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Capture with membranes

May-Britt Hägg
Professor, Dep. Chem. Eng.

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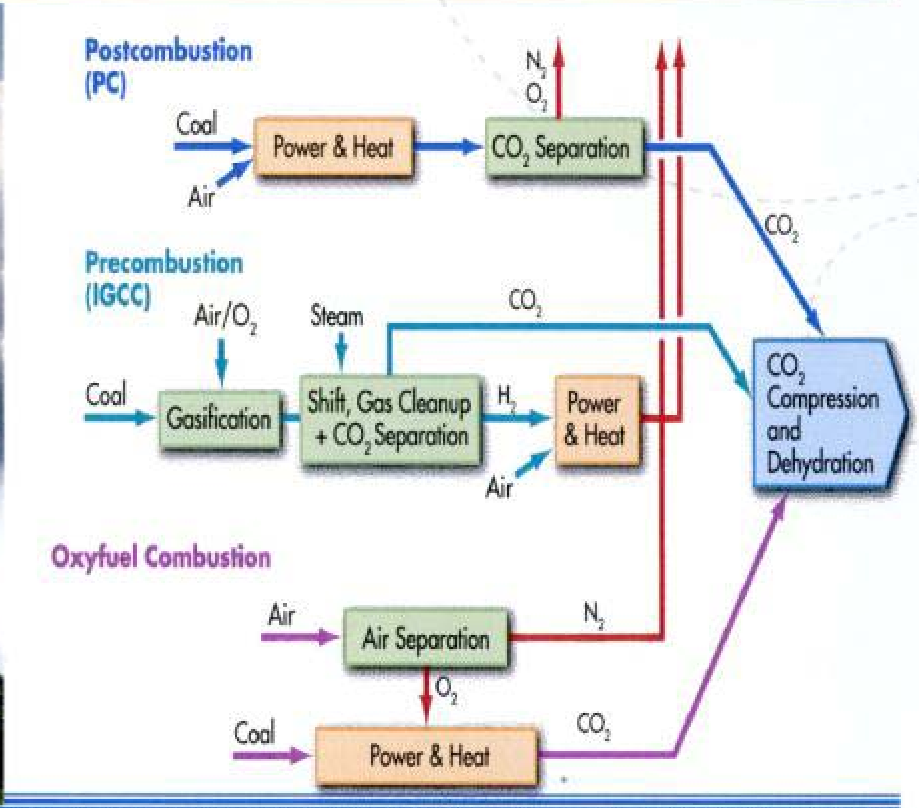
Outline of presentation

- Membrane capture technologies – brief overview
- General about driving force and separation
- New trends, examples
  - Nanocomposites
  - Facilitated transport membranes
  - Pore tailored membranes
  - Membrane contactors
  - Process solutions
- Challenges using polymer membranes
- Simulations must be mentioned
- Conclusions

CO_2 capture – membrane technologies



- *Depending on where in the process the membrane will be placed, the transport mechanisms and demands on the material will be very different*

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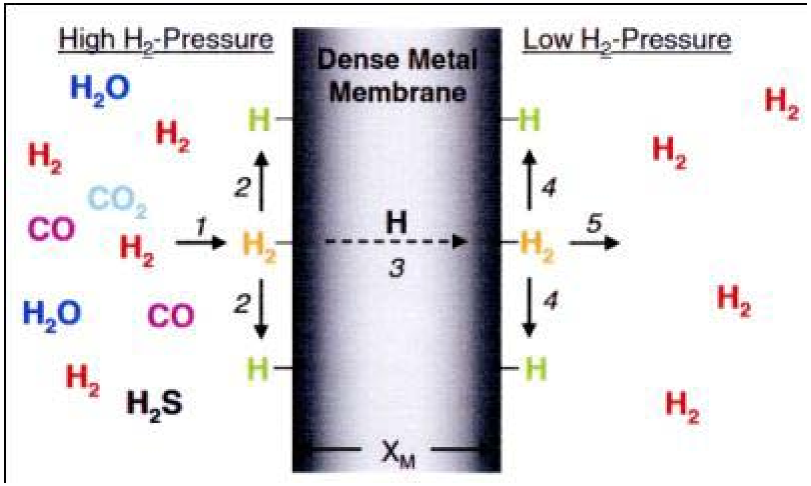
Membranes in *precombustion*



Five stage process of permeation

Permeation is by solution-diffusion

Governing equations for:

concentration of H at surface (C_H) and flux through membrane (J_{H2})

$$C_H = K_s P_{H_2}^{0.5}$$

$$J_{H_2} = -\frac{D_M K_s}{2} \frac{(P_{H_{2,Ret}}^{0.5} - P_{H_{2,Per}}^{0.5})}{X_M}$$

- Separation of $CO_2 - H_2$ at high temperature (> 300°C)
- Typical materials:
  - Pd / Pd-alloys
- Challenges:
  - Poisoning
  - Detection and elimination of defects
  - Material costs
- Engineering design
  - Complex
  - Scale-up

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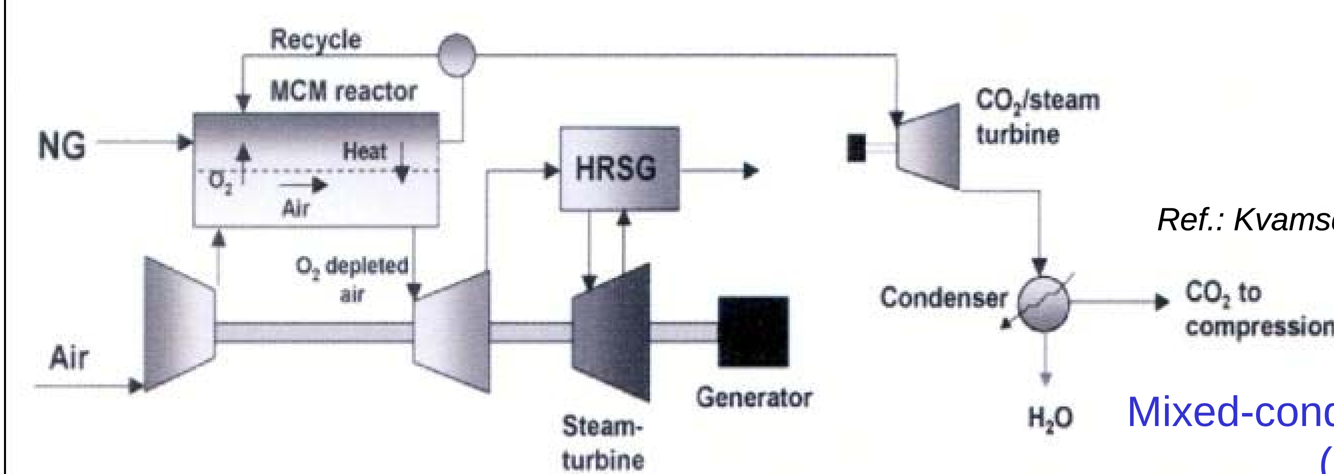
Membranes in *oxyfuel combustion*



Ref.: Kvamsdal et. al. , SINTEF Energy

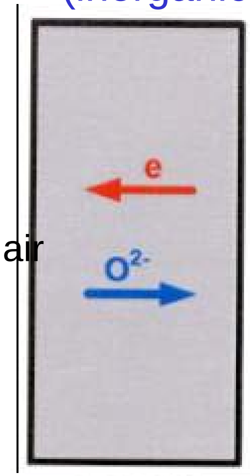
Mixed-conducting-membrane (inorganic oxide)

Demands on the material:

- High flow rate (diffusion coefficient)
- Temperature (900-1100°C)
- Chemical stability in oxidising and reducing atmosphere
- Compatible TEC (Thermal expansion Coefficient) with joined materials.
- No chemical reaction
- No reaction with joined materials (seals, interconnects etc.)

