used for the heat management in a counter current process. The length
of the pipe is 62 mm and the outer inner pipe diameter is 36 mm. Six 50 mm long honeycomb
segments are arranged one behind the other in the inner pipe.
When starting the methanation process, the heat transfer fluid assures the heating of the reactor on the one hand side, and on the other hand side while operating at steady-state, the excess heat can be removed. The cooling system aims at a constant temperature within the reactor so that the gas purity doesn’t vary along the SNG outlet.

The **micro-channel reactor** described by Brooks is designed for a comparable low educt gas flow of 90 cm$^3$/min at atmospheric pressure. Thirty channels with a length of 70 mm each form the reactor. The reactor delivers 16 g SNG per hour and excess heat of 46 W. The reactor ensures an effective heat conditioning via active side-wall cooling, which is also an oil based counter flow heat exchanger. Because of metal walls the heat is evenly distributed and the wall temperature can be effectively controlled along the length of the reactor.

![Two-phase metal reactor designs](image)

**Figure 20: Two-phase metal reactor designs [31,32,39]**

The 25 kW **plate-type reactor** from ETOGAS is, among other locations, installed as a biogas treatment test plant in Bad Hersfeld/ Germany. Online publications show operating temperatures between 250 and 550°C and a system pressure of 7 bar [39,40]. The educt gas flow of H$_2$ and CO$_2$ is slightly above 5 Nm$^3$/h for a stoichiometric proportion of 4:1 (H$_2$/CO$_2$).

The heat management in the plate type reactor is also realized by counter current heat flow. A catalytic active layer alternates with a heat exchange layer like in a sandwich construction. The heat transfer fluid can either be liquid like pressurized water and oil, or gaseous.
2.4.5 SNG Yield Estimation

In this section the conversion performance will be analysed. Therefore the SNG conversion rates of the above mentioned reactor designs are gathered in a table. A few assumptions have to be defined before assessing the SNG yield of the methanation processes. The assumptions are listed below:

- H₂ and CO₂ can be considered as educt gases without impurities that could affect the methanation reaction adversely.
- The pressure level and the temperature distribution inside the reactor is constant at steady state.
- The conversion reaction starts at steady-state conditions and at constant gas flow velocities.

The conversion performances of the three reactor concepts are listed in table 3:

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Catalyst</th>
<th>Pressure level</th>
<th>Medium temperature level in °C</th>
<th>H₂:CO₂ molar</th>
<th>CO₂ conversion rate in %</th>
<th>Gas flow/ residence time</th>
<th>CO₂ conversion rate in %</th>
<th>SNG yield in % vol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal comb reactor</td>
<td>Ni-Al₂O₃</td>
<td>8 bar abs</td>
<td>300</td>
<td>3.9</td>
<td>86.0</td>
<td>-</td>
<td>86.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>280</td>
<td>4.6</td>
<td>88.0</td>
<td>-</td>
<td>89.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td>4.6</td>
<td>90.0</td>
<td>-</td>
<td>94.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>280</td>
<td>6.2</td>
<td>86.0</td>
<td>-</td>
<td>89.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>295</td>
<td>4.0</td>
<td>16.30 cm/s /439.5 ms</td>
<td>89.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Micro-channel reactor</td>
<td>Ru-TiO₂</td>
<td>atmospheric</td>
<td>303</td>
<td>4.0</td>
<td>32.29 cm/s /221.8 ms</td>
<td>89.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70 mm</td>
<td></td>
<td></td>
<td>319</td>
<td>6.0</td>
<td>68.35 cm/s /104.8 ms</td>
<td>99.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Plate-type reactor</td>
<td>n.s.</td>
<td>7 bar abs</td>
<td>485</td>
<td>4.0</td>
<td>5 Nm³/h</td>
<td>-</td>
<td>92.0</td>
<td>-</td>
</tr>
<tr>
<td>Biogas (43 % CO₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The medium temperature within the reactors ranges between 280 – 485°C. The metal comb reactor is operated at 8 bar, between 280 and 300°C. For a stoichiometric proportion of H₂ to CO₂ the conversion rate is 86 %. A higher stoichiometric proportion causes an increase of the CO₂ conversion, but it has to be taken into account that the impurities of H₂ in the product gas will increase as a consequence.

The micro-channel reactor shows high performances up to 89.4 % for a stoichiometric educt
Power-to-SNG Concept

ratio, which is quite close to the thermodynamic optimum (see figure 17). It is remarkable, that the CO₂ conversion rate doesn’t change as the gas flow speed is doubled. Even for a quadruplication of the gas flow that is slightly overstoichiometric (H₂:CO₂ = 6.0), a conversion up to 99.8 % can be reached. Designing a methanation reactor, the residence time can be optimized by adjusting the dimensions of the reactor or the gas stream speed respectively.

Due to a small-scale PtG application the plate-type reactor from ETOGAS converts a comparatively high volume flow. The operating temperature differs significantly from the other reactors. Despite a higher temperature level, a volumetric methane yield of 92 % can be achieved.

The above presented performance data of the existing reactors allow an estimation of an implementable small-scale reactor, which form the basis for the static PtSNG plant model.

Considering the CO₂ conversion rates, it is reasonable to assume a value up to:

- η_{conversion} = 90 % CO₂ conversion ~ 90 % vol. SNG for stoichiometric proportions

Due to optimization even a higher conversion can be reached [32]. The inner wall and gas temperatures and the relative pressure level are constant at:

- T_{wall} = T_{gas} = 300 °C
- p_{reactor} = 8 bar

The impurities in the product gas are non-reacted educt gases H₂ and CO₂. According to a Ni-based 100 kW fixed-bed reactor [40], the dry product gas can be composed as follows:

![Figure 21: Estimated product gas composition according to [40]](image-url)
It is hereby notified that the above shown product gas composition is an estimation which includes assumptions according to the performance data of table 2, estimations from methanation experts of VTT [41] and the product gas composition of a 100 kW PtSNG plant at ZSW [40]. The accuracy of the percentages has to be evaluated at a test facility.

### 2.4.6 Reactor Model Development

The proposed static model, which is presented in this chapter, comprises the physical dimensioning of a metal comb reactor design.

The metal comb reactor of KIT institute serves a template for this model [31]. With regards to the model parameters, the excess heat production can be calculated.

First of all the boundary conditions of the methanation reactor have to be defined. Therefore the following aspects have to be taken into account:

- Steady-state operating conditions at constant chemical conversion rate.
- The ideal gas law is valid for the gas state variables $p_{\text{reactor}} = 8$ bar and $T_{\text{gas}} = 300^\circ\text{C}$.
- Constant gas-flow, which prohibits the appearance of hot-spots.
- Radial isothermal temperature distribution.
- Countercurrent heat management through a double wall pipe by thermal oil.
- Physical dimensions of the reactor correspond to a small-scale plant.

For achieving a high methane yield in the product gas an appropriate residence time of the reactants has to be chosen. The residence time is inversely proportional to the so called space velocity.

In literature two common definitions of volumetric gas flow rates are mentioned [42]. The first refers a gas flow to a volume of catalysts within the reactor and the second refers to the blank volume of inside of the reactor. The latter is considered for the proposed model in this work. The so called gas hourly space velocity $GHSV$ can be described as follows:

$$GHSV = \frac{\text{Volumetric flow of reactor gas} \left[ \frac{m^3}{h} \right]}{\text{Empty space volume of the reactor} \left[ m^3 \right]} = \frac{f_{\text{gas}}}{\Phi_V \cdot V_{\text{reactor}}}$$  \hspace{1cm} (19)

where $\Phi_V$ is the empty space share. This value describes the share of the reactor volume, which can be passed by the gaseous fluids.
Specht reports about a GHSV range between 2 000 and 5 000 l/h [40]. Walspurger operates a methanation plant within that range at 2 500 l/h [43]. For a SNG methanation plant at ZSW, the GHSV is 1 365 l/h.

For the following model development a **GHSV value of 2 000 l/h** is chosen. The reactor design of a metal comb reactor in a double-walled pipe is based on the reactor developed at KIT institute [31]. A cross section of the reactor is shown in figure 22.

![Draft of a double-walled pipe metal comb reactor acc. to [31]](image)

**Figure 22: Draft of a double-walled pipe metal comb reactor acc. to [31]**

The main components of the reactor are the metal comb reactor segments, which are coated with the catalysts and their support material, as described in section 2.4.1. The segments are serialized in the inner pipe of the reactor. To improve the radial heat conductivity a thermal
paste can be applied in the narrow gap between the segments outer wall and the inner pipe wall. The heat transfer medium is pumped through the slot of the double pipe. It can be seen that the gas flow and the heat transfer medium flow is arranged as countercurrent. Before the reactants enter the catalytic active area, the inrushing gas is mixed and evenly distributed in a diffuser.

The **empty space volume of the metal comb reactor** \( V_{r,\text{empty}} \) can be calculated as follows:

\[
V_{r,\text{empty}} = \Phi_V \cdot V_{\text{reactor}} = \Phi_V \cdot \frac{\pi d_{in}^2}{4} \cdot L_{\text{reactor}}
\]

(20)

with \( \Phi_V \) as the empty space share of the reactor segments which is assumed to be 0.9, \( d_{in} \) as the inner diameter of the inner pipe and \( L_{\text{reactor}} \) as the length of the reactor. Combining equations (19) and (20), the reactor gas flow \( f_{\text{gas}} \) can be calculated.

Assuming a recirculation of product gas, which in particular is described in the next section, the **reactor feed gas flow** \( f_{\text{gasfeed}} \) in m\(^3\)/h can be can be determined:

\[
f_{\text{gasfeed}} = (1 - RR) \cdot f_{\text{gas}}
\]

(21)

where RR is the recirculation rate, which in that case takes a value of 0.8. To compute the **standard volumetric feed gas flow rate** \( f_{\text{gasfeed0}} \) in Nm\(^3\)/h, the state variables have to be referred to ambient conditions at \( T_{\text{amb}} = 288.15 \) K and atmospheric pressure by a factor 8:

\[
f_{\text{gasfeed0}} = f_{\text{gasfeed}} \cdot 8 \cdot \frac{T_{\text{amb}}}{T_{\text{gas}}}
\]

(22)

The feed gas flow is composed of \( \text{H}_2 \) and \( \text{CO}_2 \) in stoichiometric proportions. Assuming the reactants as ideal gases, it means that 80 % of the feed gas flow is hydrogen and 20 % is carbon dioxide.

The dry product gas flow rate can be calculated, supposing that the entire reaction water is removed. For stoichiometric proportions and a product gas composition of 90 % methane and 10 % unreacted educts the **standard volumetric product gas flow** \( f_{\text{product0}} \) in Nm\(^3\)/h is:

\[
f_{\text{product0}} = \left( \eta_{\text{conversion}} \cdot \frac{1}{5} + (1 - \eta_{\text{conversion}}) \right) \cdot f_{\text{gasfeed0}}
\]

(23)

The factor 1/5 describes the volume reduction of \( \text{CH}_4 \) to the reactant gases.
2.4.7 Excess Heat Production

Feed gas entering the reactor inlet at the top is mixed and heated up to the temperature of approximately 300°C, where the gas kinetics allow a comparable fast methanation reaction [31]. As explained in the previous sections the hydrogenation of CO₂ is a strongly exothermal reaction (see R6). The heat production within the reactor, which is equal to the molar excess heat production $Q_{m,\text{excess}}$ in kJ/mol at steady-state conditions, can be calculated in order to dimension the heat removal properly.

\[
Q_{m,\text{excess}} = \eta_{\text{conversion}} \cdot \left[ \sum H_{\text{product}} - \sum H_{\text{educt}} \right]
\]  

\[
Q_{m,\text{excess}} = \eta_{\text{conversion}} \cdot \left[ (H(CH_4) + 2 \cdot H(H_2O)) - (4 \cdot H(H_2) + H(CO_2)) \right]
\]

The conversion efficiency $\eta_{\text{conversion}}$ is estimated as 90%. The reactants standard enthalpy has to be translated to the temperature level of the reactor inlet. The parameters and equations for the excess heat calculations can be found in annex 3.

Performing the computation of the heat production for a temperature of 300°C, the molar excess heat flow of the reaction amounts $Q_{m,\text{excess}} = -158.35$ kJ/mol. Assuming the reactants as ideal gases, one mol of gas occupies a volume of 22.4 l, so that the volumetric excess heat production in kWh/Nm³ can be determined:

\[
Q_{v,\text{excess}} = -7.07 \frac{MJ}{Nm^3} = 1.96 \frac{kWh}{Nm^3}
\]

The heat management can be realized by thermal oil, which flows through the outer pipe. Both, heating the reactor before starting the methanation process, and cooling the reactor during the operation, can be performed in combination with a heating coil and an internal cooling. The tubular heat exchanger can be introduced as a simplified model of the methanation reactor. Therefore the following assumptions have to be taken into account [44]:

- The heat exchanger is operated at steady-state conditions.
- Kinetic and potential energy, as well as heat losses to the environment are neglected.
- No phase changes during the heat transfer.
- Heat conduction in the direction of the flow is neglected.

To calculate the required thermal oil flow rate for a countercurrent heat exchanger, the heat transfer balance has to be defined:
\[ Q_{v,\text{excess}} = Q_{\text{oil}} = \rho_{\text{oil}} \cdot f_{\text{oil}} \cdot c_{\text{oil}} \cdot \Delta T_{\text{oil}} \]  
(25)

The material values, density and specific heat capacity of the thermal oil, can be taken from table data. To avoid high temperature gradients within the reactor, the oil temperature difference should be as small as possible, but great enough to remove the excess heat efficiently.

