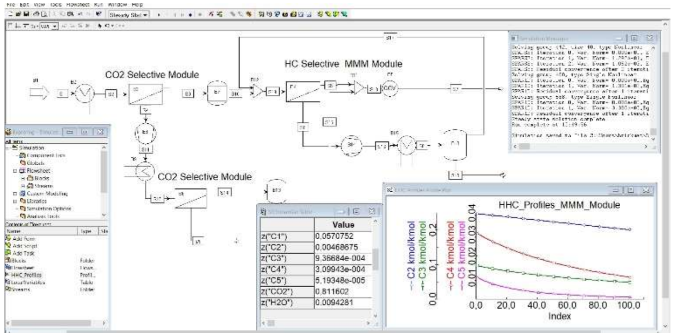
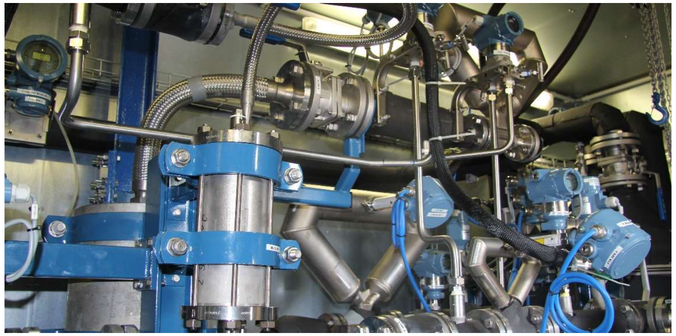
# MEMBRANE TECHNOLOGY FOR THE SEPARATION OF $H_2$ FROM NATURAL GAS



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Helmholtz-Zentrum Geesthacht
Zentrum für Material- und Küstenforschung

EERA Joint Programme FCH

Virtual, 28.10.2020

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- Introduction
- Membranes for $H_2$ applications
- Transport mechanisms
- Modules, modelling and simulation
- Application examples
- Summary and outlook



It will be a subjective, polymer membrane based perspective

# INTRODUCTION

## Potential of membrane processes

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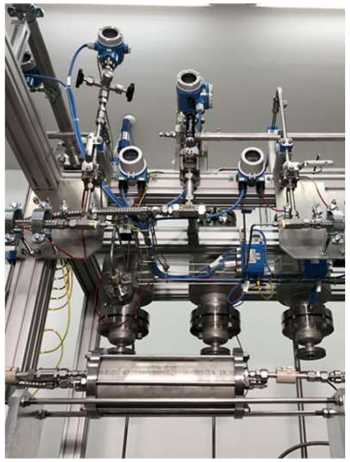
- $H_2$ separation by membranes is established
  - Ammonia synthesis
  - Refinery processes
  - Methanol production
- General advantages
  - Low energy consumption
  - Steady state process and less moving parts than PSA
  - Modular plant design and small footprint
- Well suited for
  - Process integration and hybrid processes
  - Applications in the $H_2$ economy
  - Quick start-up and shut-down
- More than just $H_2$ selective membranes



# MEMBRANE GAS SEPARATION: RENEWABLE ENERGIES AND CHANGING RAW MATERIAL BASE

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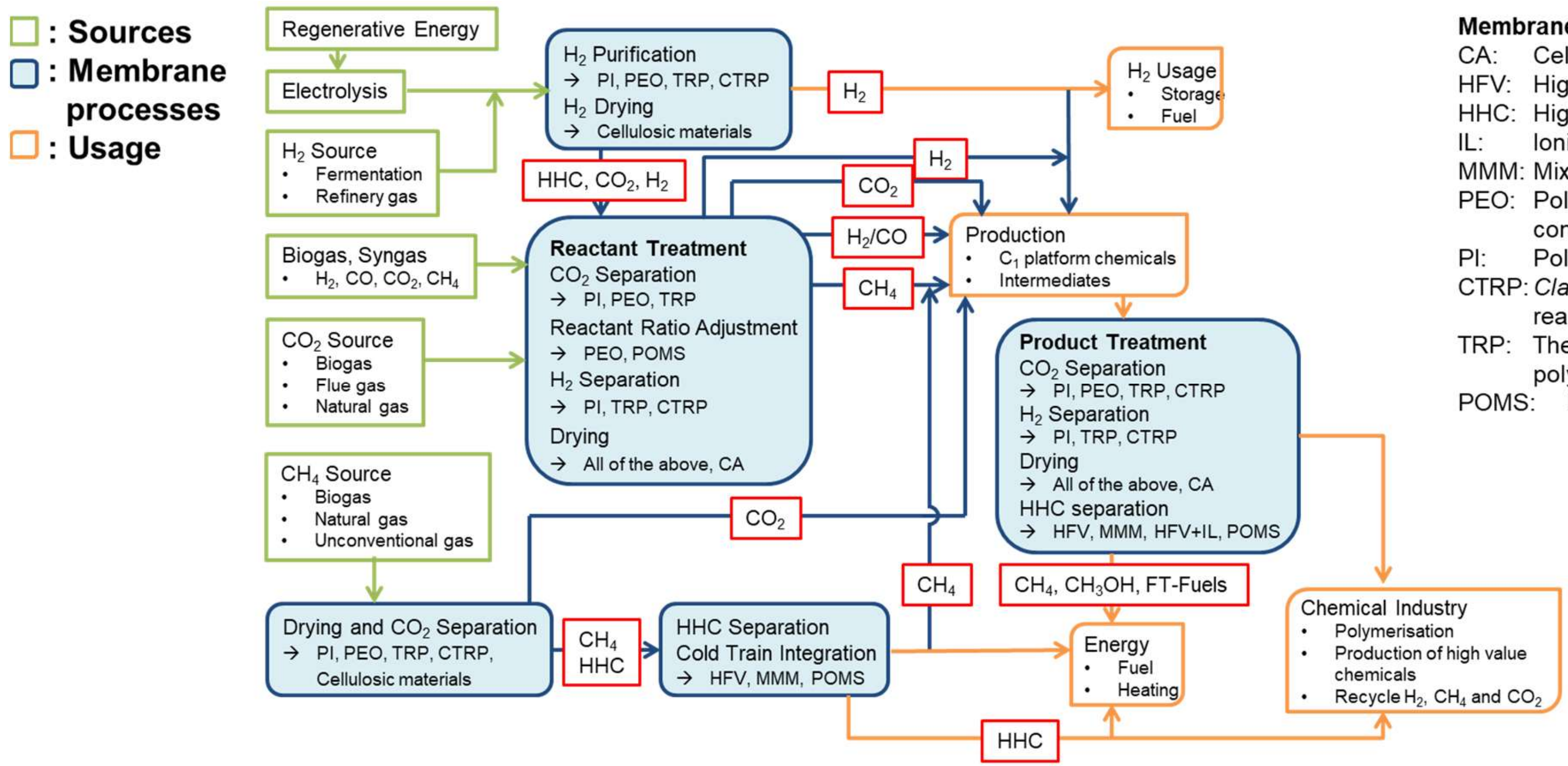


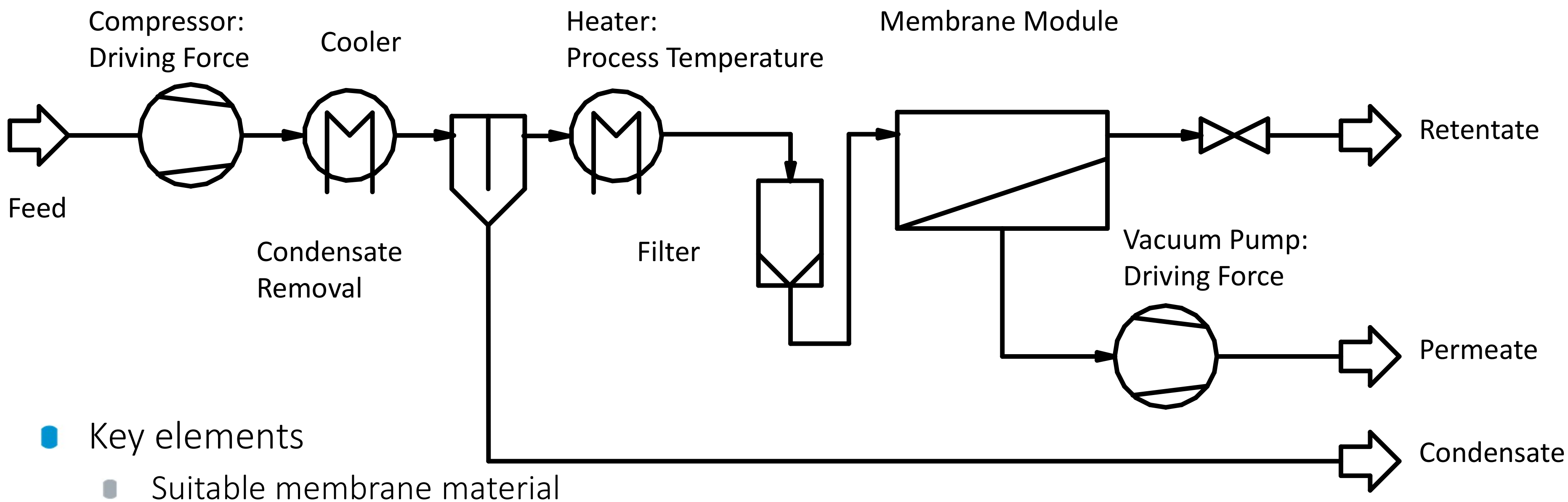

**Membrane materials**

CA: Cellulose acetate
HFV: High free volume polymer
HHC: Higher hydrocarbon
IL: Ionic liquid
MMM: Mixed matrix membrane
PEO: Polyethylene oxide containing blockcopolymers
PI: Polyimides
CTRP: *Claisen* thermally rearranged polymer
TRP: Thermally rearranged polymer
POMS: Polyoctylmethylsiloxane

