

Extraction of Green Hydrogen at Fuel Cell Quality from Mixtures with Natural Gas

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A hybrid process based on membrane and pressure swing adsorption for the extraction of green hydrogen from mixtures with natural gas at fuel cell quality is presented. The gas is supplied by the natural gas grid at high pressures (up to 60 bar). It is pre-enriched via membrane separation. Afterwards, a pressure swing adsorption (PSA) ensures the required product quality. All remaining components, separated by PSA, are returned to the grid. Beside the technological feasibility the influence of various process parameters (e.g. stage-cut, permeate conditions, PSA H₂ recovery) is analysed. Moreover, the so called HylyPure[®] process is compared with a reference process (decentral hydrogen from electrolysis).

At the current state of the work the PSA separation had to be estimated. Therefore, the hydrogen recovery was varied from 20 to 98 %. It is shown that this process is far more efficient than the reference. Even at low hydrogen recoveries it is three times more efficient.

1. Introduction

Electrical energy from renewable sources (e.g. solar power, wind) is increasing since the last years. Fluctuating electrical excess energy is a major topic and requires energy storage technologies, which became a key challenge for the energy transition.

Very promising solutions are Power-to-Gas concepts. These concepts are based on the idea that electrical excess energy is used to store energy (power) in the form of gas. For example this can be done by producing hydrogen via water electrolysis. This hydrogen can be stored, transported and converted back to electrical energy. Moreover it can be used as vehicle fuel or as feed for the chemical industry (Ausfelder et al., 2015).

This work investigates the extraction part of a concept that uses hydrogen (H₂) as an energy carrier which is gained via water electrolysis. Theoretically, the electricity source is not relevant for the hydrogen production. However, the idea is to use fluctuating renewable energy sources (e.g. from wind power). This green hydrogen is injected into the natural gas grid and transported with the stream.

Beside the advantage of low costs (e.g. existing infrastructure) the transportation via pipelines is also energy efficient. However, the grid has a certain maximum concentration limit for hydrogen. Dependent on the country this limit is 4 % (v/v) in Austria (ÖVGW, 2001) or 5 % (v/v) in Germany (DVGW, 2013).

With the current process the hydrogen can be extracted at any desired location along the gas grid. This renewable hydrogen, can then be used to supply fuelling stations or other applications. It can also be converted to electricity by fuel cells. However, a certain hydrogen quality is required (99.97 % H₂ according to ISO 14678-2:2012 (ISO - International Organization for Standardization, 2012)).

Based on membrane technology and adsorption (hybrid approach) the here presented process (see Figure 1) extracts hydrogen at fuel cell quality from mixtures with natural gas. It will be analysed for a hydrogen content between 1 and 10 % (v/v). However, the focus lies on 4 % as it is the maximum hydrogen concentration in Austria.

Natural gas is a mixture of various components (CH_4 , CO_2 , H_2 , N_2 , H_2O , H_2S , etc.). Their quantities depend on the gas source and the upgrading. However, the grid requires certain limitations of undesired components that are regulated (DVGW, 2013; ÖVGW, 2001).

The membrane separation step is used for a cost- and energy-efficient pre-enrichment (Adhikari et al., 2006). Afterwards pressure swing adsorption (PSA) provides upgrading of hydrogen to the required quality (Ruthven, 1984). Remaining PSA offgas is recompressed and returned to the grid.

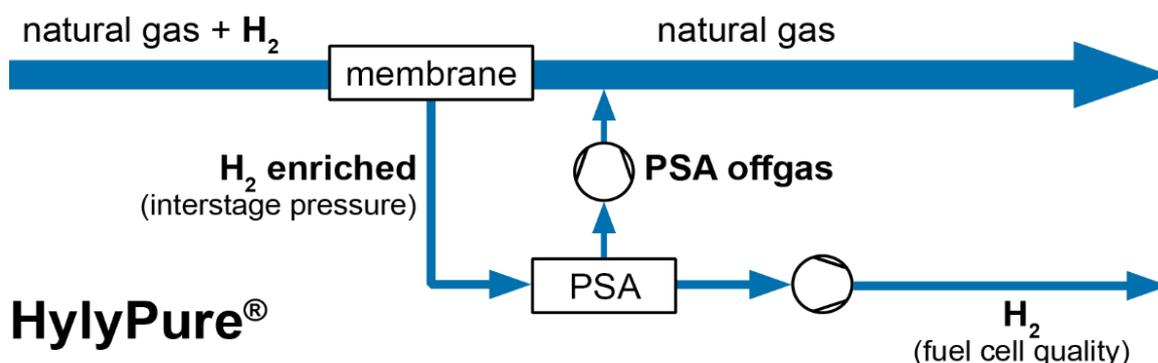


Figure 1: HylyPure® process concept

Through the combination of two different technologies and the high product quality the technological feasibility is experimentally analysed. Therefore, a lab scale plant has been developed and built. For higher flexibility the two processes are investigated separately and the combined process is examined via virtual linking.

