Separation- A key technology towards the hydrogen economy?

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Structure of the presentation

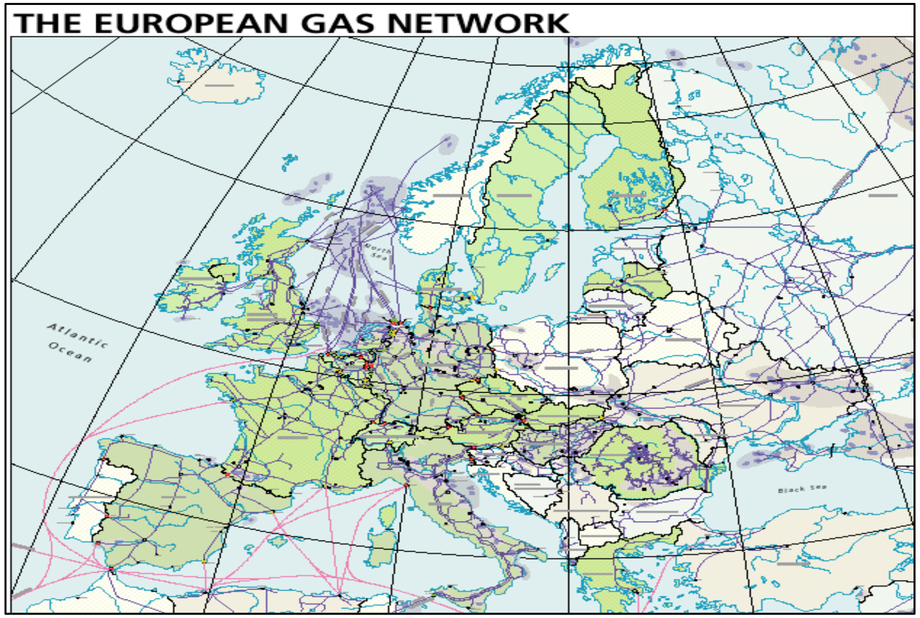
- **NATURALHY Project**
- **Separation technologies**
- **NATURALHY approach**
- **Status**
- **Future**

NATURALHY Project

Main political drivers towards H_2

- Energy security
- Reduction of CO2 emissions (Kyoto ≥8% by 2010)
- Improvements in regional air quality

