



Energy research Centre of the Netherlands

CACHET II WP1

Pd membrane engineering, development and PDU testing

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¹ECN, ²DICP, ³IMR

*Presented at the CO₂NET Annual Seminar and EC CCS conference 2011,
25th of May 2011, London, UK*



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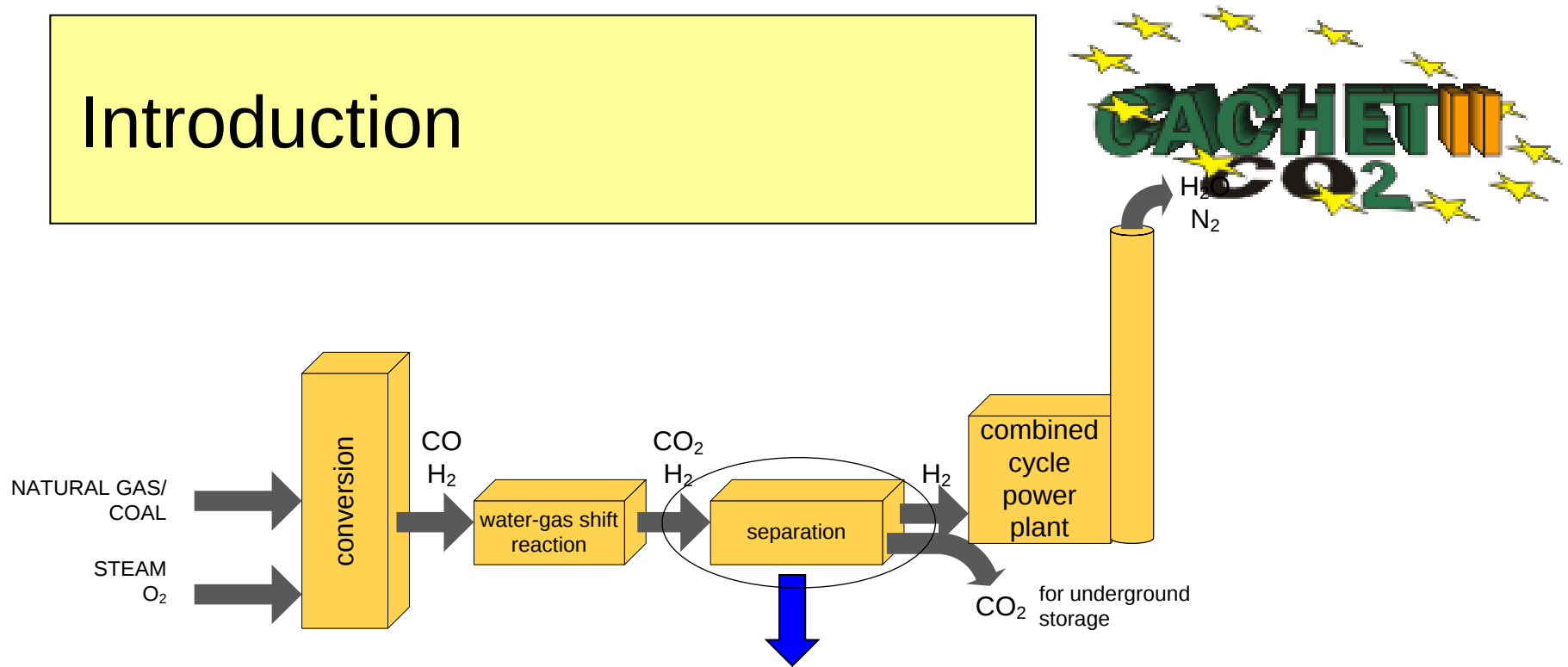


Outline

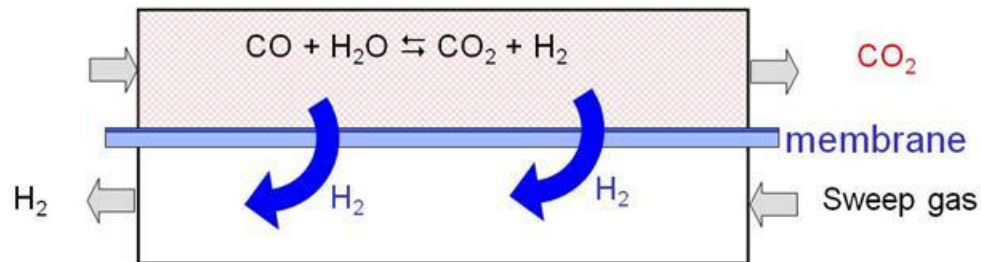


- Introduction
- Objectives
- Interaction of WP1 with other WP's
- WP1 approach/structure
- Description and status of activities
- Conclusion

Introduction



Membrane watergas shift (M-WGS)



