

IBP0962_17 COMPARISON OF POWER-TO-X TECHNOLOGIES FOR THE PRODUCTION OF FUELS FROM RENEWABLE ELECTRICITY S. Bajohr¹, N. Trudel², F. Graf³, W. Köppel⁴, T. Kolb⁵

Copyright 2017, International Gas Union

This Technical Paper was prepared for presentation at the *International Gas Union Research Conference 2017*, held between October, 24-27, 2016, in Rio de Janeiro. This Technical Paper was selected for presentation by the Technical Committee of the event according to the information contained in the final paper submitted by the author(s). The organizers are not supposed to translate or correct the submitted papers. The material as it is presented, does not necessarily represent the International Gas Union's opinion, or that of its Members or Representatives. Authors consent to the publication of this Technical Paper in the *International Gas Union Research Conference 2017 Proceedings*.

Abstract

The need to reduce the greenhouse gas in all sectors and the necessity to make the transformation in a world with power as primary energy causes enormous economic effort. To minimize this economic effort an overall analysis over all sectors and infrastructure is generally necessary. Based on these considerations first investigations show that a total electrical mobility is not realizable in the next couple of years. Especially the air and the shipping traffic as soon as the road-transport need chemical fuels. Therefore the DVGW funded a research project to evaluate the process chains of carbon based PtG- and PtL-fuels. The system boundary of the process chain is at the inlet side the electrolyzer and the CO_2 -source and at outlet side the fuel. The for the synthesis necessary carbon comes from biomass or from CO_2 found in the ambient air.

The comparison of the process efficiency to fuel for the process chains shows that PtG with biomass as carbon source has an approx. 8 % better process efficiency as PtG with CO_2 found in the ambient air and approx. 10 % better process efficiency as PtL via Fischer-Tropsch-Synthesis with biomass as CO_2 source. These differences are explainable as a result of the complexity of the process chains. Because of the huge complexity of the synthesis of Methanol or OME 3-5 the process efficiency are lower than 40 % and consequently approx. 28 % worse than PtG with biomass as carbon source. But these investigations are still running.

As a first conclusion based on the process efficiencies it can be proposed that Methan is an alternative fuel for mobility if no battery-powered vehicle is possible. But the PtL is essential for the air traffic.

1. Introduction

Germany's long-term greenhouse gas (GHG) reduction targets (80 - 95 % reduction compared to 1990 [Umweltbundesamt/klima-energie 2016]) require an energy supply based on renewable sources across all energy sectors and applications in industry, households and transport.

An energy system, which is completely based on renewable energy sources and not using cultivated biomass for energy supply must allow shifting of electricity-based energy to the heating and transport sectors. Today, approximately 25 % of Germany's total energy consumption is caused by the transportation sector, which is supplied by 94 % of fossil fuels [Umweltbundesamt/energeiverbrauch 2016].

Power-to-X (PtX) identifies technologies that transform power from renewable sources into material energy storage, energy carriers, and energy-intensive chemical products. Power-to-gas (PtG) is a technology for producing hydrogen using electrolysis and methane via methanation [Götz, 2015], while power-to-liquids (PtL) is an electricity-based process for the production of tailor-made liquid fuels (and chemicals) from H₂ and CO₂. Options for the mobility sector are e.g. CNG and LNG via the PtG route and methanol (CH₃OH), Dimethylether (CH₃-O-CH₃) or Fischer-Tropsch based fuels (C_nH_{2n+2}) via the PtL route.

¹ Dr.-Ing. Siegfried Bajohr; Senior Lecturer – Karlsruher Institute of Technology (KIT), Karlsruhe, Germany

² M. Sc. Nike Trudel; phD-student – Karlsruher Institute of Technology (KIT), Karlsruhe, Germany

³ Dr.-Ing. Frank Graf; DVGW Research center at Engler-Bunte-Institute (DVGW-EBI), Karlsruhe, Germany

⁴ Dipl.-Ing. Wolfgang Köppel, DVGW Research center at Engler-Bunte-Institute (DVGW-EBI), Karlsruhe, Germany

⁵ Prof. Dr.-Ing. Thomas Kolb; head of department – Karlsruher Institute of Technology (KIT), Karlsruhe, Germany

Using PtG and PtL technologies will enable implementing an energy supply fully based on renewable sources in the long term. The availability of PtG and PtL technologies is therefore of crucial importance and must be considered in shaping the energy systems transformation process in Germany and beyond.