# MEMBRANE GAS SEPARATION PROCESS

## Not just the membrane






- Key elements
  - Suitable membrane material
  - Membrane production and performance
  - Module that transfer membrane's properties
  - Accurate models for membrane modules
  - Process design

# GAS SEPARATION INVOLVING $H_2$

## Not just $H_2$ separation

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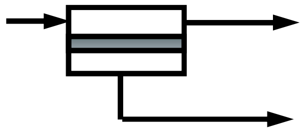
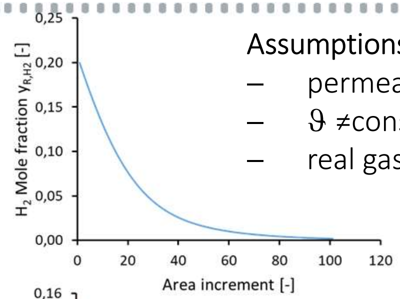
- $H_2$ separation from $CH_4$ with a polyimide (MATRIMID®) membrane

$\dot{V}_F = 100 \frac{Nm^3}{h}$
$p_F = 64\ bar$
$\vartheta_F = 25°C$
$y_{F,H2} = 0{,}20$

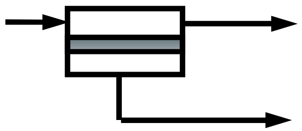


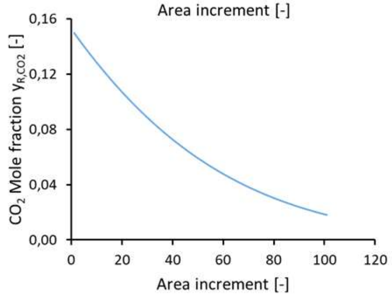



Assumptions:
- permeances = f(ϑ,p,y)
- ϑ ≠const.
- real gas (SRK EoS)

- $CO_2$ separation from / drying of $H_2$ with a PolyActive™ membrane

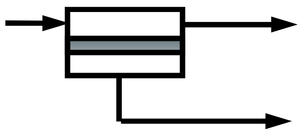
$\dot{V}_F = 100 \frac{Nm^3}{h}$
$p_F = 15\ bar$
$\vartheta_F = 25°C$
$y_{F,CO2} = 0{,}15$
$y_{F,H2O} = 0{,}001$

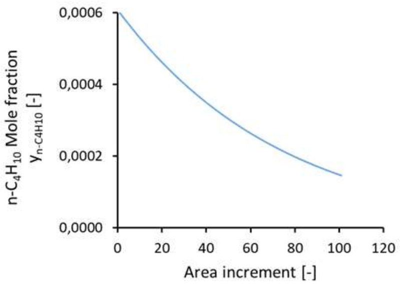





- Higher hydrocarbon (HHC) separation from $H_2$ with a silicon rubber (POMS) membrane

$\dot{V}_F = 100 \frac{Nm^3}{h}$
$p_F = 65\ bar$
$\vartheta_F = 25°C$
$y_{F,H2} = 0{,}8759$ $y_{F,C4H10} = 0{,}0006$
$y_{F,C2H6} = 0{,}016$ $y_{F,CO2} = 0{,}007$
$y_{F,C3H8} = 0{,}0005$ $y_{F,N2} = 0{,}1$





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# MEMBRANE CLASSIFICATION

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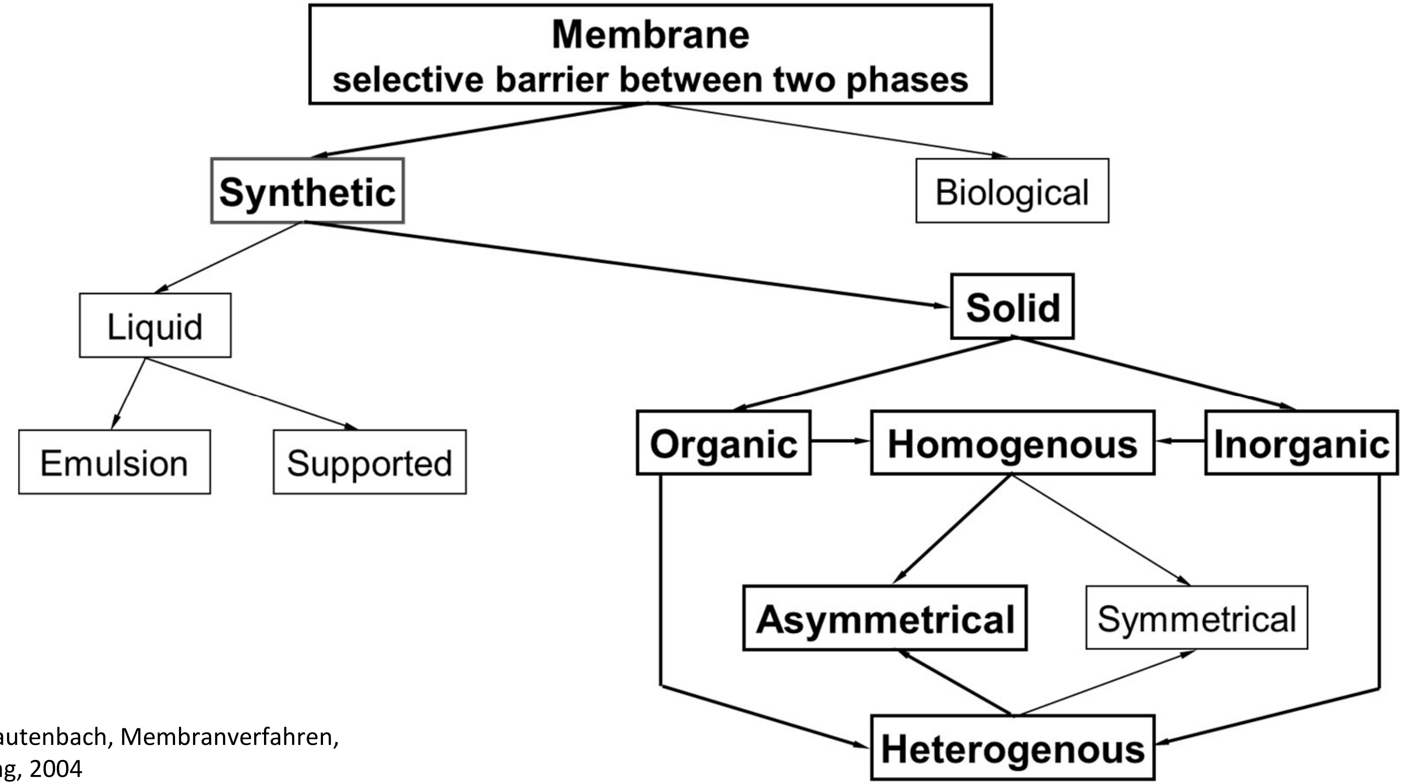


T. Melin, R. Rautenbach, Membranverfahren,
Springer Verlag, 2004

# GAS SEPARATION MEMBRANES

## Transport mechanisms

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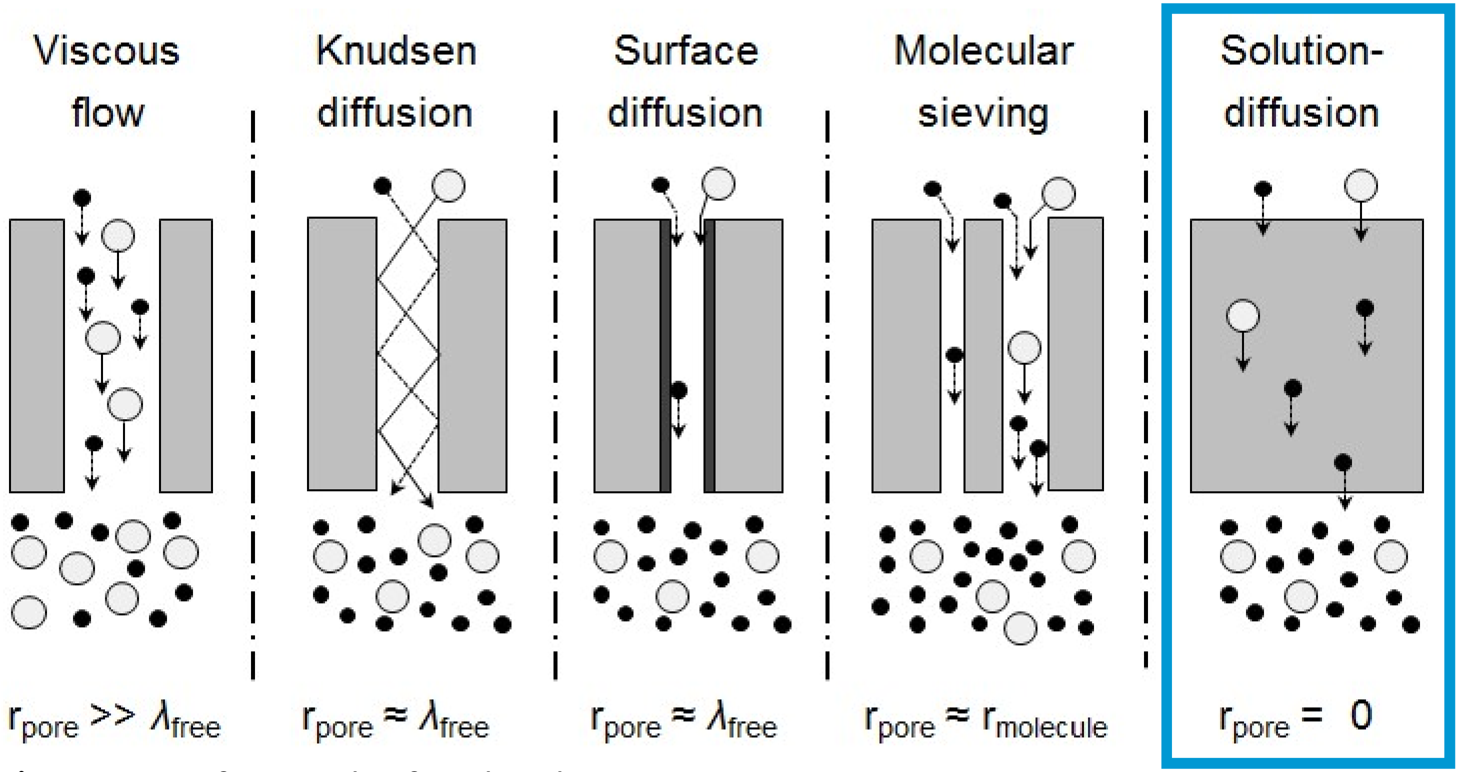


