

Demonstration of a Biogas Methanation Combined with Membrane Based Gas Upgrading in a Promising Power-to-Gas Concept

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The further development of photovoltaic and wind power as renewable energies with their production rate fluctuations both on short- and medium-time-scale result in the necessity of smarter grids and higher energy storage capacities. One very prominent and promising technology for meeting this future electric energy storage demand is the concept of power-to-gas. Here, the excess electric energy is converted to hydrogen using alkaline or PEM electrolysis. Most concepts incorporate an immediate subsequent conversion to methane using a local carbon dioxide source and a process of thermo-catalytic or biological methanation. After a final gas upgrading mainly comprising the separation of H₂, CO₂ and H₂O the produced SNG can be fed to the natural gas grid owning a huge potential for energy storage and distribution. The current work presents the joint research efforts undertaken by the authors in the field of power-to-gas processes. A process chain consisting of a coupled hydrogen dark fermentation and a biogas fermentation, a thermo-catalytic methanation step and product gas upgrading applying membrane-based gas-permeation is developed and demonstrated on laboratory scale. The described process chain has been demonstrated on a scale of roughly 0.5 m³(STP)/h and experimental results will be presented. Special emphasize is laid on the analysis of the methanation performance considering the changing content of the mixed raw biogas. It is shown that the combination of methanation with membrane-base gas separation technology provides significant advantages for process integration.

1. Introduction

Renewable energy sources have become one of the most sought after energy sources in Austria and Germany over the last decades by both the politics and the public. Recent publications predict a potential growth for renewable energy sources to up to 80 % of the produced primary energy in 2050 (Nitsch et al., 2012). A large share of this will be attributed to photovoltaics and wind power. Although they offer renewable energy they also lead to certain problems that have to be addressed. Due to their high volatility in regard to both time and place demand and supply may not match. This leads to the need for ways to store potential excess energy. Power-to-gas offers the possibility to use this energy to produce hydrogen via an alkaline or proton exchange membrane(PEM) electrolysis, which than can either be stored or transformed to methane via the Sabatier reaction or bio-methanation.

When assessing the possible alternatives for energy storage many different parameters have to be taken into account ranging from technological aspects like storage capacity and storage duration to economical ones like the overall storage costs and even social aspects like the need of structural changes in the landscape.

Table 1: Overview of storage technologies (Lehner et al., 2014)

Technology	Efficiency	Specific Energy Storage in kWh/m ³	Time Scale
Pumped hydro storage Δ= 100 m	70-85 %	0.23	h – months
Li-Ion battery pack	80-90 %	270	Min – d
Power-to-gas, Methane p = 200 bar, η _E = 60 %	30-75 %	1,200	Min – months
Compressed air	70-75%	6.9	h – months
Lead acid battery	70-80 %	75	Min – d

As can be seen in Table 1 Power-to-gas offers certain advantages. It has a large specific storage energy capacity as well as large timeframe in which the energy can be stored and withdrawn. Furthermore, the existing infrastructure of the natural gas grid offers a valid option for storage without the need of additional infrastructure. The possibility to use the natural gas grid as a storage option is one of the reasons to transform the hydrogen to methane. For the injection in the natural gas grid certain quality criteria have to be met. The gas may not contain more than 4 % (v/v) hydrogen in Austria (ÖVGW 31, 2001) respectively 5 % (v/v) hydrogen in Germany (DVGW, 2013) and the possibility to store hydrogen this way is limited compared to methane that underlies no restrictions as long as it is in the form of Synthetic Natural Gas (SNG).

Despite these positive aspects the concept of generating so called SNG as an energy storage option is still in its development. Due to the relatively complicated transformation process the financial sustainability is still unsure (Baumann et al., 2013). The reason for this is the low efficiency of 30 - 75 % (Lehner et al., 2014) compared to other available technologies. To improve upon this point further research has to be undertaken and alternative process chains have to be developed.