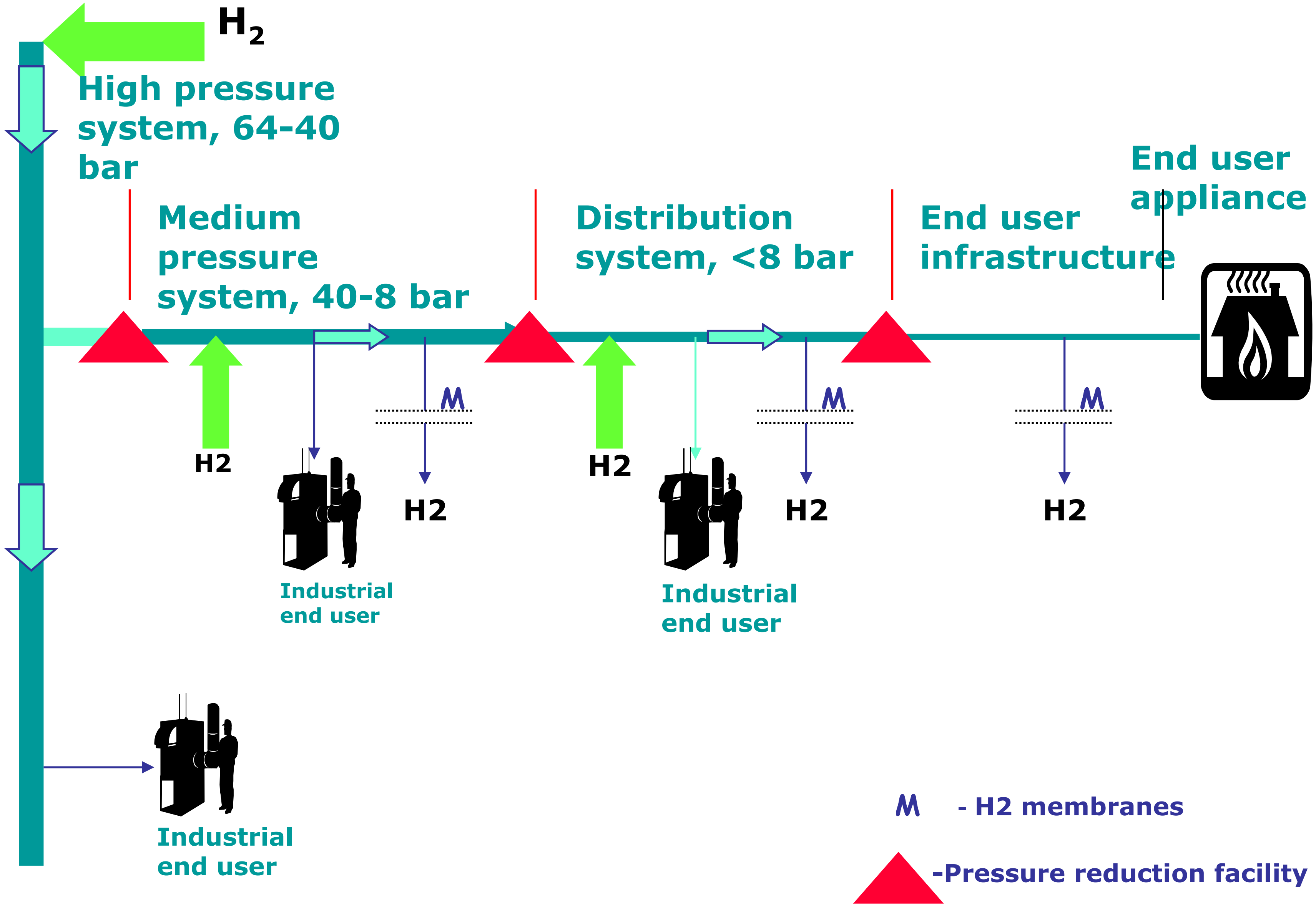
Smooth, rapid introduction of hydrogen to end-users by using existing widespread NG network system to distribute mixtures of NG and H_2



Value of Mixtures

- **Reduction of CO2 emissions (greening of gas)**
- **1% of NG energy replaced by CO_2-free H_2 results in a reduction of 9Mt/y CO_2 in the EU-25 countries**
- **Potential of pure hydrogen delivery by H_2 separation**
- **Offering hydrogen producers a connection to end-users**
- **Using existing system avoids investment in completely new infrastructure**

Hydrogen Local centres



Separation of Hydrogen

- Pressure swing adsorption (PSA)
- Membranes

Gas separation by adsorption processes widely used in

- **Petrochemicals**
- **Biochemical**
- **environmental technology**
- **oil and gas industries.**

