Confidential

Palladium membrane reactors for large scale production of hydrogen

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1. 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 $1m^2$ scale. Application of the 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.

2. 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 10-15 Nm^3/h hydrogen, operational in 2008. An overview of the results and current status of the hydrogen membrane reactor development for large-scale hydrogen production is presented.

3. 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. 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 [3]. This low cost (3.5 Euro/piece) carbon compression sealing was successfully tested for 14 mm outer diameter ceramic tubes at 100-500ºC and 1-60 bar (see Figure 1b).

Figure 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 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 50-100m^3/m^{2}hbar$^{0.5}$ 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.

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. Figure 2 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 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, 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 modeling 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.

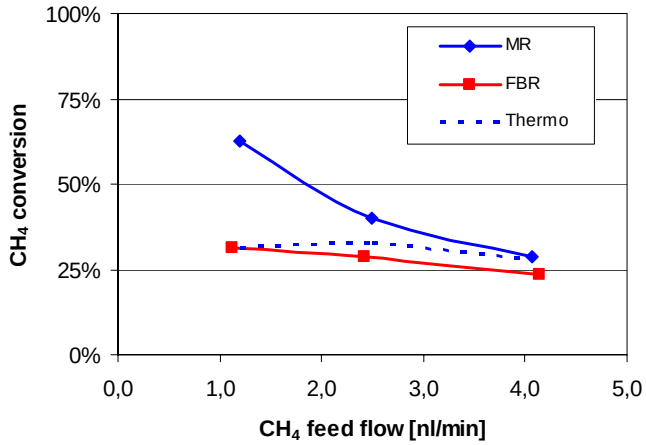

Figure 2 Methane conversion vs feed flow with a membrane reactor (MR), a fixed bed reactor (FBR) and the calculated equilibrium conversion (Thermo) (650ºC, 11 bar, feed: CH_4/H_2O=1/3).

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. 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. Calculations show that the permeate pressure has a large impact on the economics of the process. To assess the impact of this parameter on reactor performance an in-house membrane reactor model has been developed, 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 new model has been used to quantify the trade-off between the permeate pressure and operating temperature and the effect of sweep flow. The model calculations show 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 and membrane permeance the hydrogen partial pressures/permeate pressure must even be lower than the maximum case. When the temperature increases the hydrogen partial pressure on the feed side increases and therefore a higher permeate pressure can be used. 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. Lab scale membrane reformer experiments have 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.

ACKNOWLEDGEMENT

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ECN

Energy research Centre of the Netherlands

Palladium Membrane Reactor for Large scale Hydrogen Production

Yvonne van Delft, Luci Correia, Arend de Groot

Outline

- Introduction
- Background & Objective
- Feasibility & Process studies
- Membrane development & testing
- Catalyst screening
- Membrane reactor testing
- Membrane reactor modelling
- Conclusions

Energy research Centre of the Netherlands

Mission statement

ECN develops and implements high level knowledge and technologies for the transition to sustainable energy system

Trias Energetica

- Efficient use
- Renewable energy
- Clean fossil fuels

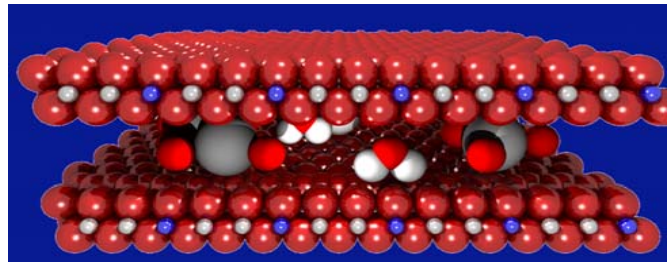
Maximum reliability

Minimum environmental burden

Optimum cost effectiveness

Current framework

Hydrotalcite



CO_2 Capture:

- Run by Hydrogen and Clean Fossil Fuel
- World: Global Climate and Energy Project
- Europe: Cachet program
- NL: Cato

Process Intensification

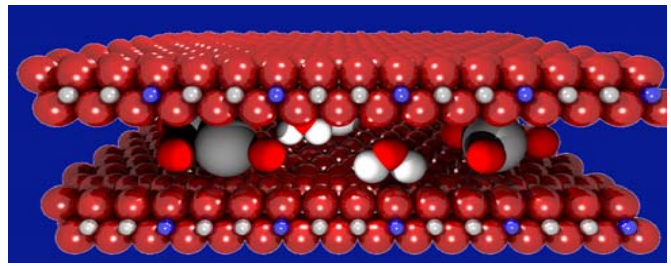
- Run by Energy Efficiency in Industry (PI)
- NL: Energy Research Subsidies
- Partners: Hygear, Continental Engineers

Membrane development

- Run by Energy Efficiency in Industry (MST)
- TU-Delft (Amarante Bottger)

Current framework

Hydrotalcite



CO_2 Capture:

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Partners: Hygear, Continental Engineers

Membrane development

Run by Energy Efficiency in Industry (MST)

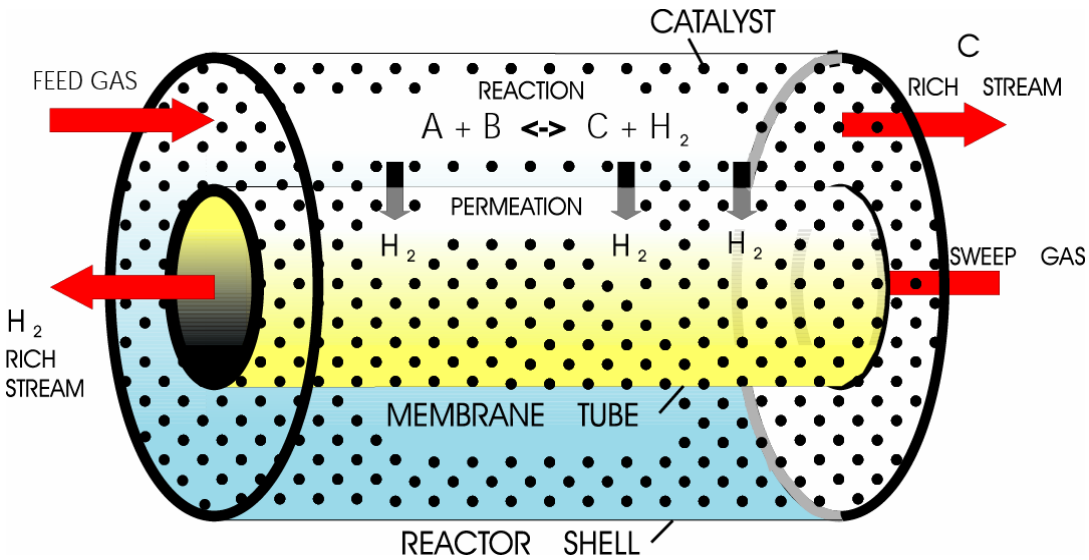
TU-Delft (Amarante Bottger)

