Thermal gasification based hybrid systems

IEA Bioenergy Task 33 special project
Thermal gasification based hybrid systems

IEA Bioenergy Task 33 special project

Author:

Dr. Jitka Hrbek, Vienna University of Technology, Austria
Abstract

Synthesis gas from thermal gasification of biomass and waste can be used in many different ways: for production of heat and electricity or for production of biofuels and chemicals.

In this special Task 33 report a production of renewable gaseous and liquid biofuels in combination with renewable hydrogen will be described. It will be shown, how the excess electricity, which could not be fed into the grid immediately in order not to be overloaded, can be stored in form of hydrogen and how this renewable hydrogen can boost the production of renewable biofuels.

It is well known that the covering of our energy demand now and in the future must be based on a combination and synergies of different technologies as well as different energy sources. Only in this way, it will be possible to leave the energy policy based on fossil fuels.

The production of renewable gaseous and liquid biofuels as a combination of different technologies: thermal gasification and electrolysis; different energy sources such as biomass and wind and/or solar energy is the focus of this work.

Energy Strategy and Energy Roadmap are the starting points of the report, further an overview on potential of biomass in EU and worldwide is given. A theoretical overview on the technology of thermal gasification and related issues, such as product gas applications: Fischer-Tropsch synthesis technology, hydrogen and methanol production as well as Bio-SNG production are described here.

Further, the power production from wind and solar energy, as well as direct employment of solar power during the thermal gasification can be found here.

The production of hydrogen using the surplus electricity from wind and solar energy through electrolysis is described in this report, including different types of electrolysers, their comparison and outlook for the future.

Special attention is given to the combinations of technologies mentioned above (Power to Gas and Power to Liquids systems) for the boosted production of renewable gaseous and liquid biofuels, based on thermal gasification.

Pilot and demonstration PtG and PtL projects, which are based on thermal biomass gasification or where the thermal gasification could be employed as a source of carbon oxides, complete this special IEA Bioenergy Task 33 report.
# Table of contents

Abstract .......................................................................................................................... 1  
Table of contents .............................................................................................................. 2  
Abbreviations ................................................................................................................... 4  
List of figures ................................................................................................................... 5  
List of tables .................................................................................................................... 7  
1.  Introduction .......................................................................................................... 8  
2.  Energy strategy ..................................................................................................... 9  
   2020 Energy Strategy .................................................................................................. 9  
   2030 Energy Strategy .................................................................................................. 9  
   2050 Energy Strategy .................................................................................................. 9  
   Energy Roadmap ........................................................................................................ 9  
3.  Future potential of biomass ....................................................................................11  
4.  Thermal gasification of biomass ..............................................................................13  
   4.1 Product gas applications ...........................................................................................15  
      4.1.1 Fischer Tropsch synthesis ....................................................................................15  
      4.1.2 Hydrogen production ..........................................................................................15  
      4.1.3 Methanol production ...........................................................................................16  
      4.1.4 Bio-SNG ...........................................................................................................16  
5.  Solar and wind power energy ..................................................................................17  
   5.1 Solar power ............................................................................................................17  
      5.1.1 Efficiency ..........................................................................................................17  
      5.1.2 Costs ...............................................................................................................18  
      5.1.3 Solar power – future contribution to power system .................................................20  
      5.1.4 Thermal gasification using solar energy .................................................................20  
   5.2 Wind power ............................................................................................................24  
      5.2.1 Efficiency ..........................................................................................................24  
      5.2.2 Capacity ...........................................................................................................24  
      5.2.3 Costs ...............................................................................................................24  
6.  Storage of fluctuating energy .................................................................................27  
   6.1 Power to Gas ........................................................................................................28  
      6.1.1 Electrolysis .......................................................................................................30  
      6.1.2 Hydrogen ..........................................................................................................36  
      6.1.3 Methanation ......................................................................................................37  
      6.1.4 Biomass gasification as a carbon source for PtG principle (SNG production) ........38  
      6.1.5 Efficiency ..........................................................................................................39  
      6.1.6 Economics of PtG systems ...................................................................................40  
      6.1.7 Power to gas applications ....................................................................................42  
      6.1.8 Power to Gas - Projects .....................................................................................44
6.2 Power to Liquids........................................................................................................58
  6.2.1 Fischer-Tropsch synthesis (F-T synthesis) ..............................................................58
  6.2.2 Methanol production ...........................................................................................64
  6.2.3 Advantages of PtL to PtG systems .......................................................................69
  6.2.4 Power to liquids - Projects ..................................................................................71
7. Summary .....................................................................................................................86
References .......................................................................................................................88
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEL</td>
<td>Alkaline electrolysis</td>
</tr>
<tr>
<td>ASU</td>
<td>Air separation unit</td>
</tr>
<tr>
<td>BFB</td>
<td>Bubbling fluidized bed</td>
</tr>
<tr>
<td>BioSNG</td>
<td>Synthetic natural gas from biological sources (e.g. biomass)</td>
</tr>
<tr>
<td>CAPEX</td>
<td>Capital expenditures</td>
</tr>
<tr>
<td>CSTP</td>
<td>Concentrated solar thermal process</td>
</tr>
<tr>
<td>CSTR</td>
<td>Continuously stirred tank reactor</td>
</tr>
<tr>
<td>DENA</td>
<td>Deutsche Energie-Agentur (German Energy Agency)</td>
</tr>
<tr>
<td>DH</td>
<td>District heating</td>
</tr>
<tr>
<td>FCC</td>
<td>Fluid catalytic cracking</td>
</tr>
<tr>
<td>FLH</td>
<td>Full load hours</td>
</tr>
<tr>
<td>GWEC</td>
<td>Global Wind Energy Council</td>
</tr>
<tr>
<td>HTAG</td>
<td>High temperature air and steam gasification</td>
</tr>
<tr>
<td>HTE</td>
<td>High-temperature electrolysis</td>
</tr>
<tr>
<td>HTSG</td>
<td>High temperature steam gasification</td>
</tr>
<tr>
<td>IRENA</td>
<td>International Renewable Energy Agency</td>
</tr>
<tr>
<td>KTH</td>
<td>Royal Institute of Technology in Stockholm</td>
</tr>
<tr>
<td>LCF</td>
<td>Line-focus solar collectors</td>
</tr>
<tr>
<td>LC0E</td>
<td>Levelized costs of energy</td>
</tr>
<tr>
<td>MCEC</td>
<td>Molten carbonate electrolysis cell</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten carbonate fuel cell</td>
</tr>
<tr>
<td>OPEX</td>
<td>Operating expense</td>
</tr>
<tr>
<td>PEM</td>
<td>Polymer electrolyte membrane</td>
</tr>
<tr>
<td>PFC</td>
<td>Point-focus solar collector</td>
</tr>
<tr>
<td>PFR</td>
<td>Plug flow reactor</td>
</tr>
<tr>
<td>PtG</td>
<td>Power-to-Gas technology</td>
</tr>
<tr>
<td>PtL</td>
<td>Power-to-Liquids technology</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>ROI</td>
<td>Return of investment</td>
</tr>
<tr>
<td>SG</td>
<td>Steam generator</td>
</tr>
<tr>
<td>SNG</td>
<td>Substitute natural gas</td>
</tr>
<tr>
<td>SOEC</td>
<td>Solid oxide electrolysis cell</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>TCI</td>
<td>Total capital investment</td>
</tr>
<tr>
<td>WWII</td>
<td>World war II</td>
</tr>
</tbody>
</table>
# List of figures

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Figure Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Summary of EU biomass potential (Mtoe) over categories</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>Contribution of each biomass resource category to the global potential of biomass for energy use in 2050</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>Schematic diagram for hydrogen production during biomass gasification</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>Future module prices in different scenarios based on the historical “learning rate”</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>Cost of electricity from new solar power plants in Southern and Central Europe</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>Cost of electricity from new solar power plants in North America, Australia, India and Mena region</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>Cost of electricity and contribution to power system per technology, in Germany 2035</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>Reactor concept</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>System scheme for modeled concentrating solar gasification facility</td>
<td>21</td>
</tr>
<tr>
<td>10</td>
<td>Solar-biomass power generation system</td>
<td>22</td>
</tr>
<tr>
<td>11</td>
<td>Hybrid power generation system</td>
<td>23</td>
</tr>
<tr>
<td>12</td>
<td>Marginal efficiency change with increase of heat input from CSTP</td>
<td>23</td>
</tr>
<tr>
<td>13</td>
<td>Summary of Expert Survey Findings</td>
<td>25</td>
</tr>
<tr>
<td>14</td>
<td>Estimates of Median-Scenario LCOE</td>
<td>25</td>
</tr>
<tr>
<td>15</td>
<td>Power-to-gas process chain</td>
<td>28</td>
</tr>
<tr>
<td>16</td>
<td>Roadmap PtG</td>
<td>29</td>
</tr>
<tr>
<td>17</td>
<td>Pilot projects in Germany</td>
<td>29</td>
</tr>
<tr>
<td>18</td>
<td>Equilibrium cell voltage as function of temperature for different pressure</td>
<td>30</td>
</tr>
<tr>
<td>19</td>
<td>Functional principle of three types of electrolysis</td>
<td>31</td>
</tr>
<tr>
<td>20</td>
<td>Comparison of selling prices of AEL, PEM and SOEC systems</td>
<td>33</td>
</tr>
<tr>
<td>21</td>
<td>Costs comparison and target markets for 2025 between SOEC, PEM and alkaline based electrolysers</td>
<td>35</td>
</tr>
<tr>
<td>22</td>
<td>Market prospective of hydrogen producers by electrolysis</td>
<td>36</td>
</tr>
<tr>
<td>23</td>
<td>Coupling of two-bed steam gasifier and electrolysis for PtG (methane) and PtL</td>
<td>39</td>
</tr>
<tr>
<td>24</td>
<td>Sankey diagram of the PtG process efficiency</td>
<td>40</td>
</tr>
</tbody>
</table>
53  Effect of electricity price on payback period and ROI  74
54  Methanol/DME synthesis based on electrolysis assisted gasification of wood  75
55  Principle of a pressurized bubbling fluidized bed gasifier from Carbona  76
56  Sankey chart of mass flows in the gasification concept  77
57  The Sunfire process Power to liquids  79
58  Blue crude breakdown  83
59  Audi e-diesel plant in Laufenburg  85

List of tables

Nr.  Page
1  Most important gasification reactions  14
2  Comparison of alkaline and PEM technologies  33
3  Comparison of some properties of alkaline water electrolysis and PEM electrolysis  34
4  Store&Go demonstration sides characteristics  54
5  Audi e-gas project data  57
6  Raw and final products from hydrocracking  63
7  Raw and final products before and after FCC  63
8  Summary of performance metrics  66
9  Gasoline and methane production with and without adding of extra hydrogen  68
10  Biofuels output potential  69
11  Scenario 1 - dual fluidized bed gasifier with FT synthesis  72
12  Scenario 2 - dual fluidized bed gasifier with FT synthesis with steam generation process  72
13  Scenario 3 - Winddiesel  72
14  Gasifier mass and heat balance  76
15  Technical specifications of electrolysis module by Sunfire  80
16  First commercial plant for the production of blue crude – project details  82
1. Introduction

The Earth offers a huge amount of renewable energy in different forms. Wind-, solar- and geothermal energy, ocean power and biomass energy are just some of them. The potential of this renewable energy is so huge that it would be possible to stop using fossil fuels and switch just to renewables to cover or even exceed our energy demand. The switching from fossil to renewable energy would solve more environmental problems at the same time, but our energy technology and infrastructure is not advanced enough to go this way immediately. Unfortunately, we are still not able to utilize this renewable energy efficiently and store the surplus of fluctuating energy such as wind and solar energy in smart forms directly, economic feasible and without considerable losses.

It is clear that not just one renewable energy source will be able to cover our energy demand, but only combined share of renewable sources will be the right way for the future.

Energy scenarios and roadmaps indicate that intermittent renewable energy sources such as wind power and solar photovoltaic will be crucial for the power supply in the future. On the other hand, the dramatic reduction in generation cost of solar and wind power production in the last years makes it difficult for biomass-based power to compete in costs with those renewable sources.

Anyway, not the competition but synergies of different technologies and energy sources is the right way to the future. Each source and technology have their pros and cons, and the clue for their employment is their right combination.

Therefore, biomass, which is moreover a scarce resource, should be used in applications in which solar and wind cannot compete so well, for example production of fuels, chemicals and materials and preferably in combination with these fluctuating energy sources. Biomass as a source of energy is available anytime, in comparison with wind and solar ones and can therefore help by balancing the grid as well.

This report describes the thermal gasification based hybrid systems, which means in this case, the combinations of different technologies for production of biofuels, called also electrofuels. Volatile energy surplus (solar, wind), which is converted through electrolysis in hydrogen and usage of this renewable hydrogen in thermal gasification process for production of gaseous (PtG) or liquid (PtL) products.

PtG and PtL can help reduce CO₂ emissions in various sectors of consumption in that the renewable gaseous or liquid fuels replaces fossil ones in mobility, industry, heat supply and power generation. As an electricity storage method, PtG and PtL can also contribute to compensating the increasing fluctuations in electricity generation from wind and solar energy, and facilitate long-term use of electricity that could not be integrated directly into the electricity grid.

An important motivation behind hybrid systems is the possibility to switch between different energy sources in an optimal way. Usually one or more of the following drivers can be expected [1]:

- Increase in self-sufficiency in terms of energy and reliability
- Reduction in emissions, lower environmental impact
- Avoided cost of purchase of oil or electricity (especially peak power cost)
- Lower maintenance requirement for biomass or oil boiler
- Increase in component lifetime and efficiency
- Optimized dimensioning of system components
- Avoided investment in storage system (bioenergy is storable) or in new production capacity (waste heat recovery)
2. Energy strategy

2020 Energy Strategy
By 2020, the EU aims to reduce its greenhouse gas emissions by at least 20% (from 1990 levels), increase the share of renewable energy to at least 20% of consumption, and achieve energy savings of above 20%. All EU countries must also achieve a 10% share of renewable energy in their transport sector.

Through the attainment of these targets, the EU can help combat climate change and air pollution, decrease its dependence on foreign fossil fuels, and keep energy affordable for consumers and businesses. [2]

2030 Energy Strategy
EU countries have agreed on a new 2030 Framework for climate and energy, including EU-wide targets and policy objectives for the period between 2020 and 2030. These targets aim to help the EU achieve a more competitive, secure and sustainable energy system and to meet its long-term 2050 greenhouse gas reductions target.

The strategy sends a strong signal to the market, encouraging private investment in new pipelines, electricity networks, and low-carbon technology. The targets are based on a thorough economic analysis that measures how to cost-effectively achieve decarbonisation by 2050.

The cost of meeting the targets does not substantially differ from the price we will need to pay in any case to replace our ageing energy system. The main financial effect of decarbonisation will be to shift our spending away from fuel sources and towards low-carbon technologies. [3]

Targets for 2030
- a 40% cut in greenhouse gas emissions compared to 1990 levels
- at least a 27% share of renewable energy consumption
- at least 27% energy savings compared with the business-as-usual scenario.

2050 Energy Strategy
The EU has set itself a long-term goal of reducing greenhouse gas emissions by 80-95%, when compared to 1990 levels, by 2050. The Energy Roadmap 2050 explores the transition of the energy system in ways that would be compatible with this greenhouse gas reductions target while also increasing competitiveness and security of supply.

To achieve these goals, significant investments need to be made in new low-carbon technologies, renewable energy, energy efficiency, and grid infrastructure. Because investments are made for a period of 20 to 60 years, policies that promote a stable business climate, which encourages low-carbon investments, must start being made today. [4]

Energy Roadmap
The European Commission’s 2011 Energy Roadmap set out four main routes to a more sustainable, competitive and secure energy system in 2050: energy efficiency, renewable energy, nuclear energy, and carbon capture and storage. It combined these routes in different ways to create and analyze possible scenarios for 2050.

Conclusions of the analysis [5]:
- Decarbonizing the energy system is technically and economically feasible. In the long run, all scenarios that achieve the emissions reduction target are cheaper than the continuation of current policies.
- Increasing the share of renewable energy and using energy more efficiently are crucial, irrespective of the particular energy mix chosen.
- Early infrastructure investments cost less, and much of the infrastructure in the EU built 30 to 40 years ago needs to be replaced anyway. Immediately replacing it with low-carbon alternatives can avoid costlier changes in the future. According to the International Energy Agency, investments in the power sector made after 2020 would cost 4.3 times as much as those made before 2020.
- A European approach is expected to result in lower costs and more secure energy supplies when compared to individual national schemes. With a common energy market, energy can be produced where it is cheapest and delivered to where it is needed.
3. Potential of biomass

In the Atlas of EU biomass potentials [6] all biomass types are presented, there are three sectors under which the biomass categories have been classified: agriculture, forestry and waste biomass.

Under these main sectors, there are categories of dedicated biomass production such as biofuel crops, woody and grassy crops, stem wood production and by-products and waste categorized in primary, secondary and tertiary levels.

In the figures below a summary of the relative contribution is shown.

![Figure 1: Summary of EU biomass potential (Mtoe) over categories](image)

The largest potential is in the agricultural residues class. This class consists of manure, straw and cutting and prunings from permanent crops. The second largest contribution comes from round wood potential, although one can doubt whether this feedstock should really be included as the price of it is far above levels at which bioenergy can compete with competing uses of wood. The third place is covered by the waste group and the additional harvestable round wood potential. The contribution of tertiary forestry residues should not be underestimated as price levels of these potentials are generally more likely to be in the limits of commercial bioenergy production.

Many scenarios predict a potential in biomass worldwide. However, published estimates of the total global bioenergy production potential in 2050 ranged from 33 to 1,135 EJ annually [7], from which 0 to 358 EJ annually came from woody biomass [8]. Energy crops from surplus agricultural land have the largest potential contribution of 0-988 EJ/year [7].

Overall, differences between the various scenarios are due to large differences in demand and energy mix, because of variations in population dynamics, and economic and technological development.

Following figure shows a contribution of each biomass resource category to the global potential of biomass for energy use in 2050.
In the near future biomass is going to be a limited resource. A key for biomass usage is sustainability. Biomass can be used to provide heat and electricity as well as liquid biofuels and biogas for transportation. However, without structural changes to the energy system, the production of biomass energy crops and removal of biomass residues from forest and agricultural systems for energy production can result in negative environmental, economic, or social impact. Moreover, unsustainable biomass production would erode the climate related environmental advantage of bioenergy.

