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PALLADIUM ALLOY MEMBRANES FOR ENERGY EFFICIENT MEMBRANE REACTORS

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Abstract

In ECN's vision hydrogen separation membranes will play a key role in future power production systems and industrial chemical production processes. The driving force for the application of these membranes is that during reaction favourable thermodynamics can be utilised to increase efficiency while elegantly CO_2 can be captured under high pressure or chemical products can be obtained cost-effectively.
Applications envisaged and currently investigated are:
- process integrated hydrogen membrane reactors for reforming, water gas shift and production of paraffins with parallel removal of hydrogen,
- small-scale efficient hydrogen production with membrane reactors,
- hydrogen recovery from industrial (waste) streams.

In the above processes membrane separation can only be economically 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. Membrane development at ECN focuses on the development of thinner and cheaper metallic membranes with higher hydrogen permeation rates. Important activities concern the development of reproducible manufacturing techniques for porous stainless steel supported thin layer palladium alloy membranes, improvement of long-term stability and prevention of performance decrease due to poisonous adsorbing gas components such as CO or sulphur. The research is guided and supported by advanced process studies and flowsheet calculations using membrane reactor simulators and membrane reactor testing under simulated realistic conditions. This paper gives an overview of the results and current status of the membrane materials development as part of the R&D trajectory of hydrogen membrane reactors at ECN.

Palladium Alloy Membranes for Energy Efficient Membrane Reactors

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Outline

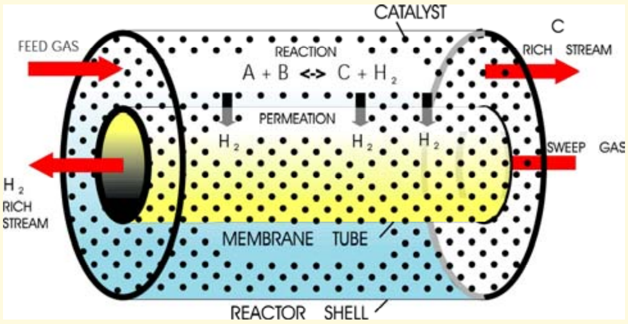
- Introduction
- Background & Objective
- Feasibility & Process studies
- Membrane development & testing
- Catalyst screening
- Membrane reactor testing
- Conclusions

Hydrogen Membrane Reactor

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

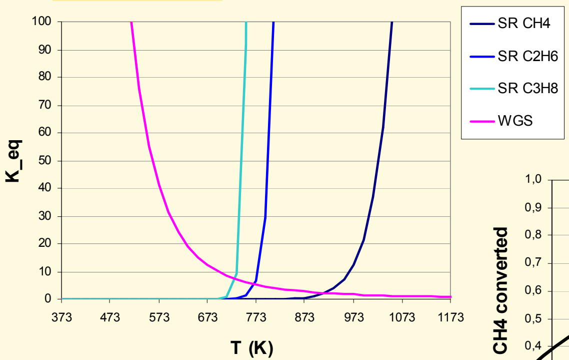
Water-gas shift: $CO + H_2O \rightleftarrows H_2 + CO_2$ (ΔH = - 41 kJ/mol)

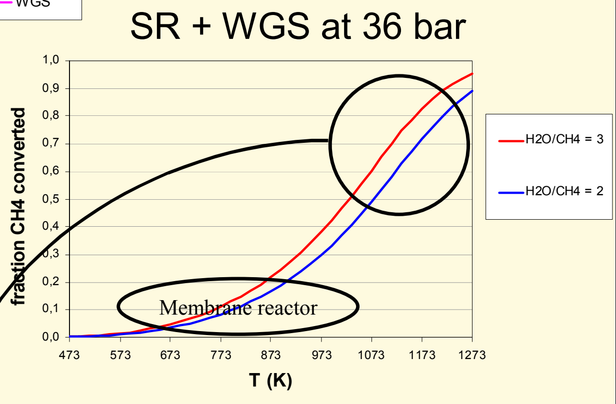
$$CH_4 + 2\,H_2O \rightleftarrows 4\,H_2 + CO_2$$