Palladium Membrane Reactor

Steam reforming: $CH_4 + H_2O \rightleftharpoons 3\,H_2 + CO$ ($\Delta H = 206$ kJ/mol)

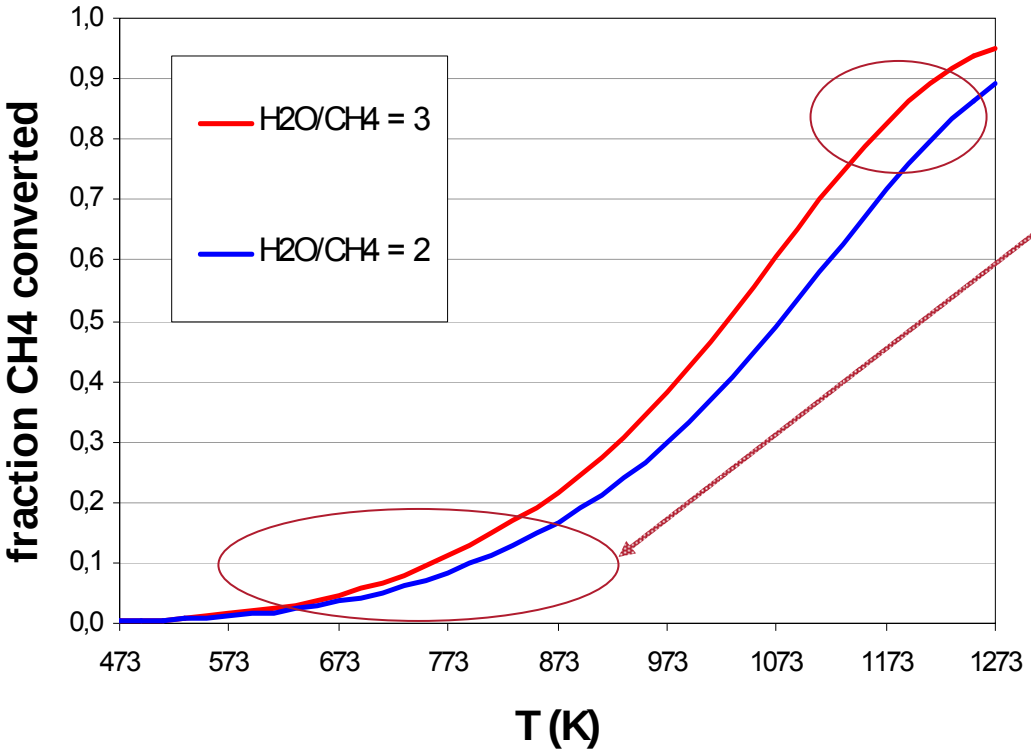
Water-gas shift: $CO + H_2O \rightleftharpoons H_2 + CO_2$ ($\Delta H = -41$ kJ/mol)

$$CH_4 + 2\,H_2O \rightleftharpoons 4\,H_2 + CO_2$$



Reactor modelling

SR + WGS at 36 bar



High methane conversion:

- Demands high temperature
- Shift equilibrium with membrane reactor

Palladium 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 5-15 Nm^3/h.

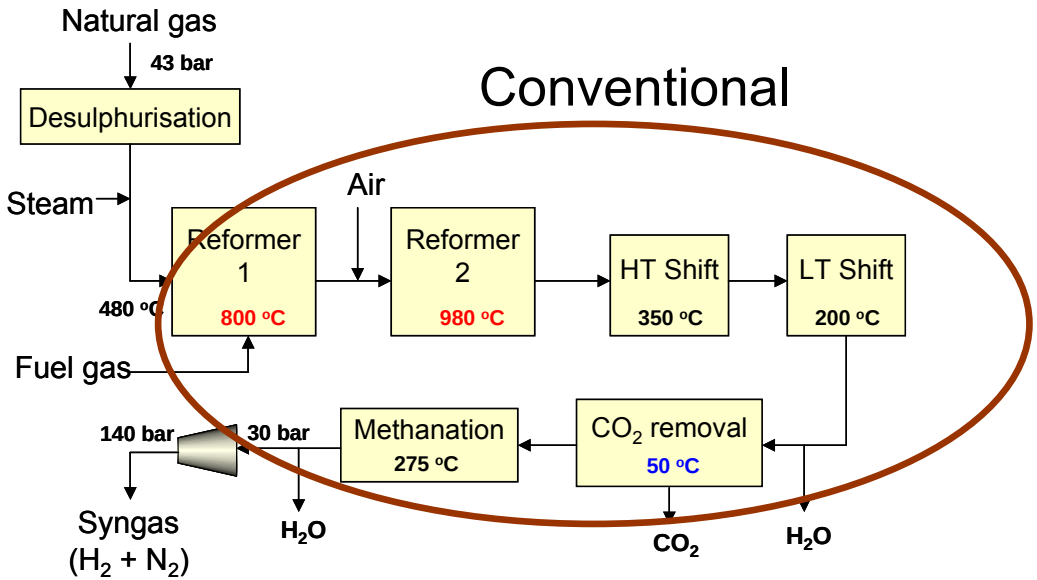
Applications in the Netherlands:

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

Actual Industrial Consumption	458 PJ/year
Estimated Energy Saving Potential	24 PJ/year

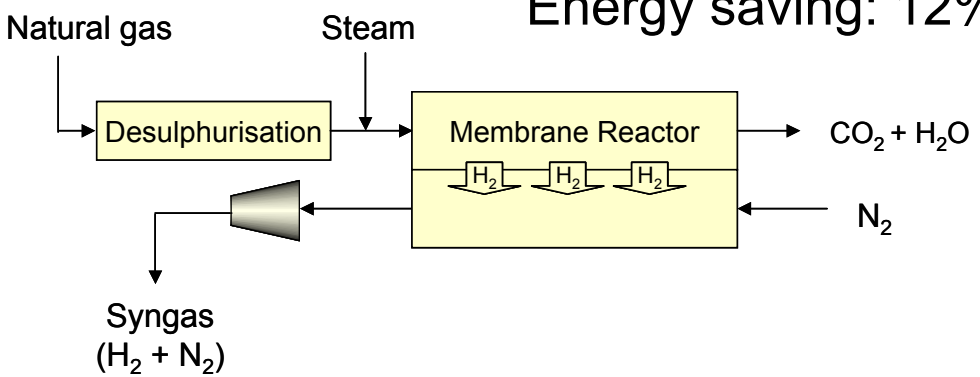
Total saving potential 5%!