Removing hydrogen → shift equilibrium

Introduction



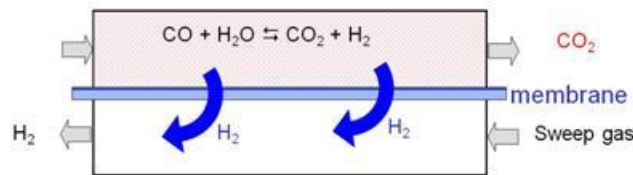
- Critical issues in the field of Pd-membranes:
 - Manufacturing and testing of upscaled membranes up to 1 m
 - Membrane seals and integration into industrial installations
 - Long term performance stability of membrane plus seal
 - H₂-separation and M-WGS

Membrane performance:

$$J_{H_2} = Q(T) \cdot (p_f^n - p_p^n)$$

- High H₂-selectivity
- Stable permeance $Q(T, t)$:
 - Mass transfer
 - Contaminants
 - Inhibition effects

Membrane watergas shift (M-WGS)



Removing hydrogen → shift equilibrium

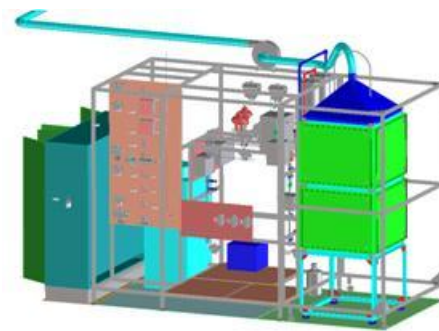
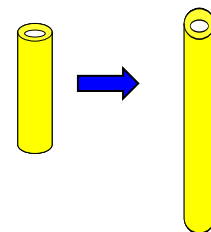
In case WGS integrated:
Water gas shift catalyst:

- Stable activity
 - gas composition (inlet → outlet)
- Stable selectivity:
 - no by-products