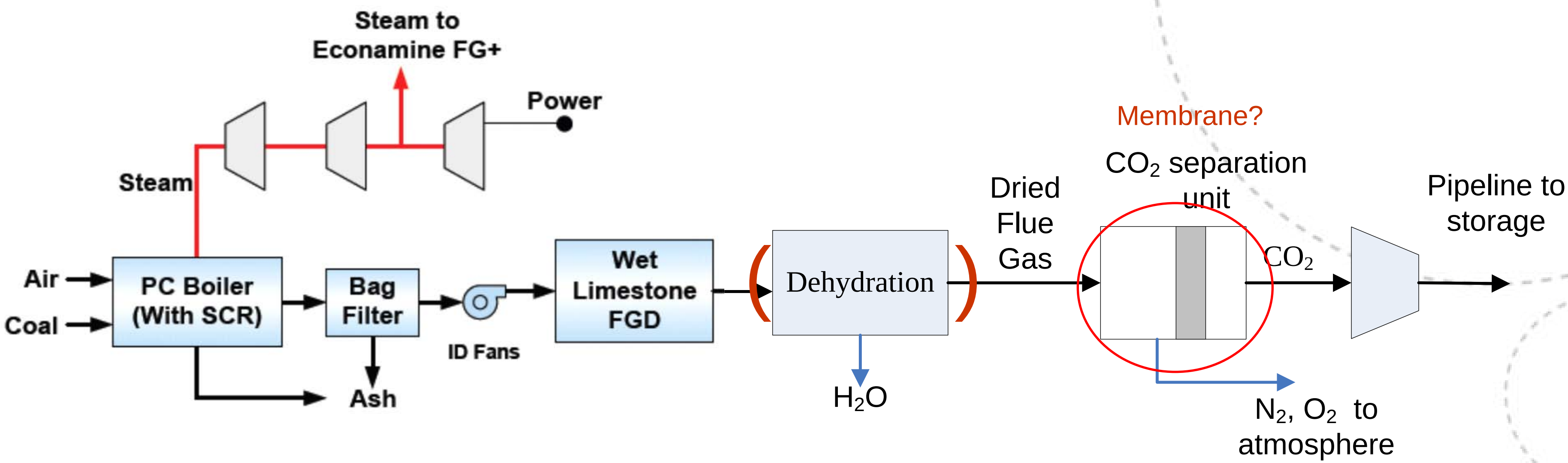
Strong demands on the module sealing!

Air → O_2 depleted air
$O_2 + 4e \rightarrow 2O^{2-}$



$2O^{2-} \rightarrow O_2 + 4e$

Membranes in *post combustion*



- Process design based on a typical coal fired power plant
- SO_2, NO_x, VOC and fly ash are removed to given spesifications
- Dehydration unit may complicate the process if needed for the membrane
- Feed gas components to membrane are basically (H_2O), N_2, CO_2, and O_2
- Feed gas at atmospheric pressure, temp. ~50° – 70°C

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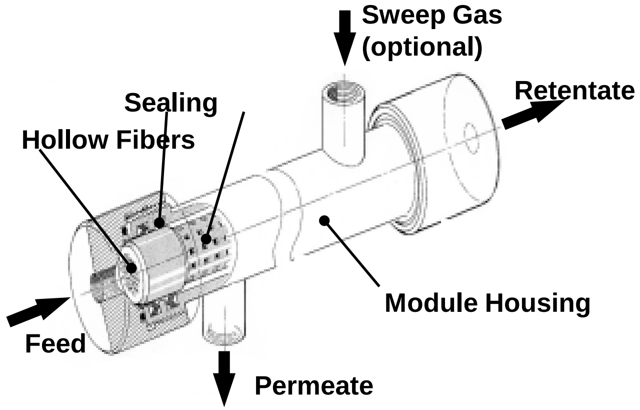
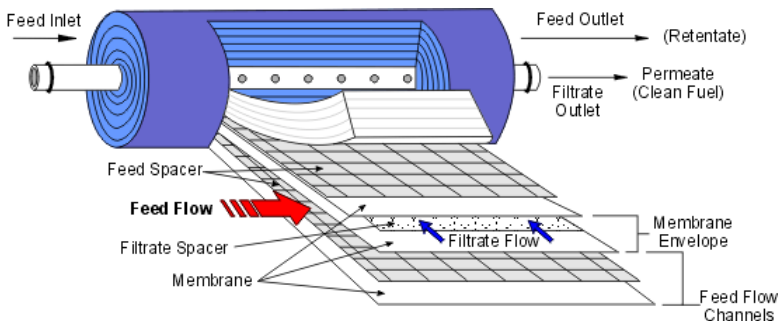
Polymeric membranes for gas separation have been in commercial use since 1980's





Areas of applications:

- ✓ H_2-recovery
- ✓ Air separation (high purity N_2)
- ✓ CO_2 removal from Natural Gas
- ✓ VOC recovery from gas streams

- Standard polymeric materials are: derivates of cellulose acetate and polyimides
- Separation depends on trade-off between permeability and selectivity (the ”upper-bond”) and the driving force available

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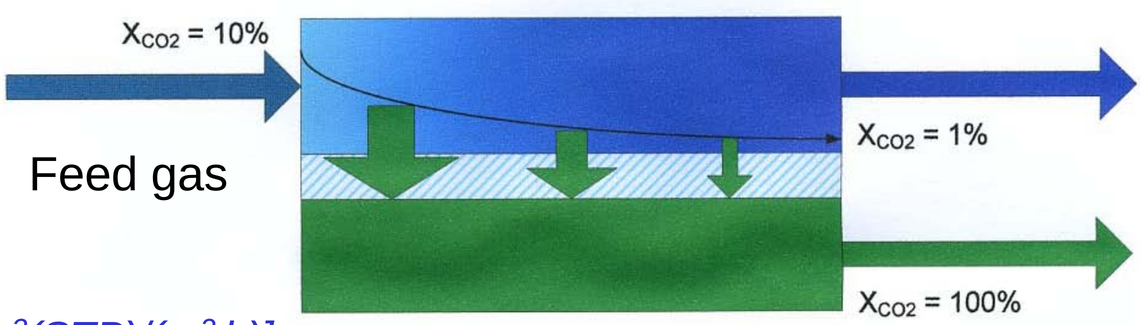
The driving force in a standard membrane



