BIOCOMEM

Bio-based copolymers for membrane end products for gas separations

Start date of project: 01/06/2020 **Duration: 3,5 years**

WP7 – Dissemination, and Exploitation

D7.27 BIOCOMEM long term learning measures (courses and workshops)

Topic:	BBI2019.SO3.R10: Develop bio-based high-performance materials for various and demanding applications
Funding scheme:	Research and innovation actions
Call identifier:	H2020-BBI-JTI-2019

Due date of deliverable: 30-11-2023	Actual submission date: 12-01-2024	Reference period: 01-12-2021 – 30-11-2023
Document classification code: BIOCOMEM-WP7-D7.26-DLR-TUE-08182023-v0.1.docx		Prepared by: TUE

Version	DATE	Changes	CHECKED	APPROVED
v0.1	19-12-2023	First Release	TUE	
V0.2	07-03-2022	Communication formats review	Tecnalia	Oana David

This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No 887075

Dissemination Level		
PU	Public	X
PP	Restricted to other program participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for BioCoMem partners of the consortium (including the Commission Services)	
CON	Confidential, only for BioCoMem partners of the Consortium	

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1. EXECUTIVE SUMMARY

1.1. Description of the deliverable content and purpose

As part of work package 7 of Biocomem, (Exploitation, Dissemination and Communication) TUE together with all partners has developed and executed activities related to long term learning measures.
In the second part of the project, from M19 to M42, two webinars took place at M37 and the final at M42. BioCoMem knowledge and results were included into courses for university students for the two academic partners UM and TUE.
It was not possible to organize visits at the demo sites. First, the company owning the Demo site where the membrane module was installed (DMT) had to leave the project due to internal reorganization. Although DMT kindly agreed to allow for the demo campaign at its premises using its own resources as in kind contribution, it was not possible to include also on-site demo visits on top of their commitment with testing at TRL5. Second, the lab scale set-up at TUE did not receive the membrane module until the last month of the project, so there was no time left for such visits.
A winter school is going to take place at TUE, gathering speakers from MACBETH and AMBHER EU projects. A BioCoMem presentation held by a TUE member is included in this school.

2. ACTIVITIES ON LONG-TERM LEARNING MEASURES

2.1 Webinars

Webinar "Biobased membranes for CO_2 separation"
Date: June 26th 2023 – 10:00-12:00
A first dedicated BioCoMem webinar to discuss the main methodologies, challenges and achievements of the BioCoMem project has been held on June 26th . Speakers have been Dr. Angeles Ramirez/ Dr. Sergey Shishatskiy (Hereon), Dr. Oana David (Tecnalia), Dr. Rouzbeh Ramezani (Eindhoven University of Technology), Stefan Frehland (Quantis).
Link to watch the registration here**. Slides of the presentation attached as Appendix.**

Webinar "Pathways to demonstrate the BIOCOMEM technology for future bio-based membranes deployment in industry"
Date: November 24th 2023 – 10:00 – 12:30
A second BioCoMem webinar has been held on November 24th to discuss about the main results achieved during the project, and included presentations from Dr. Katrien Bernaerts (University of Maastricht), Dr. Oana David (Tecnalia), Dr. Sergey Shishatskly (Hereon), Dr. Rouzbeh Ramezani (Eindhoven University of Technology), Andrea Randon (Eindhoven University of Technology).
Link to watch the registration here**. Slides of the presentation attached as Appendix.**

2.2 Other activities

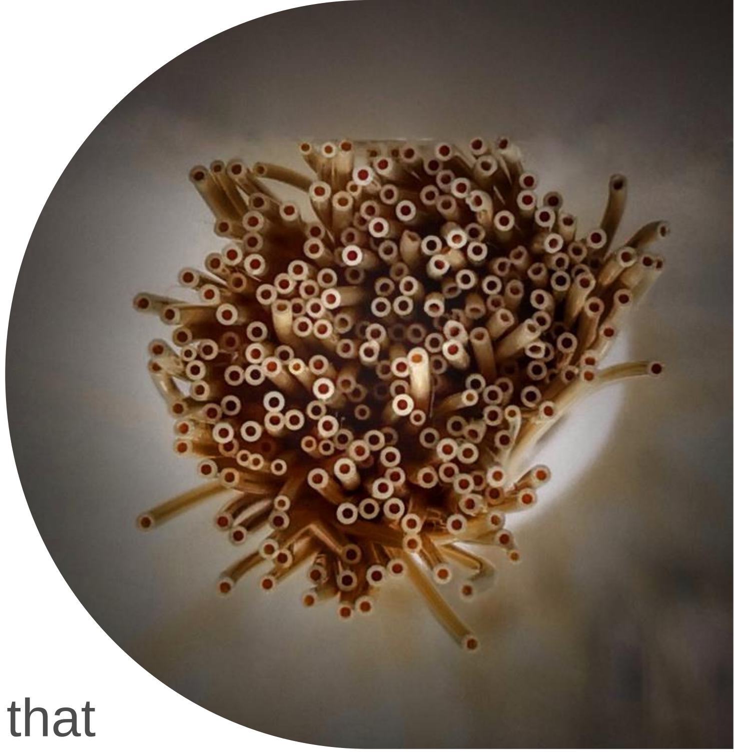
- TUE will host the MACBETH-AMBHER winter school on January 29th – 30th. Relevant project partners will give a lecture in this course. Some partners will be also invited to send employees/students for the school. TUE is currently organizing the event (flyer preparation, registration for attendees, agenda). We have added in the program one lecture that will focus on the BioCoMem project (Membrane modelling tools - by Dr. R. Ramezani). Full winter school agenda can be found here
- To reach bachelor and master students, the following courses integrate the knowledge and the results generated in BIOCOMEM: Separation technology, Process design (TUE); Advanced Macromolecular Chemistry: Biopolymers synthesis, modification and characterization (UM);

In addition, the following thesis was successfully carried out within the BioCoMem project at TUE:

- Sterre Spruit - Modelling of Solubility in Bio-Based Dense Polymeric Membranes (Bachelor thesis).
- Leonardo Varnier – Design and optimization of membrane processes for carbon capture purposes (Master thesis)

APPENDIX
Presentations from the BioCoMem webinars enclosed here.

Bio-based copolymers for membrane end products for gas separations



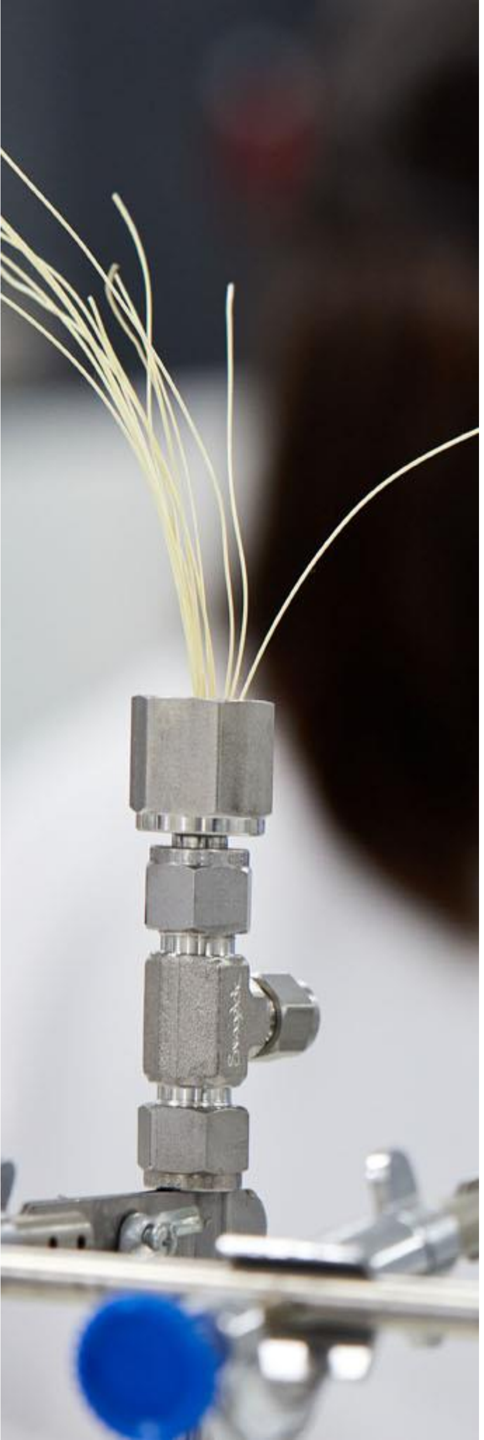
BBI JU contribution: €2.35 million

Duration: June 2020 – May 2023

Feedstock: agricultural, biowaste

The overarching objective for the BIOCOMEM project is to demonstrate that membrane-based separation techniques using PEBA-type (Polyether block amide) copolymers are more efficient than their heat-based equivalent methods. This reduces the overall environmental impact of separation technology on three different levels:

- Application: direct CO_2 capture
- Use of membrane technology with a higher efficiency and lower energy use than other separation options
- The development of membranes based on bio-based precursors for membrane preparation



Bio-based copolymers for membrane end products for gas separations

Project lead: Tecnalia (Spain)