Figure 2: Contribution of each biomass resource category to the global potential of biomass for energy use in 2050 [7]
4. Thermal gasification of biomass

Thermal gasification is a complete breakdown of the biomass particles at high temperatures (700-1200°C) into a combustible gas, volatiles and ash in an enclosed reactor (gasifier) in the presence of any externally supplied oxidizing agent (air, O₂, H₂O, CO₂, etc.) when equivalent ratio (ER) is 0 < ER < 1.

ER = 1 if the stoichiometric amount of oxidising agent is present. Stoichiometric amount is the theoretical amount of air or any other oxidizing agent required to burn the fuel completely.

Gasification is an intermediate step between pyrolysis and combustion. It is a two-step, endothermic process. During the first step the volatile components of the fuel are vaporized at temperatures below 600°C by a set of complex reactions. No oxygen or other reactive agent is needed in this phase of the process.

Hydrocarbon gases, hydrogen, carbon monoxide, carbon dioxide, tar and water vapour are included in the volatile vapours. Char (fixed carbon) and ash are the by-products of the process, which are not vaporized. In the second step, char is gasified through the reactions with oxygen, steam, carbon dioxide and/or hydrogen. In some gasification processes (indirect gasification), some of the unburned (not gasified) char is combusted in a separate reactor or reactor zone to release the heat needed for the endothermic gasification reactions. Main gasification products are gas, char, and tars. Gasification products, their composition and amount are strongly influenced by gasification agent, temperature, and pressure, heating rate and fuel characteristics (composition, water content, granulometry). Gaseous products formed during the gasification may be after cleaning and conditioning further used for heating, electricity production or synthesis. The main product gas components are CO, H₂, CO₂, H₂O, CH₄ and other hydrocarbons.

The following table shows the most important gasification reactions.
Table 1: Most important gasification reactions

<table>
<thead>
<tr>
<th>Reaction Description</th>
<th>Chemical Equations</th>
<th>ΔH</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary devolatilization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary tar (CH₅Oₓ)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass → CO, H₂, CO₂, CH₄, C₂H₄, H₂O</td>
<td>[eq. 1]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tar cracking and reforming</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary tar → CO, CO₂, CH₄, C₂H₄, H₂</td>
<td>[eq. 2]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Homogenous gas-phase-reactions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary tars → C, CO, H₂</td>
<td>[eq. 3]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂ + 0,5 O₂ → H₂O</td>
<td>-242 kJ/mol</td>
<td>H₂ – Combustion (oxidation)</td>
<td></td>
</tr>
<tr>
<td>CO + 0,5 O₂ → CO₂</td>
<td>-283 kJ/mol</td>
<td>CO - Combustion (oxidation)</td>
<td></td>
</tr>
<tr>
<td>CH₄ + 0,5 O₂ → CO + 2 H₂</td>
<td>-110 kJ/mol</td>
<td>CH₄ - Combustion (oxidation)</td>
<td></td>
</tr>
<tr>
<td>CH₄ + CO₂ → 2 CO + 2 H₂</td>
<td>+247 kJ/mol</td>
<td>Dry reforming reaction</td>
<td></td>
</tr>
<tr>
<td>CH₄ + H₂O → CO + 3 H₂</td>
<td>+206 kJ/mol</td>
<td>Steam reforming methanisation</td>
<td></td>
</tr>
<tr>
<td>CO + H₂O → CO₂ + H₂</td>
<td>-40,9 kJ/mol</td>
<td>Water-gas-shift reaction</td>
<td></td>
</tr>
<tr>
<td>Heterogenous reactions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C + O₂ → CO₂</td>
<td>-393,5 kJ/mol</td>
<td>Partial carbon oxidation</td>
<td></td>
</tr>
<tr>
<td>C + 0,5 O₂ → CO</td>
<td>-123,1 kJ/mol</td>
<td>Boudoar equilibrium</td>
<td></td>
</tr>
<tr>
<td>C + CO₂ → 2 CO</td>
<td>+159,9 kJ/mol</td>
<td>Water gas reaction (steam reforming)</td>
<td></td>
</tr>
<tr>
<td>C + H₂O → CO + H₂</td>
<td>+118,5 kJ/mol</td>
<td>Steam reforming</td>
<td></td>
</tr>
<tr>
<td>C + 2 H₂ → CH₄</td>
<td>-87,5 kJ/mol</td>
<td>Methane production (hydrogasification)</td>
<td></td>
</tr>
</tbody>
</table>
4.1 Product gas applications

The current R&D on applications for synthesis gas from biomass, apart from CHP is mainly focused on transportation fuels and only very little on chemicals. Most of R&D is performed on Fischer Tropsch- and SNG synthesis, hydrogen production as well as production of methanol, ethanol and mixed alcohols.

Therefore, in the following, a short description of the most product gas applications will be given.

In comparison with product gas, synthesis gas consists mainly of hydrogen and carbon monoxide. In some cases, also small amounts of carbon dioxide or methane are present. To use the product gas from a biomass gasifier as synthesis gas, there are several properties, which have to be taken into account:

- $H_2:CO$ ratio
- Amount of inerts, like nitrogen
- Amount of methane and higher hydrocarbons
- Catalyst poisons like sulphur-, nitrogen- and chlorine components
- Operation pressure

For most synthesis a $H_2:CO$ ratio of 2 is required. This ratio is normally adjusted in a separate catalytic reactor before the synthesis reactor, where some $CO+H_2O$ is converted to $H_2+CO_2$ by the water gas shift reaction. If the gasifier produces already the correct $H_2:CO$ ratio, the exothermal water gas shift reaction can be avoided, which reduces investment and operation costs and increases the efficiency as well.

In the case of SNG synthesis processes, the presence of methane and hydrocarbons can be beneficial. However, hydrocarbons need to be converted (e.g. via steam reforming) into syngas in Fischer-Tropsch, methanol, hydrogen, etc. synthesis processes.

Impurities like nitrogen act as inerts during the synthesis and their concentrations have to be as low as possible. The inerts reduce the partial pressures of the reactive species $H_2$ and $CO$ and by this effect reduce the conversion. Especially for synthesis reactions, where the product is separated as a liquid and where recycle of remaining unconverted gas is done (e.g. methanol), the inerts have to be bled off, as they would otherwise be accumulated. Also for production of BioSNG the inerts have to be below 1 vol.%, as otherwise the heating value of the BioSNG will not fulful the requirements of natural gas.

4.1.1 Fischer Tropsch synthesis

Fischer–Tropsch (FT) synthesis is based on the conversion of a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. This technology, a key component of gas to liquids technology, produces synthetic fuels and chemicals from biomass, coal or natural gas.

Details regarding thermodynamics, reactors, catalysts and products of FT synthesis will be described later in the chapter 6.2.1.

4.1.2 Hydrogen production

Hydrogen is one of the most promising energy carriers for the future. Several investigations on hydrogen production methods have been conducted over the past decades. Biomass is potentially a reliable energy source for hydrogen production. It is renewable, easy to use and CO$_2$ neutral. Therefore, it is expected that biomass gasification process will be available for large-scale hydrogen production.

Hydrogen can be produced from the gasification product gas through the steam reforming and water-gas shift reactions. Using a dual fluidized bed gasification system with CO$_2$ adsorption along
with suitable catalysts, it is possible to achieve a hydrogen yield up to 70 vol% directly in the gasifier [9].

![Schematic diagram for hydrogen production during biomass gasification](image)

Figure 3: Schematic diagram for hydrogen production during biomass gasification [10]

Furthermore, the costs of hydrogen production by biomass gasification in very large scale are competitive with natural gas reforming [11].

### 4.1.3 Methanol production

Methanol, also known as methyl alcohol, wood alcohol, or wood spirits, is often abbreviated as MeOH. It can be produced from fossil or renewable resources and can be used either directly as a transportation fuel, or can be converted further to hydrocarbons (methanol to gasoline).

Further details to production of methanol from synthesis gas can be found in the section 6.2.2.

### 4.1.4 Bio-SNG

Natural gas that is produced from coal or biomass is known as "synthetic natural gas" or "substitute natural gas" (SNG). The typical catalyst for methanation is nickel and the main reaction is

\[
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{[eq. 15]}
\]

Ni-based catalysts are also active in water-gas shift and hydration of higher hydrocarbons, like olefins. Normally a H\(_2\):CO ratio of 3 is necessary, which is achieved in a water gas shift reactor before the methanation. In some types of reactors, e.g. fluidized beds, the water gas shift can be done also in parallel with the methanation, so no external adjustment of the H\(_2\):CO ratio is necessary.

The methanation can be done at atmospheric pressure, although from the thermodynamics higher pressure is preferred.

As Ni-based catalysts are sensitive to sulphur poisoning, gas treatment before the methanation is quite important, and sulphur compounds have to be removed to below 0.1ppm.

Almost all biomass gasifiers (except for high-temperature entrained-flow processes) contain some methane in the product gas, depending on the operation temperature. As methane does not have to be converted in the methanation, high methane content in the synthesis gas is a big advantage for the production of BioSNG (the overall efficiency is higher, the higher the methane content in the product gas is). So, indirect gasifiers, which have a methane content of 10 vol% or more, are especially advantageous for methanation.
5. Solar and wind power energy

5.1 Solar power

Solar power is the conversion of energy from sunlight into electricity, either directly using photovoltaics (PV), indirectly using concentrated solar power, or a combination of both. Photovoltaic cells convert light into an electric current using the photovoltaic effect.

Photovoltaics were initially solely used as a source of electricity for small and medium-sized applications, from the calculator powered by a single solar cell to remote homes powered by an off-grid rooftop PV system.

Commercial concentrated solar power plants were first developed in the 1980s. The 392 MW Ivanpah installation is the largest concentrating solar power plant in the world, located in the Mojave Desert of California [12]. With the end of 2018 Noor Complex Solar Power Plant in Morocco will overcome Ivanpah and will provide 580 MW. The project in Morocco is expected to provide electricity for over 1 million people [13].

As the cost of solar electricity has dramatically decreased, the number of grid-connected solar PV systems has grown into the millions and utility-scale solar power stations with hundreds of megawatts are being built. Solar PV is rapidly becoming an inexpensive, low-carbon technology to harness renewable energy. The current largest photovoltaic power station in the world is the 850 MW Longyangxia Dam Solar Park, in Qinghai, China [14].

The International Energy Agency projected in 2014 that under its "high renewables" scenario, by 2050, solar photovoltaics and concentrated solar power would contribute about 16 and 11 percent, respectively, of the worldwide electricity consumption, and solar would be the world's largest source of electricity. In 2016, solar power provided just 1% of total worldwide electricity production but growing 33% per annum.

5.1.1 Efficiency

Electrical efficiency is a contributing factor in the selection of a photovoltaic system. However, the most efficient solar panels are typically the most expensive, and may not be commercially available. Therefore, selection is also driven by cost efficiency and other factors.

The most efficient type of solar cell to date is a multi-junction concentrator solar cell with an efficiency of 46.0% produced by Fraunhofer ISE (December 2014). The highest efficiencies achieved without concentration include a material by Sharp Corporation at 35.8% using a proprietary triple-junction manufacturing technology (2009) and Boeing Spectrolab (40.7% also using a triple-layer design). The US company SunPower produces cells that have an efficiency of 21.5%, well above the market average of 12–18%. 

17
5.1.2 Costs

Figure 4: Future module prices in different scenarios based on the historical “learning rate” [15]

The feed-in tariff paid for electricity from large-scale photovoltaic installations in Germany fell from over 40 ct €/kWh for installations connected in 2005 to 9 ct €/kWh for those connected in 2014. This sudden reduction came as a major surprise to most industry experts and policy makers. Power produced by solar photovoltaics, long known as one of the most expensive renewable energy technologies, is today cost competitive with both wind onshore and power generated by fossil fuels in Germany. The feed-in tariff for large scale solar photovoltaic power plants in Germany installed in January 2015 is 8.7 ct €/kWh, not adjusted for inflation. This compares to a feed-in tariff for wind onshore, ranging from 6 to 8.9 ct €/kWh in Germany, and to the cost of producing power through newly built gas- or coal-fired power plants, ranging from 7 to 11 ct €/kWh. [15]

Even lower prices for solar power have been reported in sunnier regions of the world. A power purchase agreement for a 200 MW-solar farm in Dubai was recently signed for 5 ct €/kWh (5.84 $ct/kWh). Projects under construction in Brazil, Uruguay and other countries are reported to produce at costs below 7 €ct/kWh. These power generation costs largely confirm the notion that the cost of building and operating a large-scale solar photovoltaic power plant is comparable around the world, once market barriers are removed.

Depending on annual sunshine, power costs of 4-6 €ct/kWh are expected in Europe by 2025, reaching 2-4 €ct/kWh by 2050. For the next decade, this represents a cost reduction of roughly one third below the 2015 level.

These results indicate that in future, power produced from large-scale solar photovoltaic plants will be cheaper than power produced from any conventional technology in large parts of Europe. The cost of electricity produced in conventional, large-scale power plants typically ranges between 5 and 10 €ct/kWh. Cost competitiveness will thus be achieved under optimal conditions before 2025 and full cost competitiveness even under non-optimal conditions by 2050 at the latest. Further research is needed to analyze the cost competitiveness of different technologies in country and regional contexts and at different penetration rates.
In other regions of the world with higher solar irradiation, solar power will be even cheaper than in Europe. Some results indicate that solar power will become the cheapest source of electricity in many regions of the world, reaching costs of between 1.6 and 3.7 €ct/kWh in India and the Mena region (Middle East and North Africa) by 2050. Cost competitiveness with large-scale conventional power plants will be reached in these regions already within the next decade, at a cost for solar power by 2025 ranging between 3.3 and 5.4 €ct/kWh.

In North America, costs for large scale solar photovoltaics will reach 3.2 to 8.3 €ct/kWh in 2025 and 1.5 to 5.8 €ct/kWh in 2050, the wide cost range due to significant geographical differences within the region. In Australia, costs will reach 3.4 to 7.1 €ct/kWh in 2025 and 1.6 to 4.9 €ct/kWh in 2050. In both regions, cost competitiveness of solar photovoltaics at the best sites will be reached within the next decade and cost competitiveness for all sites only a number of years later.

The cost of hardware sourced from global markets will decrease irrespective of local conditions. Solar photovoltaic modules and inverters are traded already today on global markets, similar to
commodity products, and costs for other components are similarly global. While regional differences may exist due to the very young nature of utility-scale solar photovoltaic markets in different parts of the world, it is very unlikely that large differences in investment costs between different regions of the world will persist in the future.

5.1.3 Solar power – future contribution to power system

![Figure 7: Cost of electricity and contribution to power system per technology, in Germany 2035**[15]](image)

**Contribution of renewables based on scenario B2035 of grid development plan 2015, cost for other technologies based on Agora Energiewende 2014

As can be seen in the figure above, the electricity production costs of solar PVs and wind onshore will be similar by contribution to power system of about 30%.

5.1.4 Thermal gasification using solar energy

Thermal gasification is an endothermic process, where input heat is needed. This necessary heat is supplied by combustion of a part of a feedstock (direct gasification), or comes into the process from outside (indirect gasification, e.g. double bed).

A promising alternative to the conventional gasification is solar-assisted gasification process.

Sepe et al. [17] studied solar-assisted gasification process, the aim of his work was to design an efficient solar reactor configuration and to develop a computational model to assess and evaluate reactor performance. A new solar-assisted gasification reactor has been proposed in fixed bed, downdraft configuration. This type of reactor was chosen for its documented high efficiency and versatility.

![Figure 8: Reactor concept [17]](image)
Two advanced steam-gasification technologies of biomass, high temperature steam gasification (HTSG) and solar-assisted steam gasification have been thermodynamically investigated and compared with both conventional auto-thermal gasification and high temperature air and steam gasification (HTAG). A multi-phase, multi-physics 1D steady-state model has been built up to predict the biomass gasification performance, efficiency, yield and species of produced syngas at varying gasification methods and input parameters. In particular, heterogeneous and homogenous gasification reactions coupled with a radiative transfer were employed in the solar-assisted steam gasification.

The results showed that the solar-assisted steam gasification technology demonstrates its potential to produce high quality syngas (nearly 42% H₂ and 35% CO).

Moreover, it upgrades the heating value of the product syngas up to 1.4 times more than the original value, due to the additional solar energy induction. Compared with conventional auto-thermal gasification, it was found that the process efficiency can be improved from 65% to 81% if using the HTAG technology and the content of hydrogen in the syngas increased from 30% to 55% if applying HTSG. The modelling results agree considerably with the reported experimental and modelling data in literature, and able to return a direct comparison of advantage and disadvantage of each gasification method, in terms of syngas quantity and quality.

Another approach regarding the usage of solar power in combination with biomass gasification was solar-biomass generation system, where a two-stage gasifier was integrated. Zhang Bai et al. [18] proposed two different types of solar collectors, concentrating solar thermal energy at different temperature levels. They were applied to drive solar-biomass thermochemical process of pyrolysis (at about 643 K) and gasification (at about 1150 K). The product gas from the system was directly utilized by advanced combined cycle system for power generation. Numerical simulations were implemented to evaluate the on-design and off-design thermodynamic performances of the system. Results indicated that the proposed system could achieve an overall energy efficiency of 27.93% and a net solar-to-electric efficiency of 19.89% under the nominal condition.

A scheme of the proposed system can be seen in the following figure.
Thermal energy concentrated by solar collectors is used to heat feed-water to superheated steam directly or through a heat transfer fluid (i.e., synthetic oil or molten salt) and then the superheated steam drives the steam turbine for power generation.

Biomass pyrolysis as well as the feedstock preheating and steam generation is driven by mid-temperature solar thermal energy. This is concentrated by the line-focus solar collectors (LFC), which can achieve a relative increased collection efficiency than the point-focus collector (PFC) that operates in a higher temperature range.

For heating the biomass gasifier concentrated solar energy is used; the energy level of the introduced solar thermal energy in the proposed two-stage solar-biomass gasification system was improved from 0.68 to 0.9, which resulted in an energy level upgrading ratio of 32.35% compared to 21.62% in one-stage gasification mode.

The overall energy efficiency and the net solar-to-electric efficiency for the proposed novel system reached 27.93% and 19.89%, respectively. Additionally, the proposed system exhibited satisfactory thermo-dynamics performances except in December days during system off-design evaluation. In addition, the daily average net solar-to-electric efficiency achieved the improvement in the range of 8.6–21.33% compared to the one-stage gasification thermochemical system.