The **volumetric flow of thermal oil** \( f_{\text{oil}} \) is defined as follows:

\[ f_{\text{oil}} = u_{\text{oil}} \frac{\pi(d_{o,\text{in}}^2 - d_{o,\text{out}}^2)}{4} \]  
(26)

where \( u_{\text{oil}} \) is the velocity of the thermal oil and \( d_{o,\text{in}} \) is the inner diameter of the outer pipe and \( d_{o,\text{out}} \) is the outer diameter of the inner pipe.

Before starting a methanation process the steady-state condition has to be established, in order to avoid a low SNG product gas yield at the beginning. The reactor has to be tempered by the thermal oil and an additional electric heating coil. It is assumed that the internal energy of the previous methanation process is stored for the most part, so that the thermal oil provides an initial temperature of 250°C. As a consequence the thermal oil and the reactor temperature need to be raised by \( \Delta T_{\text{start}} = 50 \) K.

The **required amount of electrical power** \( P_{\text{el,oil}} \) for heating the thermal oil up to 300°C can be calculated as follows:

\[ P_{\text{el,oil}} = \dot{m}_{\text{oil}} \cdot c_{\text{oil}} \cdot \Delta T_{\text{start}} = \rho_{\text{oil}} \cdot u_{\text{oil}} \frac{\pi(d_{o,\text{in}}^2 - d_{o,\text{out}}^2)}{4} \cdot c_{\text{oil}} \cdot \Delta T_{\text{start}} \]  
(27)

with \( \dot{m}_{\text{oil}} \) as the oil mass flow, calculated by the product of \( f_{\text{oil}} \) and \( \rho_{\text{oil}} \) and \( c_{\text{oil}} \) as the specific heat capacity of the thermal oil. The data sheet of the thermal oil Mobiltherm605® from PONDUS Verfahrenstechnik GmbH [45] provides values for \( c_{\text{oil}} = 2800 \) J/kg·K and \( \rho_{\text{oil}} = 680 \) kg/m³ at 300°C. Applying equation 27 with an initial oil velocity of 0.001 m/s the **required electrical power** \( P_{\text{el,oil}} \) amounts:

\[ P_{\text{el,oil}} = 288.7 \text{ W} \]

For the determination of the required energy for tempering the reactor, the **heat capacity** \( C_{\text{reactor}} \) has to be figured out. The value for heat capacity is dominated by the metallic pipe walls (V2A steel) and the catalyst inlet support material (Al₂O₃). The heat capacity of gas is neglected in the following calculation.
\[ C_{\text{reactor}} = C_{\text{pipes}} + C_{\text{inlet}} = m_{\text{pipes}} \cdot c_{\text{steel}} + m_{\text{inlet}} \cdot c_{\text{Al}_2\text{O}_3} \]  
(28)

\[ m_{\text{pipes}} = \rho_{\text{steel}} \cdot L_{\text{reactor}} \cdot \pi \left( \frac{(d_{\text{out}})^2 - (d_{\text{in}})^2}{4} + \frac{(d_{\text{out},l})^2 - (d_{\text{in},l})^2}{4} \right) \]  
(29)

\[ m_{\text{inlet}} = \rho_{\text{Al}_2\text{O}_3} \cdot V_{\text{reactor}} \cdot (1 - \Phi_V) \]  
(30)

with \( \rho_{\text{steel}} = 8000 \text{ kg/m}^3 \), \( \rho_{\text{Al}_2\text{O}_3} = 3700 \text{ kg/m}^3 \), \( c_{\text{steel}} = 477 \text{ J/kg·K} \), \( c_{\text{Al}_2\text{O}_3} = 900 \text{ J/kg·K} \), \( \Phi_V = 0.9 \) [46,47]. All further dimensions are depicted in figure 22. The heat capacity \( C_{\text{reactor}} \) of the reactor can now be calculated:

\[ C_{\text{reactor}} = 1.764 \text{ kg}_{\text{steel}} \cdot 477 \text{ J/kgK} + 0.288 \text{ kg}_{\text{Al}_2\text{O}_3} \cdot 900 \text{ J/kgK} \]  
(31)

\[ C_{\text{reactor}} = 1100 \text{ J/K} \]

The required energy for tempering \( E_{\text{temp}} \) the reactor from 250 to 300°C can now be determined:

\[ E_{\text{temp}} = C_{\text{reactor}} \cdot \Delta T_{\text{start}} = 1.1 \frac{kJ}{K} \cdot 50 \text{ K} = 55.0 \text{ kJ} = 15.3 \text{ Wh} \]  
(32)

The time for tempering the reactor with a 288.7 W electrical heater is less than 200 seconds. In fact the time is dominated by the slow oil flow rate of oil, which needs at least 600 seconds to fill the reactor with tempered thermal oil. In conclusion tempering the reactor from 250 to 300°C requires an energy amount of 55 kJ and takes at least 10 minutes to achieve the steady-state temperature.

### 2.4.8 Reactor Plant Configuration

The methanation set-up is aligned to the PtSNG Audi plant [3]. The simplified configuration, which is shown in figure 23, contains a product gas recirculation in order to achieve the required GHSV.

Figure 23 illustrates the plant configuration of the methanation process. The feed gases \( \text{H}_2 \) and \( \text{CO}_2 \) are being fed with a constant flow rate at a stoichiometric proportion to the so called injector (1). The injector is a mixing device on the one hand side, but also a type of a pump on the other hand side. Within the injector the feed gas streams through a nozzle, which is then accelerated and causes a low local pressure. Hence a defined product gas stream is sucked to
the injector gas inlet and is mixed with the feed gas stream in the diffuser throat of the injector [48].

**Figure 23: Methanation plant configuration according to [40]**

In this way an efficient recirculation (3) of product gas can be performed, avoiding an electrical driven pump. Xingxing describes the recirculation loop of product gas as a fundamental process to assure a nearly constant reactor temperature prevent local forming of hot spots that damage the catalyst. Simultaneously fresh gas feed is preheated in the injector to ensure a constant reactor temperature and to avoid the formation of nickel carbonyls at temperatures below 200°C [33]. Due to a considerable smaller feed gas stream, the management of excess heat can be facilitated as well. Moreover a recirculation of product gases result in a longer residence time and therefore a higher CO$_2$ conversion can be expected but has to be validated by experimental tests.

As described in the previous section, the reactor is being cooled by thermal oil (2). The excess reactor heat is transferred in the double-walled pipe and can be stored, or removed by a heat sink like domestic heating, or an air cooler. The recirculation rate is set to 80% of the volumetric flow, which is explained in section 3. The Audi SNG plant is equipped with an additional water injection at the reactor inlet [3,41]. It is known that a lack of steam within the reactor leads to deposition of elemental carbon at the catalysts. It is reasonable to assume no carbon deposition effects to the above depicted plant design, because the recirculating gas is wet, compared to the Audi plant, as the methanation is carried out in a single-stage process. Nevertheless further investigations should be performed on that matter.

The wet product gas stream which is not recirculating enters a dry cooler (4). The temperature of the gas is being cooled down to ambient temperature and the condensed water is removed. The dry SNG can be compressed (5) and transported in a seasonal storage tank (6).
2.5 SNG Use Options

The subject of SNG gas properties, with respect to a SNG use as an automotive fuel or a possible gas feed into the natural gas grid will be discussed in this section. All requirements for those two use options are extracted from German gas standards:

- **DVGW Arbeitsblatt G 260** - Gas quality
- **DVGW Arbeitsblatt G 262 A** - Use of renewable energy gases at the public gas supply system
- **DIN 51624** - Automotive fuels - Compressed Natural Gas - Requirements and test methods

The technical regulation G 260 defines the gas quality and requirements of fuel gases for the public gas supply in general [49]. Terms such as basic gas, gas for conditioning, additional and replacement gases are defined, which need to be understood dealing with an SNG gas mixture of methane, carbon dioxide and hydrogen.

A basic gas is commonly supplied natural gas in the grid. Gases for conditioning can be added to the natural gas for adjusting its combustion properties. Air, nitrogen, or liquid gases belong to this category for example. Additional gases significantly differ in properties from the basic gas. The impact of change in properties of the basic gas defines the limit of the additional gas content. Hydrogen rich gases or liquid gas-air mixtures represent possible additional gases. Replacement gases can fully replace the basic gas due to its equal combustion properties. Biogas but also thermal catalytic SNG gases belong to this category, if their compositions fulfil certain requirements.

Depending on the gas composition, the technical regulation G 260 categorizes a fuel gas in three gas types. The first type defines the composition of the hydrogen rich (< 12 % vol.) gas like town gas. Due to the fact that no town gas is distributed in the gas network, since the gas system has been changed to natural gas, the first gas family became less important. The third type defines the requirements for wet or liquid gases like propane or butane and will not be further described here. The gas quality and requirements for a categorization of a gas for feeding it into the natural gas grid has to be taken in consideration. Within the second gas family the natural gas is categorized by the so called Wobbe index. The Wobbe index is the ratio of the calorific value of a gas per unit volume and the square root of its relative density for standard conditions. The determination of the Wobbe allows the assessment of the exchangeability of gases due to their heat impact in gas combustion applications. Certain limits are set for group natural gas L and group natural gas H. The Wobbe index limits and some other rel-
relevant characteristic values listed in table 4. The SNG higher heating value related Wobbe index $W_{H,n}$ for standard conditions can be calculated as follows:

$$W_{H,n} = \frac{HHV_{SNG}}{\sqrt{d}}$$  \hspace{1cm} (33)

$$d = \frac{\rho_{SNG}}{\rho_{air}}$$  \hspace{1cm} (34)

with the HHV$_{SNG}$ as the higher heating value of the SNG gas components, the relative density $d$, which is calculated by the density of the SNG gas divided by the density of air at standard conditions.

The technical regulation G 262 A applies for the feed in of renewable gases into the natural gas grid [50]. The requirements are primarily related to biogas from fermentation. It is pointed out clearly, that the standard requirements for renewable gases from other sources have not been investigated adequately due to their minor importance. The specified limits of hydrogen content in the gas are based on an insufficient state of knowledge for example. In any cases it has to be ensured that the feed in gas is dried to a maximum water content of 200 mg/m$^3$. Thus, corrosion, uncontrollable flow processes and cross-section constrictions can be avoided.

The required methane yield depends on the type of the gas grid. For a natural gas grid H, a minimum methane yield of 95 % molar is required, whereas a gas grid L allows at least 90 % methane. Nevertheless a differing minimum methane yield can be agreed with the gas grid operator, if more than 1 % molar other fuel gases exist in the feed in gas. Hence, the carbon dioxide yield is accepted when it is less than 5 or 10 % mol. respectively.

An emerging issue in the PtG industry is the maximum allowed hydrogen content for a feed in gas, especially when dealing with PtH$_2$ processes and also PtSNG systems. According to investigations, the technical regulation G 262 A states that a hydrogen content in a single-digit percentage area is uncritical, if the calorific characteristics of G 260 are fulfilled. Nevertheless, different hydrogen limits are defined depending on the field of application:

- Some manufacturers of gas turbines define the hydrogen limit to 5 % vol. due to sensitive premix burners, a few reduce the limit to 1 % vol.
- For underground storage purposes, the hydrogen content must not exceed 5 % vol. due to the risk of sulphate-reducing bacteria growth and the initiated H$_2$S-production.
- DIN 51624 sets the limit to 2 % vol. as it is defined by the natural gas tanks of gas driven vehicles.
However, the objective of current investigations aims at enabling higher hydrogen content in the natural gas grid.

Table 4: Relevant requirements for SNG as grid gas and SNG use as automotive fuel

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameter/ Equation</th>
<th>Unit</th>
<th>Min.</th>
<th>Max.</th>
<th>Nom.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion characteristics for SNG as feed in gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[49]</td>
</tr>
<tr>
<td>Wobbe Index</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural gas group L</td>
<td>( W_{L,n} )</td>
<td>kWh/Nm(^3)</td>
<td>10.5</td>
<td>13.0</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>Natural gas group H</td>
<td>( W_{H,n} )</td>
<td>kWh/Nm(^3)</td>
<td>12.8</td>
<td>15.7</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>Higher heating value</td>
<td>HHV(_\text{SNG})</td>
<td>kWh/Nm(^3)</td>
<td>8.4</td>
<td>13.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Relative density</td>
<td>( d )</td>
<td></td>
<td>0.55</td>
<td>0.75</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Composition of dry SNG as feed in gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[50]</td>
</tr>
<tr>
<td>Methane content</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural gas group L</td>
<td>% vol</td>
<td></td>
<td>90.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Natural gas group H</td>
<td>% vol</td>
<td></td>
<td>95.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide content</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural gas group L</td>
<td>% vol</td>
<td></td>
<td></td>
<td>10.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Natural gas group H</td>
<td>% vol</td>
<td></td>
<td></td>
<td>5.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Hydrogen content</td>
<td>% vol</td>
<td></td>
<td></td>
<td>5.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Water content</td>
<td>mg/Nm(^3)</td>
<td></td>
<td>-</td>
<td>200.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Requirements for SNG as automotive fuel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>Lower heating value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural gas group L</td>
<td>kWh/Nm(^3)</td>
<td></td>
<td>10.8</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Natural gas group H</td>
<td>kWh/Nm(^3)</td>
<td></td>
<td>12.8</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>kg/Nm(^3)</td>
<td></td>
<td>0.72</td>
<td>0.91</td>
<td>-</td>
<td></td>
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<tr>
<td>Methane content</td>
<td>% mol</td>
<td></td>
<td>80.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Methane number</td>
<td>-</td>
<td></td>
<td>70.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sum of carbon dioxide and nitrogen contents</td>
<td>% mol</td>
<td></td>
<td>-</td>
<td>15.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Hydrogen content</td>
<td>% mol</td>
<td></td>
<td>-</td>
<td>2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Oxygen content</td>
<td>% mol</td>
<td></td>
<td>-</td>
<td>3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Water content</td>
<td>mg/Nm(^3)</td>
<td></td>
<td>-</td>
<td>40</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The German standard DIN 51624 defines the requirements and limits for the use of natural gas with an admixture of biogas as a fuel for combustion engines [51].

