Hydrogen Membrane reactors for pre combustion CO_2 capture

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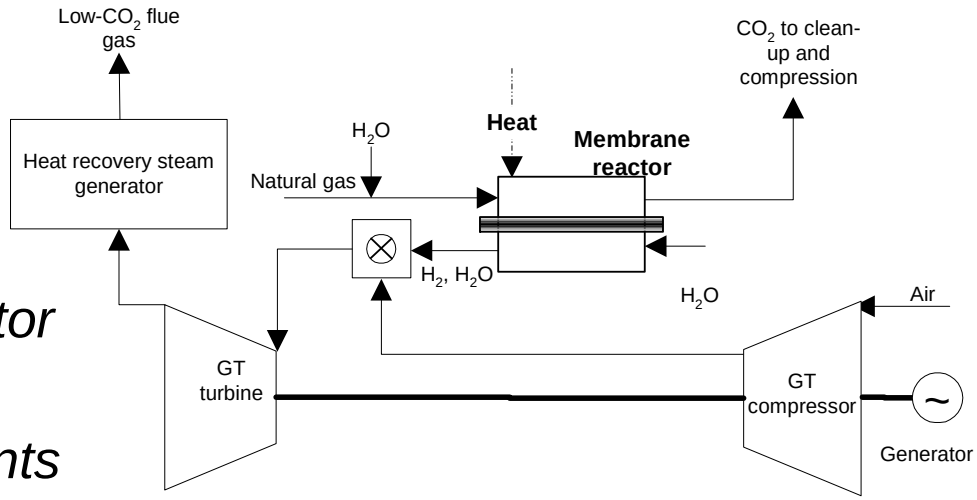
Outline

- SP1 –WP3 Membrane reactor development
- Headline results
  - *Membrane research, manufacturing and testing*
  - *PDU design and construction*
  - *System assessment and process synthesis*
- Recap

Objective

- **Develop, and evaluate the potential of Pd H_2 membrane reactors for CO_2 capture in NGCC**

- Includes
  - *Membrane development for both WGS and reforming*
  - *Performance testing*
  - *Membrane reactor design for both WGS and reforming*
  - *Bench scale membrane reactor testing*
  - *Techno economic assessments*