Also Tanaka et al. studied performance of a hybrid power generation using biomass gasification and concentrated solar thermal energy [19]. Biomass gasification was provided using bubbling fluidized bed (BFB) system, using CO2-H2O-O2 mixture and concentrated solar thermal process (CSTP).

BFB was simulated by a semi-kinetic model applying a continuously stirred tank reactor (CSTR) model for the bed behavior and a plug flow reactor (PFR) model for the freeboard reactions. Operating conditions of the plant and heat exchanger network were optimized separately. The effects of gasifying agents and heat input from CSTP on system efficiency among examined parameters were studied.

The hybrid power generating system mainly consisted of air separation unit (ASU), steam generator (SG), BFB gasifier, CSTP, gas turbine, and Rankine cycle, which can be seen in the following figure.
O₂, CO₂ and H₂O were supplied to BFB gasifier from air separation unit, exhaust gas from gas turbine and steam generator, respectively. O₂ and CO₂ were compressed to 1.5 MPa before injection. Pressure ratio of gas turbine was 10 and turbine inlet temperature was 1000 °C. CO₂ and O₂ were injected to the compressor of the gas turbine. The steam pressure and temperature of Rankine cycle was 4 MPa and 400°C. The temperature of molten salt from CSTP was 500 °C and it could be cooled down to 300 °C. Heat exchanger network was constructed independent of mass flow by using heat demands and supplies.

The effect of gasifying agent and heat input from CSTP on electric output were standing in focus of Tanaka’s work. Gasifying agent was a mixture of O₂, CO₂ and H₂O, and O₂ supply rate was adjusted to keep bed temperature at 800 °C. The mixing ratio of CO₂ and H₂O was varied from pure CO₂ to pure H₂O. Molar ratio of CO₂+H₂O to carbon in biomass was to be kept from 0.5 to 1.5. In all the cases, the electricity output was highest when pure H₂O was used at H₂O to carbon ratio around 0.5.

Following figure shows the effect of heat input from CSTP on the marginal efficiency.

As heat input from CSTP increased, the marginal efficiency increased with three distinct regions: 0-40 MW with highest increasing rate; 40-150 MW with moderate increasing rate; and constant marginal efficiency above 150 MW. The change in the rate of efficiency increase is due to pinch temperature change. When CSTP was lower than 40 MW, pinch temperature was at saturated temperature of steam to be supplied to BFB gasifier (198°C). When CSTP was around 40-150 MW, pinch occurred at inlet temperature of high pressure feed water heater in Rankine cycle (121°C) or dew point of steam in exhaust gas from gas turbine (100 °C). When CSTP was larger than around 150 MW, pinch occurred at inlet temperature of low pressure feed water heater in Rankine cycle (54°C).
5.2 Wind power

Wind power is the use of airflow through wind turbines to mechanically power generators for electric power. Wind, as well as solar power, gives variable power which is very consistent from year to year but which has significant variation over shorter time scales. It should be therefore used in conjunction with other electric power sources to give a reliable supply.

Wind turbines convert the wind’s kinetic energy into electrical power. The result of over a millennium of windmill development and modern engineering, today’s wind turbines are manufactured in a wide range of horizontal axis and vertical axis types.

5.2.1 Efficiency

Wind turbines convert around 45% of the wind passing through the blades into electricity (and almost 50% at peak efficiency [20]).

The smallest turbines are used for applications such as battery charging for auxiliary power. Slightly larger turbines can be used for making small contributions to a domestic power supply while selling unused power back to the utility supplier via the electrical grid. Arrays of large turbines, known as wind farms, have become an increasingly important source of renewable energy and are used in many countries, as a part of strategy to reduce their reliance on fossil fuels.

5.2.2 Capacity

In its Global Wind Report: Annual Market Update report, the Global Wind Energy Council (GWEC) announced that cumulative global wind power capacity grew by 12.6% to reach a total of 486.8 GW in 2016. The cumulative installed capacity is expected to reach more than 800 GW by the end of 2021. A study by the International Renewable Energy Agency (IRENA) showed that China, Germany, India and the US accounted for almost three-quarters of new wind energy capacity of 51GW in 2016 [21].

Wind energy supply has grown rapidly over the last decade. However, the long-term contribution of wind to future energy supply, and the degree to which policy support is necessary to motivate higher levels of deployment, depends also on the future costs of both onshore and offshore wind.

5.2.3 Costs

A summary of the results of 163 of the world’s foremost wind experts, was provided by Rian Wiser et al. [22]. Results suggest significant opportunities for cost reductions, but also underlying uncertainties. Under the median scenario, experts anticipate 24–30% reductions by 2030 and 35–41% reductions by 2050 across the three wind applications studied. Costs could be even lower: experts predict a 10% chance that reductions will be more than 40% by 2030 and more than 50% by 2050. Insights gained through expert elicitation complement other tools for evaluating cost-reduction potential, and help inform policy and planning, R&D and industry strategy.

The following figure is a summary of experts’ findings and shows a forecast for onshore and offshore wind industry.
Figure 13: Summary of Expert Survey Findings [22]

Note: All dates are based on the year in which a new wind project is commissioned. LCOE and LCOE drivers are shown relative to 2014 baseline values. Rather than assume that all experts have the same internal 2014 baselines, a default option was offered, which allowed experts to provide their own estimates for onshore and fixed-bottom offshore wind. Roughly, 80% of experts opted to use the default baseline values. 2014 baseline estimate for floating offshore wind was not a focus; floating offshore wind changes are therefore compared to expert-specific 2014 baselines for fixed-bottom offshore wind.

Onshore wind is expected to remain less expensive than offshore and fixed-bottom offshore less expensive than floating. However, there are greater absolute reductions (and more uncertainty) in the LCOE of offshore wind compared with onshore wind, and a narrowing gap between fixed-bottom and floating offshore, with especially sizable anticipated reductions in the LCOE of floating offshore wind between 2020 and 2030.

Figure 14: Estimates of Median-Scenario LCOE [22]
Note: Emphasis should be placed on the relative positioning of and changes in LCOE, not on absolute magnitudes. Because the 2014 baselines shown in the figure are the median of expert responses, they do not represent any specific region of the world. For any specific region, the 2014 baselines and future absolute LCOE values would vary. Additionally, because roughly 80% of experts chose to use the default 2014 baseline values for onshore and fixed-bottom offshore, the 1st and 3rd quartile as well and the median expert response for 2014 are all equivalent to those default baseline values.

As can be seen in the figure above, further reduction of production costs of wind energy can be expected in the future, which means that wind and solar energy can be rightly considered as the cheapest renewable energy sources.
6. Storage of fluctuating energy

As predicted in the studies mentioned in the last chapter, wind and solar energy will be very low cost energy in the future, thus an excess electricity from these sources could be expected.

On the other hand, solar and wind energy are fluctuating and intermittent energy sources, thus they have to be balanced for electric grid stability purposes. Consequently, long term and large capacity electricity storage is required, as well as reserve production capacity.

There are many possibilities how to store electric energy [23], some of them are listed below:

Pumped hydroelectric. Electricity is used to pump water up to a reservoir. When water is released from the reservoir, it flows down through a turbine to generate electricity.

Compressed air. Electricity is used to compress air at up to 1,000 pounds per square inch and store it, often in underground caverns. When electricity demand is high, the pressurized air is released to generate electricity through an expansion turbine generator.

Flywheels. Electricity is used to accelerate a flywheel (a type of rotor) through which the energy is conserved as kinetic rotational energy. When the energy is needed, the spinning force of the flywheel is used to turn a generator. Some flywheels use magnetic bearings, operate in a vacuum to reduce drag, and can attain rotational speeds up to 60,000 revolutions per minute.

Batteries. Similar to common rechargeable batteries, very large batteries can store electricity until it is needed. These systems can use lithium ion, lead acid, lithium iron or other battery technologies.

Thermal energy storage. Electricity can be used to produce thermal energy, which can be stored until it is needed. For example, electricity can be used to produce chilled water or ice during times of low demand and later used for cooling during periods of peak electricity consumption.

In addition to these technologies, new technologies are currently under development, such as flow batteries, super capacitors, and superconducting magnetic energy storage [23].

Anyway, there are also other possibilities, how to store electric energy in order to produce another type of energy source, it mean to convert the electricity into gaseous or liquid carrier, which could be stored as long as needed.
6.1 Power to Gas

One possibility how the electricity can be stored, distributed and made available for various energy usage ways is Power-to-Gas (PtG) concept. This concept is not new; it was first proposed in Japan in the 1980s - 1990s [24]. PtG is referred to as a system solution due to its many cross-sectoral applications and the various technologies it employs. [25]

The idea behind PtG is to convert an excess of electricity from renewable energy sources (e.g. wind and/or solar) to hydrogen or to methane. The renewable gas can be transported in the existing gas infrastructure (in case of SNG production), stored and then used in a range of applications. Likewise, the direct use of hydrogen, for instance in the mobility sector or in refineries, is possible [26].

PtG can help reduce CO₂ emissions in various sectors of consumption in that the renewable gas replaces fossil fuels in mobility, industry, heat supply and power generation. As an electricity storage method, PtG can also contribute to compensating the increasing fluctuations in electricity generation from wind and solar energy, and facilitate long-term use of electricity that could not be integrated directly into the electricity grid. Anyway, it should be mentioned that the main drawbacks of Power-to-Gas systems are still a relatively low efficiency and high costs. [27]

In the figure below a roadmap for further development of the PtG system solution presented by dena (Deutsche Energie-Agentur) Power to Gas Strategy Platform can be seen.

It identifies key areas of action and issues and associated time corridors that must be considered for a successful utilization of PtG, involving all sectors of consumption (electricity, heat, transport, material use) and the interaction of politics, industry, academia and research.

The aim of the dena Strategy Platform partners is to build a Power to Gas plant capacity of 1,000 MWel in Germany by 2022.
The actual pilot-projects status can be seen in the following map (status end of July 2018).

Different technologies must interact seamlessly for the PtG concept to work. The most important processes include electrolysis (for hydrogen production) and methanation (for SNG production).
6.1.1 Electrolysis

Electrolysis process to generate hydrogen is the core process of the PtG concept. In the electrolysis process, about 80 percent of the input energy is converted into hydrogen; heat loss in particular lowers the efficiency of the process.

The most well known type of electrolysis is water electrolysis to yield $\text{H}_2$ and $\text{O}_2$ [eq. 16]. It is an electro-chemical reaction, which can be divided into two steps. At the negatively charged cathode the reduction reaction takes place [eq. 17], while the oxidation reaction occurs at the positively charged anode [eq. 18].

Depending on the technology, the charge carrier can be $\text{OH}^-$, $\text{H}_2\text{O}^+$, or $\text{O}_2^-$.

\[
\text{H}_2\text{O} \text{ (l)} \rightarrow \text{H}_2 \text{ (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \quad \text{[eq. 16]}
\]

\[
\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + \text{O}_2^- \quad \text{[eq. 17]}
\]

\[
\text{O}_2^- \rightarrow \frac{1}{2} \text{O}_2 + 2e^- \quad \text{[eq. 18]}
\]

As can be seen in the following figure, temperature has a positive influence on the water electrolysis reaction and pressure has a negative one.

![Equilibrium cell voltage as function of temperature for different pressure (1, 10 and 20 bar)](image)

Figure 18: Equilibrium cell voltage as function of temperature for different pressure (1, 10 and 20 bar) [27]

The three electrolysis processes relevant for PtG systems are:

- Alkaline water electrolysis with an alkaline liquid electrolyte (AEL)
- Acidic or polymer electrolyte membrane (PEM) electrolysis with a solid polymer electrolyte (SPE)
- High-temperature (HTE) steam electrolysis using solid oxide electrolytes (SOEC)
6.1.1.1 Alkaline electrolysis

Alkaline electrolysis (AEL) is the most mature and well-understood technology (commercially available for decades) in comparison with the other two electrolysis technologies.

In AEL, an aqueous alkaline solution (KOH or NaOH) is used as the electrolyte. AEL works either atmospherically or under elevated pressure. Pressurized alkaline electrolyzers have a lower efficiency and produce a lower purity product than atmospheric AEL [29]. The foremost advantage of pressurized AEL compared to atmospheric AEL is that it produces compressed hydrogen (either for grid injection or further for use) with less additional energy input. This is a result of the fact that the reduction in electric efficiency of the electrolysis with increased pressure is lower than the energy needed to compress the produced hydrogen.

AEL electrolysers can be operated between 20 and 100% of the design capacity, and overload operation up to 150% is possible. This operation window makes AEL a good choice for systems such as PtG, which are coupled with a fluctuating and intermittent power supply.

Anyway, Gahleitner [30] reported about problems with intermittent and fluctuating power sources. One problem was that it took 30-60 min to restart the system following a shutdown [31], but the biggest disadvantage of AEL was that the utilized electrolytes (alkaline solution, e.g. 20 - 30 % potassium hydroxide solution) are highly corrosive, thus necessitating high maintenance costs. An overall maintenance of the system is necessary every 7-12 years [29]. According to [32], the expected lifetime for an alkaline electrolyser is currently about 30 years, which is high compared to the other considered electrolyser types. In recent years, AEL has been optimized, especially with respect to efficiency and total investment costs.

6.1.1.2 Polymer electrolyte membrane electrolysis (PEM)

PEM was first introduced in the 1960s by General Electric to overcome the drawbacks of AELs [33]. The first commercial PEM electrolyser available for purchase in 1978 [34].

The technology is based on solid polymer membranes [35]. The main advantages of PEM include faster cold start, higher flexibility, and better coupling with dynamic and intermittent systems. Furthermore, the purity of the produced hydrogen is very high [36]. The minimum load is reported to be 5%. However, this technology is currently more expensive than AEL systems (due to the costs for the membrane and the use of a noble metal catalyst), and the limited life expectancy is
disadvantageous. PEM electrolysers in the MW scale have recently become available (Proton Onsite and Siemens) [37, 38].

6.1.1.3 Solid oxide electrolysis (SOEC)

Solid oxide electrolysis (also known as high temperature electrolysis) is the most recently developed electrolysis technology but it is still at the laboratory stage [33] and individual companies are currently aiming to bring this technology to market [39].

In SOEC, ZrO₂ doped with 8 mol% Y₂O₃ is used as the electrolyte, which at high temperatures is highly conductive for oxygen ions (charge carrier), and has good thermal and chemical stability [22,23]. The high temperature reduces the equilibrium cell voltage and therefore the electricity demand [24]; however, the heat demand increases with increasing temperature. The low electricity demand is the most significant advantage of SOEC systems. Theoretically, electrical efficiencies above 100% could be achieved (endothermic mode) [40, 41].

The biggest challenges for SOEC systems are the fast material degradation and the limited long-term stability, both of which are due to high temperature operation [34].

Anyway, it was reported in [42] that an electrolyte supported solid oxide cell was operated during 23,000 h in the steam electrolysis mode. Cell voltage degradation was 7.4mV/1000 h (0.57%/1000 h), what is a low value for present SOEC. After dismantling the cell was neither broken nor fissured and showed no visible damage of the H₂ electrode; a fraction (~10%) of the O₂ electrode was delaminated. Moreover, the O₂ electrode was affected by an, at least partly reversible, pollution from the purging with compressor air.

Another aspect is that, the high temperature level means that the product stream from the electrolyser is a mixture of hydrogen and steam, and requires additional processing; thereby further increasing the capital costs.

Moreover, in literature [29, 34] could be found that SOEC systems are not stable against fluctuating and intermittent power sources, anyway, modulation in a range of 20 - 100 % of the nominal load are possible. Of course, the SOEC cannot be switched off completely.

Potential advantages include high electrical efficiency, low material cost and the options to operate in reverse mode as a fuel cell.

High-temperature electrolysis is now still not available in commercial scale and that is why the comparison, which could be seen in the following table, is focused to alkaline and PEM technologies.

As can be seen in the table below, the advantages of PEM electrolysis are that it works also at lower load areas, startup time is shorter and ramp-up from minimum load to full load is faster. As a disadvantage of PEM system lower size range could be seen as well as higher investment cost (following figure).
Table 2: Comparison of alkaline and PEM technologies [43]

<table>
<thead>
<tr>
<th></th>
<th>Alkaline</th>
<th>PEM</th>
<th></th>
<th>Alkaline</th>
<th>PEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density [A/cm²]</td>
<td>0,2 – 0,4</td>
<td>1,0 – 2,0</td>
<td>Start-up time from cold to minimum load [min.]</td>
<td>20 to several hours</td>
<td>5 - 15</td>
</tr>
<tr>
<td>Hydrogen output pressure [bar]</td>
<td>0,05 – 30</td>
<td>10 – 30</td>
<td>H₂ purity [%]</td>
<td>99,5 -99,9998</td>
<td>99,9 – 99,9999</td>
</tr>
<tr>
<td>Min. load [%]</td>
<td>20 - 40</td>
<td>5 - 10</td>
<td>System size range</td>
<td>0,25 – 760 Nm³/h</td>
<td>0,01 – 240 Nm³/h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1,8 – 5 300 kW</td>
<td>0,2 – 1 150 kW</td>
</tr>
<tr>
<td>Ramp-up from minimum load to full load [%full load/s]</td>
<td>0,13 - 10</td>
<td>10 - 100</td>
<td>Lifetime stack [h]</td>
<td>60 k – 90 k</td>
<td>20 k – 90 k</td>
</tr>
</tbody>
</table>

A distinction must be made between atmospheric pressure and pressurized electrolysis when looking at alkaline electrolysis and PEM electrolysis. Advantages of pressure electrolysis lie in the more compact construction and the possibility of direct coupling to many industrial pressure-controlled applications as well as the natural gas infrastructure.

Figure 20: Comparison of selling prices of AEL, PEM and SOEC systems [44, 45, and 46]

As can be seen in the figure above, investment costs for alkaline electrolysis are significantly lower than the costs for PEM and SOEC electrolysis systems.
The following table compares investment costs, efficiency and energy consumption of alkaline water electrolysis and PEM electrolysis.