Pressure Swing Adsorption

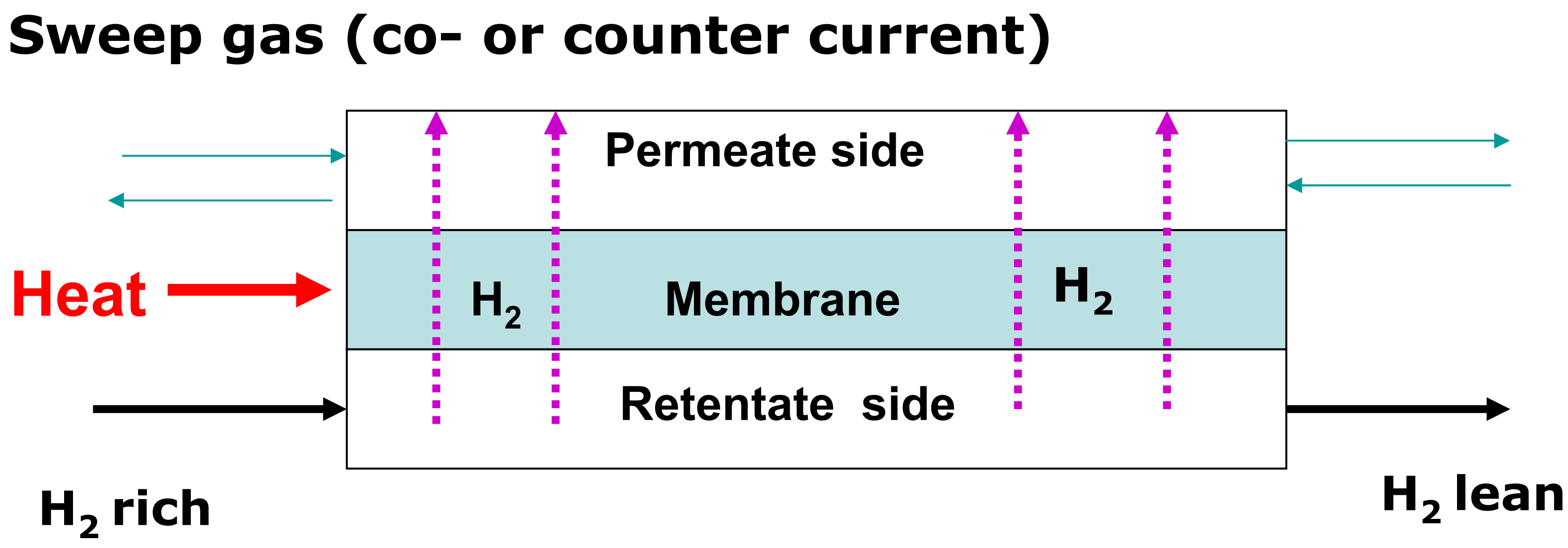
Advantages

- **Well-established commercially, especially in natural gas systems and refineries**
- **Fairly high purity H2**

Disadvantages

- **Only 80-90% of H2 is recovered**
- **Higher purity H2 product requires more energy (more freq. switching)**
- **Mechanically more complex – switching beds**
- **Higher energy usage than filters / membranes**
- **Higher capital cost**

Membrane principle



Why Membrane Separator Development?

- **Commercial systems problematic -expensive**
- **Capitalise on cost advantage for smaller scale operations**
- **Relevant to purification and membrane reactors**
- **Improvements in cost and reliability needed**
- **Need to link membrane development with packaging for process needs**

Programme objectives

Objectives

- **To develop high selectivity Pd based thin membranes for Hydrogen separation from natural gas mixtures**
- **To examine performance envelope, packaging and system issues**
- **To develop low cost carbon based membranes**

Palladium Membranes

Advantages

- **Simple, no moving parts**
- **Pure H2 product**
- **Modular for scale up**
- **Potential for lowering costs**
- **However, Still in development**
  - **Relatively low flux – large membrane area required**
  - **Palladium (most common) is very expensive**
  - **Contaminants (sulphur, other components)**
  - **Low outlet H2 pressure**
  - **High operating temperatures (>400C)**

Typical lab permeator (Univ Oxford)

Early sample

- **8 μm Pd membrane supported on ceramic substrate**
- **Graphite seal**
- **13 mm o.d x 120mmlength**
- **Sep. factor>50:1 (~99%)**
- **Further development of ceramic will allow thinner membranes (2-3 μm) with separation factor>1000:1(>99.9%)**