One approach to this is the adaption of the integration of the carbon dioxide source into the process as both hydrogen electrolysis and catalytic methanation of carbon dioxide are already well known and researched. There are several possible carbon sources that can be used. Industrial processes for example offer a constant and cheap option but must be cleaned before they can be used for the methanation, which in turn leads to a more complex setup. Furthermore, it seems illogical to look to industrial processes as a reliable carbon source, while trying to minimize their carbon emissions in first place.

A second option is offered by the separation of carbon dioxide from air. This is in line with the idea of recycling already emitted carbon dioxide but it is ineffective compared to other options as described by Sterner (2009). The third widely discussed option is the use of biogas. Compared to the previously mentioned options it has the advantage of being considered as a renewable energy source on itself and its market share is planned to be increased. Therefore, it offers a reliable carbon dioxide source for the foreseeable future (Nitsch et al., 2012). Biogas already contains a high concentration of up to 60 % of methane, while the remaining gas consists of carbon dioxide and trace components like hydrogen sulfide or ammonia depending on its origin. Normally it is upgraded and fed to the natural gas grid as SNG (Niesner et al., 2013). The remaining carbon dioxide rich gas can then be used for catalytic methanation to increase yield of methane.

Another way of using the excess carbon dioxide would be to feed the methane rich biogas stream to the methanation. The potential of this variant has been discussed for example by Trost et al. (2012) but no demonstration plants have been realized. The potential advantages of this concept are higher methane yields and a lower energy consumption than comparable processes. The set-up of a demonstration plant will be discussed in the following paragraphs.

2. Materials and Methods

A classical biogas process consists of a one- or two-stage fermentation, a gas upgrading process and a catalytic methanation as shown in Figure 1. The newly developed process presented in Figure 2 changes the order of the gas integration and upgrading.

In a first step the biogas mix is produced by a two-stage fermentation consisting of a hydrogen dark fermentation and a methane fermentation. Afterwards the product is dried using condensation at 4 °C and trace components that may have negative effects on the following process steps are removed by a multi-stage adsorption column. The gas now consisting of methane, carbon dioxide and hydrogen is lead to storage tanks. These storage tanks are basically not a necessity but provide the option to operate the following catalytic methanation at higher flowrates than the fermentation could constantly support. The refined biogas is then fed to the methanation reactor and hydrogen is added. The hydrogen was supplied in cylinders because it was not deemed necessary to prove the functionality of an electrolyzer unit. In the methanation step hydrogen and carbon dioxide are partially converted to methane and water. After an additional drying by condensation at 4 °C the upgrading of methanation product gas to grid quality was performed using a membrane unit. In theory, the permeate could

be recompressed and recycled to the methanation reactor. Due to legal restrictions this step could not be carried out in practice and remains subject to a simulative approach. In a final step the produced, concentrated gas was tested for its compliance with the applying gas grid standards of a minimum concentration of 96 % (v/v) methane and a maximum of 2 % (v/v) carbon dioxide (ÖVGW 31).

