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Hydrogen membrane reactor for industrial hydrogen production and power generation

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Abstract

Combining reaction and separation using membrane reactors has shown to offer numerous advantages for hydrogen production in future power production systems and 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. In steam reforming and water gas shift processes membrane separation can be economical viable using current thin layer palladium alloy membrane technology, however a further increase in flux and/or decrease in membrane price is absolutely needed to convince the process owners of the suitability of this promising technology. Also 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 conditions. This paper gives an overview of the results and current status of the hydrogen membrane reactor development at ECN for energy efficient industrial hydrogen production and power generation.

Dense tubular membranes with very thin Pd/Ag layers have been made on ceramic supports with electroless plating on a $1m^2$ scale. 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 $50\text{-}100 m^3/m^2 h bar^{0.5}$ can be obtained with high permselectivities. Tests with simulated reformate gas at 500ºC gave lower selectivities due to lower hydrogen permeances caused by the poisonous CO in the reformate gas. With the Pd/Ag membrane the hydrogen concentration was increased from 10% in the simulated reformate gas to 90% in the permeate. A shift in equilibrium was observed and extra hydrogen was produced without the use of a catalyst. Prior to actually testing the performance of the membrane reactor, different catalysts have been tested under simulated membrane reactor gas conditions. During 140h on stream at 500°C, the reference nickel catalyst showed significant deactivation under the simulated membrane reactor conditions, probably due to carbon deposition. The noble catalyst did not show significant deactivation and was selected for application in the membrane reactor. It was shown that methane conversions well beyond the thermodynamic limits could be reached during steam reforming at 500-600°C and 50 bar in the membrane reactor. The membrane has been on stream for more than 100 days using different feed gases and is showing acceptable performance.

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Hydrogen Membrane Reactor for Industrial Hydrogen Production and Power Generation

Yvonne van Delft, Paul Pex, Luci Correia

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Outline

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

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Mission statement
ECN develops 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

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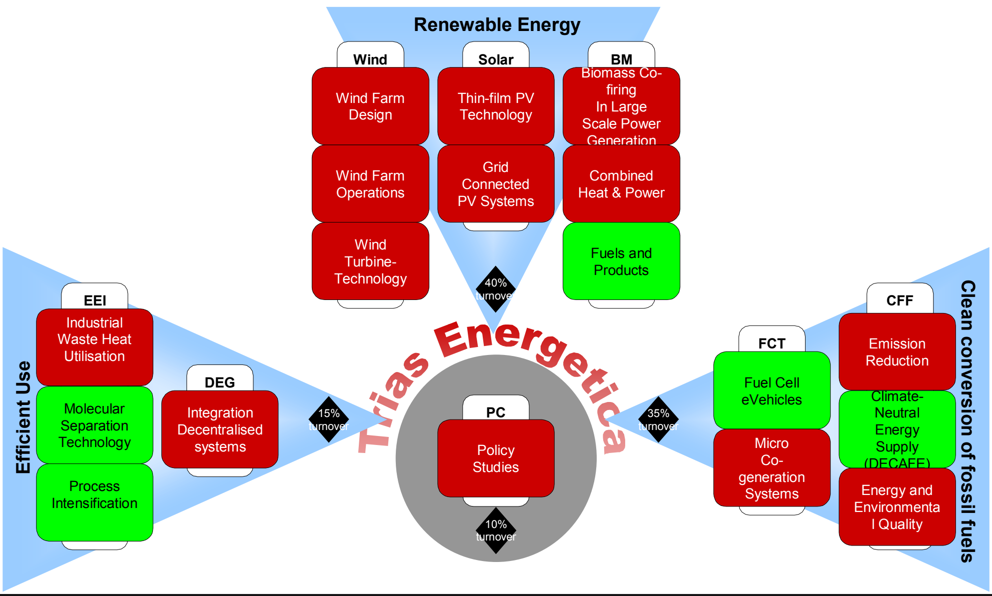
Hydrogen Membrane Technologies



