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TOWARDS APPLICATION OF PALLADIUM MEMBRANE REACTORS IN LARGE SCALE PRODUCTION OF HYDROGEN

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Abstract: Palladium membrane reactors have been identified as a promising option for hydrogen production in future power production systems and industrial chemical production processes. This paper gives an overview of the results and current status of the palladium membrane reactor development at ECN for large-scale hydrogen production.

Dense tubular Pd alloy membranes with a high hydrogen permeance have been made on ceramic supports with electroless plating on a 1m² scale. Application of a Pd membrane and a commercial catalyst in membrane reactor experiments have shown that it is possible to shift the methane conversion beyond chemical equilibrium by means of hydrogen withdrawal. A computer model of the palladium membrane reformer was developed and has been successfully used to evaluate the impact of main operating and design parameters on the reactor performance.

Keywords: Palladium membrane reactor, hydrogen production, CO₂ capture

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 CO₂ 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 CO₂ can be captured under high pressure or chemical products can be obtained cost-effectively (Jansen *et al.*, 2004).

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 Nm³/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 (Pex *et al.*, 2004a). The manufacturing process of ECN PdAg membranes contains the following steps:

- Fabrication of porous support tube with an appropriate porous structure
- Application of Pd seeds on the support, activation of the support
- Sequential electroless plating of a Pd and a Ag layer with an appropriate thickness to reach a PdAg ratio of 70/30 wt%
- Heat treatment for alloying PdAg

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. Using the above described procedure membrane tubes with a length of 0.6 to 0.85 meter and an outer diameter of 14 mm can be prepared reproducibly on a regular basis. In Figure 1a a photograph is given of these membranes. 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 (Rusting *et al.*, 2001). This low cost (3.5 Euro/piece) carbon compression sealing was successfully tested for 14 mm outer diameter ceramic tubes at 100-500°C and 1-60 bar (see Figure 1b).

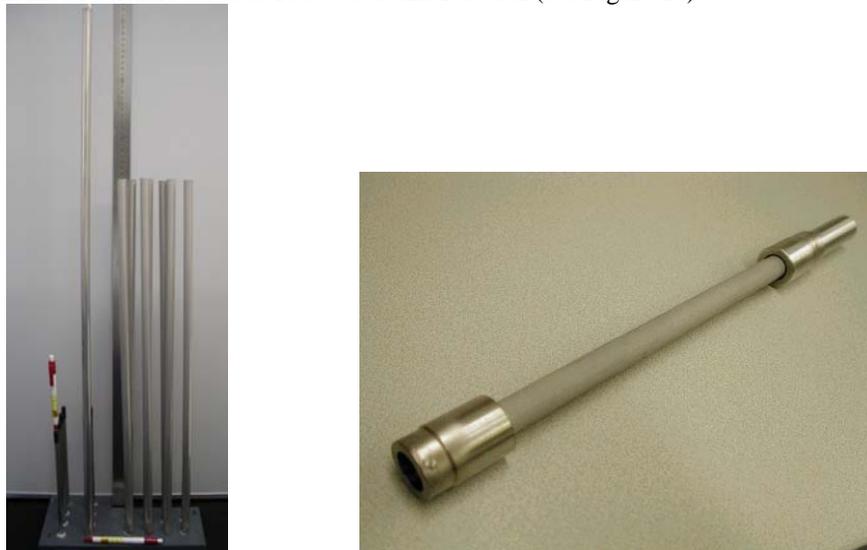


Fig. 1. Set of PdAg membrane tubes with a length of 0.6 meter (a) and a membrane with the low cost carbon compression sealing (b).

The membranes have been used for single gas permeance tests at different temperatures and for the separation of hydrogen from reformat gas, using a bench scale test system that can operate up to 500°C and 65bar feed pressure with a membrane area of about 50 cm². Hydrogen permeation measurements have shown that after initial activation very high hydrogen permeances of 50-100 m³/m²hbar^{0.5} can be obtained with sufficient permselectivities. The permeation results show a decrease in permselectivity at high feed pressures due to a leak flow through the sealing and defects in the membrane. Tests with simulated reformat gas gave lower selectivities due to lower hydrogen permeances caused by the poisonous CO in the reformat gas (Pex *et al.*, 2004b).

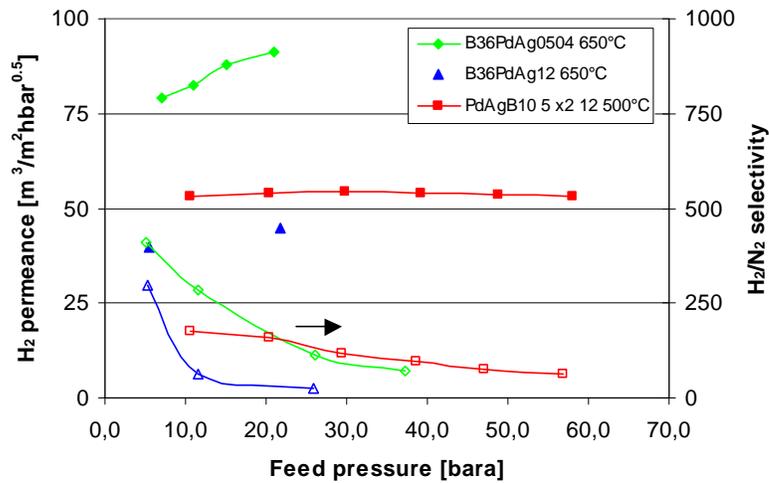


Fig. 2. Hydrogen permeance (closed symbols) and H_2/N_2 permselectivity (open symbols) vs feed pressure for different PdAg membranes.

The membrane has been on stream for more than 100 days using different feed gases and its performance is shown in Figure 3. It shows that the highest hydrogen permeance is obtained with single gas measurements as was expected. During gas separation measurements with a reformat mixture the hydrogen permeance decreases with a factor 4-5 due to absorption of other molecules like CO on the PdAg surface. The hydrogen permeance decreases even more when subsequently methane and water is fed to the membrane reactor. This is caused by the fact that in the first part of the reactor no hydrogen is available and therefore no hydrogen passes through this part of the membrane, giving a smaller effective membrane area.

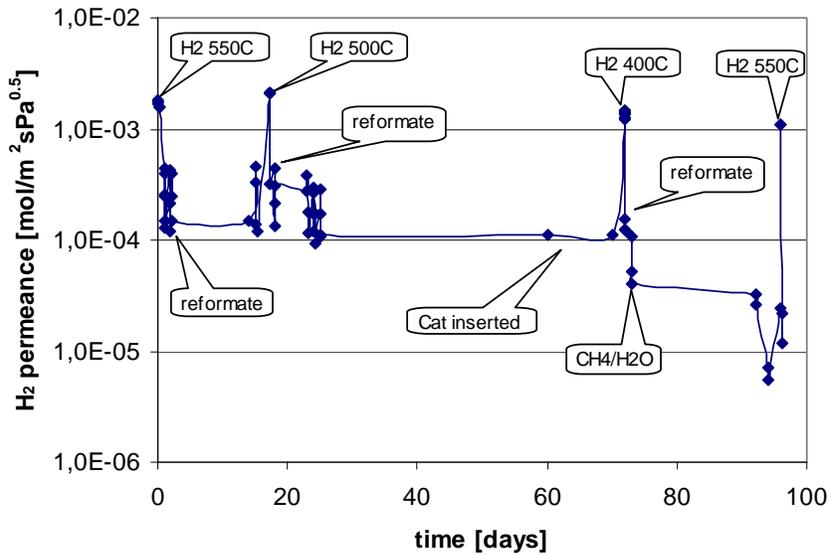


Fig. 3. Hydrogen permeance vs. time on stream ($T=400-550^\circ\text{C}$, $P_{\text{feed}}=40-50$ bar).