Reactor modelling

Equilibrium reactions



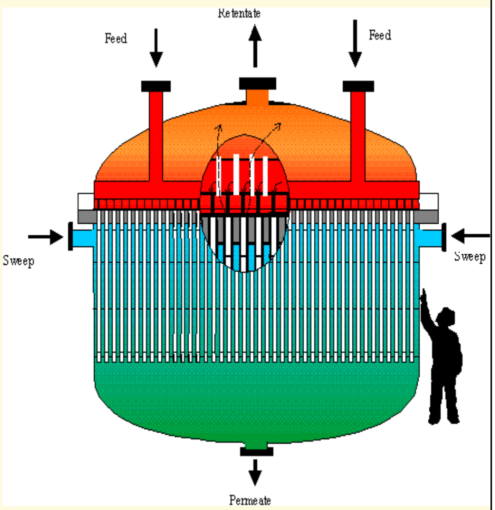


- High temperature for SR
- Low temperature required for WGS
- Very high temperature required for high methane conversion: we do not want that!

H2MR

Why do we want such technology?

- Advantages
  - integration of process steps
    - lower temperatures
    - high product yield
  - cheaper construction materials
  - compactness
  - energy savings
- Disadvantages
  - not yet proven technology
  - complex unit operation
  - less degree of freedom in design



Concept WGSMR for 100 MWe IGCC

Hydrogen Membrane Reactor

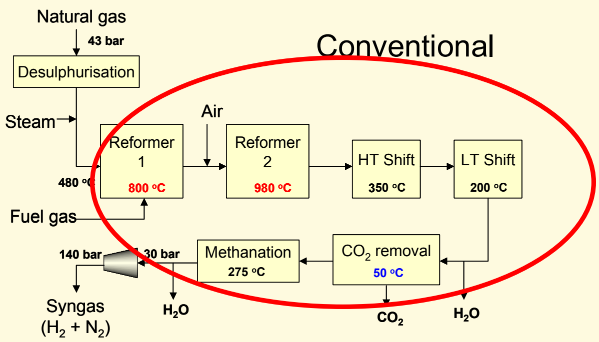
<u>Objective of the programme:</u>

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

<u>Applications:</u>

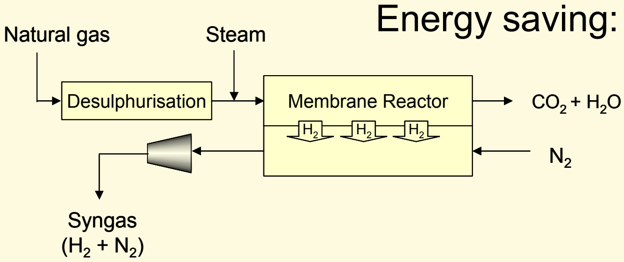
- Large scale hydrogen production in the ammonia process
- Power generation with integrated CO_2 capture
- Small scale on-site hydrogen supply
- Dehydrogenations

Process concepts
H_2 production for ammonia synthesis



Energy saving: 12%

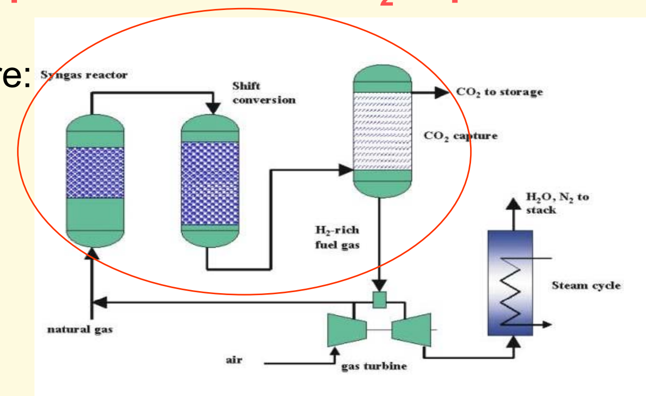
New scheme including membrane reactor

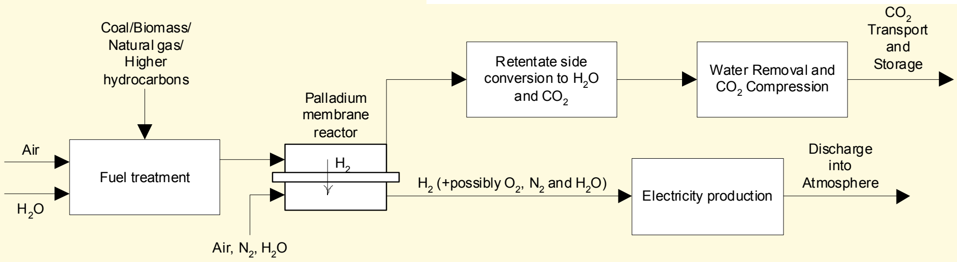


Process concepts
Electricity production with CO_2 capture

Conventional CO_2 capture: 16 to 40% increase in energy consumption!

