Thin-film composite (TFC) membrane fabrication:
polymer → membrane → module

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Institute of Membrane Research

BioCoMem

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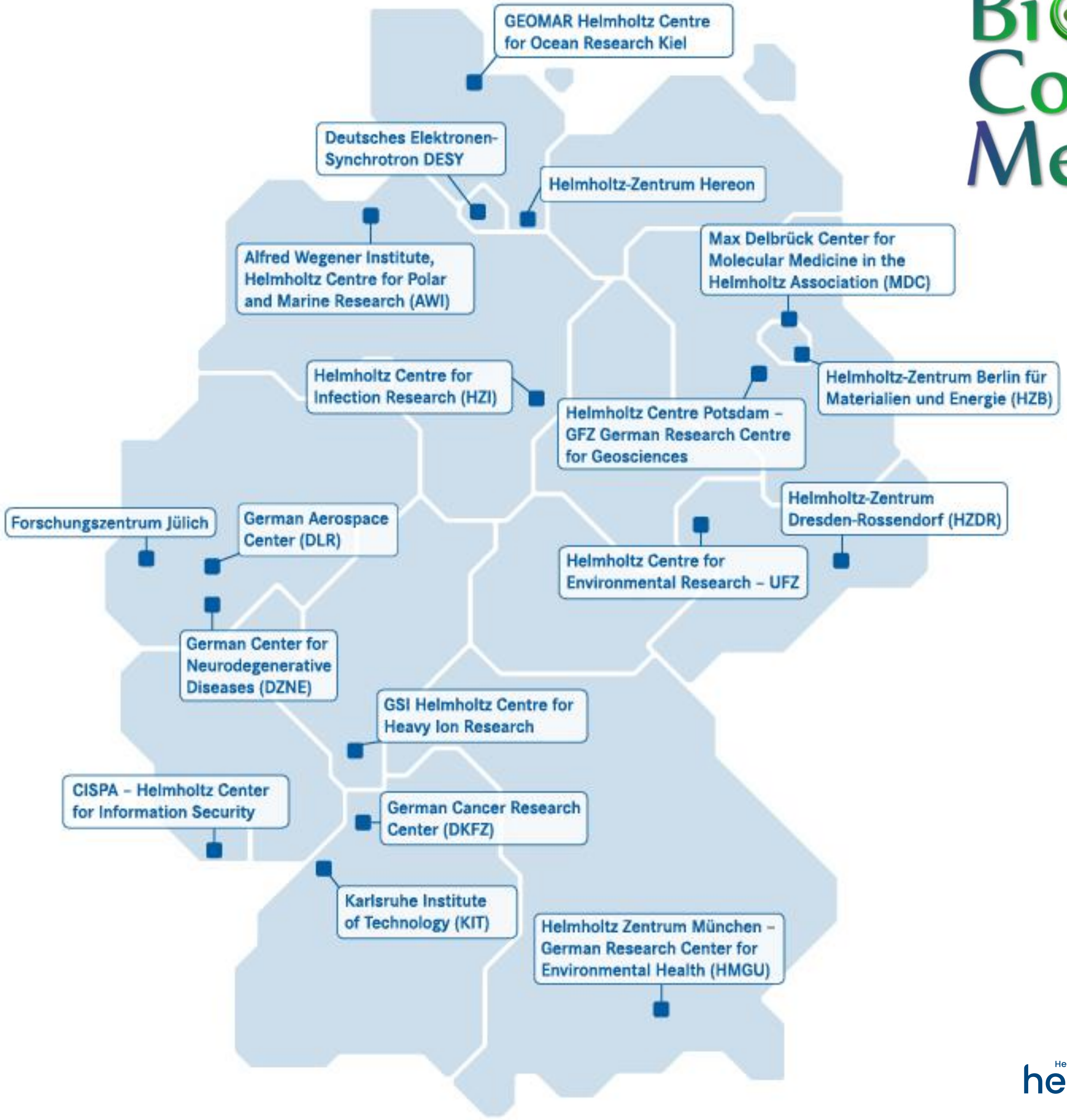
Helmholtz Association
18 Centers and their Funding

HELMHOLTZ
SPITZENFORSCHUNG FÜR GROSSE HERAUSFORDERUNGEN

Total Budget 4.8B €		
70% Federal/State		30% Third Party
90% Federal	10% State	



Helmholtz-Zentrum Hereon
15 Institutes

Helmholtz Research Programme: Information

- Institute of Active Polymers
- Institute of Hydrogen Technology
- Institute of Material and Process Design
- Institute of Materials Mechanics
- Institute of Material Systems Modeling
- **Institute of Membrane Research**
- Institute of Metallic Biomaterials
- Institute of Surface Science
- Institute of Photoelectrochemistry

Helmholtz Research Programme: Earth & Environment

- Institute of Carbon Cycles
- Institute of Coastal Environmental Chemistry
- Institute of Coastal Ocean Dynamics
- Institute of Coastal System Analysis and Modeling
- Climate Service Center Germany (GERICS)

Helmholtz Research Programme: Matter

- Institute of Materials Physics

Institute of Membrane Research:
R&D in membrane gas separation technology

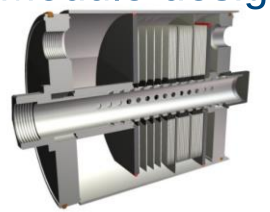
Lab. scale investigations

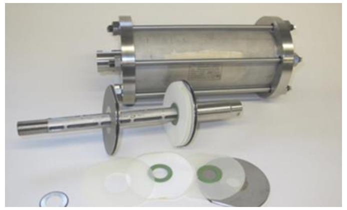
- Polymer synthesis
- Polymer modification
- Permeation behaviour

Pilot scale membrane production

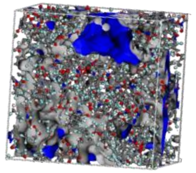
Pilot plants

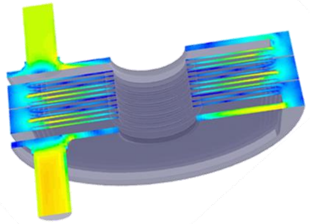
Module design

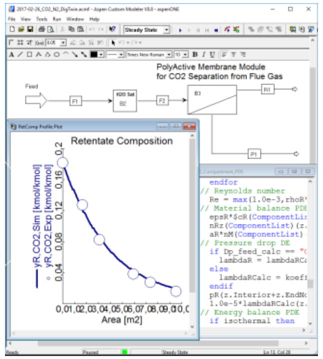




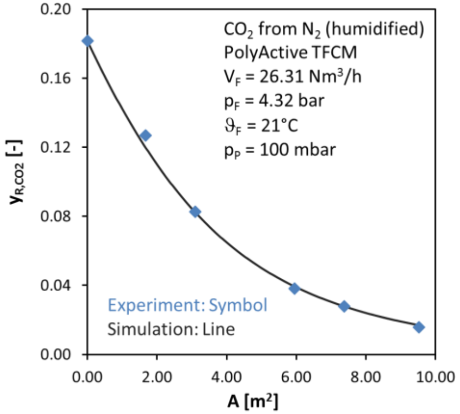
Modelling and simulation







Comp. pilot plant/simulation



Thin-film composite (TFC) membrane fabrication: polymer → membrane → module

Hereon’s role within BioCoMem project

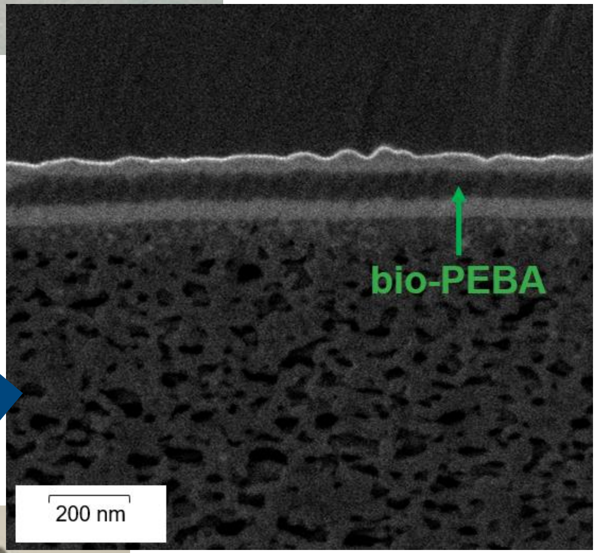
- **Objectives**:

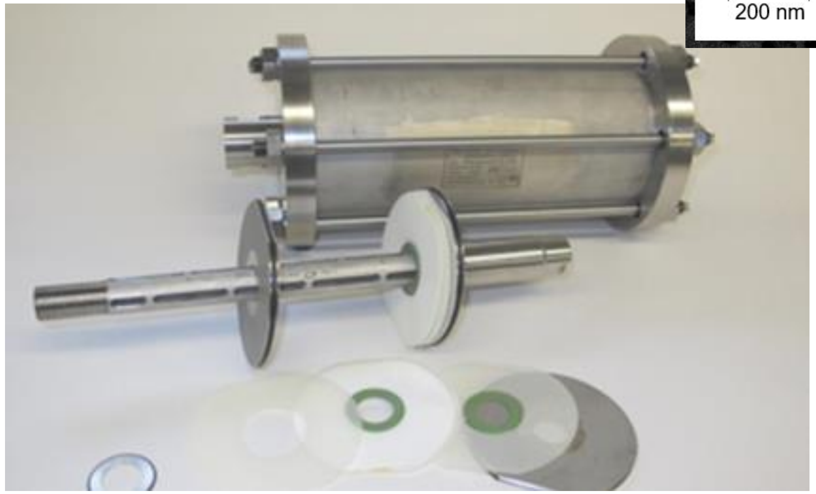
  ✓ Development of thin-film composite (**TFC)** membranes with **bio-based polyether-block-amide (PEBA) copolymers** as **selective layer** materials