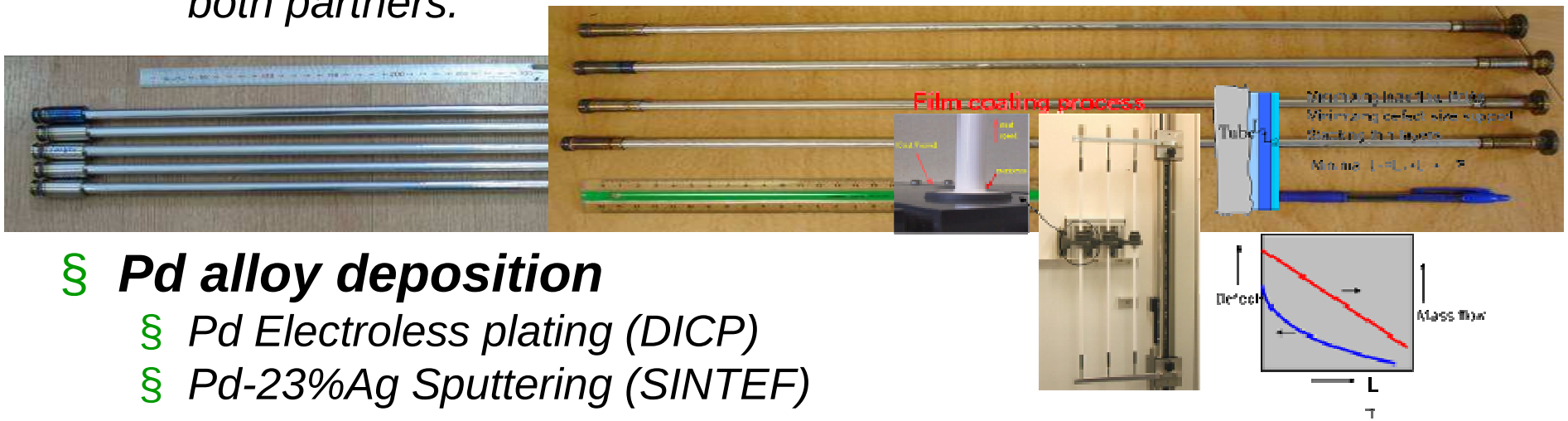


Operational approach

	Membrane	Reactor	Process
Technical Objectives*	n Flux > $2x10^{-6}$ mol/m^2sPa n Selectivity $H_2/C_xH_yO_z$ > 1000 n Lifetime > 3 years n Cost < 1500 Euro/m^2	n Optimum heat management n Size 4 kWth (0.15 m2 @ 20-25 bar dP) n Cost effective (catalyst)	n Cost of CO_2 capture reduced with 50%
Activities	n Support development n Membranes by electroless plating and sputtering n Basic testing n Sealing	n Concept engineering n Hydrodynamics: Reduce non-ideal behaviour n Manufacture reactor n Reactor testing	n Process synthesis n Technical/economic evaluation n Project guidance
Main Partners	**Sintef, Dalian** (ECN)	**ECN** (Sintef, ETC)	**PDC** (ETC, BP, ECN)

Progress

- **Membrane manufacturing**
  - *Both DICP and SINTEF have successfully scaled up their thin layer tubular membranes to a length of 50 cm, as targeted.*
  - *Multiple membranes of this length have been manufactured by both partners.*



- ***Pd alloy deposition***
  - *Pd Electroless plating (DICP)*
  - *Pd-23%Ag Sputtering (SINTEF)*
- **Membrane support development**
  - *Low cost membrane supports are available.*

Progress

- **Membrane sealings**
  - *The sealing technology for application of both types of membranes at membrane reactor conditions is available.*
  - *Long term behaviour needs to be verified*

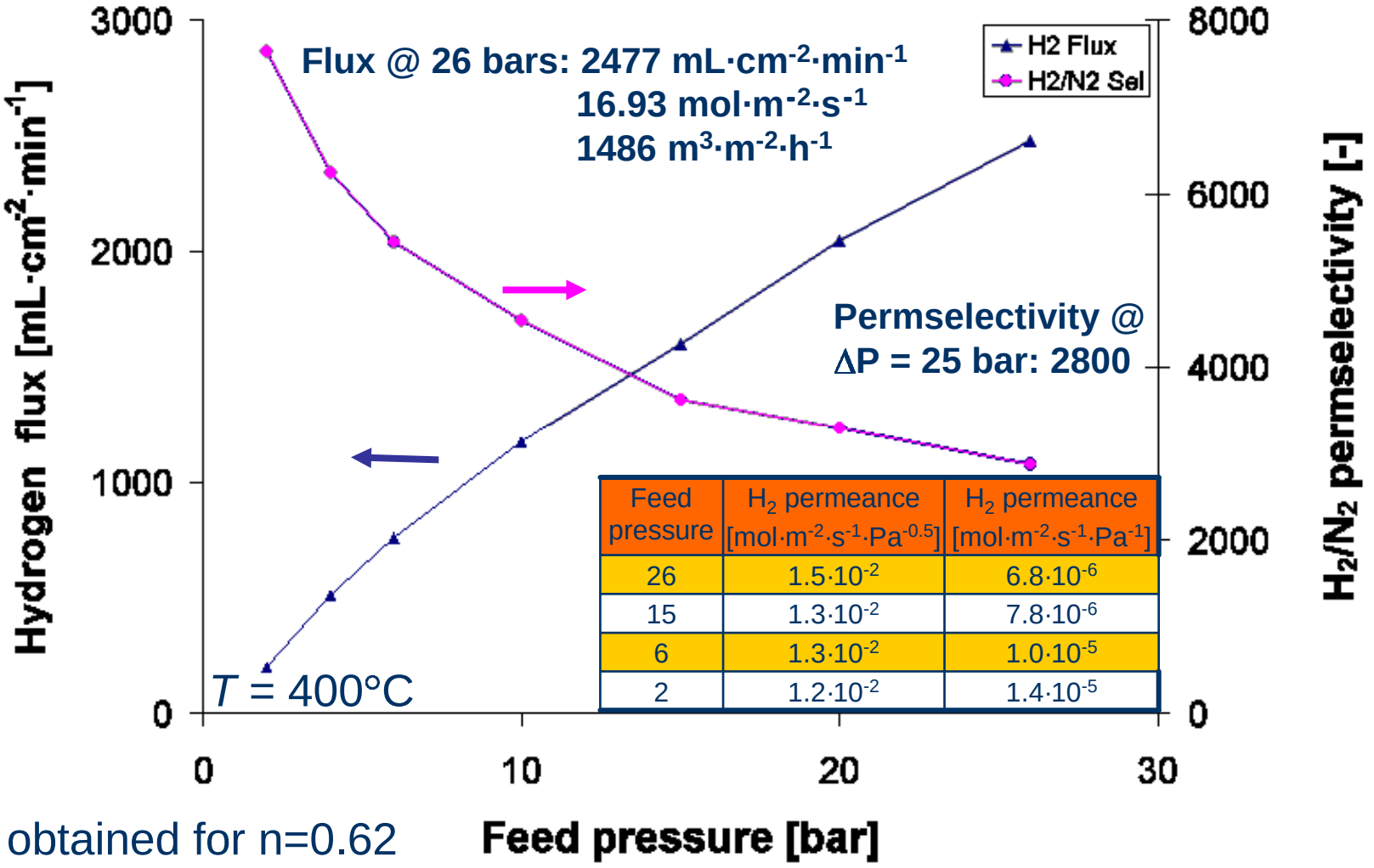
- **Membrane permeance/flux**
  - *Within the current uncertainty level the membranes measured are within the range of the CACHET targets.*