Flux = J [m^3(STP)/(m^2·h)]

$$J_{CO2} = \frac{D \cdot S}{l}\left(x_{CO2,f} \cdot p_H - x_{CO2,p} \cdot p_l\right) = \frac{P}{l}\left(x_{CO2,f} \cdot p_H - x_{CO2,p} \cdot p_l\right)$$

The membrane will separate on basis of:

- Molecular size and structure of gas components
- Physical properties of the gases (ideal / non-ideal)
- Membrane material properties
- Transport mechanism (solution-diffusion in a polymer)
- Process conditions (temperature, pressure, concentrations)

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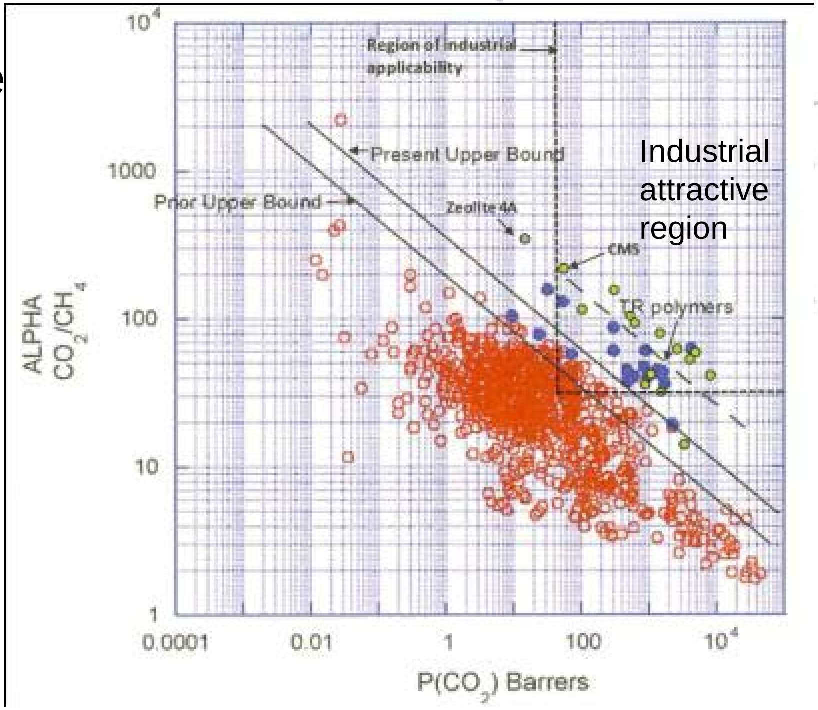
"The upper bond" with respect to driving force for polymer membranes in general

- The upper-bond must be broken for the gas pair CO_2-N_2 if membranes are to be used in ***post-combustion*.**



This can be done in several ways:

1) Nanocomposite materials
2) Facilitated transport membranes
3) Pore tailored inorganic membranes

Two other ways to neglect upper-bond:

- Using membrane contactors
- Innovative process design

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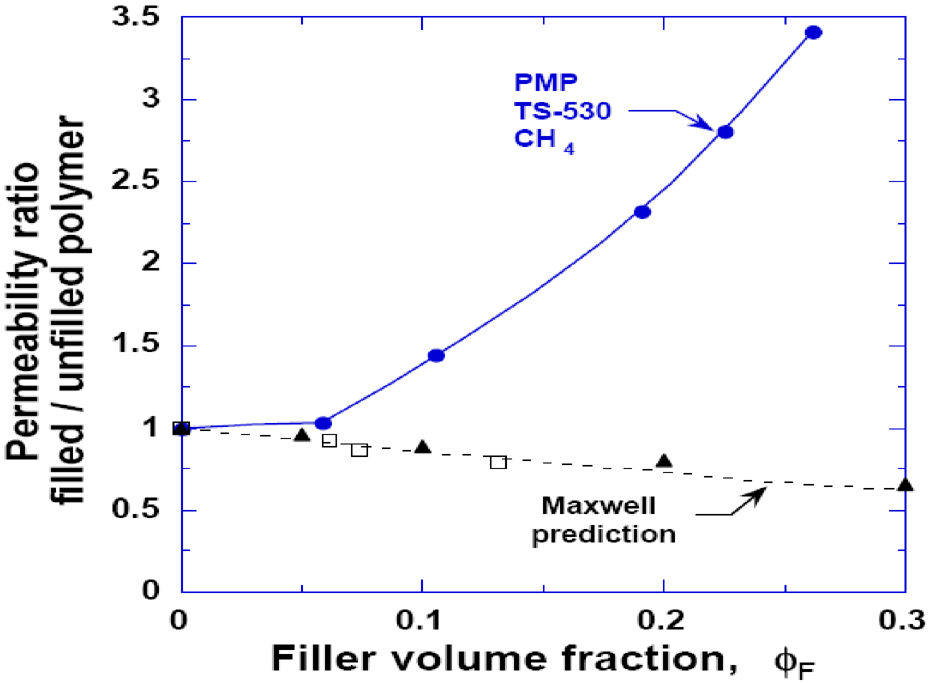
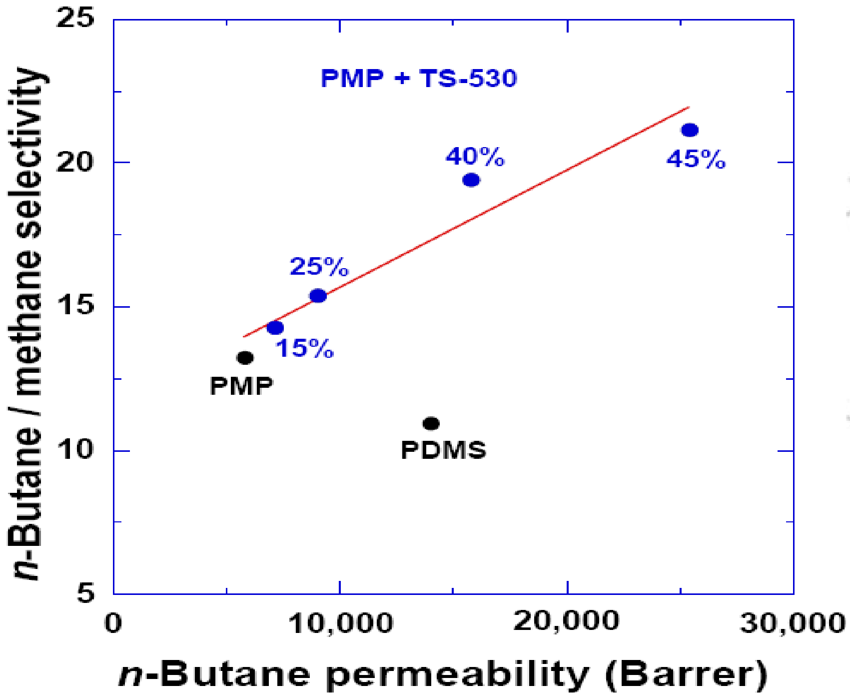
1) Nanocomposite (mixed matrix) membranes
- *the effect of adding nonporous nanoparticles*





▲: Barrer et al., *Journal of Polymer Science*, **1**, 1963
□ : Most, *Journal of Applied Polymer Science*, **14**, 1970

2 % *n*-butane / 98% methane feed;
upstream pressure = 150 psig; downstream pressure = 0 psig

Merkel *et al*., Ultrapermeable, Reverse-Selective Nanocomposite Membranes, *Science*, **296**, 519-522 (2002).