The equipment is designed for a maximal pressure of 100 bar(g) and a feed flow rate of up to 0.5 m³/h (STP). Due to the various process conditions (e.g. gas composition, pressures) and the necessity to perform transient experiments, high quality equipment was required (e.g. Coriolis mass flow controller, mass spectrometer and gas chromatography with mass spectrometer). Beside the investigation of the feasibility the experiments are further used to validate models for a process simulation that will be used for an overall process-optimisation.

As already mentioned the process contains two steps. The next sections describe the first process step (membrane) followed by adsorption.

2. Membrane

In a first step, hydrogen pre-enrichment is realised via hydrogen selective membrane. This gas permeation membrane uses the pressure difference as driving force and different permeabilities to perform the separation. Hence, the pressure on the permeate side (product side) is lower than on the feed side.

There are various different types of membranes available in literature. Due to its high hydrogen selectivity and permeability a polyimide based membrane is preferred for this kind of separation problem (Zornoza et al., 2013).

Through the faster permeation of hydrogen (than methane) the H_2 concentration is increased on the permeate side. Nevertheless, methane and several other impurities (e.g. CO_2) can be found on the permeate side. Practically, the remaining gas (retentate) is kept at almost feed pressure (decrease of several mbar) and can therefore be returned to the grid.

In lab-scale experiments the membrane is analysed and a model, based on a solution-diffusion approach that has been implemented in AspenPlus® (Lassmann et al., 2016), is validated. The experiments are examined with various feed gas concentrations and feed pressures. Moreover, the permeate pressure is varied.

Ongoing work is focused on the overall process simulation and optimisation that will be published elsewhere. As result of these investigations various pressure and stage-cut (ratio of permeate flow to feed flow) dependent hydrogen purities and recoveries are obtained. A brief overview can be seen in Figure 2. These conditions are used as inlet gas composition (and pressure) for the adsorption analysis. Permeate hydrogen concentration is between 15 and 35 % (v/v) for pressures between 1.6 and 7 bar(g) depending on the stage-cut.