Hydrogen for ammonia production



Energy saving: 12%

New scheme including membrane reactor



Base case system analysis

Three main challenges:

- 97% CH_4 conversion at low temperature (500-650°C)
- H_2 recovery > 98% => H_2 poor conditions!
  - High selective membrane operating at 500-650°C
  - Process membrane flux > 50 $m^3/m^2hbar^{0.5}$
  - Membrane price ~ 1400 Euro/m^2
  - Membrane lifetime > 2 years
- SMR strong endothermic => high heat input

Approach:

- Development of asymmetric, thin layer Pd/alloy membranes
- Catalyst screening
- Membrane reactor testing & modelling
- Basic unit design

Scale-up issues for Pd membrane reactor

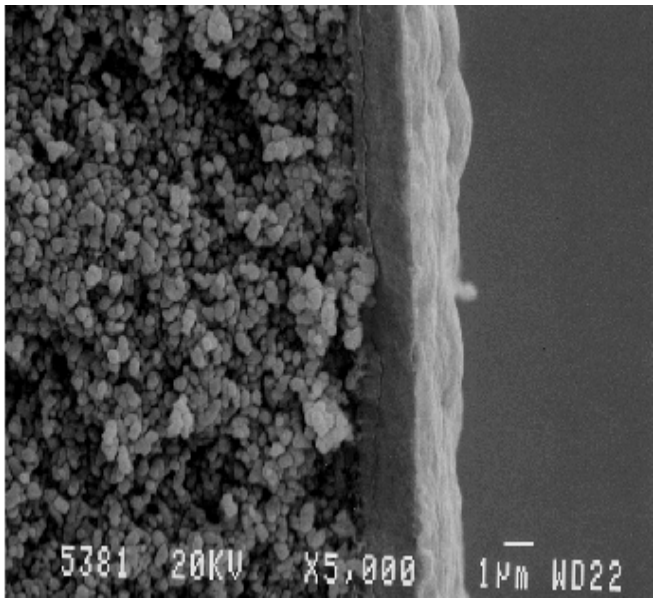
- Cost
  - Pd membrane: Pd price is 8.86 €/g (Jan, 2007), thickness 3-5 μm = 318 -530 €/m2
  - Catalyst: noble metal catalyst more active at low temperature and less risk of carbon formation, but expensive
- Poisoning by process stream impurities
  - unsaturated hydrocarbons, H2S, carbon monoxide (CO)
  - should be regeneratable in steam or air
- Embrittlement
  - resistance to thermal cycling
  - α > β (α') phase transition
- Leak-free sealing
- Stability
  - Catalyst
  - Pd membrane

How are these problems adressed?

- Cost
  - thin films of Pd on hydrogen-porous supports, minimize Pd film thickness
  - nickel/noble metal catalyst
- Poisoning
  - remove most H2S up front
  - other Pd alloys like PdCu40
- Embrittlement
  - Pd alloys reduce distortion upon hydriding/dehydriding => PdAg membranes
- Leak free sealing
  - patented carbon compression sealing
- Stability
  - proper carrier
  - depress sintering effect => new Pd alloys

Membrane development

Thin layer Pd alloy membranes



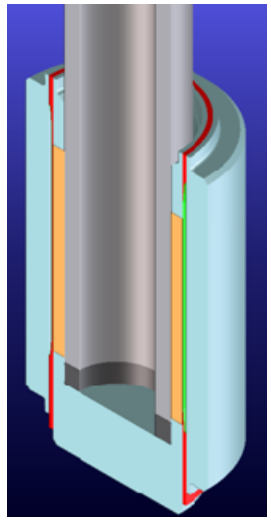
Pd/23%Ag

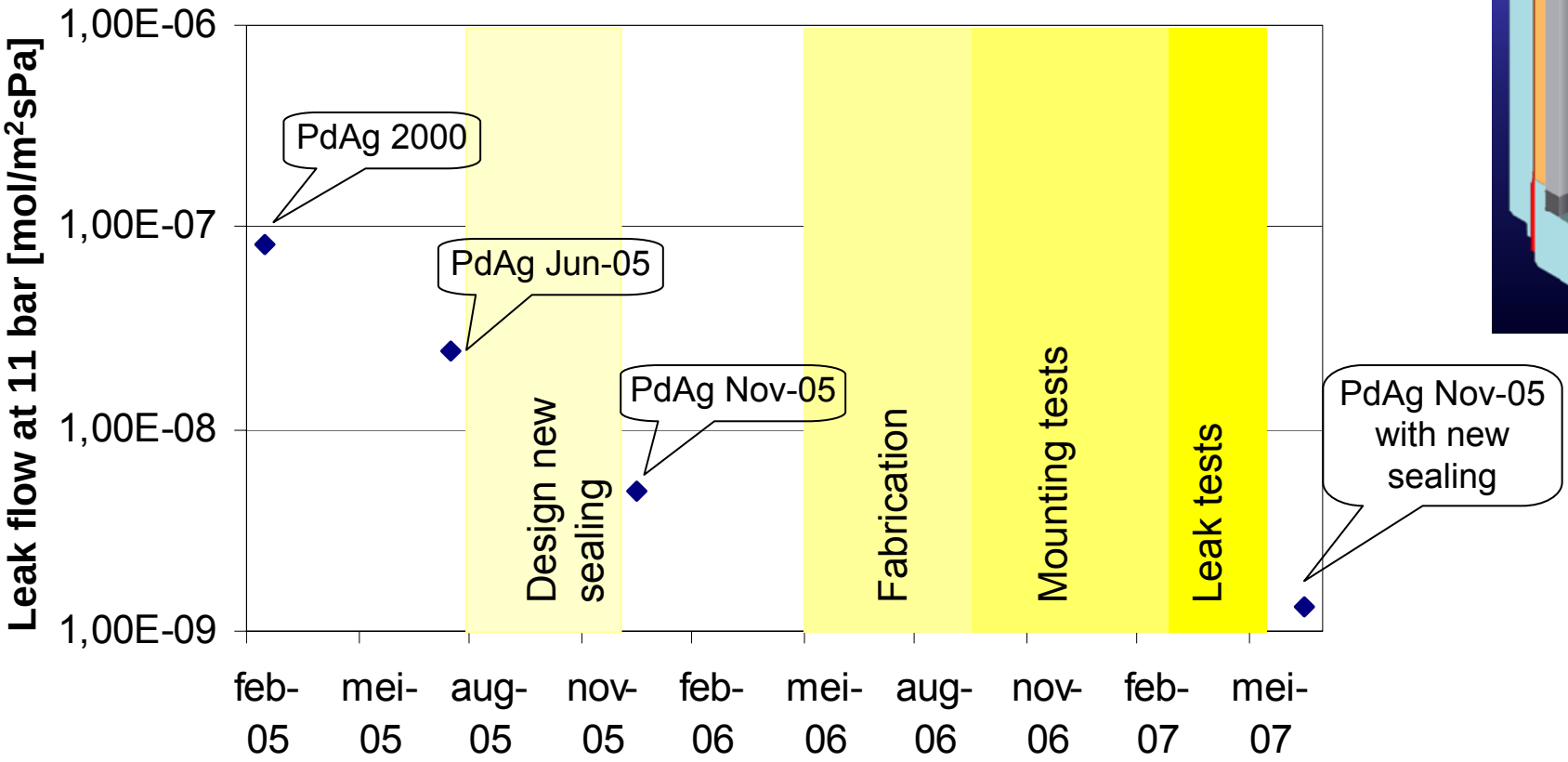
Production procedure up to 80 cm tubes:

- Recipe development plate bath
- Controlled nucleation
- Sequential electroless plating
- Annealing/alloying

Thin layer defect free membrane 3-5 μm on tubular ceramic support

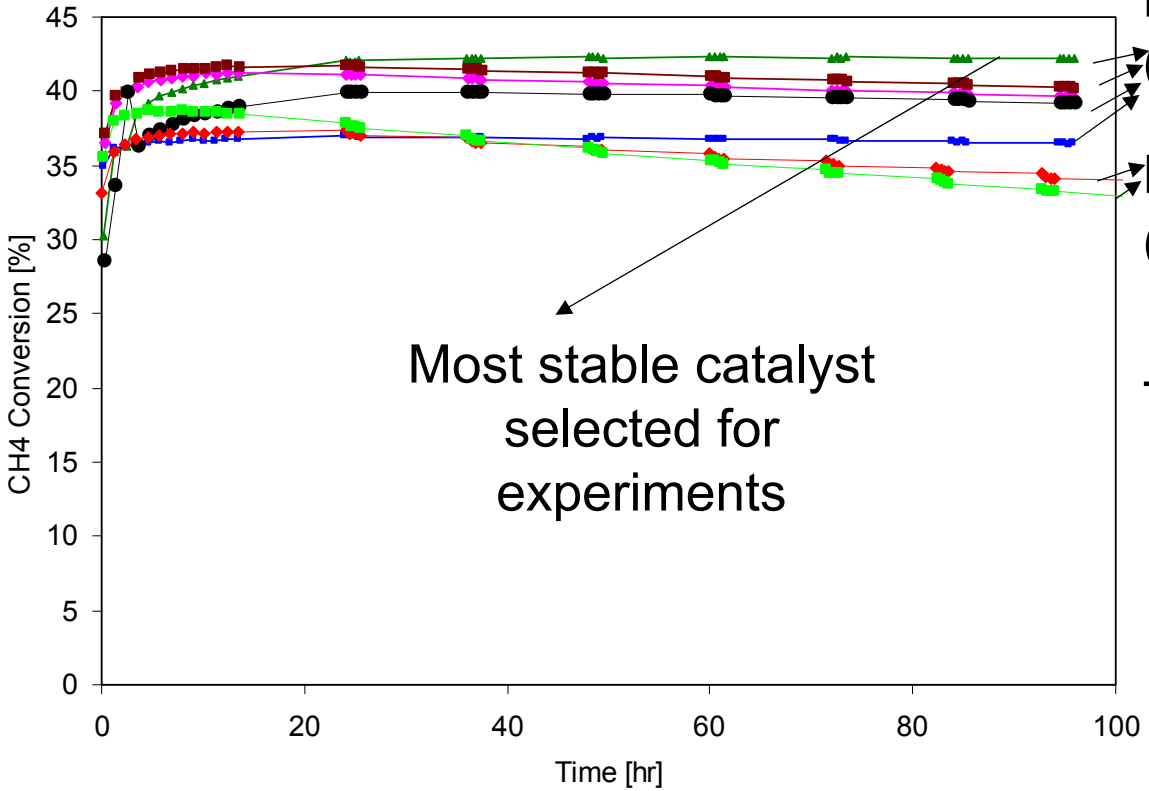
Selectivity improvement: defect control and sealing





Catalyst screening

Activity and stability at MSR conditions

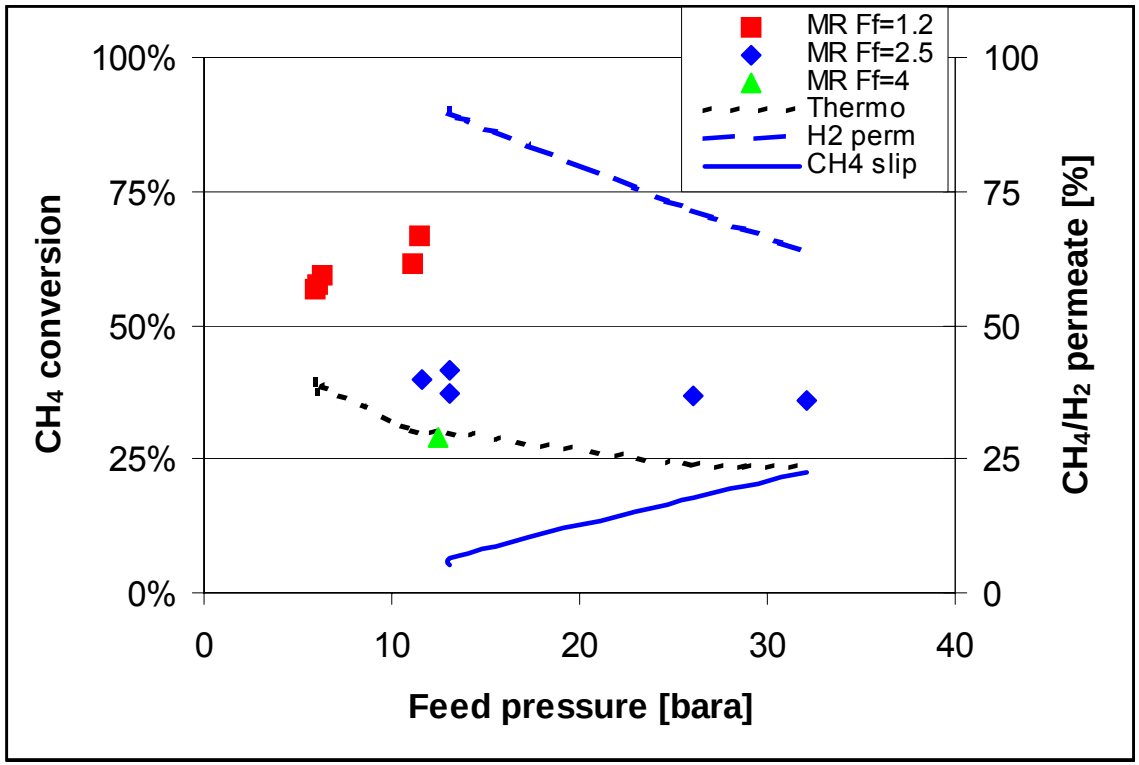


Pre-reforming catalyst (pre-commercial)

Rh-based catalyst (in-house)