$\lambda_{free}$: mean free path of molecule

# POLYMERIC MEMBRANE TYPES

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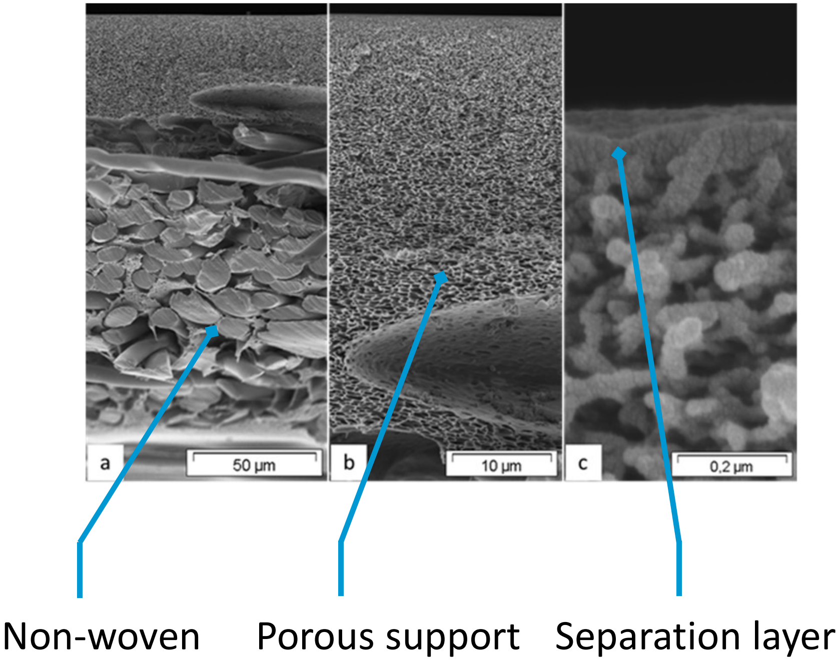
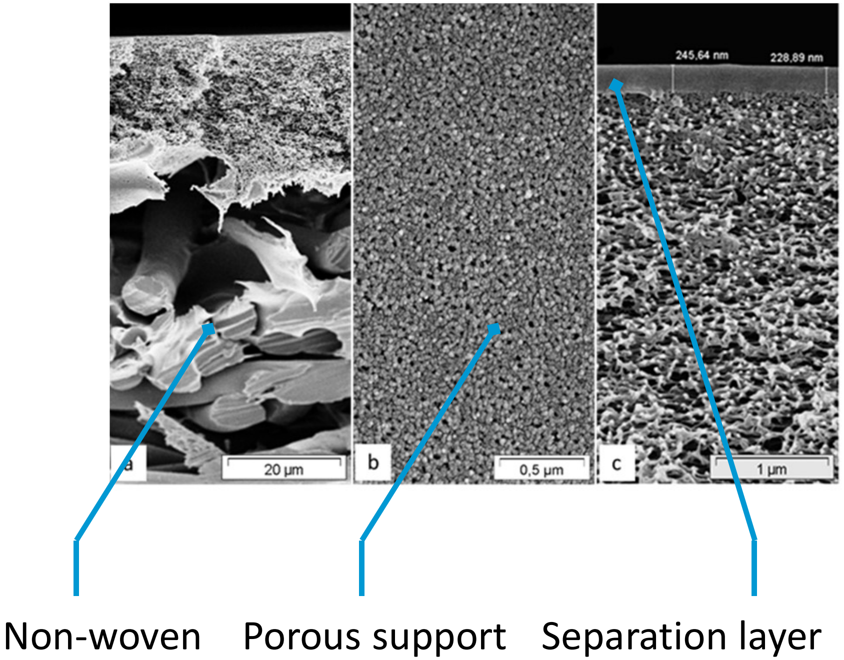
## Asymmetric membrane




## Thin film composite membrane



# POLYMERS INVESTIGATED FOR $H_2/CH_4$ SEPARATION

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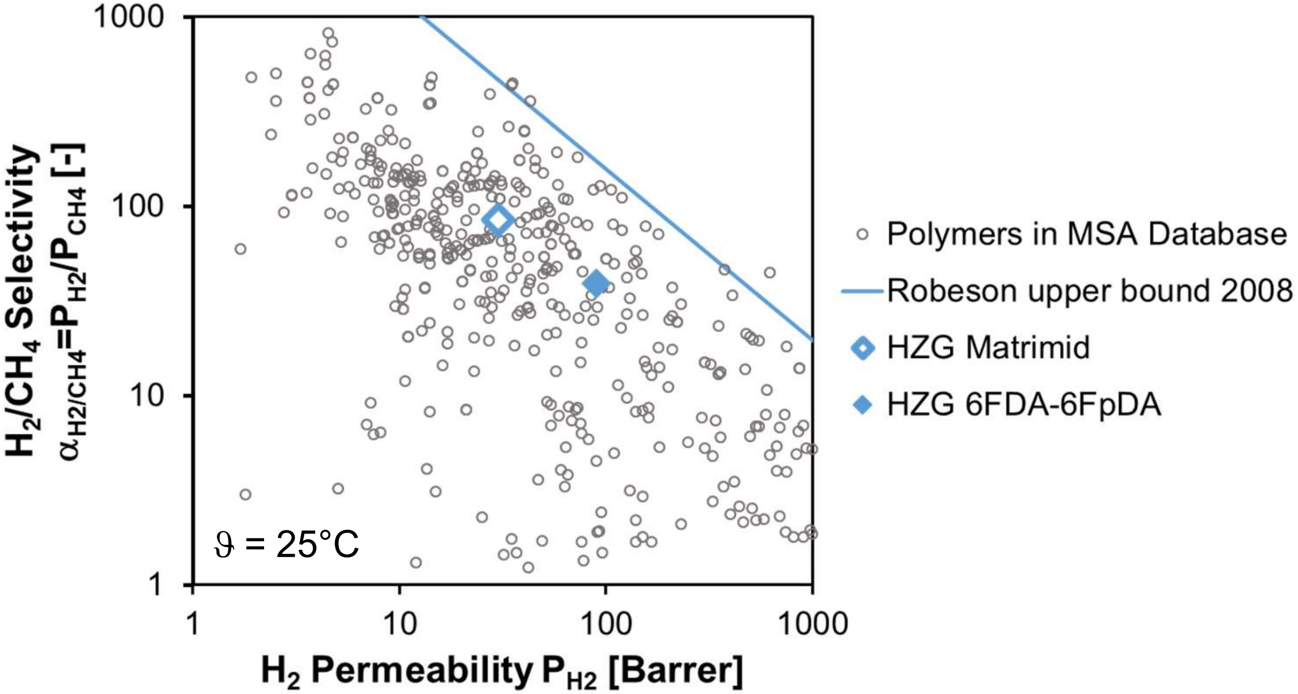


L.M. Robeson, J. Membr. Sci. 320 (2008) 390-400.
Membrane Society of Australasia Database:
https://www.membrane-australasia.org/polymer-gas-separation-membranes/