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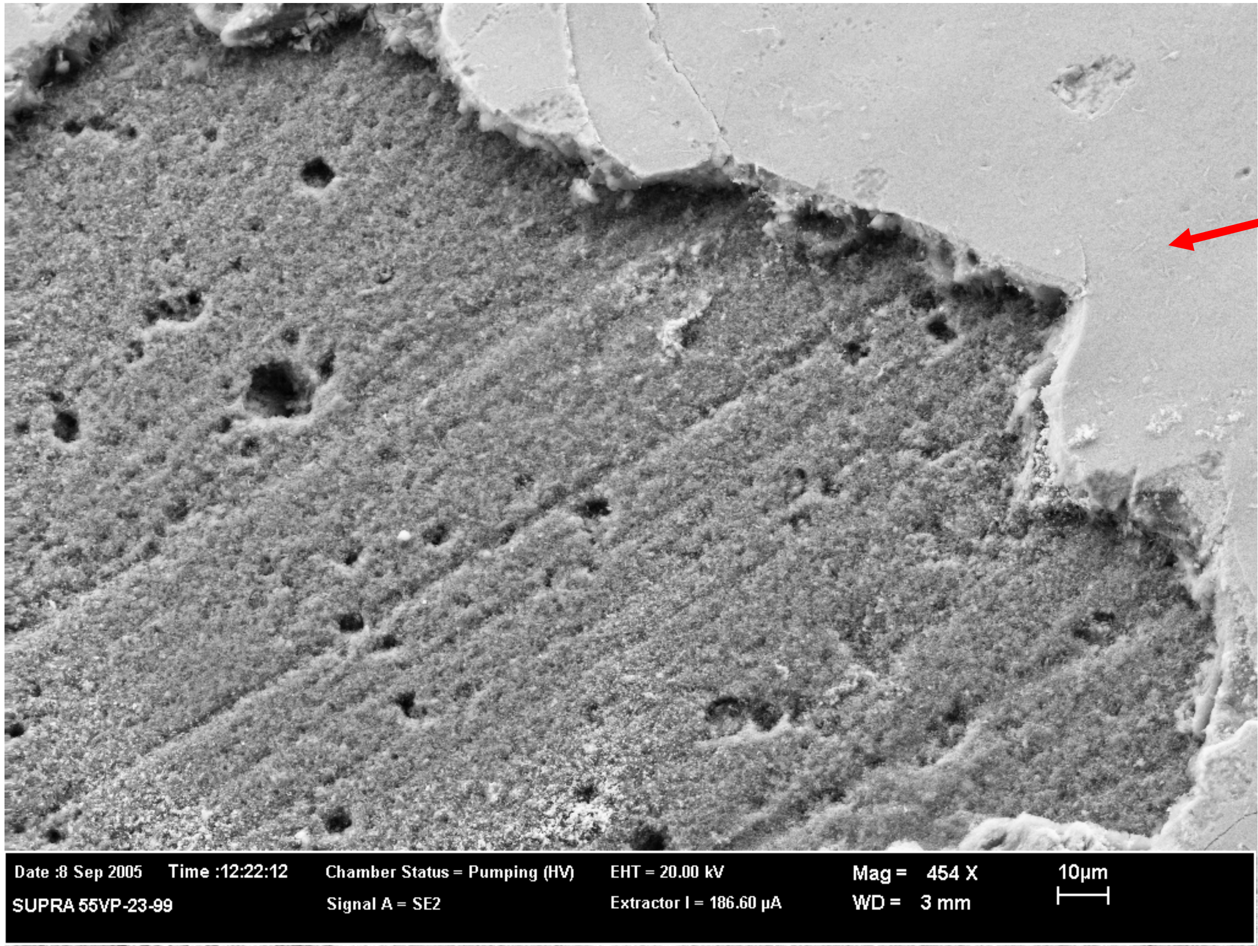
Scale up issues for Pd membranes

Flux	**Use Pd based alloys e.g. Pd/Ag** **Very thin films of Pd on porous supports**
Cost	**Price of Pd is ~$650/ounce (April, 2007)** **Thickness of Pd film will be <2µm for $500-1000/m2**
Poisoning by process stream impurities	**Unsaturated hydrocarbons, H2S, CO** **Should be regeneratable in steam or air**
Embrittlement	**Resistance to thermal cycling** **$\alpha \longrightarrow \beta$ (α′) phase transition**
Leak free sealing	**Supported membranes**

Pd membrane

High resolution SEM of substrate support for Pd alloys



10µm sol gel coating

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How do we address these problems?

■ **Cost**

– thin films of Pd on hydrogen-porous supports

– minimize Pd film thickness

■ **Poisoning**

– remove most H_2S up front

– $PdCu_{40}$ is sulphur resistant

■ **Embrittlement**

– Pd alloys reduce distortion upon hydriding/dehydriding

Technical Approach

- **Thin Pd films on supports:**
  - **Challenge is to produce perfect defect free film –very difficult**
  - **Role of support is crucial**
  - **Defect free supports problematic**
  - **Electroless plating OK for Pd but not for Pd/Ag and Pd/cu alloys**