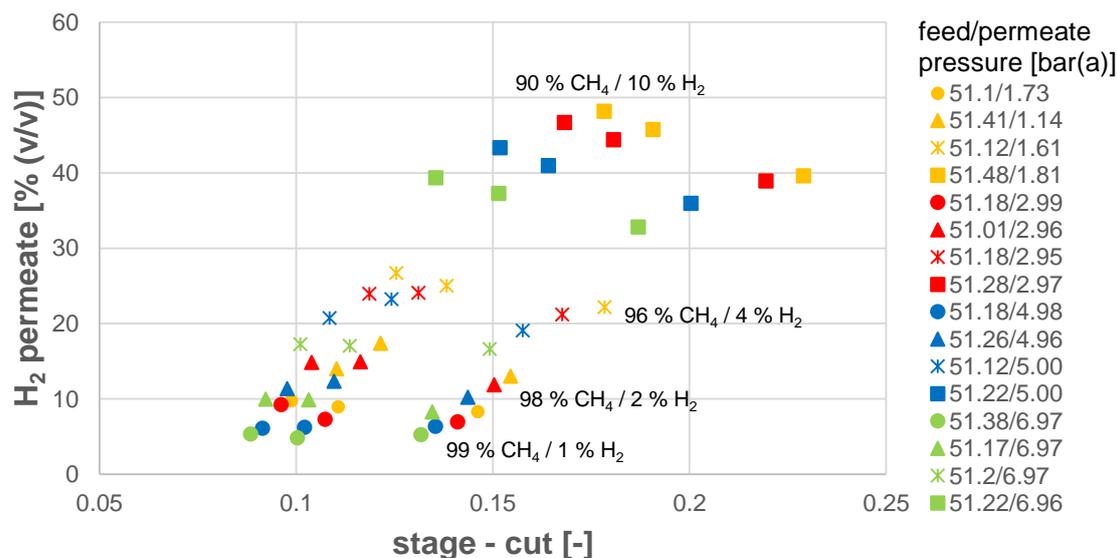


Figure 2: H₂ permeate concentration for various pressures and stage-cuts

3. Adsorption

As a second process part pressure swing adsorption (PSA) is used to ensure the required product quality. The performance of a PSA process depends on various parameters. Beside the number of adsorber columns and their dimensions (e.g. length-to-height ratio), the switching time and the used material plays a major role. There are various materials mentioned in literature (e.g. activated carbon, zeolite, silica gel, activated alumina).

In contrast to use a single material it is state-of-the-art to use multiple materials (in a layered bed) to gain the highest possible efficiency (Ribeiro et al., 2008). Based on the present impurities (e.g. CH₄, CO₂, N₂, H₂S, H₂O) activated carbon, zeolite and silica gel were taken into account. However, it is important to have the correct order to ensure that certain components do not reach particular materials (e.g. CO₂ or water vapour should not reach zeolite (Ribeiro et al., 2008)), otherwise regeneration would be difficult.

For the current process the order has to be silica gel (removal of humidity and higher carbons (Sircar et al., 2000a)), followed by activated carbon (removal of CH₄, CO₂ (Sircar et al., 2000a) and H₂S (Ritter et al., 1987)). Finally zeolite 5A is the preferred material to remove N₂ and CO (Sircar et al., 2000a).

As CH₄ and CO₂ are the major components which have to be removed, the main focus was to investigate activated carbon.

There are various different activated carbon materials on the market which makes the comparison of literature values difficult. Moreover, there were no proper parameters found for the used activated carbon (Supersorbon® C IV spezial from DonauCarbon). Subsequently, it had to be analysed. This was done with breakthrough experiments. These experiments are further used to validate a dynamic adsorption model which is required to simulate and optimise a whole pressure swing adsorption process.

3.1 Breakthrough

The usage of breakthrough experiments for the validation of adsorption models is commonly known in literature and used to gain model parameters as shown elsewhere (Lopes et al., 2011; Bastos-Neto et al., 2011). In this work they were examined in lab-scale with an adsorber (5.4 cm internal diameter; 1 m length) at various pressures (1-15 bar(g)) and feedgas compositions.

Adsorption is a highly temperature-dependent process. Therefore, the adsorber is constructed to feature a double shell wall where water-based cooling or heating can be applied. Further, ten temperature sensors are installed in the bed (evenly spreaded along the flow direction) to determine the temperature during the adsorption and the position of the adsorption front. A mass spectrometer was used to measure the gas concentration on the outlet after the volume flow rate was determined by positive displacement devices.

The experiments (examined with/without cooling and feed gas at room temperature) show on one hand the technical feasibility of the material to separate the given mixture and gain the required hydrogen concentration and on the other hand they are used for parameter extraction and model validation. Therefore, a breakthrough simulation is set up in Aspen Adsorption® and compared with the experimental data. The simulation uses an

isothermal approach with extended Langmuir isotherms and the linear driving force (LDF) model (Sircar et al., 2000b). An isothermal approach was chosen to reduce the complexity of the simulation. Figures 3 - 5 show experimental and simulated (parameters taken from (Waldron et al., 2000) breakthrough curves for different setups (e.g. various pressures, feed gas composition, applied cooling, temperature). As experimental reference temperature (so called MAT) is expressed, which is the maximum value (maximum of average from all ten sensors) during the experiment.