3. CATALYST SCREENING

In membrane reactors a customized catalyst is required for reforming of methane, which should be active at low temperatures and resistant to coke formation under the carbon-rich membrane reactor conditions. In addition,

catalyst costs should not exceed membrane costs. Prior to actually testing the performance of the membrane reactor, different catalysts have been tested under simulated membrane reactor gas conditions. Among the catalysts screened, are noble metal catalysts on various supports and a reference nickel-based catalyst. More information on the catalyst development can be found in (van Beurden, 2006). A commercial catalyst has been used for screening and testing purposes and is referred to as catalyst X₁. Figure 3 shows that during 280 h on stream at 773 K, the reference nickel catalyst and a ruthenium-based catalyst showed significant deactivation under the simulated membrane reforming conditions. The promoted noble-metal catalyst and the commercial catalyst did not show severe deactivation and were selected for application in the membrane reactor.

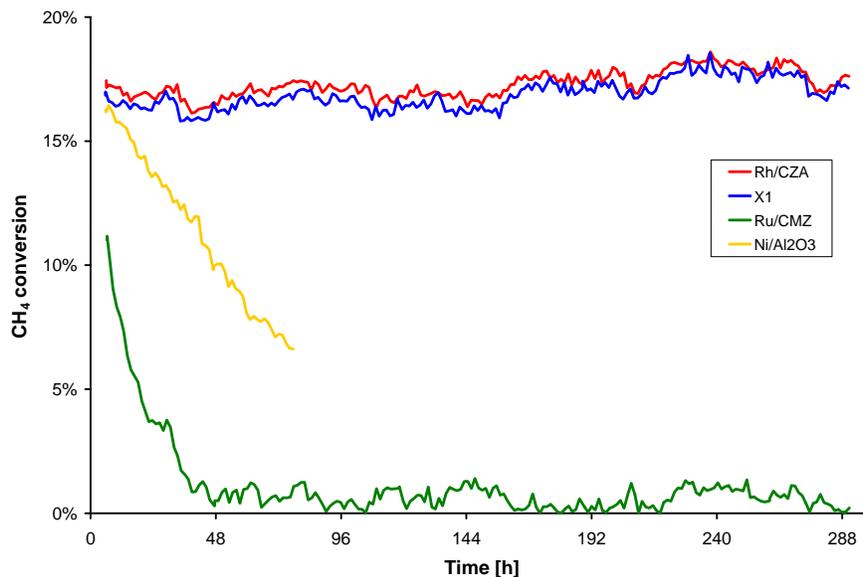


Fig. 4. Catalyst stability under simulated membrane reformer conditions (2.7% CH₄, 14.3% H₂O, 5.0% CO₂, 0.6% CO; 500°C, 3.5 bar).

4. MEMBRANE REACTOR TESTING

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 reactor is placed in an electrically heated oven. Figure 5 presents the results of one-tube membrane reactor reforming tests in which the feed flow has been varied. A preheated feed stream consisting of a CH₄/H₂O mixture is supplied to the single tube membrane reactor consisting of a membrane tube placed in a catalyst bed. The nitrogen sweep flow is introduced in co-current mode to prevent back permeation of hydrogen. It can be seen that, especially at low feed flow rates, permeation shifts the equilibrium to considerably higher conversions, and beyond the chemical equilibrium. For practical application of membrane reactors higher conversions are required than those obtained in the experiments presented here. Membrane reactor modelling shows that this is due to the low membrane surface area/feed flow ratio used, so for higher conversions longer membranes or lower feed flow rates are to be used.

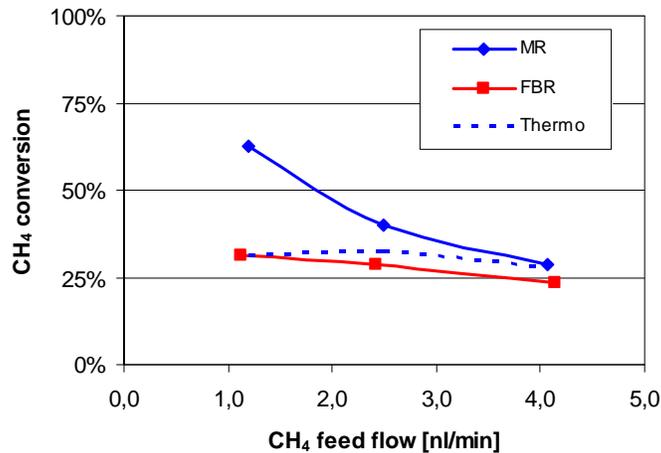


Fig. 5. Methane conversion vs feed flow with a membrane reactor (MR), a fixed bed reactor (FBR) and the calculated equilibrium conversion (Thermo) (650°C, 11 bar, feed: CH₄/H₂O=1/3).

5. MEMBRANE REACTOR MODELLING AND DESIGN

One of the critical items for application of the hydrogen membrane reactor for large scale hydrogen production is the compression of the hydrogen to the desired pressure. The separation of hydrogen by a membrane is a pressure driven process. To have a sufficient driving force for the separation and an economical feasible membrane surface area, the separated hydrogen is supplied at low pressures. For a lot of applications the hydrogen must be available at high pressure, so often recompression with an expensive and energy consuming compressor is necessary. The trade-off between the membrane surface area and the compression energy is depicted in Figure 6. It shows that an increase in permeate pressure decreases the compressor duty (operational costs) on one hand, but on the other hand it gives an increase in membrane surface area (capital costs).

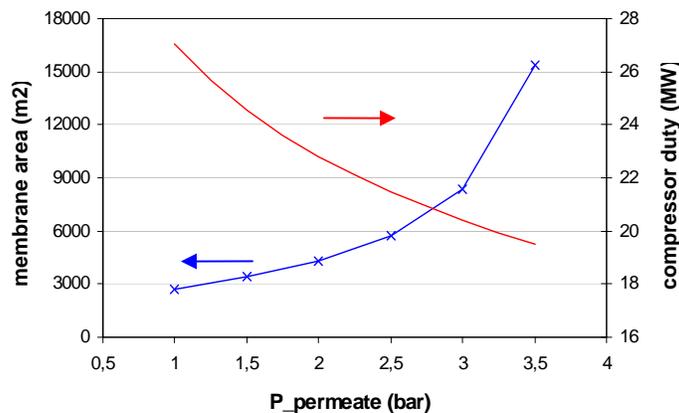


Fig. 6. Trade-off between membrane surface area and compressor duty.

Since the permeate pressure has such a large impact on the economics of the process more knowledge is needed of the impact of the main operating and design parameters on reactor performance is of great importance. To assess the impact of these parameters an in-house membrane reactor model has been developed (van Delft and Pex, 2003), which can be used in flow sheeting software (such as Aspen Plus). The model predicts membrane reactor performance (conversion, hydrogen recovery) as a function of the main operating parameters and main dimensions. The one-dimensional model describes the partial pressure profiles along the membrane length coordinate. The model

combines mass and energy balances for each component on both sides of the membrane with expressions for reaction and permeation. The feed is a pre-reformed $\text{CH}_4/\text{H}_2\text{O}$ (3/1) mixture entering at 40 bara. The reactor is operated in counter-current mode, which means that the feed is flowing from left to right, sweep in the opposite direction. The new model has been used to quantify the trade-off between the permeate pressure and operating temperature and the effect of sweep flow.