The standard also categorizes natural gas to natural gas H and L regarding to their heating value, the Wobbe index has no meaning. The absolute density of the SNG gas must be in a range between 0.72 – 0.91 kg/m\(^3\). A minimum methane yield of 80 % molar, as well as maximum molar shares of 2 % hydrogen, 15 % inert gases like nitrogen and carbon dioxide and 3 % oxygen are mentioned. The water content must be below 40 mg/kg.
The essential limits for using SNG as an automotive fuel are mentioned in table 4. The methane number is of great importance for assessing the combustion properties of an automotive gas. The methane number defines the knock resistance of a combustible gas. The higher the knock resistance, the better the combustion properties for a compressing gas. It can be calculated, knowing the composition of SNG gas in volumetric percentage. A gas with 85 % vol. methane and 15 % vol. hydrogen has a methane number of 85 for example. If there is 5 % carbon dioxide, 5 % hydrogen and 90 % methane in the SNG gas, the methane number rises up to 95. According to Bohatsch, a methane number of 100 corresponds to a RON (Researched octane number) of 130, which is approximately 30 % higher than conventional gasoline (RON 95) [52]. The higher octane number is compensating the 30 % lower volumetric energy density of methane compared to conventional liquid fuels such as gasoline. Consequently gaseous and liquid fuels for combustion engines need to be compared with their average fuel consumption in kilogram fuel per 100 km.

In order to categorize the assumed SNG product gas the parameters of the assumed composition (figure 21) will be calculated applying inter alia equation 33 and 34:

\[
HHV_{SNG} = 0.9 \times HHV_{CH_4} + 0.049 \times HHV_{H_2} = 10.13 \frac{kWh}{Nm^3}
\]

\[
d = \frac{\rho_{SNG}}{\rho_{air}} = \frac{0.751 \ kg/m^3}{1.204 \ kg/m^3} = 0.62
\]

\[
W_{H,n} = \frac{HHV_{SNG}}{\sqrt{d}} = 12.83 \frac{kWh}{Nm^3}
\]

According to DVGW Arbeitsblatt G 260 the assumed SNG gas lies within the upper limit of natural gas group L.

\[
LHV_{SNG} = 0.9 \times LHV_{CH_4} + 0.049 \times LHV_{H_2} = 9.12 \frac{kWh}{Nm^3}
\]

According to DIN 51624 the assumed SNG gas lies below the required lower heating value of natural gas group L for using SNG as a fuel. In order to fulfil the requirements of the standard, the SNG needs to be conditioned with small portions of propane or butane.
3 Power-to-SNG System Evaluation

The model calculations are aligned to the system set up. In order to provide a complete guidance for the evaluations made in this section, figure 24 illustrates a comprehensive overview of this section.

Figure 24: Chapter overview for the PtSNG system evaluation
In section 3.1 the focus is on the power input of the proposed PtSNG system. The probability distribution of residual load is highlighted, as it serves the basis for the calculation of the next section. In section 3.2 the results of hydrogen production calculations for a 5 kWel PEM PV-connected electrolyser is shown. Daily hydrogen production rates, as well as the yearly hydrogen production volume will be computed for 2013 at the reference site. In the end the PEMEL lifetime is determined. Section 3.3 delineates the hydrogen intermediate storage in pressurized bottles. The dimensioning of the storage capacity is carried out and the operational mode of both, the hydrogen intermediate storage and carbon dioxide provision are defined. Section 3.4 presents the dimensioning of the methanation reactor. The cumulated produced SNG volume and the excess heat occurrence, which result from the methanation plant design of section 2.4, are described subsequently. In section 3.5 the potential of energy utilization will be calculated. Firstly the driving range of the produced SNG is determined. Secondly an assessment of excess heat integration in hot water and domestic heating system of a single-family three-person household is given.

3.1 Residual Load System Input

As the PV plant is connected to the 230 V AC bus, the input power to the system is the difference between the PV generated electricity and the electricity that is consumed by the household. The consumed power is synthesized by the German H0 power profile, which can be considered as an average electricity consumption of plenty of households. From a purely energetic point of view, the profile represents an accurate energy consumption of the average German household. However, temporary load peaks are not displayed. Thus a realistic residual load curve certainly differs from the synthetic curve. Nevertheless, to represent an average household and calculate the energy conversion in a static model, a synthesized residual load curve is an accurate approximation for a typical German three-person household.

Assuming the electrolyser’s electrical input as 5 kW, the yearly residual load cannot completely be converted by the PtSNG system. Particularly in summer time the residual load exceeds the threshold of 5 kW. In that case the surplus of power has to be fed into the grid. Figure 25 delineates the convertible residual load (positive, blue curve) and the power, which is fed into the grid (negative, yellow curve) for the reference plant in Lütjensee, Germany.
The negative part of the graph can be interpreted as an energy flow, which crosses the system boundaries of the domestic AC bus to the electricity grid. The electricity, which is demanded from the grid in times of no irradiation, is not depicted.

By the installation of a 5 kW electrolyser, it can be observed, that mostly in summer time, but also in the late spring and early fall, the residual load power exceeds the nominal power of the PtSNG system. Nevertheless, the 5 kW conversion plant limits the grid feed to a maximum of 4.5 kW, hence the distribution grid could be relieved by a minimum percentage of approximately 50 %. The grid relief is even higher in respect of the AC-DC rectifier efficiency. At nominal PEM electrolyser load (5 kW) the rectifier efficiency amounts 94 % in the proposed configuration. Thus, the actual residual load input can be about 5.3 kW due to the electricity coupling losses. For the following gas yield calculations, this fact is respected.

Figure 26 visualizes the frequency distribution of the residual load. Most of the residual load occurs between 0 and 1 kW. Between a broad range from 2 to 8 kW, the residual load occurs nearly for the same probability. High loads above 8 kW are negligible seldom.

Considering a 5 kW conversion plant, at 80 % of the occurring residual load (unequal to zero), a PtSNG conversion takes place without the necessity of feeding excess energy to the grid. For the remaining 20 % of the time, at which the 5 kW is exceeded, the excess load has to be fed into the grid.
It can be summarized that the residual load curve of a PV plant typifies a certain characteristic like high shares of low loads. Hence it is reasonable to take those characteristics for a dimensioning or system optimization measures into account.

As mentioned above at 20 % of the time, when the residual load is greater than 5 kW, the PtSNG system operates with a connection to the grid to get rid of the surplus energy that cannot be converted to gas. From an energetic point of view even 86 % of PV generated RE can be used in the household storage system and only 14 % of the energy necessarily flows to the electricity grid, mainly in summer time.

3.2 Hydrogen Generation of PEMEL

In the figure 27 above the occurrence of residual load is displayed again. Here, it is referred to the design case, in which a PtSNG unit with a 5 kW PEMEL is connected to the AC bus of the household. In the figure below, the system efficiency of the PtSNG unit is plotted according to the developed Matlab® model, presented in section 2.2.3. In order to get an impression of the applicability of connecting the PtSNG unit to a PV power source it is worth comparing both graphs.

As can be seen in both graphs, the upper power limit exceeds 5 kW. This can be explained by the switching losses of AC/DC rectifier, whose maximum efficiency is 94 % at nominal power. Hence approximately 5.3 kW can be fed to the PtSNG system to lie within the electrical limit of 5 kW nominal load of the PEMEL. 20 % of the residual load occurrence has the value
of 5.3 kW. This load level represents all conditions, in which the residual load is above the PtSNG electrical nominal power. For the remaining 80 %, the load profile is aligned to the natural load profile of a PV plant.

The PEMEL system efficiency curve can be divided into two characteristic regions. The first region between 0 - 0.5 kW load is mainly affected by the rectifiers performance (1). As already mentioned, the low load performance of the AC/DC rectifier is negatively affected by its switching losses. Focusing on the residual load range below 200 W, where a major part of the residual load occurs, the system efficiency is strongly decreasing.

However, the maximum power point of the PEMEL system lies in a favourable residual load range at about 0.5 kW. The linear decreasing region of the efficiency curve behaves due to the

Figure 27: Comparison of residual load occurrence and PEMEL performance
characteristics of the PEMEL (2), which is mainly influenced by the ohmic losses (figure 8). Excluding the low residual load range, the PEMEL system efficiency mainly operates between 75 % and 60 % conversion efficiency. In times, the nominal power of the PtSNG system is exceeded, the unit operates with an efficiency of about 60 % at nominal load. To sum it up, approximately 2/3 of the electric energy fed into the PtG unit is stored in chemical energy via hydrogen.

Based on both, the PV-characteristic residual load occurrence and the PEMEL system performance curve, a curve fitting can be performed in order to optimize the hydrogen conversion efficiency. Similar to the annual yield of a PV plant (kWh/kWp), the conversion quality of a PtG system can be quantified by a \textbf{hydrogen conversion quality value}:

\[
\text{Hydrogen conversion quality} = \frac{Nm^3_{H_2}}{kW_{PEMEL}}
\]  

The conversion quality value is the ratio of the yearly cumulated volume of generated hydrogen per kW installed electrolyser power. It allows the beneficial adjustment of the PEMEL size.

Furthermore the influence of the variation of electrical input can be analysed to assess the options of offering grid services. Electricity can be purchased from the electricity exchange. This external energy from the grid affects the residual load profile. The impact of the additional grid electricity can easily be analysed by the determination of the conversion quality value.

In figure 28 the hydrogen production rates of two exemplary days in 2013 are depicted.

![Figure 28: Hydrogen production rates for two exemplary days](image)
The red plot visualizes the hydrogen production rate of a partly-cloudy day in the spring time. It is reported that the sun shone approximately 4 hours at that day. Due to the occurrence of clouds, the electricity generation is volatile, which is then fed to the PEMEL electrolyser system. The hydrogen production starts at 09:00 am Central European Time and ends about 05:30 pm. Most of the daytime the upper residual load limit of 5.3 kW is not exceeded. At 03:00 pm the upper limit is reached and electricity has to be fed to the grid. At that point the PEMEL operates at nominal point with a production rate of approximately 0.84 Nm$^3$/h.

In contrast, the blue plot visualizes the hydrogen production rate of the sunniest day in 2013. At that day the sun shone about 12 hours and except in the morning, no clouds came up. Hence more than half of the sunshine duration, the PtG plant works at nominal load. Due to less clouds and a higher solar altitude in summer, the generated volume of hydrogen is more than twice of the day in spring time. However, these plots are results of the static Matlab\textsuperscript{®} model. The electrolyser conversion performance needs to be evaluated by series of real tests focussing also on the dynamics of a PEMEL, which is tracking a volatile electricity input.

The necessity of a seasonal storage dealing with solar energy is shown in figure 29. The daily generated hydrogen volume is depicted for every day of 2013 at the reference site. As expected, the hydrogen production is weak in the winter time and considerably more productive in the summer time.

Nonetheless, even in summer time periods of low hydrogen productions occur, but all in all the hydrogen yield behaves in accordance to the seasonal altitude of the sun.
A fundamental assumption that is part of the hydrogen yield calculation is the efficiency losses due to cell degradation of the PEMEL stack, in other words the lifetime efficiency $\eta_{\text{time}}$, which is further explained in section 2.2.4. According to the literature mentioned in that section, the cell degradation is expected to be almost constant at 7 $\mu$V per operational hour of the PEMEL. Assuming the PtSNG system is designed for 20 years, an average value $\eta_{\text{time}}$ summarizes the cell degradation losses to a constant efficiency value, which is used for the above mentioned hydrogen production calculation.

In figure 30 the average lifetime efficiency is plotted against the yearly operating time. The efficiency linearly depends on the time.

![Figure 30: Average Lifetime efficiency of the PEMEL stack](image)

At the reference site, the PEMEL operates approximately 2,800 hours in 2013. As a consequence the average lifetime efficiency amounts 90.6 %, which is assumed to be constant for 20 years of PEMEL operation for the yield calculation. Including the lifetime efficiency in the system efficiency, the average system efficiency $\eta_{\text{sys ave}}$ amounts 61.5 % for the reference site. The average system efficiency can also be consulted as an indicator to evaluate the PEMEL performance.