BBI JU contribution: € 2 353 438

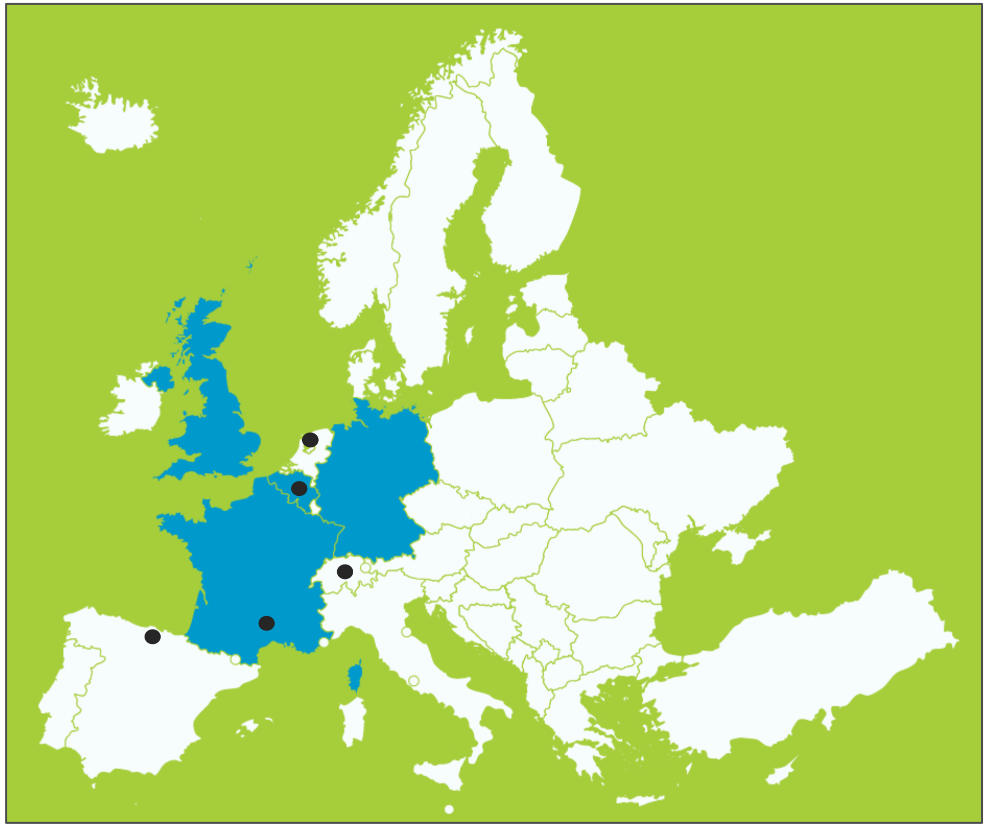
Duration: 01.06.2021 – 31.05.2023

2 HES

2 RTOs

2 SMEs

1 Large Company



tecnalia MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Maastricht University

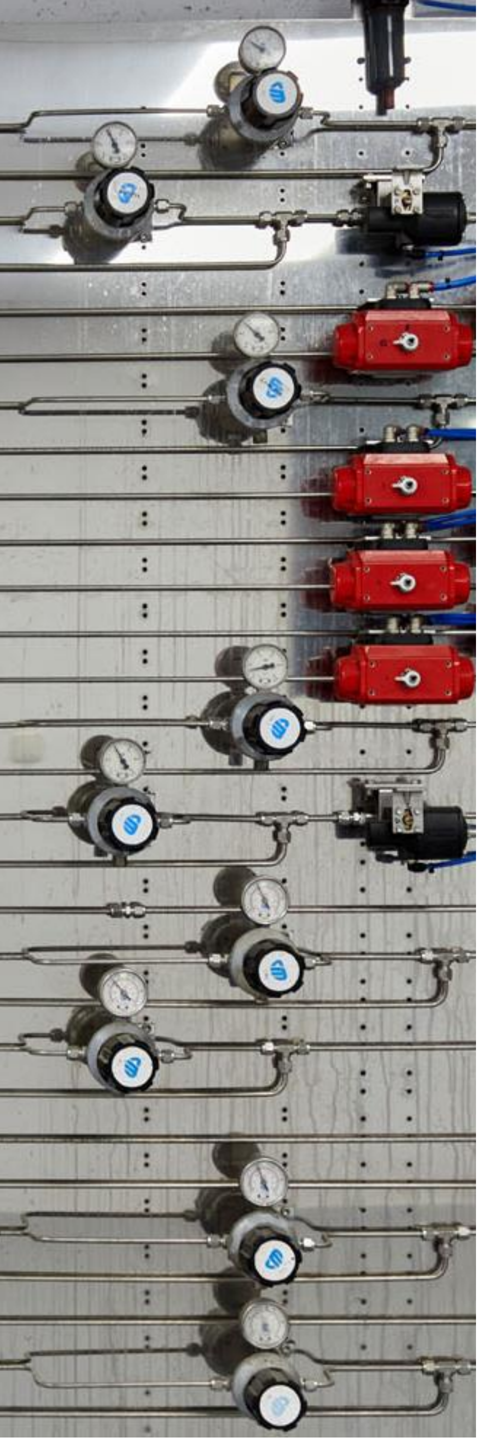
TU/e

B4PLASTICS

Quantis

Helmholtz-Zentrum hereon

ARKEMA



Context and Objectives

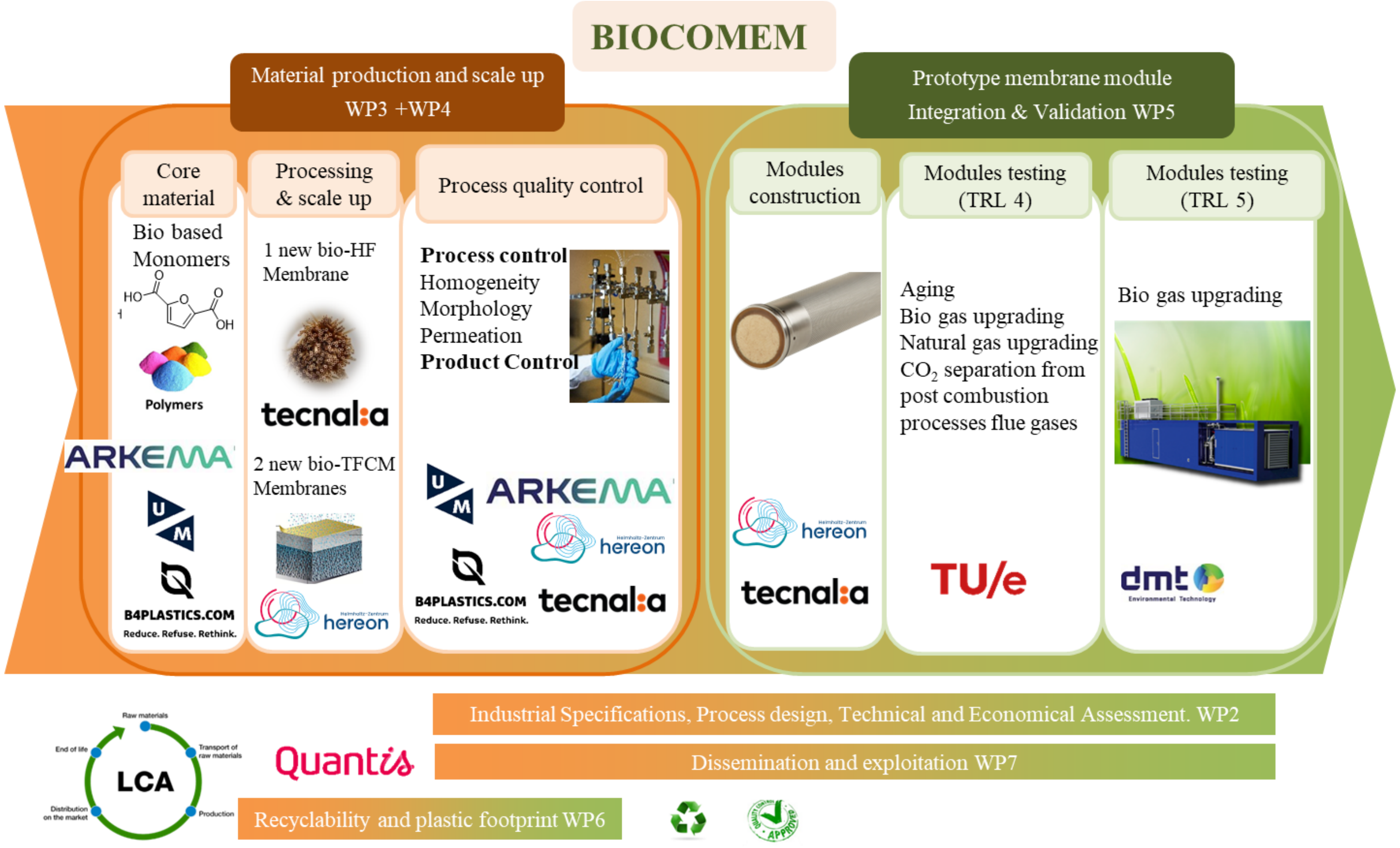
- **Context/main challenge**

  Increase the application of membrane-based separation technology in order to:
  - decrease the energy consumption
  - increase the overall sustainability
  - reduce the environmental impact

  of separation processes in the chemical industry.

- **Objectives:** develop bio-based gas separation membranes using polyether-block-amide copolymer type (PEBAs) chemistry with improved functionality for:
  – higher processability into monolithic hollow fiber membrane
  – higher gas separation performance
  – higher resistance to chemical attack (aging)

BIOCOMEM value chain and main activities



Work that has been carried out

Material Production and scale up:

- Core material:
  - 5 new Bio-PEBA co-polymers have been developed at lab scale.
  - One fatty acid derived Bio-PEBA co-polymer is being develop at pilot scale.

Processing and scale up:

- Bio-membrane development at lab scale: all 5 new Bio-PEBA have been characterised for gas permeation
- Bio-membrane up-scaling activities:
  - the selected fatty acid derived Bio-PEBA is currently processed into monolithic hollow fiber membrane (Prototype B)
  - The reference Bio-PEBA is processed into thin film composite hollow fiber membrane by dip coating (Prototype A)

Benefits to society and the environment

Use of biomass instead of fossil fuels as feedstock is expected to result in a reduction of GHG emissions (to be confirmed by the Life Cycle Assessment along the project).

BIOCOMEM project specifically works also on recyclability of material and on use of nontoxic and bio-based solvents, so that the large-scale production of membranes can be made more environmentally friendly.

BIOCOMEM technologies are more energy efficient than state of the art technologies (PSA, cryogenic distillation, ..)

BIOCOMEM products contribute directly to CO_2 capture from technical processes.