At current, PtL considerations are at the very beginning. There are manifold approaches, but the most promising options are still to be identified. Therefore, an ongoing DVGW study focusses on evaluation of PtL processes to produce market-near liquid fuels. The most promising routes are evaluated by comparing process efficiency, short- to mid-term applicability, as well as economics.

Special attention is drawn on the comparison of PtL with gaseous fuels from PtG processes, as PtL processes will define the benchmark for the application of PtG processes in future energy systems.

This contribution to the IGRC will show some exemplary results of the ongoing study and will give you an insight into the considerations and approaches which have to be taken into account if reliable predictions are wanted.

2. Process Chains

For the evaluation of possible process chains from power and/or biomass to fuels suitable for current mobility systems, one approach is their breakdown into modular building blocks which can afterwards be rearranged into full process chains. The following figure 1 shows the building blocks used for this work.



Figure 1: Building blocks for process evaluation

Generally, all processes need a suitable carbon and hydrogen source. The hydrogen sources included in this work are water (H₂O) which can be converted into hydrogen (and oxygen) via electrolysis (PEM, alkaline, SOEC) and biomass (approximated formula of $CH_{1.5}O_{0.67}$ which can stand in for most woody biomasses) which can be converted into a hydrogen containing synthesis gas via gasification. In the case of the utilization of biomass this is also used as a carbon source for the fuels produced via synthesis reactions. Additional or alternative carbon can be obtained from the ubiquitous CO_2 found in the ambient air. As the concentration is only about 400 ppm the effort to separate CO_2 from the air and to concentrate it for the following synthesis reactions is very high. Current systems for carbon capture from ambient air consume about 2.3 kWh of energy (thermal and electric) per kg of CO_2 [climeworks, 2017].

Other carbon sources already available from fossil fuels (e. g. flue gases from power plants or off gases from industry) were not taken into account, as their availability after the "Energiewende" is uncertain. Nevertheless, the modular building blocks used in this study allow substituting one carbon source with another if calculations on transition scenarios on the way to complete fossil carbon free fuels are wanted.

The processes shown in figure 2 were chosen as the most mature and realizable technologies. They were built from the different modules and evaluated regarding availability, possible plant sizes, efficiency and compatibility with the current transportation systems.

In this work the results shown will focus on "conventional" fuels like gasoline, diesel, CNG and LNG. More exotic fuels like OME (oxymethylene ether) or methanol are not considered here in detail but will be discussed in future works as the studies on these are not finished yet. Therefore the results shown on the next pages will be

International Gas Union Research Conference 2017

subdivided into processes for CNG and LNG production (chapter 2.1) and processes for liquid fuel productions (chapter 2.2).



Figure 2. Overview of examined processes

2.1. Processes for CNG and LNG production

Renewable CNG and LNG is built via (catalytic or biological) methanation reaction[Götz, 2017; Kopyscinski; 2009; Rönsch, 2016; Bailera, 2016] which is shown in eq. (1).

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \Delta_R H = -165 \text{ kJ/mol}$$
(1)

If a CO containing synthesis gas is used (mostly from gasification processes) then eq. (2) has to be included.

 $CO + 3 H_2 \rightleftharpoons CH_4 + H_2O$ $\Delta_R H = -206 \text{ kJ/mol}$ (2)

Both reactions are strongly exothermic and efficient heat extraction from the reactors involved is mandatory for all processes using catalysts and operating at temperatures of about 300 °C. In case of the biological "cold" methanation heat extraction is no big issue but the energy on the low temperature level of about 50 °C can rarely be used.

Looking at the reactions involved the incorporation of biomass into a process chain necessitates its conversion to synthesis gas containing H_2 and the carbon carriers CO and CO₂. Eq. (3) shows the conversion reaction of woody biomass into synthesis gas via fluidized bed gasification. This type of gasification was chosen for all processes aiming at CH₄ as product as in the gasification significant amounts of methane are formed.