For Pd alloys Sputtering methods being investigated

  - **Deposit thin coherent film of Pd/Ag on defect free support**
  - **Silicon wafers and ultra-fine filter materials used**
  - **Deposit on substrate, seal and manifold**

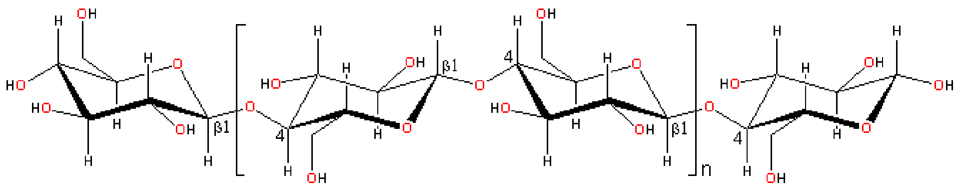
Experiments with H_2S and THT in CH_4

CETH

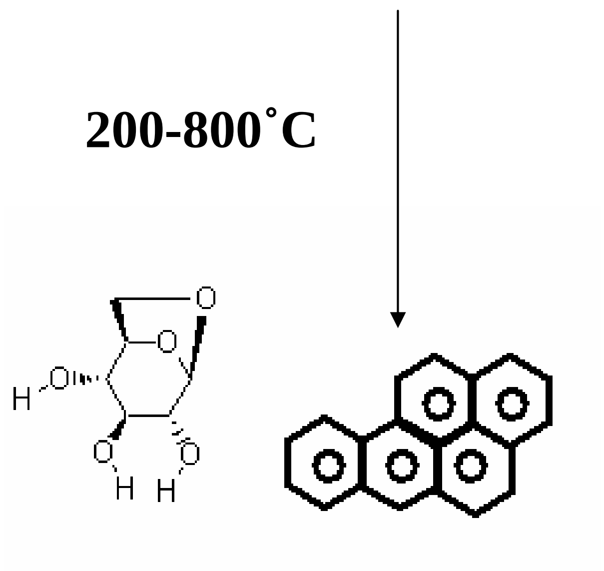
Characteristics	Units	Pd-40Cu	Pd-23Ag
Pd content	Weight %	60	77
Standard flux (25 μm thick)[1]	Std. cc H_2/cm^2•min	50 [2]	79 [3,4]
Normalized flux [5]	Std. cc H_2/cm^2•min	83	102
Embrittled by hydrogen	N/A	No	No
Poisoned by sulfur	N/A	No	Yes