BioCoMem

Local impacts

key partners
- key components suppliers
- RTOs and Universities
- system manufacturer (total or partial)
- system/technology integrators
- Public administrations
- finantial entities

key activities
- R&I, O&M, design, engineering and commercial capacities
- fast response vs. failure

key resources
- Process Design
- Detailed Engineering
- Key components:
  - *Feedstock*
  - *Monomers*
  - *Polymers*
  - *Membranes*

value propositions
Fabrication, sales and/or O&M of CO_2 separation systems based on:

- Membrane separation system for refrigerant gas mixtures separation
- Membrane separation system for post combustion flue gas treatment

"Pay per use" based on refrigerant production or CO_2 capture

customer relationship
- Operation and Manteinance (continuous follow-up)
- customer attention
- personalized services

exploitation channels
- commercial network
- public contests

customer segments
Large CO_2 emitters:
- *Cement plants (lime and dolomite sector included)*
- *Power plants*
- *Refineries*
- *Steel Industry*

Refrigerant consumers:
- *Food and healthcare*
- *Consumer electronics industry*
- *Households*
- *Automotive Industry*

CO_2 consumers:
- *EOR*
- *Beverage Carbonation*
- *Food packaging*
- *Urea production*
- *Methanol production*

cost structure
- O&M resources
- components
- manufacturing costs
- design costs
- certifications
- commercial cost
- financial costs

revenue streams
- O&M services
- systems commercialization
- licensing and engineering services
- Refrigerant sales
- CO_2 sales

Fabrication and/or O&M of separation systems | Product direct sales or self consuption | Both Business Models

Bio-based copolymers for membrane end products for gas separations

BioCoMem

PEBA polymer synthesis pathways to membrane processing

Assoc. Prof. dr. Katrien Bernaerts (UM)

Dr. Marcin Ślęczkowski and Dr. Amol Ichake (UM)

Dr. Oana David (Tecnalia)

WEBINAR: Pathways to demonstrate the BIOCOMEM technology for future bio-based membranes deployment in industry

November 24th – 10:00 – 12:30

Bio-based Industries Consortium

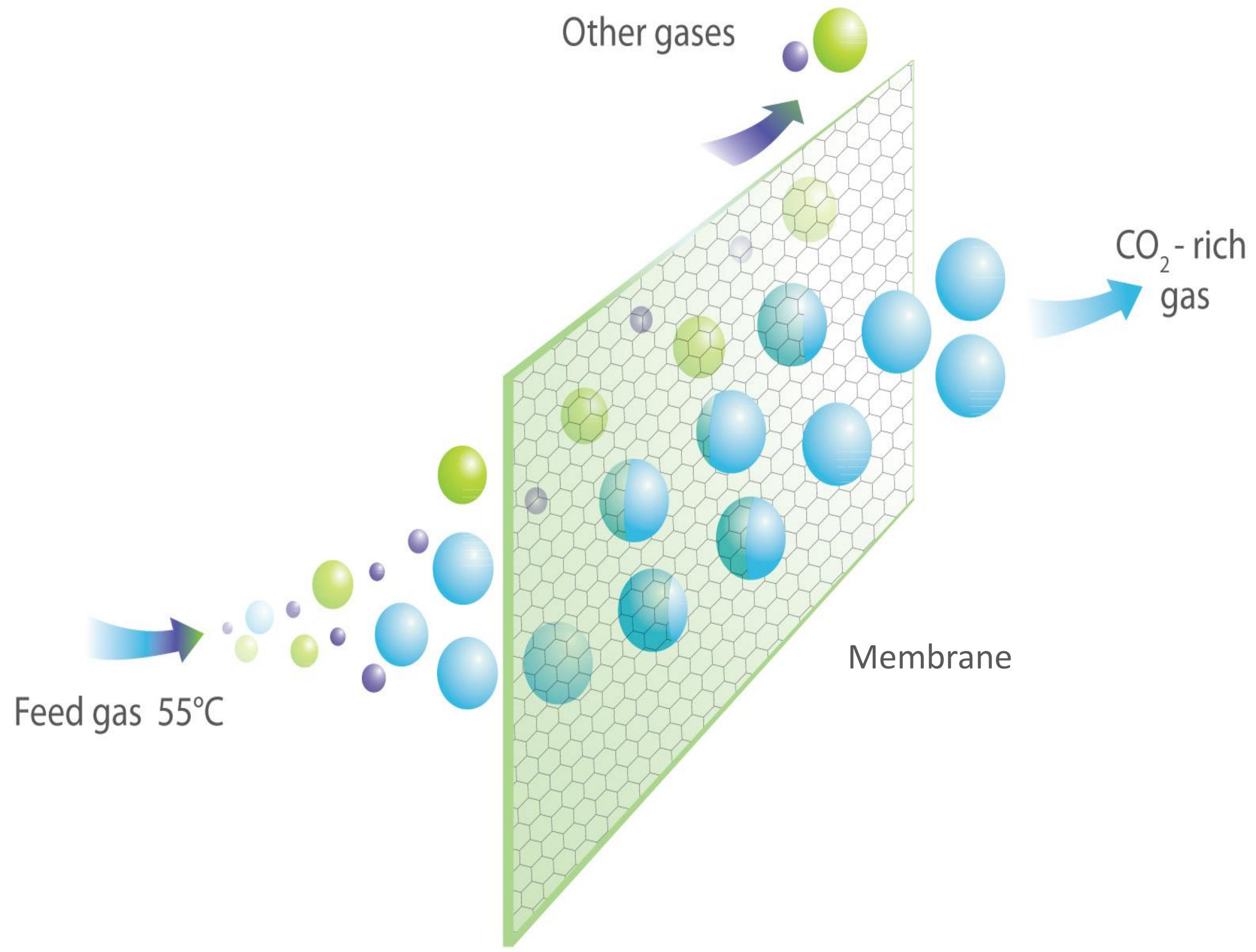
BBI JU

This project has received funding from the Bio Based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation programme, under grant agreement No 887075.

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

Introduction

Gas separation membranes



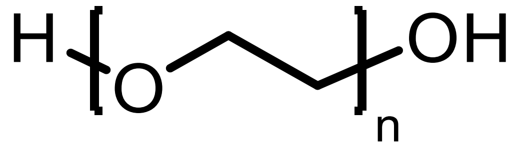
- Permeability is the rate at which gaseous molecules permeate through membrane
- Selectivity is the ability of membrane to separate the gas molecule from their mixture

Membrane materials for gas separation

Membrane

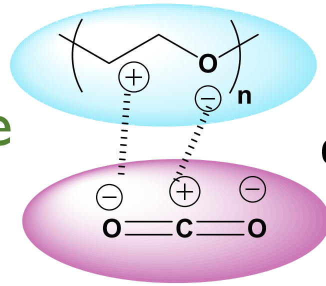
Inorganic (e.g. Silica, zeolites)	**Metallic**	**Polymeric**
✓ Can withstand aggressive conditions as well as high temperatures ○ High cost, modest reproducibility, brittleness and low permeability	✓ Mostly used for hydrogen separation ○ Associated with high cost and scalability issues	✓ Easy processability ✓ easy tunability

Polymeric gas separation membranes



Advantages

- Especially for CO_2 capture



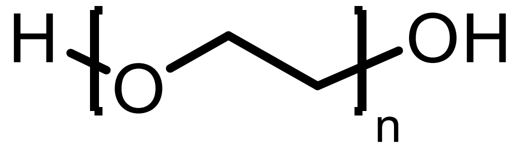
quadrupole-quadrupole interaction

- PEG-based polymers show a considerable CO_2 solubility, and the CO_2 selectivity mainly stems from the solubility selectivity.

Disadvantages

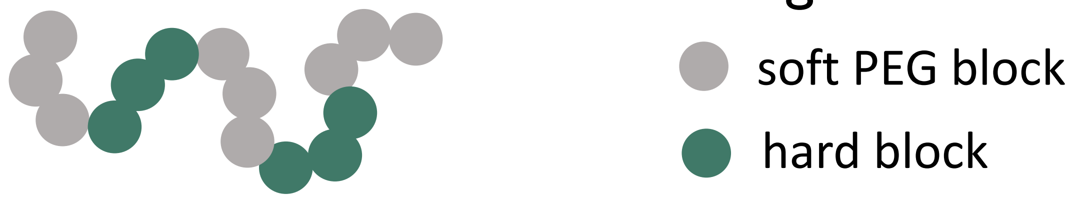
- Permeability Selectivity Trade-off
- Swelling and Plasticization
- Membrane Aging
- Limited Resistance to Fouling
- Mechanical Strength

Polymeric gas separation membranes

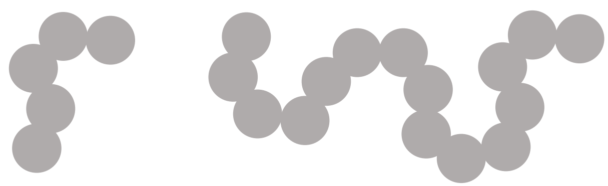


Various approaches to overcome these limitations

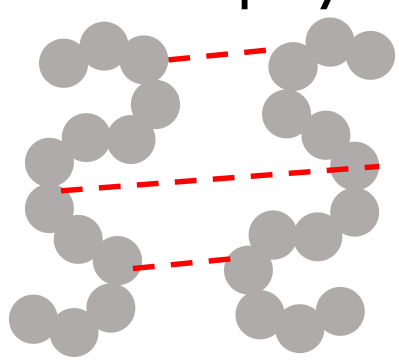
- Block copolymerization with other hard segments



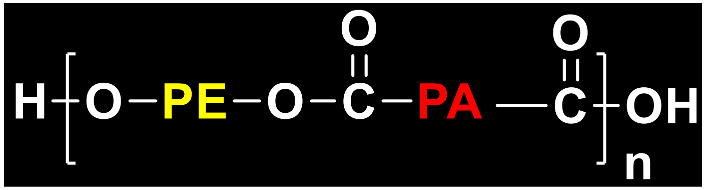
- Blending with low molecular weight PEG and PEG-derivatives



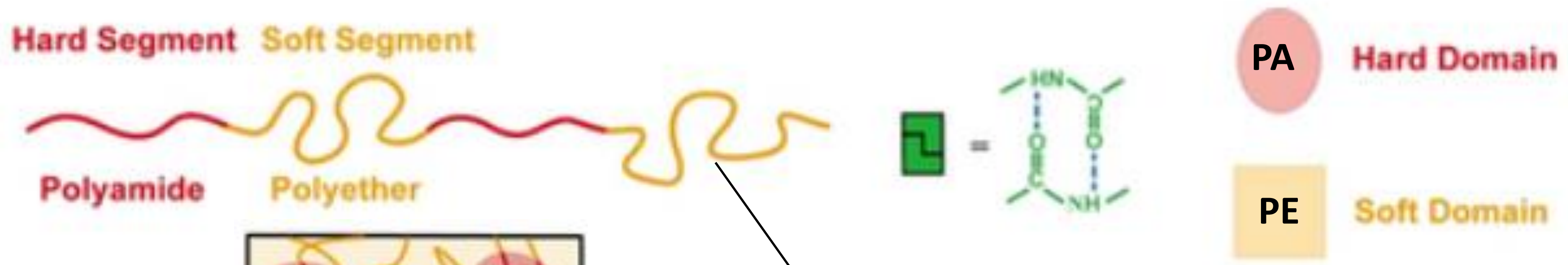
- Crosslinking to form PEG polymer network.