Table 3: Comparison of some properties of alkaline water electrolysis and PEM electrolysis (source: dena)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Alkaline electrolysis</th>
<th>PEM electrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment costs</td>
<td>800 – 1500 €/kW</td>
<td>2 000 – 6 000 €/kW</td>
</tr>
<tr>
<td>Efficiency relative to upper calorific value (HHV)</td>
<td>67 – 82 %</td>
<td>44 – 86 %</td>
</tr>
<tr>
<td>Specific energy consumption</td>
<td>4 – 5 kWh/Nm³H₂</td>
<td>4 – 8 kWh/ Nm³H₂</td>
</tr>
</tbody>
</table>

Current capital costs are reported at around 1000 €/kWel and 2000 €/kWel for alkaline and PEM electrolysis (1 MWel) respectively. SOEC systems are not yet widely commercially available and estimated costs lie above 2000 €/kWel [47].

PEM electrolysis should be available for <1000 €/kWel already in 2018, whereas in [45] a PEM price of 1250 €/kWel is expected for 2020.

DENA reports that the aim is to reduce the investment costs of electrolysis to 500 €/kW by 2022. Cost reduction potential arises primarily from the continuous increase in annual production quantities and the transition to series production.

Technical challenges for the use of water electrolysis in the PtG concepts include a stabilization of the specific energy consumption, the necessary power plant dynamics and the consistent extension of maintenance intervals, all required due to fluctuations in electricity generation.

Crucial for operation and efficiency of the process, however, are the peripheral components of an electrolysis system such as lye pumps, pressure regulators and product gas separators. Frequent load changes and full shutdowns stress these mechanical components by unsettling the heat balance, thereby shortening the system’s service life [25].

PEM electrolysers have technical advantages for use in PtG plants, as already mentioned they follow fluctuating power input better than alkaline electrolysers do. They respond more quickly to load changes, even in the lower partial load range, and quickly reach operating temperature in their startup phase.

However, further advancements of alkaline electrolysers were also made in terms of the mentioned aspects. Investment costs for PEM electrolysers are still much higher than for alkaline electrolysers.

An interesting view of hydrogen production costs is offered in the following figure, where the SOEC, PEM and alkaline electrolysers are compared. Electricity costs of 50 €ct/MWh, 100 €ct/MWh and 150 €ct/MWh (large industry with high electricity consumption, medium-sized industry and SME) are assumed to calculate hydrogen production costs.
Figure 21: Costs comparison and target markets for 2025 between SOEC, PEM and alkaline-based electrolysers [48]

It can be seen that 60-80 % of total costs are related to the electricity prices indicating significance of high conversion efficiencies. Target markets for hydrogen are displayed in the figure as well: industrial hydrogen (bottled), hydrogen for refineries and hydrogen for mobility. In all cases, the SOEC lowers the H₂ production costs by about 12-22 %.
6.1.2 Hydrogen

It is expected that the global hydrogen usage will substantially grow in the coming years due to the extension of (fluctuating) renewables in the grid or the decarbonisation of the transport sector. Hydrogen generated from electricity and water can be stored in large quantities over long periods and retransformed to electricity. It can be converted to synthetic natural gas or sold as a fuel for fuel cell vehicles in the transport sectors. Hydrogen can fulfil renewable quotas in refineries if the legal framework is adapted.

Hydrogen or SNG for energy storage require large units at MW-scale and very low electricity prices to become competitive. Hydrogen in industrial applications has a much higher cost tolerance if it competes with logistic H₂.

Sunfire has estimated potential business numbers for three markets [49] in Germany, UK and California (due to larger amount of renewables). Results for the period 2015 to 2020 are shown in the following figure.

![Figure 22: Market prospective of hydrogen producers by electrolysis [49]](image)

If electrolysers are used to compensate fluctuations from renewable electricity, state-of-the art technologies are PEM and alkaline based electrolysers, as mentioned above. Anyway, the greatest potential for the future seem to be SOECs.

6.1.2.1 Hydrogen storage

Currently there are two best options for the temporary hydrogen storage:

- high pressure gas tanks (350-700 bar)
- metallic hydride tanks

Hydrogen can be used as a fuel in internal combustion engines and gas turbines, or can be mixed with natural gas and burned on the steam generator burners. It is also possible to utilize it in the chemical industry and households. Anyway, the most attractive technique is hydrogen utilization in fuel cells.

However, hydrogen gas has a few unique properties that require special consideration. For example, hydrogen can leak easily and ignite a relatively low temperature. As with any fuel, safe
handling depends on knowledge of its particular physical, chemical, and thermal properties and consideration of safe ways to accommodate those properties.

Further item, which should be considered by the hydrogen utilization, is missing infrastructure of transport and storage. This can be overcome by further hydrogen converting into another energy carrier, such as SNG, for which there is already a well-developed infrastructure.

6.1.3 Methanation

Hydrogen generated from the electrolysis process can be stored or further used or it can be converted into methane using carbon monoxide or carbon dioxide in a downstream methanation process to produce synthetic natural gas (SNG). This process can be catalytic or biological.

This report focuses on catalytic methanation and not on biological process.

The most relevant reactions during the methanation process:

\[
\begin{align*}
\text{CO}_2(g) + 4\text{H}_2(g) & \leftrightarrow \text{CH}_4(g) + 2 \text{H}_2\text{O}(g) & \Delta H^\circ = -165.1 \text{kJ/mol} \quad [\text{eq. 19}] \\
\text{CO}(g) + 3\text{H}_2(g) & \leftrightarrow \text{CH}_4(g) + \text{H}_2\text{O}(g) & \Delta H^\circ = -206.3 \text{kJ/mol} \quad [\text{eq. 20}] \\
\text{CO}_2(g) + \text{H}_2(g) & \leftrightarrow \text{CO}(g) + \text{H}_2\text{O}(g) & \Delta H^\circ = +41.2 \text{kJ/mol} \quad [\text{eq. 21}] \\
2 \text{CO}(g) & \leftrightarrow \text{C}(s) + \text{CO}_2(g) & \Delta H^\circ = -172.5 \text{kJ/mol} \quad [\text{eq. 22}]
\end{align*}
\]

Catalytic methanation reactors are usually operated at temperatures between 200°C and 550°C and at pressure range 1 to 100 bar. As a catalyst in methanation reaction metals such as Ni, Ru, Rh and Co could be used. Mostly Ni catalysts are used because of its high activity, good methane selectivity and low material costs. However, a high purity of the fed gas is required due to the sensitivity of nickel catalysts to sulphur contaminants.

The methanation reaction is highly exothermic, thus a good temperature control in the reactor is a significant issue to prevent thermodynamic limitation and catalyst sintering.

There are four types of reactors developed:

- fixed bed
- fluidized bed
- three-phased
- structured reactors

Fixed-bed reactors as well as fluidized-bed reactors are established technologies, while the other reactor concepts are in the development phase.

6.1.3.1 Adiabatic fixed-bed reactors

Adiabatic fixed-bed reactors are usually used as series of 2-5 reactors with intercooling and gas recirculation [50,51]. Due to the adiabatic mode of operation, the catalyst must be able to withstand a broad temperature range of 250 to 700 °C. Alternatively, cooled fixed bed reactors can be applied for methanation. Usually, such a reactor contains cooling tube bundles; a further possibility is the use of cooled plates. Due to the cooling, the process setup is simpler than for adiabatic reactors, however, the reactor itself is more expensive.

6.1.3.2 Fluidized-bed reactors

The mixing of fluidized solids leads to almost isothermal conditions and offers much better temperature control. Nevertheless, due to high mechanical load resulting from fluidization,
attrition processes take place in relation to the catalyst as well as the wall of the reactor. As a consequence, the catalyst deactivation can occur [52]. A further disadvantage can be the incomplete CO₂ conversion caused by bubbling. In addition, a fluidized-bed reactor is limited by superficial gas velocity within the reactor: it cannot be too low in order to assure minimum fluidization conditions and cannot be too high in order to avoid catalyst elutriation and/or deactivation.

6.1.3.3 Three-phase reactors
Generally, slurry reactor is filled with a liquid phase, in which fine catalyst particles are suspended as a result of the gas flow. The presence of the liquid phase with high heat capacity allows an effective and accurate temperature control: the heat of reaction can be completely removed and the reactor can operate almost isothermally, leading to a simple process design. The challenges with the use of slurry reactors are a result of gas liquid mass transfer resistances and the decomposition and evaporation of the suspension liquid [53,54,55,56].

6.1.3.4 Structured reactors
Structured reactors have been developed to overcome the disadvantages of adiabatic fixed-bed reactors, namely temperature hot spots and high pressure drops. Due to their internal metallic structure, monolith reactors feature an enhancement of radial heat transport by two to three orders of magnitude due to heat conduction through the metallic structure (depending on the metallic material). [57]

A special structured reactor concept is embodied by micro structured reactors, which are very compact with a high surface-to-volume ratio. They combine high heat transfer and a small pressure drop. Drawbacks of structured reactors are the more complicated catalyst deposition on the metallic structure, as well as the difficulty of replacing the deactivated catalyst: once the catalyst has been deactivated, the whole reactor has to be equipped with a new catalyst coating.

A further development of structured reactors is the sorption enhanced methanation reaction concept. The water produced by the methanation reaction is removed from the gas phase by the catalyst carrier showing adsorbent functionality. Thereby, thermodynamic limitation of the conversion rate is reduced. For the subsequent water removal, temperature swing and/or pressure swing with or without purge gas can be applied.

6.1.4 Biomass gasification as a carbon source for PtG principle (SNG production)
The integration of biomass gasification into PtG, where SNG is the product; shows following advantages:

- Total carbon exploitation can be more than doubled
- Higher overall process efficiency (larger product yield and possibility of heat integration)
- O₂ from electrolysis can be used for gasification
- By adding hydrogen from electrolysis, the use of the water-gas shift reaction can be avoided
- Large H₂ storage can be avoided
- By non-available surplus electricity, the methanation can be operated with synthesis gas from gasification only

A principal of coupling thermal gasification with additional hydrogen from electrolysis can be seen in the following figure. A system consisting of two bed steam gasifier and electrolyser for production of methane (PtG) or FT-products (PtL) can be seen in the following figure.

During the steam gasification a gas with H₂ : CO = 2 ratio is produced, which is optimal for FT-synthesis. For methanation a gas with ratio H₂ : CO = 3 is necessary, it means further hydrogen from electrolyser is needed.
In case of FT synthesis is the usage of hydrogen from electrolyser a little bit different. The principle is based on CO₂ recycling, it means, the inert CO₂ will not be released to the atmosphere, but it will serve as additional fluidizing agent in the gasification unit as a carbon source for further reactions with hydrogen from electrolysis.

Figure 23: Coupling of two-bed steam gasifier and electrolysis for PtG (methane) and PtL (FT-products)

The additional CO₂, which is used as a fluidizing agent together with steam causes the shift of H₂ : CO ratio in favor of CO, thus the ratios between 0,5:1 and 1,9:1 can be achieved.

As a result of this technology, the same amount of FT products or methane can be produced using the smaller amount of biomass. Using other words, coupling the thermal gasification of biomass with hydrogen from electrolysis can doubled the production of FT products or methane in comparison if only product gas from gasification is used.

6.1.5 Efficiency

To assess the PtG process efficiency, the following system is examined. Current available electrolysis technologies (AEL and PEM) delivering H₂ at 25 bar with an electrical efficiency of about 70% are considered. The methanation reactor is operated at 20 bar with an efficiency of 78% (maximum chemical efficiency). CO₂ is already compressed to 20 bar for the methanation reaction (otherwise 2% efficiency loss should be taken into account).

PtG efficiency diagram can be seen below. The Sankey diagram shows two improvement potentials for PtG. First, the efficiency of water electrolysis and heat from the methanation reactor could be utilized.
The coupling of SOEC with catalytic methanation enables an efficiency of 80% (based on HHV). With the Helmeth pilot plant (project will be described later) 76% have been reached [49].

### 6.1.6 Economics of PtG systems

A major factor of the economic efficiency of PtG plants are the investment costs for electrolysis and methanation.

The investment costs for electrolysis are in the range of 800-3000 €/kW. For methanation the investment costs depend on the plant size (Outotec GmbH reported in [32]: 400 €/kW SNG for a 5 MW plant; 130 €/KW SNG for a 110 MW plant – both information for 2014 and 20 bar operating pressure).

The next important factors are the operating costs, costs and availability of CO2 for methanation and for pure hydrogen and the costs of a hydrogen infrastructure. Hydrogen storage is a significant contributor to the investment of a PtG plant. The costs for the hydrogen storage can be reduced or pass over by operating the methanation dynamically compared with a steady state.

The following figure plots SNG generation costs for the coupling of PtG with different CO2 sources (electricity price 5 €ct/kWh, heat price 4 €ct/kWh, oxygen price about 7€ct/m³).

![Figure 25: SNG generation costs for the coupling of PtG with different CO2 sources (FLH-full load hours) [32]](image-url)
Summarizing, the generation costs for H₂ and for SNG strongly depend on the annual operational time and the electricity price. Compared with natural gas (approximately 2-3 €ct/kWh), the costs are much higher. For economic feasibility, relevant annual operational times and low electricity costs are obligatory.

The choice of location has a decisive impact on the costs of a PtG plant as well. The choice of location depends on the business model of the planned plant, and must be based on the conditions of both the electricity and the gas network. For example, a plant in which methanation is to take place will benefit from proximity to a source of carbon dioxide.

Figure 26: Power to gas location factors

With the Power to Gas Strategy Platform, the Deutsche Energie-Agentur GmbH (dena) – the German Energy Agency – and its partners are supporting the use and development of the Power to Gas system solution. In the Strategy Platform, partners from business, associations and science pool their diverse expertise and experience. The core objective is to establish Power to Gas as a reliable, cost-efficient and large-scale multi-purpose option at least by the beginning of the year 2020/2025 with at least 1.000 MW of electrolysis power installed in Germany.
6.1.7 Power to gas applications

Figure 27: Power to Gas concept (Source: Fraunhofer ISE)

Power to Gas has the potential to be a versatile, cross-sectoral technology supporting the implementation of the energy transition and integrating renewable energy into the different energy consumption areas. The technology is mature and ready for use. However, until it is fully ready for the market, in particular with regard to economic use, some central regulatory parameters need adjusting.

**Mobility**

Power to Gas offers new opportunities in the transport sector to reduce climate damaging with CO₂ emissions and other pollutants, whereas the renewably produced fuel replaces its fossil equivalent. Non-biogenic fuels will have an important role to play in achieving climate protection goals. The amounts in question can only be supplied by hydrogen or methane. In addition, electricity-based fuels have a far lower impact on land use than plant-based fuels. Hydrogen and methane from renewable energy sources can be more easily produced than liquid renewable fuels.

**Industrial use**

Renewably produced hydrogen allows the substitution of hydrogen from fossil sources and may be used, for example, in fuel refineries, in the chemical industry, and in steel plants (direct reduction). Likewise, renewably produced methane can replace fossil natural gas in the industry.

**Heat supply**

The renewable gas from the Power to Gas process flows through the natural gas infrastructure to domestic and commercial heating systems, where it can replace fossil natural gas. A particularly efficient use of energy in this context is in combined heat and power plants.
A long-term storage in the electricity sector

Due to the large storage capacity of the natural gas network and the connected gas storage systems, Power to Gas has a high potential for storing large amounts of energy. If necessary, the renewable gas produced using the Power to Gas process can be reconverted in gas power plants or cogeneration plants, what is of course not too efficient and connected with losses.
6.1.8 Power to Gas - Projects

6.1.8.1 Bio-SNG production by means of biomass gasification combined with MCEC technique

A new technology developed and demonstrated at laboratory scale at KTH is the molten carbonate electrolysis cell [59].

A molten carbonate cell consists essentially of two electrodes, commonly made of alloyed Ni and NiO, and an electrolyte, consisting of a molten alkali salt, including combinations of Li2CO3, K2CO3 and Na2CO3, suspended in a porous ceramic matrix made of LiAlO2. The principal electrochemical reactions occurring in the cell converting electric power to an energy-rich gas, when fed with H2O and CO2, are shown in following figure. Water and carbon dioxide are converted to CO and H2. Carbonate ions are transported from the cathode to the anode in the electrolyte and decomposed to O2 and CO2. In the MCFC mode the reactions are reversed.

![Figure 28: Principle of molten carbonate cell](image)

Advantages of the system are:

- ability to withstand a high amount of CO content in the product gas
- advantage of integrating into a gasification system is the internal reforming of hydrocarbons in the gas
- the heat needed for the endothermic steam reforming of methane or higher hydrocarbons is taken from the cell stack, reducing the need for external cooling generally required in the stack
- Reversibility of the MCEC – there is a possibility to use the cell technology in both ways power-to-gas applications and power production, depending on needs.

Disadvantages:

- tolerable amount of hydrocarbons in the feed to up to 10 vol-% saturated hydrocarbons (including methane) and less than 0.5 vol-% of aromatic and cyclic hydrocarbons
- large amounts of heavier hydrocarbons may create problems with deposits on electrodes
- pollutants such as ammonia, alkali metals and halides on a MCFC may cause corrosion of cell components and increased loss of electrolyte by reaction and evaporation, impairing the balance of the electrolyte
- particles may be a problem for the cell, where they can clog the porous electrodes
- the presence of H2S in the product gas could lead to degradation in performance and shorten cell life
The study, provided at KTH, has been based on a literature survey and a conceptual techno-economic investigation of using a MCEC as a gas cleaning and conditioning process step in a biomass gasification system for bio-SNG production.

To enable a comparison with a real case, the GoBiGas plant has been selected as a reference case. The plant is a 32 MW feedstock dual fluidized bed biomass gasifier, consuming 3 MW of electricity and 0.5 MW of RME (tar recovered from the process) during normal operation. The output is 20 MW of bio methane, as well as 5 MW of excess heat for direct utilization for district heating (DH) and 6 MW of upgraded heat (via a heat pump) to DH. The produced bio-SNG consists of more than 95% methane and is distributed via the local natural gas grid.