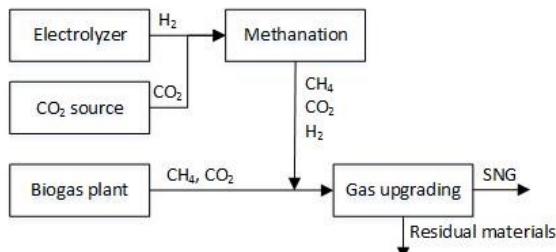


Figure 1: Classical biogas and methanation process

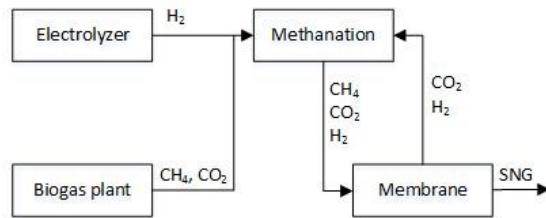


Figure 2: New process design

2.1 Two-stage fermentation

The fermentation setup used in this project consists of two separate reactors. Dark fermentation transforms hydrocarbon rich substrate to hydrogen and carbon dioxide by the use of anaerobe microorganisms. The remaining digestate is then fed to a second reactor and the organic acids are converted to methane and carbon dioxide in a classic biogas process. This setup offers distinct advantages compared to one-stage processes. Through the combination of the two processes residence time can be reduced while still offering higher conversion rate (Uneo et al., 2007). It has also been shown that general performance of two-stage fermentations is more efficient regarding energy recovery (Nathao et al., 2013). Furthermore, the overall concept presented here is able to incorporate both gas streams in the following steps without the need for complex gas cleaning or other preparation. The addition of the hydrogen produced by the dark fermentation should in theory reduce the amount of hydrogen provided by the electrolysis.

Further optimization that could be undertaken is stripping the dark fermentation with certain gases. A high hydrogen partial pressure is reported to shift the production towards more reduced substrates like ethanol or acetone. Nitrogen is supposed to improve the hydrogen yields dramatically but leads to higher costs (Kim et al., 2006) and is hard to remove. It was therefore neglected. Another option is the use of either methane or carbon dioxide for stripping as both can be supplied by the process itself without high additional costs. Carbon dioxide was also reported by Kim et al. (2006) to have positive effects on overall process but tests for this setup have been undertaken on laboratory scale and first results have not been promising due to acidification. Therefore, stripping was not included in the final demonstration plant.

The final important point for the setup of this demonstration plant was the feedstock of the fermentation. Most researchers tend to look for constant composition in their feed. This is a very reasonable step in assessing a new technology. Nonetheless, it was neglected in this work and public organic waste was used as a substrate. Unsurprisingly, the composition of public organic waste can change within weeks due to changing seasons and place of collection. This has led to a varying composition in the produced biogas as can be seen in the results. Normally, considered as a negative effect, it is used here to show the usability of this process under changing conditions.

2.2 Chemical, thermocatalytic methanation

The main reactions taking part in the methanation of carbon dioxide are already well known. The three most important ones are the Sabatier reactions for carbon dioxide Eq(1) CO and the water-gas shift reaction (Rönsch et al., 2011).



The reactor for the methanation is designed as a two-phase fixed bed reactor using a commercial Nickel bulk catalyst. The reactor design as well as the commercial catalyst are both already established technology but typically methanation is supposed to be performed at temperature levels of 250 °C and higher. Increasing temperature is supposed to significantly lower the conversion rate of carbon dioxide. The exothermic nature of the reactions taking place tend to cause temperature to reach higher levels. Peak temperatures inside the reactor higher than 650 °C are reported to be not preventable, even with additional cooling, by recent modeling studies (Schildhauer et al., 2015). The decrease of conversion rate caused by higher temperatures can be counteracted by increasing pressure. Simulations regarding this topic were conducted by

Jürgensen et al. (2015) and suggest that decrease in conversion caused by a temperature increase from 250 °C to 400 °C can be reduced by 50 % by operating the methanation at 10 bar instead of ambient pressure.

Another parameter with influence on the reaction is the gas hourly space velocity (GHSV). The GHSV is described as the quotient of the gas volume flow at STP and the volume of the catalyst.

It offers a parameter for the catalyst load. A low GHSV equals a longer retention and therefore a lower catalyst load. Based on kinetic reasons it is possible to come closer to equilibrium conditions. The potential heat accumulation has to be monitored as it may damage the catalyst and has to be monitored.

The final parameter that is of importance for the methanation is the stoichiometric ratio of hydrogen to carbon dioxide. Laboratory test runs showed the most promising results in a range of 3.7 to 4.5 for H₂:CO₂.

Taking all these factors into consideration it is easy to see that the methanation step is the most decisive factor with regard to operational parameters and should be handled carefully.

2.3 Membrane separation

The gas produced by the methanation may not fit natural gas grid standards and has therefore to be upgraded. Separation by membranes offers certain advantages in comparison to other state of the art technologies, like pressure swing adsorption, water scrubbing and chemical scrubbing. This is also suggested by membranes growing market shares (Bauer et al., 2013).