PMP = poly(4-methyl-2pentyne), PDMS= poly(dimethyl-siloxane)
TS = silica (SiO2) nanoparticles

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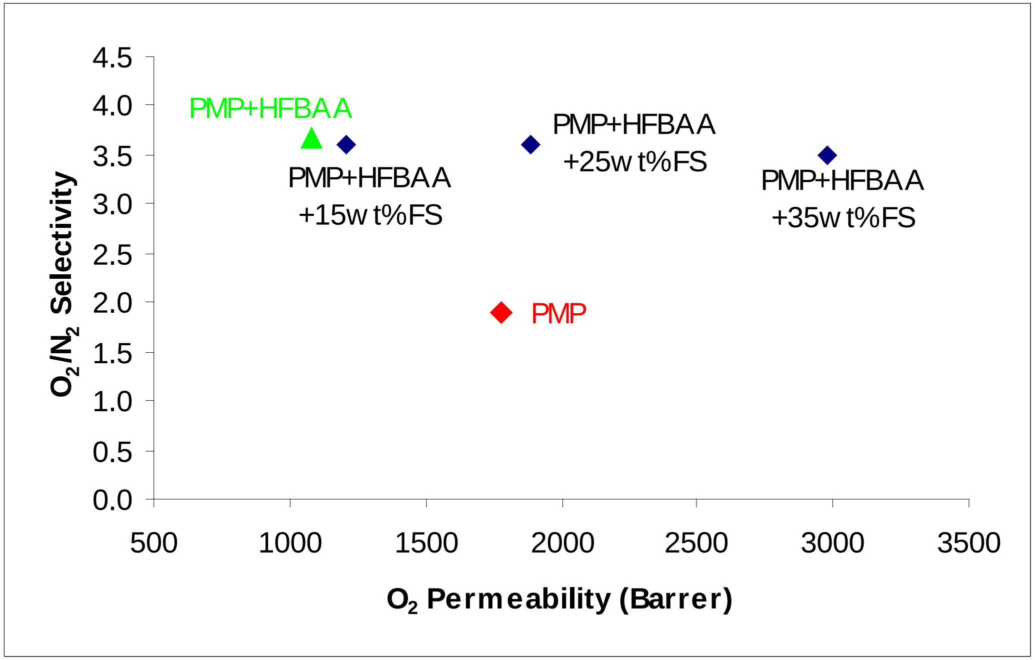
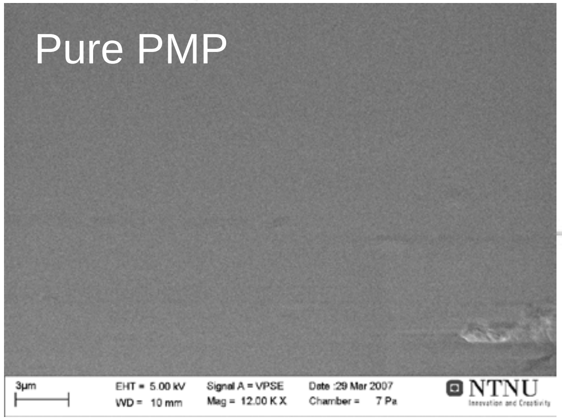
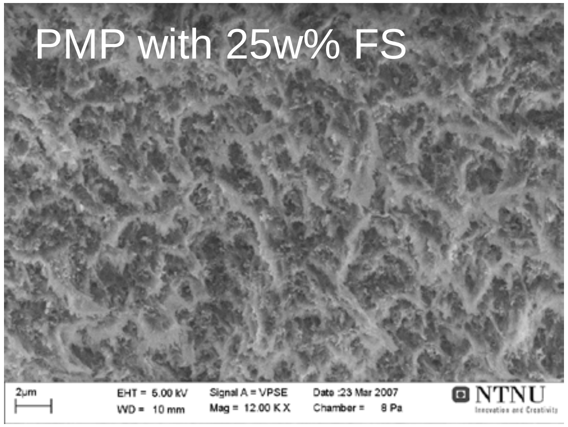
Nanocomposite material, an example:
Crosslinked PMP with FS for air separation







The effect of fumed silica (FS) content on O_2 permeability and O_2/N_2 selectivity of uncrosslinked(◆) and crosslinked PMP (▲ ◆).
Crosslinked membranes contain 2 wt% HFBAA; T=35˚**C.**
Ref.: L. Shao, Thesis NTNU 2008

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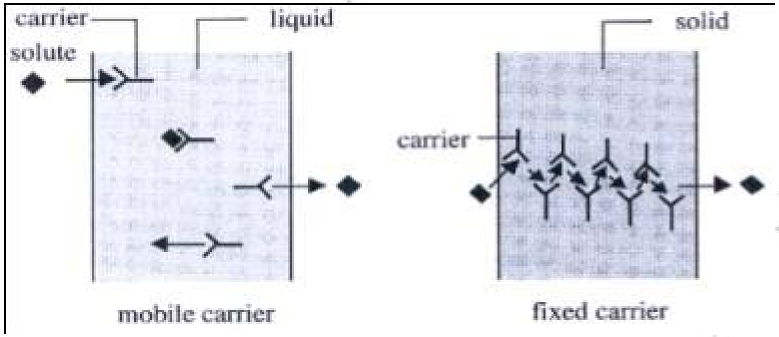
2) Facilitated transport membranes; general

Several types are available:

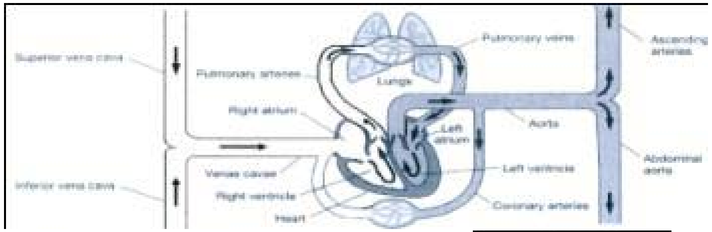
- Ion-exchange resins
- Hydrophilic polymers with CO_2-reactive salts
- Polyelectrolytes
- Biomimetic membranes
- Fixed-site carriers

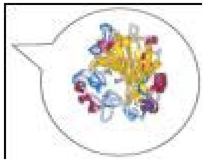


Ref.: M. Mulder, 1996

❖ The category ”blue” above, contains a mobile carrier that can react with CO_2 and diffuse acrosss the membrane – typically a *supported liquid membrane (SLM)*