  ✓ Manufacture of **membrane modules**

Intended applications:
CO_2 separation

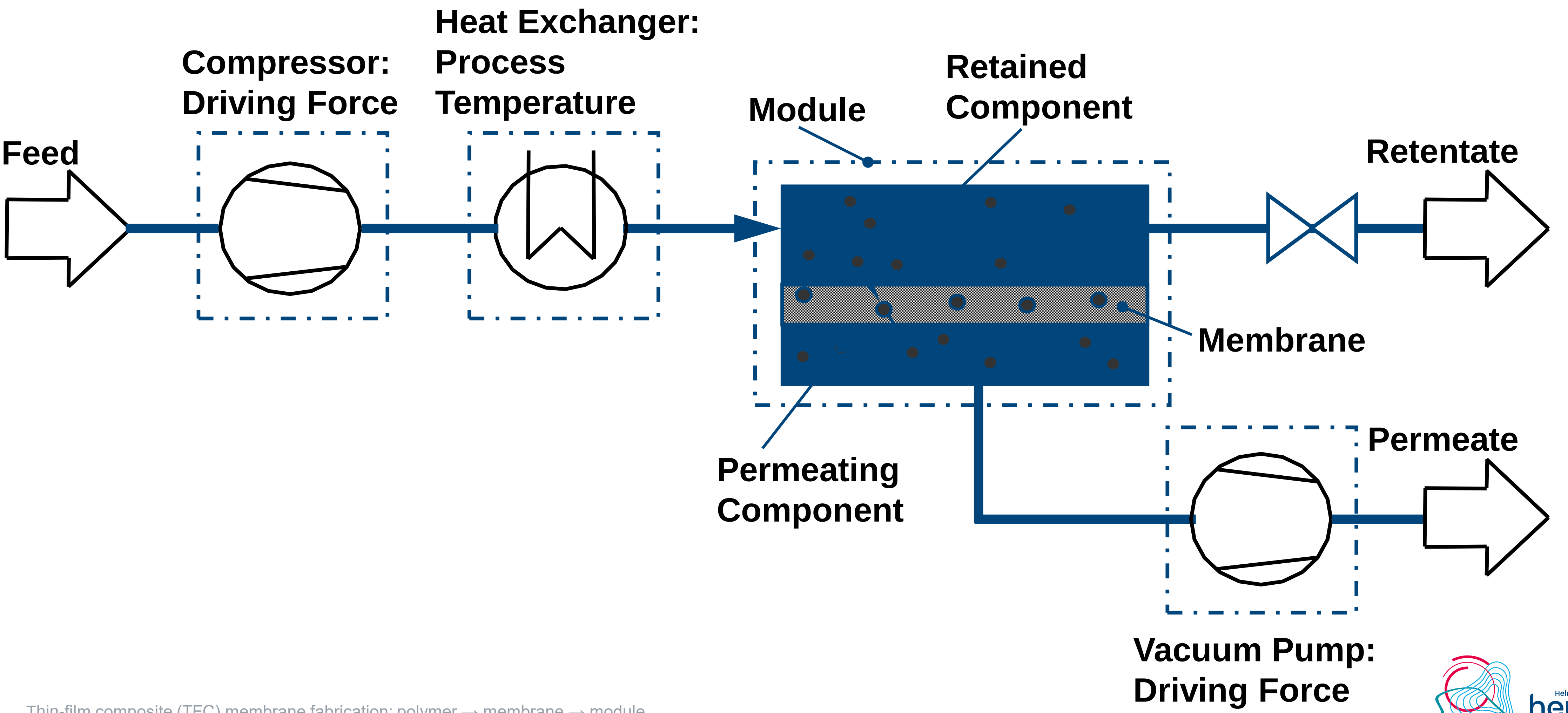
- Post-combustion flue gas treatment
- Natural gas upgrading
- Biogas upgrading





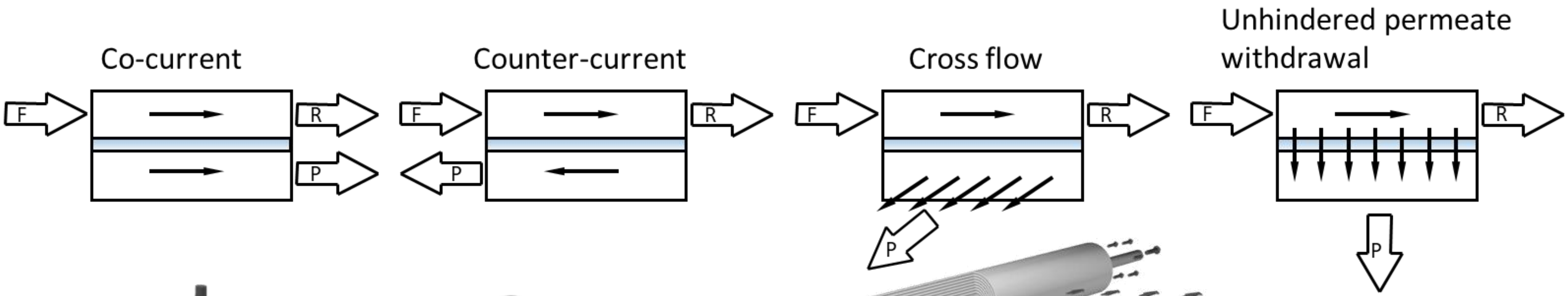
Thin-film composite (TFC) membrane fabrication: polymer → membrane → module