CH_{1.5}O_{0.67} + 0.4 H₂O → 0.5 CO + 0.3 CO₂ + 0.2 CH₄ + 0.67 H₂
$$\Delta_{\rm R}H = 28.7 \text{ kJ/mol}$$
 (3)

Regarding process evaluation the process efficiency expressed by eq. (4) which puts the chemical energy of the final (fuel) products in relation to the total energy input for the whole process chain is a suitable parameter to compare the process chains.

$$\eta_{\rm P} = E_{\rm chem,out} / (E_{\rm chem,in} + E_{\rm therm,in} + E_{\rm el,in}) \tag{4}$$

3

Looking at the first example the following figure 3 shows a possible process chain leading to the products CNG and LNG. SOEC electrolysis was chosen in this case as additional hydrogen source as heat integration from methanation can bring up the efficiency of electrolysis to more than 85 % which procures a process efficiency of 70 % for CNG and 68 % for LNG respectively.



Figure 3: Process chain for CNG or LNG based on SOEC electrolysis and fludized bed biomass gasification as carbon and (primary) H₂ source

The process chain without gasification and utilization of biomass is shown in figure 4. In this case a process for carbon(dioxide) capture from ambient air was included to supply the necessary CO_2 for catalytic methanation. Of course, the energy consumed for carbon dioxide separation from air (2.3 kWh/kg CO_2 according to [climeworks, 2017]) leads to a significant decrease of process efficiency.



Figure 4: Process chain for CNG or LNG based on SOEC electrolysis and CO₂ capture from ambient air as carbon source

Looking at biological (low temperature) methanation as an alternative to catalytic processes at elevated temperatures leads to the process chain shown in figure 5. Here CO_2 from biogas fermentation and upgrading was used as carbon source and biological methanation at 40 °C was performed as method to maximize CH_4 . As no high temperature heat from methanation is available, PEM electrolysis was used as carbon source instead of SOEC, as there is no high temperature heat available on site for process integration. The process efficiency is higher compared to the process shown in figure 4 but cannot reach the values of the process chain shown in figure 3.



Figure 5: Process chain for CNG or LNG based on PEM electrolysis, biological methanation and CO₂ from biogas upgrading as carbon source

2.2. Processes for liquid fuel production

Evaluation of PtX processes has to deal with liquid (synthesis) fuels as more conventional approach to future mobility. The sample process par excellence for PtL (Power to Liquid) processes is the Fischer-Tropsch synthesis based on biomass (high temperature) gasification. This will be done with an entrained flow gasifier producing a clean tar and Hydrocarbon free synthesis gas which is beneficial for all process chains not aiming at methane production.

A typical entrained flow gasification process for biomass feedstocks is the bioliq process invented and brought to pilot scale at KIT [bioliq; 2017]. This process demands a pretreatment of the biomass by pyrolysis (eq. (5)) in order to increase the energy density of the biomass fuel for the necessary transportation to a big scale (>> 100 MW) state of the art entrained flow gasifier. As can be seen from eq. (6) the resulting syngas contains high amounts of H₂ but not enough for the synthesis reaction.

Pyrolysis
CH_{1,5} O_{0,67} → 0,83 CH_{1,08} O_{0,22} + 0,26 H₂ O (+ 1,67 CH_{0,5} O_{1,35})
$$\Delta_{R} H = 13,7 \text{ kJ/mol}$$

(5)
Entrained Flow Gasification
CH_{1,08} O_{0,22} + 0,26 H₂ O + 0,46 O₂ → 0,83 CO + 0,17 CO₂ + 0,56 H₂ + 0,3 H₂ O $\Delta_{R} H = -59 \text{ kJ/mol}$
(6)

The amount of hydrogen can be increased by watergas shift or by addition of hydrogen from electrolysis as shown in figure 6. As excess heat is available in abundance, SOEC is chosen in the process chain. As the Fischer-Tropsch synthesis only works with CO as carbon source, all CO_2 has to be converted to CO by reverse watergas shift (RWGS) and the use of additional H₂. Following the synthesis reaction the product is upgraded to fuel grade products via hydoprocessing. It is obvious, that the additional process steps for pretreatment, RWGS and fuel upgrading in combination with the high process temperatures result in lower process efficiencies than for the methanation processes discussed before.