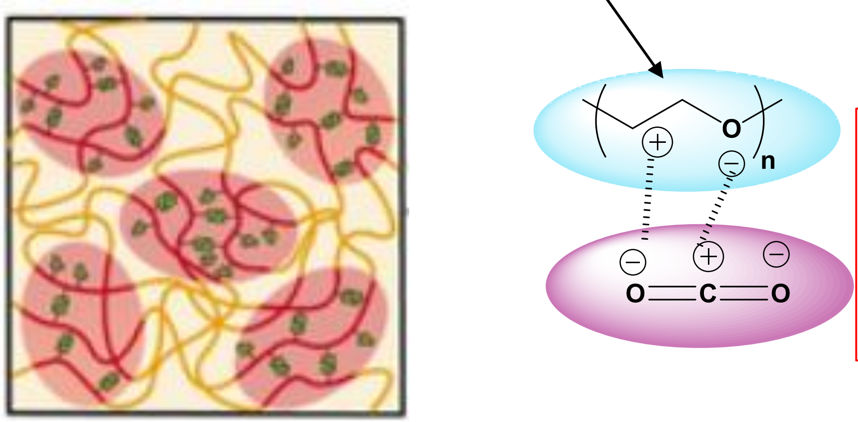


Block copolymers



poly(ether-*b*-amide) PEBA
thermoplastic elastomer





BUT: solubility issues upon processing into monolitic hollow fiber membrane

- Polyamide (PA)
- Semi-crystalline segments
- Hard PA segments provide mechanical stability

- Polyether (PE)
- Soft PE blocks,
- Owing to dipole interactions and high chain mobility, gas permeable

Process steps from monomer to membrane

Lab scale PEBA synthesis → PEBA screening → Upscaling most promising PEBA → Membrane fabrication

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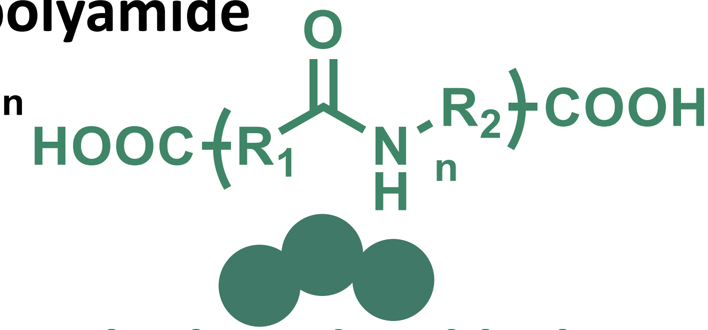
PEBA synthesis

Step 1: synthesis of COOH functionalized polyamide

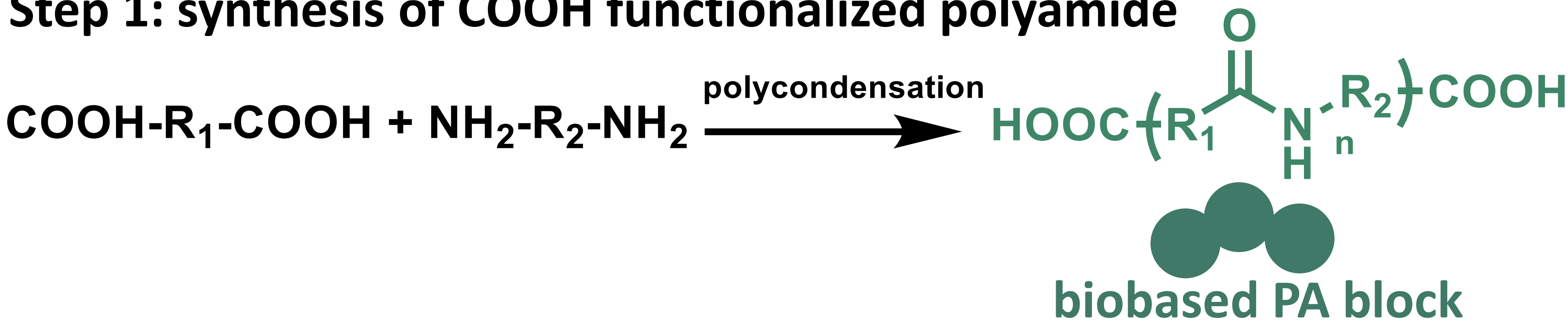
$$COOH\text{-}R_1\text{-}COOH + NH_2\text{-}R_2\text{-}NH_2 \xrightarrow{\text{polycondensation}}$$



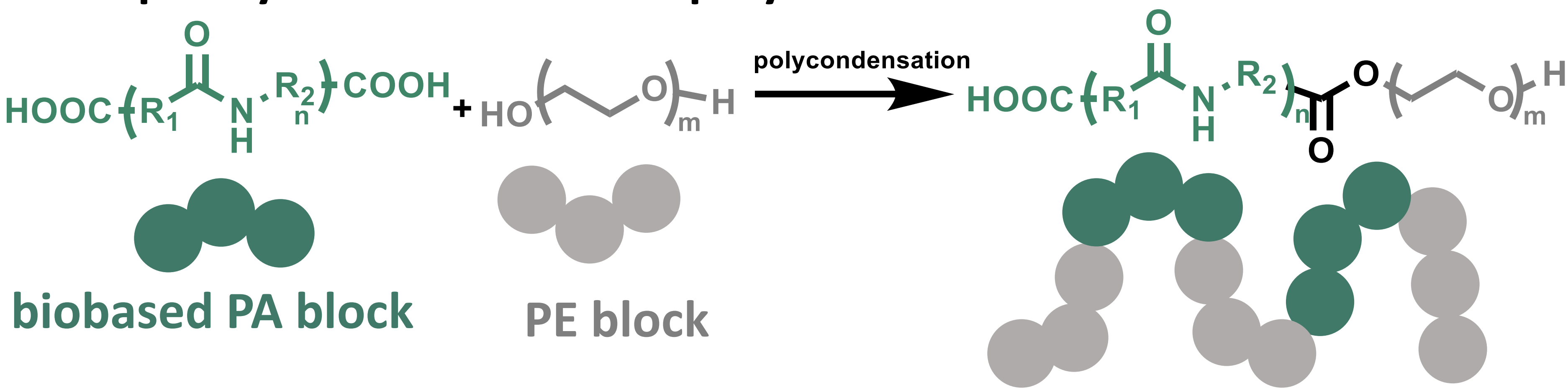
biobased PA block

PEBA synthesis

Step 1: synthesis of COOH functionalized polyamide



Step 2: synthesis of block copolymer



(PA-*b*-polyether)$_n$

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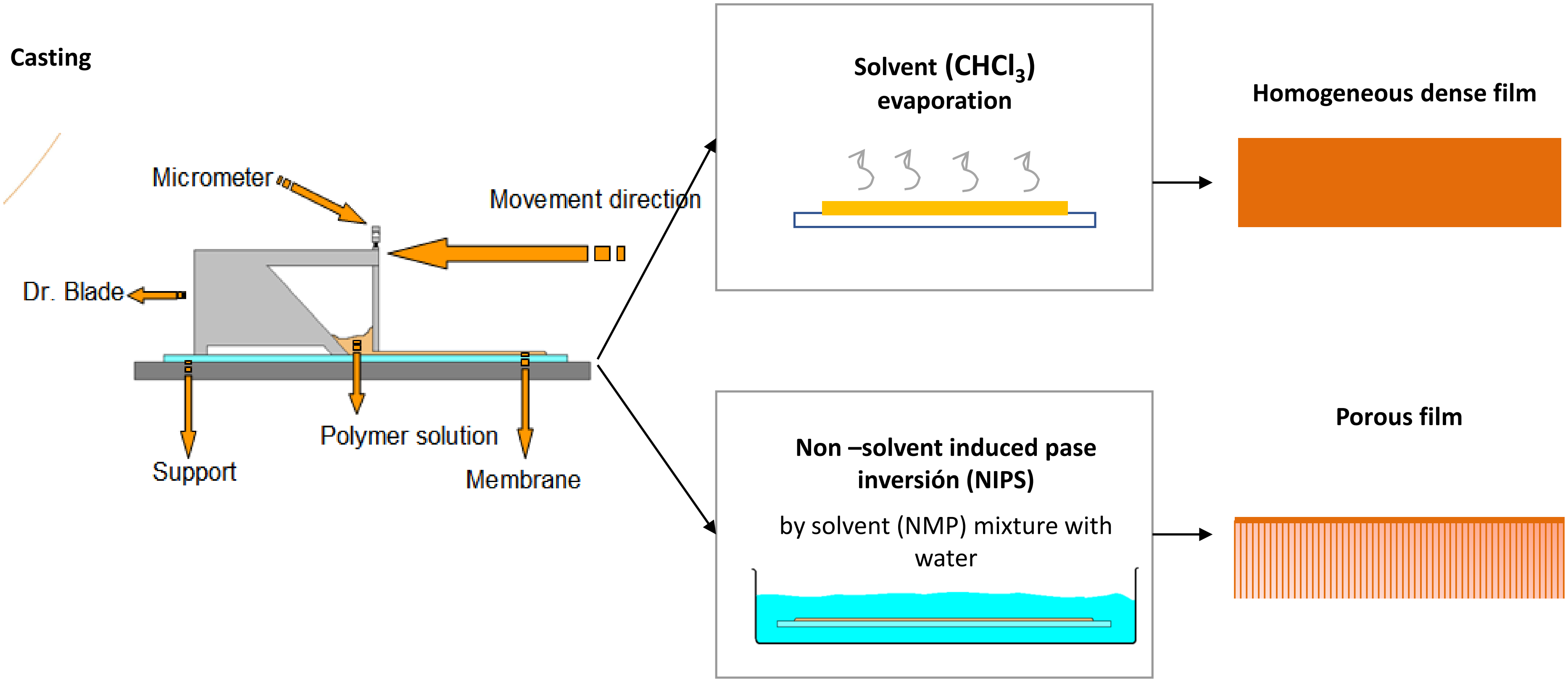
PEBA screening