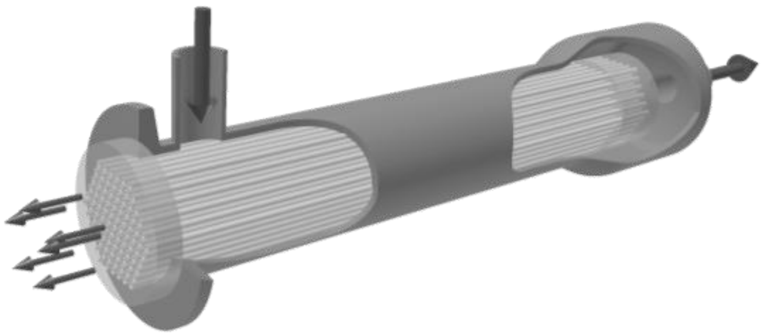
Membrane gas separation process



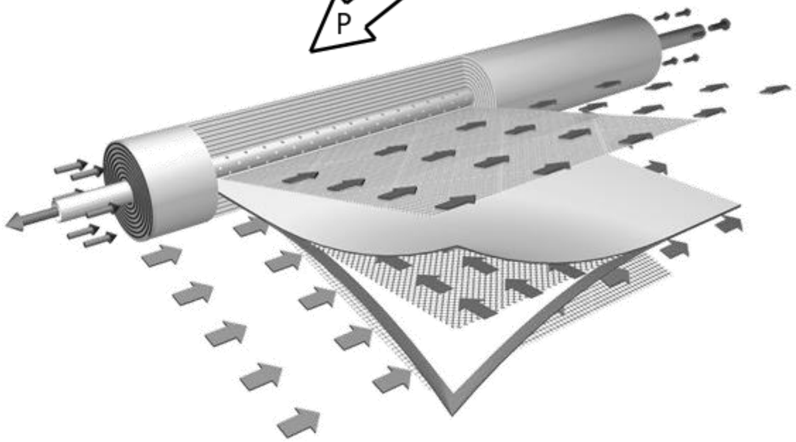
Membrane modules

Transfer membrane’s properties into process



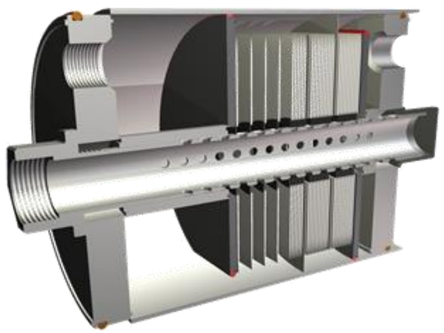


Hollow fibre/capillary/tubular module



Spiral wound module

https://doi.org/10.1016/j.desal.2006.12.009

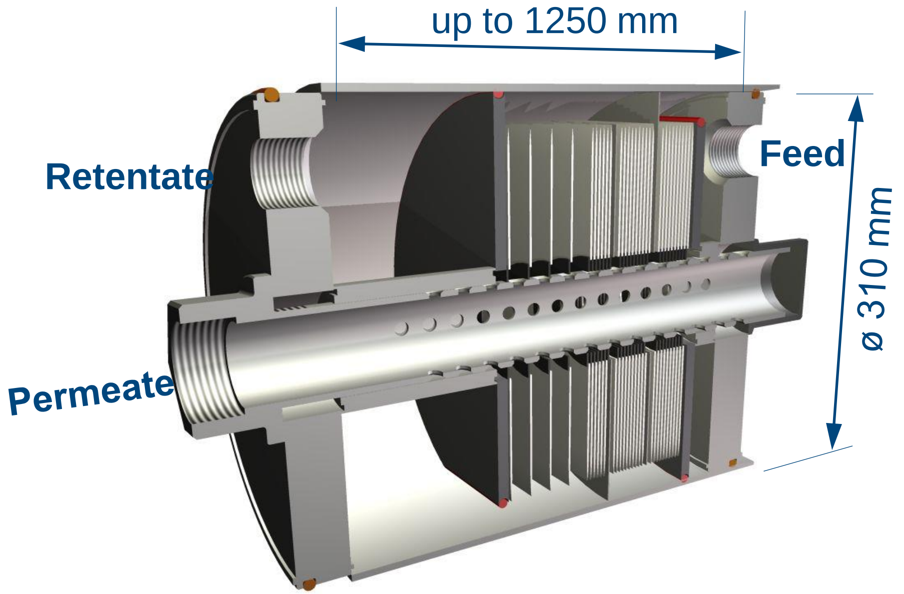


Envelope type module

Envelope type membrane modules

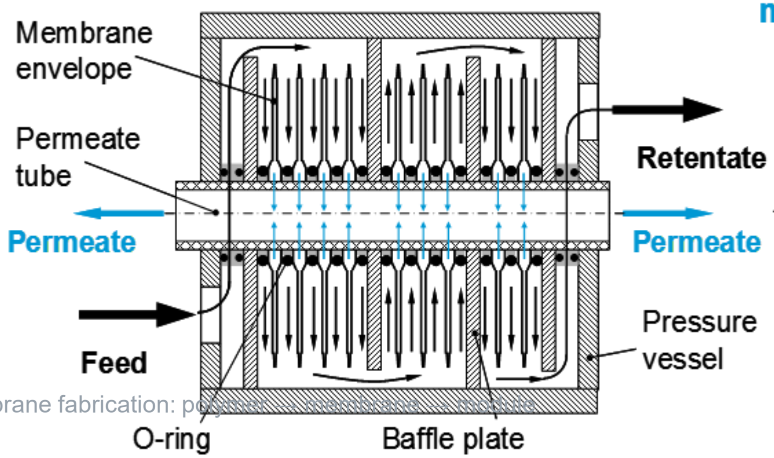
Standard module ø 300 mm

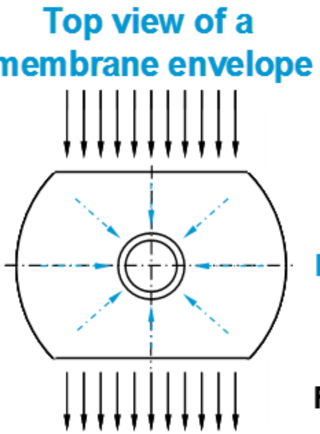
up to 75 m^2 of membrane area

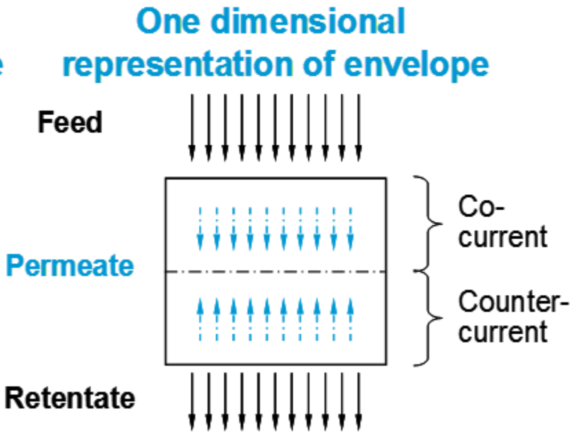


Pilot **Standard** **High pressure**

Gas flow within the module





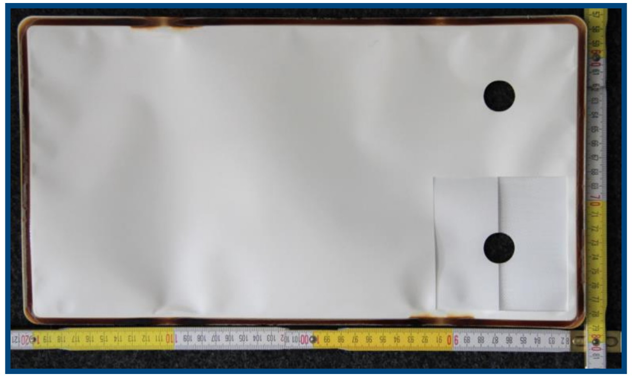


Membrane Modules: Envelope Type

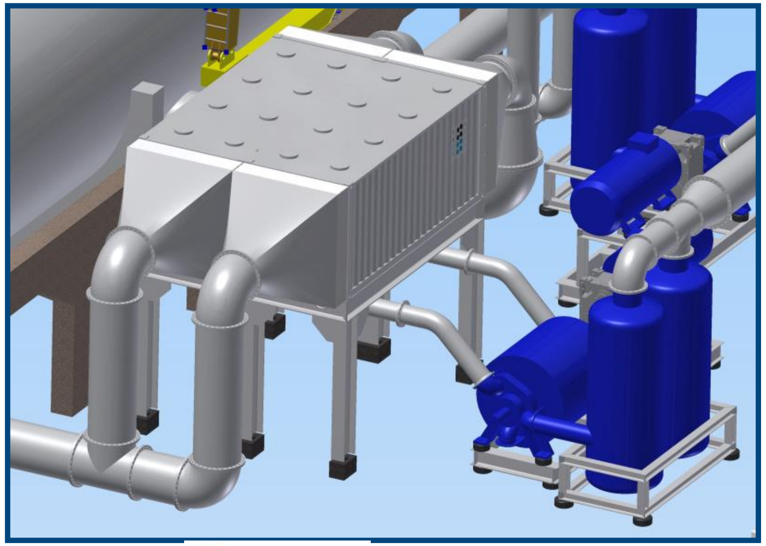
→ Standard envelope type
- ∅ 100 mm: miniplants
- A ≤ 1 m^2

- ∅ 310 mm: pilot / industrial
- A ≤ 70 m^2

→ Prototype
- Counter current flow
- Mem-Brain: Developed in collaboration with FZJ
- 0.21 m × 0.39 m
- A ≤ 5.5 m^2

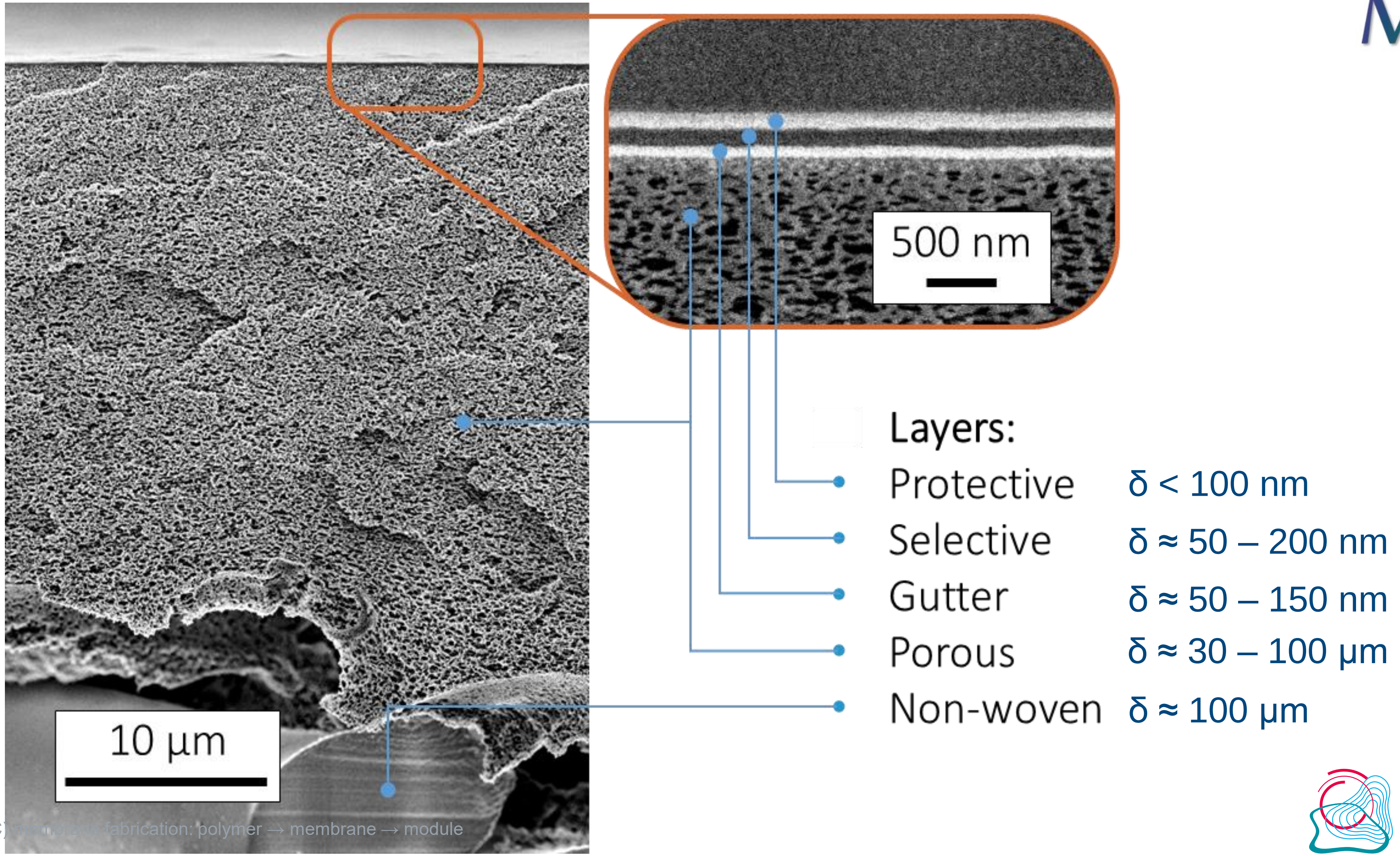


→ Scale-up concept
- Counter current flow
- 20‘ container
- Large scale applications (e.g. flue gas)
- 2.35 m × 5.89 m
- A ≤ 15 000 m^2



Portfolio Mem-Brain

TFC membrane: multi-layer internal morphology



Selective materials of TFC membranes by application

CO_2 separation
Poly(ether ester) multiblock copolymer PolyActive™
Poly(ether-block-amide) PEBAX®
Cellulose acetate / triacetate
Ethyl cellulose
Modified PDMS
Polymers of Intrinsic Microporosity PIM

VOC recovery
Poly(dimethyl siloxane) PDMS
Poly(octyl methyl siloxane) POMS
Polymers of Intrinsic Microporosity PIM
Polyacetylenes: Si; Ge; C
Teflon AF ® : 2400; 1600

H_2 separation
Polyimides
Modified PolyActive™
PIM
PPO
PEI

O_2/N_2 Separation
PVTMS
Cellulose Acetate
PDMS
PIM
PPO

Dehydration
Poly(vinyl alcohol)
TYLOSE ®
Cellulose acetate / triacetate

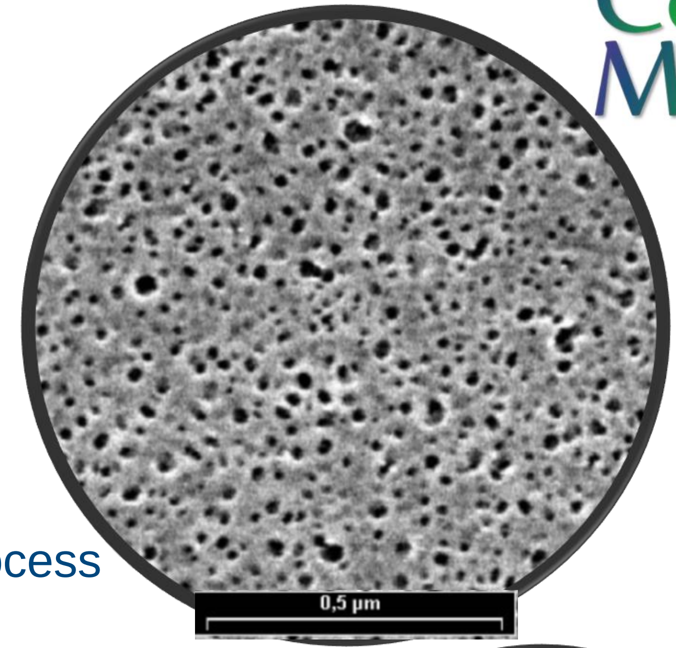
High temperature separations
Polyimides
PBI

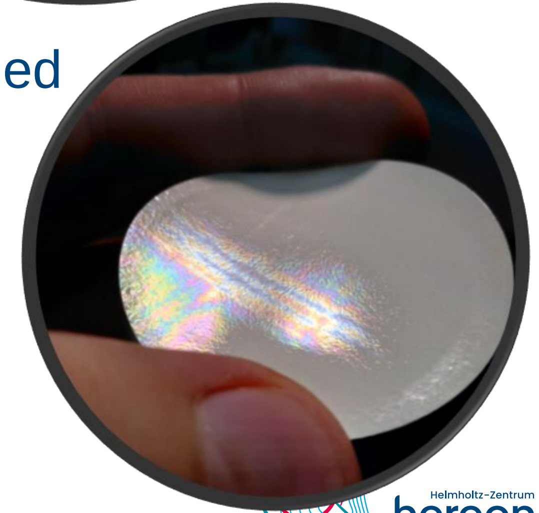
Food storage
Ethyl cellulose

Catalytic membranes
PDMS
PIM
PEBAX®
TORLON®

How to convert polymer to TFC membrane?