1 Barrer = 2,346 $10^{-16}$ kmol m $m^{-2}$ $s^{-1}$ $kPa^{-1}$

# APPLICATION AREAS AND COMPANIES PRODUCING COMMERCIAL GAS SEPARATION MEMBRANES

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| Polymer | Membrane type | Applications | Company |
|---|---|---|---|
| Cellulose Acetate | As, TFCM | $CO_2/CH_4$ | Separex (UOP), Dow, Envirogenics GASEP |
| Ethyl Cellulose | As, TFCM | $CO_2/CH_4$ | HZG |
| Poly(4-methylpentene-1) | SymF | $O_2/N_2$ | Dow |
| Polysulphone | As | $H_2/N_2$, $CO_2/CH_4$, **$H_2/CH_4$**, $H_2/CO$ | Permea (Air Products) |
| Polycarbonate, incl tetrabromo | As | $O_2/N_2$, $H_2/N_2$, **$H_2/CH_4$** | Generon, DOW |
| Poly(phenylene oxide) | As | $O_2/N_2$ | Aquillo, Parker-Hannifin,UBE |
| Polyimide | As | $O_2/N_2$, $H_20$/Air, **$H_2/(N_2$, CO, $C_{1+})$** | MEDAL (Air Liquide), IMS (Praxair), UBE, HZG |
| Polyaramid | As | $O_2/N_2$ | MEDAL (Air Liquide) |
| P84 copolyimide | As | $CO_2/CH_4$, **$H_2/CH_4$** and others | Evonik Sepuran |
| Poly(vinyl trimethyl silane) | As, TFCM | $O_2/N_2$ | USSR, HZG |
| Teflon AF, Perfluoro polymers | TFCM | VOC/$N_2$, $O_2/N_2$ | MTR, CMS |
| Poly(dimethyl siloxane)<br>Poly(octyl methyl siloxane) | TFCM | VOC/Air, $O_2/N_2$, Nat. Gas dewpointing | **HZG**, MTR, Permea, UOP |
| PEBAX, PolyActive | TFCM | $CO_2/N_2$, $CO_2/CH_4$, $CO_2$/Biogas | MTR, **HZG** |

As: asymmetric fiber or flat; SymF: symmetric hollow fiber; TFCM: Thin Film Composite Membrane

S. Shishastskiy at al., Proceedings PRES (2014).

# PRODUCTION THIN FILM COMPOSITE MEMBRANE

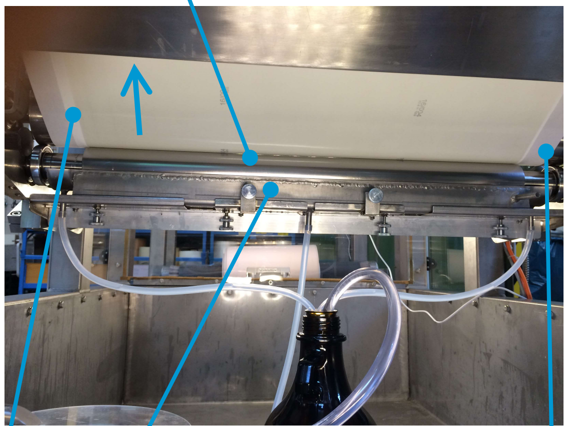


## Membrane coating machine

Batches up to 250 m length and 70 cm breadth

## Application of PolyActive™ Film

Wetted application roller and forming film



Reservoir filled with coating solution by means peristaltic pump

Poly(acrylo nitrile) layer

Polyester non-woven

# MIXED MATRIX MEMBRANES

## MATRIMID® and Activated Carbon

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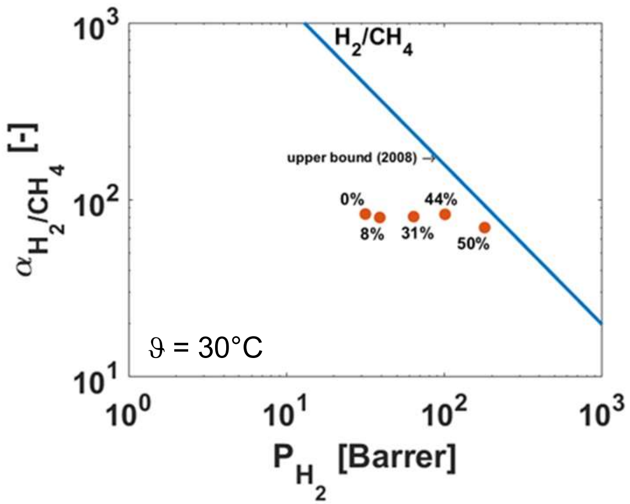


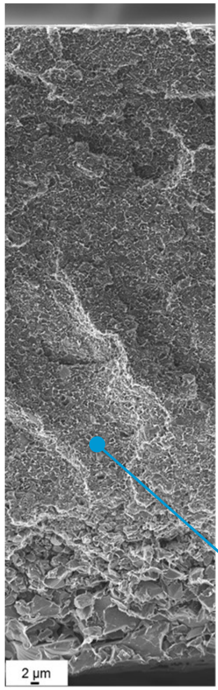


- Thick films
- Single gas measurements
- Potential for upscaling
- Asymmetric membrane required

MMM
50 vol.-% AC in
MATRIMID®

F. Weigelt et al., Polymers 10 (2018) 51.
L.M. Robeson, J. Membr. Sci. 320 (2008) 390-400.

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# MULTILAYER THIN FILM COMPOSITE MEMBRANE

## Transport visualisation

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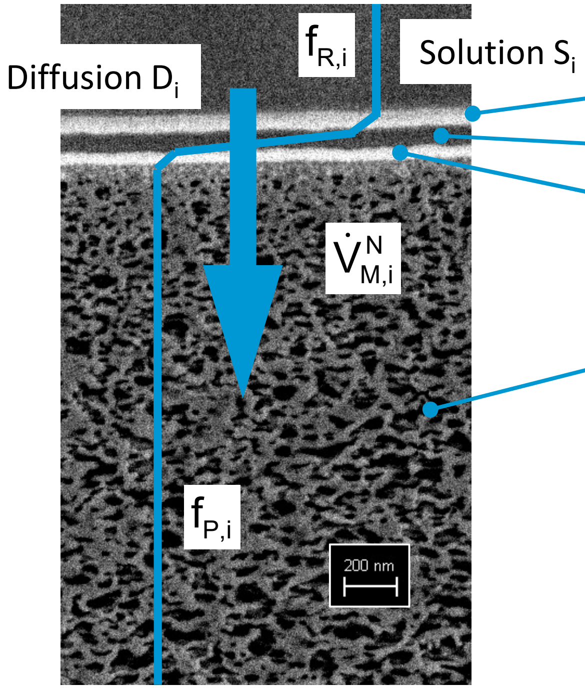


Dense protection layer (δ < 150 nm)

Dense separation layer (δ < 85 nm)

Dense gutter layer (δ < 150 nm)

Porous PAN Support (δ ~ 50 µm)

$$L_i = \frac{D_i \cdot S_i}{\delta} = \frac{\dot{V}^N_{M,i}}{A_M \cdot \left(f_{R,i} - f_{P,i}\right)}$$


S.J. Metz et al., J. Membrane Sci. 266 (2005) 51–61.
A. Car et al., Adv. Funct. Mater. 18 (2008) 2815–2823.
W. Yave et al., Nanotechnology 21 (2010) 395301.
T. Brinkmann et al., Engineering 3 (2017) 485-493.

# TRANSPORT MECHANISMS

## High flux and elevated pressure: Not only the membrane!

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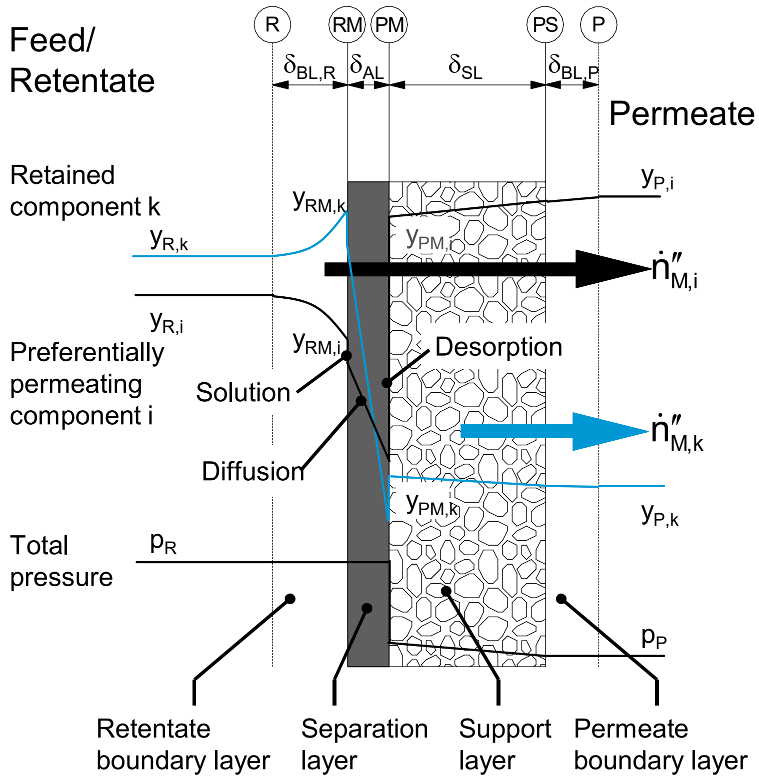
- Selective gas transport through the separation layer
  - Solution-diffusion mechanism
  - Driving force is difference of fugacities
- Real gas behaviour at high pressures
- Effect of gas flow on the retentate and permeate side
  - Concentration polarisation ($L\uparrow \Rightarrow \delta_{BL}\uparrow$, $p\uparrow \Rightarrow D\downarrow$)
  - Pressure drop
- Temperature changes
  - Joule-Thomson effect
- Transport through support layers
  - Mass transfer in porous layers