Figure 6: Process chain for liquid fuels (e. g. diesel and gasoline) based on SOEC electrolysis and entrained flow biomass gasification as carbon and (primary) H₂ source

2.3 Outlook on other PtL fuels

Not shown in this paper are the process chains for other liquid fuels like methanol or OME 3-5 which are sometimes proposed as future fuels or fuel blends of growing importance. A closer look on these process chains and their efficiencies is part of ongoing work of the authors and therefore not shown here. But as a preview on the final results which will be published at the end of 2017 it can be stated that the process efficiencies of these very complex processes are either significantly lower than the 49 % shown for the Fischer-Tropsch synthesis or the application of these fuels seems near impossible in Europe because of health issues.

Methanol is a good example for such criterions for exclusion: Methanol is a very dangerous substance because of its high toxicity coupled with its excellent solubility in water. Its direct use in Europe as fuel for cars or other transportation applications will therefore be near to impossible. As a result more "conventional" and less dangerous fuels have to be synthesized out of methanol. A good example is the synthesis of OME 3-5 (oxymethylene ether: CH₃-O-(CH₂-O)_n-CH₃ with n = 1 to 3) which needs methanol (CH₃OH) as feedstock and formaledehyde (CH₂O) as intermediate produced from methanol. Therefore, the process chain necessary from the educts H₂ and biomass or CO₂ to the final product involves many process units and is only realizable in big scale plants on a highly integrated basis. Furthermore, the total efficiency of such a process like the OME synthesis from CO₂ and H₂ will end up in values of 40 % or significantly less.

3. Summary

The results of the investigations discussed in this work can be summarized with figure 7. In this graph the process efficiencies of the process chains shown in figure 3 - 6 are shown in direct comparison. The highest efficiency can be archived with processes using biomass as carbon and (partial) hydrogen source and CH₄ as final product. Under this prefix biomass gasification coupled with SOEC electrolysis and catalytic methanation results in the highest efficiencies. However, if using CO₂ from ambient air as carbon source the efficiencies go down significantly because of the high amount of energy used for extracting CO₂ from air. In this case biological methanation becomes an attractive option. Coupled with low temperature PEM electrolysis no high temperature processes are necessary and the whole process chain becomes more suitable for simple "stand alone" solutions in smaller scale. Alas, it has to be kept in mind that biological methanation produces the same amount of heat of reaction than catalytic methanation but on the much less attractive temperature niveau of only 50 °C compared to the 300 °C available for the latter.

Aiming for a PtL substitute for conventional liquid fuels the most promising process chain is the Fischer-Tropsch synthesis path leading to gasoline, diesel and kerosene as the main products. Including the necessary product upgrading and separation the efficiencies can reach values near to 50 % if starting with biomass gasification. Using CO_2 from air this value will go down as expected. Furthermore, it has to be kept in mind that the process technology necessary for a viable Fischer-Tropsch process with high efficiencies can only be realized in scales significantly higher than 100 MW (fuel input) which makes this process demanding in biomass, CO_2 and H_2 supply. The same is true for all other processes aiming at liquid fuels (e. g. MeOH, OME 3-5) which were not discussed in detail as they are part of ongoing work. Additionally to low process efficiencies and the necessity for big plant sizes, these processes suffer from

International Gas Union Research Conference 2017

non-compatibility of their products with fuel standards and/or ambient and health issues. These facts are of mayor significance and have to be quantified more in detail and are part of the ongoing work of the authors.



Figure 7: Comparison of the process efficiency to fuel for the discussed process chains

4. Acknowledgements

The authors want to express their thanks to the DVGW for funding the studies which are summarized in their contribution to the IGRC conference.

5. References

https://www.umweltbundesamt.de/themen/klima-energie; 20.09.2016

https://www.umweltbundesamt.de/daten/energiebereitstellungverbrauch/energieverbrauch-nach-energietraegernsektoren; 15.01.2016

GÖTZ, M. et al.: Renewable Power-to-Gas: A technological and economic review.

http://dx.doi.org/10.1016/j.renene.2015.07.066

http://www.climeworks.com/co2-capture-plants.html, 15.03.2017

KOPYSCINSKI, J. et al.: Production of synthetic natural gas (SNG) from coal and dry biomass – A technology review from 1950 to 2009, 2010

RÖNSCH, S. et al.: Review on methanation - From fundamentals to current projects, 2016

BAILERA, M.: Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO₂, 2016 https://www.bioliq.de/english/55.php; 09.04.2017