❖ In the fixed-site carrier the CO_2-reactive funcionality is attached to the polymer backbone, and the CO_2 rather ”hops” from site-to-site





Ref.: M.C. Trachtenberg, 2001

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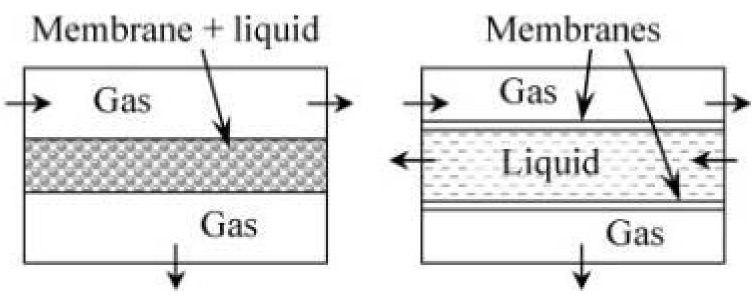
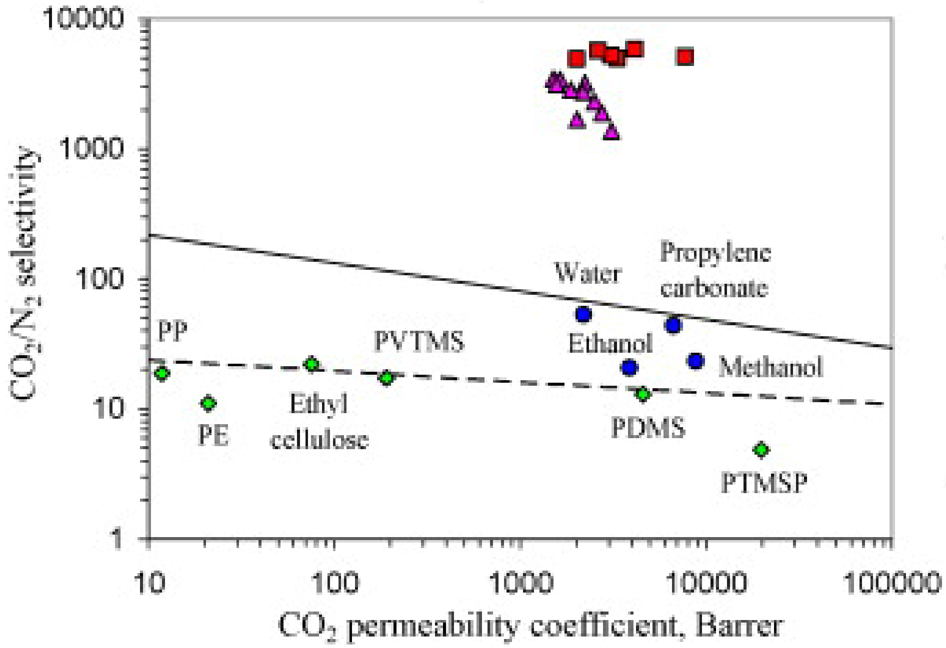
Supported (immobilized) liquid membranes
- an illustration



Left: Immobilized liquid membrane, (ILM) microporous polymer
Right: Flowing liquid membrane, (FLM) dense polymer



- Upper bond for selected polymers
- Upper bond for some solvents
- ILM using carbonate glycerol
- ILM hollow fibers using glycerol

Ref.: M.G.Shalyigyn et al. 2008

The mobile (aquous) carrier may typically be:

- Carbonates (K, Na)
- Amines
- Glycerol
- Enzymes
- Mixtures thereof

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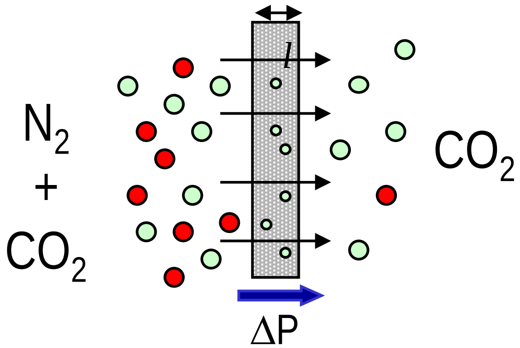
Fixed-site-carrier membrane – an example, PVAm

- Mechanism of separation: **diffusion through a non-porous membrane + carrier transport.** The **driving force** will thus be the partial pressure difference of the gases in the feed and permeate **and** the concentration difference of the complexed component



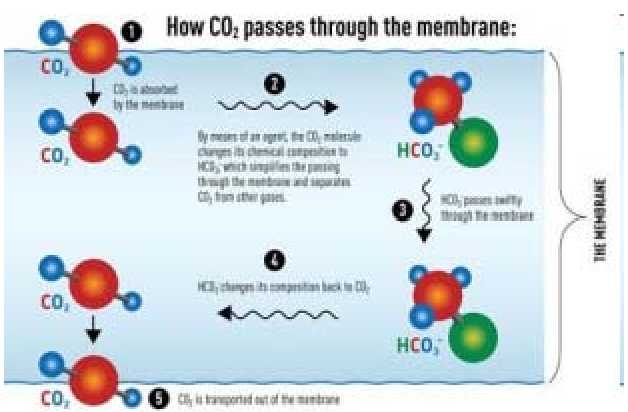
$$J_i = \frac{P_i}{l}\left(p_h x_i - p_l y_i\right)$$

1) Separation by solution-diffusion

$$P = D \cdot S \qquad c_i = S_i . p_i$$

$$J_i = \frac{D_i}{l}\left(c_{i,0} - c_{i,l}\right) + \frac{D_{ic}}{l}\left(c_{ic,0} - c_{ic,l}\right)$$

2) Carrier added

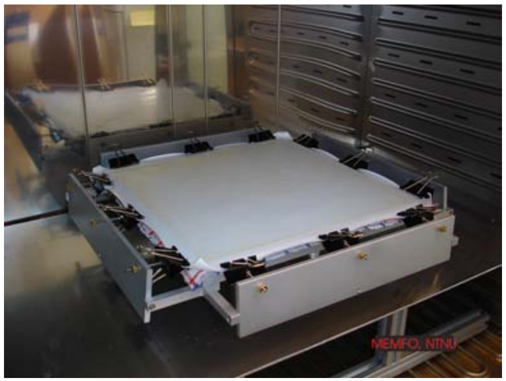


Facilitated transport in polyvinylamine (PVAm):

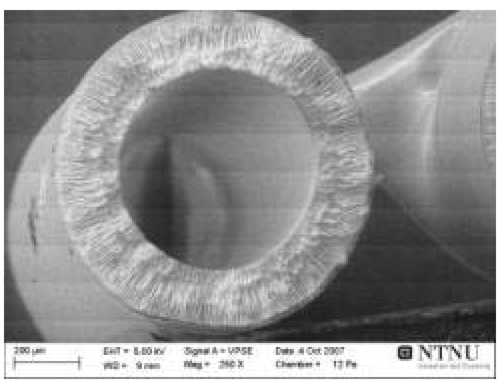
–The amino group contributes to transport of CO_2 through membrane as a bicarbonate ion (HCO_3-) in the wet membrane while N_2 is being retained.

