Membrane reformer for large scale production of hydrogen

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Towards the Application of Palladium Membrane Reactors in Hydrogen Production

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1 Introduction

A sustainable use of fossil fuels in the future will undoubtedly make use of concepts where the energy content of the fossil fuel is efficiently transferred to hydrogen. The driving force for these concepts is the possibility of capturing CO_2 elegantly while using the favourable thermodynamics to increase the efficiency of hydrogen production significantly. In ECN's vision palladium membrane reactors will play a key role in future decarbonisation of fossil fuels. Combining reaction and separation using membrane reactors will offer numerous advantages for hydrogen production both in future power production systems and in industrial chemical production processes. The application of hydrogen selective membranes for the removal of hydrogen from reforming and shift reactions gives higher conversion of these equilibrium reactions at lower temperatures while elegantly CO_2 can be captured under high pressure or chemical products can be obtained cost-effectively.

The Energy Research Centre of the Netherlands ECN works on the development of palladium membrane reactors for energy efficient industrial hydrogen production and power generation. Important research topics are the development of thinner and cheaper palladium membranes with higher permeation rates, customized catalysts, which are active at low temperatures and resistant to coke formation, and the design of a feasible large scale membrane reactor and hydrogen production process. The objective is to have a pilot membrane reactor unit, which can deliver 5 Nm^3/h hydrogen, operational in 2009. An overview of the results and current status of the hydrogen membrane reactor development for large-scale hydrogen production is presented.

2 Palladium membrane development and testing

The most common types of Pd-based membranes are self-supporting metals foils with thicknesses of 25-100 µm. These membranes have the disadvantages that they are expensive with a low hydrogen flux. The performance can be improved if their thickness can be reduced. The thinner metal layer, however, has lower mechanical strength than the thick metallic membrane. In order to meet the challenge of attaining both high selectivity and good mechanical strength, metallic membranes have been deposited on strong supports. ECN has chosen for the supported thin membrane system based on the ECN ceramic fabrication technology (tubular supports) to facilitate hydrogen flow. The metal alloy is applied on this tubular structure by sequential electroless plating followed by alloying, because this procedure can be scaled up and industrialized and showed to be the most cost-effective technique [1, 2].

By optimising the electroless plating technique it is possible to manufacture membrane layers (Pd/30%Ag) with a thickness of 3 to 5 micron on commercially available ceramic supports. Membrane tubes with a length of 0.6 to 0.85 meter and an outer diameter of 14 mm are being prepared reproducibly on a regular basis. For sealing and joining the PdAg ceramic composite membranes to metal module end plates a new graphite sealing technique has been developed and patented by ECN [3]. This low cost carbon compression sealing was successfully tested for 14 mm outer diameter ceramic tubes at 100-500ºC and 1-60 bar

The membranes have been used for single gas permeance tests at different temperatures and for the separation of hydrogen from reformate gas, using a bench scale test system that can operate up to 500ºC and 65bar feed pressure with a membrane area of about 50cm^2. Hydrogen permeation measurements have shown that after initial activation very high hydrogen permeances of 50-100$m^3/m^2hbar^{0.5}$ can be obtained with sufficient permselectivities. Tests with simulated reformate gas gave lower selectivities due to lower hydrogen permeances caused by the poisonous CO in the reformate gas [4]. The membrane has been on stream for more than 100 days using different feed gases and showed a stable performance.

3 Membrane reactor testing and modelling

Membrane reactor experiments have been performed in a single tube membrane reactor with a 17.4 cm long PdAg membrane with a diameter of 1.4 cm that was placed in a catalyst bed using a commercial low temperature reforming catalyst. The results of one-tube membrane reactor reforming tests in which the feed flow has been varied are presented. A preheated feed stream consisting of a CH_4/H_2O mixture is supplied to the single tube membrane reactor. The nitrogen sweep flow is introduced in co-current mode. It can be seen that, espe-

cially at low feed flow rates, permeation shifts the equilibrium to considerably higher conversions, and beyond the chemical equilibrium. Membrane reformer tests have been performed successfully for 4 weeks at 560°C. After 3 weeks continuous stable performance at 86% methane conversion the conditions were optimized and 92% methane conversion was reached. During these 4 weeks the membrane selectivity decreased from 1000 to 100. The test results are compared with results from membrane reactor modelling.