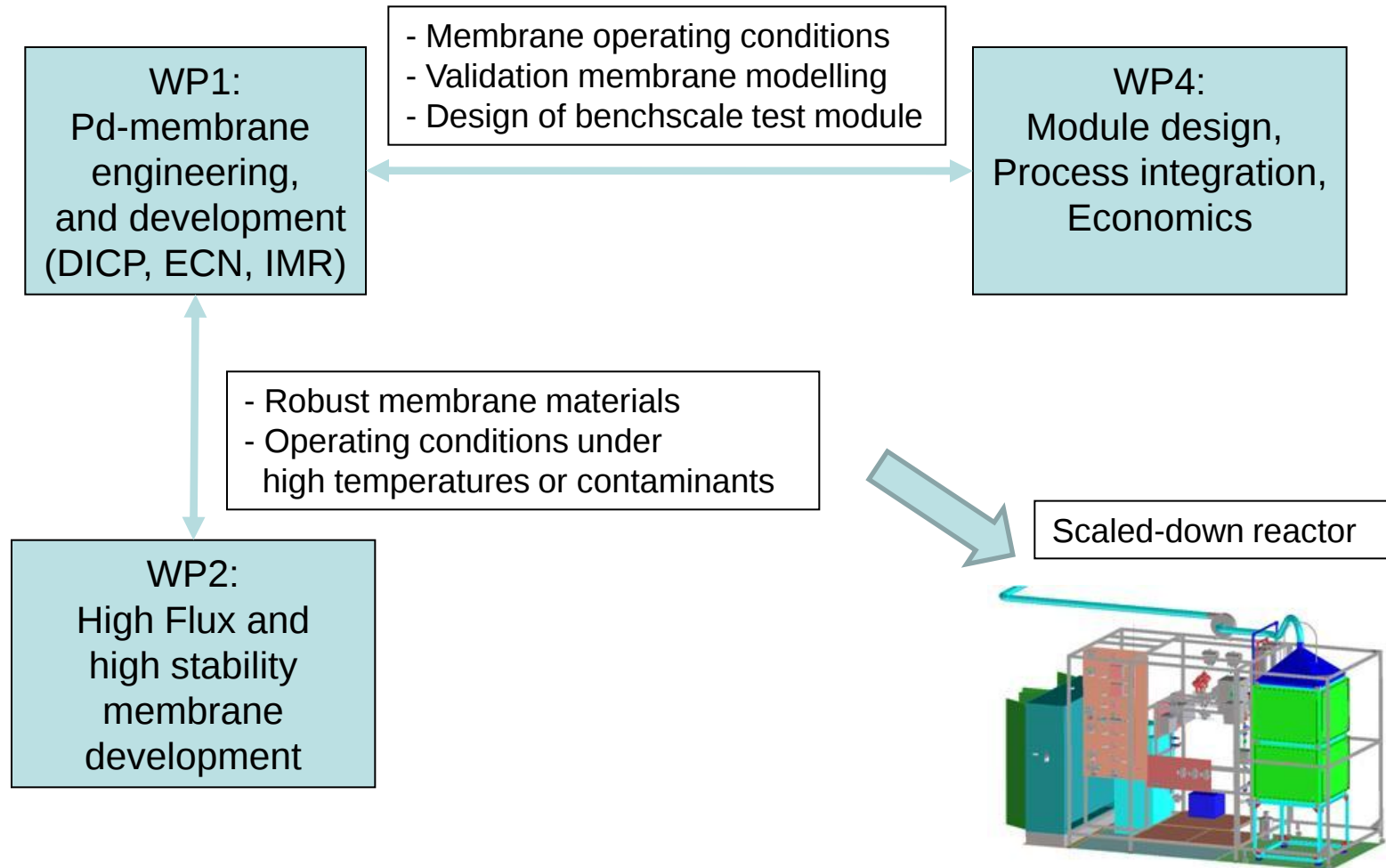
Objectives



1. Membrane production: Upscaling to 1 m membranes
2. Long term separation testing (150 days) with 5 cm long membranes and different seals at DICP
 - Less than 2% decline in hydrogen flux
 - Selectivity for H₂-separation > 200
3. Scaled down version of a full scale multi-tube M-WGS reactor with 1 m long membranes to be tested over 1000 hours at ECN:
 - Production of at least 95 % pure hydrogen
 - Capture of at least 90% CO₂



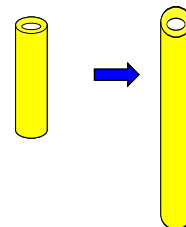
Interaction with other workpackages



WP1 structure/approach



1. Scaling up Pd membranes (DICP) to a length of 1 m

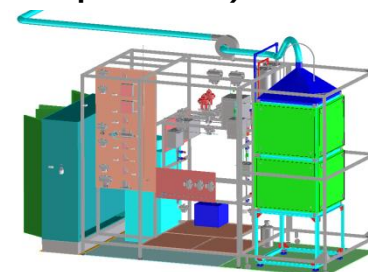


2. Development of improved sealing technology (IMR, ECN)



3. Membrane performance testing (ECN, DICP):

- Long-term stability testing of single Pd membranes (0.05 - 0.5 m) and seals
- Membrane (0.5 to 1 m) testing at DICP and ECN (multi tube in parallel)
 - Non-integrated/integrated (H_2 -separation and M-WGS)

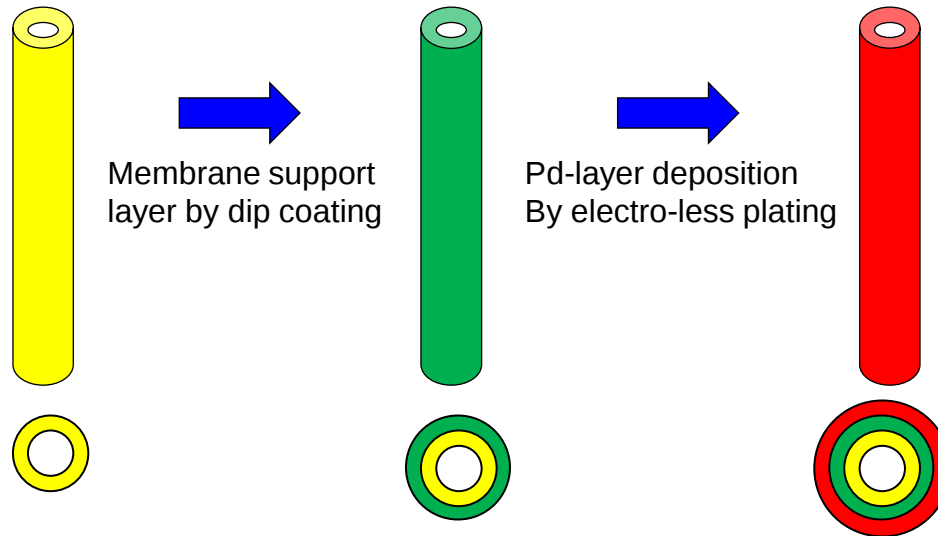


4. Construction and testing of scaled down full scale WGS membrane (1 m) reactor for at least 1000 hours (ECN)

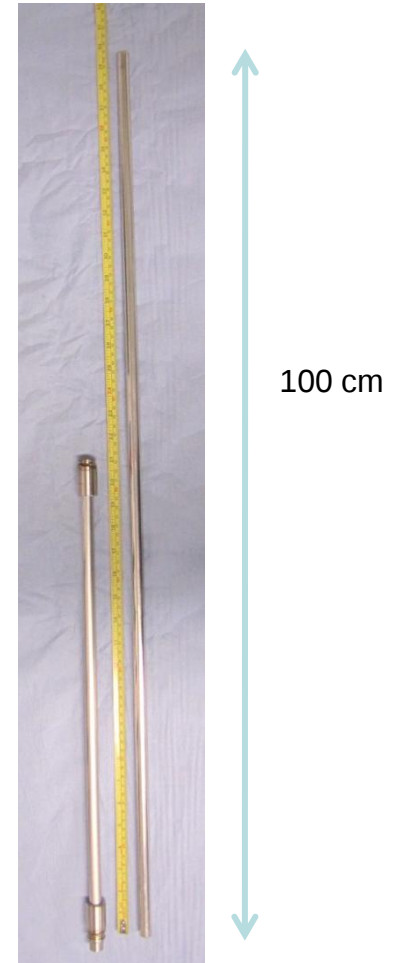
Membrane scale-up and production



- Aim: Scale-up to 1 m membranes
 - ECN supplies porous supports (alumina)
 - DICP will scale up Pd-layer deposition