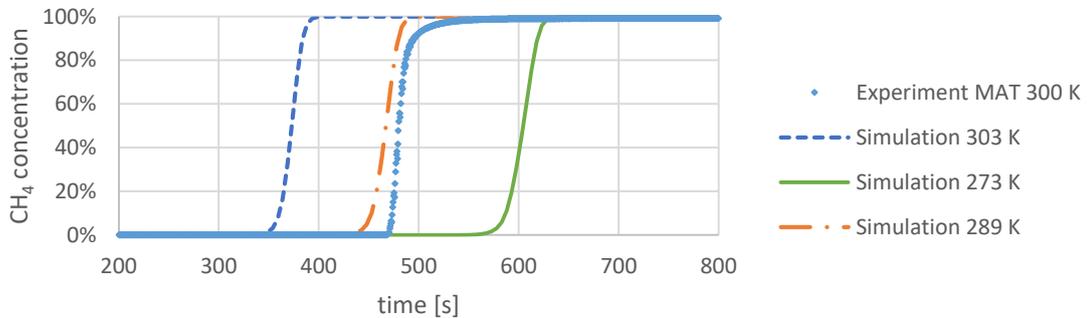


Figure 3: Adsorption at 1 bar of 100 % (v/v) CH_4 with 289 K cooling water

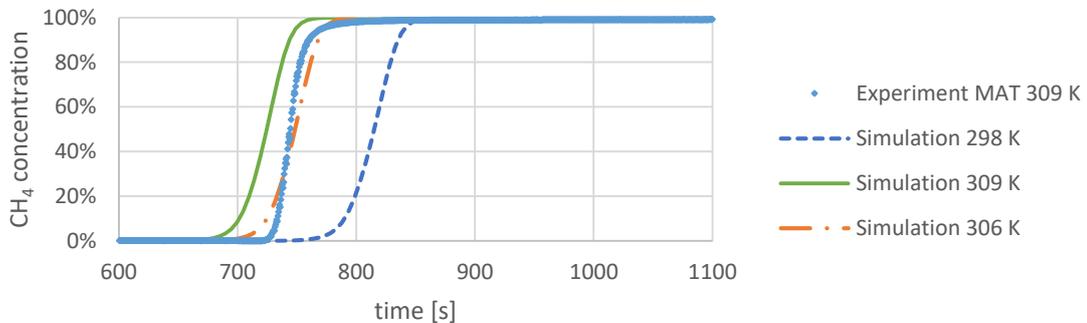


Figure 4: Adsorption at 3 bar of 100 % (v/v) CH_4 , adiabatic

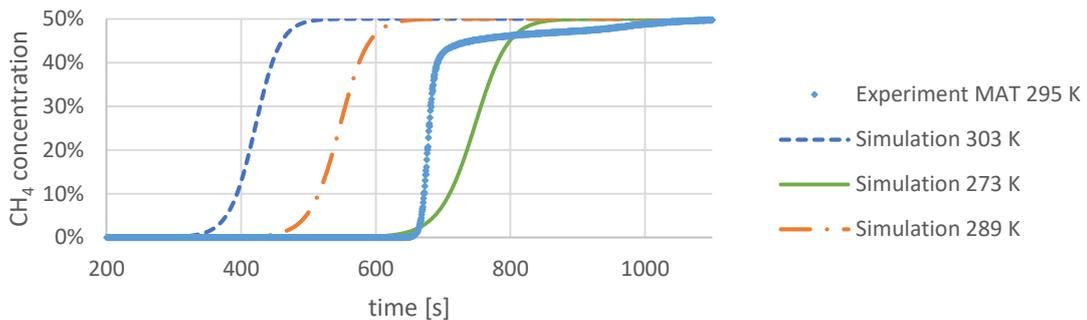


Figure 5: Adsorption at 1 bar of 50:50 % (v/v) $CH_4:H_2$ with 289 K cooling water

It can be seen that the breakthrough time depends on the feed composition, temperature and pressure. During the experiments the typical temperature increase in the adsorption front was observed. Subsequently a proper temperature for the isothermal simulation had to be chosen. The importance of this parameter is displayed by various simulation curves and it can be seen that it has a significant influence. Figure 4 shows that the adiabatic experiment and the isothermal simulation are in good agreement by using 306 K.

By comparing Figure 3 and 5 it can be seen that the experimental data has a steeper breakthrough in case of the reduced methane content. On the contrary, the breakthrough in Figure 3 is faster. Furthermore, the MAT is 5 K higher in Figure 3. However, the simulated data for both setups require a reduced MAT, which is most probably caused by the cooling. Nevertheless, this result requires further investigation.

In conclusion, these experiments show, that the measured breakthrough occurs later than the modelled (isothermal; by using the MAT). This leaves a safety bond for uncertainties. However, it also ensures the technical feasibility by using the taken model and parameters for the PSA simulation. Nevertheless, higher productivities are possible due to longer cycle times and a higher productivity. Subsequently, this needs further investigation.

3.2 Pressure Swing Adsorption

In the next step a multi adsorber PSA is essential for a full process realization. Currently, this is under development and will be validated via experiments. However, a simple first recovery estimation was done.