- Find suitable solvent for polymer:
  - Friendly for health and environment
  - Volatile, but not too much. Optimum b.p. 70 - 120°C
  - Should dissolve polymer, solution can form gel at > 5 wt.%
- Take appropriate support:
  - Stable against polymer solution
  - As high surface porosity of porous membrane as possible
  - Stable against the pressure and temperature of the separation process
  - Suitable for membrane envelope formation by glueing or melting
- Find lowest concentration of polymer solution when polymer film is still formed
- Deposit polymer solution onto support
- Evaporate solvent
- Observe the formed polymer layer and enjoy colors
- Test the membrane and compare results to properties of the polymer
- Repeat until you transfer polymer properties to membrane





Preparation of TFC membrane

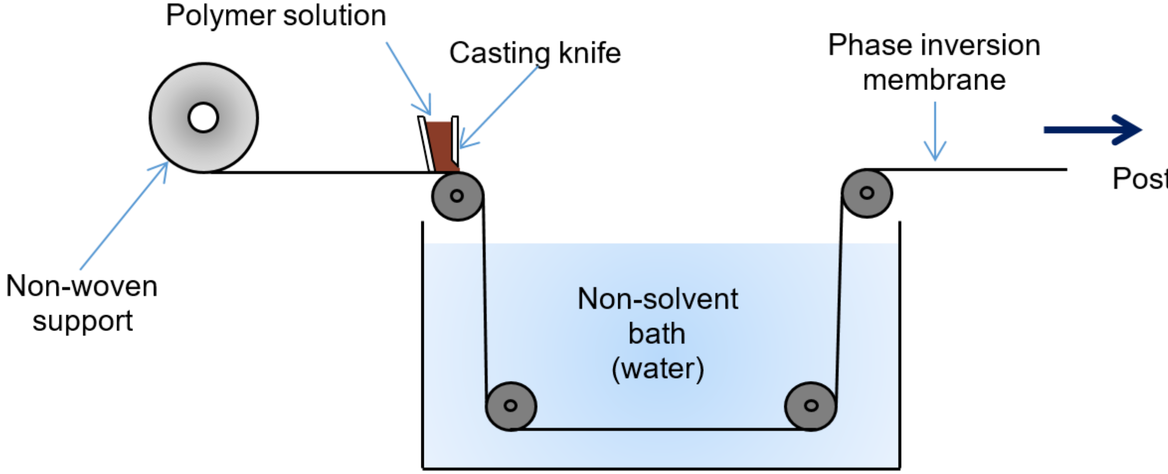
Preparation of porous support by **phase inversion**:

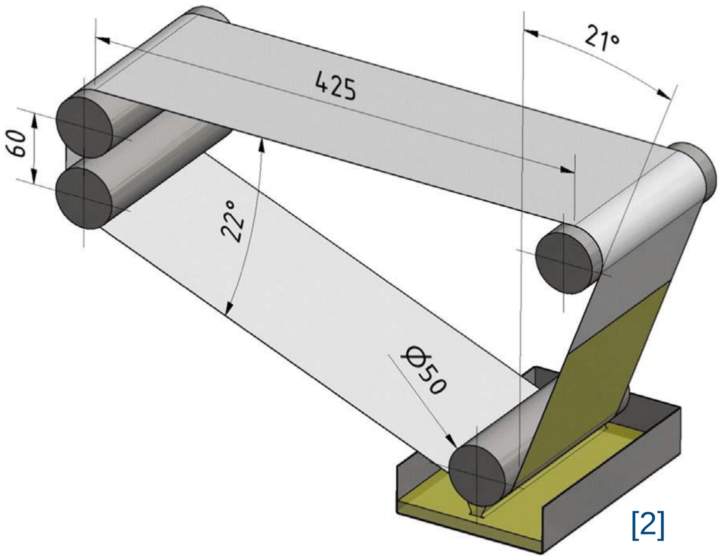
Poly(acrylonitrile) (**PAN**) on polyester (**PES**) non-woven fabric

Coating of poly(dimethylsiloxane) (**PDMS**)-based **gutter** layer

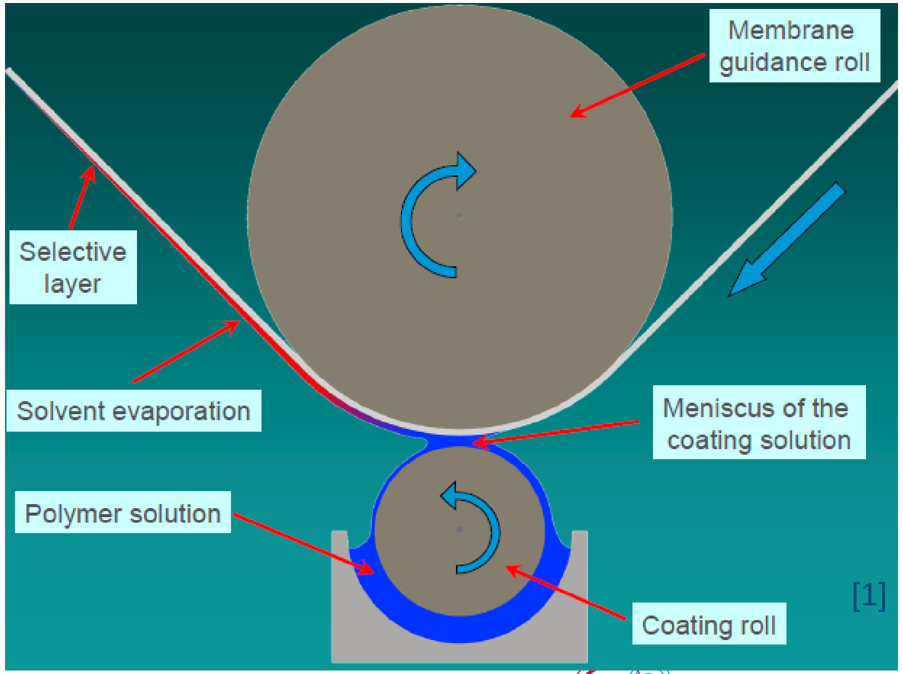
Deposition of **PEBA selective** layer by dip coating

In the case of pilot scale machine: coating of PDMS-based **protective** layer





[2]



[1]

[1] Image courtesy of T. Wolff.
[2] Grünauer et al., Journal of Membrane Science, Vol. 518, 15, Pages 178-191 **(2016)**.

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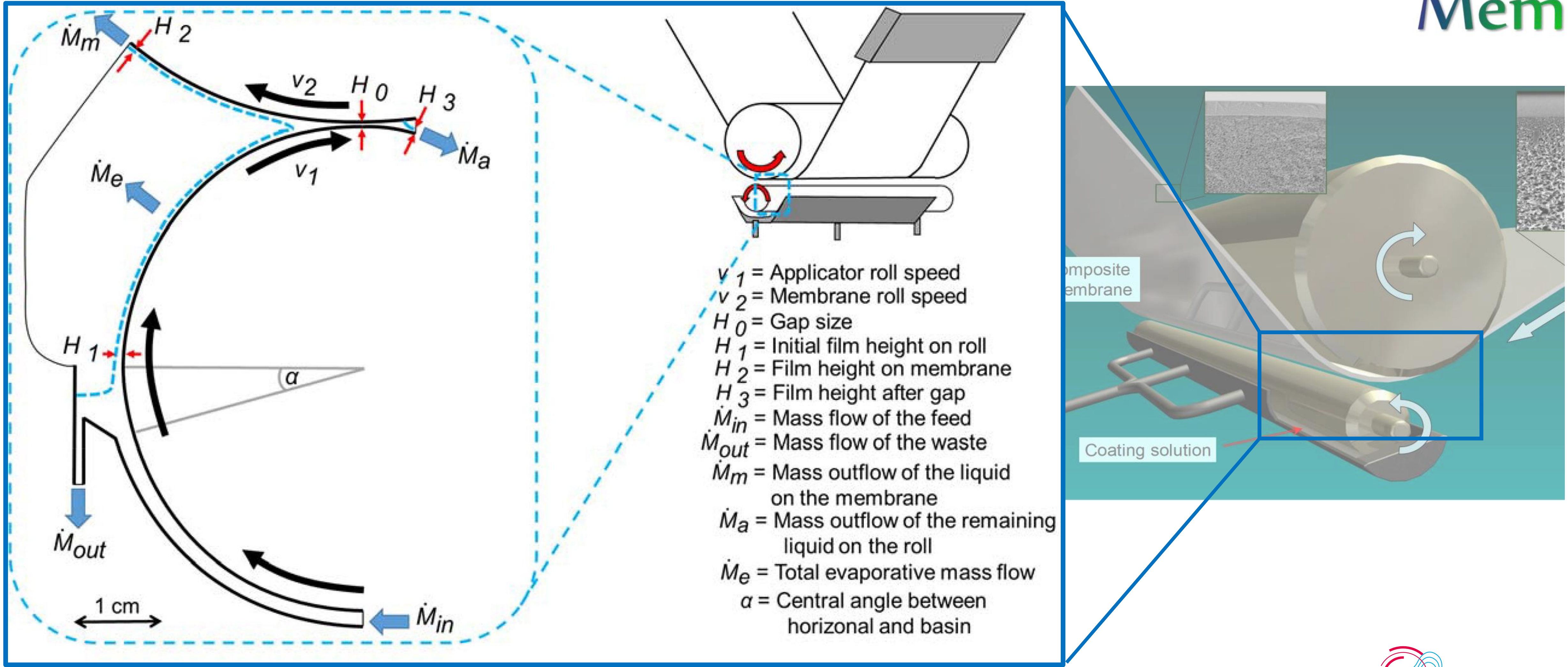
Modelling of processes occurring in solution meniscus during TFC membrane formation