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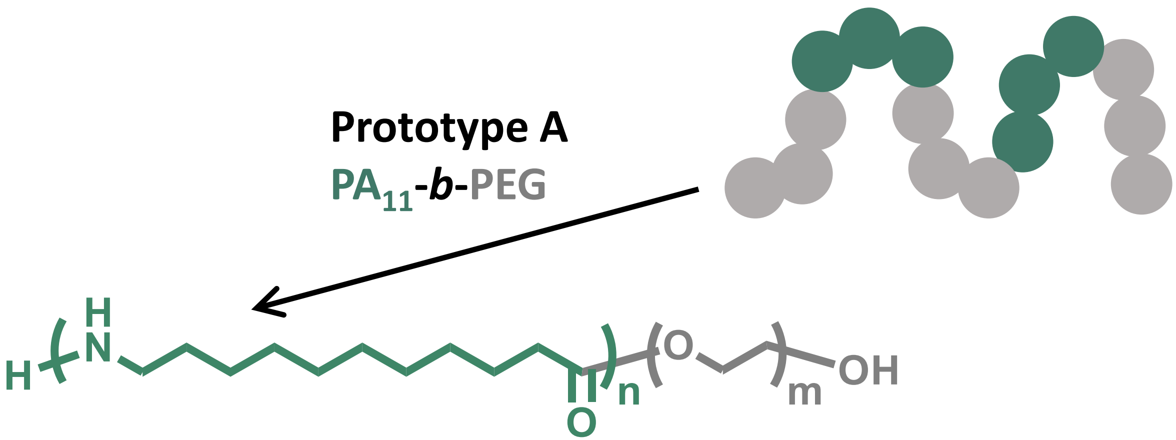
BIOCOMEM results

PEBA with improved processability/solubility

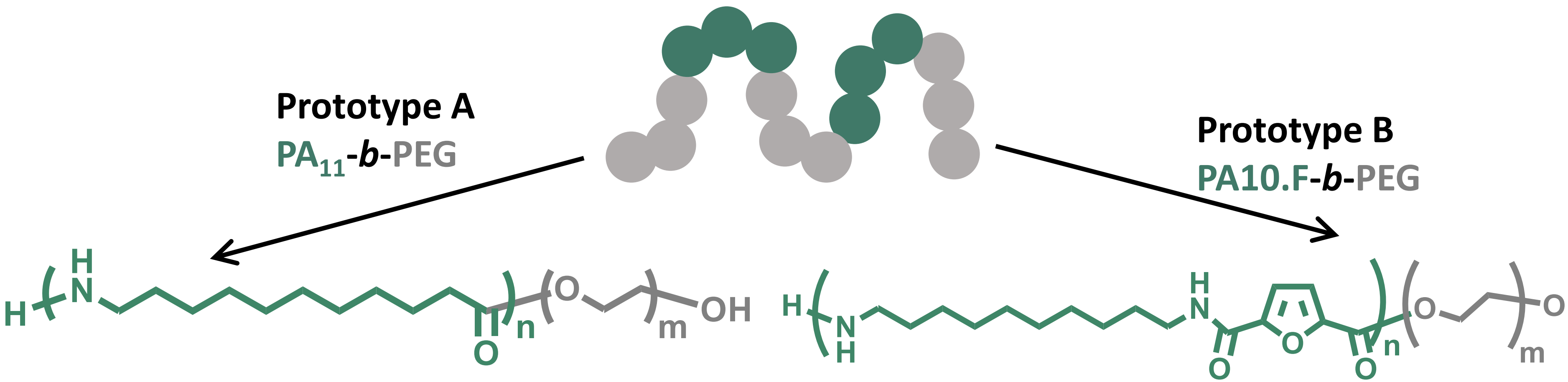
Prototype A
PA_{11}-***b***-PEG



PEBA reference with solubility issues

PEG: T_m = 13 °C; ΔH_m=40 J/g
PA: T_m=149 °C; ΔH_m=29 J/g

PEBA with improved processability/solubility



PEBA reference with solubility issues

PEG: T_m = 13 °C; ΔH_m=40 J/g
PA: T_m=149 °C; ΔH_m=29 J/g

Goals:

- better solubility then prototype A
- less crystalline PA,
  compensate for mechanics via aromatic
- biobased PA

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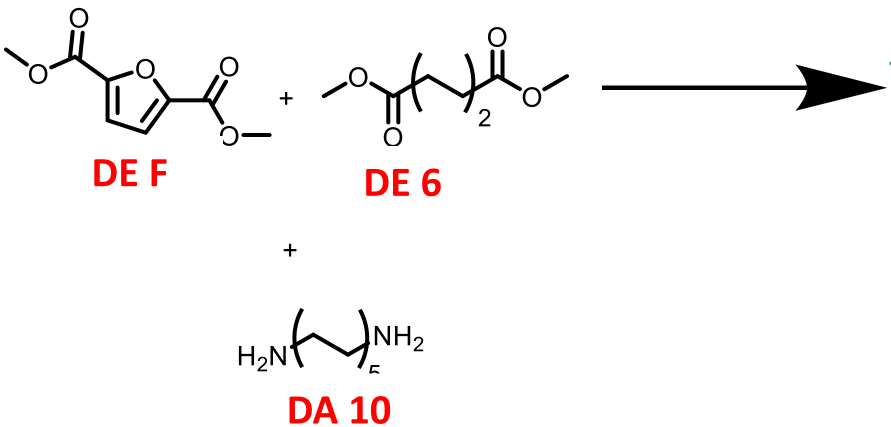
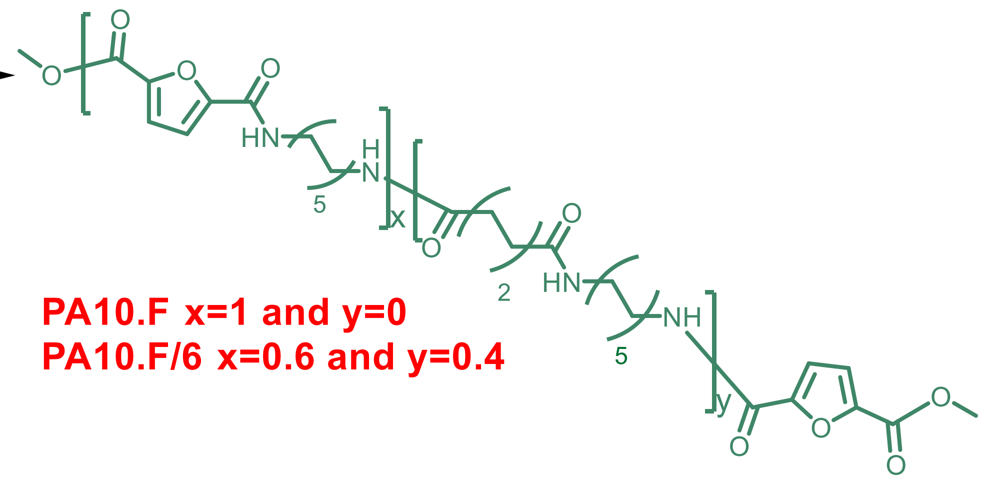
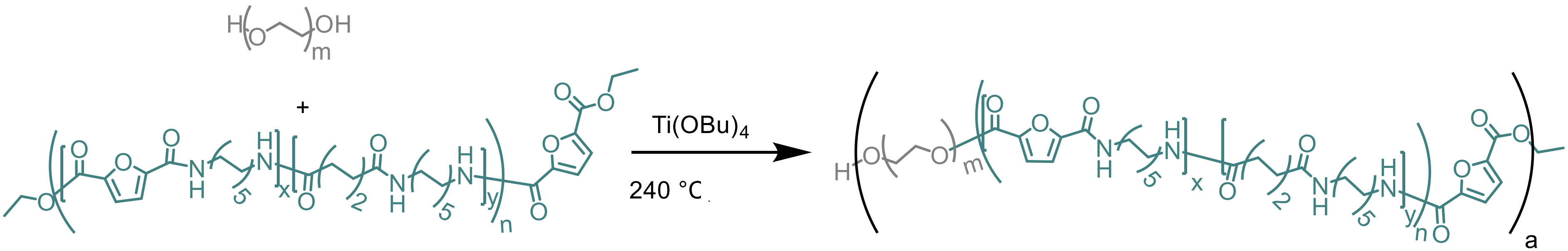
Prototype B synthesis