- Status:
 - 1 m membranes have been manufactured



New sealing technologies



- Aim: Improved seal stability and seal dimensions
 - Stability up to 500°C under WGS-conditions
 - Improved seal footprint ensuring mass transfer optimized catalyst bed thickness

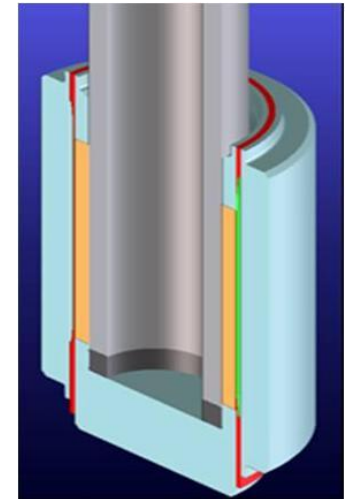
- Status:
 - Seals have been developed
 - Seals are in the process of validation

New sealing technologies



1/ Patented ECN compression seal based end-cap

- Sealing material: Graphite
- End-cap: stainless steel
- Design pressure = 38 barg
- Design temperature = 700 °C



2/ Patented IMR-seals:

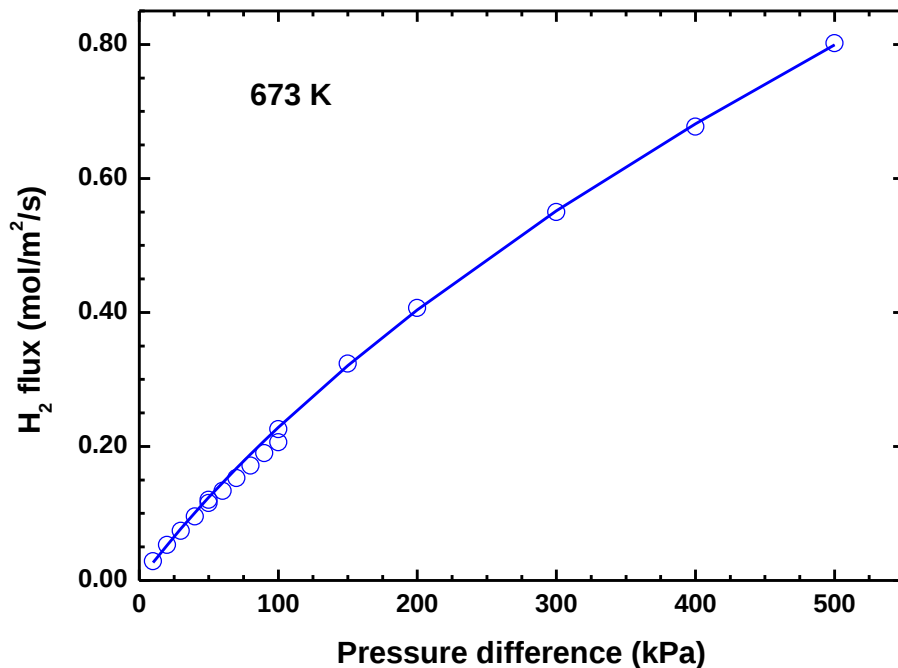
- Direct metal-ceramic joint
- Thermo-shock stability > 10 cycles (RT – 700°C)
- Smaller footprint
- Design pressure = 50 bar
- Design temperature = 500-700 °C



Membrane performance



- 0.5 m long DICP Pd membranes with 5-7 μm thick Pd layers and ECN seals



- Typical H₂ permeation rate:
 $1.75 \times 10^{-2} \text{ mol/m}^2/\text{s}/\text{Pa}^{0.5}$
 $\times \exp(-12.9 \text{ kJ/mol}/RT)$
 $\times (P_{\text{feed}}^{0.5} - P_{\text{perm}}^{0.5})$
- Typical ideal selectivity at 673 K:
 ~ 10000 ($P_{\text{feed}}/P_{\text{perm}} = 500/100 \text{ kPa}$)