Progress

- **Membrane stability**
  - *Based on stability tests performed it is concluded that membranes are sufficiently stable to be used for tests in a bench scale reactor can be fabricated.*
- **Membrane selectivity**
  - *Membrane selectivity is sufficient for the application. (>1000)*
- ***Membrane costs***
  - *No detailed analysis performed yet.*

Membrane performance

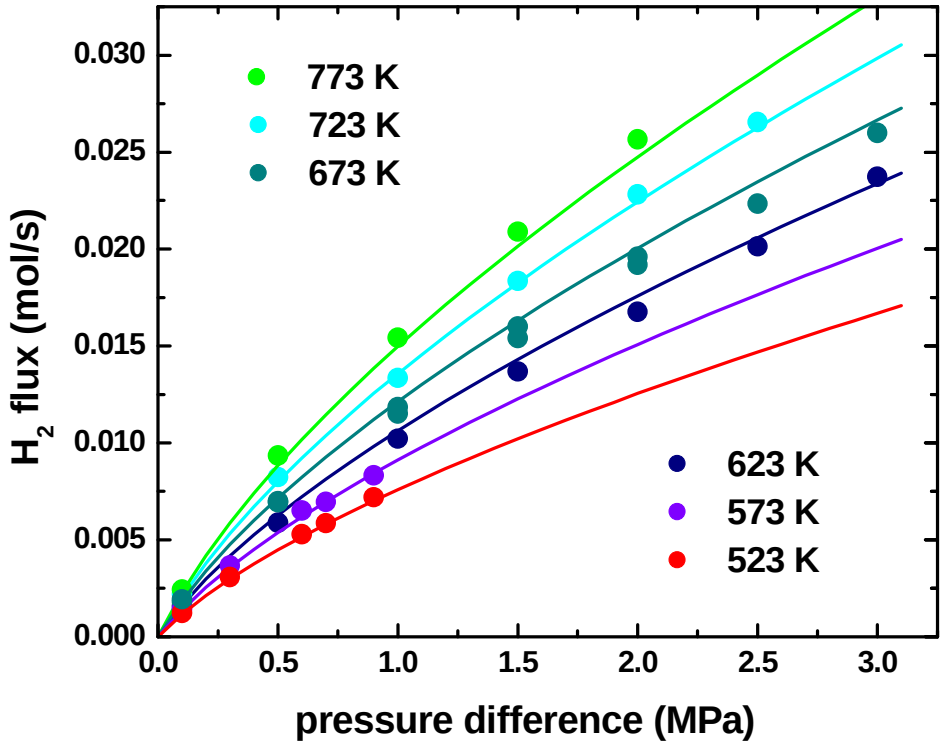
- Pure H_2 flux and H_2/N_2 permselectivity – 1.9 μm PdAg