Five different scenarios were evaluated:

1. the model run for standalone GoBiGas plant (without the integrated MCEC) in order to reproduce the actual plant operation
2. the model run for integrated GoBiGas and MCEC with a district heating option
3. the model run for integrated GoBiGas and MCEC with a condensing turbine option
4. the model run for integrated GoBiGas and internal reforming MCEC with district heating option
5. the model run for integrated GoBiGas and internal reforming MCEC with condensing turbine option

The overall conclusion is that the results are positive, as the mass and energy balance shows that the production of bio-SNG can be boosted by up to 60%, integrating a MCEC, compared to the same biomass input as in a standalone operation of the GoBiGas plant. The conclusions from the conceptual study are as follows:

- The mass and energy balance showed that the production of bio-SNG can be boosted by up to 60% for scenarios assuming internal reforming of tars without the need of an additional carbon source, in other words for the same biomass input as in a standalone operation of the GoBiGas plant.
- The economic assessments further revealed the price ranges for biomass, SNG and renewable electricity that would allow for a wider margin in terms of the IO index for the process configurations considered, as compared to the standalone SNG plant. Under the assumed economic conditions, renewable electricity prices higher than 26 €/MWh would make the integration of a MCEC infeasible. Furthermore, the sensitivity analysis shows that for a renewable electricity price of 26 €/MWh, the biomass feedstock price and the natural gas market price need to be below 26 €/MWh and above 30 €/MWh, respectively, in order to receive a positive IO index for all of the scenarios.
- The produced oxygen is also of high value, directly as a product for sale or to be used internally by the gasification process in a direct gasifier when production of a syngas is desired. This implies a possibility of using direct gasifiers at smaller scales for syngas production, as supply of pure oxygen is a cost-limiting factor in this case. A direct
gasifier is generally less complex compared to indirect systems, as exemplified when comparing single direct and dual indirect fluidized bed gasifiers.

- The introduction of a MCEC in the gas cleaning and conditioning process of a biomass gasification system provides process intensification with a potential integration of three process units into one.
- Based on today’s size of commercial MCFC systems, using 3.7 MW size units, stacked to power plants up to 60 MW, and utilizing natural gas, a similar scenario for applying the MCEC technology is foreseen.
- The possibility to operate the MCEC in a reverse MCFC mode is beneficial and increases the usefulness of the overall system, promoting continuous operation of the cell technology and thus optimizing the economy in relation to the price of electricity or Bio-SNG.

There are a number of technical issues related to a MCEC such as sulphur tolerance and tolerance towards other impurities, and extent of hydrocarbon steam reforming depending on process conditions that need to be addressed before the potential of a MCEC can be concluded. Anyway, based on positive results of this study further investigations regarding MCEC and process evaluation are planned.

The whole report can be found also at the IEA Bioenergy Task 33 website in the section “Other publications and reports”.

46
6.1.8.2 Integrated high-temperature electrolysis and methanation for effective power to gas conversion (HELMETH) [49]

The objective of the HELMETH project was the proof of concept of a highly efficient PtG technology with methane as a chemical storage and by thermally integrating high-temperature electrolysis (SOEC) with methanation. This thermal integration balancing the exothermal and endothermal processes is an innovation with a high potential for a most energy-efficient storage solution for renewable electricity, without any practical capacity and duration limitation, since it provides SNG as a product, which is fully compatible with the existing pipeline network and storage infrastructure.

The whole report is available at the IEA Bioenergy Task 33 website in the section “Other publications and reports”.

The first target was the elaboration of the conditions and scenarios for an economic feasibility of the PtG process towards methane as chemical storage, without significantly deteriorating the CO2-balance of the renewable electricity.

Second target was the demonstration of the technical feasibility of a conversion efficiency > 85 % from renewable electricity to methane, which is superior to the efficiency for the generation of hydrogen via conventional water electrolysis.

The focus within this project lay in the development of a complete pressurized PtG system consisting of a pressurized steam electrolyser module, which is thermally integrated with an optimized carbon dioxide methanation module. The HELMETH project has proven and demonstrated that the conversion of renewable electricity into a storable hydrocarbon by high-temperature electrolysis and methanation is a feasible option.

Both units can be coupled and thermally integrated towards highest conversion efficiencies by utilizing the process heat of the exothermal methanation reaction in the high-temperature electrolysis process. Schematic HELMETH concept can be seen in the following figure.

Figure 30: HELMETH Power-to-Gas concept with potential applications [49]
Starting from (surplus) renewable energy, steam is converted electrochemically into oxygen and hydrogen in pressurized SOEC. After mixing the hydrogen with CO₂, both are catalytically converted by the exothermic CO₂-methanation reaction into methane and water. After condensing the produced water, the remaining methane (SNG) can be directly injected in the natural gas grid if certain quality criteria are fulfilled. The heat of reaction from the methanation is used to produce steam for the electrolysis, which in turn produces the required hydrogen. Both units are therefore thermally integrated/coupled.

The working principle of the HELMETH PtG concept is based on a hydrogen production through SOEC technology and a following CO₂-methanation unit, what can be seen in a figure bellow.

![Figure 31: Scheme of thermal integration of SOEC and methanation unit](image)

**Pressurized SOEC**
Compared to low-temperature electrolysers like Alkali or PEM, an electrolysis of steam offers the benefit of a reduced energy consumption, furthermore high temperature electrolysis has a remarkable higher electrical efficiency compared to other electrolysis techniques; the advantage is in the range of 15 %. Due to the higher temperatures, the specific electric energy demand is lower for HTEs than for the competing technologies. This results in potentially higher electrical system efficiencies of up to 90 % based on the lower heating value, as a significant share of energy input can be provided by heat or waste heat from industrial processes, respectively.

![Figure 32: Energy demand of electrolysis technologies at the thermodynamic optimum](image)
A high temperature electrolyser was designed to be operated at high pressure up to 15 bar.

Generally, the influence of pressure on SOEC performance is low. The advantage is seen at system level in an integrated process at higher pressures, e.g. PtG with coupled methanation that operates above 10 bar. The pressurized operation of the high temperature electrolyser allows to save this compression step and instead to generate the hydrogen at the required pressure of the following process step.

*Methanation unit*

In order to develop a cost- and performance optimized concept, cooled reactors with boiling water cooling were chosen. For the operation of the methanation module, an optimal boiling water temperature of 250 °C was found. A simplified reactor concept is shown in the figure below.

**Figure 33: CO₂-methanation reactor design**

For future plants the low boiling water temperature of 250 °C and the corresponding steam pressure of 40 bar offers the potential of significantly reducing the size of the pressure vessels. With this reduced pressure compared to the current maximum of 87 bar (300°C), vessel thicknesses can be reduced and therefore the size of the vessels, resulting in even lower heat losses at hot stand-by.

*Coupling of the both units*

For the coupling, it was planned to have as less interfaces as possible, from the fluidic as well as from the electrical and signal point of view. The minimum number of fluidic connections is two: the steam outlet from the methanation cooling circuit to the electrolyser and vice versa, the hydrogen output from the electrolyser to the methanation unit. The steam was converted to hydrogen in the electrolyser.

For the combined operational tests, the methanation module was operated at a stable operating point with a gas feed-in pressure of 10 bar. The required hydrogen was drawn from a line that included the SOEC outlet and bottled hydrogen. From a methanation point of view the main focus was on a stable steam supply for the electrolysis. Steam from the methanation module cooling system was generated at 250 °C (40 bar) and then reduced in pressure down to 12.7 bar.

However, the steam flow control in the electrolyser showed unexpected and strong fluctuations and a stable operation was hardly achievable or for very short duration. Therefore, only part load operation could be achieved for a short time in the coupled mode. Full load would have required a longer and voltage stable operation in the exothermal mode to obtain higher temperatures and therefore lower resistance with the possibility for higher current density.

Synthetic (substitute) natural gas (SNG) that is produced by the coupled high-temperature electrolysis and methanation, so-called Power to Gas (PtG) applications, will be the key outcome.
of the HELMETH project. SNG can be used either for storage of surplus renewable electricity in the natural gas grid or direct usage of compressed natural gas (CNG) for transport applications.

The business case PtG is challenging for the following reasons:

- Using surplus renewable electricity allows only a limited number of operation hours (<2000) during the year
- Taking an electricity price of 4-5 €ct/kWh results in a SNG price of 5.7-7.1 €ct/kWh (70% efficiency assumed) if only operational costs are considered. The market price of natural gas is in the range of 2-3 €ct/kWh. Thereby, SNG is not directly competitive.
- Surplus wind power and photovoltaics are, at least in Germany, also recompensed if the units are idling due to a low demand in the grid. The EEG (German Renewable Energy Act) prevents alternative usage of surplus electricity. If this compensation would be stopped, it is not clear which market price will establish for surplus electricity.

PtG needs sophisticated business concepts in order to be viable. Legislation (in Germany - Renewable Energy Act) forces currently a monetary compensation of the renewable energy producers, even if the electricity cannot be supplied to the grid. On the other hand, natural gas is currently cheap and there is an overabundance of gas in the market, which results in a low incentive of buying ‘green’ gas. Results of the project will therefore be the investigation of business cases, where PtG could work and to elaborate legislative or similar measures that needs to be taken in future, if the technology is available.

The economic feasibility of PtG is mainly determined by the electricity price and the investment cost of the electrolyser and methanation modules, which can be seen in the following figure. Most critical for the business cases is the production of hydrogen. Electricity takes about 50% of the total costs (related to 1 kWh of natural gas). It is therefore the main leverage to improve the economics by increasing the conversion efficiency or buy surplus renewable electricity at lower costs. Investment costs amounts at about 25% of total costs. Here, the electrolyser is assumed to have a range of 8.2 to 15.2 m€ (for 6.6 MW power it leads to 1240 … 2300 €/kWel). Methanation is estimated to 7.3 m€ and gas processing costs are about 1.6 m€.
Summary and conclusions of the HELMETH project:

- A detailed theoretical analysis of an integrated pressurized high-temperature electrolyser and methanation unit has been performed. It has been shown that the upper efficiency limit is 89 %HHV, where a practical efficiency limit is at about 85 %.
- Sunfire optimized and operated the worldwide first pressurized high-temperature electrolyser system. The system works at pressure levels up to 15 bar with a stack operation at 850 °C and an input power of up to 10 kWel. It could be shown that the stack performance at elevated pressure is the same like at ambient pressure and that high steam conversion rates up to 90 % can be achieved. Electrolyser efficiencies above 100 %HHV have been proven to be easily possible for a full-scale system. As a drawback it was shown, that the pressure vessel and pressure control are costly and risky. Even if a constant operation regime at different pressure levels could be achieved, small disturbances of the flow or pressure control can result in differential pressure spikes that might damage the stack.
- KIT developed and built a multistep CO2-methanation module working with a boiling water cooling. Extensive tests in stand-alone mode were performed in order to characterize the methanation module performance. The gas pressure was varied from 10 to 30 bar and a load modulation from 20 to 100%. Boiling water cooling that can be operated at up to 300 °C (87 bar) showed an extremely stable and effective heat removal capability, while being able to control the temperature in a range of plus/minus 0.05 °C. An optimal boiling water temperature of 250 °C was determined.
- The methanation module produced SNG with hydrogen contents below 2 vol.-% and therefore excelling the quality target by far.

Figure 34: Economics of PtG concept [49]
• Coupled operation was limited by the challenges in the steam mass flow control at the electrolyser inlet, resulting in large pressure fluctuations and unstable steam conversion rates. Therefore, the coupling wasn’t completely successful.

• An important outcome of HELMETH was also the identification of technical obstacles, which should be in focus in future developments towards reaching technological maturity, namely the accurate flow and pressure control of steam at high pressures and the thermal insulation at high pressures.

• An economic feasibility is given provided that the costs of the electrolyser system can be reduced to below 2000 €/kW, which seems to be possible by 2020.

• Long-term stability of cells and stacks, dynamic operation, RSOC cycling and H2 polishing are identified as main obstacles before market penetration can be started.

• PtG this market is challenging due to low natural gas prices as competing fuel and limited yearly hours where surplus renewable electricity is available. In order to bring PtG into the market, the regulatory framework needs to be adjusted.

• HTE is the only electrolyser technology that has the potential to be competitive with natural gas due to its high conversion efficiencies.

• The generation of syngas with co-electrolysis of steam and CO2. This technology is still in its infancies, so that fundamental questions like long-term durability of cells or carbon formation risks during recuperative the cool-down of product gas need to be answered.
6.1.8.3 STORE & GO

Even if the thermal gasification of biomass is not CO₂ source in this project and other sources are used (biogas; waste water; atmosphere), it worth to mention it here. The reason is that the project does not focus just on the production of renewable gas, but evaluates also its utilization.

The project Store&Go [48] focuses on the integration of PtG into the daily operation of European energy grids to investigate the maturity level of the technology. Three different demonstration sites in Germany, Switzerland and Italy offer highly diverse testing grounds for PtG:

- available energy sources (high wind power; PV and hydro; PV and wind power)
- local consumers (low consumption; municipal region; rural area)
- electricity grid type (transmission grid; municipal distribution grid; regional distribution grid)
- gas grid type (long distance transport; municipal distribution grid; regional distribution grid)
- type of CO₂ source (biogas; waste water; atmosphere)
- heat integration (veneer mill; district heating; CO₂ enrichment)

Moreover, three different innovative methanation processes will be developed and improved from Technology Readiness Level 5 (TRL) close to maturity (TRL 6–7):

- catalytic honeycomb/structured wall methanation reactors
- biological methanation
- modular milli-structured catalytic methanation reactors

Figure 35: Store&Go project [48]
These technologies will be demonstrated at a considerable scale between 200 kW and 1 MW in 3 different demonstration environments for a runtime of about two years. The resulting product – synthetic natural gas (SNG) – will be injected into the existing grid and delivered to customers. The image above shows the innovative STORE&GO approach with respect to the technology and the integration with the power grid, which is also part of the project.

Characteristics of the three demonstration sides can be seen in the following table.

Table 4: Store&Go demonstration sides characteristics

<table>
<thead>
<tr>
<th>Demonstration site Falkenhagen/Germany</th>
<th>Demonstration site Solothurn/Switzerland</th>
<th>Demonstration site Troia/Italy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Representative region with respect to typical generation of RES</td>
<td>Rural area in the North East of Germany with high wind power production and low overall electricity consumption</td>
<td>Municipal area in the Alps region with considerable RES from PV and hydro production.</td>
</tr>
<tr>
<td>Connection to the electricity grid</td>
<td>Transmission grid</td>
<td>Municipal distribution grid</td>
</tr>
<tr>
<td>Connection to the gas grid</td>
<td>Long distance transport grid</td>
<td>Municipal distribution grid</td>
</tr>
<tr>
<td>Plant size (in relation to the EL power input)</td>
<td>1 MW</td>
<td>700 kW</td>
</tr>
<tr>
<td>Methanation technology to be demonstrated</td>
<td>Isothermal catalytic honeycomb/structured wall reactors</td>
<td>Biological methanation</td>
</tr>
<tr>
<td>CO₂ source</td>
<td>Biogas or bioethanol plant</td>
<td>Waste water treatment plant</td>
</tr>
<tr>
<td>Heat integration possibilities</td>
<td>Veneer mill</td>
<td>District heating</td>
</tr>
<tr>
<td>Existing facilities and infrastructure</td>
<td>2 MW alkaline electrolyser, hydrogen injection plant</td>
<td>350 kW PEM electrolyser, hydrogen injection plant, district heating, CHP plant</td>
</tr>
</tbody>
</table>

27 partner organizations and companies from all over Europe collaborate in the STORE&GO project to integrate Power-to-Gas technology into the future European energy system. The project is funded by the European Union’s "Horizon 2020 research and Innovation program".

The project is at the beginning phase now, more actual information can be found at the project website: https://www.storeandgo.info
6.1.8.4 AUDI e-fuels projects

Audi e-fuels projects are briefly described below, also here the thermal gasification is not the source of CO₂ by e-gas or e-diesel projects, anyway, also in these cases the gasification could be employed as well.

Figure 36: Audi e-fuels [61]

**Audi e-gas project**

An overview on Audi e-fuels can be seen in the figure above. The aim of PtG Audi projects is a coupling of the electricity sector and the gas, mobility and heat sectors.

In the following figure, a concept of SNG (e-gas) production is displayed. As can be seen as CO₂ source biogas plants are mentioned here, but thermal gasification plants could be employed as well to provide CO₂ for methanation process.

Figure 37: Audi PtG concept (source: Audi)

In the photos below an electrolyser and methanation unit can be seen.
As can be seen in the figure below, the duration time from the start of methanation process to reach the necessary gas quality is only 6 minutes.

The research phase of this project is finished and since 2013 is the e-gas fed into the gas grid. The facility produces about 1,000 tons of e-gas, it means about 2,800 tons CO₂ per year are bound into the process. Since 2014 a new car type Audi A3 g-tron is on the market, which can be fueled with e-gas. The solved e-gas is registered by Audi (the customers have a special Audi e-gas card) to know the amount, which should be fed into the grid again.

Audi e-fuels vehicles show best-in-class emission values and show the highest CO₂-reduction in the mobility sector.
Figure 40: e-gas emissions

The project partners are SolarFuel GmbH, Center for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW), Fraunhofer Institute for Wind Energy Systems and EWE Energie AG.

An overview of the project data can be seen in the following table.

<table>
<thead>
<tr>
<th>Project name</th>
<th>Audi e-gas project</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type</strong></td>
<td>Commercial</td>
</tr>
<tr>
<td><strong>Status</strong></td>
<td>Operational</td>
</tr>
<tr>
<td><strong>Start up</strong></td>
<td>25.06.2013</td>
</tr>
<tr>
<td><strong>El. input</strong></td>
<td>6.000 kWel.</td>
</tr>
<tr>
<td><strong>H₂ production</strong></td>
<td>1.300 m³/h</td>
</tr>
<tr>
<td><strong>SNG production</strong></td>
<td>300 m³/h</td>
</tr>
<tr>
<td><strong>CO₂ source</strong></td>
<td>Biogas facility EWE AG</td>
</tr>
<tr>
<td><strong>Waste heat utilization</strong></td>
<td>In biogas facility</td>
</tr>
<tr>
<td><strong>Location</strong></td>
<td>Werlte, Germany</td>
</tr>
</tbody>
</table>
6.2 Power to Liquids

Power-to-liquids (PtL) is a further possibility how to use an electricity surplus from renewable volatile energy sources in a combination with CO₂ to produce liquid biofuels, which could be used in aviation, ship transportation, heavy load transportation and there where fuels with high energy density are necessary.

The PtL technology based on thermal biomass gasification offers a possibility to produce FT liquids (gasoline, diesel and kerosene), methanol and DME.