Long term stability testing

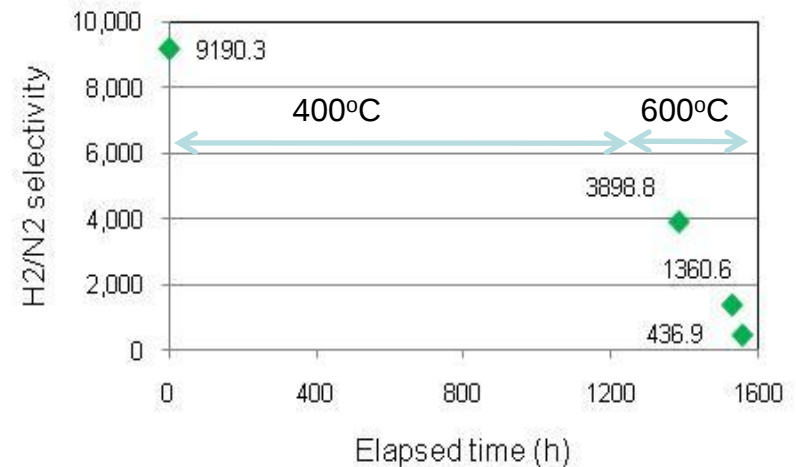
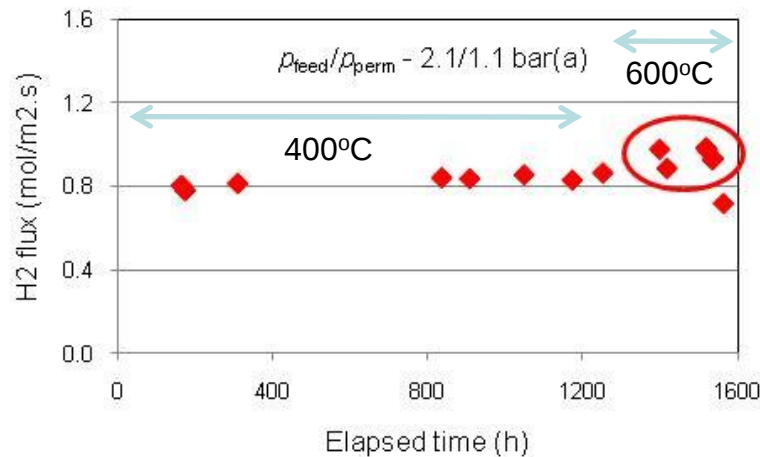


- Aim:
 - Demonstration of stability membranes, support and sealing under realistic testing conditions:
 - High pressure 25-40 bar
 - Simulated WGS conditions
 - 150 days testing
- Status:
 - Stable membrane performance demonstrated up to 1200 hours (50 days)

Long term stability testing



- Test on two parallel ECN Pd membranes 0.5 m with ECN seals
 - 1-2 micron thick Pd-layer
 - Testing condition: $P_{\text{feed}} / P_{\text{perm}} = 2.1 / 1.1 \text{ bar(a)}$ pure hydrogen
 - Operating temperature: 400 and 600°C



- H₂ flux (400°C, $P_{\text{feed}} / P_{\text{perm}} = 2.1 / 1.1 \text{ bar}$): 0.8 mol/m².s
- H₂ permeance stable up to 1200 h at 400°C: decrease in selectivity by factor 2.5
- H₂ permeance and selectivity drops after exposure to 600°C
- post test analysis: pinhole/cracks on the membranes and leakage in the seals

Testing of long membranes

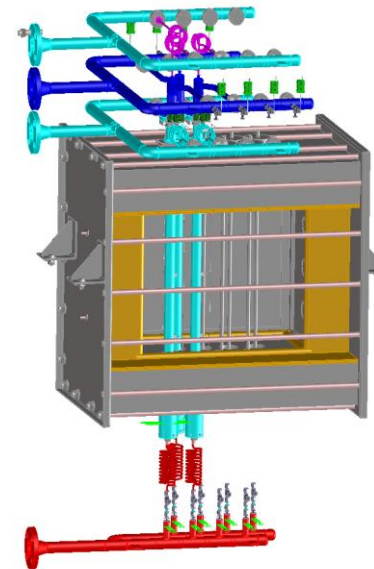
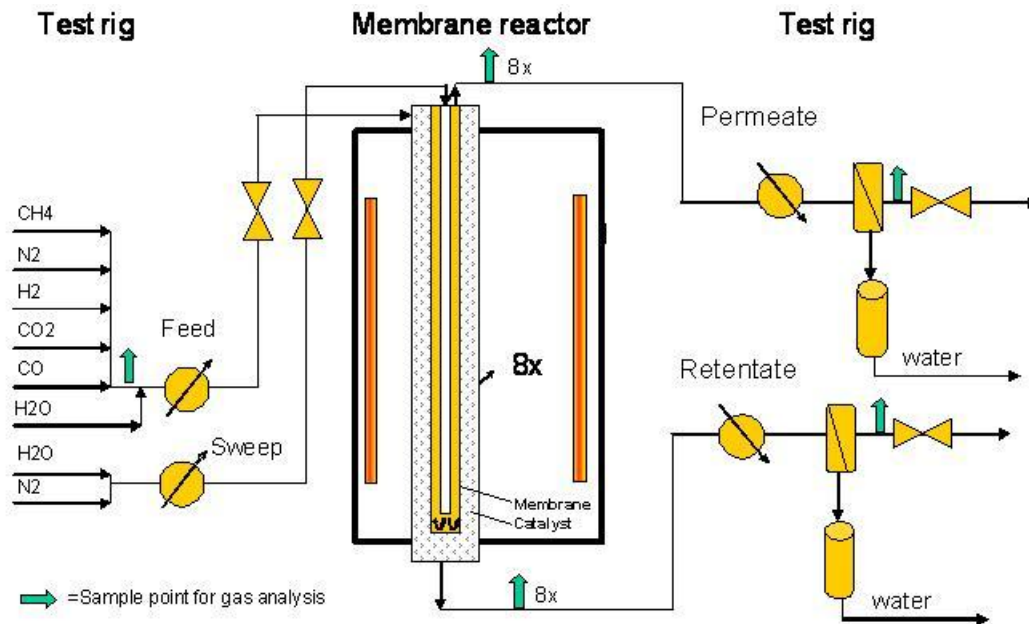