On the plus side, membranes offer flexibility in regard to scaling due to their modular design and in process integration (Makaruk et al., 2010). Their investment and operation costs are reported to be in the lower range with only water scrubbing being slightly cheaper for plants up to medium scale (250-1,000 Nm³/h) (Niesner et al., 2013), but it does not offer the same quality of cleaning.

Also the general setup of a membrane is relatively easy and small in comparison to the other options as it only consists of a removal unit for trace components, a compressor and the membrane module itself. Both auxiliary equipment items are already included for the methanation in this case and the gas is provided in pressurized form. After the upgrading the cleaned methane remains in pressurized form on the permeate side while the permeate contains mostly carbon dioxide as well as small amounts of methane and hydrogen.

The potential loss of methane may be higher for simple designs than the loss of comparable processes (Niesner et al., 2013). A possible solution concerning this problem is the recycle of the permeate stream to the methanation as it is neither diluted nor chemically polluted. This topic is subject to further simulative research.

Summing up, the flexibility in sizing and integration, the potential cost advantages and the possibility to negate the disadvantages of membranes by the recycling of the permeate stream create a prime example for their use. The most important factors for the installation of membrane modules are their selectivity and size. Both of those have to fit the actual problem to generate satisfying results. For the use in the field of biogas upgrading many membranes have been tested and polyimide (PI) based membranes offer well established option with selectivity for CO₂:CH₄ of up to 40 (Basu et al., 2009). Based on the good separation offered by PI and the high expected methane concentration in the feed gas to the membrane a one-stage membrane separation is deemed sufficient.

2.4 Auxiliary equipment

Three cooling units are installed for the condensation of water at different points in the plant. Plate heat exchangers are used to cool the gas down to 4 °C. A two-stage piston compressor compresses the biogas from ambient pressure up to a maximum pressure of 16 bar. Additionally, a multi-stage adsorption column ensures the removal of potential catalyst and membrane poisons prior to the methanation. ZnO is used for hydrogen sulfide removal and two different types of activated carbon ensure the removal of ammonia and different volatile organic compounds.

3. Results and Discussion

Based on the research conducted beforehand and additional laboratory experiments the parameters were varied in the ranges given in Table 2.

Table 2: Range of parameters

p in bara	T _{Reactor} in °C	GHSV in h ⁻¹	H ₂ :CH ₄ ratio
10-14	430-540	2,000-4,000	3.7-4.5

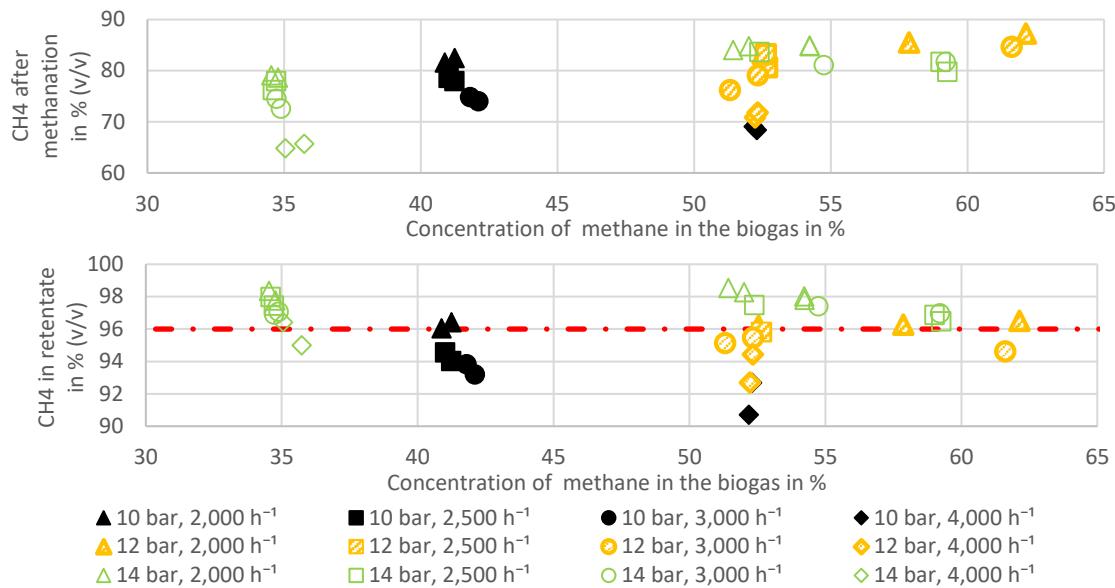


Figure 3: Effects of CH₄ in biogas on the concentration of CH₄ in methanation product and membrane retentate