4 Conclusions

Palladium membrane reactors have been identified as a promising option for hydrogen production in future power production systems and industrial chemical production processes. For this purpose an R&D programme on the development of palladium membrane reactors hydrogen membrane reactors is being carried out at ECN, which focuses on thinner and cheaper palladium membranes with higher permeation rates, customized catalysts and the design of a feasible large scale membrane reformer.

Dense tubular Pd alloy membranes with a high hydrogen permeance have been made on ceramic supports with electroless plating on a $1m^2$ scale. Permeation and gas separation measurements have shown that next to scaling-up of the fabrication of thin defect free Pd composite membranes also the sealing between the ceramic tube and the fixation in a metallic tube sheet remains a critical item for the hydrogen membrane reactor development. Lab scale membrane reformer experiments have shown that methane conversions above 90% could be reached during steam reforming at 550°C and 28 bar in the membrane reformer during a stable operation of 4 weeks. A computer model of the palladium membrane reformer was developed and has been used successfully to evaluate the impact of main operating and design parameters on the reactor performance.

5 Acknowledgements

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6 References

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Background

The (petro) chemical industry in the Netherlands is responsible for one sixth of the total energy use. A substantial part is used to produce industrial hydrogen. This takes place in huge reformer units where methane reacts with steam to become hydrogen and carbon monoxide. One promising new concept, which maximizes the energy efficiency of SMR (steam methane reforming), is the hydrogen membrane reformer (H_2MR).

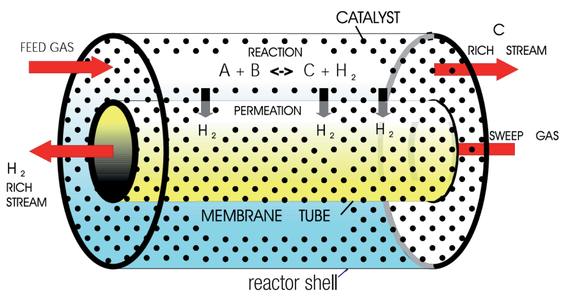


Figure 1: The H_2MR concept

H_2MR is basically a membrane assisted reformer that not only drives reactions beyond traditional equilibrium levels but also enables CO_2 to be captured under high pressure in large scale power production plants.

Objective

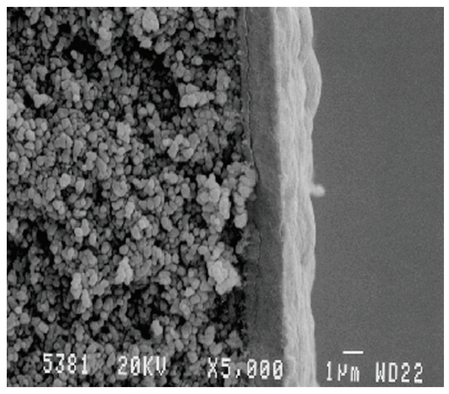
Development of a H_2MR which delivers 5 Nm^3/h hydrogen.

Applications in the Netherlands:
- Large scale hydrogen production in the ammonia process
- Power generation with integrated CO_2 capture
- Small scale on-site hydrogen supply
- Dehydrogenations

Potential energy savings in NL is 24 PJ/y.
For large scale hydrogen production for the ammonia synthesis, savings can be 7% compared to the conventional process with an estimated payback time from 1.3 to 5.7 years.

Hydrogen selective membranes

The critical enabling technology for H_2MR is the hydrogen selective membrane. ECN has developed the technology to apply a very thin layer of Pd on a ceramic support tube to enable low cost and reliable hydrogen separation. Currently, membranes can be produced which have a lifetime of several thousands of hours under different conditions at temperatures up to 450ºC.



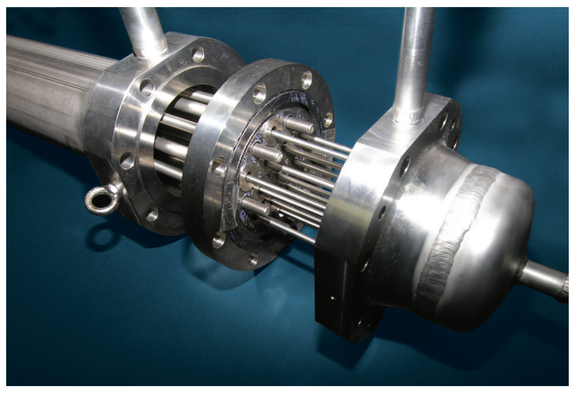


Figure 2 Cross section 4-5 µm Pd membrane and 13-tube module

Bench scale MR performance

- CH_4/H_20 = 3, T=530-590°C, Pf=25-42 bara
- stable operation for 40 days
- max. CH_4 conversion 98 %
- high H_2 single gas permeance (116 $m^3/m^2hbar^{0.5}$ at 600ºC)
- max. H_2/CH_4 selectivity 1000