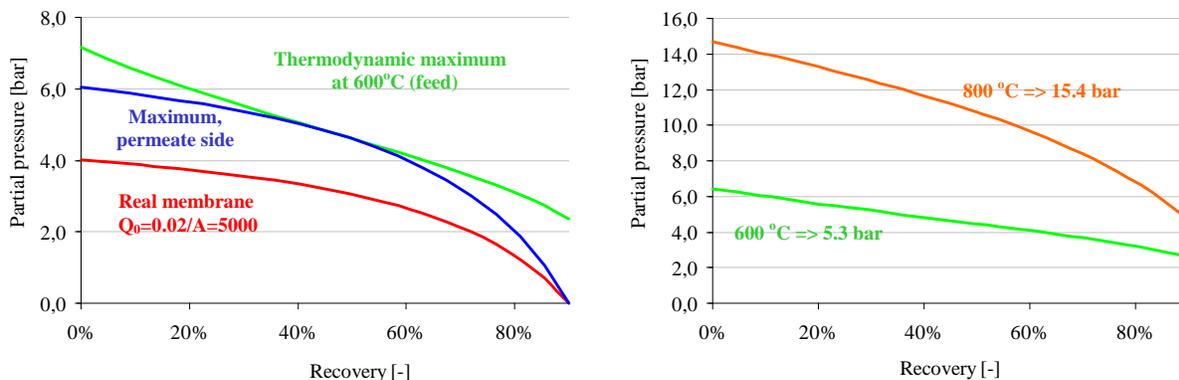


Fig. 7. Hydrogen partial pressure profiles vs the hydrogen recovery for both sides of the membrane (a) and for the feed side at different temperatures (b)

Figure 7a shows the partial pressure profile of hydrogen at both sides of the membrane in the membrane reformer as a function of the hydrogen recovery at 600°C. It can be seen that there is a maximum hydrogen partial pressure at the permeate side and therefore a maximum permeate pressure to have a sufficient driving force for separation. With a realistic membrane surface area (A) and membrane permeance (Q_0) the hydrogen partial pressures/permeate pressure must even be lower than the maximum case. When the temperature increases to 800°C the hydrogen partial pressure on the feed side increases and therefore a higher permeate pressure (15.4 in stead of 5.3 bar) can be used (see Figure 7b). Unfortunately a higher reactor temperature means also an increase in energy and lower system efficiency. The reactor design should therefore be focused on obtaining the highest permeate pressure at the lowest reactor temperature.

6. CONCLUSION

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. Two noble metal catalysts, an in-house developed and a commercial catalyst with sufficient stability and activity under membrane reactor conditions were found and selected for application in the membrane reformer. It was shown that methane conversions well beyond the thermodynamic limits could be reached during steam reforming at 650°C and 11 bar in the membrane reformer. 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.

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Palladium membrane reactor for large scale hydrogen production

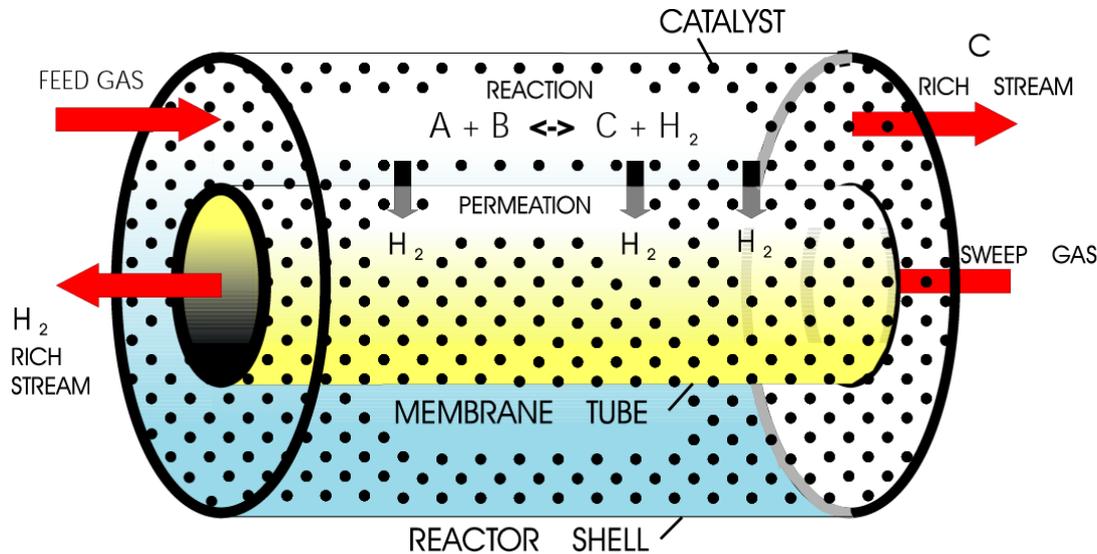
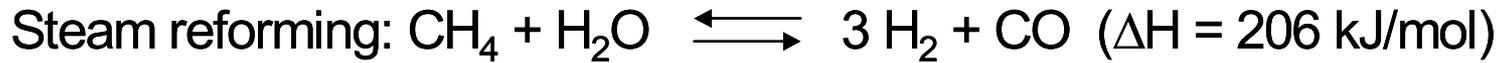
Yvonne van Delft, Marija Sarić, Arend de Groot



Outline

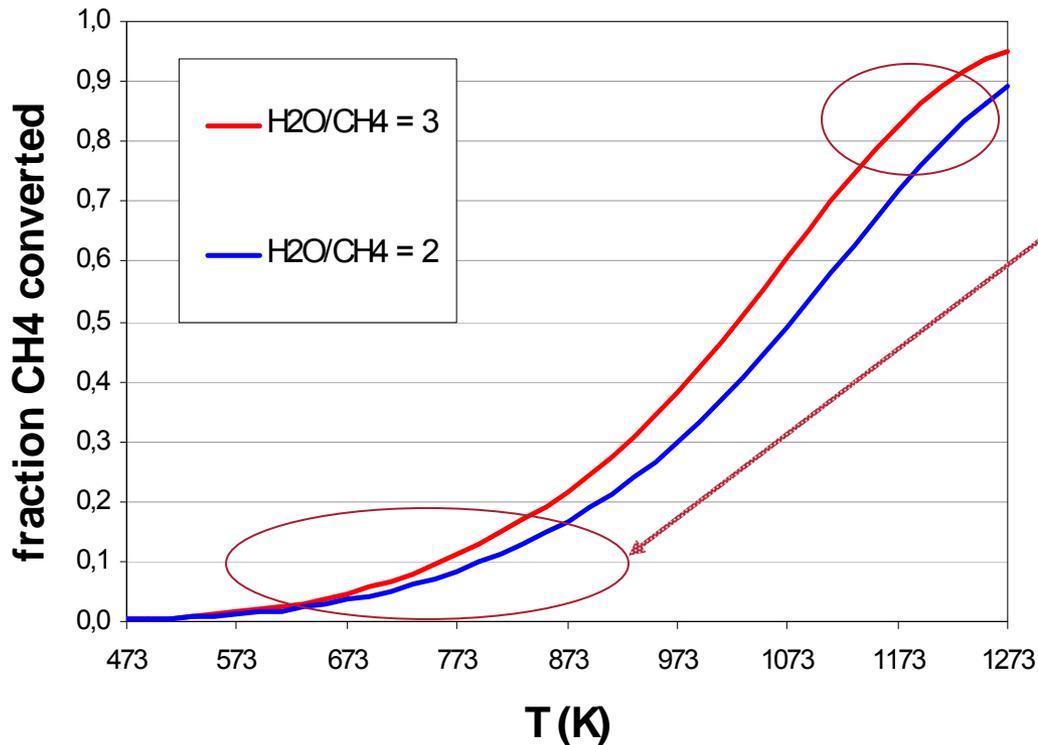
- Introduction
- Background & Objective
- Approach
- Results:
 - Palladium membrane performance
 - Stability of catalysts in membrane reactor conditions
 - Single tube membrane reactor performance
 - Comparison with 1-D membrane reactor model
 - Economic evaluation
- Summary
- Outlook