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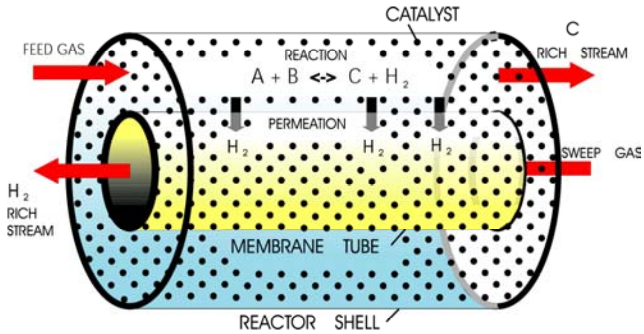
Hydrogen Membrane Reactor

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

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

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



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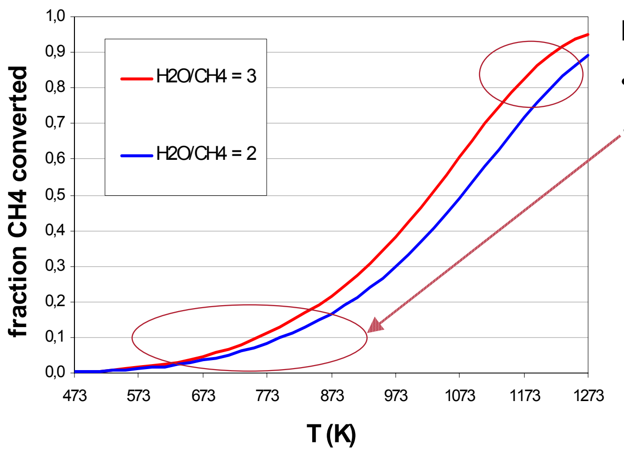
Reactor modelling

SR + WGS at 36 bar



High methane conversion:

- Demands high temperature
- Shift equilibrium with membrane reactor

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Hydrogen Membrane Reactor

Objective of the programme:

- Development of a hydrogen membrane reactor for
  - energy efficient industrial hydrogen and chemicals production
  - electricity production with energy efficient integrated CO_2 capture

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%!

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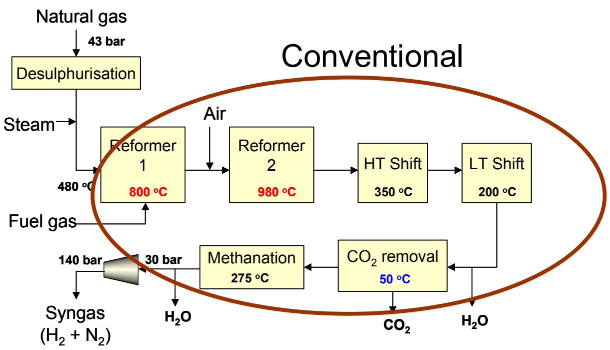
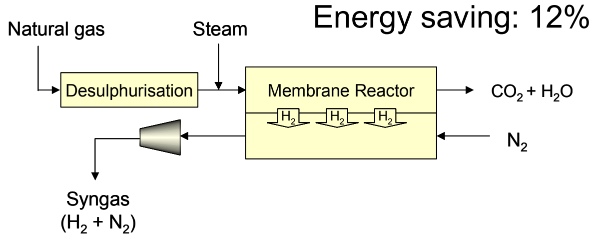
Process concepts
H_2 production for ammonia synthesis

Conventional



Energy saving: 12%

New scheme including membrane reactor



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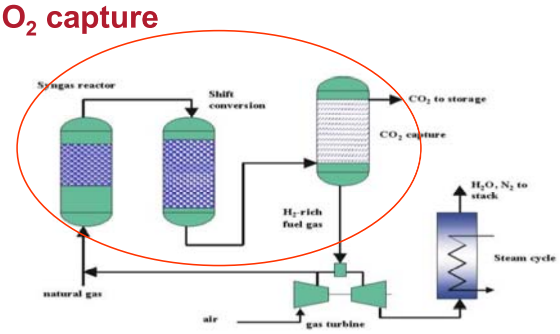
Process concepts

Electricity production with CO_2 capture

Conventional CO_2 capture:

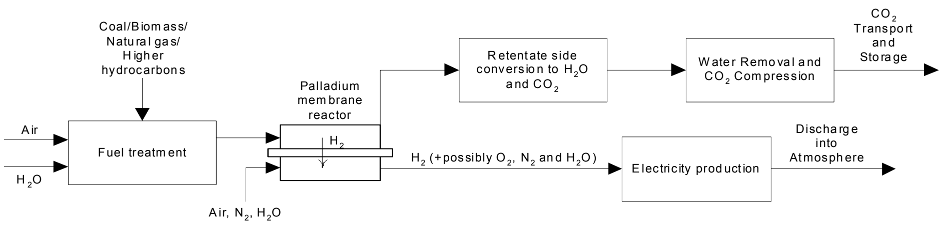
16 to 40% increase in

energy consumption!