A yearly operational time of 2,800 hours would result in an operational time of 56,000 hours after 20 years, which is remarkably higher than the specified stack lifetime of many manufacturers. However there is no universally valid rule, which defines the end of a PEMEL lifetime. Several literature report an unproblematic operation of 60,000 h [25] up to 100,000 h in military applications [53].
Due to high costs of the electrolyser’s stack, it would be reasonable rather to operate the PEMEL with a lower efficiency, than changing the stack after a couple of years to gain a few percent more efficiency.

### 3.3 Hydrogen Intermediate Storage & Carbon Dioxide Supply

In order to provide a steady-state operation of the methanation reactor, the volatile hydrogen production flow needs to be buffered through an intermediate storage by pressurized bottles. If the storage capacity is reached, a constant hydrogen flow is released to the methanation reactor until the storage pressure equals the pressure level of the methanation reactor. At the same time the second reactant CO$_2$ is fed in stoichiometric proportions to the hydrogen stream. The intermediate storage and the methanation reactor should be dimensioned properly. One possible option is that the storage discharge takes place after sunset, so that the storage is emptied before the sun rises in the morning. Alternatively the methanation reactor can be sized in that way, that the required constant hydrogen gas flow is bigger than the maximum hydrogen flow generated by the PEMEL. The second option is preferable due to space savings and to lower costs. The final evaluation of the methanation reactor gas flows is the objective of section 3.4.

For dimensioning the hydrogen intermediate storage, the daily produced hydrogen must be taken into consideration. It is reasonable to size the storage according to the hydrogen volume that is generated at the day of the highest gas conversion in 2013. Moreover an appropriate storage capacity should be provided to reduce the number of methanation operations and thus the energy expenditure for preheating the methanation reactor.

According to equation 18 to calculate the hydrogen storage capacity, two parameters $n_b$ number of 50 l bottles, and the pressure difference between $p_i$ and $p_u$ have to be chosen. The latter is calculated with 30 bar for $p_i$ and 9 bar for $p_u$. $P_i$ results from the operating pressure of the PEMEL and $p_u$ is defined by the pressure level of the methanation reactor (8 bar). To avoid a backflow of reactor gases the hydrogen discharge stops at 9 bar bottle pressure. For a first approach five 50 l gas bottles are assumed. With the proposed values 5.2 Nm$^3$ hydrogen gas can be stored in the intermediate storage.

In figure 29 the highest gas yield can be determined on 3 June 2013. Approximately 8.1 Nm$^3$ hydrogen is produced at that day. Consequently it exceeds the capacity of the intermediate gas storage. In order to avoid a down regulation of the PEMEL, the methanation reactor should convert more hydrogen than the maximum hydrogen gas flow rate provided by the PEMEL.
The PtSNG model can now be extended by the intermediate storage component. For this the yearly cumulated hydrogen volume must be taken into consideration. Figure 31 visualizes the cumulated hydrogen and the intermediate storage discharge periods.

In the end of the year 2013 approximately 1120 Nm$^3$ hydrogen is generated. Only 24% of the hydrogen is produced in the first and fourth quarter of 2013. About 76% is produced from late spring to fall, but it should be noted that the share could be even higher if the excess electricity in summer could also be converted to gas instead feeding it into the grid (see also figure 26).

Each of the 154 red crosses stands for a full discharge of the hydrogen intermediate storage and a subsequent methanation process at steady-state. The charge-discharge cycle of hydrogen storage is at least one day in the summertime. But in the wintertime the hydrogen bottles are being filled over a much larger period of time up to four weeks. It needs to be examined if the whole PtSNG system keeps on working in wintertime or if the methanation unit should be shut down due to disproportional energy expenditure to preheat the cooled down methanation reactor. Then a certain amount of residual RE would be discarded and has to be fed into the grid.
The methanation reactor is supplied with compressed CO$_2$, which is stored in gas bottles at a pressure level of 250 bar. The replacement of bottles should be performed manually. Hence the bottle dimension and the weight matter. Due to the high pressure the CO$_2$ bottle dimension can be selected small. Two 13.4 l bottles provide about 10.4 Nm$^3$ carbon dioxide gas. Due to the stoichiometric proportion of 4:1 this enables the methanation of 41.6 Nm$^3$ hydrogen gas. As a consequence the CO$_2$ bottles need to be changed approximately 26 times in the reference year. The weight for one bottle is 18.2 kg.

### 3.4 Methanation and Excess Heat Production

In the first instance the focus of this section is on the feed gas flow rates, the SNG yield and the excess heat production of the methanation unit. The equations for all calculations regarding the methanation process are explained in section 2.4.6 and 2.4.7. All assumed model parameters are summarized in annex 4.

As explained in the previous section the methanation reaction starts when the hydrogen intermediate storage is full. Then the reactant gases enter the reactor with a constant gas flow rate. This enables the reactor to operate at steady-state, which is essential for a consistent high quality of the SNG product gas.

For the dimensioning of the reactor the GHSV is going to be used. This value characterizes the flow velocities of gases within the reactor. Assuming a **GHSV of 2000** and an **empty space reactor volume $\Phi_V$ of 0.9**, the **volumetric flow of gas** within the reactor $f_{gas}$ can be described using equation 19:

$$f_{gas} = 2000 \frac{1}{h} \cdot 0.9 \cdot V_{reactor}$$

The volume of the reactor is sized according to the metal comb reactor of KIT institute [31] and can be computed by equation 20:

$$V_{reactor} = \frac{\pi d_{in}^2}{4} \cdot L_{reactor} = \frac{\pi (0.04 m)^2}{4} \cdot 0.6 m = 7.54 \times 10^{-4} m^3$$

Thus, the value of volumetric gas flow within the reactor is 1.36 m$^3$/h, which is equal to a flow velocity of approximately 30.0 centimetres per second.

Due to an 80 % product gas recirculation rate, the feed gas flow rate is considerably smaller than the reactor gas flow rate. The feed gas flow rate is computed by equation 21:

$$f_{gasfeed} = (1 - RR) \cdot f_{gas} = (1 - 0.8) \cdot 1.36 \frac{m^3}{h} = 0.27 \frac{m^3}{h}$$
For reasons of a uniform format for calculation, the feed gas flow rate is converted to standard cubic meters per hour. According to equation 22, the standard volumetric feed gas flow rate $f_{gasfeed0}$ can be determined:

$$f_{gasfeed0} = f_{gasfeed} \times 8 \times \frac{T_{amb}}{T_{gas}} = 0.27 \frac{m^3}{h} \times 8 \times \frac{288.15 K}{573.15 K} = 1.09 \frac{Nm^3}{h}$$

The feed gas stream is composed of the reactants H$_2$ and CO$_2$ in a stoichiometric proportion of 4:1. Considering the reactants as ideal gases, the volumetric proportion equals the stoichiometric proportion. Thus, 80% of the feed gas flow is CO$_2$ and 20% is H$_2$. This results in feed gas flow rates:

$$f_{gasfeed0}^{H_2} = 0.872 \frac{Nm^3}{h}$$  

$$f_{gasfeed0}^{CO_2} = 0.218 \frac{Nm^3}{h}$$

Consequently a full discharge of the hydrogen intermediate storage takes about 6 hours. The subsequent methanation is therefore completed in less time than the storage is charged during the daytime.

The dry SNG product gas flow rate $f_{product0}$ can be computed applying equation 23. The conversion efficiency $\eta_{conversion}$, which describes the reaction rate of CO$_2$ to CH$_4$, is assumed to be 0.9. Factor 1/5 describes the volume reduction that is happening during the methanation process. This factor refers to all reacted gases, so that it is multiplied with the conversion efficiency and the feed gas flow rate. 10% of the feed gas, which is not reacted, must also be taken into account, as is it a gaseous component of the dry product gas.

$$f_{product0} = \left( \eta_{conversion} \cdot \frac{1}{5} + (1 - \eta_{conversion}) \right) \cdot f_{gasfeed0}$$

$$f_{product0} = \left( 0.9 \cdot \frac{1}{5} + (1 - 0.9) \right) \cdot 1.09 \frac{Nm^3}{h} = 0.305 \frac{Nm^3}{h}$$

The dry SNG product gas stream amounts approximately 300 litres per hour. This flow rate is constant at any time the methanation reactor operates. As already explained, the steady-state reaction conditions are ensured by the intermediate hydrogen storage.

In Figure 32 one blue bar represents a hydrogen discharge or a methanation process respectively. The height of the bars describes for the cumulated amount of SNG product gas, which
is produced in 2013, beginning from January 1. The red crosses stand for the amount of excess heat occurring at the particular day, when the methanation process is operating.

![Figure 32: Yearly cumulated SNG volume and excess heat production](image)

Considering the SNG gas volume first it can easily be comprehended that the productivity of the conversion system is generally the lowest during the first and last months of the year 2013. After the first month, the methanation production gains weight and has the highest operational frequency in late June and early July, where the methanation unit operates almost every day. Furthermore there is a period of high productivity in the late May, and even in the early May and short periods in March and late September the operation frequency is considerably high.

The maximum SNG product gas volume is produced at day 151 in late May (31.05.2013) with a SNG volume of approximately 4.3 Nm$^3$. The day of the highest SNG yield differs from the day of the highest generated hydrogen volume which is about half a week later as depicted in figure 29. This fact can be explained by the way of how the intermediate hydrogen storage is operating. The storage is only discharged, if the maximum capacity is reached. If the storage is filled up to 90\% at the end of one day and the following day additionally generates a big amount of hydrogen, then the storage discharge takes place at the same time, the storage is charged. It is technologically feasible, as the hydrogen product gas flow rate of the PEMEL is smaller than the required hydrogen reactant gas flow rate for the methanation process. In percentage terms the gas flow rate is at least 3.5\% higher.
The cumulated amount of excess heat of the methanation reactor is visualized by red crosses. The excess heat ranges from 3.6 kWh to 8.4 kWh per day. It can be seen that there is a certain lower quantity limit of heat. The lower limit is defined by the size of the intermediate storage. The excess heat usage is an essential aspect to improve the level of utilization of a PtSNG system.

To examine the degree of fulfilment of heat demand of a household, the excess heat time curve needs to be compared with the heat load curve of an exemplary household.

### 3.5 Energy Utilization

This section contains the evaluation of SNG product gas utilization and the assessment of excess heat integration in hot water and domestic heating system of a single-family household.

#### SNG as a fuel

Main objective of this work is to estimate the potential of a domestic PtSNG system to replace fossil fuels in the transportation sector. It is proposed to calculate the distance that could be covered using SNG as a fuel for a conventional natural gas engine. The fuel consumption of a VW Passat is estimated as 4.4 kg/100 km [54]. Due to complexity, the evaluation is carried out neglecting the CNG refuelling unit, that includes the compression up to the required pressure level of 200 bar. The covered distance can be calculated as follows:

<table>
<thead>
<tr>
<th>SNG volume (Nm³)</th>
<th>SNG density (kg/Nm³)</th>
<th>SNG mass (kg)</th>
<th>SNG fuel consumption (kg/100 km)</th>
<th>Driving range (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>391.0</td>
<td>0.75</td>
<td>293.3</td>
<td>4.4</td>
<td>6 665</td>
</tr>
</tbody>
</table>

The driving range that is covered by the SNG gas is approximately 6 700 km, which is more than half of the yearly average distance of a single German car [55]. The reachable distance is supposed to be improved in a sensitivity analysis in section 4.2.

#### Excess heat integration

To evaluate the potential of excess heat integration in hot water supply and domestic heating, the occurrence of excess thermal energy has to be compared to the heat load profile of an exemplary German household. Excess thermal energy shows up at both units, the PEMEL and the methanation reactor, as both reactions are exothermal. A significant difference is the temperature level of heat. The PEMEL thermal heat occurs at a moderate temperature of 60 –
80°C, whereas the methanation excess heat temperature is about 300°C. In the following simplified illustrations, the temperature level is solely reflected in the amount of thermal energy and the evaporation effect of water is not taken into account in this work. The results of the excess heat integration calculation are depicted in figure 33.

Figure 33: Heat consumption (a), production (b) and coverage (c) curves

The consumption load profile (a) refers to a three-person household in Würzburg/ Germany. The data were provided on request by Thomas Staudacher, the author of an article in the German journal Energiewirtschaftliche Tagesfragen [56]. The assumptions underlying to the heat load curve are summarized in table 6. Staudacher states that the site Würzburg represents a comparably accurate mean value for a German average household, as the solar irradiance is close to the average German irradiation, in respect to solar heat gain. The heat demand is di-
vided into two categories. The first category refers to hot water provision. The heat demand for hot water is almost constant for the whole year. The domestic heat demand is variable and strongly depends on the season as well as on the outside temperature. The overall heat demand is approximately 45 kWh/day in the wintertime and 5 kWh/day in summer.

Table 6: Assumptions for the heat consumption curve of an exemplary household [56]

<table>
<thead>
<tr>
<th>Hot water demand</th>
<th>Domestic heat demand</th>
<th>Daily degree number</th>
<th>Global radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>650 kWh/(person·a)</td>
<td>51 kWh/m²·a</td>
<td>3 167 °C</td>
<td>1 116 kWh/(m²·a)</td>
</tr>
</tbody>
</table>

The heat production of the PtSNG system is depicted in figure 33 (b). According to the solar altitude, the heat production gains importance in summer. Particularly in the summer months, the heat production is significant high and oftentimes higher than 20 kWh/day. The major part of excess heat results from the PEMEL. Moreover the heat production is spread widely from the beginning of March to the end of September. Nevertheless, the excess heat occurrence is considerably more volatile than the heat consumption.