Hydrogen Membrane Reactor



Reactor modelling

SR + WGS at 36 bar



High methane conversion:

- Demands high temperature
- Shift equilibrium with membrane reactor

Hydrogen Membrane Reactor

Objective of the programme:

- Development of a hydrogen membrane reactor for energy efficient industrial hydrogen and chemicals production
- Build and test a hydrogen membrane reactor which delivers 5 Nm³/h.

Applications in the Netherlands:

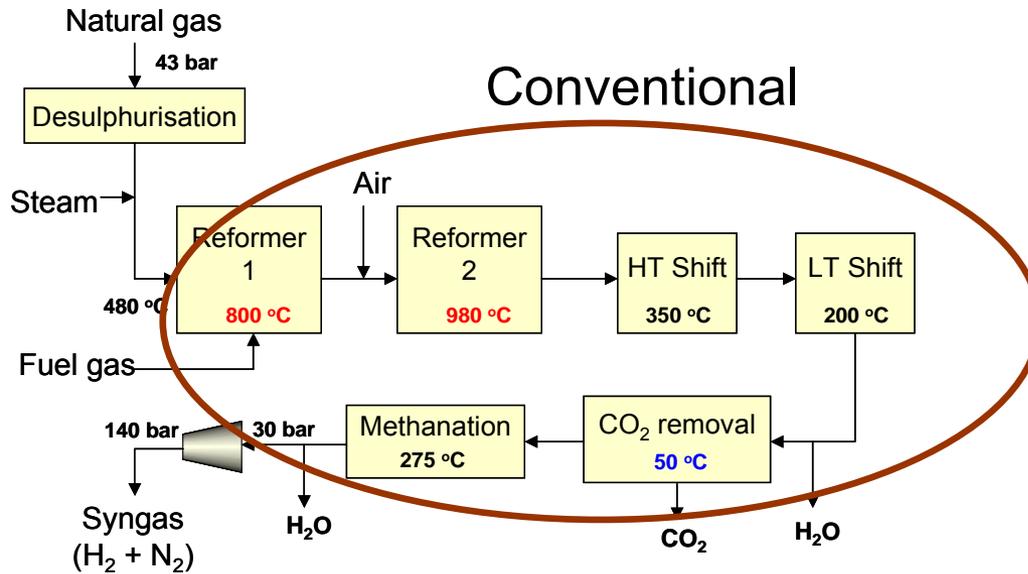
- Large scale hydrogen production in the ammonia process
- Power generation with integrated CO₂ capture
- Small scale on-site hydrogen supply
- Dehydrogenations

Actual Industrial Consumption 458 PJ/year

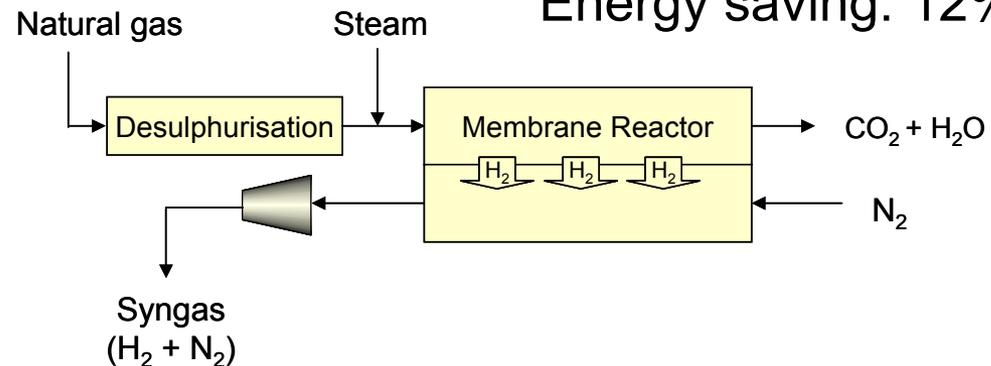
Estimated Energy Saving Potential 24 PJ/year

Total saving potential 5%!