This evaluation estimates the required amount of electric energy per m^3 H_2 product gas. Various permeate conditions (from Figure 2) are taken as inlet feed and the PSA hydrogen recovery is varied. Further on, it is assumed that the hydrogen product stream has the required hydrogen concentration at interstage (permeate) pressure. The PSA offgas contains all the methane and the residual hydrogen.

The amount of energy required for the compression (PSA offgas and PSA product-gas) is calculated isentropic with an overall compression efficiency of 72 %. As pressure levels, the pipeline pressure is used for the offgas and a reference pressure for the product gas. Since the reference process is hydrogen production via water electrolysis, the amount of specific energy and pressures for units in the range of 10 - 40 m^3/h (STP conditions) are compared. These are 4.2 to 4.8 kWh/m^3 for hydrogen product pressure at 25.81 bar(a) (Ivy, 2014).

Figure 6 shows the results of the required amount of energy per m^3 of hydrogen (STP conditions), compressed to 25.81 bar(a) for various interstage pressures and recoveries. As it can be seen, the required amount of energy, even with small PSA hydrogen recoveries, is below the reference process (4.2 kWh/m^3). Moreover, it is shown that the PSA recovery has a great influence. It is much higher than those of the chosen interstage pressure. However, a higher interstage pressure level is more efficient for the overall process.

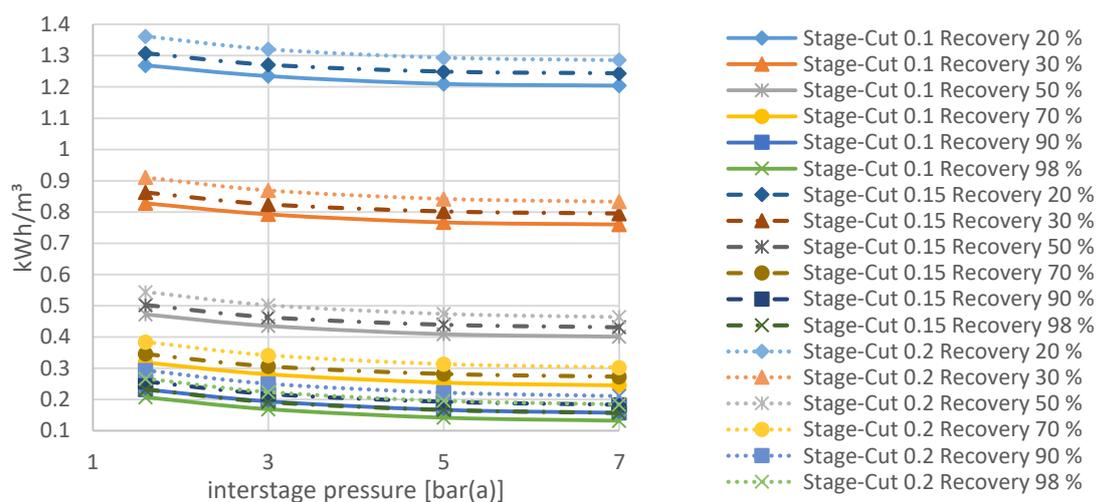


Figure 6: Process energy requirements for various interstage pressures and PSA recoveries

4. Conclusions and Outlook

This work presents the so called HylyPure[®] process that is able to extract hydrogen at fuel cell quality from mixtures with natural gas. With this process the hydrogen, which has been added to the natural gas grid, can be extracted at various locations. Therefore, energy efficient decentral hydrogen supply can be realised. It consists of a membrane pre-enrichment step followed by a pressure swing adsorption. Through the combination of two technologies it has a high potential for process optimisation via process simulation. Hence, proper models and parameters are required. On one hand, they are gained via permeation experiments for the membrane and on the other hand, breakthrough investigations are examined for the adsorption.

Currently, the adsorption properties are still under investigation so a hydrogen recovery variation (for the PSA) was used to give a first estimation for the overall required amount of energy. According to these estimations the required specific energy demand for hydrogen at 25.8 bar(a) is in the range of 0.13 to 1.4 kWh/m^3 which is at least 3 times smaller than those of a reference process (decentral hydrogen electrolysis; 4.2 kWh/m^3).

To gain the full potential of this hybrid process further experimental work as well as process simulation and optimisation is required.

Acknowledgments

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