– CO_2 transport through the membrane is attributed to this carrier effect along with the Fickian diffusion.

The FSC-membrane for CO_2-capture developed at NTNU is currently being upscaled to a small pilot in collaboration with industry and also demonstrated at EDP power plant, Portugal



This is what we have – large sheets



This is what we want in a pilot – hollow fibers

Process conditions:

- Humidity of gas stream; >75%RH
- Temperature should be below 70°C
- Pressure 2 – 8 bar

Current results (in lab):

CO_2-permeance > 1 $m^3(STP)/m^2 \cdot h \cdot bar$

CO_2/N_2 selectivity > 200

$$J_A = \frac{D_A}{l}(c_{A,0} - c_{A,l}) + \frac{D_{AC}}{l}(c_{AC,0} - c_{AC,l})$$

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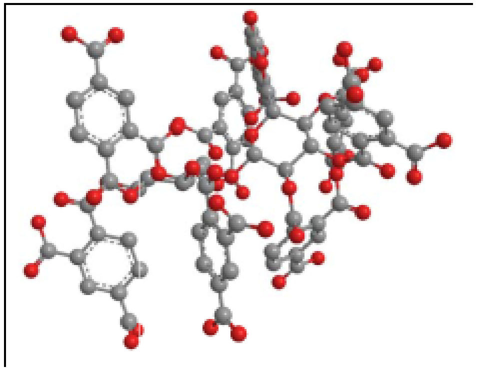
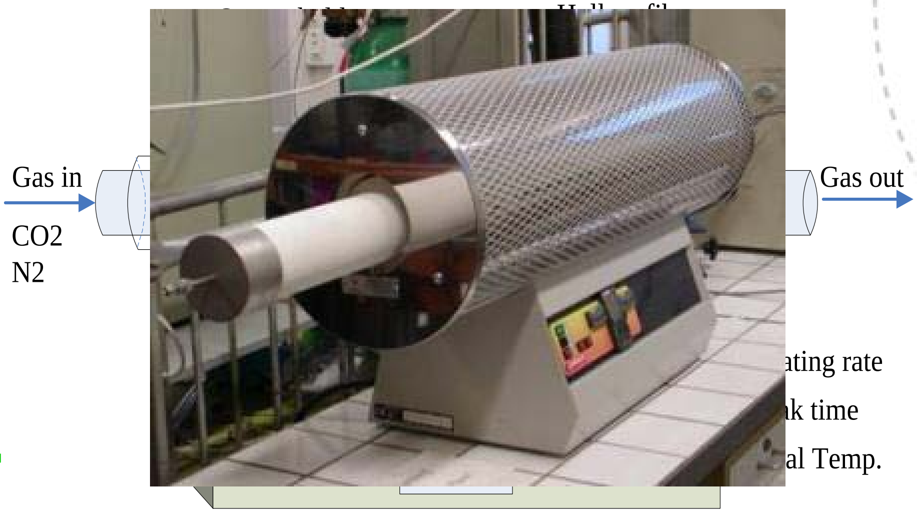
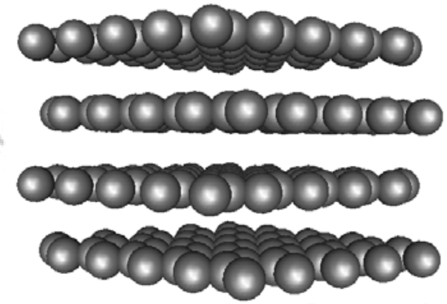
3) Pore tailored membranes; example: Carbon MS



Cellulosic precursor



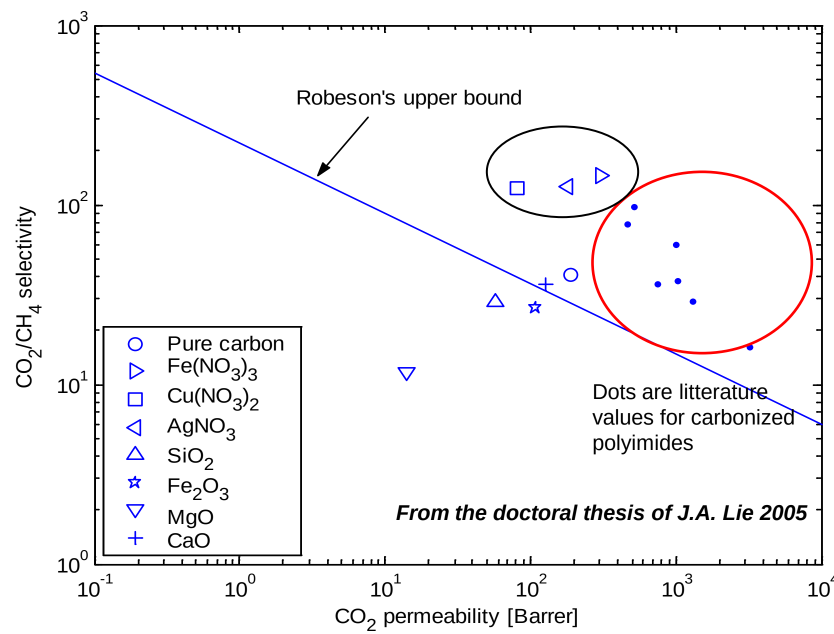


Ideal carbon structure

Tailoring the pore size:

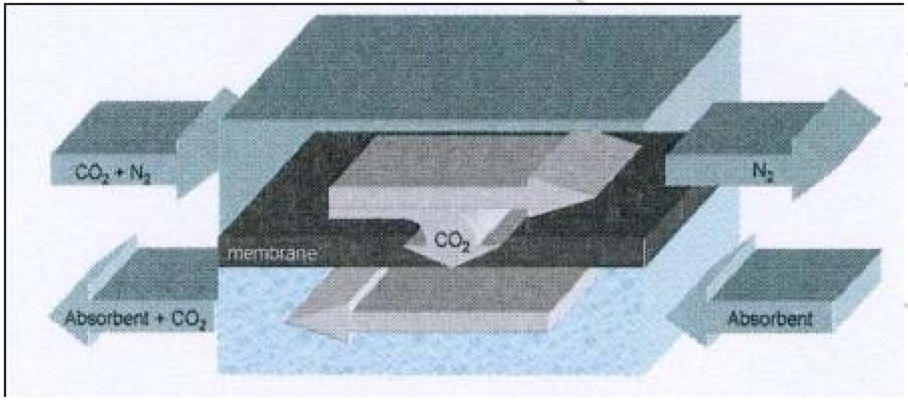
Carbonization parameters

- Temperature (500-1000 °C)
- Heating rate
- Soak time
- Atmosphere (vacuum or purge gas)
- Purge gas flow rate



Other types: Membrane contactor for CO_2-removal

- The membrane function is
  - To be a barrier between the gas and absorbent liquid
- Advantages:
  - Compact system
  - No direct contact between gas and liquid phases
  - Reduces problems such as liquid entrainment and foaming
  - Lower Δp