Carbon based membranes

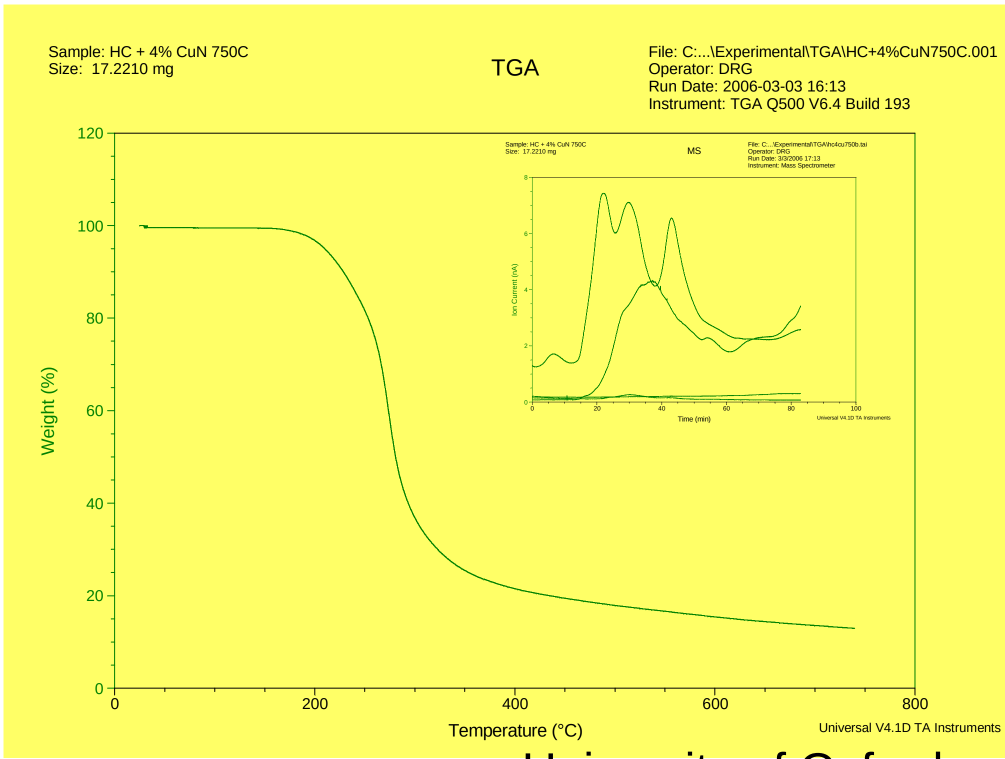
CMS Formation



+ MeSalt/MeO



Levoglucosan **Benzopyrene**



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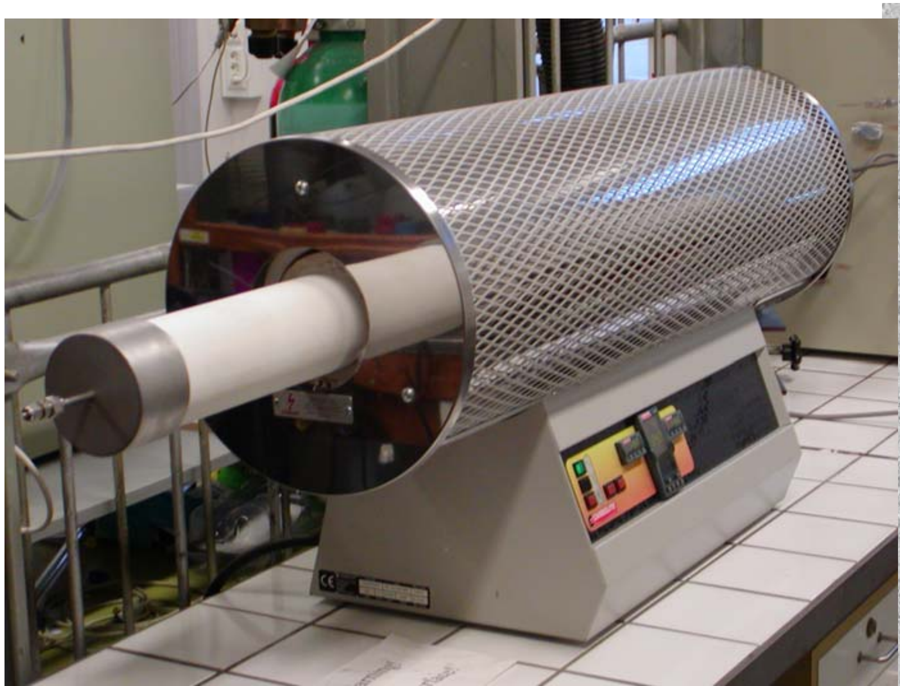
CMS Mixed Gas Results (30% H_2 in CH_4)

Material	Test Temp oC	Test feed pressure bar	H2 permeability Barrer	Selectivity	H2 permeance M3(STP)/m2.h (12 microns)
HC+Cu 550ºC	90	4	1502	679	0.34
HC+Cu 650 ºC	30	2	700	181	0.16
HC+cu 650 ºC	30	6	648	541	0.15
HC+Cu 650 ºC	80	2	1230	218	0.28
HC+Cu 650 ºC	80	6	1155	532	0.26