Feed pressure	H_2 permeance [mol·m^{-2}·s^{-1}·Pa$^{-0.5}$]	H_2 permeance [mol·m^{-2}·s^{-1}·Pa^{-1}]
26	$1.5 \cdot 10^{-2}$	$6.8 \cdot 10^{-6}$
15	$1.3 \cdot 10^{-2}$	$7.8 \cdot 10^{-6}$
6	$1.3 \cdot 10^{-2}$	$1.0 \cdot 10^{-5}$
2	$1.2 \cdot 10^{-2}$	$1.4 \cdot 10^{-5}$

Best fit obtained for n=0.62

Membrane Performance



Pd membrane

1.2 μm thick, 13.4 cm long

58.9 cm^2 area

H_2/N_2 selectivity

773 K: 8100 (0.1 MPa)
3500 (2.0 MPa)

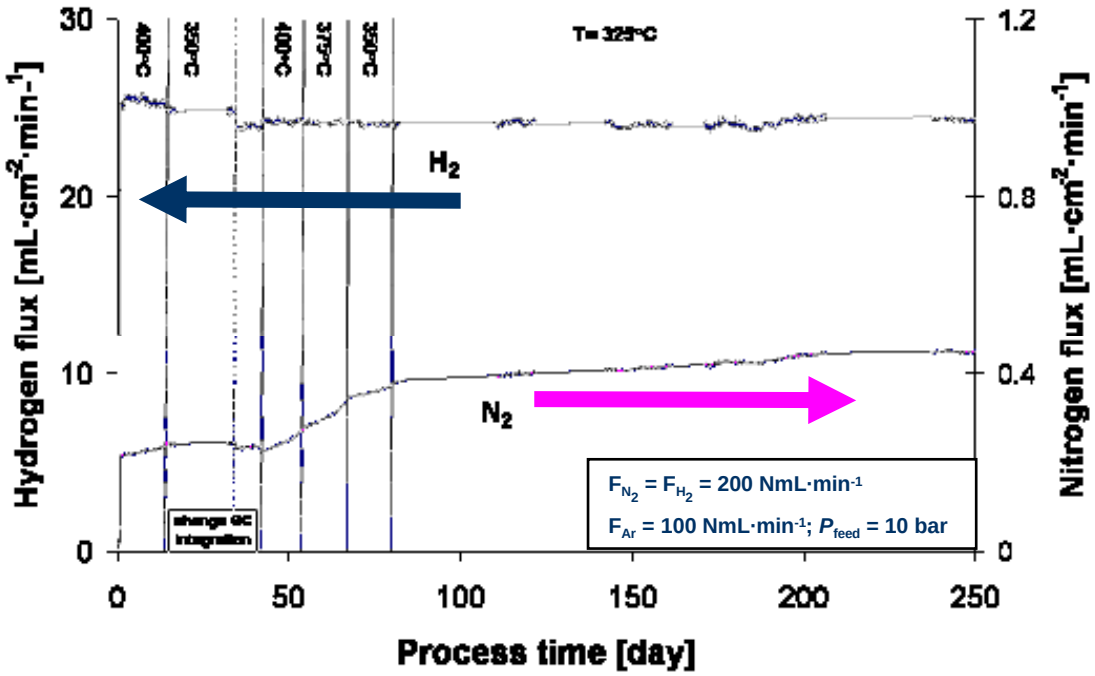
673 K: 7350 (0.1 MPa)
2750 (3.0 MPa)

$$Q_{H2} = 1.96\times10^{-3}\ mol/m^2/s/Pa^{0.64} \times \exp(-9.14\ kJ/RT) \times (P_1^{0.64} - P_2^{0.64})$$

nonlinear pressure dependence

Long-term stability – continuous operation

- **H_2 and N_2 flux over 250 days – P_{feed} = 10 bar**



H_2 permeance ~ $3 \cdot 10^{-6}$ mol·m^{-2}·s^{-1}·Pa^{-1}

H_2/N_2~ 1000

- P_{N_2} (initial) = $1.7 \cdot 10^{-9}$ mol·m^{-2}·s^{-1}·Pa^{-1} (400°C)
- P_{N_2} (250 days) = $3.1 \cdot 10^{-9}$ mol·m^{-2}·s^{-1}·Pa^{-1} (325°C)