New process with MR: CO_2 capture cost can be reduced with 50%





Results
Base case system analysis

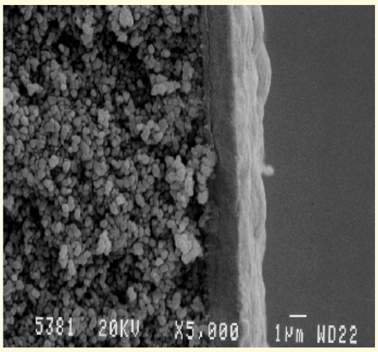
Three main challenges:

- 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 $m^3/m^2hbar^{0.5}$
- SMR strong endothermic => high heat input

Approach:

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

Results
Thin layer Pd alloy membranes



Pd/23%Ag

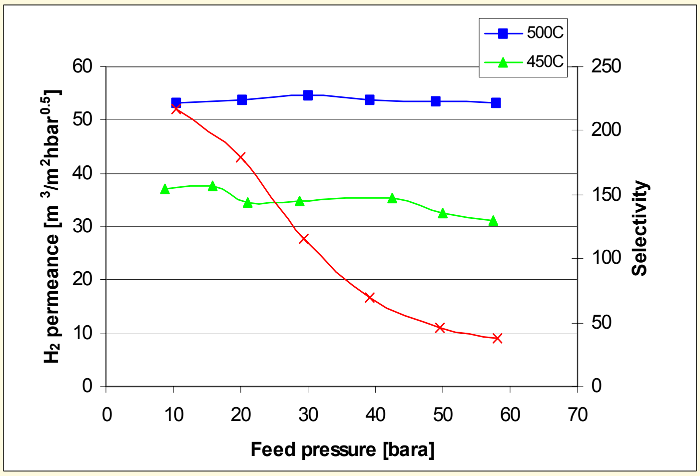
Production procedure:

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

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

Results

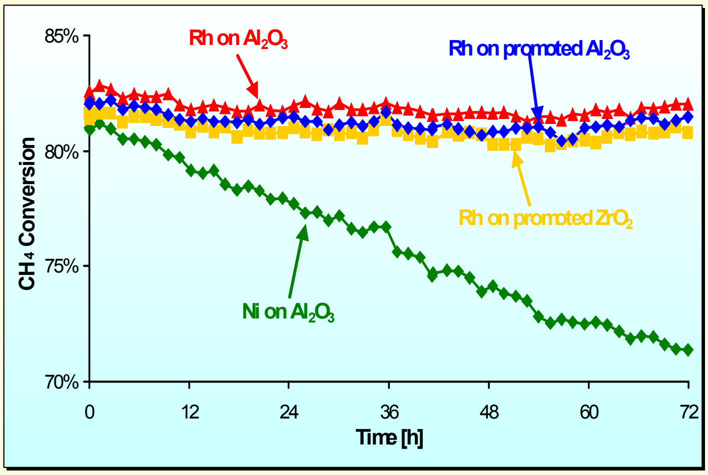
Performance measurements Pd/Ag membranes