Figure 3 shows the effects of the methane concentration on the methanation reactor respectively the gas upgrading. For the methanation the concentration of methane in biogas is an important factor. A lower GHSV and higher pressure improve the results. Comparing this to the data after the membrane unit shows some significant differences. The dot dashed line indicates the threshold for the standard of the natural gas grid. The importance of the GHSV appears to be the same as before. Instead of the methane concentration supplied by the fermentation the pressure level is now the deciding factor as a pressure of 14 bar offers the necessary product gas quality even for methane concentration of under 35 % in the biogas.

The conversion of carbon dioxide was calculated at rate of 92 – 98 % as shown in Figures 4 and 5. Neither temperature nor pressure seem to have a predictable impact on it. While not changing the conversion rate in a predictable way the temperature does influence the concentration of methane in the gas after the methanation step. Increasing the temperature from 440 °C to 520 °C leads to a decrease of 15 to 20 % (v/v)methane (see figure 4). Increasing the pressure on the other hand from 10 to 14 bar causes an increase of the upper and lower boundaries of the methane concentration in the retentate by 3 to 4 %.

4. Conclusion

It has been demonstrated that combination of catalytic methanation and gas separation by membrane offers a good option for biogas upgrading. Even with methane feed gas concentrations as low as 35 % (v/v) the targeted gas quality could be reached as the gas upgrading provided by the membrane unit fully negates this effect. It was shown that reactor cooling is of high importance to maintain high methane yields. Further possibilities for the process setup can also be derived from the result. A higher pressure level is mainly beneficial for the membrane unit it should be possible to decouple the pressure levels of methanation and gas separation. This opens up the possibility to further increase results of the membrane by operating at higher pressure levels.

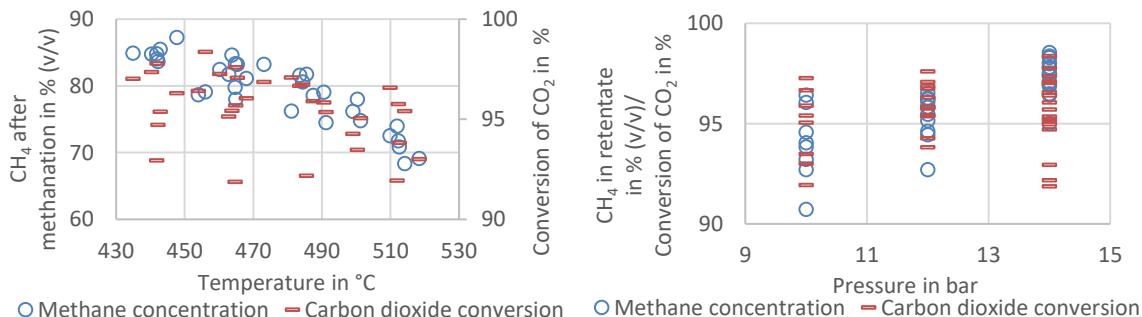


Figure 4: Temperature effects on the reactor

Figure 5: Pressure effects on reactor and membrane

Higher pressure levels may also lead to higher losses of methane in the gas upgrading step making a recycling of the permeate mandatory. This should pose no problems for the methanation step as it was shown that carbon dioxide conversion rates are high despite high methane concentrations in the feed. Adding a second stage to the membrane unit is another option to increase the recovery of methane. Both aspects - decoupling of the pressure levels and recycling of the methane stream - are currently under research using process simulation.

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