Step 1: polyamide synthesis

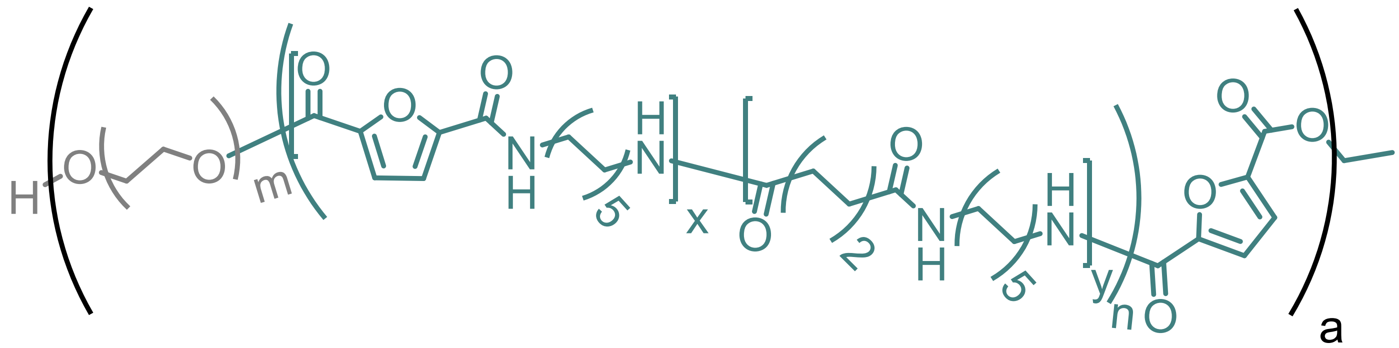




Step 2: PEBA synthesis



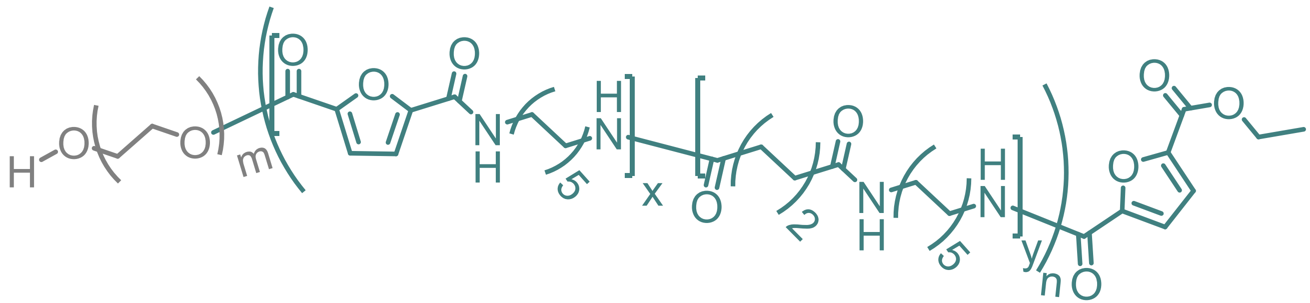
Prototype B synthesis



PA (DA.DE)	$M_{n,PA}$ [g/mol]	$M_{n,PEG}$ [g/mol]	$M_{n,PEBA}$ [g/mol]	Đ	wt% PA/PEG	T_g[°C]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	$\Delta H_{m,PEG}$ [J/g]	$\Delta H_{m,PA}$ [J/g]
PA10.F	900	1500	22 000	1.60	40/60	-45	30	-	143	-.
PA10.F	1500	1500	7 000	1.35	48/52	-45	37	-	140	-
PA10.F/6 x=0.6, y=0.4	1500	1500	8 500	1.51	41/59	-60	48	-	148	-

Polymer is too low M_n and shows poor mechanical properties at temperatures above melting of PEG block.

Prototype B screening



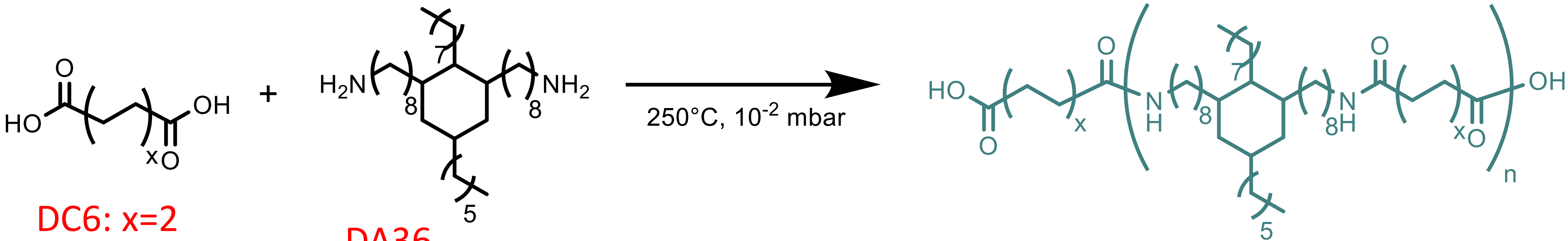
PA (DA.DE)	$M_{n,PA}$ [g/mol]	$M_{n,PEG}$ [g/mol]	$M_{n,PEBA}$ [g/mol]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	CO_2 permeability (Barrer)	CO_2/N_2 selectivity	CO_2/CH_4 selectivity	NIPS membrane formation?
10.F	900	1500	22 000	30	-	20,87	22,5	n.d	no
10.F	1500	1500	7 000	37	-	150	12,6	n.d	no
10.F/6 x=0.6, y=0.4	1500	1500	8 500	48	-	Could not form a dense film			no

Issues membrane evaluation:

- Polymer properties obstacle protocols with temperatures above 50 ℃ are used to prepare membranes.
- high degree of crystallinity of PEG block is detrimental for CO_2 absorption properties

Modified Prototype B – synthesis route A

Step 1: polyamide synthesis

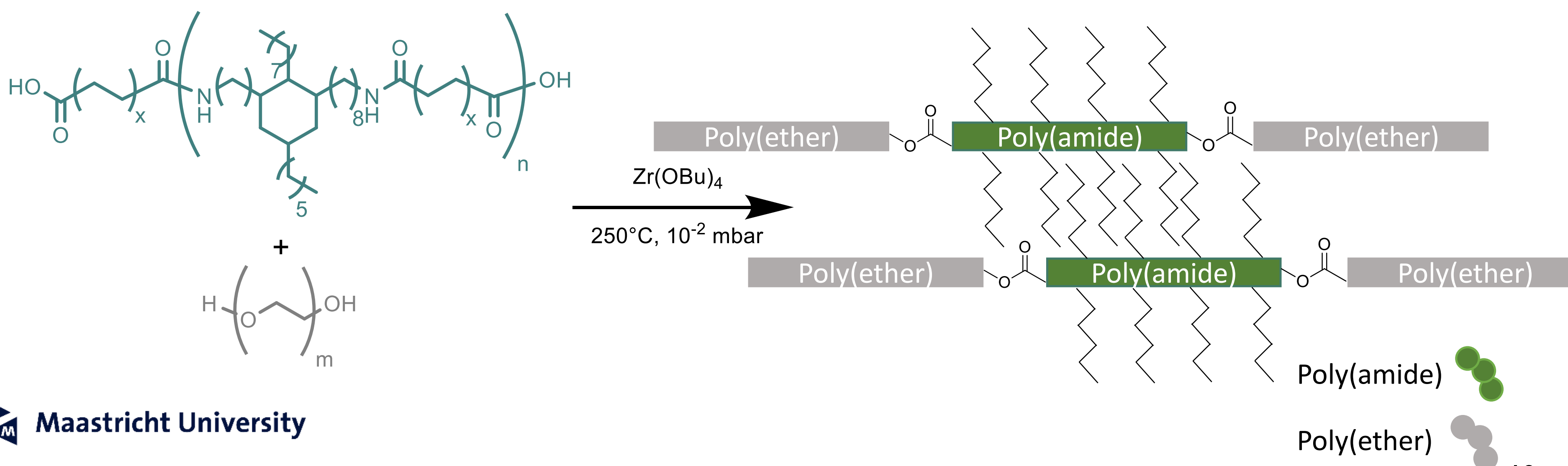


DC6: x=2
DC10: x=4

DA36

PA36.6 or PA36.10

Step 2: PEBA synthesis



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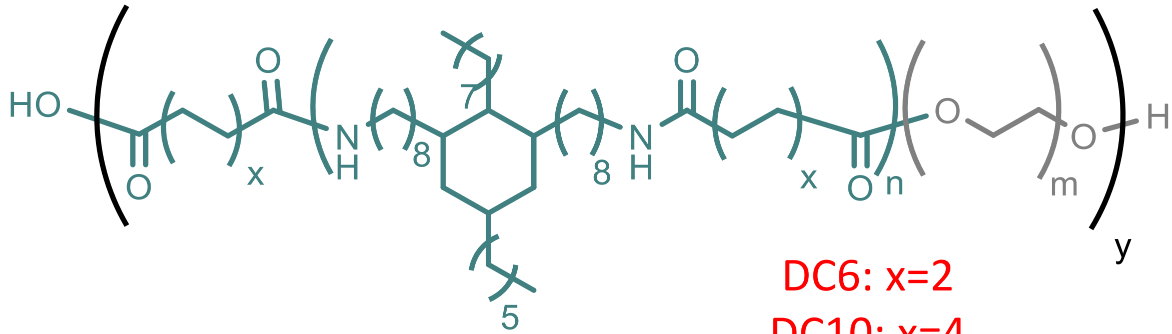
Modified Prototype B – synthesis route A