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

Results

Catalyst stability at MSR conditions



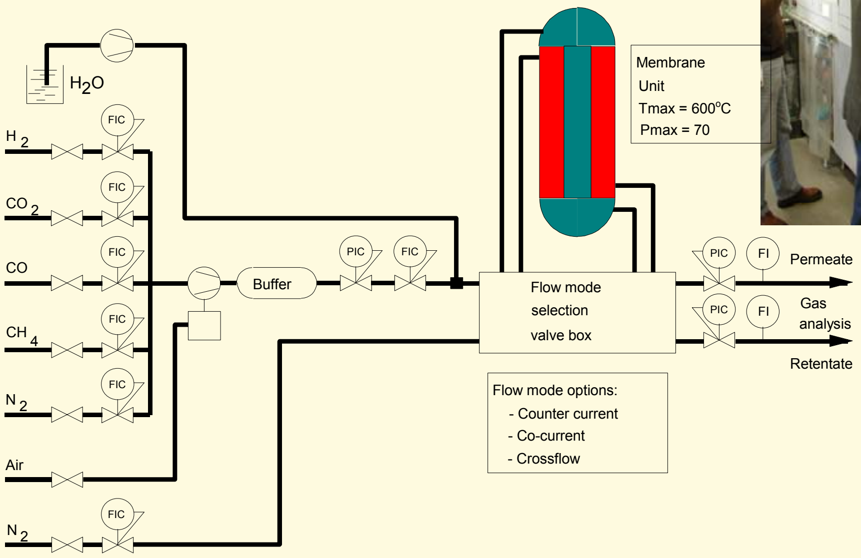
T=500°C, P=3.5 bar

• eq conversion:

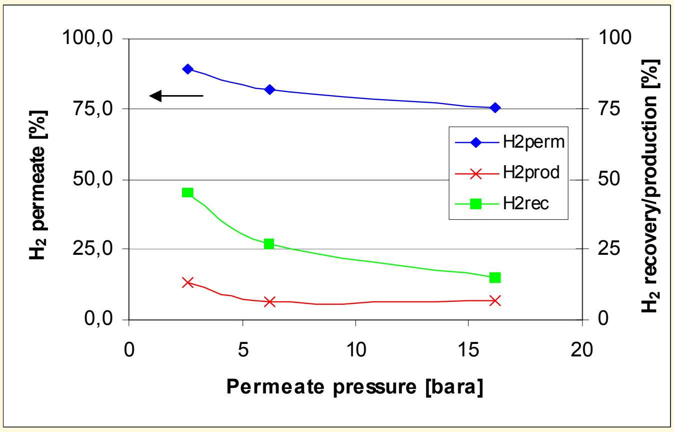
SR 41%, MSR 85%

•High activity and stability at MR conditions

Results
Bench scale MR test installation



Results
Membrane Reforming process testing



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

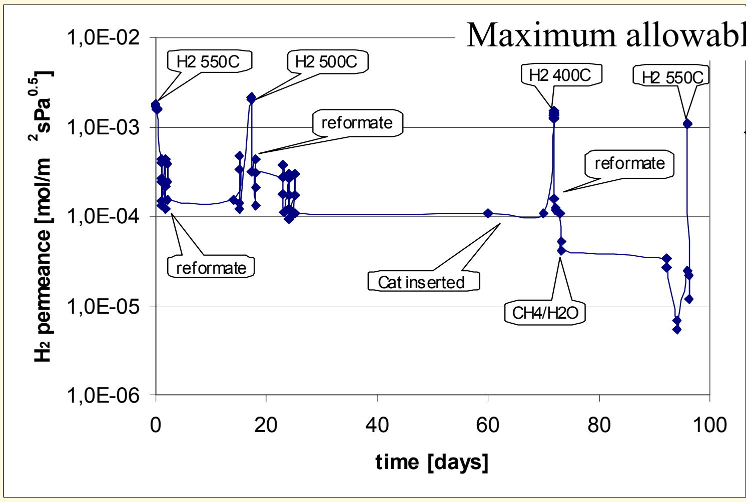
Preliminary Results
Membrane reformer testing

T (°C)	Pf (bar)	Feed flow (nl/min)	Feed (%)		Permeate* (%)					CH_4 conversion (%)	
			CH_4	H_2O	H_2	CH_4	CO_2	CO	H_2O	MR	eq
400	50	5	15.9	36.3	47.2	32.4	0.7	0.0	19.7	5.5	4.5
	50	2.5	16.2	34.4	29.3	23.6	0.8	0.0	46.3	14.3	4.5

balance N_2, * corrected for N_2 sweep gas

- Combined reaction and separation:
  - Catalyst shows good activity
  - Hydrogen separation with decreased permeance
  - High CH_4 and H_2O leakage
- At low feed flows increased CH_4 conversion

Results
Membrane Reforming process testing



Maximum allowable membrane cost:

1400 €/m²

100 €/m²

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

Conclusions and future work H2MR

- Conclusions
  - Composite Pd/alloy membrane promising technology
  - Process concepts indicate feasible operation
  - Increased methane conversion at 400°C
- R&D issues
  - Performance at 600°C (CH_4 conversion > 90%)
  - Increase selectivity: sealing, membrane
  - Stability: fouling, poisoning, carbon deposition
  - Detailed MR design, construction

Acknowledgements

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Thank you for your attention!