Comparing the heat consumption of the household with the excess heat production of the entire PtSNG system, the seasonal fluctuations between the heat demand in wintertime and the surplus heat in summertime become obvious. Between day number 150 and 240 the heat coverage (c) is about 100 % due to low heat consumption and a high heat production. It has to be noted here, that a large amount of energy is dissipating to the atmosphere, as there is no heat demanded. A heat requiring carbon dioxide capture from air could be an option for an additional heat sink in the summer. As expected, the heat coverage in the winter months is negligible low. Particularly during the seasonal changes not only the hot water demand is covered, but also a certain share of domestic heat requirements are served.

All in all, assuming that PtSNG excess heat can be stored for one day, the average heat coverage of the household is 22.5 %. The sensitivity analysis will indicate whether the heat coverage can be improved. Another efficiency indicator is the maximum share of excess heat usage, which is 59.9 % for the base case. In order to avoid energy losses, this value sounds promising. However it should be kept in mind that the calculated excess heat represents an upper limit, assuming that the entire excess heat can potentially be recovered.

A user guidance for applying the developed Matlab® simulation model is provided in annex 5.
4 Results and Discussion

4.1 Technology Readiness Level

In order to assess an evolving technology according to its technological feasibility, the development stage needs to be determined. Technology Readiness Levels (TRL) are measures that identify the maturity of an innovation that stands before the marketing stage. According to the European Commission, the 9 TRLs are defined as follows [57]:

- TRL 1 - basic principles observed
- TRL 2 – technology concept formulated
- TRL 3 – experimental proof of concept
- TRL 4 – technology validated in laboratory
- TRL 5 – technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies)
- TRL 6 – technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies)
- TRL 7 – system prototype demonstration in operational environment
- TRL 8 – system complete and qualified
- TRL 9 – actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies)

Both main components of the proposed small-scale PtSNG system, the PEM electrolyser and the methanation, can be categorized separately.

For the purpose of tracking a strongly volatile electricity input, the **PEMEL technology** is an extensively researched technology. All components for the electrolyser system set-up are technologically available. The PEMEL’s characteristic fast response time is an exclusive benefit towards the alkaline electrolyser technology. Due to the stack configuration, the electrolyser cells’ electrical resistance is comparatively low, that allows a high current density up to 2.0 A/cm². The low current density implies a compact stack design, which is important for a domestic small-scale plant. The simulation in this work shows an average PEMEL efficiency about 61.5 %. The product gas is high purity and compressed hydrogen, which fulfils the re-
quirements of the subsequent methanation reactor. The maximum efficiency amounts up to 75% and it is expected that the lifetime of the electrolyser stack will last more than 20 years of operating time. More than 20 years of field experiences were made in military sector and in RE demonstration plants around the world. Even though the trend is towards a higher electrical power per stack, the majority of demonstration plants doesn’t exceed the kW level. PEMEL technology manufacturers produce plug & play plants in mini-series, in order to meet the demand for research projects. Nevertheless the PEM technology shows a few drawbacks, as the demand of noble metals like platinum is high. Current research is carried out in the substitution of noble metals, increasing the current density, enhancing the chemical compression up to 200 bar output pressure and boosting the stack lifetime. The excess heat integration for small-scale electrolyzers is from the view of efficiency desirable, but has not been implemented yet. The implementation of MW-scale demonstration plants and the simultaneous development of the PEM fuel cell promise an optimistic future. The technology readiness level is located between a demonstration technology stage TRL 7 and a completed and qualified technology, TRL 8.

Compared to the electrolyser technology, the methanation reactor for RE is definitely not as advanced as the electrolyser technology, as the methanation unit is assembled to the evolving electrolyser technology. Methanation reactors and appropriate catalysts are well studied in biomass methanation plants. The challenge is to design a suitable reactor concept for the new environment of a domestic small-scale unit. From reaction engineering criteria the methanation of the gaseous reactants H$_2$ and CO$_2$ is less complicated in case the gas feed is constant by a hydrogen buffer as proposed in this work. However the reactor design and an effective heat management have to be determined in order to achieve a high quality SNG gas, which can be used without an additional gas upgrade. In this work a metal comb reactor design was chosen according to a laboratory plant at KIT Karlsruhe and a heat management was integrated. But also related concepts like plate-type reactors and tube reactors show promise. The thermodynamic reaction kinetics holds out the prospect of a high quality SNG product gas, especially at high pressures. Demonstration plants from ETOGAS and ZSW in Germany have shown, that a small-scale and single stage methanation reactor in a PtSNG plant (25 kW electrical input) delivers SNG gas, which fulfils the requirements of feeding it directly into the natural gas grid. Besides the above mentioned research efforts the focus is also on renewable CO$_2$ sources and the influence of a varying hydrogen supply. The technology readiness level ranges between lab-scale validation (TRL 4) and demonstration technology (TRL 6) as some
research projects found out, that the methanation unit is easy to construct and comparatively low in cost.

Both technologies, PEMEL and the methanation reactor, are at technology readiness levels that go beyond the lab-scale stage. The PEMEL technology is considered as more mature than small-scale methanation but due to a far less complex set-up, the methanation reactor will probably overcome the maturity gap soon.

4.2 Sensitivity Analysis

A sensitivity analysis is a commonly used approach for identifying important parameters that dominate model behaviours. The sensitivity analysis is carried out by defining promising cases to improve the PtSNG performance with a primarily focus on the SNG gas yield and a secondary focus on excess heat utilization. To achieve proper results from the sensitivity analysis, meaningful performance indicators have to be defined. Most of the proposed indicators were characterized in the previous section but on the following, the performance indicators will be summarized in short form.

4.2.1 Performance Indicators

**SNG volume and driving range:** The SNG volume is the sum of all SNG volumes in Nm$^3$ that is produced in one year at the reference site. With an average SNG density of 0.75 kg/Nm$^3$ and assuming a fuel consumption of 4.4 kg per 100 km, the potential range in km can be calculated. These performance indicators assess the PtSNG system in terms of conversion quantities.

**PtSNG system efficiency:** The efficiency is the classical definition of a plant’s performance, which refers the energy yield of the system’s output to the residual energy input in %. The system efficiency compares the electrical energy of the residual load to the Lower Heating Value (LHV) of the cumulated product gas SNG. The LHV of SNG is preferred to the HHV as a car engine cannot use the calorific value effect. Considering the PtSNG system efficiency, the quality of the conversion path -electrical energy to chemical energy- can be evaluated. However it has to be noted that the PtSNG system efficiency cannot be applied to calculate the potential excess heat production, as the definition includes a simplification of the methanation reaction in particular, where the reactant gas stream CO$_2$ and the product water is not accounted. To involve the excess heat considerations the released reaction heat has to be calculated exclusively.
Household heat coverage: The household heat coverage refers to the current usable amount of excess heat production to the current heat consumption of the exemplary household. The excess heat production is calculated by the summation of all reaction heat that occurs along the chemical conversion path. For the PEMEL unit it also includes the heat, which is produced due to electrical resistors. Matching the daily produced excess heat with the daily required heat for hot water and domestic heating the average share of heat coverage can be calculated in %. In other words, the household heat coverage represents the maximum share of fossil fuels which can be avoided by the heat integration of the PtSNG system.

\[
\text{Household heat coverage} = \frac{\text{Usable Excess Heat}}{\text{Heat Consumption of Household}}
\]  

(37)

Excess heat usage: This indicator is the share [%] of used excess heat to the total amount of excess heat, which is produced for one year.

\[
\text{Excess heat usage} = \frac{\text{Used Excess Heat}}{\text{Total Excess Heat}}
\]  

(38)

Waste heat: The waste heat is the amount of thermal energy in kWh\text{th} which is released to the atmosphere.

These six performance indicators are evaluated in the sensitivity analysis. In the following, three different cases are characterized in order to perform the sensitivity analysis and to point out the system optimization potential. The size of the PV plant (10.8 kWp) and the household heat consumption, that underlie the calculations of the sensitivity analysis, are not changed in the cases. All changes will be performed within the PtSNG system or the residual load input varied by input electricity from the grid.

4.2.2 Case Descriptions and Results

Case 0 and Case I: In order to analyse the influence of the system size on the PtSNG performance, the nominal power of the PtSNG system is varied from 1 to 8 kW. Case 0 is the base case scenario, which includes the 5 kW PtSNG conversion unit that is exclusively fed by the rooftop PV plant. In the following case study the nominal power of the PtSNG system is varied in 1 kW steps up to 8 kW.

- **Case 0 5 kW** PtSNG system nominal power
- **Case I 1 kW** PtSNG system nominal power
- **Case I 2 kW** PtSNG system nominal power
- **Case I 3 kW** PtSNG system nominal power
- **Case I 4 kW** PtSNG system nominal power
- **Case I 6 kW** PtSNG system nominal power
- **Case I 7 kW** PtSNG system nominal power
- **Case I 8 kW** PtSNG system nominal power

According to the varying nominal power, the plant dimension has to be adjusted in the Matlab® model as well. Therefore the cell area needs to be changed to the new load conditions, as the current density must be the same. Due to the base case, every installed kW refers to 14 cm² cell area. The results of the sensitivity analysis for case I are shown in figure 34 and table 7.

The SNG volume and the corresponding driving range increases with an increasing nominal power. The gradient is slightly decreasing from low to higher capacities and seems to reach the highest level close behind 8 kW. This curve progression is caused by the natural load profile of a PV plant. As already mentioned and described in figure 26, the low load occurrence is considerably high and it drops exponentially for higher loads.

The system efficiency is rising at approximately 1.3 % per installed kW. Due to the fact, that the methanation efficiency is decoupled from the volatile input and its efficiency is constant,
the PEMEL system alone causes the efficiency increase with an increased nominal power. Apparently the PEMEL efficiency curve fits better to the PV load profile (see figure 27), if the nominal power is higher.

Table 7: Results from the sensitivity analysis for case I

<table>
<thead>
<tr>
<th>Case</th>
<th>SNG volume/driving range [Nm³] / [km]</th>
<th>PtSNG system efficiency [%]</th>
<th>Household heat coverage [%]</th>
<th>Excess heat usage [%]</th>
<th>Waste heat [kWh]th</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 kW</td>
<td>128 / 2 182</td>
<td>50.8</td>
<td>12.4</td>
<td>91.6</td>
<td>103.3</td>
</tr>
<tr>
<td>2 kW</td>
<td>216 / 3 733</td>
<td>51.5</td>
<td>16.4</td>
<td>74.7</td>
<td>520.0</td>
</tr>
<tr>
<td>3 kW</td>
<td>290 / 4 943</td>
<td>52.2</td>
<td>19.4</td>
<td>67.4</td>
<td>875.7</td>
</tr>
<tr>
<td>4 kW</td>
<td>347 / 5 915</td>
<td>52.6</td>
<td>21.2</td>
<td>63.0</td>
<td>1 166.0</td>
</tr>
<tr>
<td>5 kW</td>
<td>391 / 6 665</td>
<td>53.5</td>
<td>22.5</td>
<td>59.9</td>
<td>1 393.7</td>
</tr>
<tr>
<td>6 kW</td>
<td>423 / 7 210</td>
<td>54.0</td>
<td>23.4</td>
<td>58.1</td>
<td>1 547.2</td>
</tr>
<tr>
<td>7 kW</td>
<td>445 / 7 585</td>
<td>54.7</td>
<td>23.7</td>
<td>57.6</td>
<td>1 605.9</td>
</tr>
<tr>
<td>8 kW</td>
<td>457 / 7 790</td>
<td>55.6</td>
<td>23.8</td>
<td>57.7</td>
<td>1 635.5</td>
</tr>
</tbody>
</table>

By varying the nominal power from 1 kW to 8 kW the driving range changes from approximately 2 200 km to 7 800 km. It can therefore be ascertained that the residual load from a 10.8 kWp PV plant cannot cover the average driving range of a single German car of about 12 000 km at all.

Focussing on the excess heat integration into the domestic heating system, the replacement of demand for fossil fuels in the household heating system can be diminished up to 23.8 % at 8 kW. The curve progression corresponds to the SNG volume curve for low nominal power, but it remains constant for nominal power bigger than 5 kW, as an increase of the power mainly affect a surplus of operational time in the summer time, where the domestic heat demand is considerably small. The same effect can be observed for the excess heat usage. From 6 to 8 kW the excess heat usage stays almost at the same level of about 58 % and increases exponentially for a lower nominal power. The most variation can be observed for the waste heat. As the excess heat amount of the PtSNG system is low at a low nominal power and the heat demand for hot water is constant for the whole year (see figure 33), there is only a small amount of heat, that has to be released to the atmosphere in the midsummer. The waste heat amount significantly increases from 1 to 6 kW as the heat demand for domestic heating cannot be covered due to a seasonal mismatch of demand and supply (see also figure 33).

**Case II:** The second case is supposed to optimize the system efficiency by adding electricity from the grid at certain residual loads. The issue of a poor low load performance of the
PEMEL was already explained in section 3.2. Again, one drawback of the electrolyser is the large efficiency drop at loads below 5% of the nominal load. Viewing figure 27, it becomes visible that a noticeable share of PV residual load occurs at low loads, when the weather is cloudy and during the time of sunrises/sunsets. Nevertheless it is advantageous that the point of maximum efficiency is quite close to the low load efficiency drop. Hence it is reasonable to boost the low load efficiency by adding electricity from the grid, so that at any time, the load is below the maximum efficiency load of 562 W, additional power is fed to the PtSNG conversion system, understanding that the produced SNG gas is not one hundred percent renewable.