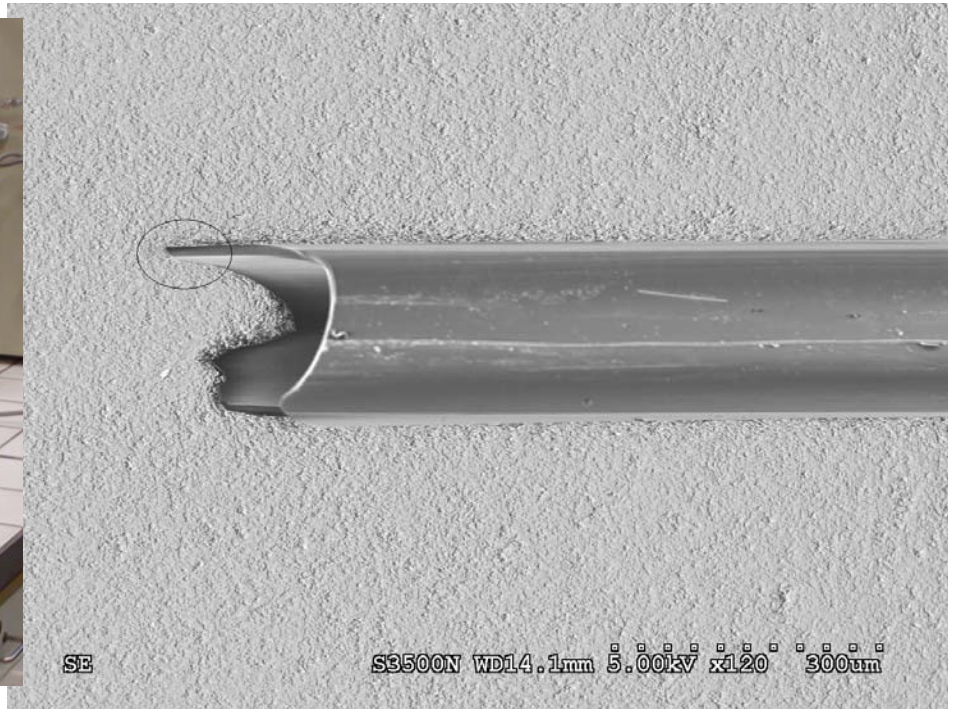
- **Insensitive to pressure in the application range (2-6 bar)**
- **Significant increase in permeability with temperature**
- **80% H2 recovery, >90% purity possible at 30 C**

SEM of hollow carbon membrane

Challenge is to achieve close control of the pore tailoring and carbonization procedures. Work is focussed on making defect free larger membranes or hollow fibres (NTNU)



Temperature programmed furnace for carbonization of precursor films



SEM of hollow carbon fibre

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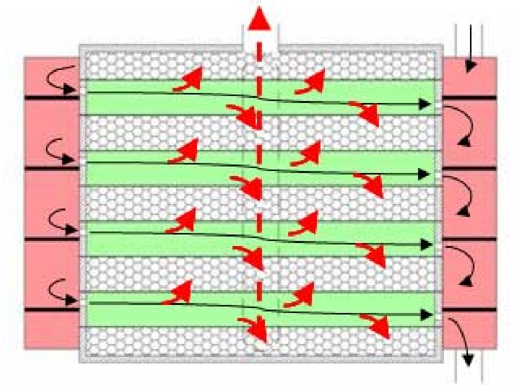
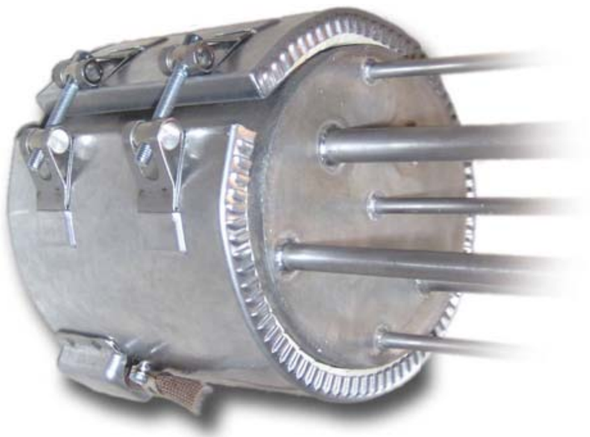
Packaged Pd membrane