PtL production comprises three main steps:

1. Hydrogen production from renewable electricity using the electrolysis principle
2. Provision of renewable CO₂ and its conversion
3. Synthesis to liquid hydrocarbons with subsequent upgrading/conversion to refined fuels

There are following principle pathways to produce renewable PtL fuels, which will be mentioned in this report:

- Fischer-Tropsch (FT) synthesis and upgrading
- Methanol (MeOH) synthesis and conversion

6.2.1 Fischer-Tropsch synthesis (F-T synthesis)

F-T synthesis, which was already briefly described in the section on product gas applications, can be divided, depending on the temperature, into low-temperature (LTFT, 200-260°C) and high-temperature (HTFT, 300-350°C) Fischer-Tropsch synthesis.

During the LTFT (up to 260°C) a higher fraction of higher-boiling hydrocarbons (above 360°C) is produced. Also the total distillate yield is higher than during HTFT. Higher temperature leads to faster reactions and higher conversion rates but also tends to favor methane, olefin and aromatics production. Typical pressures range is from one to several tens of atmospheres. Increasing the pressure leads to higher conversion rates and also favors formation of long-chained alkanes, both of which are desirable. Even higher pressures would be favorable, but the benefits may not justify the additional costs of high-pressure equipment and costs for compression.

The following figure shows C-H-O system to produce liquid hydrocarbons from water and CO₂ using the F-T synthesis.
The production starts with electrolysis, where H₂O is split to H₂ and O₂. As a next step the reaction H₂ and CO₂ takes place and CO₂ is reduced to CO or H₂ reacts directly with CO, the water produced is condensed out. In further step, the hydrocarbons are produced using Fischer-Tropsch synthesis process.

### 6.2.1.1 Thermodynamics

During the FT process, saturated as well as unsaturated hydrocarbons are produced. Following equations describe exothermic FT reaction.

\[
\begin{align*}
    n\text{CO} + 2n\text{H}_2 & \rightarrow (\text{CH}_2-\text{)}^n + \text{H}_2\text{O} & \Delta H_{300K} = -165 \text{kJ/mol} & \text{[eq. 23]} \\
    2\text{CO} + \text{H}_2 & \rightarrow (\text{CH}_2-\text{)} + \text{CO}_2 & \Delta H_{300K} = -204 \text{kJ/mol} & \text{[eq. 24]} \\
    3\text{CO} + \text{H}_2 & \rightarrow (\text{CH}_2-\text{)} + 2\text{CO}_2 & \Delta H_{300K} = -244.5 \text{kJ/mol} & \text{[eq. 25]} \\
    \text{CO}_2 + \text{H}_2 & \rightarrow (\text{CH}_2-\text{)} + \text{H}_2\text{O} & \Delta H_{300K} = -125.2 \text{kJ/mol} & \text{[eq. 26]} \\
    \text{CO} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{CO}_2 & \Delta H_{300K} = -38.8 \text{kJ/mol} & \text{[eq. 27]}
\end{align*}
\]

However, not only desired compounds (alcohols, paraffin and olefin) are produced during this process, also undesired ones are formed (aldehydes, ketones, ester, acids and carbon).

### 6.2.1.2 Reactors

Four types of FT reactors, which are shown in the following figure, should be mentioned here:

- Multi tubular fixed-bed reactors (A)
- Slurry reactors (B)
- Microchannel reactors (C)
- Fluidized bed reactor (D)
Multi tubular fixed-bed reactors

These fixed bed reactors were the first reactors, which were installed in commercial scale already before and after WWII. This type of reactors is robust, but it´s drawbacks are complicated scale up, high-pressure drop, not sufficient heat removal, low catalyst workload, the catalyst particles have to be very small because of the pressure drop and heat removal, used catalyst must be regularly removed and exchanged by fresh one, which is related to higher costs.

Slurry reactors

Slurry reactors were developed to overcome the problems of multi-tubular reactors. In comparison the slurry reactors are easier to design and cheaper. Heat removal is in slurry reactor done by internal cooling coils. The synthesis gas is bubbled through the waxy products and finely-divided catalyst which is suspended in the liquid medium. This also provides agitation of the contents of the reactor. The advantages of this reactor type are that higher temperatures can be reached without sintering of the catalyst, lower pressure drop of catalyst surface, easier removal of the catalyst and lower catalyst consumption. A big disadvantage is the need for separation of the catalyst and waxes as well as the possible poisoning of the whole catalyst because of the good mixture conditions. The slurry reactor consists of a freeboard. Based on the hydrodynamics in slurry reactor is the up-scaling too complicated and related to high cost demonstration status.

Fluidized bed reactors

Fluidized bed reactors were developed to overcome the problems of fixed-bed reactors as well as to increase the efficiency. This technology suits just for high-temperature Fischer–Tropsch synthesis (nearly 340 °C), because the FT synthesis process takes place in gas phase. The advantages of this reactor type are considerable better heat transfer and temperature controlling, and possibility to use also smaller catalyst particles to avoid interparticle diffusion. The better mixing is ensured with fluidization of catalyst particles and higher contact between gas and solid phase. Replacement of the used catalyst by the fresh one is easier and possible also during the process. A disadvantage of this reactor type is necessary further equipment (e.g. cyclones).

Microchannel reactors

Microchannel reactors are compact reactors that have channels with diameters in the millimeter range. These small channels dissipate heat more quickly than conventional reactors with larger channel diameters in the 2.5 – 10 cm range, so more active catalysts can be used. Mass and heat transfer limitations reduce the efficiency of the large conventional reactors used for Fischer–Tropsch, steam reforming reactions and hydroprocessing. The use of microchannel processing makes it possible to greatly intensify chemical reactions enabling them to occur at rates 10 to 1000 times faster than in conventional systems.
6.2.1.3 Catalysts

A variety of catalysts can be used for the Fischer–Tropsch process, but the most common are the transition metals such as cobalt, iron, and ruthenium. Nickel could also be used, but tends to favor methane formation. By LTFT cobalt or iron based catalyst are mostly used, whereas in HTFT only iron based catalysts are used.

The advantage of the cobalt based catalysts is a much longer lifetime. Less unsaturated hydrocarbons and alcohols are produced compared to the iron based catalysts. On the other hand, iron based catalysts are more tolerant to sulphur and can be also used to adjust the H2:CO ratio, if it is lower than 2 by means of water-gas shift reaction.

Anyway, in commercial scale cobalt and iron based catalysts are mostly used.

**Cobalt based catalysts**

The significant properties of Co-based catalysts are their high activity and selectivity. They are stable and suitable for diesel fuels production. The disadvantage is high price; thus, the optimal usage is necessary. Based on this the catalyst is mostly as an impregnation on a carrier used. Mostly used carriers are alumina oxide (Al₂O₃), silica oxide (SiO₂) and titan oxide (TiO₂).

The activation of a catalyst is provided by reduction with hydrogen by temperature of about 450°C. This high temperature can cause the sintering of the catalyst that is why the promotors are used (noble metals – Ru, Pt, and Re) to decrease the temperature bellow 400°C. This process does not influence the selectivity of the catalyst and the hydrogenation rate of CO will be increased. The regeneration of the catalyst should be made regularly with e.g. thermal treatment with H₂.

Deactivation of the catalyst can be caused by plugging with high molecular waxes and also with carbon deposits. By high partial pressure of H₂O the sintering and oxidation of catalyst can occur and non-active Co-bounding can be formed.

The process temperature influences the selectivity of the catalyst; e.g. higher temperature causes influence on selectivity of methane.

**Iron based catalysts**

Fe-based catalysts provide an attractive (cheaper) alternative to Co-based catalysts for the Fischer–Tropsch synthesis (FTS). They lead to more olefin products and to lower CH₄ selectivity than Co-based catalysts over a wide range of temperature and H₂/CO ratios. Also the iron catalysts are used in combination with a carrier (SiO₂, Al₂O₃, TiO₂, MgO, ZrO₂). The activation of Fe-based catalysts is more complex that by Co-based ones.

Catalysts for Fischer – Tropsch synthesis are very sensitive again impurities which can poison them. Such impurities as NH₃, HCN, H₂S, COS. HCl causes corrosion of catalysts. Alkaline metals could cause deposits on the catalyst. Tars are deposited, cause poisoning of catalyst and contaminate the products. And particles (dust, soot, ash) can cause fouling of the reactor.

The removal limit is based on an economic optimum determined by catalyst stand-time and investment in gas cleaning. But generally, all these impurities should be removed to a concentration below 1 ppmV.
6.2.1.4 Products of Fischer-Tropsch synthesis

Products of F-T synthesis is a mixture of not converted synthesis gas, gasoline, diesel and waxes. The typical product distribution is shown in the figure below.

![Figure 43: Products of FT synthesis - ASF-model [63]](image)

After the FT process further processing is necessary to obtain the separated the products. Hydrocracking and fluid catalytic cracking are suitable methods for products separation. The composition of the FT raw products depends on the FT process and its operation. Higher temperatures of the process lead to lighter and more olefinic products. Products selectivity can be also controlled by the composition of synthesis gas. In addition, the catalyst can be tailored to promote or suppress olefins and oxygenated formations. [63]

**Hydrocracking**

During the fractionated distillation, the products as gasoline, diesel and waxes are separated. Diesel fraction could be used as a fuel immediately after this process step because of its high cetane number. Gasoline must be further processed because of its low rate on aromatics. The most difficult process is the processing of wax fraction. During the hydrocracking the long-chain-compounds are split into short-chain-compounds with the hydrogen. In the following table can be seen that by the hydrocracking the yield on diesel and kerosene increases.
Table 6: Raw and final products from hydrocracking [63]

<table>
<thead>
<tr>
<th>Raw products</th>
<th>Final products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ratio [m-%]</td>
</tr>
<tr>
<td>Naphtha</td>
<td>39</td>
</tr>
<tr>
<td>Diesel</td>
<td>42</td>
</tr>
<tr>
<td>Waxes</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fluid catalytic cracking (FCC)

During the FCC the distillation and isomerization of gasoline fraction takes place. The wax-fraction is converted into gas, gasoline, light cycle oil and rest. The products and their ratios can be seen in the following table.

Table 7: Raw and final products before and after FCC [63]

<table>
<thead>
<tr>
<th>Raw products</th>
<th>Final products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ratio [m-%]</td>
</tr>
<tr>
<td>Naphtha</td>
<td>39</td>
</tr>
<tr>
<td>Diesel</td>
<td>42</td>
</tr>
<tr>
<td>Waxes</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.2.2 Methanol production

Methanol is produced from synthesis gas by the hydrogenation of carbon oxides over a suitable (copper oxide, zinc oxide, or chromium oxide-based) catalyst according to:

\[ \text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} \]  \hspace{1cm} [eq. 28]

\[ \text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \]  \hspace{1cm} [eq. 29]

The first reaction [eq. 28] is the primary methanol synthesis reaction. A small amount of CO₂ in the feed (2-10%) acts as a promoter of this primary reaction and helps maintain catalyst activity. The stoichiometry of both reactions is satisfied when \( R \) in the following relation is 2.03 minimally. In many cases H₂ builds up in the recycle loop, which leads to an actual \( R \) value of the combined synthesis feed (makeup plus recycle feed) of 3 to 4.

\[ R = \frac{\text{H}_2 - \text{CO}_2}{\text{CO} + \text{CO}_2} \]

The methanol synthesis reactions are exothermic and give a net decrease in molar volume. Therefore, the equilibrium is favoured by high pressure and low temperature. During the process, heat is released and has to be removed to keep optimum catalyst life and reaction rate. Typically, about 0.3% of the produced methanol reacts further to form side products as dimethyl ether, formaldehyde or higher alcohols.

The catalyst deactivates primarily because of loss of active copper due to physical blockage of the active sites by large by-product molecules, poisoning by halogens or sulphur in the synthesis gas, which irreversibly form inactive copper salts, and sintering of the copper crystallites into larger crystals, which then have a lower surface to volume ratio.

Conventionally, methanol is produced in two-phase systems: the reactants and products forming the gas phase and the catalyst being the solid phase. The production of methanol from synthesis gas was first developed at company BASF in Germany in 1922. This process used zinc oxide - chromium oxide catalyst with poor selectivity, and required extremely vigorous conditions—pressures ranging from 300–1000 bar, and temperatures of about 400 °C. In the 1960s and 70s the more active Cu/Zn/Al catalyst was developed allowing more energy-efficient and cost-effective plants, and larger scales. Processes under development at present focus on shifting the equilibrium to the product side to achieve higher conversion per pass. Examples are the gas/solid/solid trickle flow reactor, with a fine adsorbent powder flowing down a catalyst bed and picking up the produced methanol; and liquid phase methanol processes where reactants, product, and catalyst are suspended in a liquid. Fundamentally different could be the direct conversion of methane to methanol, but despite a century of research this method has not yet proven to be economically feasible.
Methanol is nowadays mostly produced from fossil fuels such as coal and methane. For PtL systems methanol can play an important role as a bio fuel if it is produced from renewable energy sources. For the production process of renewable methanol, it is necessary to consider:

- storage of hydrogen
- production, storage and distribution of methanol (methanol synthesis, tanks, pipelines, fuel filling stations)
- methanol utilization (Otto motor, gas turbine, gas and steam plants, heat pumps, fuel cells vehicles)

At the moment there is no existing infrastructure for direct usage of methanol as by e.g. SNG, but the its production is relatively simple and efficient and also partly compatible with fossil fuels infrastructure.

Anyway, there is a possibility to produce gasoline from methanol and this can be used immediately in existing infrastructure without any doubts.
6.2.2.1 Methanol to gasoline

The conversion of methanol to gasoline proceeds essentially according to reaction

\[ n\text{CH}_3\text{OH} \rightarrow (\text{CH}_2)\_n + n\text{H}_2\text{O} \]  \[\text{eq. 30}\]

\((\text{CH}_2)_n\) represents here a wide range of paraffinic and aromatic hydrocarbons produced during the gasoline synthesis step.

The methanol feed is pumped to 2.27 MPa followed by vaporisation and superheating to 297°C in heat exchange with the hot reactor effluent. An adiabatic fixed-bed dehydration reactor is used to convert the feed to an equilibrium mixture of methanol, DME and water. The effluent exits the reactor at 407°C and 2.17 MPa, is admixed with recycle gas and fed to a second reactor where it is converted to gasoline.

Figure 46: Two-step methanol-to-gasoline synthesis section [64]

Mass and energy flows comparison during thermal biomass gasification using oxygen or steam as fluidizing agent in combination with or without additional hydrogen from surplus electricity to produce gasoline or methane was provided by Hannula [64].

All plants consumed 100 MW (LHV) of wet (50 wt%) biomass residues, corresponding to 5,92 kg/s flow of dry biomass into the process.

Table 8: Summary of performance metrics [64]
Configurations:

- **OG**: Oxygen gasification and gasoline production
- **SG**: Steam gasification and gasoline production
- **OG+**: Oxygen gasification and gasoline production + extra hydrogen to syngas
- **SG+**: Steam gasification and gasoline production + extra hydrogen to syngas
- **OM**: Oxygen gasification and methane production
- **SM**: Steam gasification and methane production
- **OM+**: Oxygen gasification and methane production + extra hydrogen to syngas
- **SM+**: Steam gasification and methane production + extra hydrogen to syngas

Figure 47: Simulated energy flows for gasoline configurations featuring hydrogen enhancement
Following table offers an overview on boosting the process adding the hydrogen to synthesis gas (CO₂ from syngas utilized) to produce gasoline or methane.

Table 9: Gasoline and methane production with and without adding of extra hydrogen [64]

<table>
<thead>
<tr>
<th></th>
<th>Oxygen gasification</th>
<th>Oxygen gasification + extra hydrogen</th>
<th>Steam gasification</th>
<th>Steam gasification + extra hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline production [MW]</td>
<td>51,8</td>
<td>134</td>
<td>51</td>
<td>98</td>
</tr>
<tr>
<td>Methane production [MW]</td>
<td>66,8</td>
<td>205,4</td>
<td>63,7</td>
<td>139,9</td>
</tr>
</tbody>
</table>

The highest overall efficiency is attained by non-enhanced methane production via oxygen gasification (green field) and the lowest by enhanced gasoline production via oxygen gasification (yellow field). The addition of electrical input to the process contributes to additional synfuel produced. With the state-of-the-art alkaline electrolyser technology chosen for this work, 48.4 - 55.1% energy conversion efficiencies from electricity to synfuel (LHV) can be achieved. Mass yields lay in the range of 193 - 226 kg/tonne (dry biomass) for the non-enhanced configurations but can be dramatically increased up to 694 kg/tonne (dry biomass) with maximal hydrogen enhancement.

Carbon flow – difference between oxygen and steam gasification:

In oxygen gasification, where heat is generated within the gasifier by partial oxidation, all CO₂ leaves the gasifier as synthesis gas, whereas in steam gasification, where oxidation reactions take place in a separate reactor with air, part of the CO₂ “escapes“ further processing as nitrogen-diluted flue gas.

The second significant difference in carbon flows relate to the way syntheses operate. In methane production, all compounds in the fresh syngas feed end up in the product (with the exception of reaction water that is removed by means of condensation), while in methanol and gasoline production a stream of purge gas is removed from the recycle loop to avoid build-up of inerts in the system. Some carbon is thus inevitably lost from the process, contributing to lower overall carbon conversion.

Hannula evaluated also process economics. The first parameter was TCI (total capital investment). TCI for steam gasification are estimated to be 7-22 M€ lower than for oxygen gasification process. These reductions are caused by the lack of oxygen, water-gas shifting and CO₂ removal. The configuration with enhanced hydrogen have higher TCIs. For all configurations, methane-producing plants feature the lowest TCIs, ranging from 173 to 190 M€, while for gasoline-producing plants the TCIs range from 227 to 272 M€.

The corresponding break-even electricity prices are also calculated. For gasoline configurations, hydrogen enhancement becomes feasible when the average annual cost of electricity drops below 35.4 €/MWh (OG+) or 33.9 €/MWh (SG+). For methane configurations, the break-even thresholds are 27.7 €/MWh (OM+) or 25.1 €/MWh (SM+).