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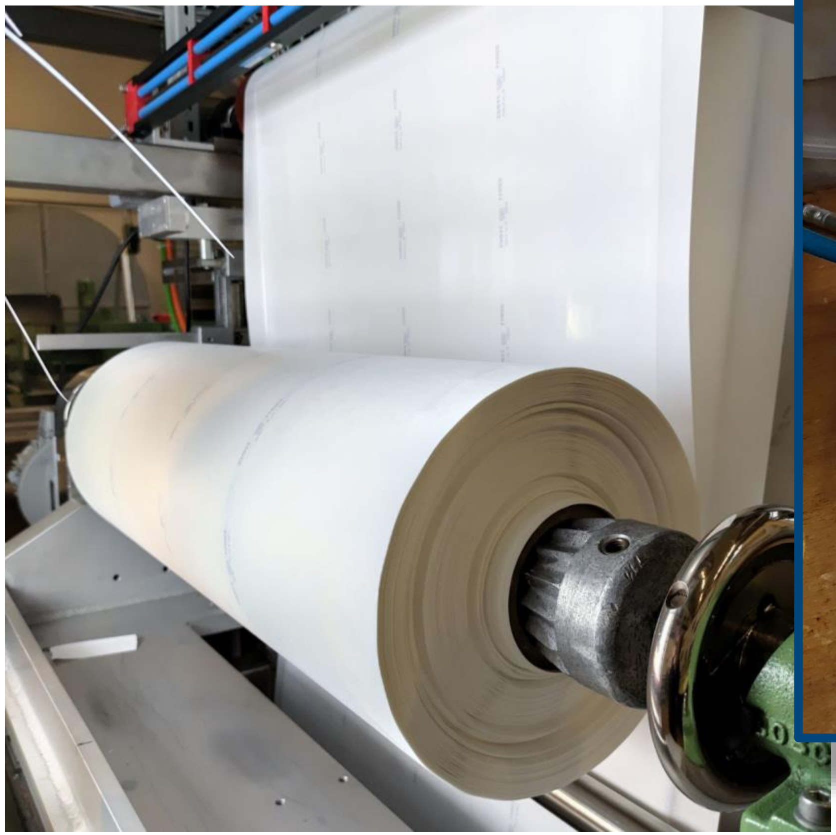
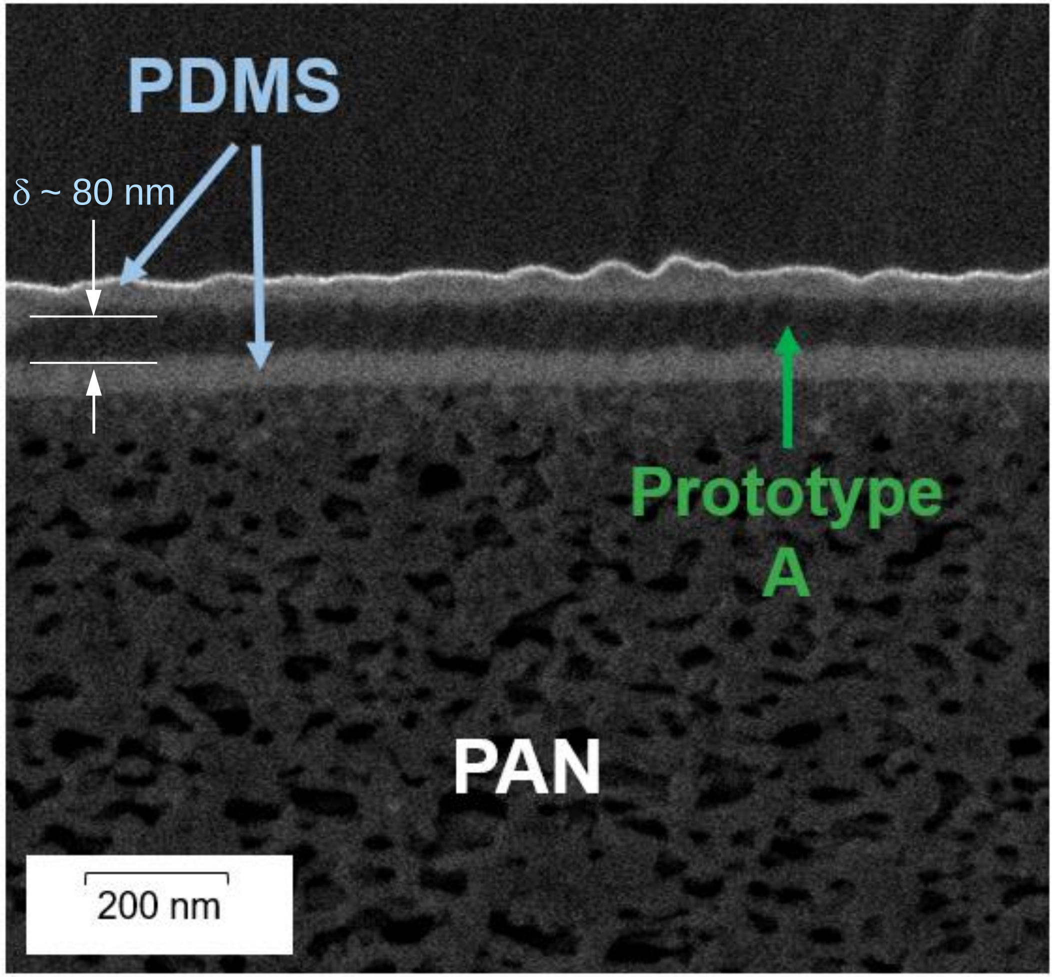
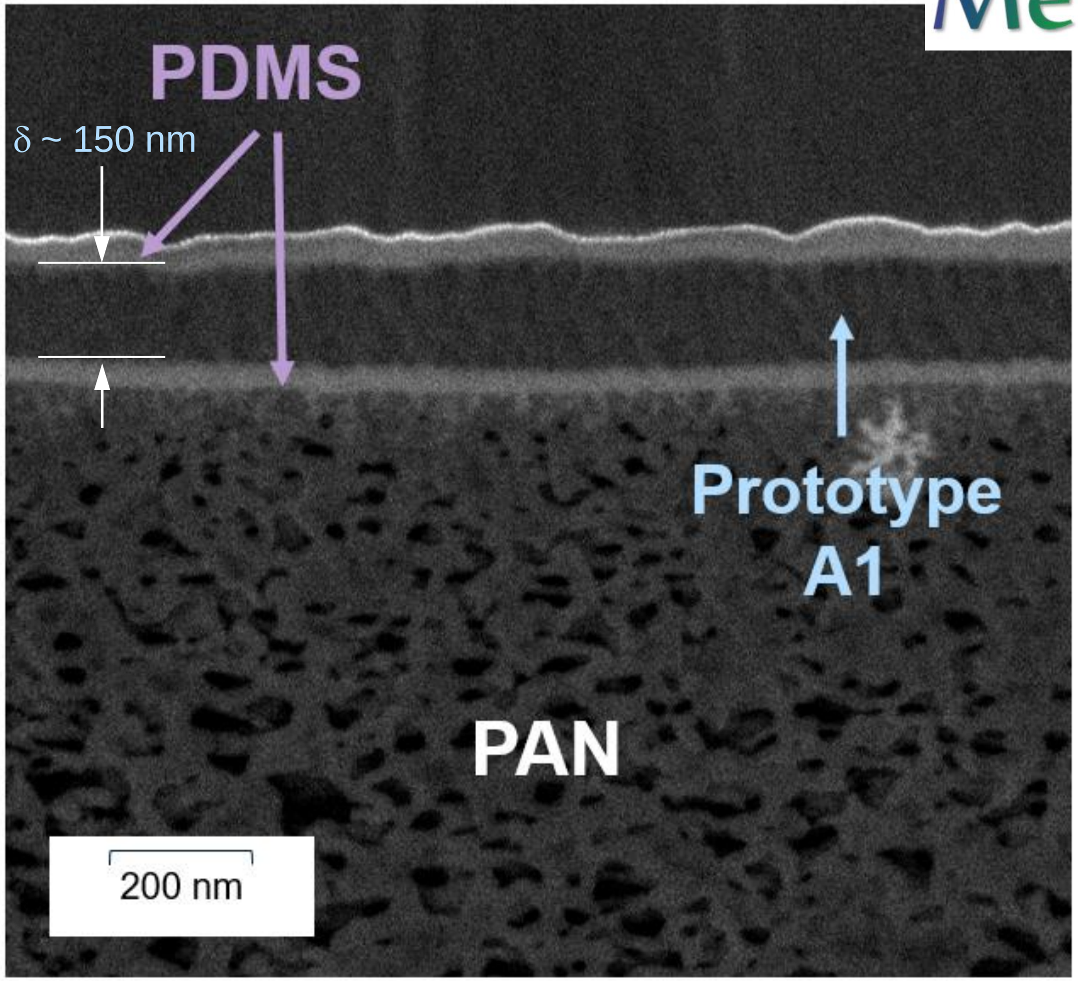
TFC membrane samples for quality control tests