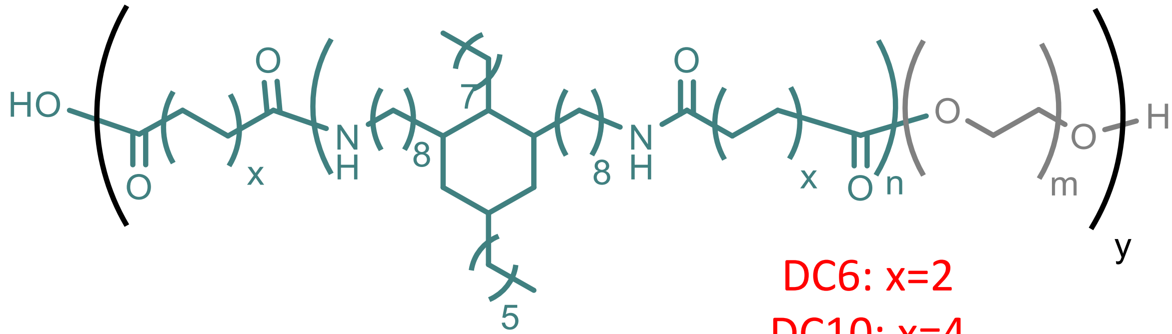
DC6: x=2

DC10: x=4

PA (DA.DC)	$M_{n,PA}$ [g/mol]	$M_{n,PEG}$ [g/mol]	$M_{n,PEBA}$ [g/mol]	Đ	wt% PA/PEG	T_g[°C]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	$\Delta H_{m,PEG}$ [J/g_P	$\Delta H_{m,PA}$ [J/g]
36.6	**3200**	1500	33 000	1.49	**67/33**	<-40	31	102	89	13
36.6	**2100**	1500	27 500	1.61	**59/41**	<-40	34	100	93	11
36.6	**1200**	1500	28 000	1.56	**48/52**	<-40	40	98	86	5
36.10	2600	1500	24 000	1.45	62/38	<-40	41	92	92	14

$M_{n,PEBA}$ lower then expected due to sublimation

Modified Prototype B – screening route A



DC6: x=2

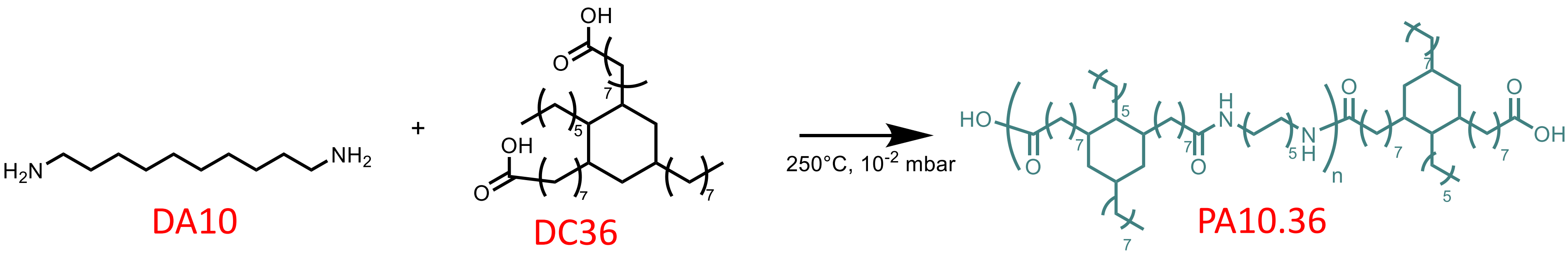
DC10: x=4

PA (DA.DC)	wt% PA/PEG	$M_{n,PEBA}$ [g/mol]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	CO_2 permeability (Barrer)	CO_2/N_2 selectivity	CO_2/CH_4 selectivity	NIPS membrane formation?
36.6	**67/33**	33 000	31	102	139,4	24,3	8,0	no
36.6	**59/41**	27 500	34	100	234,4	29,0		no
36.6	**48/52**	28 000	40	98	45,1	23,9	8,4	no
36.10	62/38	24 000	41	92	70,9	22,6	7,6	no

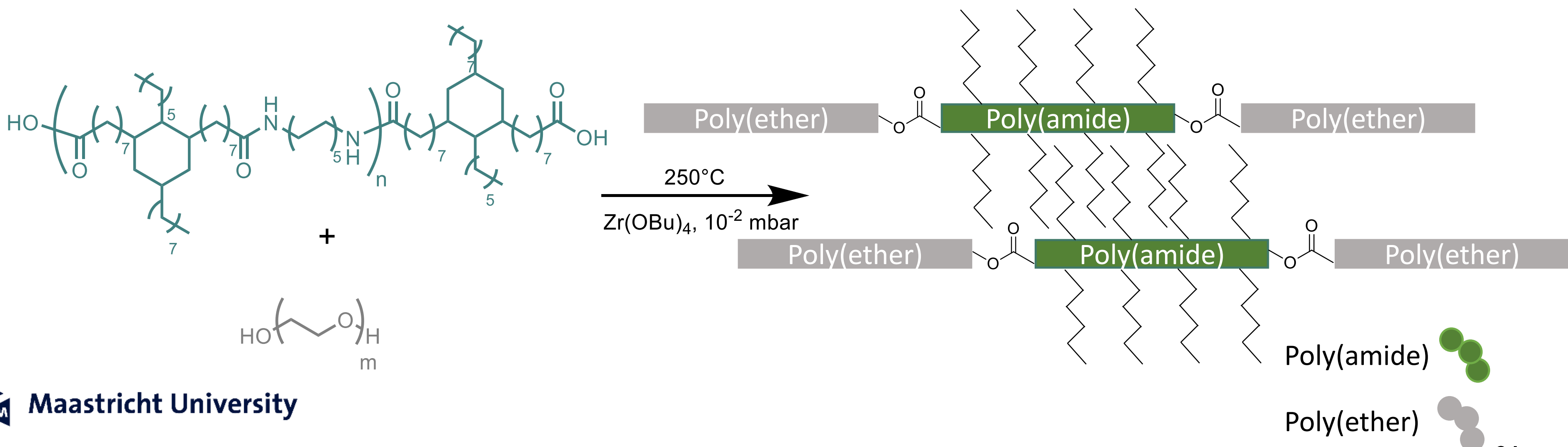
- Screening experiments at 35 °C. If $T_{m,PEG}$ > 35 °C, bad gas separation performance because of lack of mobility in the PEG phase
- NIPS membrane formation not succesfull

Modified Prototype B – synthesis route B

Step 1: polyamide synthesis

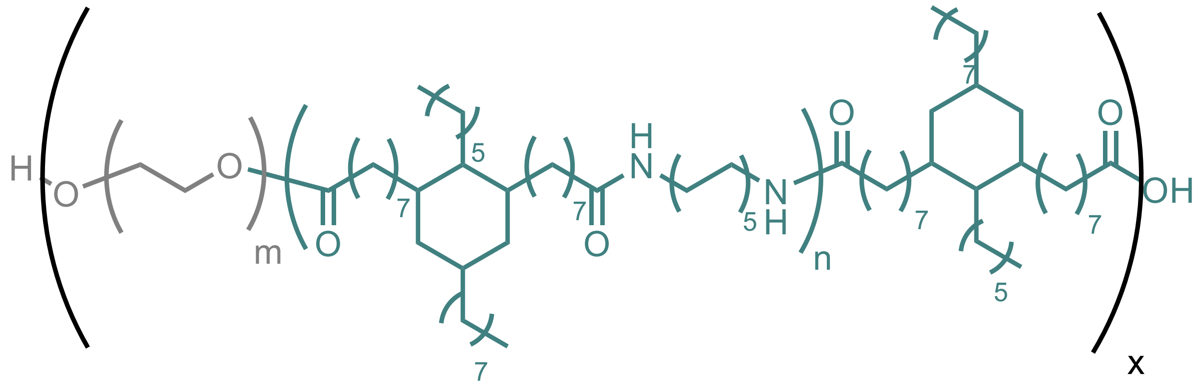


Step 2: PEBA synthesis



Maastricht University

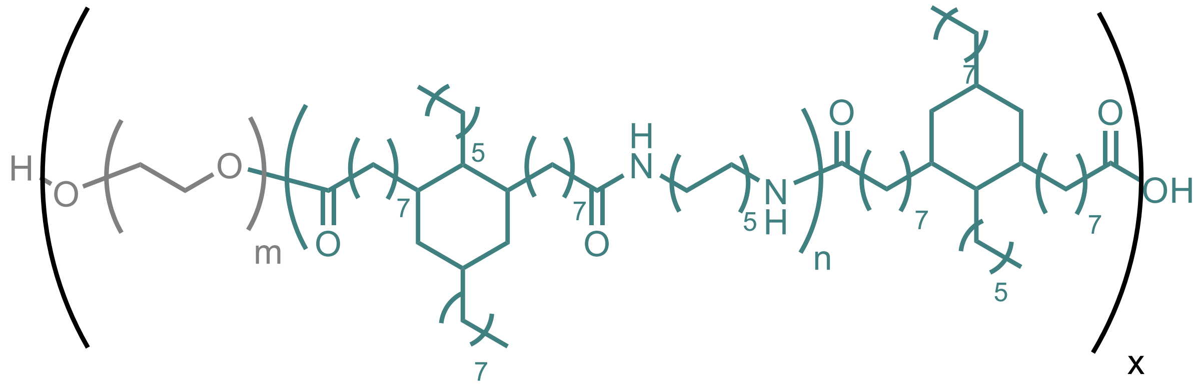
Modified Prototype B – synthesis route B



PA (DA.DC)	$M_{n,PA}$ [g/mol]	$M_{n,PEG}$ [g/mol]	$M_{n,PEBA}$ (g/mol)	Đ	wt% PA/PEG	T_g [°C]	$T_{m,PEG}$ [C]	$T_{m,PA}$ [°C]	$\Delta H_{m,PEG}$ [J/g]	$\Delta H_{m,PA}$ [J/g]
10.36	2000	1500	48 000	2.23	60/40	n/d	16	80	57	20
10.36	2300	1500	43 000	1.77	64/36	-60	14	79	64	19
10.36	2600	**3350**	34 300	2.07	36/64	n/d	54	78	113	12

Maastricht University

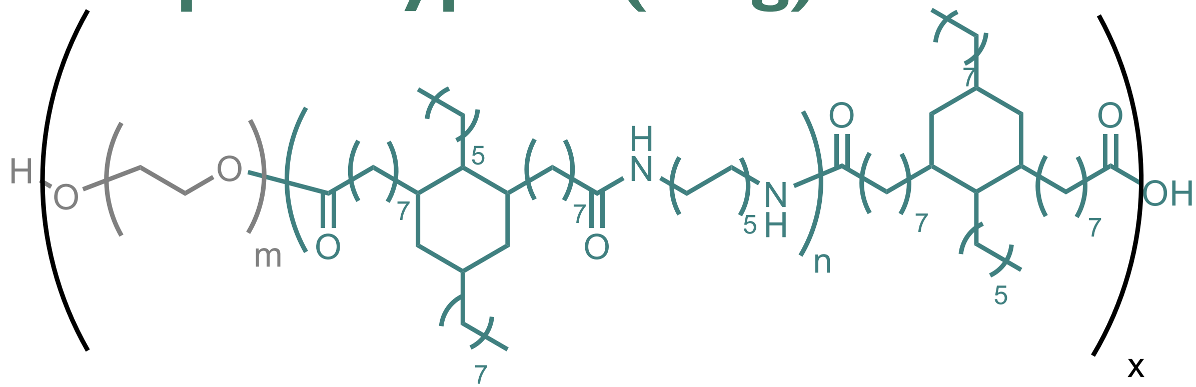
Modified Prototype B – screening route B