Ref.: figure from the PhD-work of K. N. Seglem

Pore radius in membrane <u>depends on La Place eq.:</u>
ΔP; over membrane
γ; surface tension of liquid
$\cos\theta$; wetting angle

$$r_p = \frac{2\gamma}{\Delta P}\cos\theta$$

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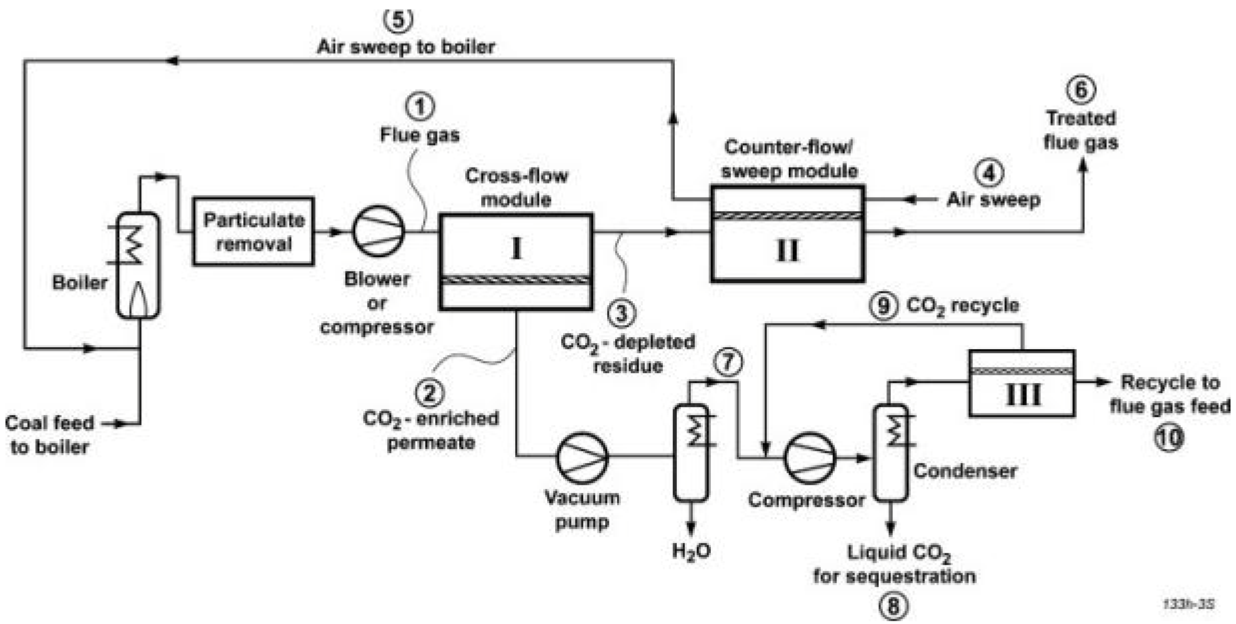
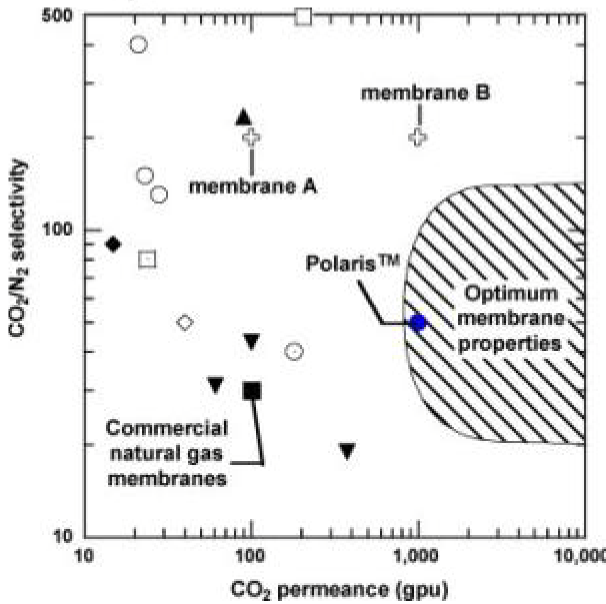
..not only the membrane itself, but also creative process solutions are important..





- ***Ref.: T.C. Merkel et al., J. Membr. Sci., 359 (1-2) 2010: Two step process, counter-current sweep***
- This membrane has a permeance of 1000 GPU (~2.7 m^3(STP)/($m^2 \cdot h \cdot bar$)), with only a selectivity $CO_2/N_2 = 50$ *(→ high flux, low selectivity)*
- This design dramatically reduces the membrane area and energy demand while also meeting the product spesification for CO_2 purity (> 95%)
- Challenges are in the process design rather than the membrane

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Challenges using polymer membranes for CO_2 capture in flue gas streams

CHALLENGES TO BE ADRESSED

1. ”Standard” polymers may swell
2. Driving force may be too low for ”standard” membranes
3. Durability towards SO_2, NOx, fly ash not good over time
4. Permeance or selectivity is too low

ACTIONS

1. Materials can be crosslinked, gas may have to be dried
2. Work on the process design or redesign the membrane
3. FGD must be installed / filters for fly ash
4. Still not good enough?

   WORK ON A DIFFERENT MATERIAL!

Creative design for materials with optimized separation properties for CO2 is ongoing all over the world – also with the Memfo group at NTNU