- **Case II: PtSNG system efficiency boost by adding grid power at low loads**

Figure 35 compares the performance indicators of case II to the base case of PtSNG system.

![Figure 35: Variation of performance by adding grid power at low loads](image)

By adding grid power at 5% of the nominal power both, the SNG volume and the system efficiency, increase by 4% compared to the base case. The growth of the SNG volume is due to the increase of the PtSNG system efficiency.

**Table 8: Results from the sensitivity analysis for case II**

<table>
<thead>
<tr>
<th>Case</th>
<th>SNG volume/driving range</th>
<th>PtSNG system efficiency</th>
<th>Household heat coverage</th>
<th>Excess heat usage</th>
<th>Waste heat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Nm$^3$] / [km]</td>
<td>[%]$_{\text{LHV}}$</td>
<td>[%]</td>
<td>[%]</td>
<td>[kWh]$_{\text{th}}$</td>
</tr>
<tr>
<td>0</td>
<td>391 / 6 665</td>
<td>53.5</td>
<td>22.5</td>
<td>59.9</td>
<td>1 393.7</td>
</tr>
<tr>
<td>II</td>
<td>407 / 6 938</td>
<td>55.7</td>
<td>23.2</td>
<td>60.0</td>
<td>1 439.1</td>
</tr>
</tbody>
</table>
It is important to note that the household heat coverage as well as the amount of waste heat increases, whereas the excess heat usage remains almost constant. In general, a gain in the household heat coverage implies that more excess heat is produced in wintertime, which entirely can be integrated to the domestic heating system. However, as low loads also occur in the summertime, the amount of waste heat increases too. The excess heat shows slight gains compared to the base case.

In total the variation of the performance indicators are comparatively small in contrast to the variations in case I.

**Case III A-C:** The third case is primarily supposed to increase the yearly generated SNG product gas volume and therefore the range in kilometres by adding electricity from the grid when there is a surplus of RE. Secondarily the PtSNG excess heat integration is considered, as the advantageous side effect is expected to be the most profitable in winter times. Due to the seasonal variation of solar energy, a grid support is desirable in wintertime. In contrast to solar energy, the wind energy production has its peaks in autumn and during the wintertime.

A German study from “Agora Energiewende” analyses the future potential of Power-to-Heat (PtH) in Schleswig-Holstein/Northern Germany for the year 2023, based on the yearly RE feed-in data from 2011 [58]. Annex 6 visualizes the expected RE excess grid power and the corresponding annual load duration curve for that year. It can be seen that there is surplus RE in the grid at approximately 3000 hours. Furthermore the majority of excess power occurs during the winter half-year. It is reasonable to assume that 60 % of the excess power occurs in the six winter months. Assuming that 200,000 PtSNG are installed in Germany and each of them offers grid services with up to 5 kW, one third of the excess power potential could be used. Hence the potential of PtSNG amounts 600 hours in 182 days. Theoretically the PtSNG unit can be fed with RE from the grid for about 23 hours per week at full load neglecting other storage technologies on the market. For analysing the SNG yield of a single PtSNG unit, that is fed by RE from the grid in six winter months, the following cases can be assumed:

- **Case III A:** 5 kW grid power at 2 days per week for 5 hours
- **Case III B:** 5 kW grid power at 4 days per week for 5 hours
- **Case III C:** 2.5 kW grid power at 5 days per week for 5 hours

The variations of case III to case 0 are shown in figure 36. Adding 5 kW grid power for two days in case III A, causes a SNG volume increase of about 19 % that covers a driving range of
approximately 8000 km. Doubling the time of grid supported operation is doubling the additional generated SNG up to 9 150 km, which is more than three-quarters of the average driving range of a single car. As expected the efficiency is slightly dropping in all cases, as higher loads than 500 W result in a lower PEMEL efficiency. Due to the fact that the grid power in case III A and B is constant, the efficiency change is doubled too. Case III aims at offering

the grid operator an option for load management in the wintertime, when the majority of the surplus RE is wind energy. A valuable side effect of the grid connected operation in winter is that almost all excess heat can be integrated in the domestic heating system of the household, as the heat demand in the winter months is considerably high. In case III B approximately 20 % more excess heat can be used than in case 0, so that the value for household heat coverage changes by 70 % to more than 38 % in total. At the same time the additional waste heat is comparatively low.

Table 9: Results from the sensitivity analysis for case III

<table>
<thead>
<tr>
<th>Case</th>
<th>SNG volume/ driving range [Nm³] / [km]</th>
<th>PtSNG system efficiency [%]</th>
<th>Household heat coverage [%]</th>
<th>Excess heat usage [%]</th>
<th>Waste heat [kWh]th</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>391 / 6 665</td>
<td>53.5</td>
<td>22.5</td>
<td>59.9</td>
<td>1 393.7</td>
</tr>
<tr>
<td>III A</td>
<td>466 / 7 943</td>
<td>52.5</td>
<td>30.7</td>
<td>66.7</td>
<td>1 428.1</td>
</tr>
<tr>
<td>III B</td>
<td>536 / 9 136</td>
<td>51.7</td>
<td>38.3</td>
<td>71.0</td>
<td>1 472.8</td>
</tr>
<tr>
<td>III C</td>
<td>487 / 8 301</td>
<td>52.9</td>
<td>31.9</td>
<td>67.4</td>
<td>1 439.3</td>
</tr>
</tbody>
</table>
To sum it up, on the basis of the presented data in the cases I-III, the system sizing (case I) and the opportunity of adding grid power in wintertime (case III) have a big potential to gain a better performance in terms of driving range and excess heat integration. The influence of adding low loads to improve the system efficiency (case II) is relatively low. In case III the driving range can be boosted up to 9 150 km. The PtSNG system efficiency stays above 50 % for all cases. It turns out that the system efficiency increases with an increased nominal load. The heat integration can be improved most effectively by adding grid power in the winter months. However it has to be kept in mind that the excess heat integration is neglecting any heat losses, as it is considered as a potential estimation.

4.3 Cost Estimation

This section gives a rough estimation about the system investment costs and revenues. Firstly, the investment costs for the PEMEL are broken down into cost elements, as the electrolyser is the cost defining factor of the PtSNG system. Secondly, the actual investment costs for the entire PtSNG system will be estimated. Finally the investment costs and the revenues of the small-scale PtSNG unit will be compared in a break-even situation, where the investment costs is a function of the number of produced units.

The cost breakdown of the PEMEL is considered as a rough determination of which component subsystem contribute the most cost in order to provide a general overview of the significance of the different cost defining aspects. The PEM electrolyser system includes the cell stack, AC-DC power electronics, the cooling system and a gas drying unit. Proton OnSite, a leading US manufacturer for military and laboratory applications, discloses their cost breakdown as follows:

![Cost breakdown of a lab-scale PEMEL from Proton OnSite](image)

Figure 37: Cost breakdown of a lab-scale PEMEL from Proton OnSite [25]
Almost half of the costs for a PEM electrolyser are accounted for the flow fields and separators. As explained in section 2.2.5, the flow fields and current collectors are supposed to minimize the electrical losses to the inside of the cell and they promote the efficient removal of the gaseous product. A big potential for cost reduction is given, as the flow field has a high mass percentage and contains noble metals like gold, iridium and platinum. Research efforts focus on mass reduction by nano-coatings and the replacement of noble metals with stainless steel alloys [25].

One quarter of the investment costs are labour costs. Small-scale PEM electrolysers for laboratory purposes are produced in small series up to a dozen of plants at once. The labour costs are significantly high for system components that are not standardized and require manual work. Cost reduction potential is expected according to standardization processes and automation of a high-volume production.

The core of the PEMEL cell is the Membrane-Electrode-Assembly (MEA). The membrane Nafion® is a widely used proton conductor, as the gas crossover rates are close to zero. However the acidity of Nafion® is high, hence base metals need to be coated with a more noble metal. The research focuses on thin film catalyst layers, which are composed of a porous platinum-carbon composite. Due to the small dimensions of the MEA (thickness~1.5 μm), the material costs for noble metals are comparable low. However a cost reduction potential is given by reducing the acidity induced cell degradation that limits the lifetime of the electrolyser.

The AC/DC rectifier and electrical balance of the electrolyser system is the third biggest cost portion. The power electronics can be considered as an advanced technology as the efficiency of the rectifier is close to 100% for a broad power range. An optimization of the alignment to the requirements of a volatile operated PEMEL and a cost reduction potential according to an economy-of-scale can be expected.

There are no further quantified information concerning the investment costs for a metal comb methanation reactor. In the following, a rough cost estimation is carried out based on the description of the laboratory set up at KIT institute in Karlsruhe/Germany [31]. Furthermore, the oil cooling system and hydrogen storage is accounted as well. The cost assumptions for a small-scale application are listed in table 10. The methanation reactor itself causes low costs. Double-walled heat pipes are produced in high volumes and therefore comparatively cheap, as well as commercially available Ni-catalyst.
Results and Discussion

Table 10: Cost estimations for the methanation reactor and other system elements

<table>
<thead>
<tr>
<th>Ni-catalyst</th>
<th>Double-walled pipe &amp; metal comb segments</th>
<th>Injector</th>
<th>Heat transfer oil</th>
<th>Oil circulation pump</th>
<th>Cylinder bottles</th>
<th>SNG compressor</th>
<th>Control electronics</th>
<th>Labour costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 €</td>
<td>450 €</td>
<td>150 €</td>
<td>400 €</td>
<td>100 €</td>
<td>250 €</td>
<td>400 €</td>
<td>300 €</td>
<td>800 €</td>
</tr>
</tbody>
</table>

Other system elements like for the reactor cooling system and gas storage and compression technology is available on the market too. The labour costs constitute approximately one third of the system elements costs, as installation is manual work. All in all, the costs for the methanation reactor and system elements account about 3 000 €.

Figure 38 depicts the size-dependent PtSNG system investment costs. The curve progression is based on an exponential function for the electrolysers’ capital costs, given in a technical report from NREL (National Renewable Energy Laboratory/USA) [66].

Both, the PEM electrolyser costs and the costs of the entire PtSNG system, which is about 30 % higher than the electrolyser costs, are depicted. The capital costs per kW are rapidly increasing for low nominal power. The curves fall moderately for a power level greater 15 kW. However the system costs for the proposed 5 kW PtSNG conversion system tremendously high. The capital expenditures (CAPEX) for the entire PtSNG system would roughly constitute 50 000 €, if operational, maintenance and depreciation costs are neglected.
The revenues of the PtSNG system can be calculated for a lifetime of 20 years, assuming a price for natural L-gas that can be substituted in the transportation sector and saved energy for the domestic heating of a three-person household. For case 0, where the PtSNG plant is only fed by the 10.8 kWp rooftop PV plant, the revenues account as follows:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>294</td>
<td>2 160</td>
<td>1.00</td>
<td>6.9</td>
<td>443</td>
</tr>
</tbody>
</table>

More detailed financial aspects, including a bank loan and a discount rate of 6 % are shown in annex 7. Comparing the roughly estimated investment costs to the revenues, the small-scale PtG plant is far away from being economically feasible. For the financial estimation the present investment costs for a small-scale PtSNG plant supposed to be 10 000 €/kW.

However, these costs are far too high for being economically, but as explained in section 4.1 the technology readiness level of the PtSNG system has not reached the commercialization stage (TRL 9). In the light of past experience investment costs for prototypes are significantly higher than the proven technology that is produced in high volumes. The correlation between a decreasing product price per unit with an increased number of produced units is called learning curve, which was discovered by Theodore Wright (Wright’s Law) [69]. Wright’s empirical law says that if the volume of produced units is doubled, the costs is reduced by a constant percentage. The percentage is called Learning Rate (LR). The learning curve (figure 39) was verified for several technologies and increased its prominence by the significant price fall for semiconductor memories for computer, the so called Dynamic Random-Access Memory (DRAM).

The LR for DRAM is 40 %. Other technologies like flat screens (LR = 35 %) [69] and photovoltaic modules (LR = 8.1 - 22.8 %) provide an outlook for a possible learning curve for PtG technology. The most recent example in the semiconductor industry is the learning curve of PV modules [70]. The average learning rate of PV technology is about 20 %, but the learning rate within the PV technology differs dependent on the cell type. The conventional crystalline silicon technology dominates the solar PV industry. The learning rate is about 22.8 % and promises a healthy outlook in the foreseeable future. In contrast the PV cell type CIGS, which refers to the thin-film technology, has a low learning rate, as the efficiency is lower and the
price per installed watt is too high compared to proven Si cells that are available on the market. As can be seen in figure 39, the learning curves differ depending on the technology and the type of one technology as well. The break-even costs are calculated in annex 7.

![Figure 39: Learning curves in the context of 5 kW PtSNG plant [68,70]](image)

The learning rate for flat screens is considered as a rapidly growing technology. Assuming that industrial-scale MW plants reach their commercial stage if between 6 000 - 200 000 units are produced in, a learning rate comparable to that of crystalline Si-PV modules is necessary to lower the price per unit to 1 000 €/kW.