New process with MR:

CO_2 capture cost can be reduced with 50%



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Base case system analysis

<u>Three main challenges:</u>

- 97% CH_4 conversion at low temperature (400-600°C)
- H_2 recovery > 98% => H_2 poor conditions!
  - High selective membrane operating at 400-600°C
  - Process membrane flux > 50 $m^3/m^2 hbar^{0.5}$
  - Membrane price ~ 1400 Euro/m^2
  - Membrane lifetime > 2 years
- SMR strong endothermic => high heat input

<u>Approach:</u>

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

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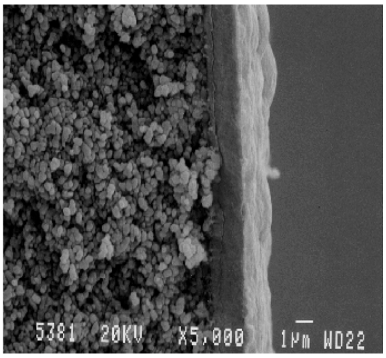
Membrane development

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

Costs: Pd= 6,000 €/kg: 3µm thickness= 225€/m^2 !

Ceramic support tube: 700 €/m^2 !

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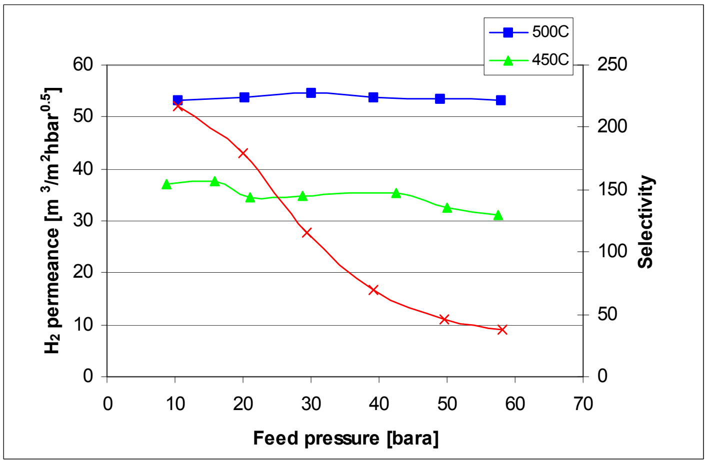
Performance measurements Pd/Ag membranes



- Tubes 80 cm length
- High H_2 permeance
- Max selectivity = 220 => improve sealing!

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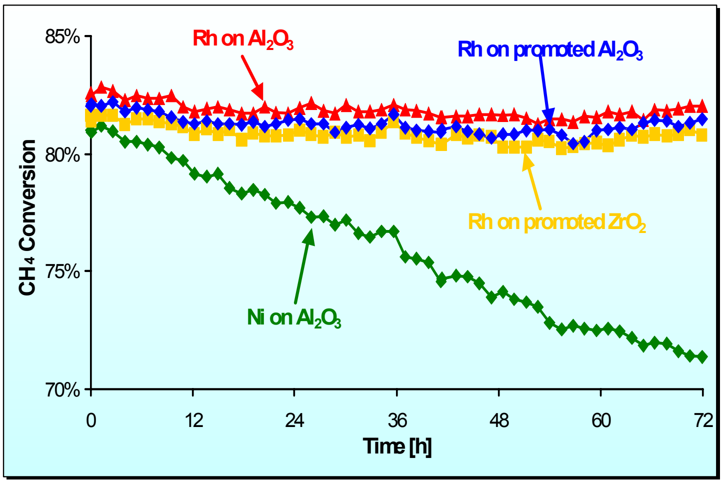
Catalyst development