# ASSESS THE PERMEATION PERFORMANCE

## Example: MATRIMID® polyimide for $H_2$ separation

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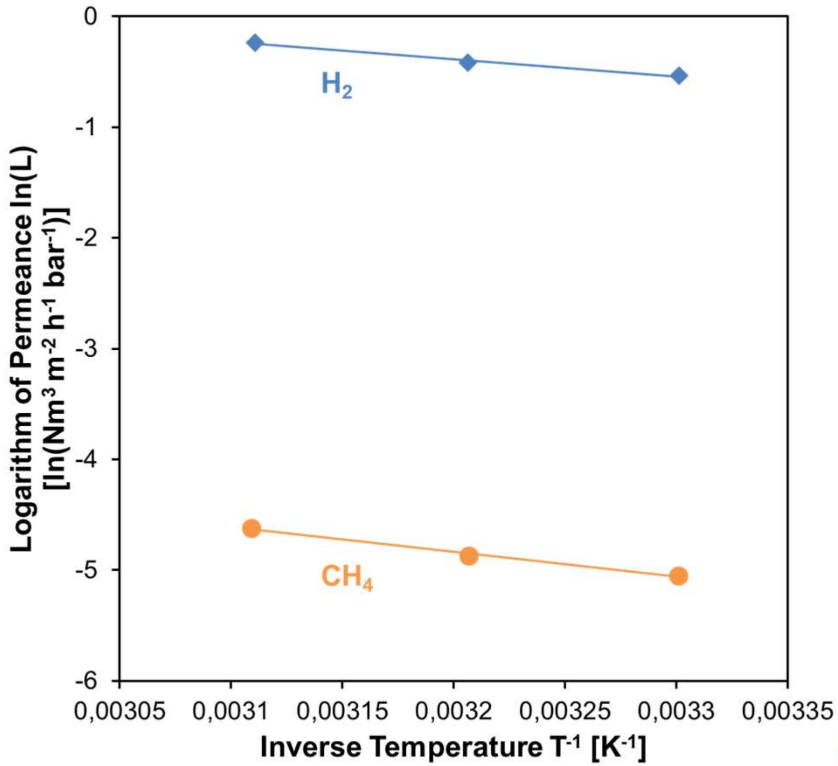
Single gas permeation measurements

- Pressure increase method:
  - ϑ = 30 to 50°C; p <1,3 bar
  - No swelling detected
  - Nearly ideal gases

⇒ Prediction of multicomponent permeation using single gas experimental data

- Arrhenius type relationship:

$$L = L_{\infty}^{0} \cdot exp\left(\frac{-E}{R \cdot T}\right)$$



# INFLUENCE OF PRESSURE RATIO AND SELECTIVITY

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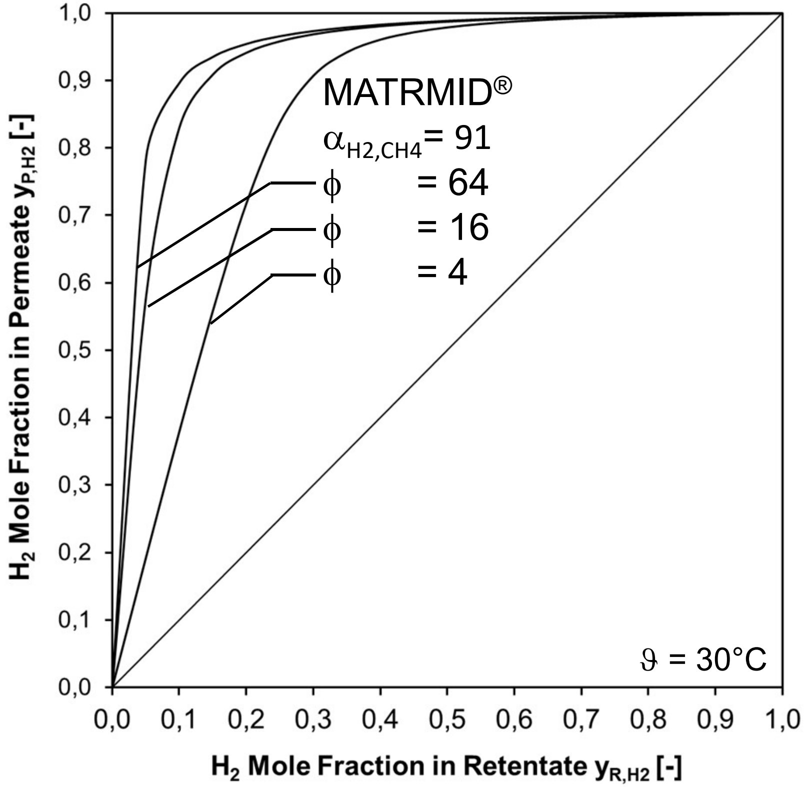


## $H_2/CH_4$ separation

- MATRIMID®
- Selectivity
  $\alpha_{H2/CH4} = 91$
- Pressure ratio
  $\phi = p_F/p_P$

$$y_{P,i} = \frac{\frac{1}{2}\cdot\left[1+\phi\cdot\left(y_{F,i}+\frac{1}{\alpha-1}\right)\right]}{-\sqrt{\left[\frac{1}{2}\cdot\left[1+\phi\cdot\left(y_{F,i}+\frac{1}{\alpha-1}\right)\right]\right]^2-\frac{\alpha\cdot\phi\cdot y_{F,i}}{\alpha-1}}}$$

$$\alpha = L_i/L_j;\ \phi = p_F/p_P$$


T. Melin, R. Rautenbach, Membranverfahren,
Springer Verlag, 2004

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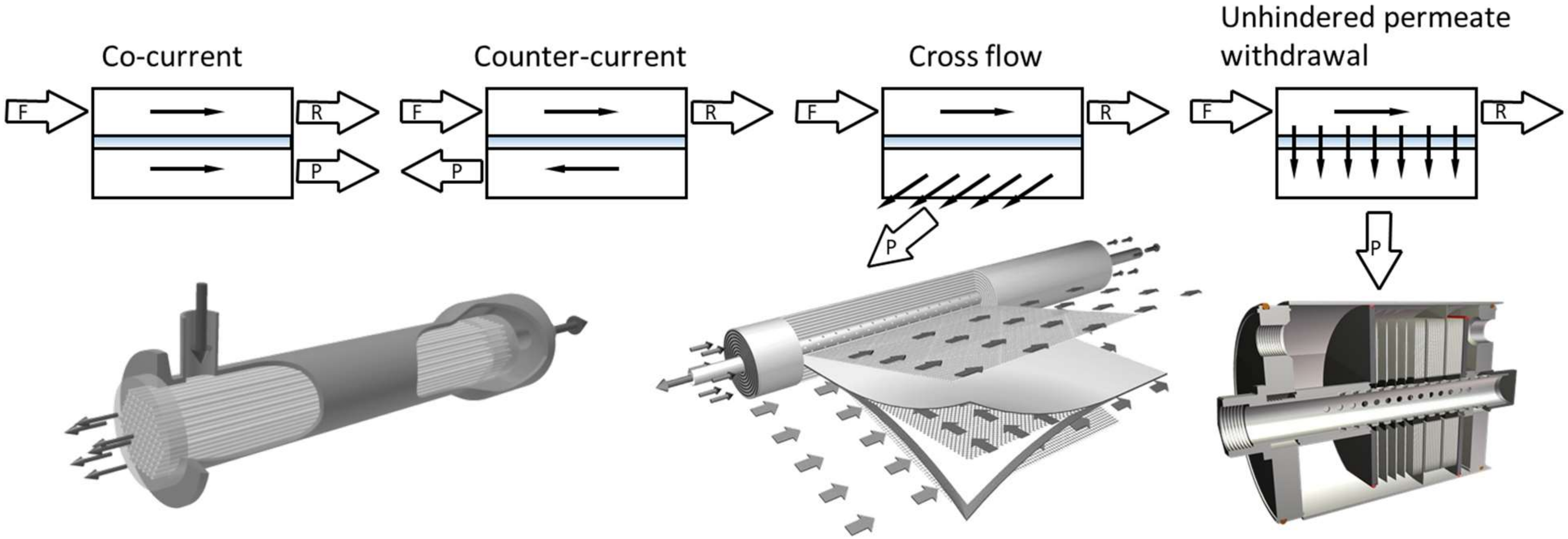
# MEMBRANE MODULES

## Transfer membrane's properties into process






- Hollow fibre/capillary/tubular module
- Spiral wound module
- Envelope type module