Morphological characterization of TFCMs:
Bio-PEBA Prototype A and Prototype A1





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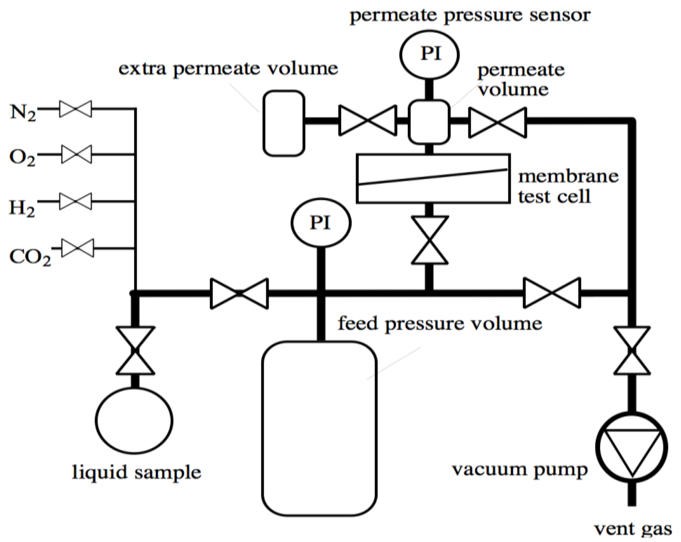
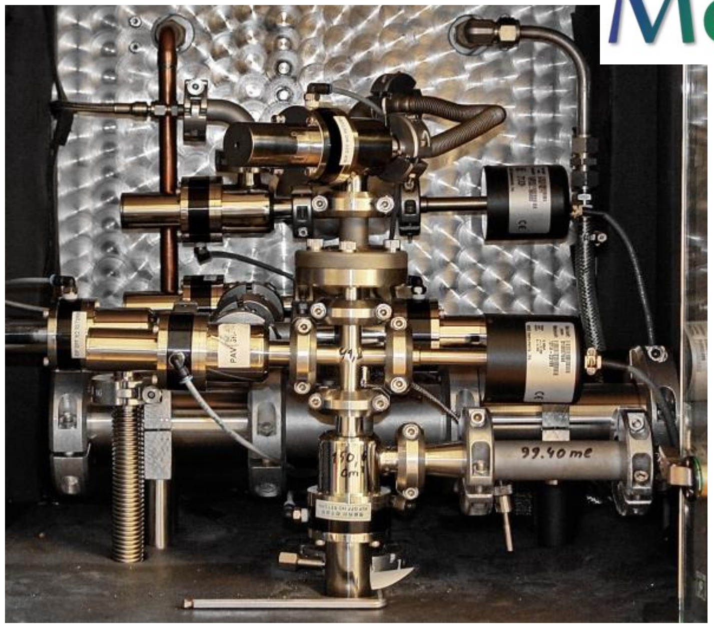
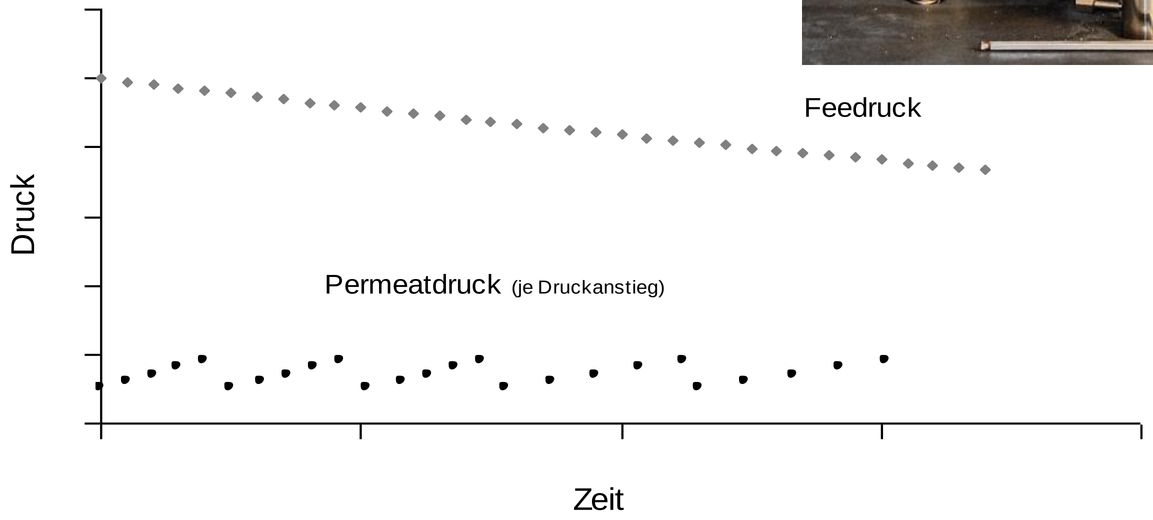
Pressure increase method for determination of single gas permeances

- Automated evaluation of permeation behaviour of single gases
- Determination of temperature dependency
- Consideration of swelling influence
- Fundamental data for permeation modelling



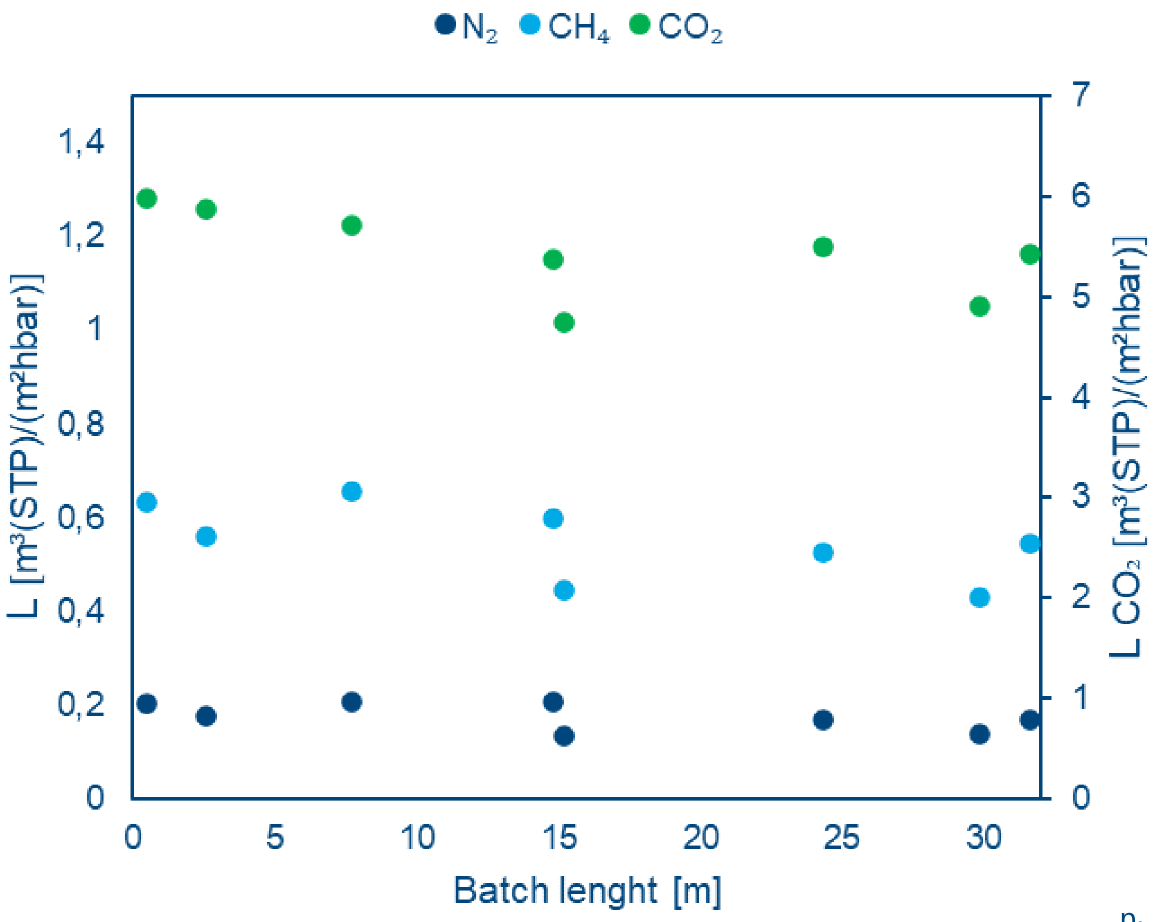


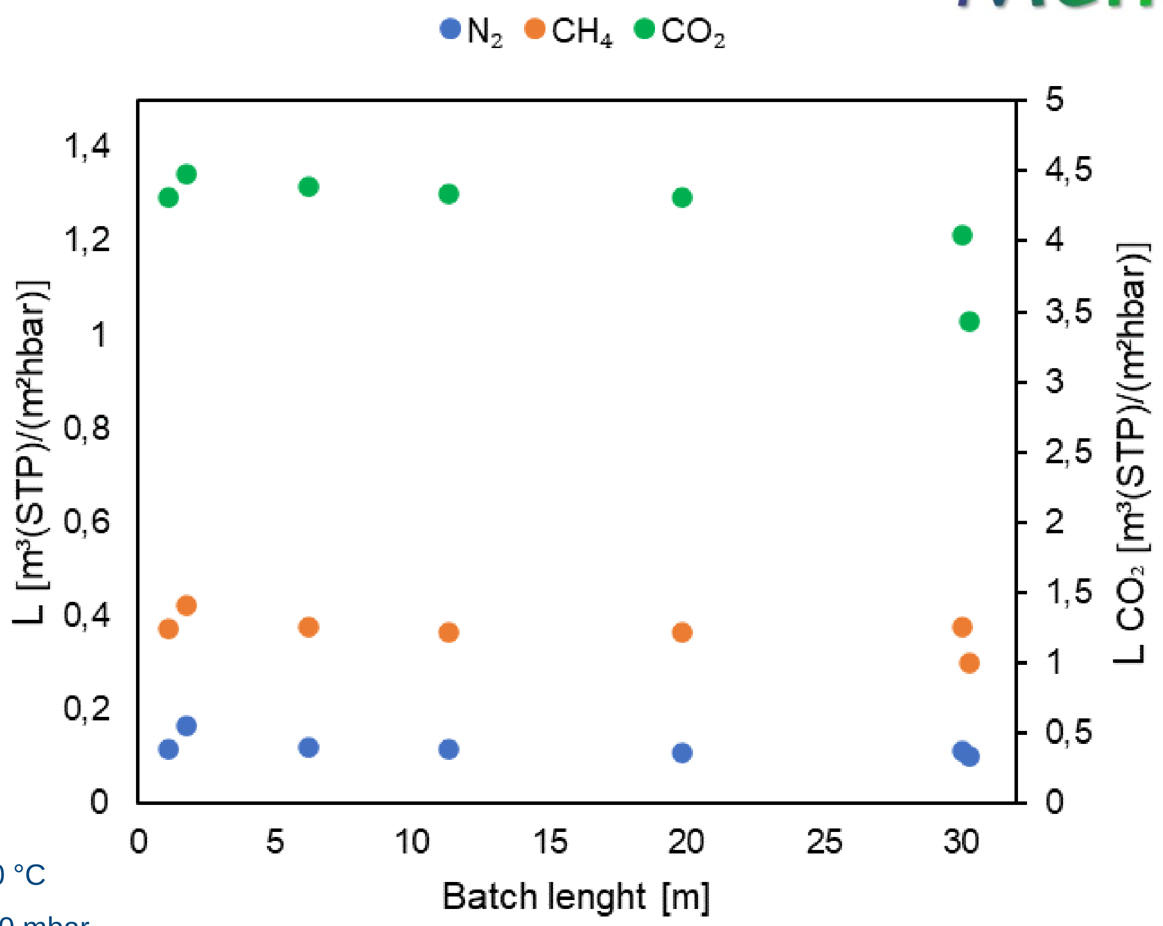


Summary of upscaled membranes

TFCM (PDMS + bio PEBA + PDMS + PAN + PES)	Produced membrane area [m²]	Permeance [m³(STP)/(m²hbar)]			Permeance [GPU]			Selectivity [-]	
		N_2	CH_4	CO_2	N_2	CH_4	CO_2	CO_2/N_2	CO_2/CH_4
Prototype A	9,9	0,18	0,55	5,5	65	204	2000	31	9,9
Prototype A1	9,0	0,13	0,38	4,3	46	142	1600	34	11
Prototype C	5,4	0,09	0,26	2,8	34	97	1000	30	11