Activity and stability at MSR conditions



T=500°C, P=3.5 bar

• eq conversion:

SR 41%, MSR 85%

•Rh catalysts show high activity and stability at MR conditions

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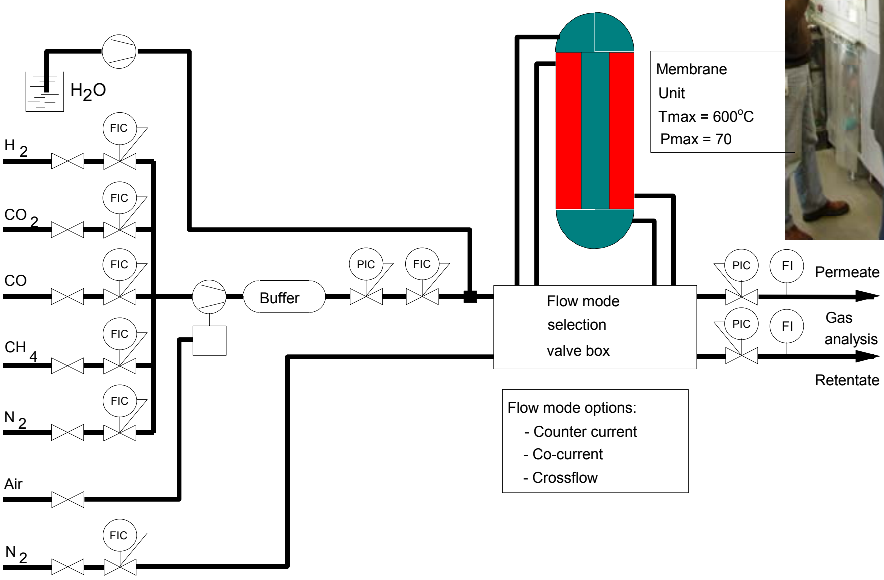
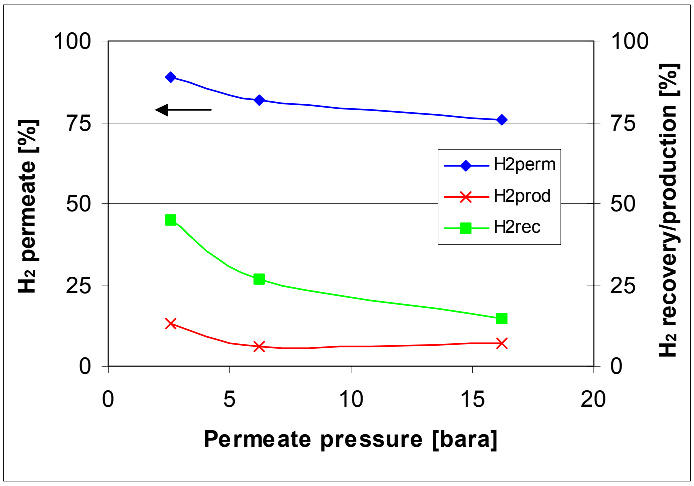
Membrane reactor testing

Bench scale MR test installation



Membrane Reforming process testing - 1



Reformate separation:

- 75-90% H_2 in permeate
- H_2 recovery 50%
- strong effect permeate pressure
- extra hydrogen produced without cat

500°C; Pf 40 bara reformate: $H_2/CH_4/CO_2/H_2O$ = 10/23/1.5/65.5

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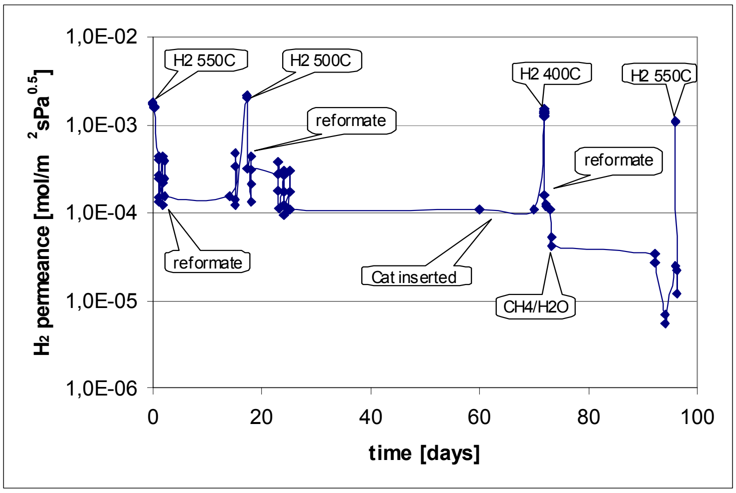
Membrane Reforming process testing - 2