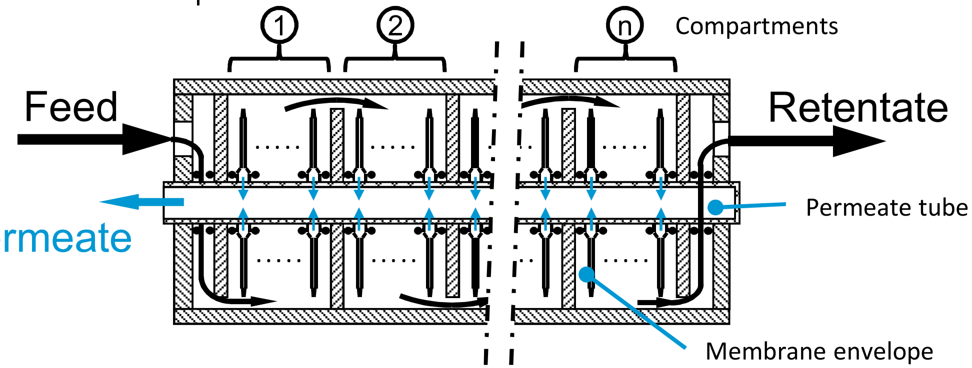
# ENVELOPE TYPE MODULE

## Flow patterns



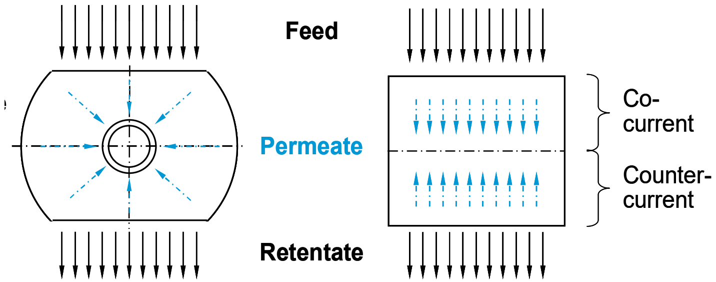
Pilot scale module

Module flow patterns




Top view membrane envelope

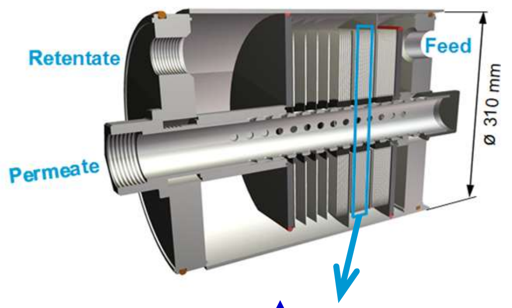
One dimensional representation

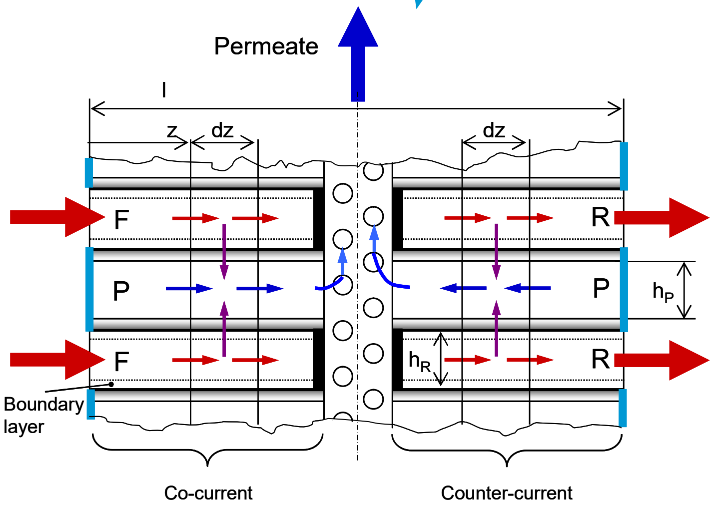



- Sub-divided into compartments
- Velocity can be controlled
- Short permeate pathways
- Adjustable membrane area
- No adhesives

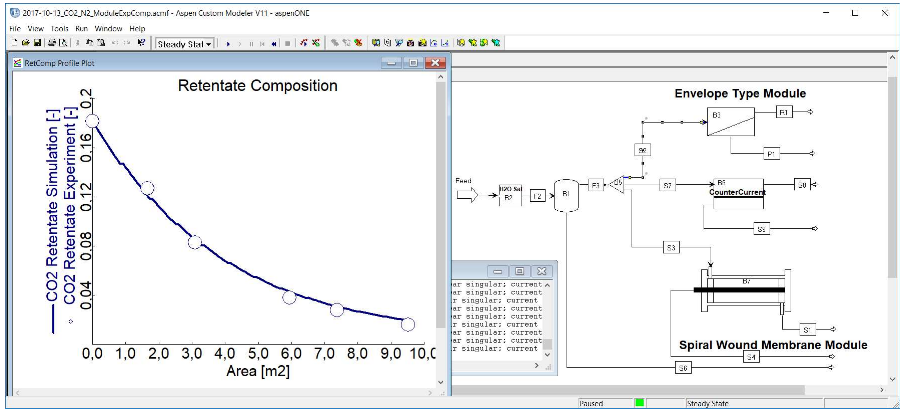
# COMPUTER AIDED SIMULATION OF ENVELOPE TYPE MEMBRANE MODULE





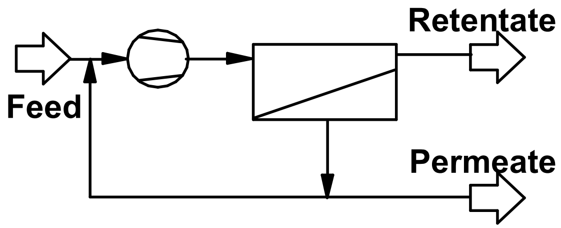

- Flow patterns: differential balances feed and permeate
- Permeation
- Equation of state
- Transport properties
- Concentration polarisation
- Implementation: Aspen Custom Modeler®




T. Brinkmann et al., Chem. Ing.Tech. 85 (2013) 1210–1220.

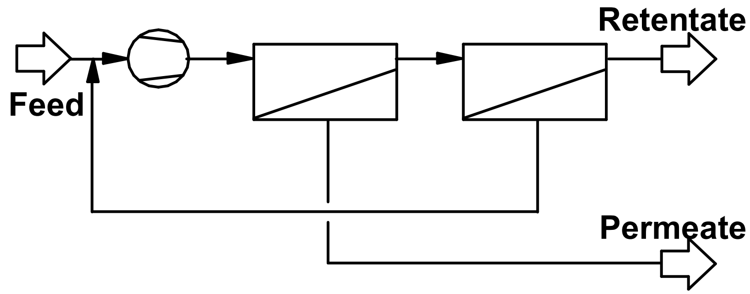
# MULTISTAGE CONCEPTS:
# ONE AND TWO STAGE CASCADES





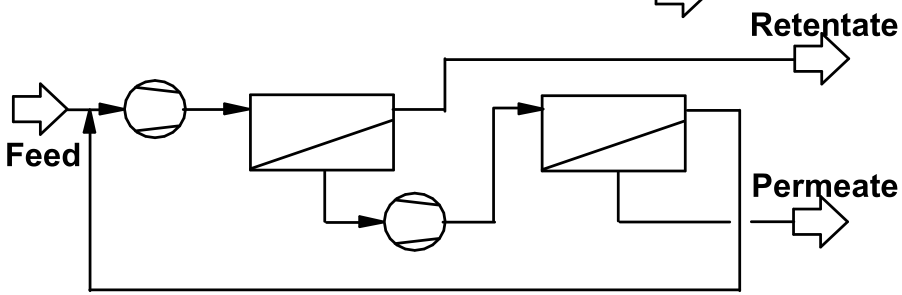

**Single stage (permeate recycle)**

- Retentate is product, minimise losses to permeate
- Increased membrane area




**Two stage stripping cascade (permeate recycle)**

- Retentate is product




**Two stage rectifying cascade (retentate recycle)**

- Permeate is product

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# CLASSICAL APPLICATION

## $H_2$ Recovery in refineries No. 1

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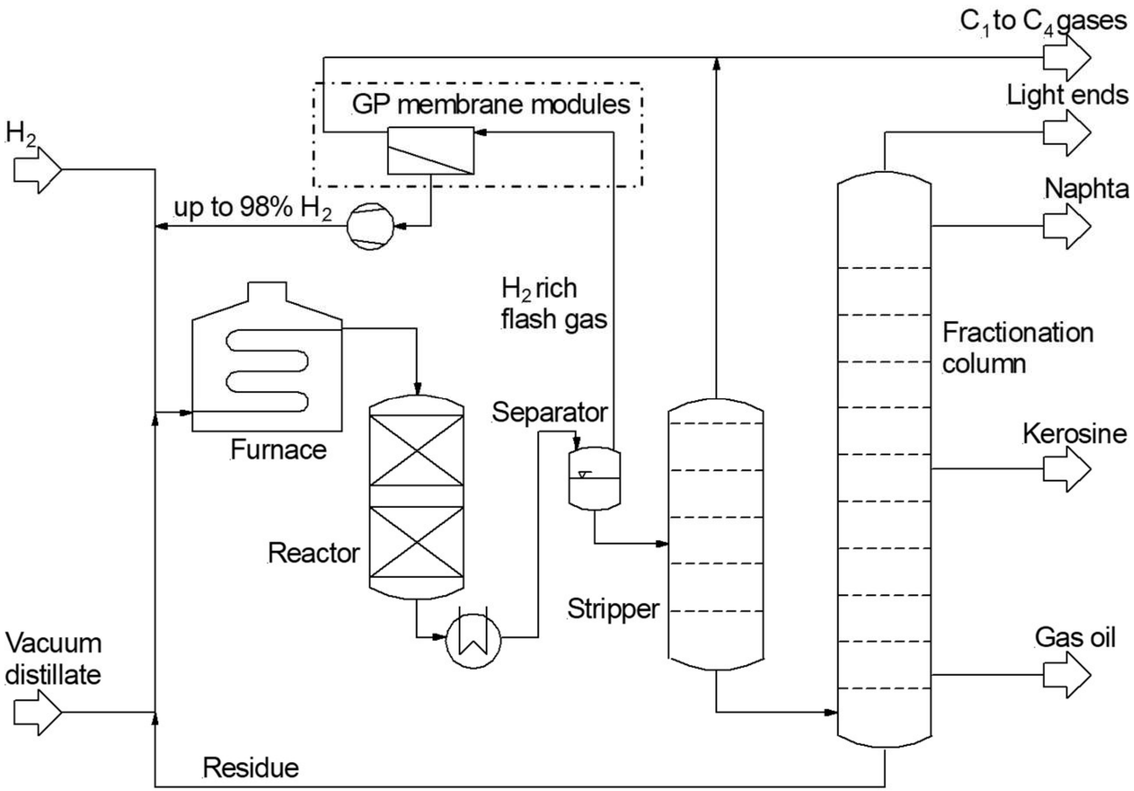
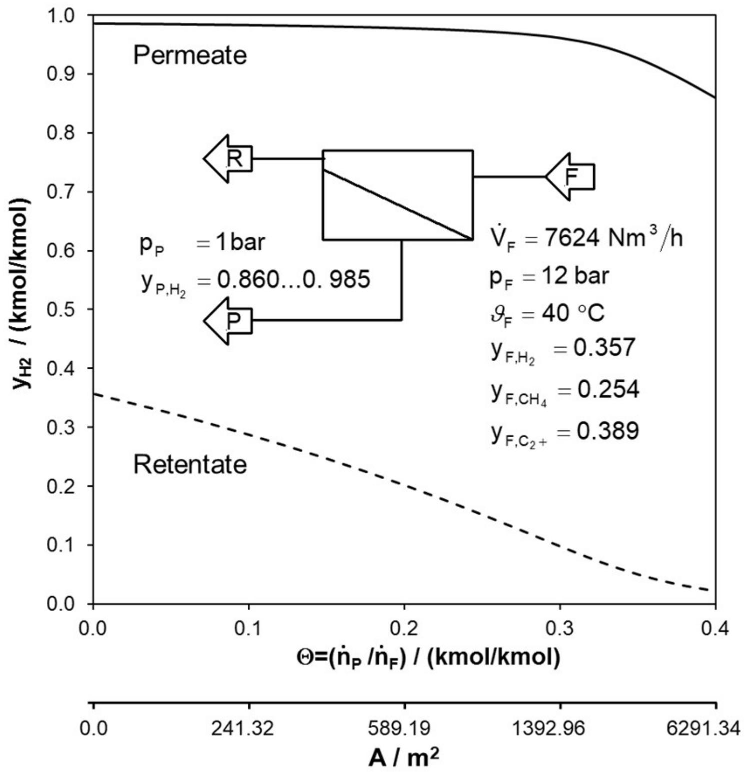