Quality control during TFC membrane preparation
Prototype A (left) vs. Prototype A1 (right)



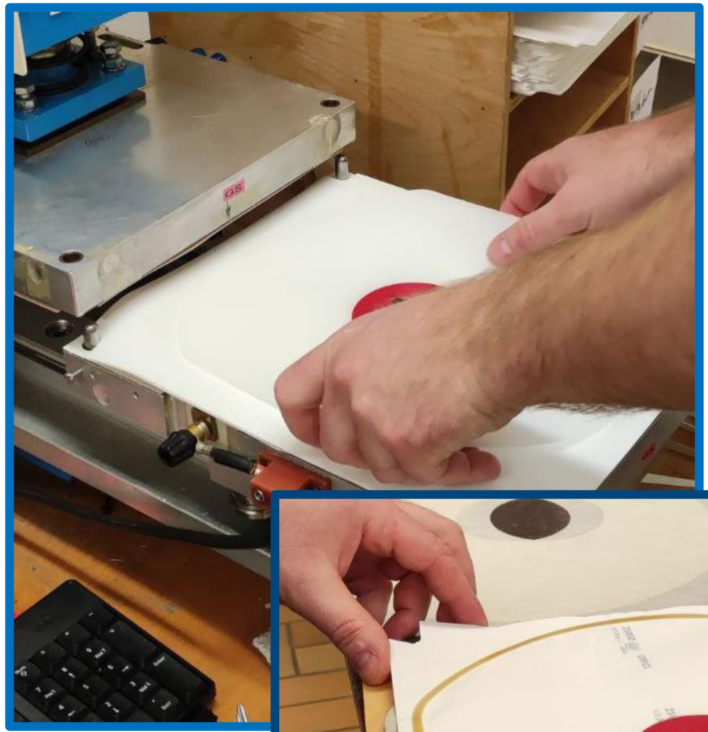


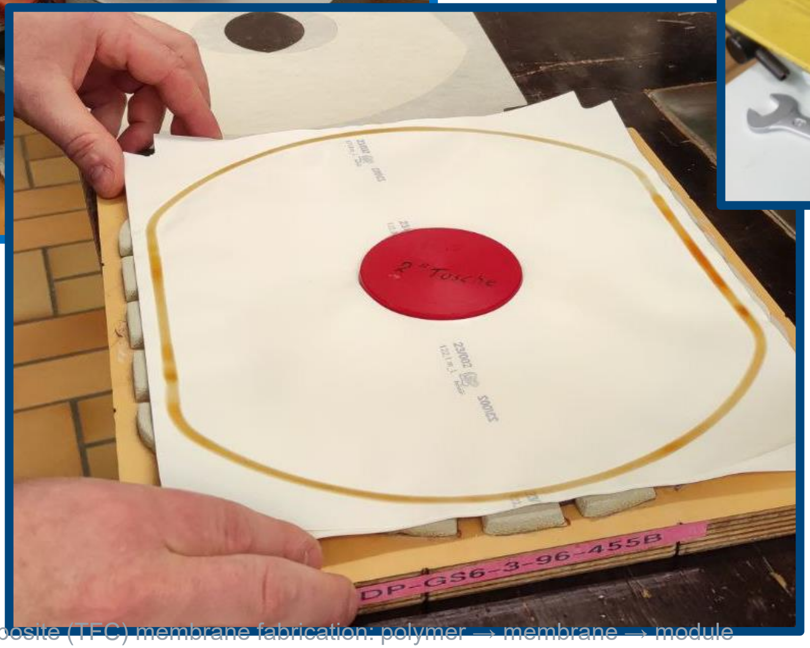
T = 30 °C

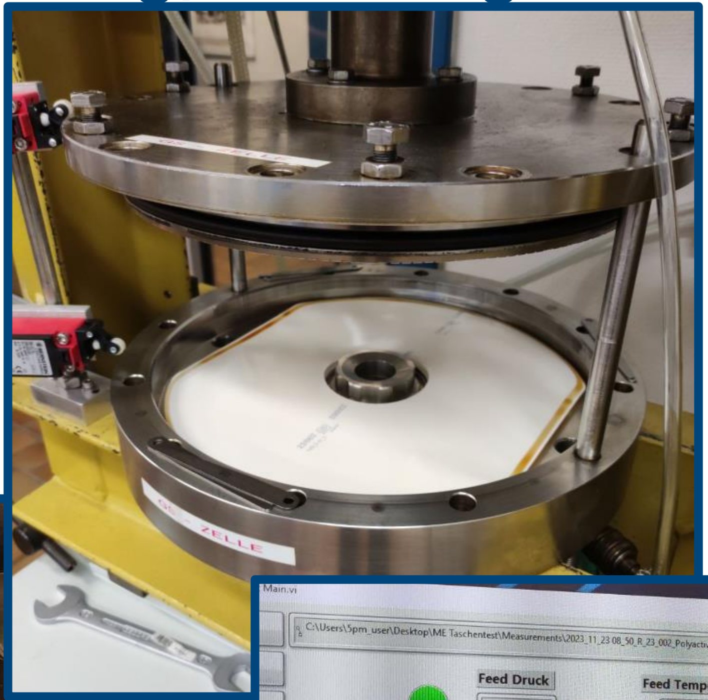
p_{feed} = 800 mbar

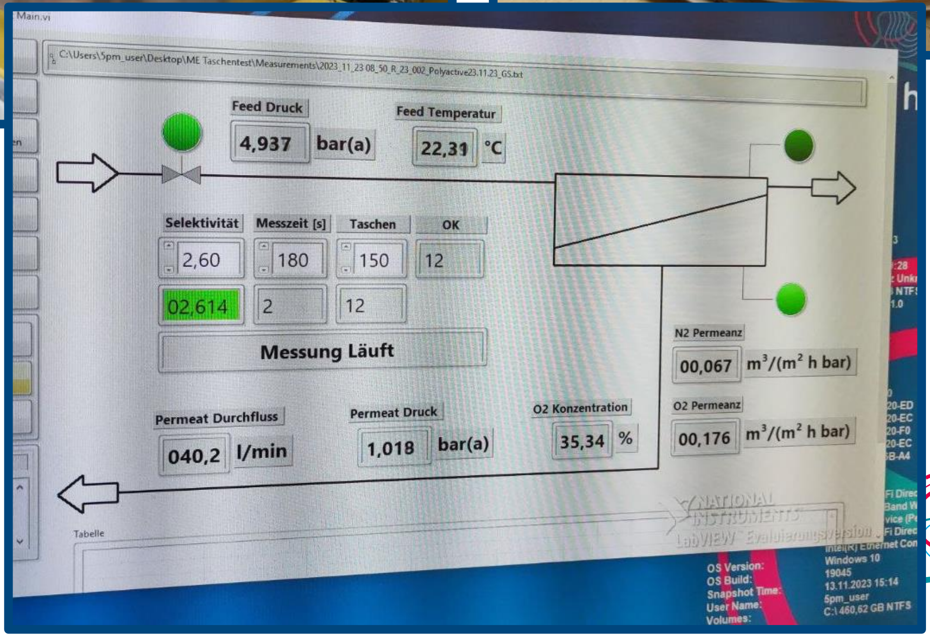
A_M = 8,3 cm^2

Membrane envelopes – labor intensive: cutting, welding, cutting, testing, stacking