T=500°C, P=3.5 bar

Membrane Reforming process testing 2005

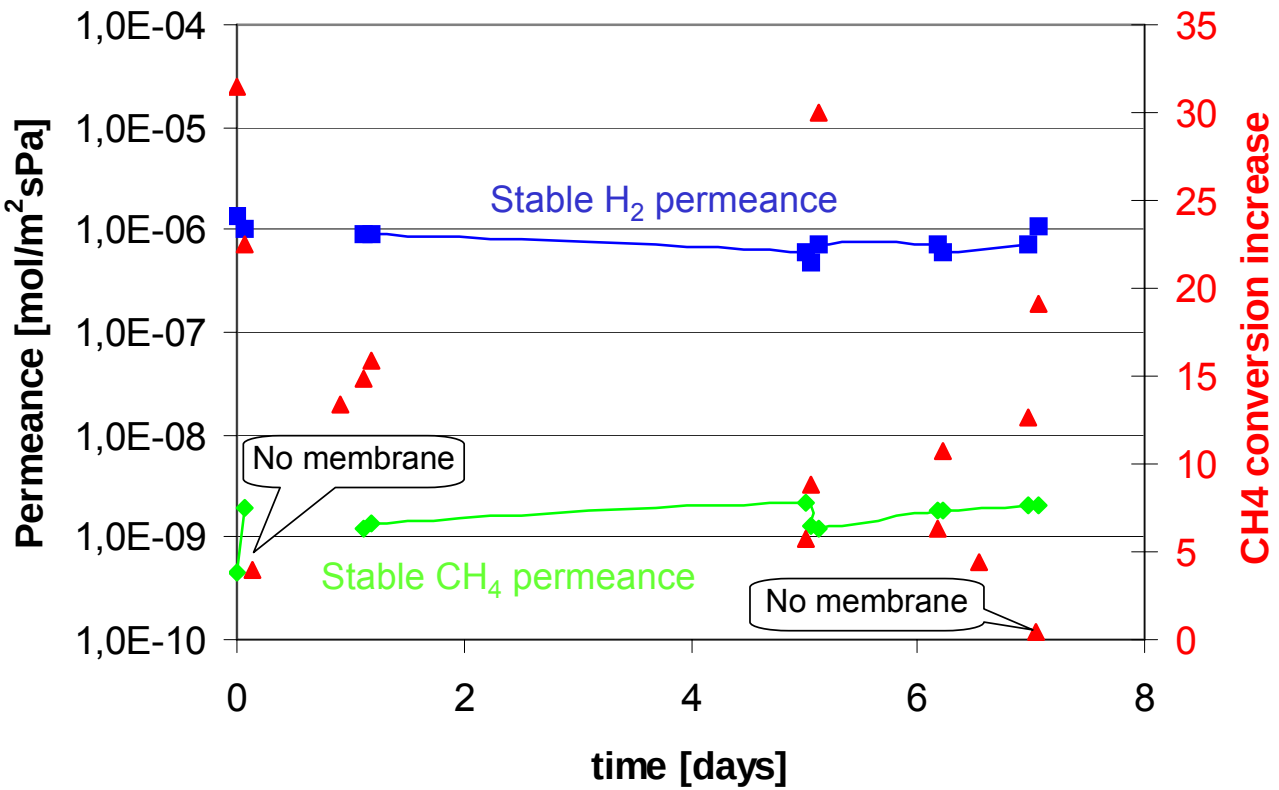


Membrane reformer:

- At higher feed pressures increased CH_4 conversion
- BUT not at very high feed pressures due to high CH_4 slip
- Still 64-91% H_2 in permeate