- **Stable performance for 250 days = 6000 hours**
  - Also stable performance in WGS, P_{feed} = 10 bar, for 100 days

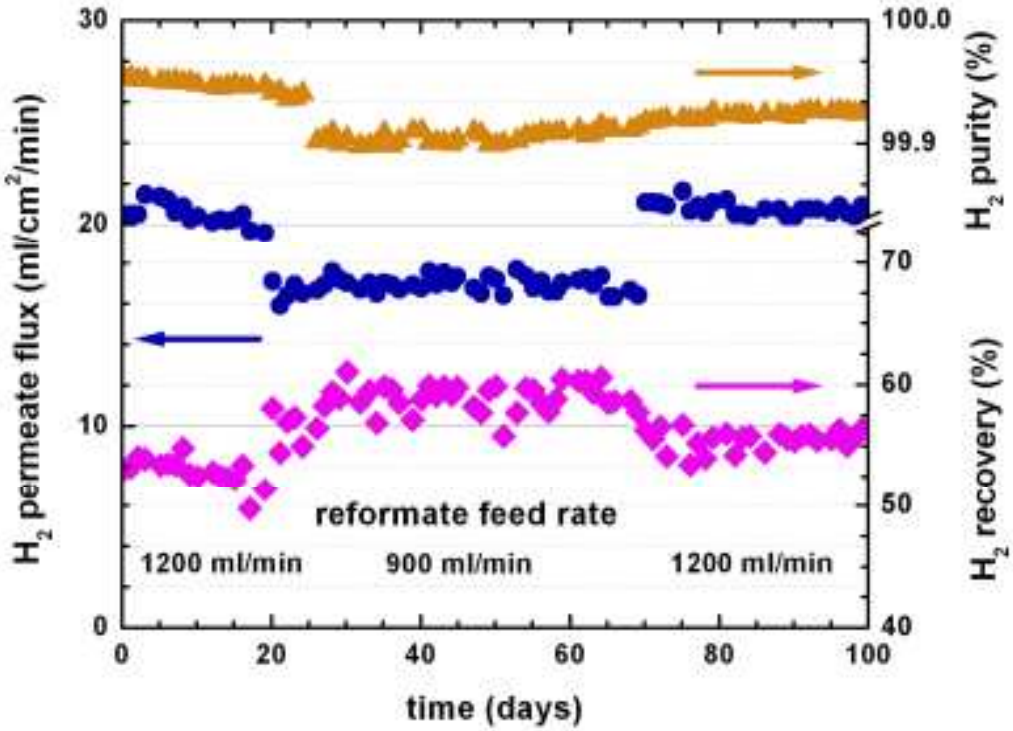
Gas	[%]
H_2	57.5
CO_2	18.7
H_2O	18.7
CO	3.8
CH_4	1.2

Progress
Long-term Stability

- **Reformate separation at 400 °C, P_{feed} = 1.1 MPa, P_{perm} = 0.1 MPa**
  feed: 59% H_2, 13% CO, 5% CO_2, 22.5% H_2O, < 0.5% CH_4, N_2