- Aim:
 - Determination of basic permeance data of membranes:
 - Operating temperatures: 400-600 °C (Accelerated testing)
 - Pressures: around 30 bar
 - Single gases (H_2/N_2), mixtures (H_2 with N_2 , CO , CO_2) and syngas.
 - Data will be used as benchmark for reactor model and design tool in WP4
 - Screening commercial WGS catalyst:
 - Stable WGS catalyst performance
 - No by-products

Testing of long membranes



- Equipment:
 - Process development unit (PDU) at ECN;
 - 8 membrane reactors in parallel



Testing of long membranes

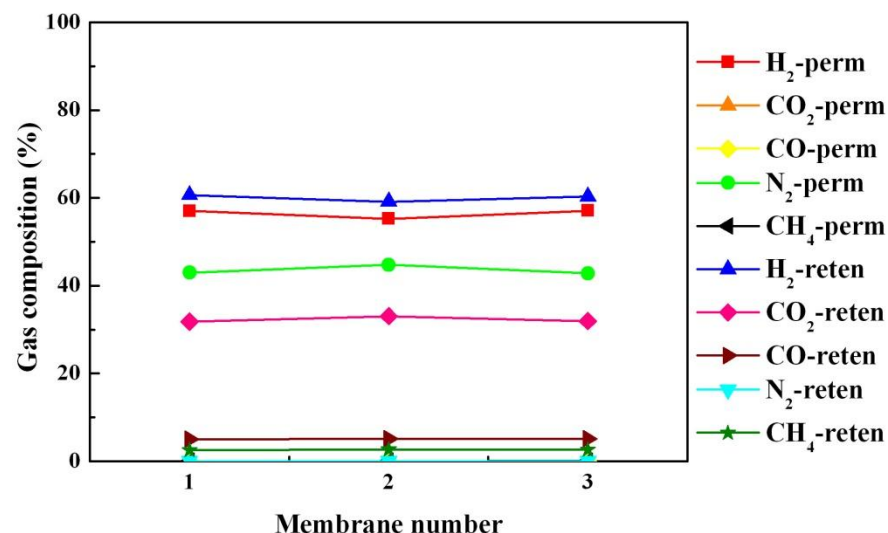
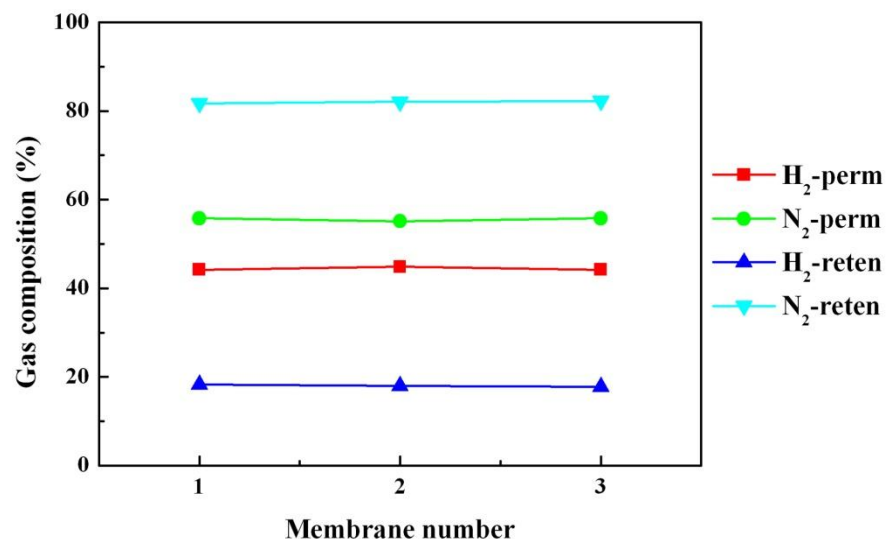