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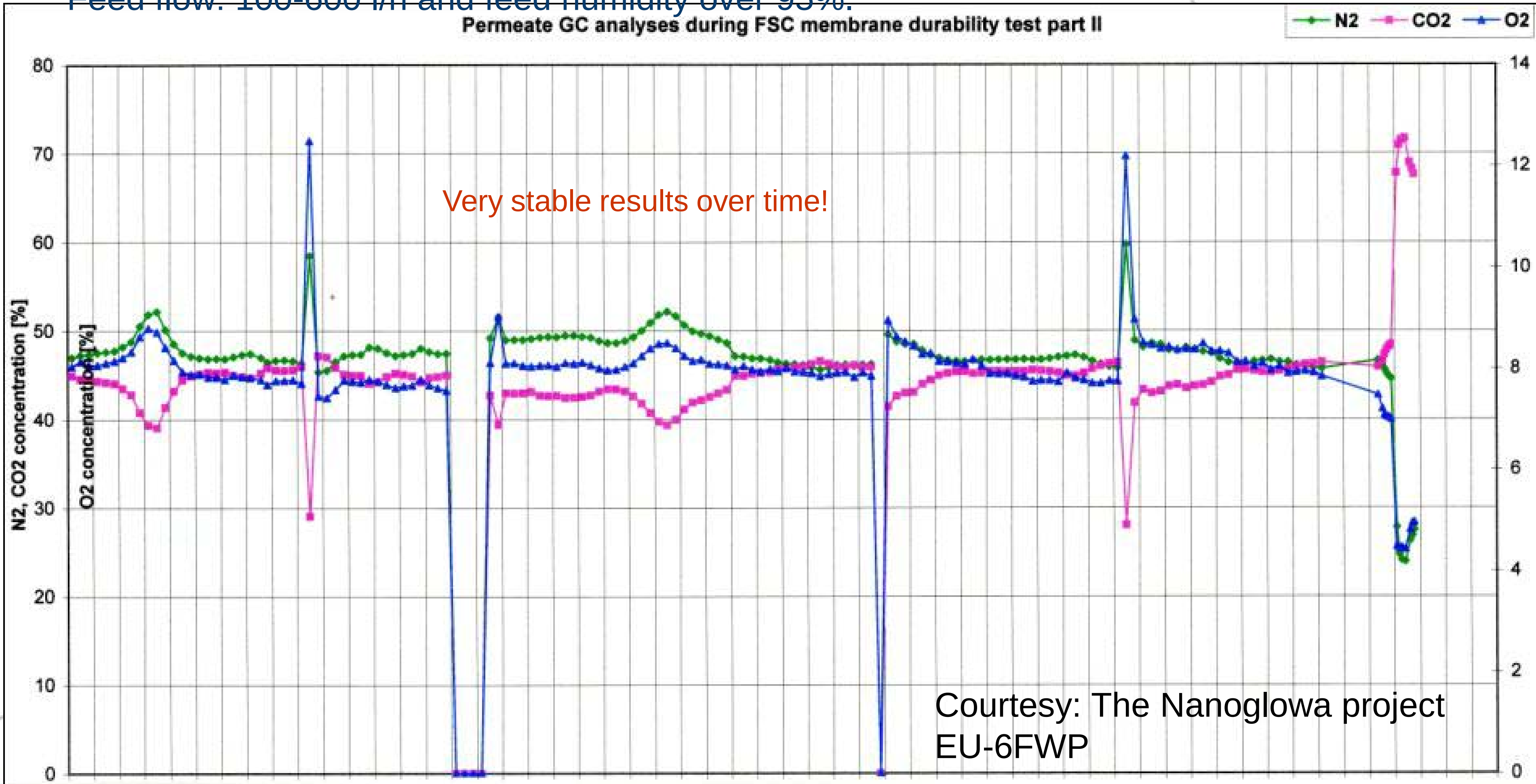
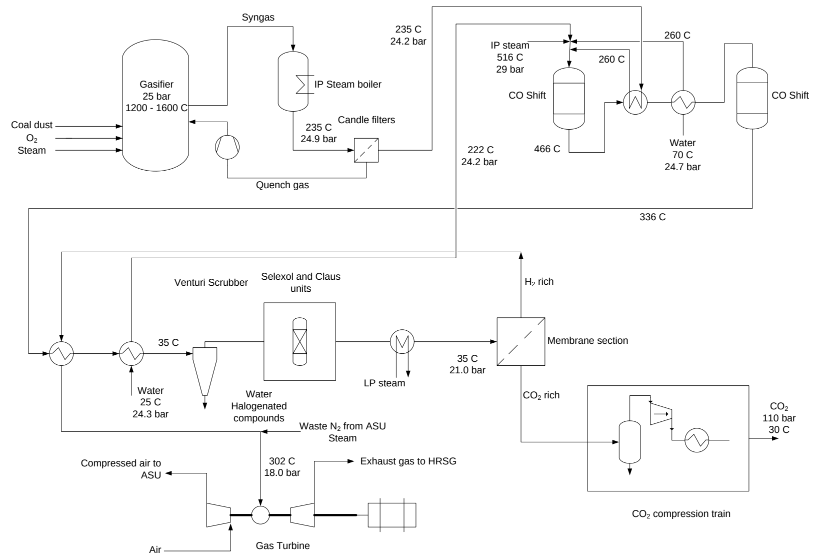
Durability of the FSC-membrane developed at NTNU has been tested, for 500 hours (synthetic flue gas) and currently real flue gas (coal), 2 weeks (ongoing)

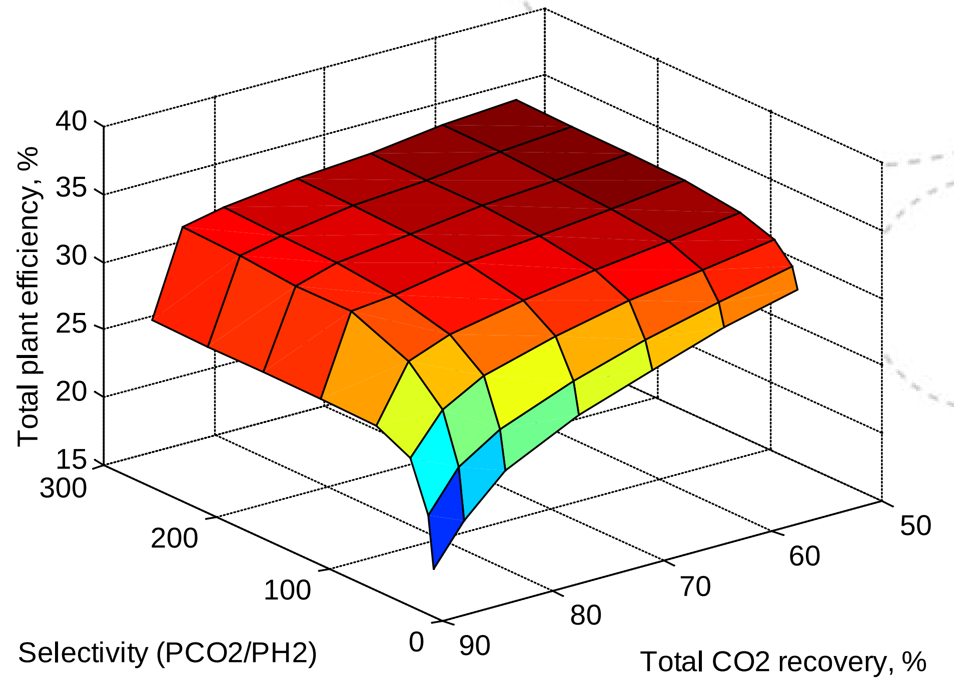
Process conditions : P feed 1.05-1.3 bar, permeate vacuum 250-100 mbar,
Feed:16 %CO_2 78% N_2, 5% O_2, 200 ppm SO_2, 200 ppm NOx
Temperature: 30°C and 50°C,
Feed flow: 100-600 l/h and feed humidity over 95%.



Courtesy: The Nanoglowa project EU-6FWP

Simulations/modeling and experiments should go hand in hand





- *IGCC (precombustion)* – flow diagram (left) with demands on membrane performance with respect to plant efficiency (right)

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Conclusions

- Membranes are clearly one of the emerging technologies for CCS
- There are already pilot testing ongoing (Europe, USA)
- Membranes represent an environmental friendly technology, no solvents – no hazardeous by-products
- Compact, modular solutions with small footprint (area)
- With optimized separation properties (the material), less demand on energy than (current) absorption processes

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Thank you for your attention

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Statoil

NanoGloWa EU-6FWP

Our ”Memfo” membrane group for good research