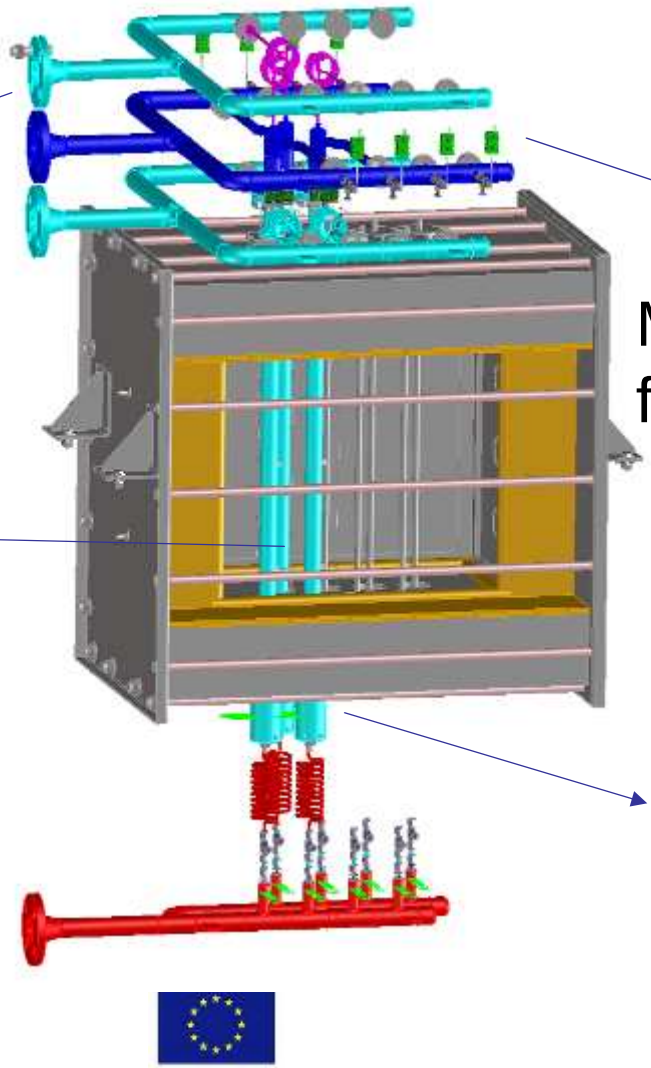
- **Membrane**
  - *5.5 μm thick Pd layer on ceramic support*
  - *4.2 cm long, 18.5 cm^2 area*

- **Membrane stability**
  - *H_2 flux, purity (> 99.9%) and recovery are stable during 100 day test*
  - *membranes are sufficiently stable to be used for tests in a bench scale reactor*