CETH examining packaged concepts





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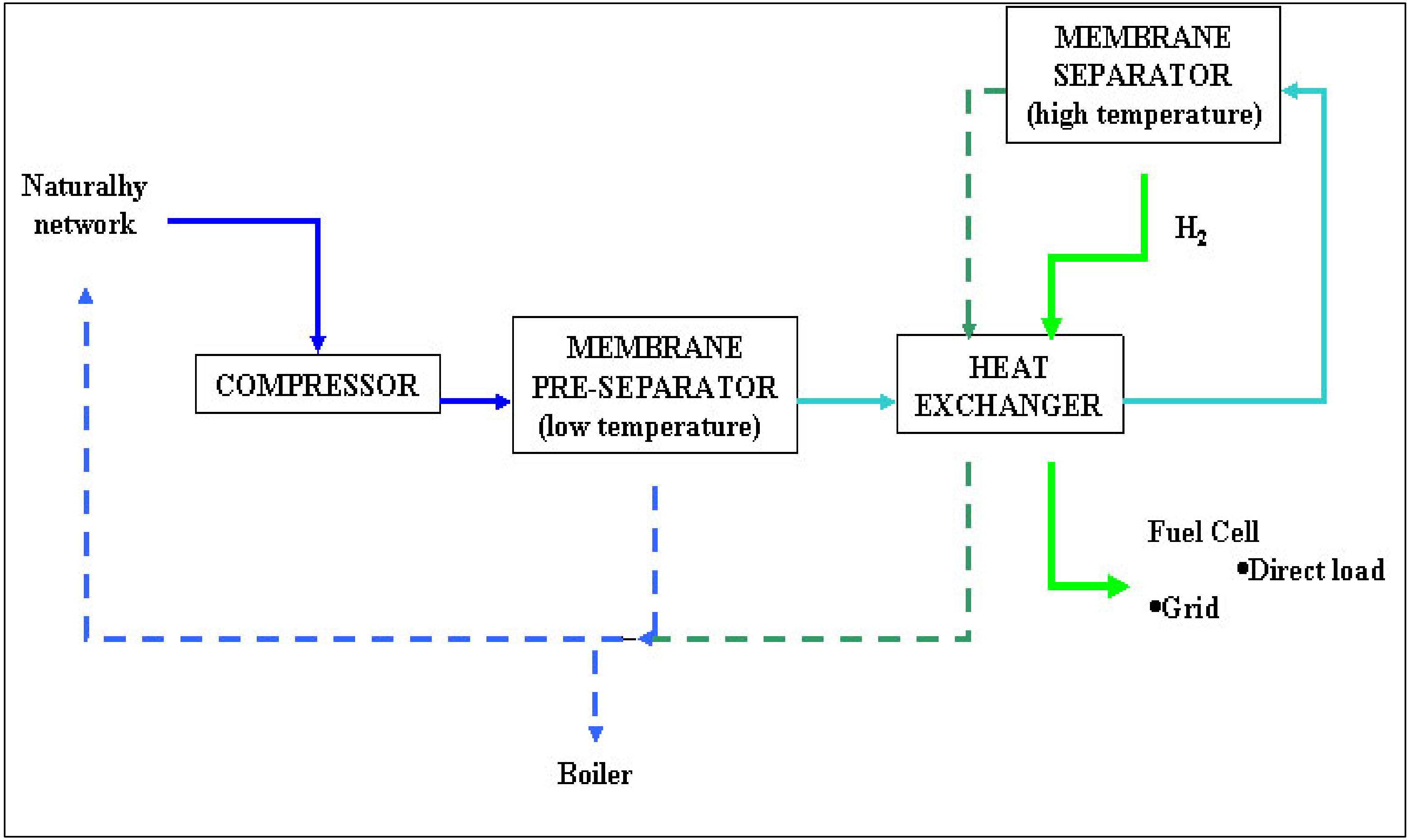
Process Design



Summary
Palladium Alloy Membranes

- **Most cost effective for small scale production**
- **Cost depends on flux obtained/unit area**
- **Flux is function of (thickness, partial pressure drop, temperature, poison concentration)**
- **Need very thin membranes**
- **Typical results for 5 microns from 65% H_2 in CH_4 at 5 bar and 450°C is 17 $m^3/hr/m^2$**
- **Target is reliability in thin films** **pin holes, thermal/mechanical stress, poisons**
- **Support material critical**
- **Need to consider issues of packaging**

Summary

- **Thin Pd based membranes offer potential but technically challenging**
  - » **work at relatively high temperature**
  - » **provide pure hydrogen**
- **Carbon based membranes: low cost with good flux, work at relatively low temperature**
- **Separation system may involve both types**
- **Packaged systems**