Maximum allowable membrane cost:

← 1400 €/m²

← 100 €/m²

400-550°C; Pf 40-50 bar reformate = $H_2/CH_4/CO_2/H_2O$

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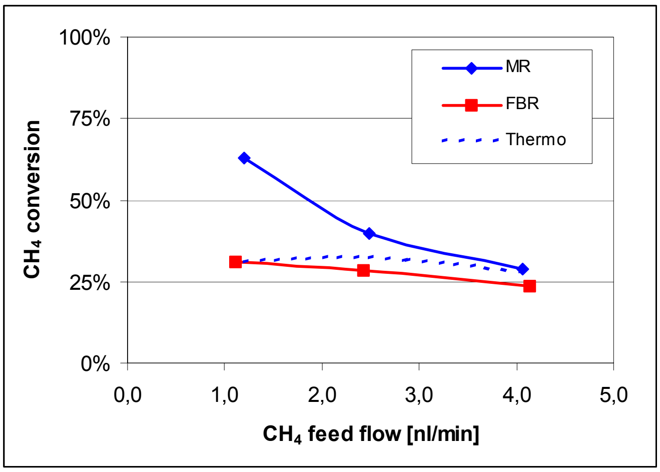
Membrane Reforming process testing - 3



Membrane reformer:

- Catalyst shows good activity
- At low feed flows increased CH_4 conversion

650°C; Pf 11 bara feed: CH_4/H_2O = 1/3

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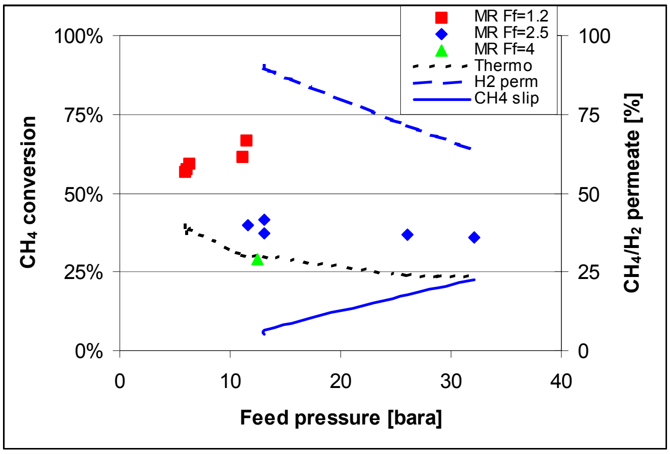
Membrane Reforming process testing - 4



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

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Conclusions and future work H2MR

Conclusions

- Successful MR-reforming experiments performed
- Increased methane conversion at 650°C
- Composite Pd/alloy membrane promising technology
- Process concepts indicate feasible operation

R&D issues

- Performance at 40 - 50 bar feed pressure (CH_4 conversion > 90%)
- Sealing at high pressure
- Stability: fouling, poisoning, carbon deposition, grain growth
- Detailed MR design, construction

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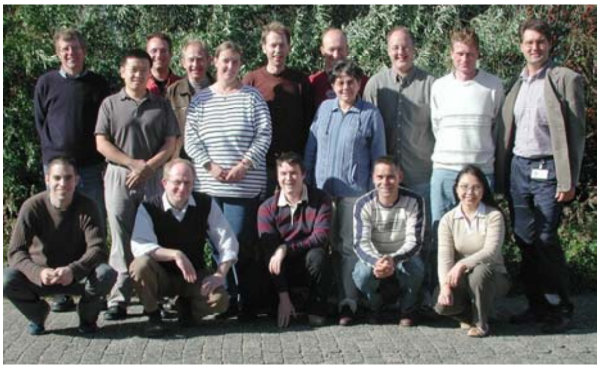
Acknowledgements

Colleagues and co-workers



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Thank you for your attention!

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