650°C; feed: CH_4/H_2O = 1/3

Membrane Reformer process testing 2007-1

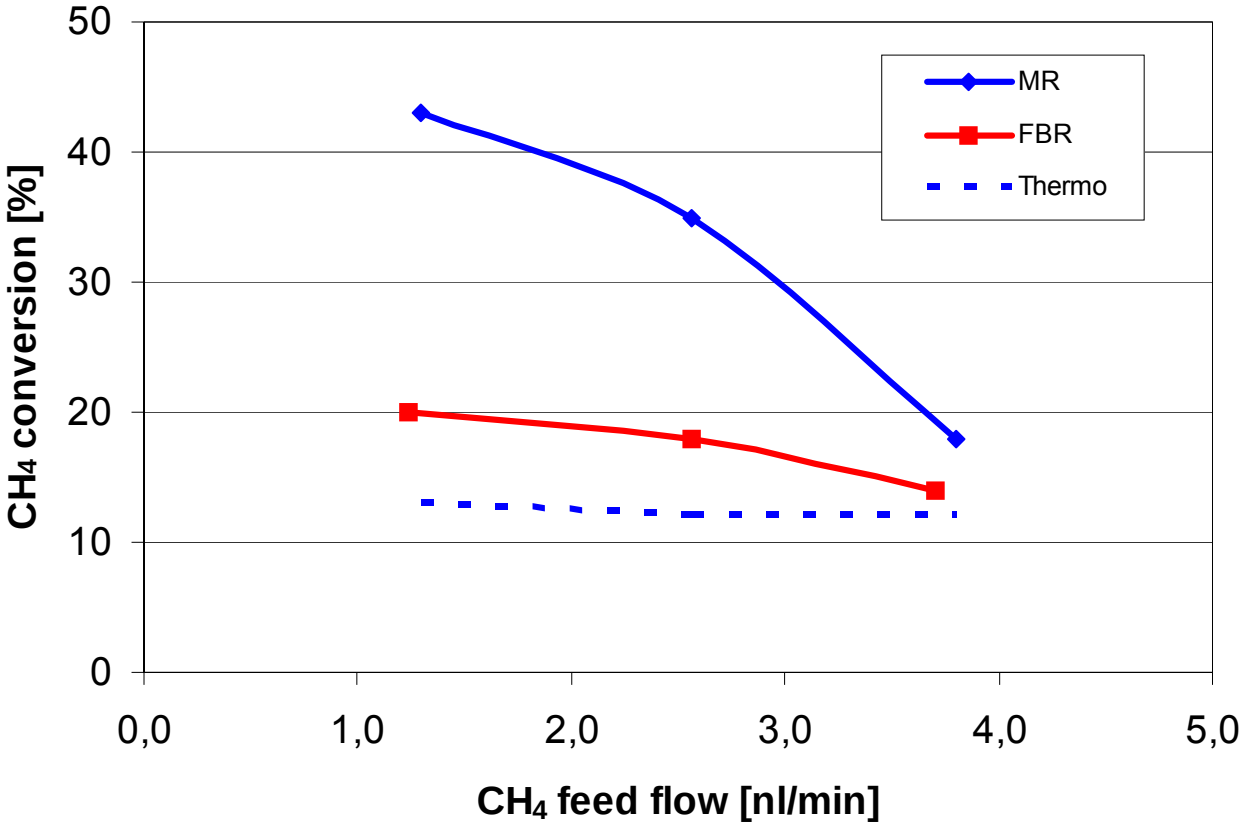


500°C, feed: CH_4/H_2O = 1/3

Depending on conditions CH_4 conversion may increase with >30%

H_2/CH_4 sel > 1000

Membrane Reformer process testing 2007-2



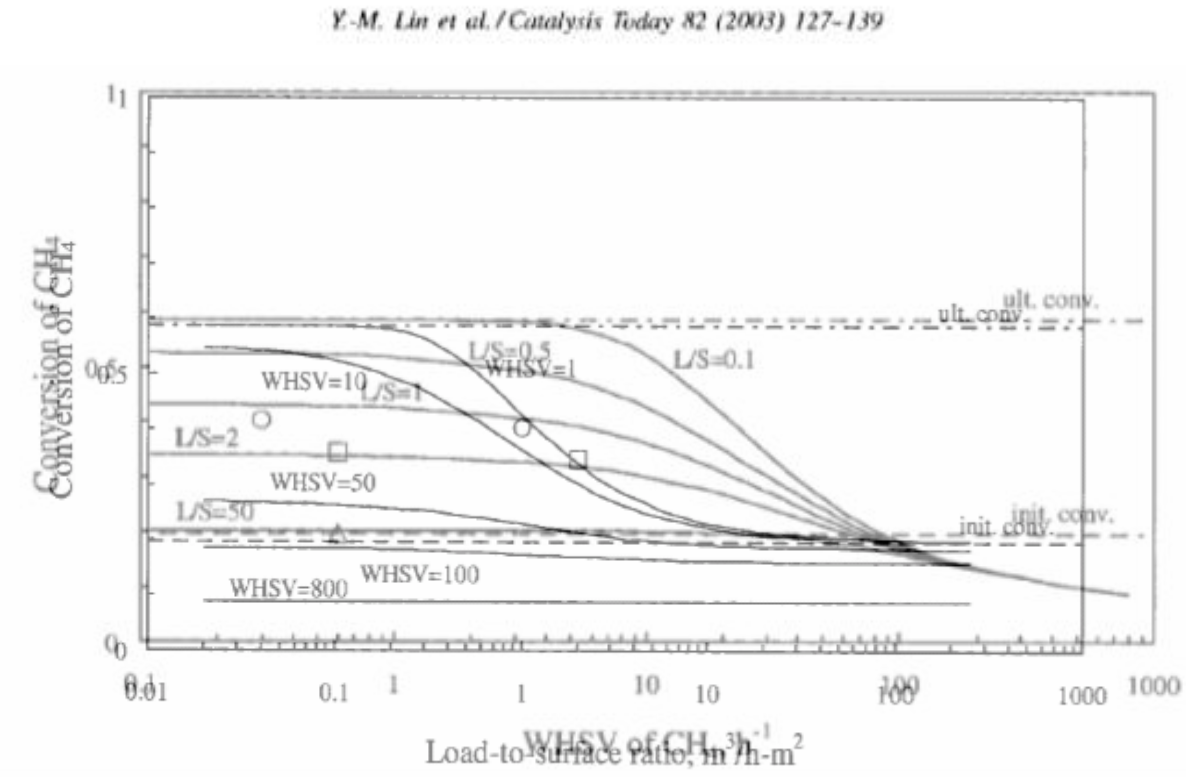
Results:

- Maximum 30% increase in CH_4 conversion
- Large effect of feed flow on CH_4 conversion
- Maximum CH_4 conversion 54%

500°C; Pf 38 bara feed: CH_4/H_2O = 1/3

Membrane reactor model

Reference case



T = 500 °C

P_reactor = 9 atm

P_perm = 1 atm

A_mem = 60 cm^2

Feed = $CH_4 + H_2O$

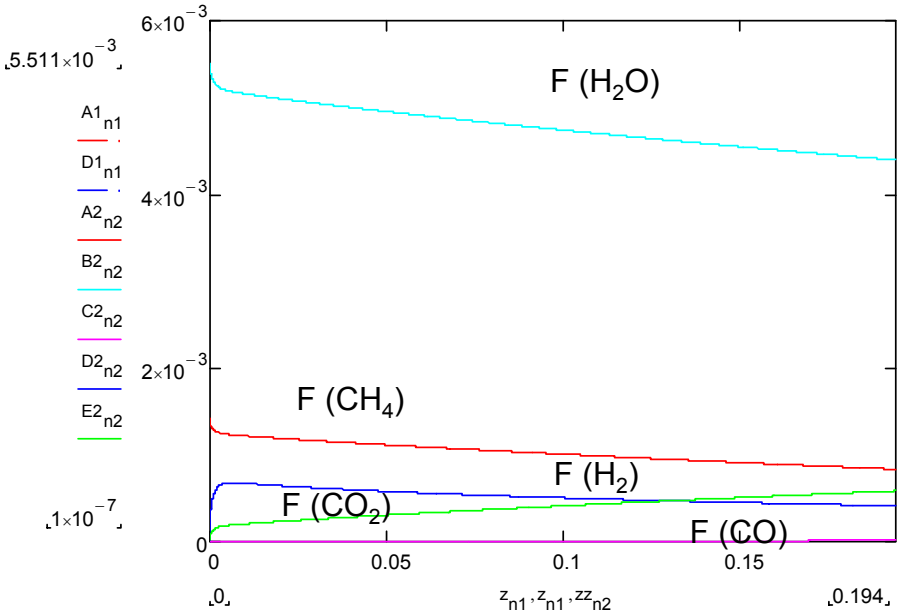
[3 : 1]

Sweep = none

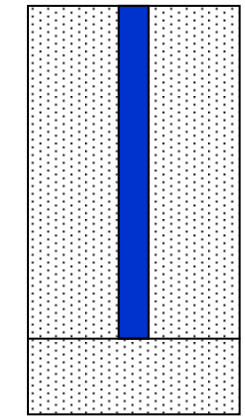
$$WHSV = \frac{\text{mass flow CH4 in feed}}{\text{Weight catalyst}}$$

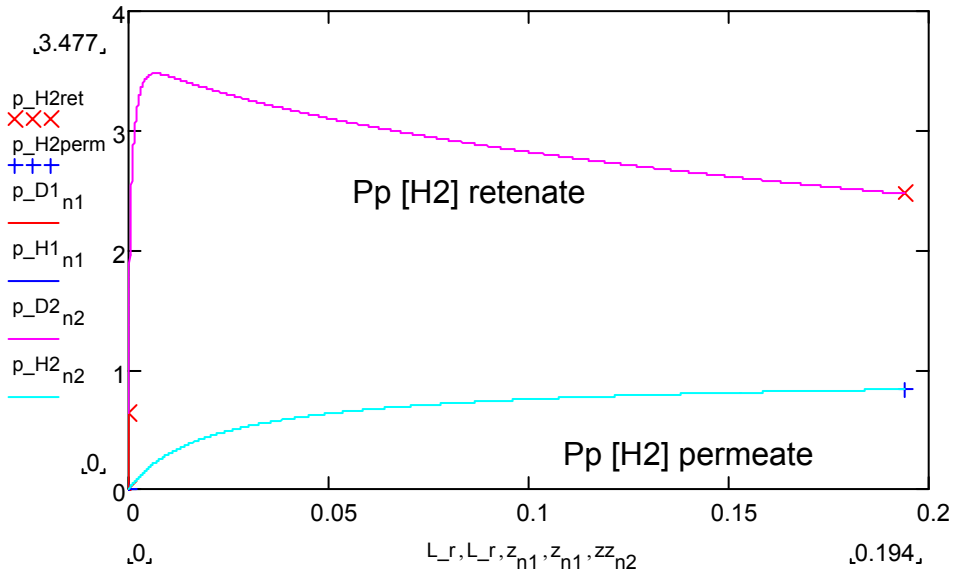
$$L/S = \frac{\text{volume flow CH4 in feed}}{\text{Membrane area}}$$