Hydrogen for ammonia production

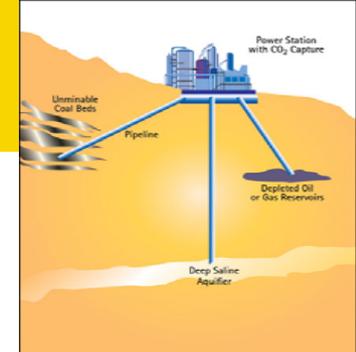


Energy saving: 12%

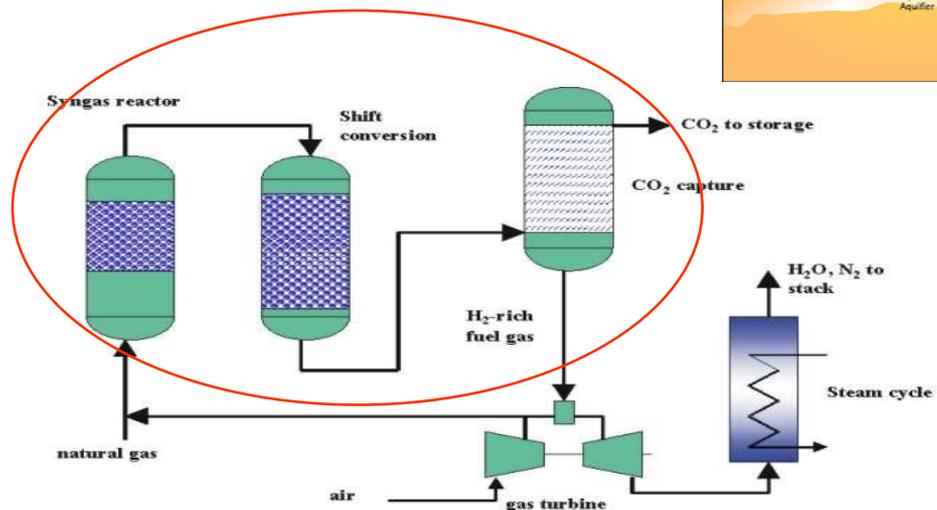


New scheme including membrane reactor

Electricity production with CO₂ capture

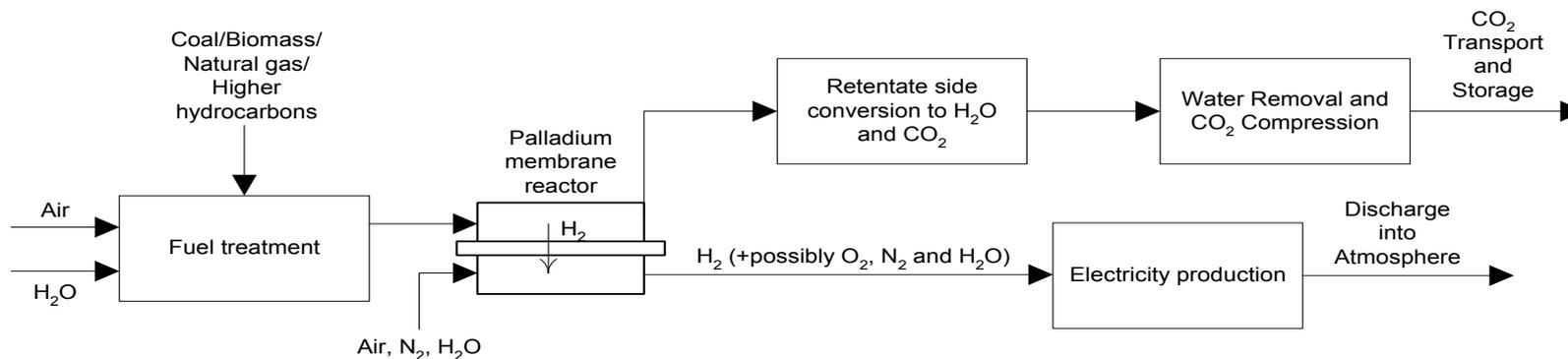


Conventional CO₂ capture:
16 to 40% increase in energy consumption!



New process with MR:

CO₂ capture cost can be reduced with 50%



Base case system analysis

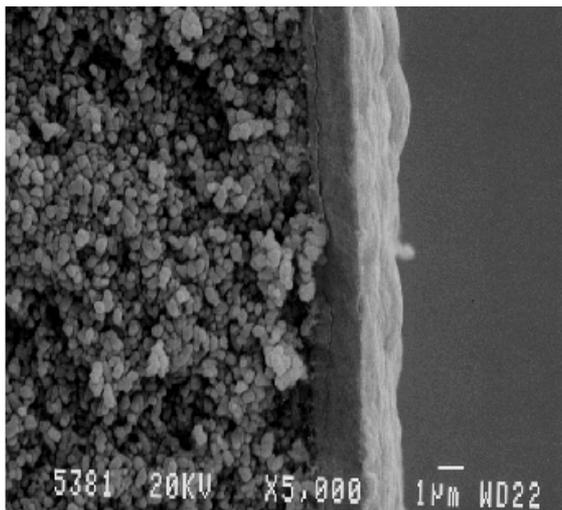
Three main challenges:

- 97% CH₄ conversion at low temperature (500-650°C)
- H₂ recovery > 98% => H₂ poor conditions!
 - High selective membrane operating at 500-650°C
 - Process membrane flux > 50 m³/m²hbar^{0.5}
 - Membrane price ~ 1400 Euro/m²
 - Membrane lifetime > 3 years
- SMR strong endothermic => high heat input

Approach:

- Development of asymmetric, thin layer Pd membranes
- Catalyst screening
- Membrane reactor testing & modelling
- Economic evaluation
- Pilot membrane reformer design (5 Nm³/h), construction and testing

Palladium membrane development



Thin layer defect free Pd membrane 3-6 µm
on tubular ceramic support

Production procedure up to 90 cm tubes

Quality Pd membranes:

-high selectivity (1000-7000)

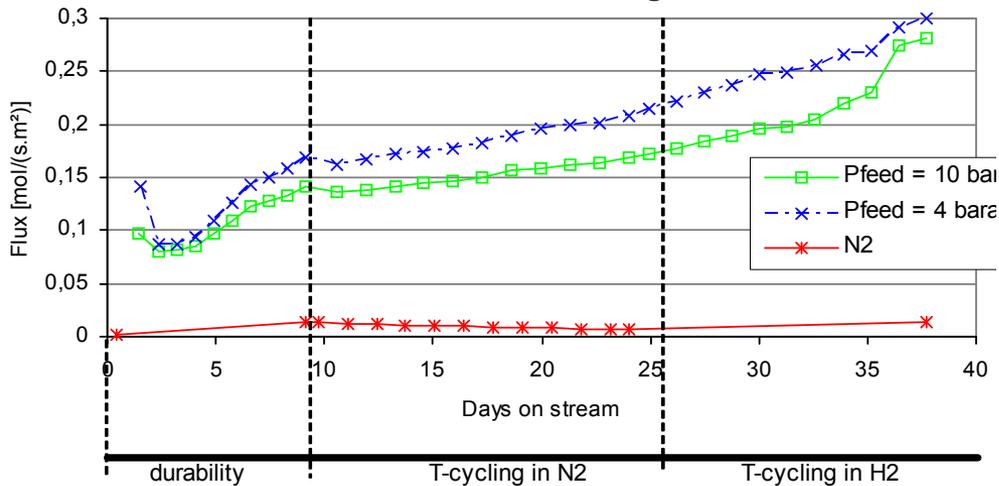
-H₂ permeance 32-48 Nm³/m²hbar^{0.5} at 450°C