Progress

Reactor design



Flange connections to test rig

Manifolding with flexible connections

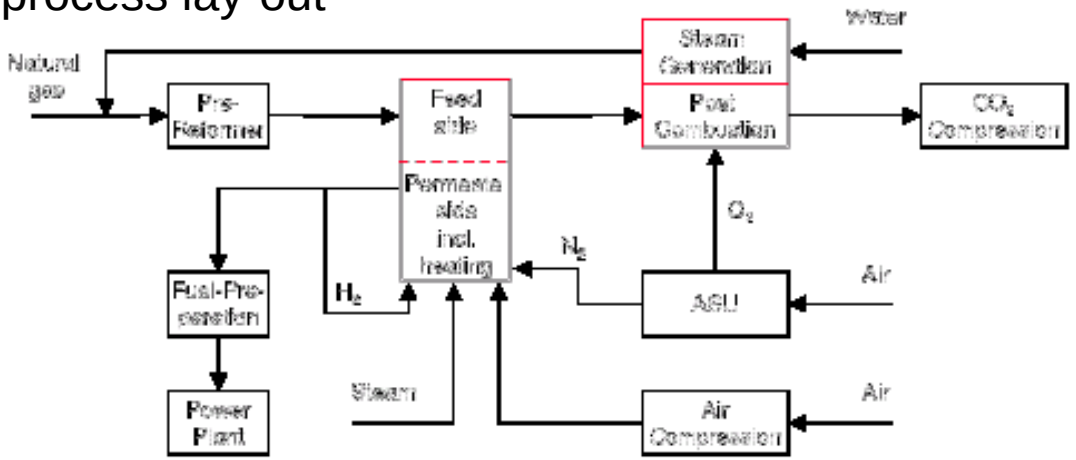
Kanthal heater oven

Removable tubes

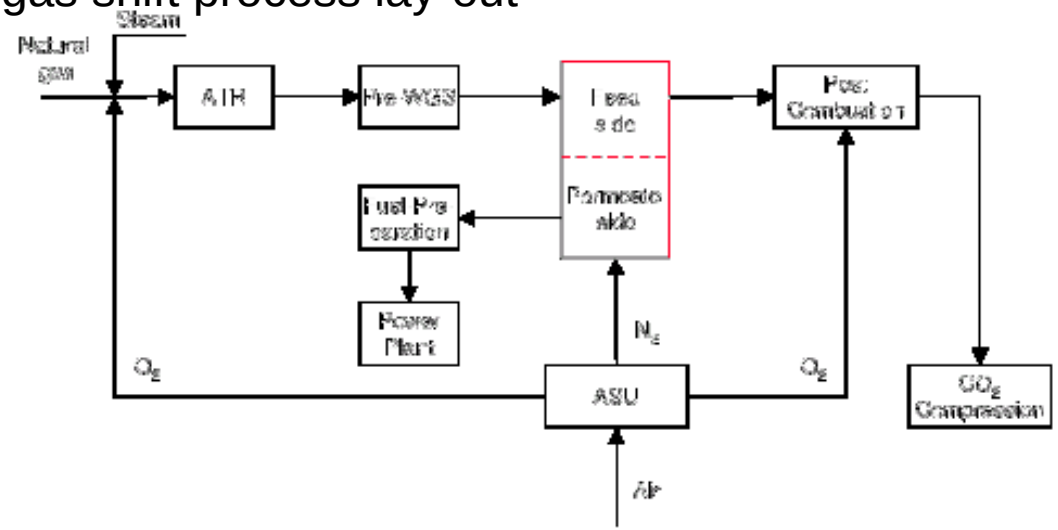
Progress

Progress

Membrane reformer process lay-out

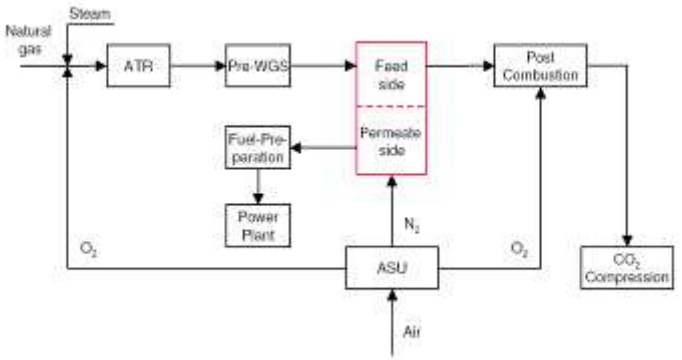


Membrane water gas shift process lay-out

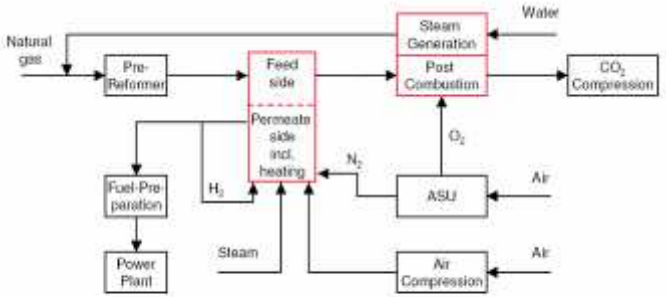


Progress

- **Techno-Economic's**
  - ***MWGS***
    - *Capture rate 99%*
    - *The LHV efficiency is about 47,5%*
    - *Avoidance costs 71 €/ton*



  - ***MREF***
    - *Capture rate 99%*
    - *H_2 fuel recompression*
    - *The LHV efficiency is about 45%*
    - *Avoidance costs 107 €/ton*



Recap-1

Reforming

- Pd membranes manufactured by electro less plating with length up to 50 cm
- Sealing has been tested at 700 °C and 38 bars
- Pd membranes are stable under H_2 up to 30 bar with H_2/N_2 selectivity better than 2500
- H_2 flux sufficient for membrane reactor testing in PDU
- 99.9% H_2 purity at 90% recovery

Water Gas Shift

- Thin Pd/Ag membranes (2-3 µm) manufactured by magnetron sputtering, length up to 50 cm
- After long term testing H_2/N_2 selectivity still above 1000
- H_2 flux sufficient for membrane reactor testing in PDU
- Long term stability at temperatures up to 450 **£** C

Recap-1

Cost estimates show relative high COE and CO_2 avoided

- Due to high natural gas prices
- Due relative low efficiencies
- Based on 2008 cost estimates

PDU test rig ready to deliver first test results

- Non integrated WGS (3 membrane tubes DICP)
- Integrated WGS (3 membrane tubes SINTEF)
- Reforming (8 membrane tubes DICP)

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See also: www.CACHETCO2.eu