- Validation Process Development Unit (PDU):
 - Flow distribution over 3 different DICP membranes (0.5 m long)

**WGS-
reaction test**

H₂/N₂ mixture, 30/19.57 l/min, 31/15 bara

WGS mixture, 90/19.57 l/min, 27/15 bara



H₂/N₂ mixture

WGS-mixture

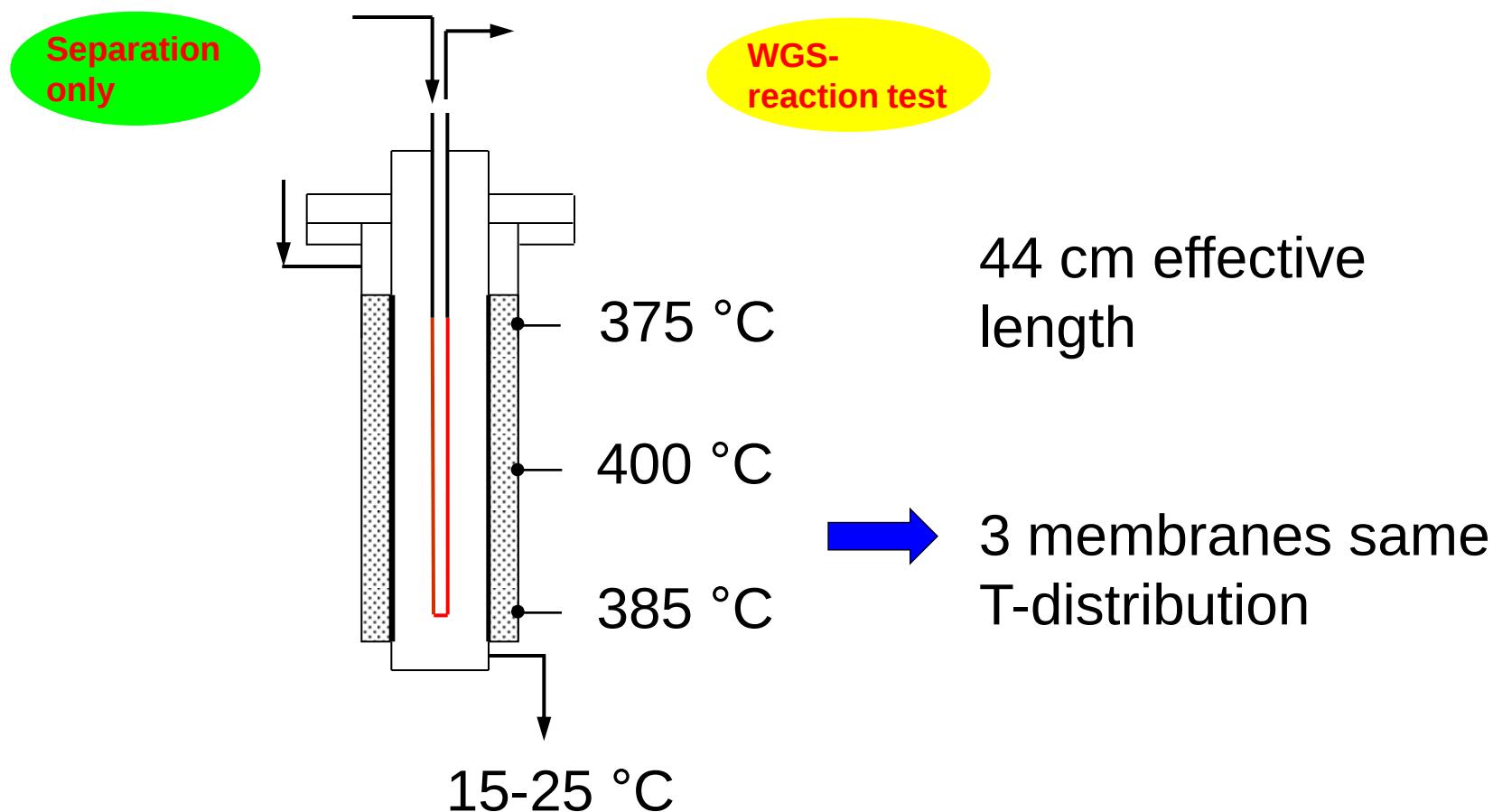


Flow distribution: Relative difference <6%

Testing of long membranes



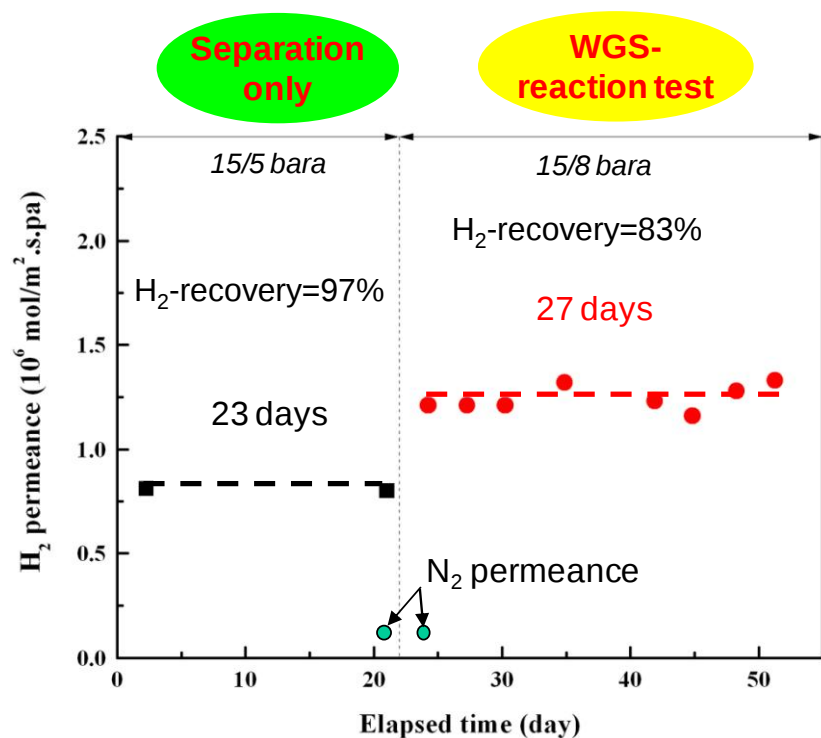
- Validation Process Development Unit (PDU):
 - Temperature distribution over membrane length



Testing of long membranes



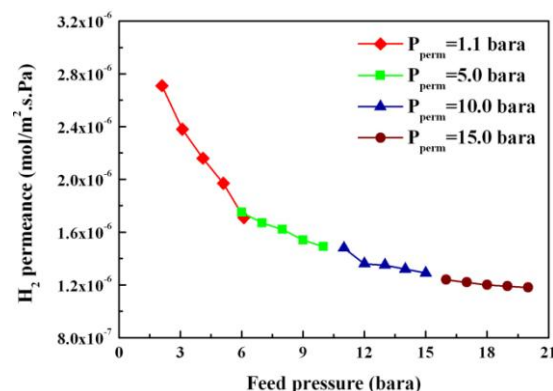
- PDU-testing of 3 DICP Pd membranes 0.5 m with ECN HTTP seals
 - Pure H₂/Pure N₂ permeance, separation and shift test (NGCC)



→ 1.2E-6 mol/m².s.Pa

→ 8E-7 mol/m².s.Pa

→ 2.6E-9 mol/m².s.Pa



➡ Stable membrane performance for both non-integrated and integrated for a total period of 50 days

Testing of long membranes



- Choice of WGS catalyst (non expensive base metal catalyst):
 - Two commercial catalyst (A (Fe-Cr) and B (alternative)) have been examined
 - Watergas shift stability as function of H_2O/H_2 and H_2O/CO -ratio
- Resulting gas composition for stability catalyst performance:
 - Cat A (Fe-Cr): $H_2O/H_2 > 0.5^*$ (high H_2O/H_2 , prevent reduction) and $H_2O/CO > 2$
 - Cat B: low H_2O/H_2 allowed* and safe operation at $H_2O/CO \leq 2$: vulnerable to H_2S

NGCC	Low H_2O/H_2	High H_2O/H_2
S/C ratio in ATR	1.4	1.4