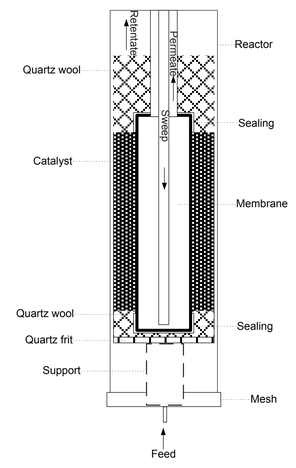


Figure 3: Catalyst in annulus arrangement

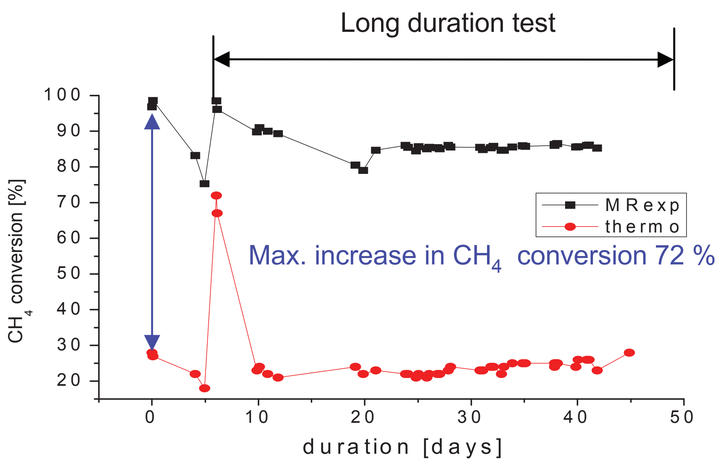


Figure 4 Thermodynamic and measured CH_4 conversion

MR modelling

- 1-D isothermal MR model shows good comparison with bench scale MR experiments.

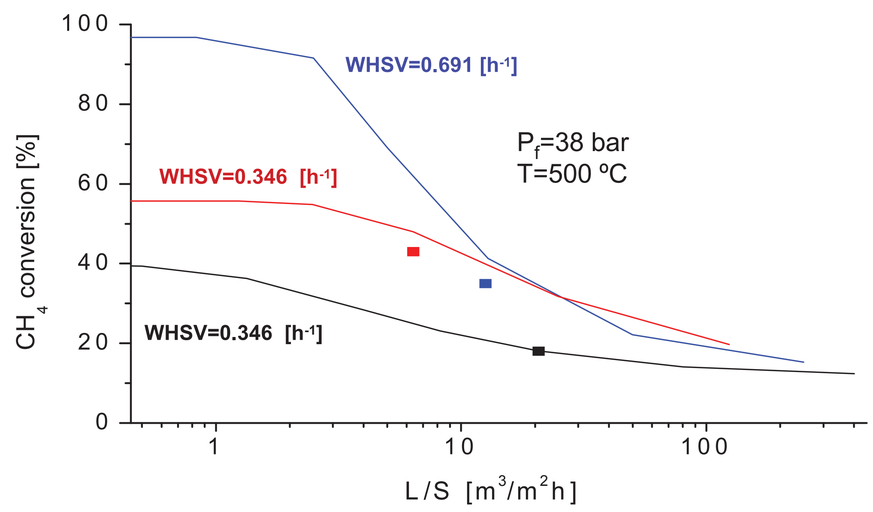


Figure 5 Comparison CH4 conversion (line –model, dot – experiment)

Future work

- Confirm overall performance of new pilot membrane reformer design, which has large similarities with the standard 5 Nm^3/h reformer from HyGear for on-site hydrogen production.
- Validation of available design models.
- Study operational aspects (e.g. heat management, start-up/cooling down, dynamics) for both pilot H_2MR.
- Update of technical economic evaluations.
- Increase the catalyst and membrane lifetime at high T.

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