# CLASSICAL APPLICATION

## $H_2$ Recovery in refineries No. 2




- $H_2$ recovery in refineries established since 1980s
- Maximum purity: 98 to 99 mol.-%
- High purity for low stage cut (=recovery)
- Proven in industrial, multicomponent processes
- Example MATRIMID®

# COUPLING OF ENERGY GASES INTO THE SYSTEM

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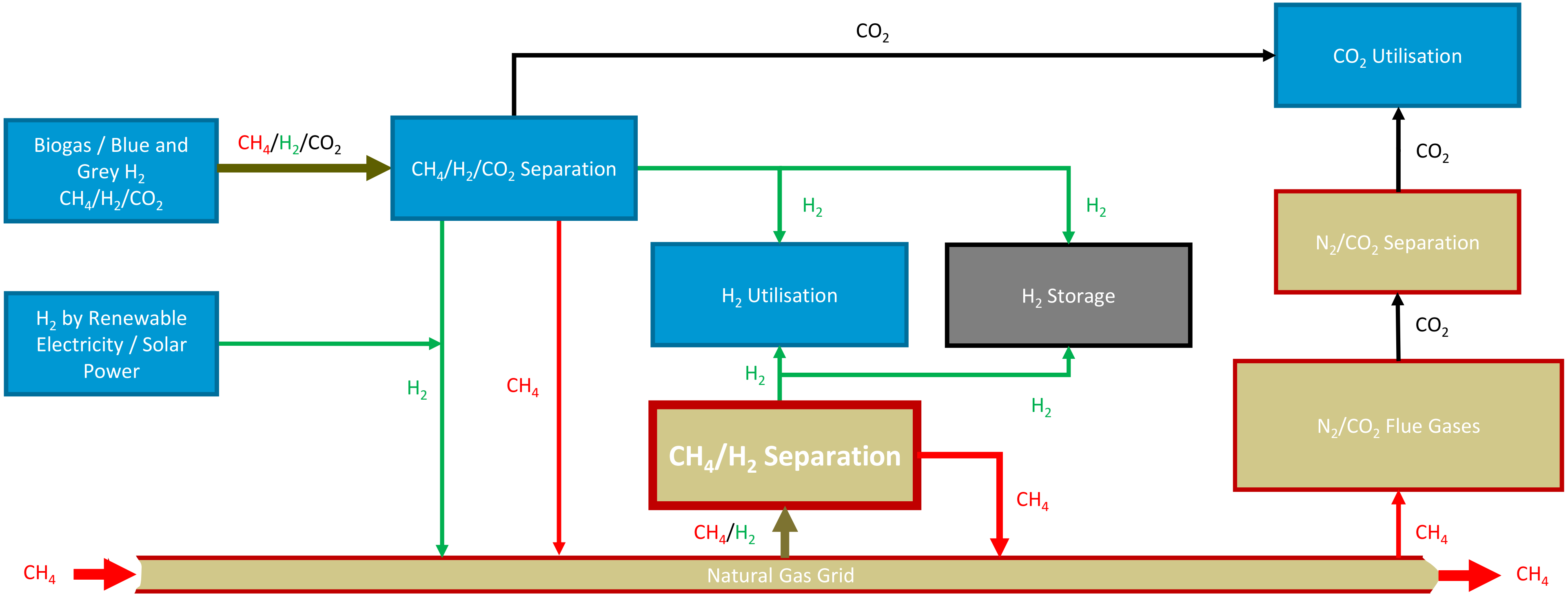


- Not shown: Drying, water always preferentially permeates

# $H_2$ SEPARATION FROM NATURAL GAS

## One stage MATRIMID® membrane

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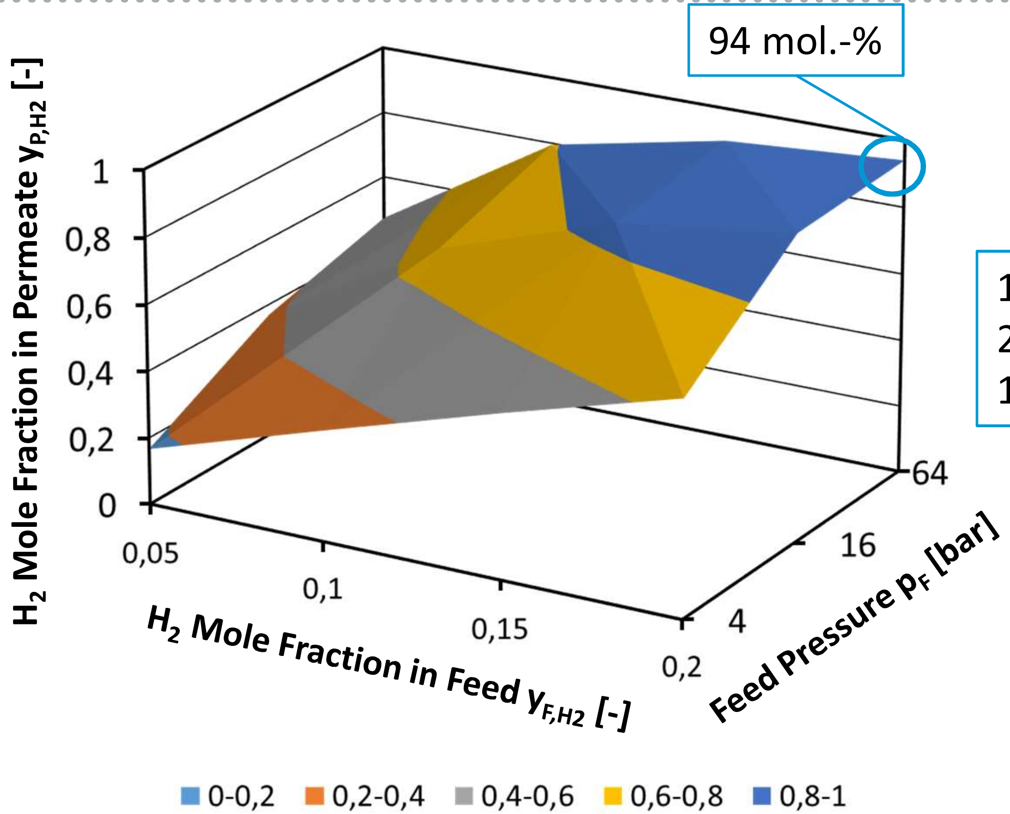