Efficiency, %	45.09	44.41
CO ₂ capture, %	99.9	99.9
Net Electricity, MW	437.4	431.2
H ₂ recovery, %	98.23	98.27
Membrane area, m²	4560	5900
H ₂ permeated, kmol/hr	11083	11100
Membrane flux, mol/m ² .s	0.6751	0.5226

*vendor spec

➡ Non expensive commercial catalyst available for M-WGS

Reactor testing



■ Aim:

- Reactor design for 1 m membranes based on scaled down full scale WGS membrane reactor design from WP4
- 1000 h test with 1 m DICP Pd membranes using ATR gas and/or coal gas
- No test with H₂S
- The reactor will be tested under different conditions, temperatures between 350 and 500 °C, different pressure level for feed and outlet.

■ Status:

- Design of reactor in progress
- This test will be performed at the end of the project (Q3 and 4 2012)

Overall conclusions



What has been achieved:

- Membrane upscaling to 1 m length
- Membrane stability proven for 1200 hours at 400°C:
 - Integrated and non-integrated
- Non-expensive commercial WGS catalysts identified

Overall conclusions



What has not been achieved yet:

- Demonstration of seals with lower footprint, no slip:
 - Seals in validation process
 - 150 days testing
- Long term M-WGS testing
- Benchscale 1 m long membrane WGS reactor testing

Future activities



Next logical steps within CACHET2:

- Demonstration stability membrane plus improved seal in 150 days testing
- Long term M-WGS testing
- Benchscale 1 m long membrane WGS reactor testing