Calculated profiles in the Pd membrane reactor



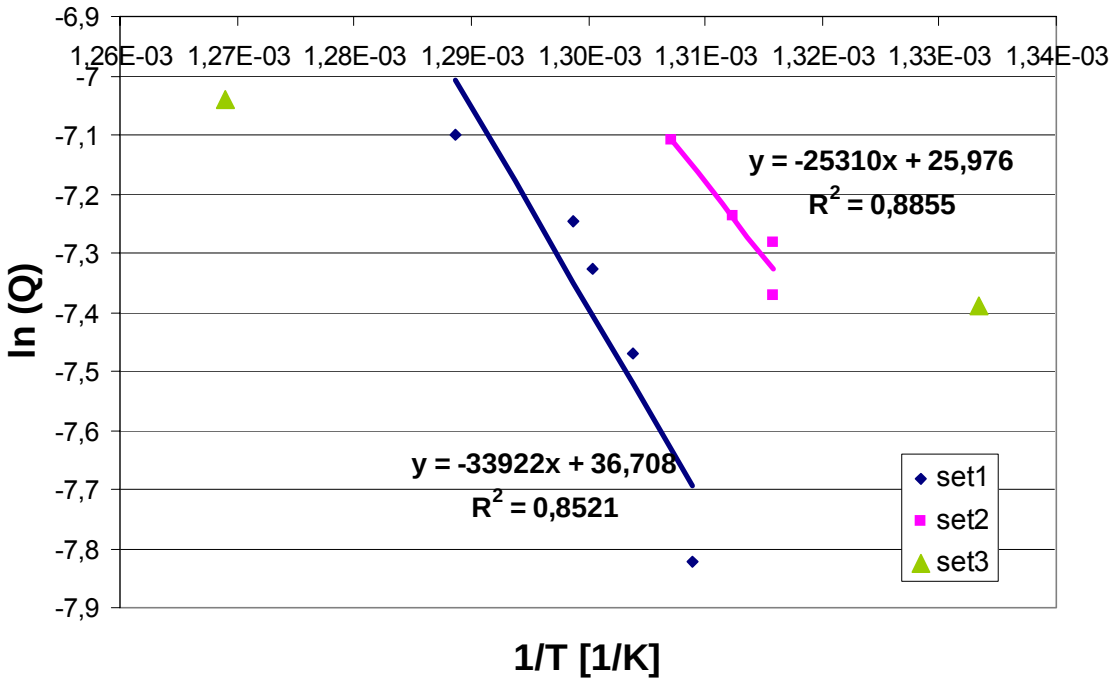
L_{mem} = 0.194 m
D=0.0141 m
M_{cat} = 111.2g
V_{cat} =130ml
Co-current flow
Isothermal





Membrane reactor model

Input hydrogen permeance



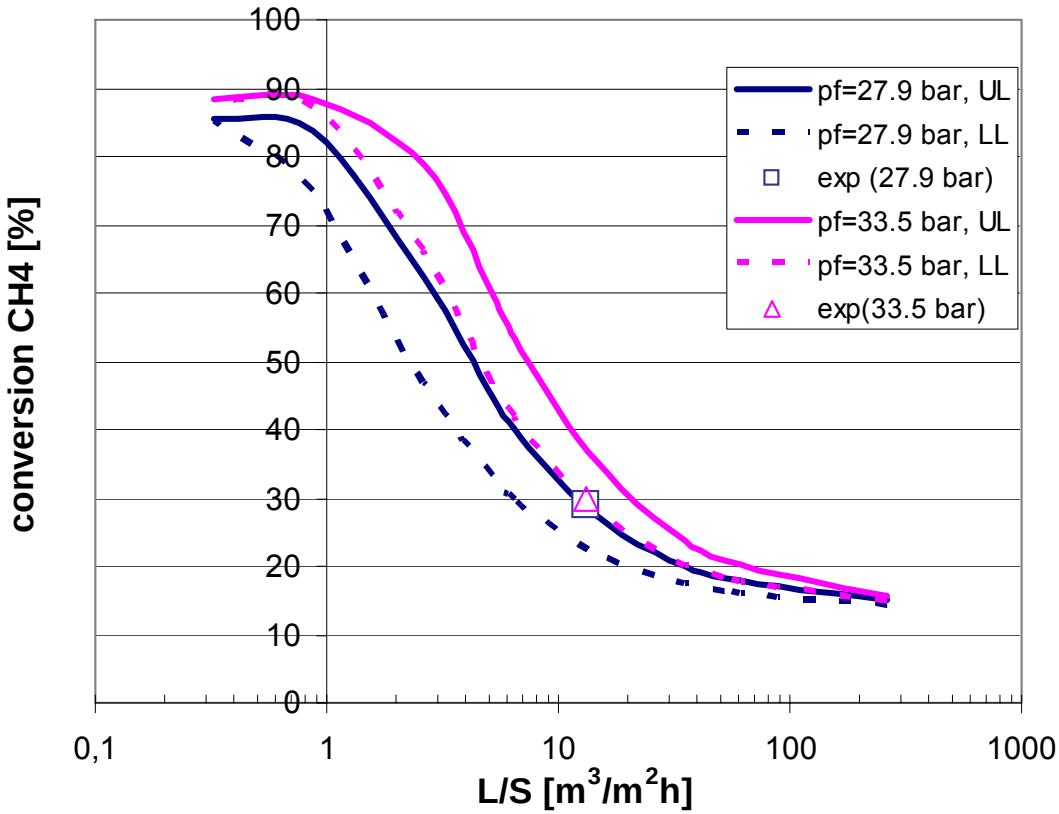
Input based on performance during MR experiments

$Q=Q_0*e(-E_a/RT)$

	Q_0 [mol/m²sPa^0.5]	Ea [kJ/mol]	
equation I	8.75E+15	282	**Lower limit**
equation II	1.91E+11	210.4	**Upper limit**