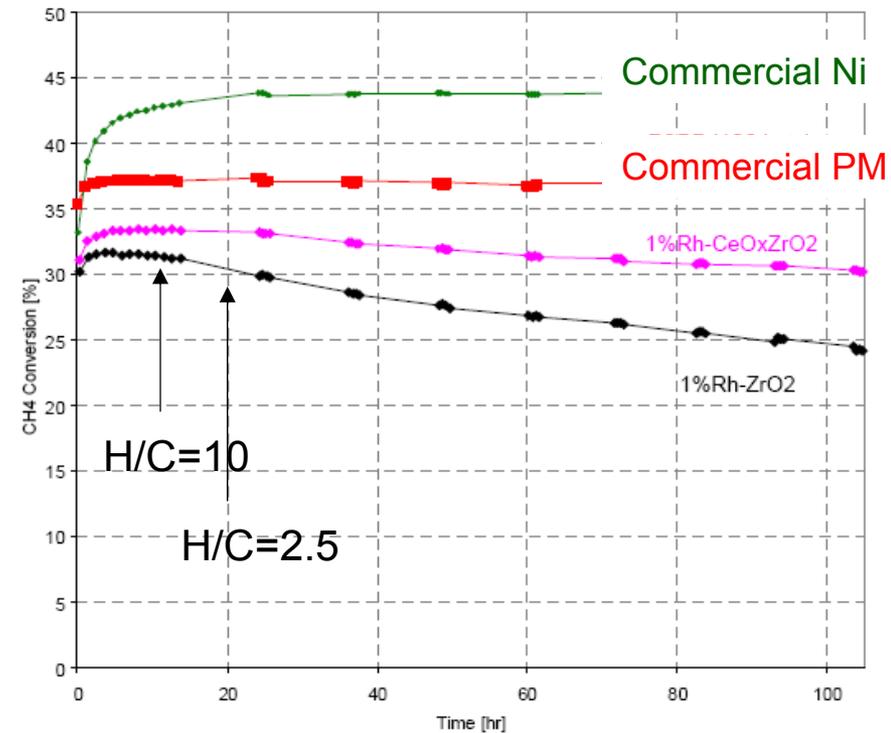
Membrane and catalyst stability

Pd membrane

H₂ flux @ 450°C and dP=2 bar
ECN Pd 102, 136 mm length



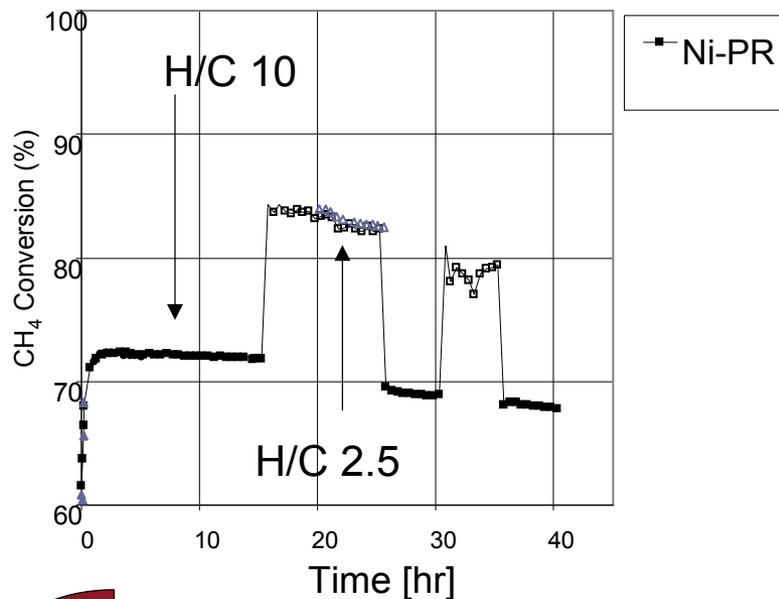
Reformer catalyst



At 450-500°C good stability,
but

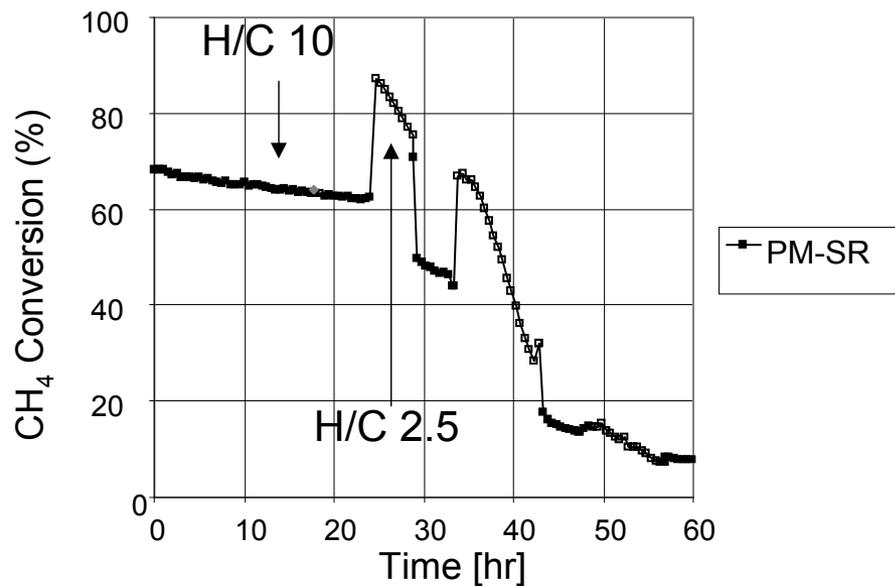
But, at 600°C:

Commercial Ni cat



Modest stability loss

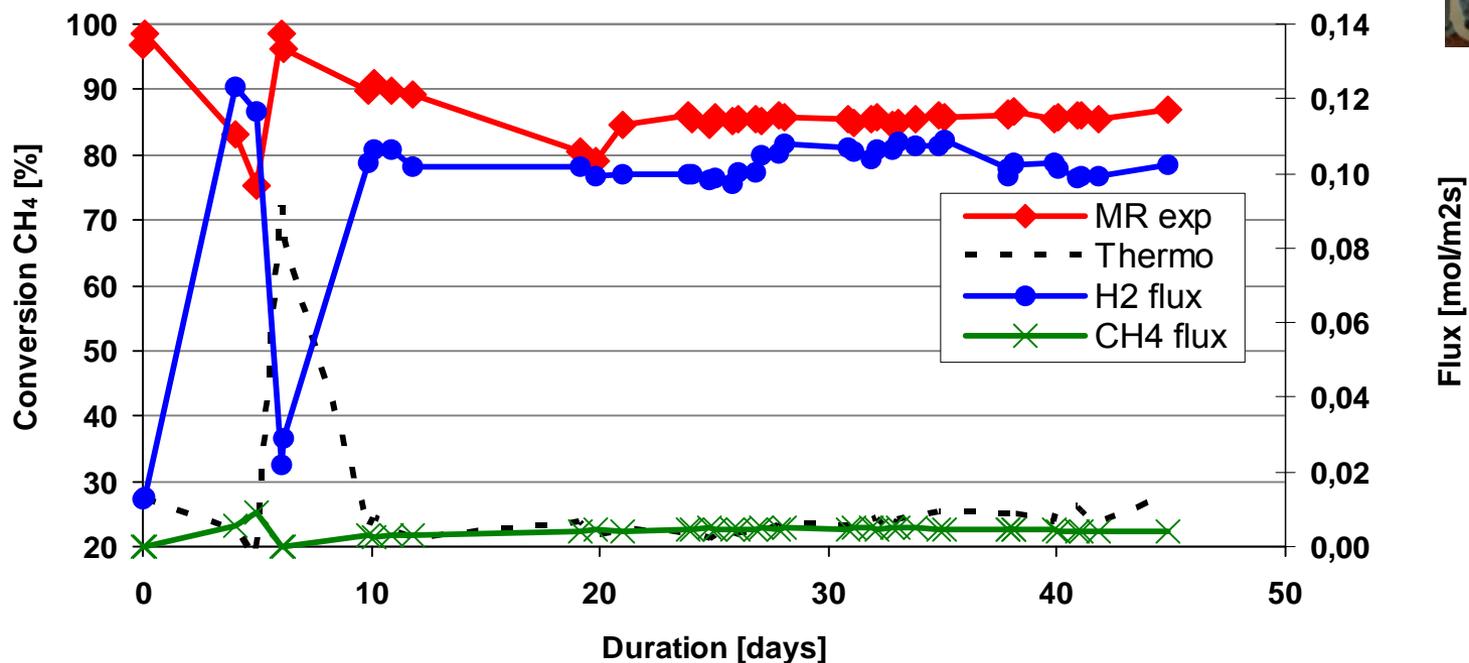
Commercial Precious Metal cat



Dramatic stability loss after exposure to H/C 2.5

Further research on optimization Ni catalyst

Membrane reformer testing

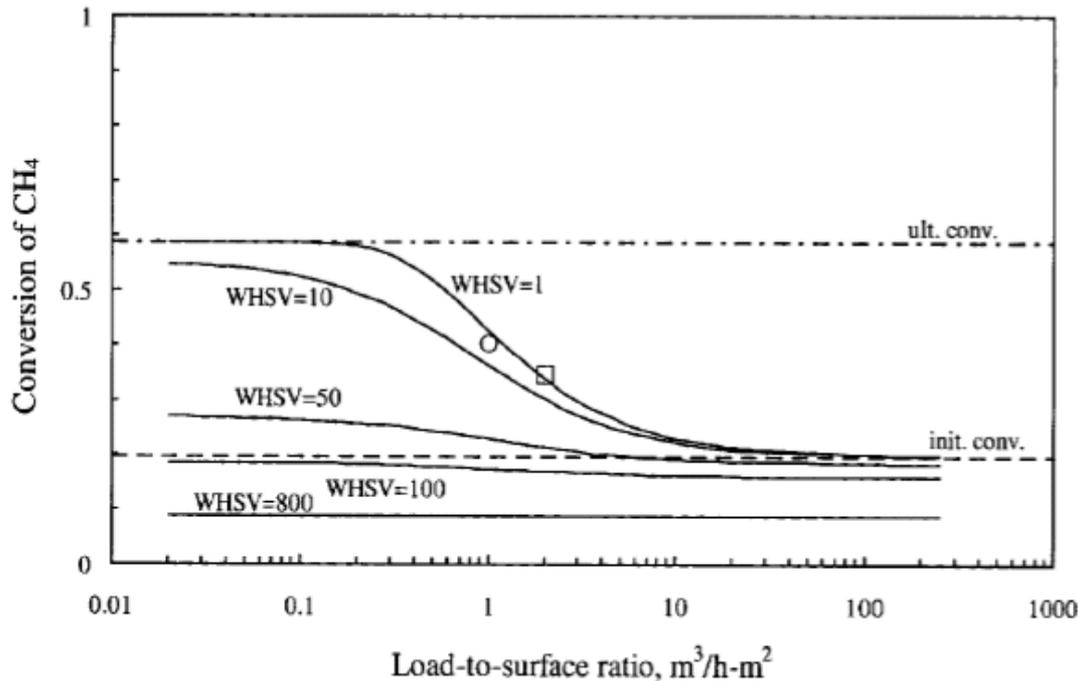


530-590°C; Pf 25-42 bara feed: CH₄/H₂O = 1/3, NiLaMgAl₂O₄ ;
 3.8 μm Pd/αAl₂O₃, 155 cm², co-current, N₂ sweep

1-D membrane reactor model

Reference case

Y.-M. Lin et al. / Catalysis Today 82 (2003) 127-139



T = 500 °C

P_{reactor} = 9 atm

P_{perm} = 1 atm

A_{mem} = 60 cm²

Feed = CH₄ + H₂O
[1 : 3]

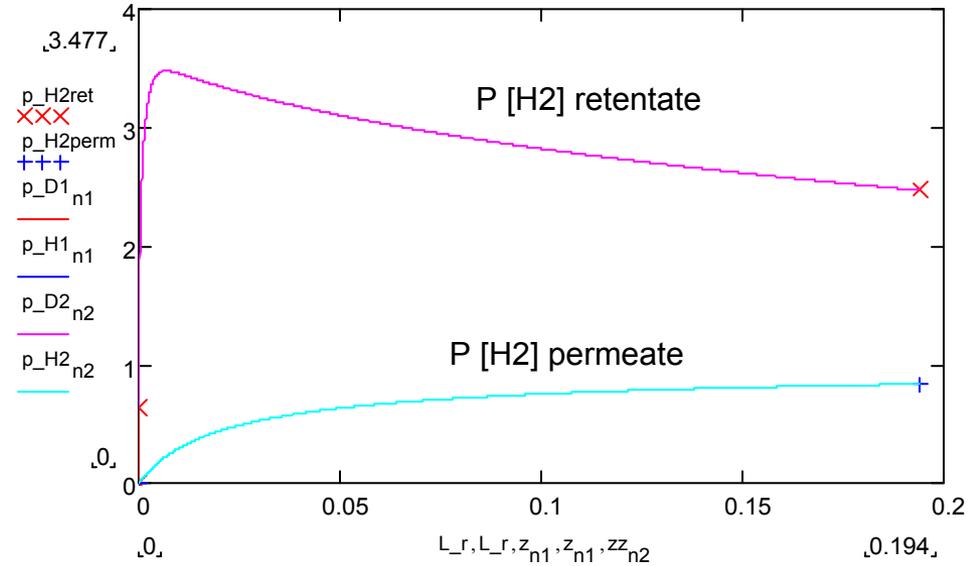
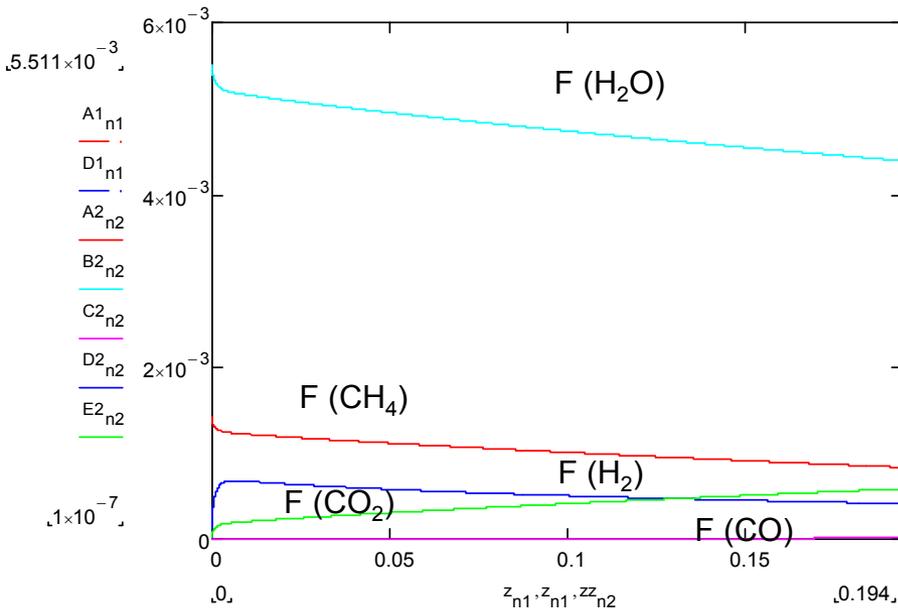
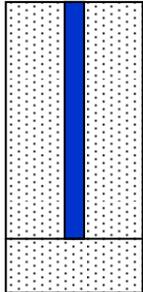
Sweep = none

$$\text{WHSV} = \frac{\text{mass flow CH}_4 \text{ in feed}}{\text{Weight catalyst}}$$

$$\text{L/S} = \frac{\text{volume flow CH}_4 \text{ in feed}}{\text{Membrane area}}$$