As a summary following should be pointed out:

- All the examined plant configurations are based on technologies that are either commercially available or at the very least successfully demonstrated at pre-commercial scale
When the production of synthetic biofuels is maximally enhanced by an external hydrogen source (used to hydrogenate also the gasification-derived CO₂ to synfuels), the following increases in fuel output can be observed:
  - 2,2-fold (methane) or 1,9-fold (gasoline) for designs featuring steam gasification
  - 3,1-fold (methane) or 2,6-fold (gasoline) for designs featuring oxygen gasification

Overall carbon conversions can be achieved with enhanced configurations:
  - 67,0% (methane) and 58,4% (gasoline) for steam gasification
  - 98,0% (methane) and 79,4% (gasoline) for oxygen gasification

Based on the cost analysis, the conversion of gasification-derived CO₂ to fuels with external hydrogen becomes economically feasible when low-carbon hydrogen can be acquired at a cost that is lower than:
  - 2.2 €/kg (methane) and 2.7 V/kg (gasoline) for enhanced designs featuring steam gasification
  - 2.4 V/kg (methane) and 2.8 V/kg (gasoline) for enhanced designs featuring oxygen gasification

Following table offers overview on potential biofuels output in the EU by 2030 for selected plant configurations based on 197 Mt/a residue availability. Total energy demand of 221 Mt for road transport is assumed in EU 2030. [65]

Table 10: Biofuels output potential [65]

<table>
<thead>
<tr>
<th>Configuration</th>
<th>OG</th>
<th>OG+</th>
<th>OM</th>
<th>OM+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residue availability, 15 wt%</td>
<td>Mt/a</td>
<td>197</td>
<td>197</td>
<td>197</td>
</tr>
<tr>
<td>Residue availability, 0 wt%</td>
<td>Mt/a</td>
<td>167</td>
<td>167</td>
<td>167</td>
</tr>
<tr>
<td>Primary energy supply, 15 wt%</td>
<td>TWh/a</td>
<td>765</td>
<td>765</td>
<td>765</td>
</tr>
<tr>
<td>H₂ requirement</td>
<td>TWh/a</td>
<td>778</td>
<td>1152</td>
<td></td>
</tr>
<tr>
<td>Electricity requirement</td>
<td>TWh/a</td>
<td>1161</td>
<td>1720</td>
<td></td>
</tr>
<tr>
<td>Biofuel output</td>
<td>Mt/a</td>
<td>33</td>
<td>85</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Mtoe/a</td>
<td>35</td>
<td>91</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Mbbld/d</td>
<td>0.7</td>
<td>1.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

As can be seen in the table above, in 2030 it could be theoretical possible to cover the transport fuel demand from 41% (gasoline) and 63% (methane). However, it should be pointed out that biomass residues are dispersed in the nature and that is why the maximum potential could not be achieve in an economically feasible way. Anyway, if only forest residues would be taken in account, the hydrogen enhancement would still allow to supply 18-28 Mt/a of renewable synfuels, displacing 8-13% of road transport fuel demand in 2030.

At the European level, maximal hydrogen enhancement of the total feedstock potential would create an additional demand for 778-1152 TWh/a of hydrogen or 1162-1720 TWh/a of low-carbon electricity if hydrogen is to be produced via water electrolysis using 67% (LHV) efficient alkaline electrolysers.

6.2.3 Advantages of PtL to PtG systems

The European Union promotes in its programs the usage of renewable fuels, already in 2020 share on biofuels should be remarkable. Between 2020-2025 electro mobility should play an important role and hydrogen powered transportation should be relevant after 2030.

A significant advantage of the FT gasoline and diesel is the fact that they could be used in already existing filling stations immediately and without further investment costs. Furthermore, FT process can be operated isothermally and the FT catalyst is less sensitive to load changes. The slurry reactor is already state of the art and can be operated by different load changes. On the other
hand, three-phase reactors for methanation are in development phase, furthermore the methanation process by loads fluctuation it is still unclear.

The environmental benefits of PtL are significant when using electricity, CO$_2$, and water from renewable sources. Greenhouse gas emissions of PtL can be made carbon-neutral when using renewable electricity and CO$_2$ from biomass gasification or biogas (fermentation).

As a synthetic fuel, PtL offers improved combustion with fewer pollutants, which makes it attractive for production of e.g. aviation fuels. By the way, in aviation today, only jet fuels from FT process have already satisfied all tests for being used as drop-in fuels.
6.2.4 Power to liquids - Projects

6.2.4.1 Project WINDDIESEL [66]

Figure below displays, how the thermal biomass gasification process is extended by the Winddiesel concept.

The idea behind is that a biomass-to-liquid plant based on FT synthesis is operated for more than 8000 hours per year as a base load. Electrical peak power is used to generate H₂ via electrolysis, if it is available. During base load operation, biomass is converted into syngas, which has an optimal H₂/CO ratio of 2:1 for the attached FT-process.

The conversion to hydrocarbons take place in the FT reactor, completed finally by upgrading processes like hydroprocessing, rectification, etc.

When H₂ is injected into the process chain, the gasification zone of the FICFB gasifier is fluidized with CO₂, or a mixture of CO₂ and steam. The CO₂ required for fluidization is separated from the syngas and recycled to the gasifier. This decreases the H₂/CO ratio, thus additional H₂ can be injected with the consequence of fluctuating flows of syngas correlated with H₂-feed.

The production conditions of the FT process can be set in a way that the products obtained are almost completely compatible to diesel fuel and gasoline. This is of inestimable value as the filling station infrastructure for these alternative fuels including the products from Winddiesel technology exists already completely. Because there is no need for any investment in that field an important structural market barrier for Winddiesel products are lacking.

In near future, only methane from PtG could be a competitive product to Fischer Tropsch fuels.

Further advantage of this concept is as the H₂ should come from excess electricity, the Winddiesel plant that is based on biomass gasification and FT synthesis can be operated in its main parts with high annual operating hours. The addition of H₂ from excess electricity brings about only a surplus in product yield and conversion rate of the used biomass but is not necessary for the synthesis process.
Economic analysis of Winddiesel project

Table 11: Scenario 1 - dual fluidized bed gasifier with FT synthesis

<table>
<thead>
<tr>
<th>Facility size</th>
<th>50 MW</th>
<th>200 MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment cost</td>
<td>€86.650.000</td>
<td>227.450.000</td>
</tr>
<tr>
<td>Annual profit</td>
<td>3.876.600</td>
<td>20.217.225</td>
</tr>
<tr>
<td>Profit/Inv. costs</td>
<td>4,5</td>
<td>8,9</td>
</tr>
<tr>
<td>Payback time</td>
<td>years</td>
<td>11,2</td>
</tr>
</tbody>
</table>

Table 12: Scenario 2 - dual fluidized bed gasifier with FT synthesis with steam generation process

<table>
<thead>
<tr>
<th>Facility size</th>
<th>50 MW</th>
<th>200 MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marginal costs generated eco power</td>
<td>€61,50</td>
<td>69,00</td>
</tr>
<tr>
<td>Investment cost</td>
<td>€103.050.000</td>
<td>270.050.000</td>
</tr>
<tr>
<td>Annual profit</td>
<td>4.603.600</td>
<td>23.984.125</td>
</tr>
<tr>
<td>Profit/Inv. costs</td>
<td>4,5</td>
<td>8,9</td>
</tr>
<tr>
<td>Payback time</td>
<td>years</td>
<td>11,2</td>
</tr>
</tbody>
</table>

Table 13: Scenario 3 - Winddiesel

<table>
<thead>
<tr>
<th>Facility size</th>
<th>50 MW</th>
<th>200 MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full load electrolysis/y</td>
<td>hours</td>
<td>3.460</td>
</tr>
<tr>
<td>Investment cost</td>
<td>€150.350.000</td>
<td>412.250.000</td>
</tr>
<tr>
<td>Annual profit</td>
<td>6.723.751</td>
<td>36.643.188</td>
</tr>
<tr>
<td>Profit/Inv. costs</td>
<td>4,5</td>
<td>8,9</td>
</tr>
<tr>
<td>Payback time</td>
<td>years</td>
<td>11,2</td>
</tr>
</tbody>
</table>

As can be seen in the table above, at least 3.460 full load hours of electrolyser are necessary to see this scenario as an attractive and competitive way of the process.

However, not only load hours of electrolyser influence competitiveness of the process, further relevant factors are e.g. profit from produced oxygen during electrolysis, investment costs of electrolyser, etc. In the following figure, it can be seen the dependence of full load hours on profit from produced oxygen.

![Figure 49: Dependence of Break-Even Point Winddiesel on profit from oxygen sale](image)

The dependence on investment costs of electrolyser are shown in the figure bellow.
The next factors influencing the economy of the process are feedstock price and payback time.

By the feedstock price below 15 EUR/MWh will be feedstock of lower quality expected, which could cause several problems during the gasification process (e.g. feeding, gas cleaning, etc.).

Significant factor to make the “Winddiesel” process attractive and competitive is funding. In this case funding about 50% could be possible due to CO₂ savings potential and innovation principle. But also without any funding, could be this process competitive. Details can be seen in the following figure.
It is possible to influence the fractions of FT products by the choice of catalyst. Shift to higher wax production is still a possibility, furthermore based on the actual wax prices on the market is this highly recommended. Actually, wax prices above 2 EUR/kg can be expected. Figure above shows the effect of wax prices on payback period and ROI. As can be seen, lower wax prices cause clearly worse economy of the process. On the other hand, more diesel and less waxes can be produced by low wax market prices.

Figure 52: Effect of wax price on payback period and ROI

Figure 53: Effect of electricity price on payback period and ROI

Figure above shows effect of electricity price from volatile sources (PV, wind). As can be seen, lower electricity prices causes better economy of the project.

The whole report can be found also at the Task 33 website in the section "Other publications and reports".
6.2.4.2 Project GreenSynFuel [67]

The purpose of the project was to select and validate technology concepts for the establishment of a Danish production of green synthetic fuels primarily for fuel cells. The feasibility of the selected concepts is assessed through a techno-economic calculation, which includes mass and energy balances and economics including CAPEX and OPEX assessments.

The project “GreenSynFuels” focuses on two concepts:

1. Methanol/DME synthesis based on electrolysis assisted gasification of wood
2. Methanol/DME synthesis based on biogas temporarily stored in the natural gas network

In this report, the attention will be paid only to the first concept.

Figure 54: Methanol/DME synthesis based on electrolysis assisted gasification of wood [67]

The project “GreenSynFuel” focuses on large-scale plants, therefore, the plant with input of 1.000 tons wood per day was in consideration. The resulting methanol output will be about 1.050 tons methanol per day.

The methanol synthesis plant was combined with an electrolyser, so in comparison to a traditional methanol synthesis plant operating on biomass gasification without electrolysis, the plant methanol output is doubled and the methanol production efficiency is boosted from 59 % to 71 %. The total plant efficiency was 81.6 %.

The economic analysis revealed that green methanol can indeed be produced at prices very close to the current oil price (1.5-2 times the existing oil price, February 2010). Interestingly, it was found from the studies that the methanol production prices are not favored by the expected increasing market of cheap electricity, as the general energy prices are expected to increase.

The methanol production stays in front of this project, but also further synthetic green fuels may be produced based on this concept.

Baseline study of GreenSynFuels project:

- biomass resources – description of a potential in Denmark
- gasification – technology description
- gas conditioning and upgrading (cleaning)
- methanol synthesis
- electrolysis
For this project, a pressurized (10 bar) bubbling fluidized bed gasifier from Carbona, which is shown in following figure, was chosen. Wood pellets served as a feedstock. As the gasifier was pressurized, CO₂ was used to pressurize the inlet biomass feed. Furthermore, bed material was continuously added at the feed line. Steam and oxygen entered the gasifier at the lower part of gasifier, near the bottom as can be seen in the figure.

![Image of pressurized bubbling fluidized bed gasifier](image)

Figure 55: Principle of a pressurized bubbling fluidized bed gasifier from Carbona [67]

Mass and heat balances are displayed in the table below.

Table 14: Gasifier mass and heat balance

<table>
<thead>
<tr>
<th></th>
<th>INPUT</th>
<th>OUTPUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>11.57</td>
<td>207.5</td>
</tr>
<tr>
<td>Bed material</td>
<td>0.10</td>
<td>0.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>3.03</td>
<td>0.6</td>
</tr>
<tr>
<td>Steam</td>
<td>2.58</td>
<td>0.9</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.40</td>
<td>0.0</td>
</tr>
<tr>
<td>Total IN</td>
<td>17.69</td>
<td>208.9</td>
</tr>
</tbody>
</table>

A novel concept is shown in a following Sankey chart. In the SOEC assisted gasification concept the production of the electrolysis unit is controlled by the balancing of the stoichiometric ratio of the methanol synthesis process, therefore hydrogen from electrolysis is added to adjust the necessary ratio. The produced hydrogen is added after the H₂S wash, omitting the shift reactor and CO₂ wash. Thus, more CO₂ is exploited in the process as during the traditional methanol production plant based on gasification of biomass. The oxygen used in the gasifier is produced by the SOEC in excess quantities. The tar reformer is in this case also heated by the purge gas from the methanol synthesis reactor. Excess heat is recuperated using production of steam at two pressure levels, 120 and 38 bar. The high pressure steam is overheated to 520 °C. Electricity is produced in two counter pressure steam turbines with an assumed isentropic efficiency of 85%. The remaining excess heat between 60 and 90 °C is used for district heating. The SOEC is operated in thermo-neutral state, i.e. excess heat is used to generate and superheat the feed of steam.
In the near future biomass is going to be a limited resource. Therefore, upgrading of biomass, with other renewable energy sources such as sun or wind, will become very relevant in the future. In that context, it is important to introduce carbon efficiency as a measure of how well a given plant is to preserve carbon in the process. The carbon efficiency calculated for the SOEC concept was 84% and only 42% for the traditional concept. It means, adding hydrogen produced from electrolysis to the methanol synthesis process significantly improves the carbon efficiency. The reason is also that amount of CO₂ could be used for methanol production, which is removed in the conventional systems without electrolysis in order to adjust C/H ratio.

**Economic analysis**

Three different scenarios were analyzed:

1. Gasification only – methanol from oxygen gasification of wood pellets only
   - CO₂ is purged from the process in order to ensure the optimal C/H ratio
2. Balanced SOEC – methanol from mixed hydrogen from electrolysis and oxygen gasification of wood pellets
   - The optimal balanced mix of C/H ratio is obtained by mixing hydrogen from electrolyser with the gasified and cleaned up product gas
3. Turn down SOEC/Alkaline
   - Similar as option 2, however the control strategy is to turn down electrolyser to 1/3 of the rated capacity when the electricity price is too high.
   - This gives the ability to use the plant actively as regulating power towards the grid.

As conclusions of economic analysis, it is believed that green methanol will become cheaper than conventional gasoline if the oil hits 120 USD/barrel in the near future or 141 USD/barrel in 2025. These figures are based on available gasification units and SOEC. In order to realize this potential, further development of gas purification (char removal) and SOEC needs to be conducted. When the calculations are made based on the already existing alkaline technology the relative oil price needs to be 147 USD/barrel based on energy input prices of 2010.
**Conclusions of the project GreenSynFuel:**

Considering a traditional gasification plant approx. 500 tons methanol can be produced from 1,000 tons of wood. (1,000 t wood = 523 t methanol).

However, when adding hydrogen to adjust the equilibrium of the methanol synthesis reaction, the plant output is doubled, the plant can therefore produce over 1,000 t methanol from 1,000 t wood (1000 t wood = 1053 t methanol).

Surprisingly high plant efficiencies were found, on a traditional gasification plant with oxygen input a methanol production efficiency of (\(\eta_{\text{meoh}} = 59.2\%\)) was found, and for the electrolysis-assisted plant a methanol production efficiency of (\(\eta_{\text{meoh}} = 70.8\%\)) was found. Therefore, not only electrolysis can double the production output, it can also boost the plant methanol production efficiency. The total efficiency of the two analyzed concepts was however similar (\(\eta_{\text{tot}} = 81.6\%\)), as district heating is better recovered in the traditional plant concept.

The economic analysis was conducted using a simple CAPEX/OPEX approach. The results of the analysis showed that if SOEC and other critical plant components were readily available today, green methanol can be produced at an oil equivalent price of 120 USD/barrel. Considering the current oil price (approx. 100 USD/barrel), the feasibility gap is quite small for a green substitute. The analysis also showed that the production cost is likely to increase in the future, due to the expected increase in energy prices (biomass and electricity), even though the number of available hours of cheap spot market electricity will increase as a function of wind energy penetration to the energy system.
6.2.4.3 Sunfire projects

In the Sunfire projects the air as a CO₂ source is used, anyway it should be mentioned in this report, while CO₂ from thermal gasification of biomass and waste could be used as well.

Sunfire was founded in 2010 by Carl Berninghausen, Christian von Olshausen and Nils Aldag. The company is supported by business angels (‘Sunfire Entrepreneurs Club’), INVEN Capital, the ERP Startfonds at the KfW bank, Total Energy Ventures and Electranova Capital, which is financed, in turn, by the EDF Group and Allianz.

Sunfire GmbH develops and manufactures steam-electrolysers (SOEC) and high-temperature fuel cells (SOFC).

The Power-to-Liquid (PtL) technology developed by the Dresden based startup company Sunfire, consists of three key elements, as displayed in figure below: (1) high-temperature solid-oxide steam-electrolysis, (2) CO₂ conversion via reverse water-gas shift reaction, and (3) Fischer-Tropsch synthesis. A first economic analysis based on numbers from 2014 was conducted. The electric energy costs for the production of synthetic fuels (plant and operating costs where not yet included) were estimated to 7 Eurocents per kilowatt-hour [68]. The total production costs would be much higher. Compared to the novel approach, fossil fuels were estimated to 6 Eurocents per kilowatt hour, based on crude oil price of $100 per barrel in 2014 [69].