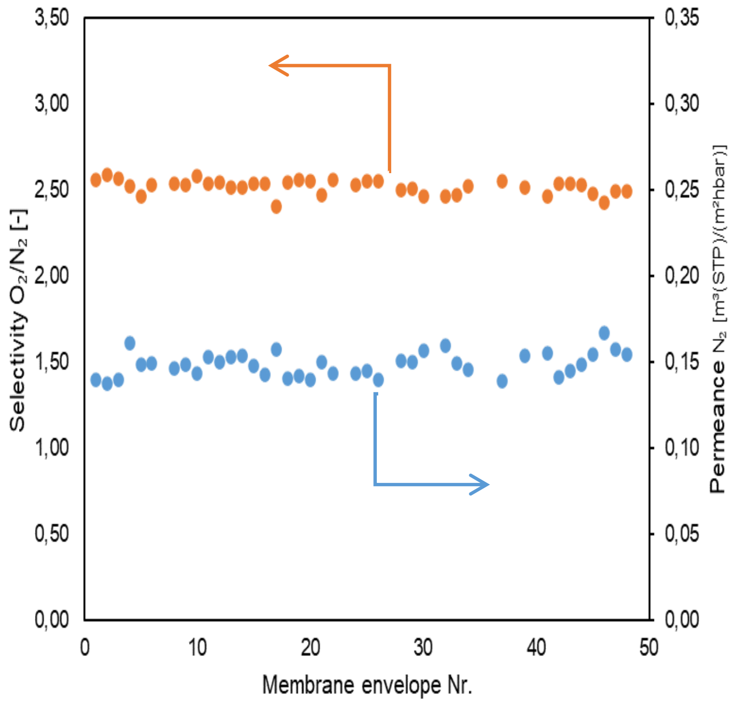




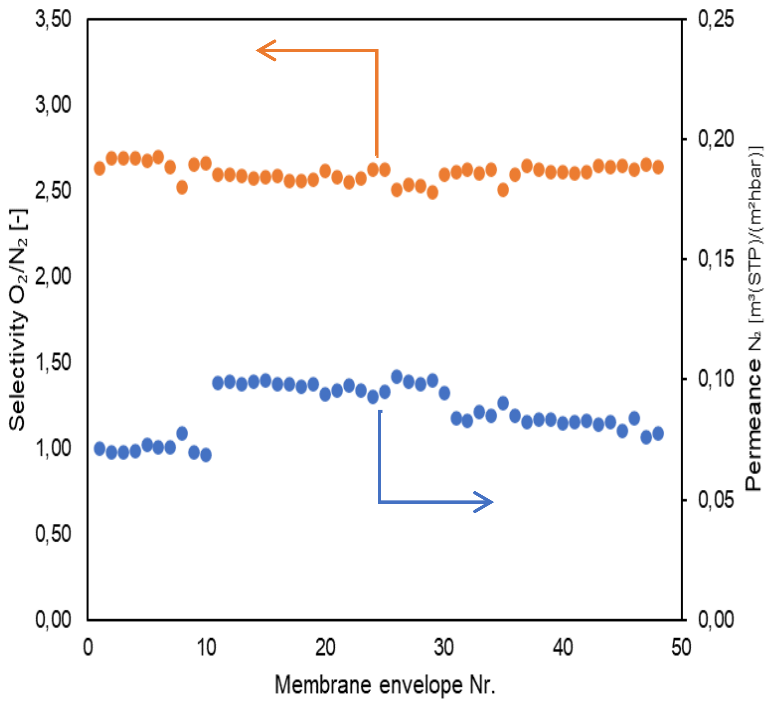


Comparison of envelope quality for different PEO based TFC membranes

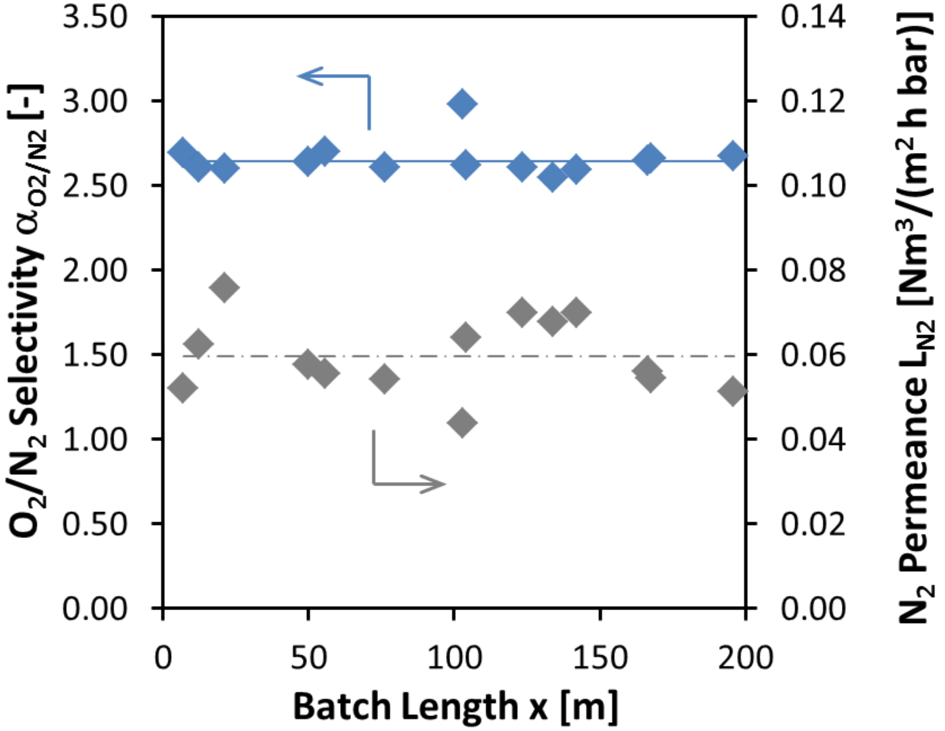
Prototype A



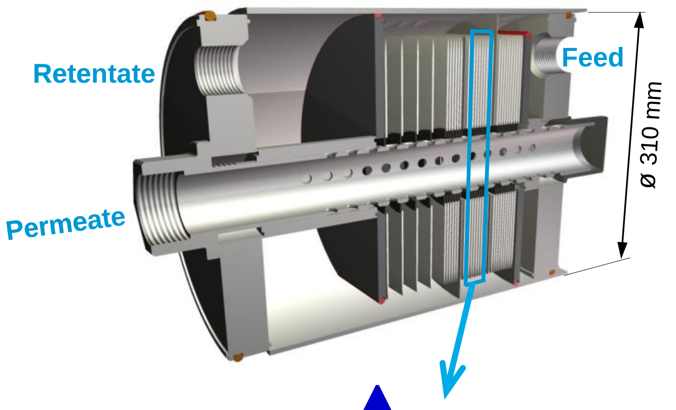
Prototype A1

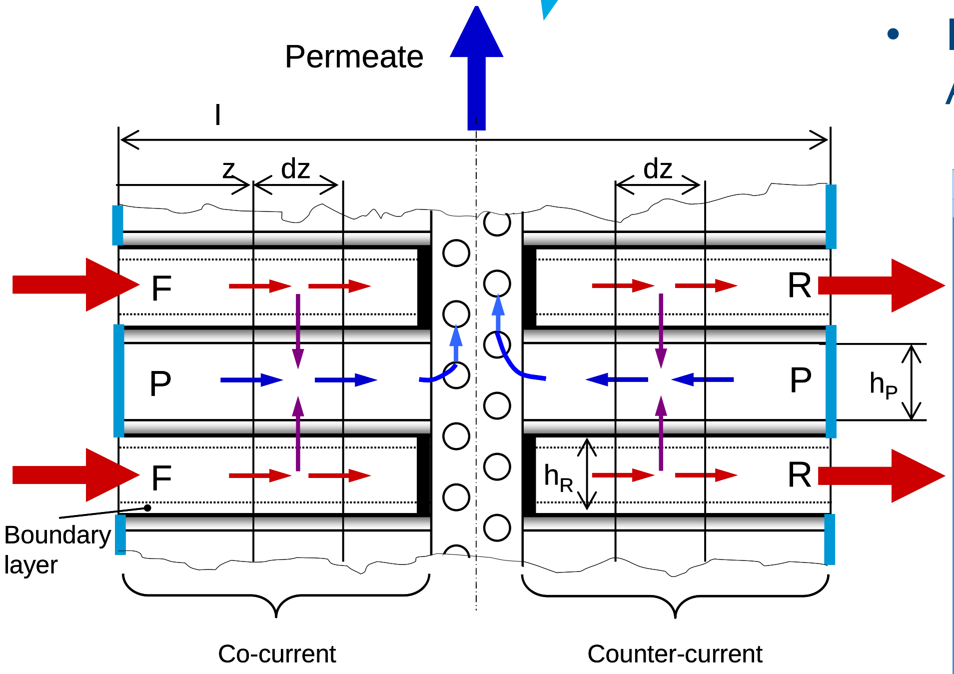


PolyActive™

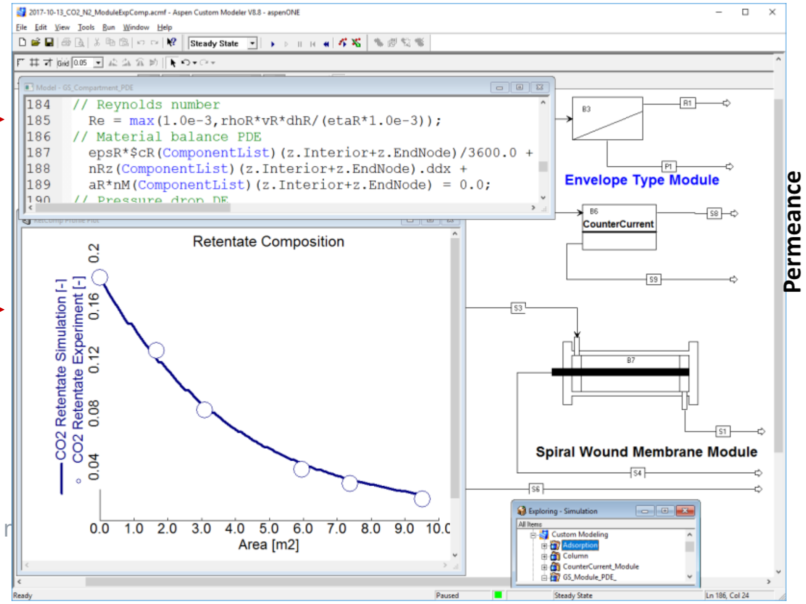


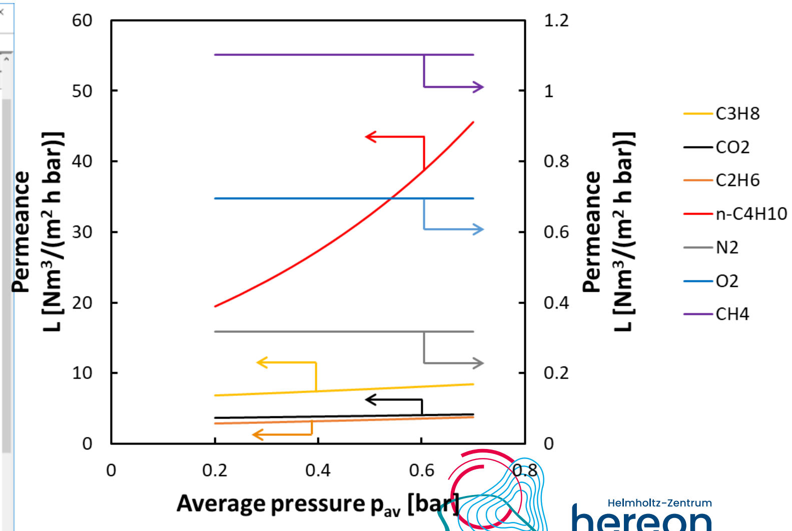
Simulation model – envelope type module





- Boundary conditions: feed definition and permeate pressure
- Flow patterns:
  differential balances feed and permeate
- Permeation equation
- Equation of state
- Transport properties
- Concentration polarization
- Implementation:
  Aspen Custom Modeler®





Conclusions

1. Separations processes based on polymeric membranes are highly accepted by industry.
2. Polymeric membranes are not an ultimate tool for solving any separation problem: process design should/could combine membranes with conventional methods such as absorption, adsorption, *etc.*
3. Multilayer design of TFC membranes gives developer flexibility in a material choice. Each layer is serving specific task: mechanical stability, permeate drainage, smooth support, permeance and selectivity, protection.
4. TFC membranes give the possibility for industrial application of experimental materials.
5. The new generation of TFC membranes developed within the BioCoMem is based on nearly 50 years of experience in membrane R&D and shows the way forward for the use of new materials with unique selective properties (polymers, carbons, ionic liquids, porous sorbents, etc.).

Thank you for your attention!

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Angeles.Ramirez@hereon.de

For module and membrane process design issues:
Torsten.Brinkmann@hereon.de

For technology transfer issues:
Friedrich.Rantzau@hereon.de>

BioCoMem

BBI JU

Bio-based Industries Consortium

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The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio Based Industries Consortium

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