Assuming that small-scale PtSNG applications have a bigger market, as the number of consumers is significantly higher (~400 000 - 40 000 000 units), a learning rate between 12.4 % and 19.0 % has to be achieved, to reach the estimated break-even costs.
5 Summary and Outlook

5.1 Conclusion

The objective of this thesis was a technical feasibility study and development of a household scale Power-to-Gas conversion plant, in order to provide a long-term renewable energy storage option. In a nutshell, the technical feasibility of converting PV electricity in a SNG storage medium was confirmed.

In the beginning of the work it was shown that a 10.8 kWp PV rooftop plant produces a lot of surplus volatile electricity that has to be fed to the national grid. A chemical conversion of the so called residual energy, that occurs primarily in the summer time, to a storage medium like methane (SNG) constitutes a seasonal storage opportunity of RE. SNG can be provided on site as a fuel for conventional car engines. A part of the excess heat from the conversion process could cover the heat demand of the household.

The PtSNG unit consists of two main components, an electrolyser and a methanation reactor. As the requirement of a small-scale conversion unit is a strongly volatile electricity input, the PEM electrolyser technology shows the most promising option. The PEMEL enables a fast response to load changes, a compact design, low maintenance and an operating range between 0-100 % of the nominal power. A Matlab® model of the PEM electrolyser system was developed that shows the dependency of the PEMEL load on the system efficiency. It was ascertained that the electrolyser system efficiency is strongly dependent on the AC/DC rectifier performance for loads smaller than 5 % of the nominal power. The maximum HHV related efficiency is about 75 % at 10 % of the nominal power and is linearly decreasing to 62 % at nominal load. Including the efficiency losses, due to cell degradation over time, the hydrogen product gas flow rate was calculated for the available residual load on site.

The produced hydrogen is pressurized up to 30 bar and needs to be buffered, as the flow is volatile and therefore not compatible for the subsequent methanation. The system was modelled with five 50 l cylinder bottles, in which the gaseous hydrogen is stored until the storage is full. Then the entire storage is discharged with a constant hydrogen flow rate, which enters the methanation unit together with the reactant carbon dioxide in stoichiometric proportions. Carbon dioxide is provided by compressed gas bottles, which have to be replaced manually.
As the idea of a small-scale methanation reactor is comparably new, there are very few concepts available in literature. Core of the proposed reactor is a metal comb structure, which is coated with Ni-catalysts. Six metal comb segments are assembled in the inner pipe of a double-walled pipe. The cooling is realized by a countercurrent flow of thermal oil through the outer pipe. Based on demonstration plants from ETOGAS, ZSW and KIT, the methanation process parameters as well as the expected SNG yield could be chosen for a Matlab® reactor model. According to the demonstration plants, a small-scale reactor is capable to deliver SNG product gas, which meets the quality requirements of natural gas group L and could be used as a fuel for combustion engines. However the usage of SNG gas in the networks of public gas supply is not clarified. Technical regulations and standards are specifically formulated for biogas from fermentation. These regulations need to be adjusted for the specifics of SNG gas.

Both, the PEMEL and the methanation reactor model enable to calculate the yearly produced hydrogen and SNG volumes for the reference site. As the conversion steps in the PtSNG plant are exothermal, the excess heat production is also computed in order to assess the potential of excess heat integration for domestic heating. The results have shown that the produced SNG volume can cover a driving range of approximately 6700 km in the reference year. Furthermore the domestic heating demand can be covered up to a maximum of 22.5 % by excess heat integration. A sensitivity analysis turned out that the influence of the PtSNG system size on the product gas volume is big for a nominal power from 1 kW up to 6 kW. A key factor to improve the produced SNG volume is the grid connected mode, in which surplus RE from the grid is fed to the PtSNG system in the wintertime. In concrete terms, the SNG volume could be increased by 38 % and the household heat coverage even about 70 %.

Finally a rough cost estimation was carried out to identify the most cost-intensive components of the PtSNG system. Due to the fact that the PtG conversion technology has not reached the commercialization level the investment costs for the entire system are rather high. By far the most expensive component is the PEM electrolyser. The electrolyser is produced in small series and most system elements are handmade and not standardized. Moreover the stack contains noble metals, which have to be minimized. The remaining components of the PtSNG system like the methanation unit, the cooling system and hydrogen storage are comparable low-cost as their elements are available on the market. However the entire system costs are too high for being economically feasible. If the PtSNG technology experiences the same learning curve like PV modules, the investment cost may be amortized for a number of around 1 000 000 units.
Which role the small-scale PtG conversion technology in an emerging RE storage market takes is on the one hand side dependent on further technical and economic modifications of the plant itself, but on the other hand side it is strongly dependent on the advances of market competitors like electric motors and battery technology, which are serious alternatives in the transportation sector.

The small-scale PtSNG technology may profit from the contemporary trend of upscaling the electrolyser units. If the MW-scale electrolysers prove their worth, learning effects and standardization processes will be transmitted to the entire industry and the high cost issues might be coped. Proceedings in the closely related PEM fuel cell technology promise findings in fields of substitution of noble metals, as well as better membrane materials and improving the stack lifetime. It is reasonable to assume that the methanation research is intensified, when problems in the electrolyser technology are overcome, as the methanation reactor is a subsequent conversion unit. Applicable small-scale reactor concepts like the metal comb design or a related structures, needs to be validated in order to guarantee a high quality SNG gas, which does not require any gas upgrade for a usage. Materials and components of the reactor set-up are commercially available on market and low in costs. The next step will be to develop an effective integration of excess heat to cover the consumers’ heat demand, as approximately 50 % of the system power input turns into heat. However it has to be pointed out, that even if the PtSNG system efficiency is comparably low the Power-to-Gas path provides the only option for a seasonal storage of surplus RE.

5.2 Recommendation for Further Work

Obtaining a more accurate PEMEL simulation model, further system efficiency dependencies can be added to the existing static model. Even though the influence of pressure and temperature differences within the cell stack are comparably low, a dynamic model could quantify the performance changes for start-up phases and rapid load variations. A second step can be to investigate the influence of a highly dynamic operation of the stack lifetime, as different PEMEL suppliers and operators mention very different cell degradation rates. Currently most electrolyser research projects mainly focus on the production of hydrogen gas, neglecting making the excess heat of a small-scale electrolyser available for heat integration. The system cooling could be achieved by water cooling as the low-temperature heat is suitable for domestic heating or alternative concepts like the capture of CO₂ from air.
The proposed metal comb methanation reactor needs to be validated in experimental tests due to secure operation mode and the real product gas composition, which is mainly affected by the temperature and pressure level and the residence time of the reactants within the reactor. The temperature could be varied according to the physical limits of the nickel catalyst. As the conversion efficiency improves at higher pressures, the pressure level could be raised up to 20 bar, also to avoid throttling of hydrogen gas which is available at 30 bar. Reactor concepts like the plate-type reactor, tube reactors or microchannel reactors or a variation of all, could also be tested. In order to achieve a high quality SNG product gas, which is close to the maximum conversion potential of CO₂, a recirculation of product gas can be implemented as proposed in section 2.4.8. The main objective of the methanation unit must be to guarantee a consistently high quality of SNG gas, so that the gas usage is not limited by the quality standards for feeding it in the natural gas grid or using it as a fuel for the engine of a car.
6 References


71. Breyer C., Tsupari E., Tikka V., Vainikka P. 2015. Power-To-Gas as an emerging profitable business through creating an integrated value chain. 9th IRES
7 Annex

Annex 1: Equations and parameters for modelling a PEM electrolyser cell

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameter / Equation</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Global constants</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absolute pressure</td>
<td>( p )</td>
<td>30</td>
<td>bar</td>
<td>[22]</td>
</tr>
<tr>
<td>Temperature</td>
<td>( T )</td>
<td>333.15</td>
<td>K</td>
<td>[22]</td>
</tr>
<tr>
<td>Gas constant</td>
<td>( R )</td>
<td>8.314472</td>
<td>J/mol·K</td>
<td></td>
</tr>
<tr>
<td>Faraday constant</td>
<td>( F )</td>
<td>96485.34</td>
<td>C/mol</td>
<td></td>
</tr>
<tr>
<td>Transferred electrons</td>
<td>( n )</td>
<td>2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td><strong>Variables</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current density</td>
<td>( i )</td>
<td>0.0...2.0</td>
<td>A/cm²</td>
<td>[13]</td>
</tr>
<tr>
<td>Stack current</td>
<td>( i )</td>
<td>0.0...140</td>
<td>A</td>
<td>[27]</td>
</tr>
<tr>
<td>Cell voltage</td>
<td>( V_{\text{cell}} = E_{\text{rev}} + V_{\text{act}} + V_{\text{ohm}} + V_{\text{conc}} )</td>
<td></td>
<td>V</td>
<td>[13]</td>
</tr>
<tr>
<td>Cell efficiency</td>
<td>( \eta_{\text{cell}} = \frac{1.482}{V_{\text{cell}}} )</td>
<td></td>
<td>-</td>
<td>[17]</td>
</tr>
<tr>
<td>Reversible cell voltage</td>
<td>( E^0 = 1.229 - 0.9 \cdot 10^{-3} (7 - 289) )</td>
<td></td>
<td>V</td>
<td>[15]</td>
</tr>
<tr>
<td>Standard reversible cell voltage</td>
<td>( E_{\text{rev}} = E^0 + \frac{RT}{nF} \ln\left(\frac{1}{1/\sqrt{p}}\right) )</td>
<td></td>
<td>V</td>
<td>[12, 15]</td>
</tr>
<tr>
<td>Reversible cell voltage</td>
<td>( V_{\text{act}} = V_{\text{act.a}} + V_{\text{act.c}} )</td>
<td></td>
<td>V</td>
<td>[14]</td>
</tr>
<tr>
<td>Tafel equation</td>
<td>( V_{\text{act}} = \frac{RT}{nF \ln\left(\frac{i}{n_i g_{\text{act}}}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table><p>ight)} ) |          | V       | [14]      |
| Cathode charge transfer coefficient     | ( a_c )            | 0.5      | -       | [14]      |
| Anode charge transfer coefficient       | ( a_a )            | 0.433    | -       | [14]      |
| Cathode exchange current density, PI/Nafion, 60°C | ( I_{g_c} ) | 0.391 | A/cm² | [14] |
| Anode exchange current density PI/Nafion, 60 °C | ( I_{g_a} ) | 0.0005 | A/cm² | [14] |
| <strong>Ohmic overvoltage</strong>                   | ( V_{\text{ohm}} = \frac{\delta_m}{\sigma_m} \cdot i ) |          | V       | [15]      |
| Ohmic resistance                        | ( \sigma_m = (0.005139 \lambda - 0.00326) e^{12689(\frac{1}{102 - T})} ) |          | -       | [15]      |
| Membrane humidification                 | ( \lambda )        | 20       | -       | [15]      |
| Membrane thickness                      | ( \delta_m )       | 1.5      | μm      | [11]      |
| <strong>Concentration overvoltage</strong>           | ( V_{\text{conc}} = \frac{RT}{nF} \ln\left(\frac{1 - \frac{i}{i_L}}{i_L}\right) ) |          | V       | [16]      |
| Limiting current density                | ( i_L )            | 2.0      | A/cm²   | [13]      |</p>
Annex 2: Equations and parameters for modelling the PEMEL system efficiency

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameter/ Equation</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PEMEL system efficiency</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System efficiency</td>
<td>[ \eta_{sys} = 100 \cdot \eta_{cell} \cdot \eta_{loss} \cdot \eta_{aux} \cdot \eta_{time} ]</td>
<td>%</td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>Hydrogen losses</td>
<td>[ \eta_{loss} = \frac{i - i_{loss}}{i} = 0.99 ]</td>
<td>-</td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td>Power auxiliary losses</td>
<td>[ \eta_{aux} = \frac{\eta_{DC}}{1 + \xi} ]</td>
<td>-</td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>AC/DC coupler efficiency</td>
<td>[ \eta_{DC} = \frac{0.95}{1 + 1/j} ]</td>
<td>-</td>
<td></td>
<td>[29]</td>
</tr>
<tr>
<td>Parasitic power ratio</td>
<td>[ \xi = 0.05 \cdot \frac{P_{nom}}{P_{op}} ]</td>
<td>-</td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>Nominal PEMEL load</td>
<td>[ P_{nom} = 5000 \text{ W} ]</td>
<td>W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operational PEMEL load</td>
<td>[ P_{op} = V_{op} \cdot I ]</td>
<td>W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operational voltage</td>
<td>[ V_{op} = 1.8 \cdot N_{cell} ]</td>
<td>V</td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>Number of cells connected in series</td>
<td>[ N_{cell} = 20 ]</td>
<td>-</td>
<td></td>
<td>[27]</td>
</tr>
<tr>
<td>Average cell degradation</td>
<td>[ \eta_{life} = \frac{V_{cell}}{V_{cell, halftime}} ]</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell Voltage at half lifetime</td>
<td>[ V_{cell, halftime} = V_{cell} + V_{deg} \cdot t_{halftime} ]</td>
<td>V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average voltage degradation rate</td>
<td>[ V_{deg} = 7 \text{ \mu V/h} ]</td>
<td>(\mu\text{V/h})</td>
<td></td>
<td>[13,17,25]</td>
</tr>
<tr>
<td>Operation time after 10 years</td>
<td>[ t_{halftime} = 28000 \text{ h} ]</td>
<td>h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen flow rate</td>
<td>[ f_{H_2} = \eta_{sys} \cdot \frac{N_{cell} \cdot V_{cell} \cdot I_{cell}}{HHV_{H_2} \cdot 1000 \frac{W}{KW}} ]</td>
<td>Nm³/h</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Annex 3: Equations and parameters for modelling the methanation excess heat