![Power-to-Liquids](image)

Figure 57: The Sunfire process Power to liquids [71]

The high-temperature electrolyser of the Sunfire project reaches an electrical efficiency of more than 90 % from power to H₂ by integrating waste heat from Fischer-Tropsch. It is designed to operate reversible as both, fuel cell and electrolyser, which creates a unique business model. The fuel cell/electrolyser is able to produce high caloric chemicals, when renewable excess energy is available. In times of energy penury, the system supplies electricity by converting stored high caloric chemicals. Consequently, the novel technology creates a new income as operation reserve of the electrical grid. [70]

Specifications of electrolysis modules can be seen in the following table.
Table 15: Technical specifications of electrolysis module by Sunfire [71]

<table>
<thead>
<tr>
<th>Power (per module) a)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Rated electrical power (AC):</td>
<td>150 kW</td>
</tr>
<tr>
<td>Load variation (H₂ output):</td>
<td>0 to 125 % b) c)</td>
</tr>
<tr>
<td>Electric efficiency (AC):</td>
<td>82 % LHV c)</td>
</tr>
<tr>
<td>Specific electric energy (AC):</td>
<td>3.7 kWh/Nm³ c)</td>
</tr>
<tr>
<td>H₂ production:</td>
<td>40 Nm³/h c)</td>
</tr>
<tr>
<td>H₂ pressure (after compression):</td>
<td>10 bar (g)</td>
</tr>
<tr>
<td>H₂ purity (after gas cleaning):</td>
<td>99.999 %</td>
</tr>
<tr>
<td>Steam input:</td>
<td>Saturated steam: 40 kg/h @ 150 °C</td>
</tr>
<tr>
<td></td>
<td>Pressure: 3 bar (g)</td>
</tr>
<tr>
<td>Electrical interface:</td>
<td>3 phase, 380/400/480 VAC; 50 Hz/60 Hz</td>
</tr>
<tr>
<td>Noise:</td>
<td>&lt; 60 dB @ 3 m distance</td>
</tr>
<tr>
<td>Ambient temperature:</td>
<td>−20 °C to +40 °C</td>
</tr>
<tr>
<td>Communication:</td>
<td>Communication for remote monitoring and control</td>
</tr>
</tbody>
</table>

In the table can be seen an average performance at beginning of life. Performance over its operation life may vary due to integration and installation concept as well as operating conditions.

a) Modules can be multiplied to meet hydrogen demand. All products are offered in standard containers
b) Idle mode close to operating temperature is possible
c) At 100% rated power performed at standard testing conditions and beginning of life

The three key elements electrolyser/fuel cell, reverse water gas shift reaction, and Fischer-Tropsch reaction were combined and developed in an industrial relevant scale within the Sunfire project. Based on the research results, the Sunfire team designed and constructed a PtL demonstration plant that was worldwide the first of its kind. Currently, the plant is able to produce one barrel per day of synthetic diesel fuel from CO₂, water, and renewable energy [72]. It is noteworthy that this synthetic liquid fuel is free of any sulfur, nitrogen, aromatic compounds, or fossil oil, and hence performs superior as compared to fossil fuels. Due to the Fischer-Tropsch unit, in addition to synthetic fuels, kerosene for aviation and waxes for the cosmetic industry can be produced by the Sunfire technology (TRL 6).
In April 2015, the German Federal Minister of Education and Research, Johanna Wanka, fueled her official car with the first five liters of the so called “e-diesel”, refined from Sunfire’s “Blue crude” for a test drive, which was recognized worldwide by global media coverage.

FIRST COMMERCIAL PLANT FOR THE PRODUCTION OF BLUE CRUDE PLANNED IN NORWAY [71]

Nordic Blue Crude, Sunfire, Climeworks and the plant manufacturer EDL Anlagenbau start with the planning of a plant which shall produce 10 million litres per year. Production in the industrial park Heroya in Norway shall start in 2020.

Price of Synthetic crude oil substitute called Blue Crude, which is a CO2-neutral alternative for mobility and chemical sector should be less than 2.00 Euros. Nordic Blue Crude relies on affordable renewable electricity from hydropower and CO2 generated directly from ambient air.

The plant should supply up to 13,000 cars with e-fuel and annually avoids 21,000 tons of CO2 emissions from fossil fuel.

It will be operating with an electric capacity of 20 megawatts, producing 8,000 tons of Blue Crude per year. The synthetic Blue Crude consists of various hydrocarbons – making it comparable with crude oil. Refineries can use it as raw material for waxes, but also petrol, diesel, kerosene and even rocket fuel.

About 3,000 products, which are currently made from crude oil, could be manufactured on the basis of Blue Crude – from chewing gums and credit cards to sneakers and smartphones all the way to climate-neutral fuels. Thus, a replacement is created, which can be employed directly by utilizing the existing production processes and distribution networks, without any complex renewals or adjustments.

The clean tech company Nordic Blue Crude AS, located in the harbour and industrial city of Porsgrunn, will operate the power-to-liquids plant and already markets the synthetic crude oil substitute to manufacturers of cars, trucks, trains, airplanes and ships as well as to specialized chemical refineries and other customers.

Since 2016 the company holds the exclusive rights for Norway and Sweden. In the long-term up to ten similar plants could become reality in Scandinavia.

Blue Crude is created in a highly efficient, three-stage process, developed by Sunfire and consists of a patented power-to-liquid procedure employing nothing but water, CO2 and renewable energy – in Norway the continuously available, cost-efficient green energy from hydropower is put to use.

The core element is the steam electrolysis process (SOEC) that efficiently splits steam into its components hydrogen and oxygen. Subsequently the CO2 is transformed into carbon monoxide (CO) and then the synthesis towards Blue Crude is effectuated. The gaseous CO2, employed as carbon source, is partly extracted on-site from the ambient air by using the Direct Air Capture (DAC) technology, developed by the Swiss company Climeworks. Especially the exploitation of the waste heat from the Sunfire process makes the DAC technology highly efficient.

The timetable and details of the project plans could be seen in the following table.
Table 16: First commercial plant for the production of blue crude – project details [73]

<table>
<thead>
<tr>
<th>H22017 – H1/2019</th>
<th>Preparation of Commercial Scale, FEED, Commercialization &amp; Financing</th>
<th>Equity</th>
<th>€2.5 Million</th>
</tr>
</thead>
</table>

1) **Front End Engineering Design (FEED)**

Completing the FEED study for the 10 million litres plant so that the construction of the plant can be initiated. The purpose of this phase is to get clarification on key assumptions for the construction of the factory and test and finetune the technology in order to generate further soft Intellectual Property (IP). Although the principles of the production are based on known technology and have been tested on a smaller scale, some processes have not been tested on an industrial scale. In this phase therefore, significant resources will be involved in the design, development and engineering of the plant. These include:

- Preparing and filing the documents needed in order to obtain the required permits to initiate construction;
- Adaption and cost assessments of the Reverse Water Gas Shift (RWGS) unit and of the Electrolysis and final SynGas unit;
- Basic engineering and commissioning of the Fischer-Tropsch unit;
- Industrial environment analysis and technical embedding of the Sunfire system;
- Design and finetuning of the refining processes in line with the requirements for both logistic and customer;
- Unit integration, balance of plant design, optimization of output and mix and confirmation and finetuning of FEED conclusions; and
- Modularization and ramp up for optimal cost risk balance towards (1,700 Barrels per Day (BPD) 100 million litre Industrial plant.

2) **Consolidate Commercialization & Distribution**

Develop financial forecasts for the Industrial plant project profitability and environmental outcomes based on CAPEX, OPEX, distribution and off-take agreements achieved, finetune the ideal potential product streams. Define the impacts on society and environment so that investors and authorities can make decision toward investments.
3) Setting Up the Finance of the Commercial Pilot Plant

Closing the finance agreements with equity partners, Enova and Bank finance;

<table>
<thead>
<tr>
<th>Timeframe</th>
<th>Description</th>
<th>Equity</th>
<th>Commercial Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/2019 – H1/2020</td>
<td>Construction of the pilot plant 10 million litres/year (170 BPD)</td>
<td>Enova</td>
<td>£12.4 Million</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bank Financing</td>
<td>£23.3 Million</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>£37.3 Million</td>
</tr>
<tr>
<td>2020 – 2023</td>
<td>Construction of the industrial plant 100 million litres / year (1,700 BPD)</td>
<td>Equity</td>
<td>Commercial Stage</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Enova</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bank Financing</td>
<td></td>
</tr>
</tbody>
</table>

A distribution and wholesale networks will be established to sell the products. The Blue Crude and E-Fuel Certificates will be sold to large Transporters (End users) such as ferry companies, airlines and train service providers.

As mentioned above, the selling price should be about 2€/l and production cost about 1€/l.

A breakdown of production cost can be seen in the following figure.

![Figure 58: Blue crude breakdown](image)

Cost breakdown:
- €70M investment, gives €0.29/litre inclusive interest of 4% for 75% loan financing, with Enova support €0.19/litre
- €0.67/M personnel ann. gives €0.06/litre
- CO2: Swap vs. sale of oxygen
- Electricity: 16kWh/litre. Power= € 0.026/kWh (10 yrs., 8,000 hrs., pos. net loss), GWh= €0.006/kWh, 160 GWh/year is 16 kWh/litre = €0.48/litre
- Refining = €0.05/litre
- Distribution = €0.11/litre
- Total production cost = €0.99/litre
Project stakeholders:

Key stakeholders

**Sunfire** - is a developer and manufacturer of novel galvanic energy converters, which allow transforming solar or winding power into renewable fuels and vice versa with a game-changing efficiency. The Dresden-based firm’s vision is to bridge the gap between the power, fuel, and gas grid in order to make renewable energy available everywhere at reasonable costs. Sunfire’s customers include Air Liquide, Audi, Boeing, ThyssenKrupp, Total and Vaillant. Today, Sunfire employs nearly 100 employees.

**Nordic Blue Crude (NBC) – project coordinator**, will produce high quality, carbon neutral, synthetic fuels and other fossil replacement products, based on water, Carbon dioxide and renewable power.

**Climeworks AG** - is a spin-off company of ETH Zurich providing solutions for efficiently capturing CO2 from ambient air (“direct air capture”, DAC). The company is following its vision of closing the carbon cycle by offering its customers location-independent and environmentally friendly CO2.

**Herøya Industripark** - Landowner and provider of local infrastructure at construction site. The park is operated by Norsk Hydro, one of Norway largest companies and one of the leading aluminum producers in the world offers the following services: industrial sites with electricity grid, cooling water, steam, gas etc., along with good access to road and shipping.

**Yara & Praxair** - the former is a major manufacturer of fertilizer and supplier of CO2. Praxair handles and distribute the CO2 from Yara. Praxair in return will get the O2 that the process generates.

**Statkraft** - largest renewable power producer in Europe, will likely be contracted as supplier of renewable hydro power. For further expansion of the business model, other renewable energy developers will be approached.

**Enova** - is owned by the Norwegian Ministry of Petroleum and Energy and contributes to reduced greenhouse gas emissions, development of energy and climate technology and a strengthened security of supply.

**Norwegian Government** - NBC has met with several leading politicians engaged in the areas of climate and transportation. On a national level, it is assumed that Norway is very eager to protect industry like NBC and has no plan to introduce costly regulations and taxes.

Investors:

Tuft Invest AS owned by Ronald Tuft the founder of Norway’s largest transport company Litra and largest Refugee Reception company Hero. Other investors include Konsulent 1 owned by Jørn Lein-Mathisen, founder of Oslo International Hub and former secretary to Norway’s current prime minister, Åsmund Mandal former Director of FMC, Chijioke Igwe, CEO, Deltalift Resources Nigeria Ltd and Nnamdi Agbim, CEO Interterkel Group.

NBC plans to raise approximately €3 million to secure its upcoming FEED study in addition to €18 million for the construction of the Pilot Plant.
6.2.4.4 AUDI e-diesel project [61]

Together with the partners Ineratc GmbH and Energiedienst Holding AG, the Audi company has plans for a new pilot facility for the production of e-diesel in Laufenburg, in Canton Aargau (Switzerland). For the first time, the energy needed will be supplied from the renewable source of hydropower. The planned facility will have a capacity of around 400,000 liters (105,669 US gal) per year.

Audi e-diesel has the potential to make conventional combustion engines operate almost CO2-neutral. To produce it, the power-to-liquid plant converts surplus hydropower into synthetic fuel. A chemical principle is applied: The green power generated on site in the hydroelectric power station produces hydrogen and oxygen from water by means of electrolysis. In the next step, the hydrogen reacts with CO2, using an innovative and very compact microprocess technology. The CO2 can be obtained from the atmosphere or from biogenous waste gases as well as from thermal gasification and, as with all Audi e-fuels, is the only source of carbon. Long-chain hydrocarbon compounds are formed. In the final process step, these are separated into the end-products Audi e-diesel and waxes, which are put to use in other areas of industry. The following figure offers an overview of the process.

![Figure 59: Audi e-diesel plant in Laufenburg [61]](image)

Construction work started in 2018.

This is now Audi’s second partnership in a pilot facility that operates according to the power-to-liquid principle. Audi has already been working together with the energy technology corporation Sunfire in Dresden since 2014. There, Sunfire was exploring the manufacturing of e-diesel using the above principle, but involving different technologies.

As CO2 source, the biogas and CO2 from the air were employed in the project with Sunfire. To produce the hydrogen a high temperature electrolysis process was utilized.

The Ingolstadt carmaker is also researching the manufacture of e-gasoline together with specialist partners.
7. Summary

The aim of this report was the explanation of the thermal gasification based hybrid systems principal as well as the description of relevant actual projects.

The attention was given especially to Power to Gas (PtG) and Power to Liquids (PtL) technologies, but also direct usage of the thermal solar energy for thermal gasification was mentioned as well.

On this place, it is necessary to mention the advantages and disadvantages of solar, wind and bioenergy and why it is of a great relevance to use these sources in a combination.

The great advantage of solar and wind energy is the fact that they are renewable and their prices decreased rapidly in the last years, what makes them to be the cheapest renewable energy sources on the market now. A lot of cheap excess energy could be produced, but on the other hand this excess electrical power could not be fed into the electric grid immediately in order not be overloaded, but have to be stored. In this case, batteries revealed to be expensive and not intended for a long time energy storage, thus another possibilities were explored.

Disadvantage of wind and solar energy is their fluctuation and intermittence. In contrast to wind and solar energy, the energy from biomass and waste is stable and not fluctuating, but as a source, it is limited in amount.

It was shown, how the renewable hydrogen, produced using electrolysis from an excess wind or solar energy, could be further utilized in a combination with carbon oxides from thermal gasification product gas. In this way, higher amount of renewable energy carriers (the amount can be doubled) in gaseous or liquid forms; using the same amount of biomass could be produced due to better employment of carbon oxides, especially CO₂.

Different types of electrolysers (Alkali, PEM and SOEC) were described and compared each other in this report. Whereas alkali and PEM electrolysers are commercially already available, SOEC, which have a great potential in many aspects are still in a laboratory or pilot scale. Anyway, also by SOEC was a considerable progress made during the last years, so the commercialization of SOEC is awaiting in a short time.

This report describes the technology as well as economic feasibility of gasification based PtG and PtL concepts. The most important factors influencing the price of the final renewable fuels are:

- costs of renewable hydrogen
- costs of biomass
- size of gasification unit
- number of operating hours/year of electrolyser and gasifier
- heat utilization
- usage or selling of high purity oxygen from electrolysis
- subsidy

The price of renewable hydrogen is dependent on type and size of electrolyser as well as on number of operating hours. If only excess electricity (peaks) would be used for hydrogen production, the load (operating hours) of electrolyser would be low, which makes hydrogen price higher, in comparison to the full load over the year.

In case of gasification unit, preferably large-scale gasifiers with about 8000 operating hours/year should be employed for feasible concepts. Important issue is also heat from the process, which should be utilized for district heating or in the process itself. The economics of the gasification process is significantly influenced also by the biomass costs. PtG or PtL process can be more beneficial, if also income from oxygen sale could be included into calculations, as well as subsidy.
As it was shown by e.g. the HELMETH project (PtG), the renewable SNG, which costs 5,7-7,1 €ct/kWh could not compete without subsidy with the fossil natural gas, which price is about 2-3 €ct/kWh. The similar picture was shown also by projects focusing on PtL, also here the prices of renewable fuels were 2-3 times higher than price of their fossil twin brothers.

As a summary, it could be said, that even if technology of PtG and PtL would be advanced enough to be employed now, the crucial fact for the market penetration is the oil price nowadays, what is a benchmark for the economic feasibility of renewable-based technologies. The very low oil price makes PtG and PtL uncompetitive, but isn´t it finally time to realize what the real prices of fossil fuels should be in order to their impacts to our environment?

For the progress of renewable energy employment, not only research on technology, but also advantageous political framework, as a main driver is essential.

On this place is also important to mention, that there is no existing market with surplus electricity at the moment, e.g. in Germany the surplus of electricity, which could not be fed into the grid is recompensed also if units were idling.

That is why the author would like to appeal to politicians, which have the courage and power to go finally off beaten track of fossils and support the renewable energy, which is the key of a healthy life on the Earth, without smog and all the ecological disasters caused by climate change. Let the responsibility towards future generations is more important than the power of money.

Source: Dan Piraro, text adapted by Jitka Hrbek
References

8. Sorensen B. Long-term scenarios for global energy demand and supply: four global greenhouse mitigation scenarios. Energy & Environment Group, Roskilde University, 1999, Roskilde, Denmark
20. The wind energy fact sheet
23. EPA, Electricity storage
(https://www.epa.gov/energy/electricity-storage)
(http://dx.doi.org/10.1016/S0921-5093(99)00092-1)
25. DENA – Power to Gas
(http://www.powertogas.info/fileadmin/content/Downloads/Brosch%C3%BCren/dena_PowertoGas_2015_engl.pdf)
26. Hydrogen mobility Europe
(https://h2me.eu/)
(http://www.messesauber.de/doc/files/e3_1_13_merzel_script.pdf)
(www.dvgw-innovation.de/fileadmin/dvgw/angebote/forschung/innovation/pdf/g3_01_12_tp_b_d.pdf)
(https://doi.org/10.1016/J.IJHYDENE.2015.03.133.)
(http://dx.doi.org/10.1109/JPROC.2011.2156750)
(http://dx.doi.org/10.1016/j.ijhydene.2013.01.151.)
(http://www.dvgw-innovation.de/fileadmin/dvgw/angebote/forschung/innovation/pdf/1411hacker.pdf)
37. Siemens: “Grüner” Wasserstoff.
(http://www.industry.siemens.com/topics/global/de/magazine/process-news/antriebstechnik/seiten/pemelektrolyse.aspx)
38. Proton Onsite: M1, M2. (http://protononsite.com/products/m/#taboverview.)


48. Store&Go project, https://www.storeandgo.info

49. Report on the overall system design and operation tests of the combined system (HELMETH project)


58. Goetz M.: Renewable Power-to-Gas: A technological and economical review; Renewable Energy 85 (2016); 1371-1390
59. F3 project: Bio-SNG production by means of biomass gasification combined with MCEC technique
61. Audi steps up research into synthetic fuels (www.audi-mediacenter.com)
68. The German R&D Program for CO2 Utilization—Innovations for a Green Economy (https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4884562/)
70. BMBF (2015f) Technologies for Sustainability and Climate Protection: Chemical Processes and Use of CO2, Final Conference. Federal Ministry of Education and Research (BMBF)