1-D membrane reactor model

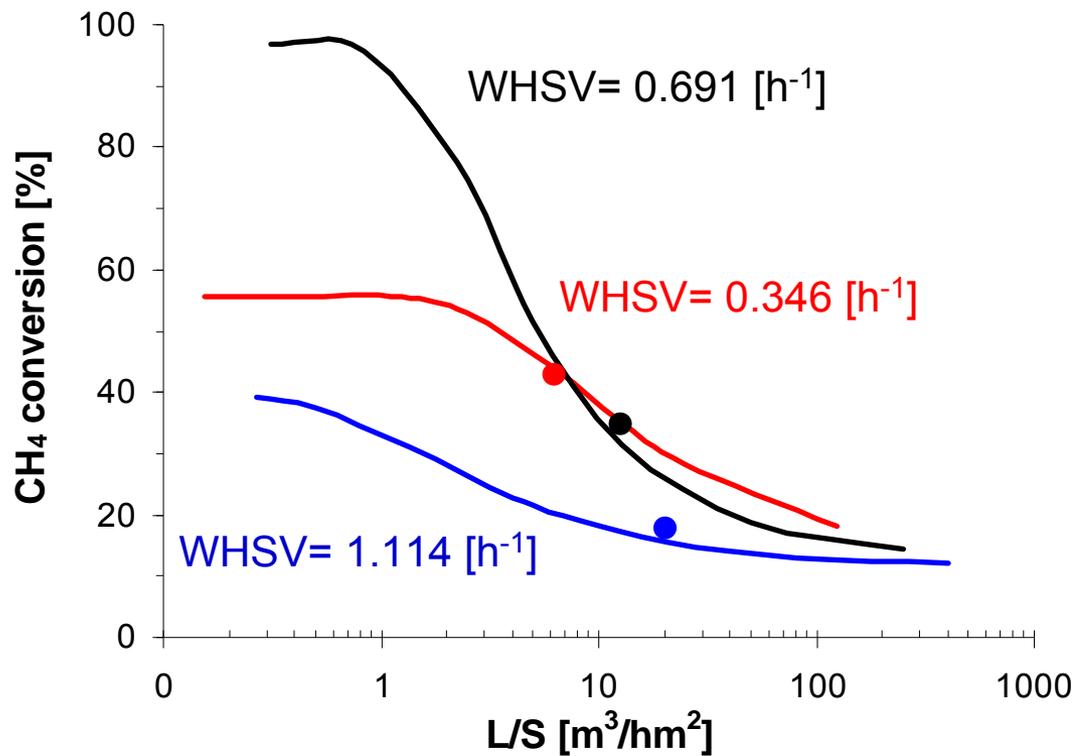
Profiles



$L_{mem} = 0.194 \text{ m}$
 $D = 0.0141 \text{ m}$
 $M_{cat} = 111.2 \text{ g}$
 $V_{cat} = 130 \text{ ml}$
 Co-current flow
 Isothermal

1-D membrane reactor model

WHSV dependency

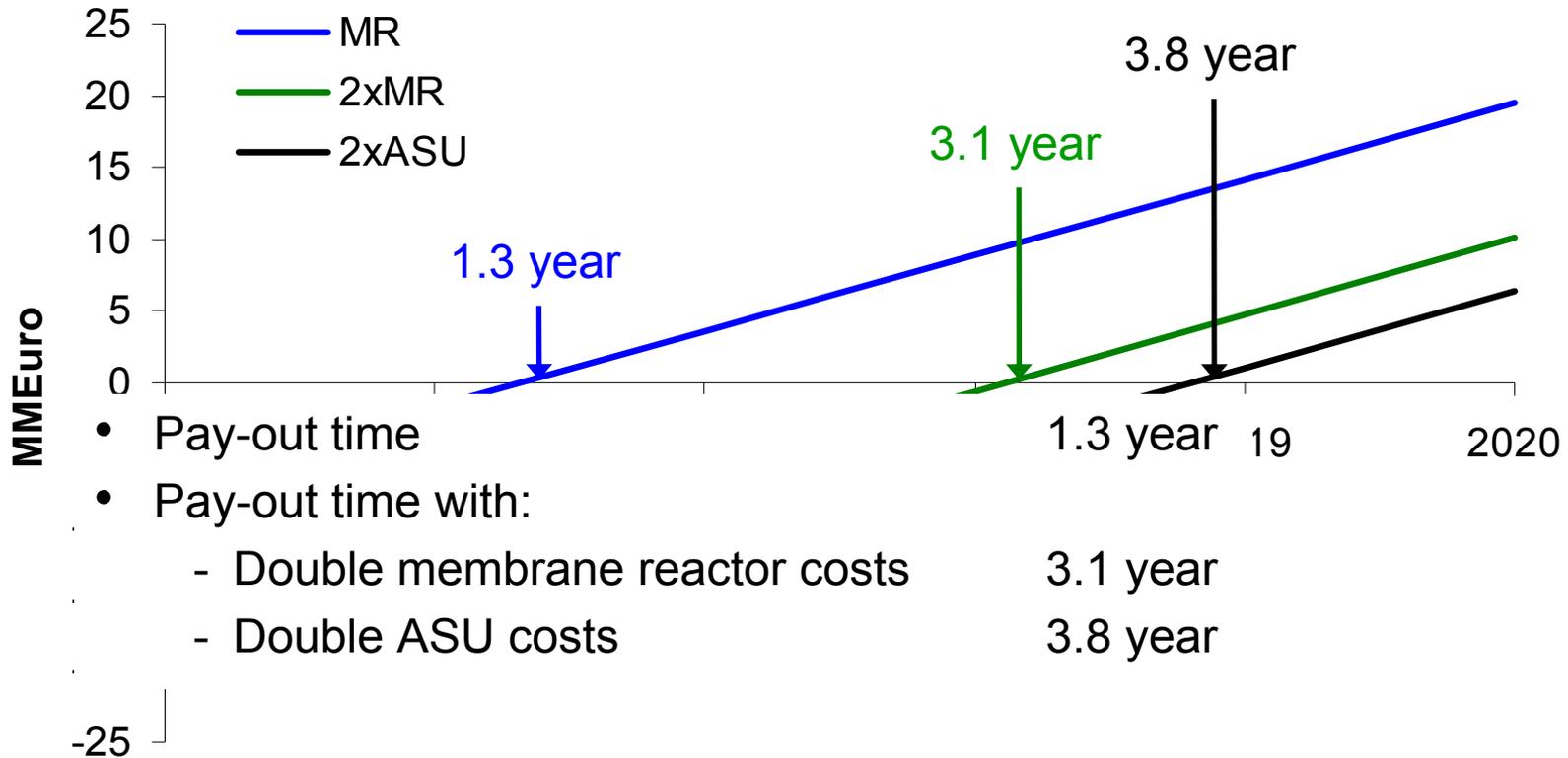


Input model:

- P_f= 38 bar, T = 500°C, P_p= 1 bar
- H₂ permeance during MR test

| Exp | conv CH ₄ [%] | calc CH ₄ conv. [%] |
|------|--------------------------|--------------------------------|
| MR9 | 43.0 | 43.7 |
| MR10 | 18.0 | 15.5 |
| MR2 | 35 | 31.3 |

Economic evaluation MR: Hydrogen for ammonia



5 Nm³/h pilot membrane reformer



- Multitube membrane reactor for membrane reforming and membrane water gas shift
- Max 600°C, 40 bar
- First tests started

Summary and outlook

Summary

- Successful reproducible MR-reforming experiments:
 - 99% conversion possible (up to 70 % higher than equilibrium conversion)
 - Stable membrane reformer operation, stable conversion for 40 days
- 1-D isothermal membrane reformer model shows good comparison with bench scale experiments
- Economics large scale hydrogen production for NH_3 synthesis looks feasible:
 - for newly built front end
 - 7.5 % fuel savings $\sim 1 \text{ PJ/yr} \Rightarrow 1/5$ of predicted savings in NL
 - pay-out time 1.3 year \Rightarrow price ASU and membrane unit determine to a great extent the ultimate feasibility

Outlook

- Study catalyst deactivation and catalyst-membrane interaction during membrane reformer testing
- Increase catalyst and membrane life time at high T
- Testing 5 Nm^3/h membrane reformer
- Study operational aspects pilot membrane reformer
- Update technical economical evaluations
- Technology transfer to market

Technology transfer to market

Prototype hydrogen separation modules
(www.hysep.com):

- From single short tubes ($\sim 40 \text{ cm}^2$),
- To full length multi tubular ($1/8$ to $1/2 \text{ m}^2$)



Partners:

- CRL Energy (New Zealand)
- University of the Basque Country (Spain)
- Technip KTI (Italy)
- N-GHY (France)



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- **Partners**
HyGear, Continental Engineers, Twente University
BP, Sintef, DICP, PDC, NTUA, Chevron



Thank you for your attention



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