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameter/ Equation</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reactor Excess Heat</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar Excess Heat Flow</td>
<td>[ Q_{m, excess} = \eta_{conv} \cdot [(H(CH_4) + 2H_2O) - (4H_2 + H(CO_2))] ]</td>
<td>-158.35 kJ</td>
<td>kJ/mol</td>
<td>[33]</td>
</tr>
<tr>
<td>CH₄ Enthalpy at 300 °C</td>
<td>H(CH₄)</td>
<td>-60.8 kJ</td>
<td>kJ/mol</td>
<td>[33]</td>
</tr>
<tr>
<td>H₂O Enthalpy at 300 °C</td>
<td>H(H₂O)</td>
<td>-231.8 kJ</td>
<td>kJ/mol</td>
<td>[33]</td>
</tr>
<tr>
<td>H₂ Enthalpy at 300 °C</td>
<td>H(H₂)</td>
<td>8.0 kJ/mol</td>
<td>kJ/mol</td>
<td>[33]</td>
</tr>
<tr>
<td>CO₂ Enthalpy at 300 °C</td>
<td>H(CO₂)</td>
<td>-380.7 kJ</td>
<td>kJ/mol</td>
<td>[33]</td>
</tr>
<tr>
<td>Volumetric Excess Heat Flow</td>
<td>[ Q_{v, excess} = \frac{Q_{m, excess}}{V_M} ]</td>
<td>-7.07 MJ/Nm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar Volume of Ideal Gas</td>
<td>[ V_M = 0.0224 \text{ Nm}^3/\text{mol} ]</td>
<td>Nm³/mol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Annex 4: Equations and parameters for modelling the methanation process

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameter/Equation</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constant Reaction Conditions</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactor Inlet Temperature</td>
<td>$T_{\text{inlet}}/T_{\text{gas}}$</td>
<td>573</td>
<td>K</td>
<td>[31]</td>
</tr>
<tr>
<td>Reactor Pressure</td>
<td>$p_{\text{reactor}}$</td>
<td>8</td>
<td>bar</td>
<td>[31]</td>
</tr>
<tr>
<td>Stoichiometry</td>
<td>$n_{\text{H}<em>2}/n</em>{\text{CO}_2}$</td>
<td>4</td>
<td></td>
<td>[40]</td>
</tr>
<tr>
<td><strong>Dry Product Gas Composition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$ Conversion Rate</td>
<td>$\eta_{\text{conv}}$</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane Volume Fraction</td>
<td>$\phi_{\text{CH}_4}$</td>
<td>90</td>
<td>% vol</td>
<td>acc. to [40]</td>
</tr>
<tr>
<td>Hydrogen Volume Fraction</td>
<td>$\phi_{\text{H}_2}$</td>
<td>4.9</td>
<td>% vol</td>
<td>acc. to [40]</td>
</tr>
<tr>
<td>Carbon Dioxide Volume Fraction</td>
<td>$\phi_{\text{CO}_2}$</td>
<td>5.1</td>
<td>% vol</td>
<td>acc. to [40]</td>
</tr>
<tr>
<td><strong>Reactor Modelling</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Hourly Space Velocity</td>
<td>$GHSV = \frac{f_{\text{gas}}}{\phi_{\text{v}} \cdot V_{\text{reactor}}}$</td>
<td>2000</td>
<td>1/h</td>
<td>[40]</td>
</tr>
<tr>
<td>Volumetric Reactor Gas Flow</td>
<td>$f_{\text{gas}}$</td>
<td>1.36</td>
<td>m$^3$/h</td>
<td></td>
</tr>
<tr>
<td>Volume of Reactor</td>
<td>$V_{\text{reactor}} = \frac{\pi d_{\text{in}}^2}{4} \cdot l_{\text{reactor}}$</td>
<td>0.679</td>
<td>dm$^3$</td>
<td></td>
</tr>
<tr>
<td>Empty Space Share</td>
<td>$\phi_{\text{v}}$</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactor Length</td>
<td>$l_{\text{reactor}}$</td>
<td>600</td>
<td>mm</td>
<td>acc. to [31]</td>
</tr>
<tr>
<td>Inner Diameter of Inner Pipe</td>
<td>$d_{\text{in}}$</td>
<td>40</td>
<td>mm</td>
<td>acc. to [31]</td>
</tr>
<tr>
<td>Outer Diameter of Inner Pipe</td>
<td>$d_{\text{out}}$</td>
<td>42</td>
<td>mm</td>
<td>acc. to [31]</td>
</tr>
<tr>
<td>Inner Diameter of Outer Pipe</td>
<td>$d_{\text{in,outer}}$</td>
<td>75</td>
<td>mm</td>
<td>acc. to [31]</td>
</tr>
<tr>
<td>Outer Diameter of Outer Pipe</td>
<td>$d_{\text{out,outer}}$</td>
<td>77</td>
<td>mm</td>
<td>acc. to [31]</td>
</tr>
<tr>
<td>Reactor Feed Gas Flow at 8 bar</td>
<td>$f_{\text{gas,feed}} = (1 - RR) \cdot f_{\text{gas}}$</td>
<td>0.27</td>
<td>m$^3$/h</td>
<td></td>
</tr>
<tr>
<td>Recirculation Rate of Reactor Gas</td>
<td>RR</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard Volumetric Feed Gas Flow</td>
<td>$f_{\text{gas,feed}0} = f_{\text{gas,feed}} \cdot \frac{T_{\text{amb}}}{T_{\text{gas}}}$</td>
<td>1.09</td>
<td>Nm$^3$/h</td>
<td></td>
</tr>
<tr>
<td>Ambient Temperature</td>
<td>$T_{\text{amb}}$</td>
<td>298</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Standard Volumetric Product Gas Flow</td>
<td>$f_{\text{product}0} = \left(\eta_{\text{conv}} \frac{1}{2} + (1 - \eta_{\text{conv}})\right) f_{\text{gas,feed}0}$</td>
<td>0.31</td>
<td>Nm$^3$/h</td>
<td></td>
</tr>
</tbody>
</table>
Annex 5: Guidance for the Matlab® simulation model

The script and functions, as well as the input data for simulating the entire PtSNG system are on the enclosed DVD. The main script (“PtSNGSystemMain”), from which the following program parts are extracted, can be found on the DVD too.

```matlab
fileNameyear = 'Lutjensee Site duration curve calculation new yearly 2013.xlsx';

% entire xls yearly table in a matrix
ryH0year = xlsread(fileNameyear);
% 1D Vector
ryH0year = ryH0year(:,5);

for i=(1:length(ryH0year))
    if ryH0year(i)>5.3008
        ryH0year(i)=5.3008;
    end
end
```

The input data originates from an excel sheet (.xlsx). The fifth column of the excel sheet contains the residual load of the household, which is supposed to be the input data. The data are filtered by a for-loop to values smaller than 5.3008 kW for a 5 kW system, as the AC/DC rectifier has an efficiency of 94 % at nominal load.

```matlab
% Energy of the residual load input
InputEnergy = sum(ryH0year/4);

% Whole year matrix of IPV current inputs
daymatrix = reshape(ryH0year,[96,365]);
IPVMatrix = daymatrix/36*1000;

% Reshaping the matrix to a 1 coulumn vector IPV
IPV = reshape(IPVMatrix,[36040,1]);
etaDC = 0.95./(1+1./(IPV*147.2444/max(IPV)));
rectifierEfficiency = independent
Idcout = IPV.*etaDC; %Current after the rectifier
[etacell] = Fetacell(Idcout); %Calculates the current resulting of PEM cell efficiec
[etasys0] = Fetasys0(Idcout); %Consider parasitic power and 1% hydrogen losses
etalifetime = FPEMLifetime(ryH0year); %Takes the efficiency losses caused by cell de

% PEM system efficiency including cell, syso and etalifetime efficiencies, Idcout as
etasys = etacell.*etasys0.*etalifetime;
```

“IPVMatrix” converts the volatile power input into a volatile current flow, as the voltage of the PEMEL stack is assumed to be constant at 36 V. The main model calculations start with “Idcout”. The residual load current vector “IPV” is multiplied with the performance of the AC/DC rectifier. “Idcout” is the input vector for three functions “Fetacell”, “Fetasys0” and “FPEMLifetime”. The product of all vectors results in the system efficiency “etasys”. The volatile hydrogen production flow can now be calculated as follows:
The yearly cumulated SNG product gas volume of the methanation reactor can be calculated as follows:

```matlab
% yearly cumulative sum of produced hydrogen in Nm3
Hydrogenvolsum = cumsum(HydrogenVolume);

% Hydrogen intermediate storage periods
[Storageperiods] = FHydrogenStoragePeriods(Hydrogenvolume).*1170;%Hydrogenvolsum;
Storageperiods(Storageperiods==0)=NaN;

% SNG Production Calculation in Nm3
SNGConversion = 0.29; % = 0.9*0.2+0.1 -> 90 % Conversion of CO2— cr;
H2Share = 5/4; % needed, because SNG production calculated by 1
SNGvolsum = Hydrogenvolsum.*Storageperiods/1170.*H2Share.*SNGConversion; % yearly sum
```

In the first step the cumulated hydrogen volume is computed. The function “FHydrogenStoragePeriods” is including the hydrogen intermediate storage behaviour. The “StoragePeriods” vector is inserted in the SNG production model “SNGvolsum”, which delivers the cumulated SNG volume as a vector for the reference year. The constants “SNGConversion” and “H2Share” result from the assumptions made in the thesis, as a volume reduction and a CO2 conversion of 90 % is proposed.

Furthermore the excess heat calculation of the methanation reactor can be calculated, assuming an excess heat flow of 7.07 MJ/Nm³:

```matlab
% Excess Heat Production of Methanation per Discharge [MJ], calculated by feed gas
MethaneinSNGgas0 = FCumSumBack(SNGvolsum); % delivers the daily generated SNG g
MethaneinSNGgas0(MethaneinSNGgas0 == 0) = NaN;
Qexcess = 7.07; % MJ/Nm3 SNG product gas, the conversion efficiency is alr
ExcessHeatMeth = MethaneinSNGgas0.*Qexcess/3.6; % Excess heat production per disch
```

In the end of the script, the model related figures are plotted. Figures 1-3 refer to the code that was mentioned above. Figures 4-7 also include a heat load profile (‘Heat-LoadProfile_Wuerzburg.xlsx’) of a site in Wuerzburg. In general the principle for the heat considerations is the same as for the residual load excel sheet. The required data is imported from the excel sheet into the Matlab® script and is then being processed, which is not further explained here.
Annex 6: Renewable excess electricity in the Northern Germany grid (2011) [58]
Annex 7: Financial evaluation of a small-scale PtSNG unit investment via bank loan [71]

Equations

\[ ae = \sum_i(s_i - c_i) \]

\[ s_i = p_i \cdot q_i \]

\[ c_i = capex_i \cdot crf_i + opex_i \]

\[ crf_i = \frac{WACC \cdot (1 + WACC)^{N_i}}{(1 + WACC)^{N_i} - 1} \]

\[ WACC = \frac{E}{E+D} k_E + \frac{D}{E+D} k_D \]

Descriptions

- (ae) annualized earnings of an investment
- (s_i) annual revenues of component i
- (c_i) annualized cost of component i
- (p_i) specific price per component
- (q_i) quantity of component i
- (capex) capital expenditures
- (opex) annual operational expenditures
- (crf) capital recover factor
- (WACC) weighted average cost of capital
- (N_i) lifetime of component i
- (E) Equity, (D) Dept, (k_E) return on equity, (k_D) cost of dept

<table>
<thead>
<tr>
<th>s</th>
<th>Capex</th>
<th>Opex</th>
<th>WACC</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>[€/a]</td>
<td>[€]</td>
<td>[€/a]</td>
<td>[-]</td>
<td>[a]</td>
</tr>
<tr>
<td>443</td>
<td>50 000</td>
<td>80</td>
<td>0.06</td>
<td>20</td>
</tr>
</tbody>
</table>

\[ crf = \frac{0.06 \cdot (1 + 0.06)^{20}}{(1 + 0.06)^{20} - 1} = 0.087 \quad 1/a \]

\[ c = 50 000 \cdot 0.087 \cdot \frac{1}{a} + 80 \cdot \frac{\€}{a} = 4439 \frac{€}{a} \]

\[ ae = 443 \frac{€}{a} - 4439 \frac{€}{a} = -3996 \frac{€}{a} \]

Costs and revenues differ from each other in an order of one magnitude. The capex for the break-even point of a 5 kW PtSNG plant is calculated as follows:

\[ c_{\text{break-even}} = ae \]
\[ c_{\text{break-even}} = CAPEX_{\text{break-even}} \cdot 0.087 \frac{1}{a} + 80 \frac{\text{€}}{a} = 443 \frac{\text{€}}{a} \]

\[ CAPEX_{\text{break-even}} = 4172 \text{ €} \]

The **break-even costs per kilowatt** are:

\[ CAPEX_{\text{break-even}} = 834 \frac{\text{€}}{kW} \]