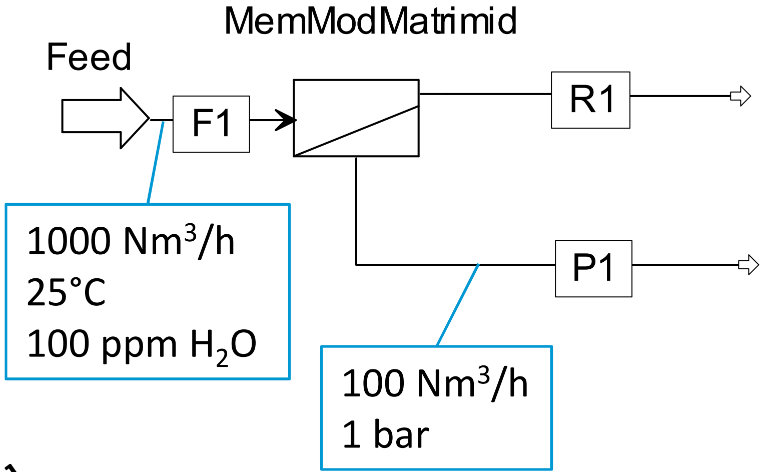

# $H_2$ SEPARATION FROM NATURAL GAS

## Two stage MATRIMID® membrane

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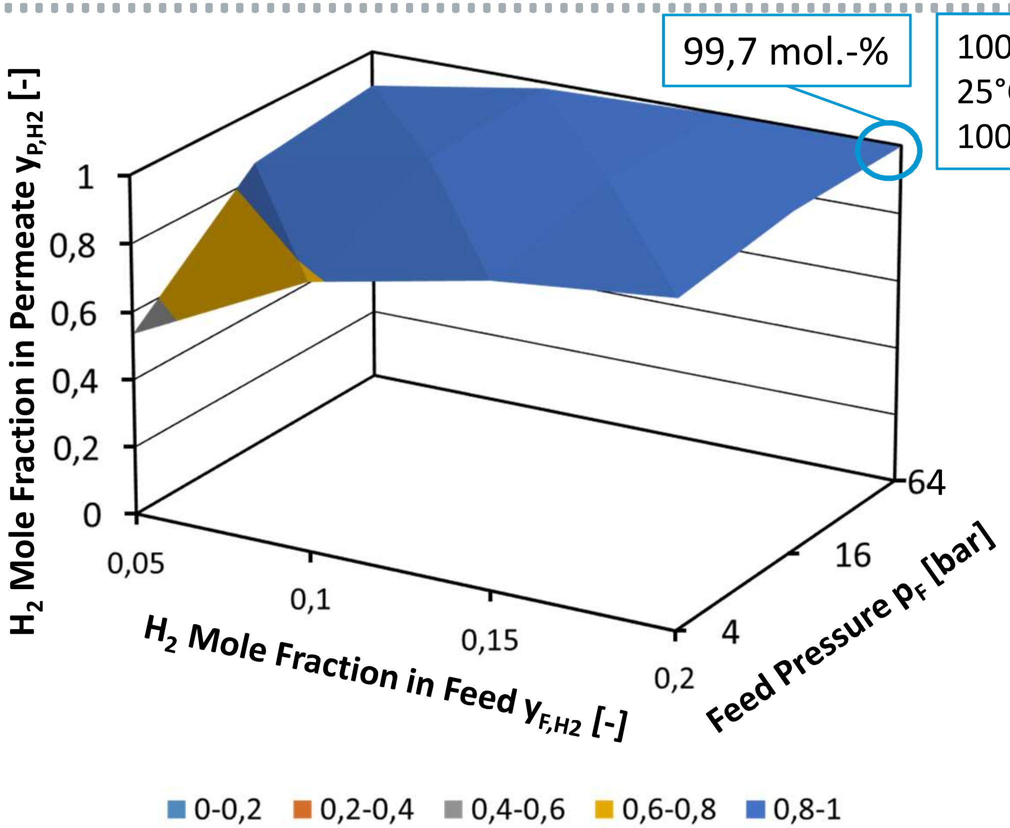


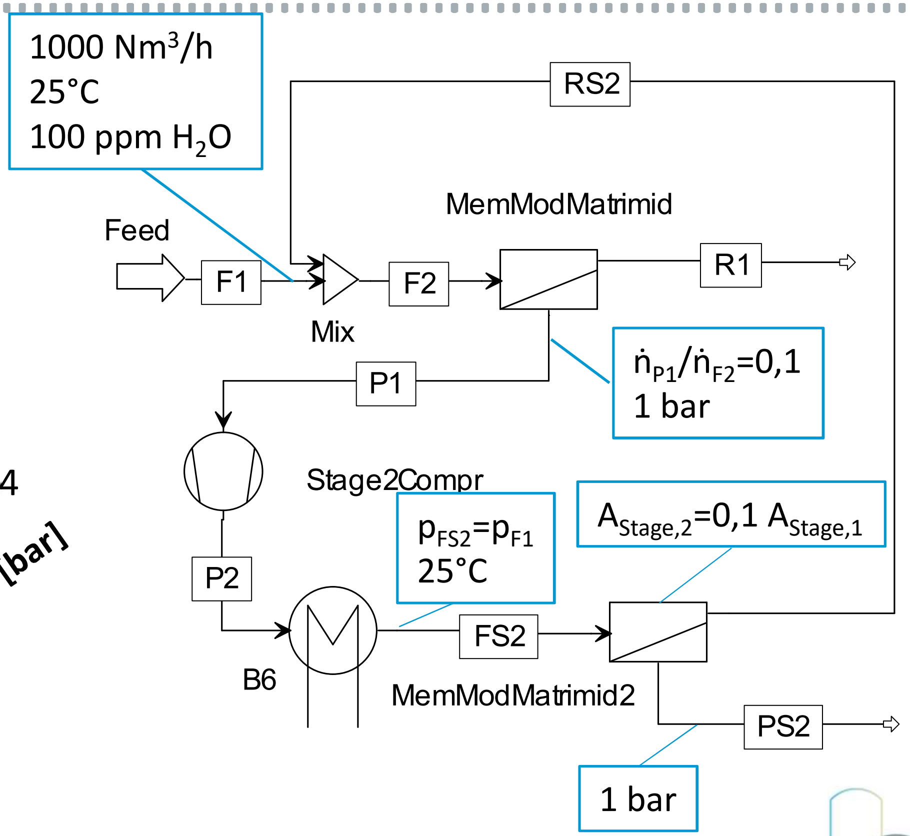

# HIGH TEMPERATURE $H_2$ SEPARATION

## Polymeric membranes at temperatures up to 250°C

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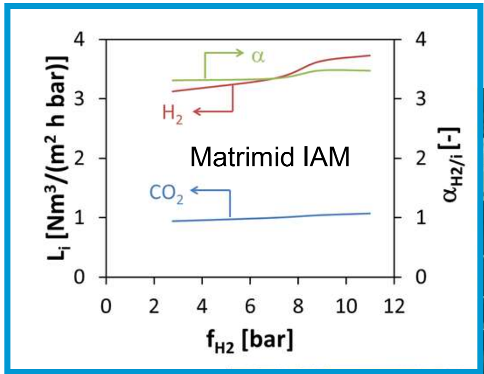


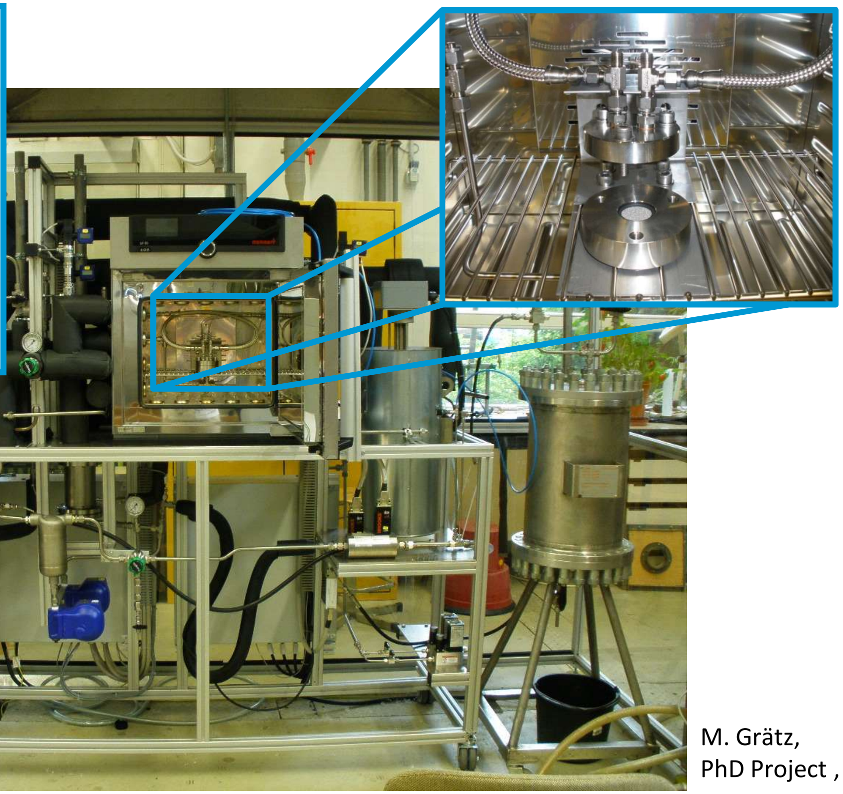

Ternary mixture ($H_2$, $CO_2$, $N_2$)

$y_{F,N2}$ = 0.4
$y_{F,H2}$ = 0.12 – 0.54
$\vartheta$ = 200°C
$p_F$ = 20 bar
$p_P$ = 1.05 bar

M. Grätz,
PhD Project , TUHH

# SUMMARY

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- Membrane technology proven for $H_2$ separation
- Well suited for applications in renewable energies
- Easily scalable for different sizes
- Comparatively simple process design
- Need for recompression
- To dos
  - Improved membrane materials
  - Investigate other separation $H_2/NH_3$,…
  - Where are membrane operations suitable?
  - What membranes are required?
  - Use digitalisation to couple knowledge sources

# FOR PEOPLE AND THEIR FUTURE ENVIRONMENT

Acknokledgements:
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# VIELEN DANK!

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