Membrane reactor model

Feed pressure dependence



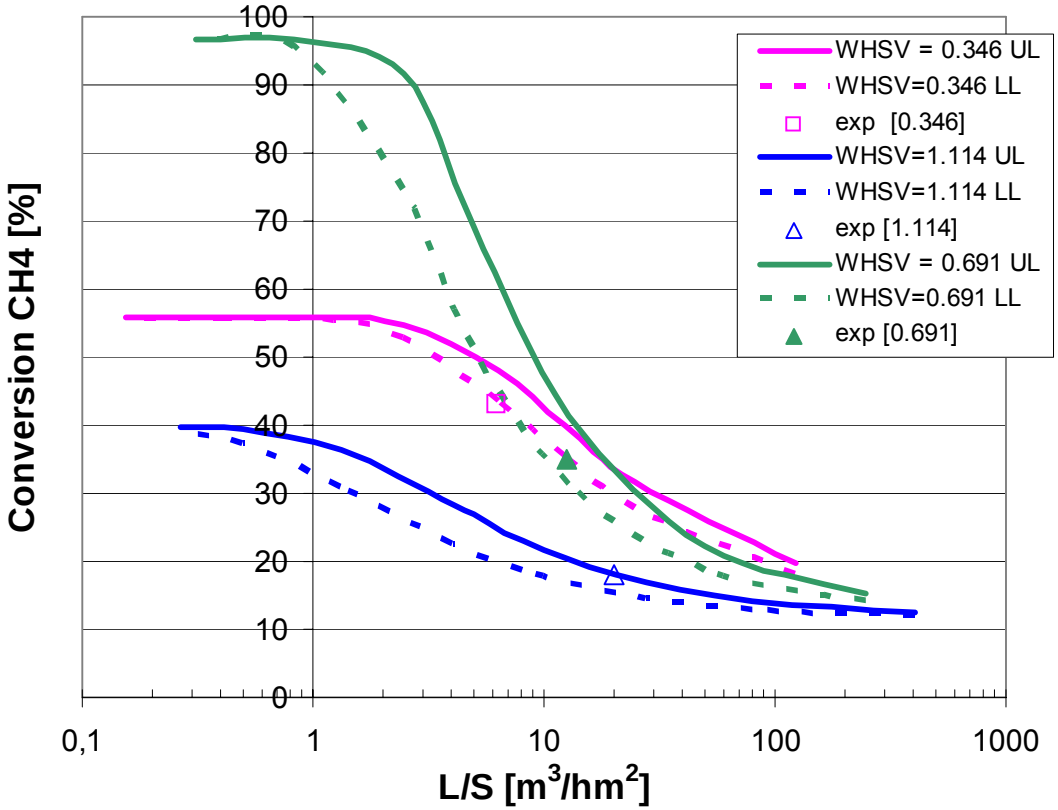
Input model:

- upper and lower limit H_2 permeance
- avg Pp
- avg Tmem

Exp	conv CH4 [%]	calc CH4 conv. [%] upper	calc CH4 conv. [%] lower
MR5	29	28.4	22.6
MR6	30	36.7	29.4

Membrane reactor model

WHSV dependence



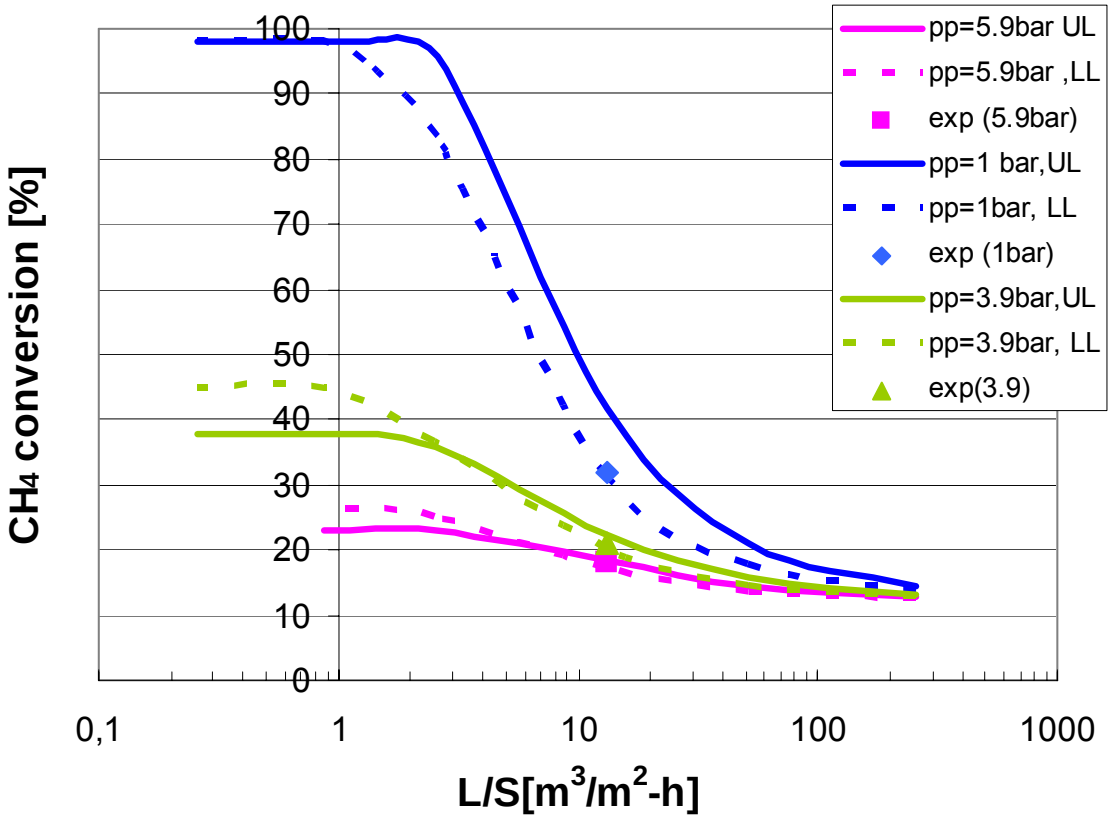
Input model:

- upper and lower limit H_2 permeance
- avg Pp
- avg Tmem

Exp	conv CH4 [%]	calc CH4 conv. [%] upper	calc CH4 conv. [%] lower
MR9	43.0	48	43.7
MR10	18.0	18.1	15.5
MR2	35	41.3	31.3

Membrane reactor model

Permeate pressure dependence



Input model:

- upper and lower limit H_2 permeance
- avg Tmem

Exp	conv CH4 [%]	calc CH4 conv. [%] upper	calc CH4 conv. [%] lower
MR7	18.0	18.3	17.4
MR8	21.0	22.5	20.4
MR15	32.0	41.9	31.2

Conclusions and future work H2MR

Conclusions

- Successful MR-reforming experiments 2005 reproduced
- Increased methane conversion
- Stable performance for 1 week
- Higher conversions are feasible at low WHSV and L/S area value

R&D issues

- Performance at 40 - 50 bar feed pressure (CH_4 conversion > 90%)
- Long term stability
- Detailed MR design, construction

Other activities

- Entering the market with hydrogen separation modules
  - From single short tubes (~40 cm2),
  - To full length multi tubular (1/8 to 1/2 m2)

Acknowledgements

Colleagues and co-workers

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Thank you for your attention!