PA (DA.DC)	wt% PA/PEG	$M_{n,PEBA}$ [g/mol]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	CO_2 permeability (Barrer)	CO_2/N_2 selectivity	CO_2/CH_4 selectivity	NIPS membrane formation?
10.36	60/40	48 000	16	80	228,8 ±8,2	27,5 ±1,64	9,2 ±0,7	yes
10.36	64/36	43 000	14	79	219,0 ±0,2	26,9 ±0,14	8,7 ±0,02	yes
10.36	36/64	34 300	54	78	40,1	27,3	8,8	no

Good gas separation properties and NIPS membrane formation succesfull with short PEG (low crystallinity)

Synthesis of upscaled PEBA modified prototype B (3 kg)



PA (DA.DC)	$M_{n,PA}$ [g/mol]	$M_{n,PEG}$ [g/mol]	$M_{n,PEBA}$ [g/mol]	Đ	wt% PA/PEG	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	$\Delta H_{m,PEG}$ [J/g]	$\Delta H_{m,PA}$ [J/g]
10.36*	2300	1500	43 000	1.77	**64/36**	14	79	64	19
10.36	2300	1500	52 900	2.19	**55/45**	13	77	28	14
11 endcapped with DC36	1000	1500	82 900	2.57	42/58	24	122	49	5
11/10.36	2100	1500	44 700	2.04	**56/44**	20	94	30	13
11/10.36	6000	1500	50 200	2.38	**78/22**	15	105	20	20

* Only upscaled to 100 g

Membrane properties upscaled PEBA Modified prototype B

Sample	PA (DA.DC)	wt% PA/PEG	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	CO_2 permeability (Barrer)	CO_2/N_2 selectivity	CO_2/CH_4 selectivity	CO_2/H_2 selectivity
Polyactive	$PEG1500_{77}PBT_{23}$		27	110	115	45.6	n.d.	n.d.
Prot A	11	40/60	25	160	311	45	14.07	9.35
Prot B1	10.36	64/36	14	79	219	26.9	8.7	n.d.
Prot B2	10.36	55/45	13	77	354	28.83	8.99	5.48
Prot B3	11 endcapped with DC36	42/58	24	122	360	36.13	10.9	7.46
Prot B4	11/10.36	56/44	20	94	343	30.13	9.25	5.37
Prot B5	11/10.36	78/22	15	105	106	21.02	7.16	2.81

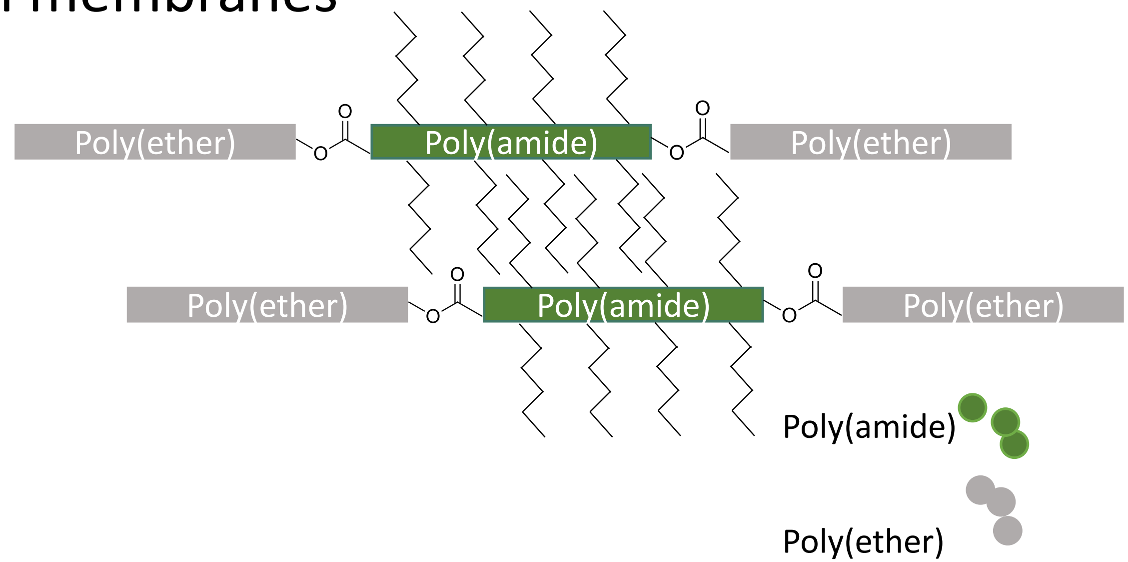
Test conditions: 35 °C and 3 bar Δp for all samples, except Polyactive 30 ºC, 300 mbar

Conclusion:

- Higher PEG content better for gas separation properties
- Prot B3 best tradeoff between processability and gas separation

Conclusions

- Succesfull synthesis of a new class of PEBA for gas separation membranes



- Dimer fatty acid in the polyamide block increases solubility/processability into membranes
- Gas separation properties of screening results very promising

Thin-film composite (TFC) membrane fabrication:

polymer → membrane → module

Angeles Ramirez-Kantun, M.Sc.
Dr. Sergey Shishatskiy
Dr. Torsten Brinkmann

24.11.2023

Institute of Membrane Research

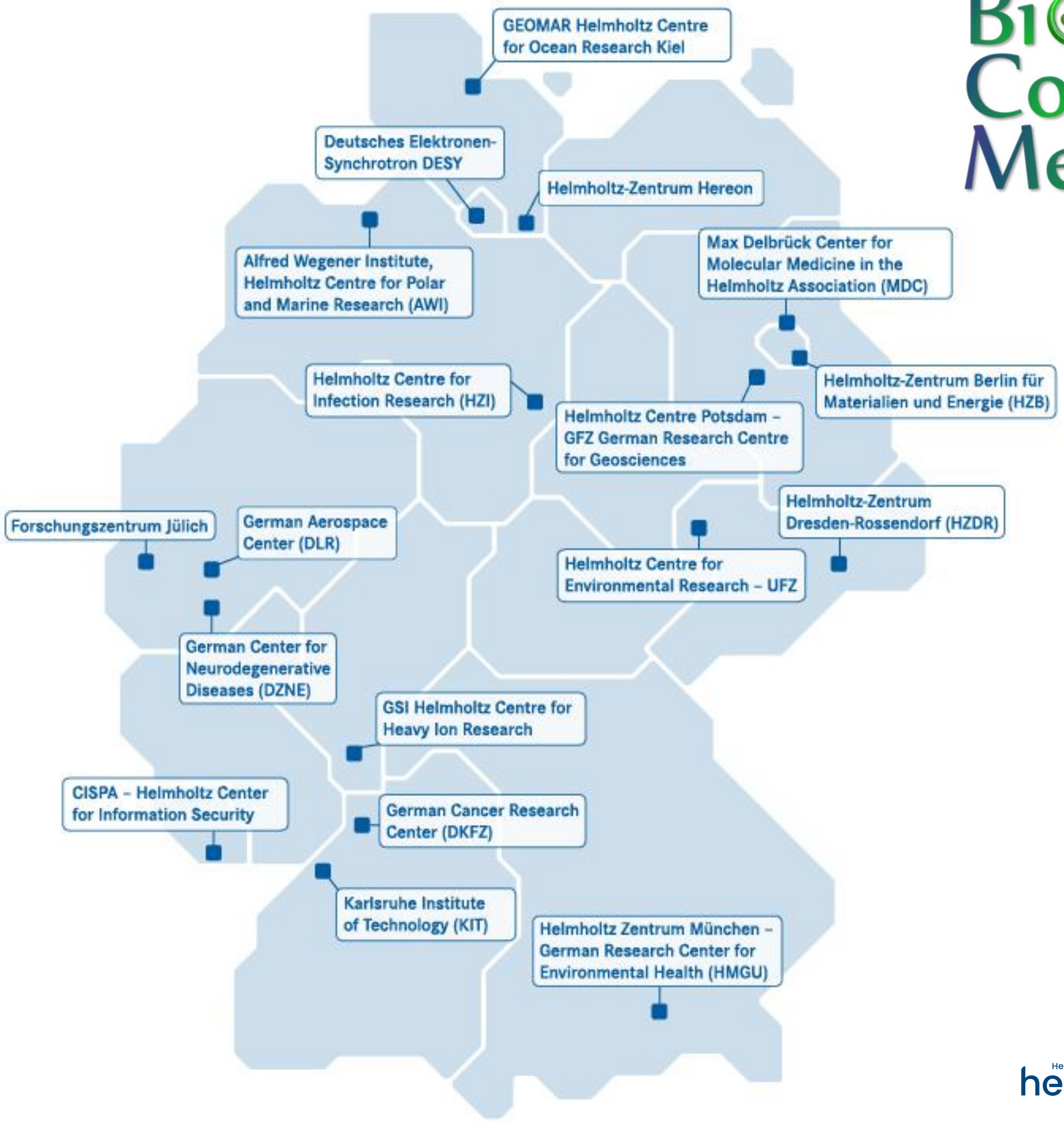
BioCoMem

Helmholtz-Zentrum hereon

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	



BioCoMem

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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

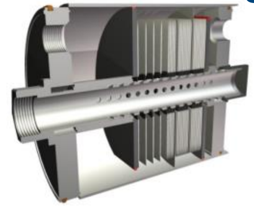
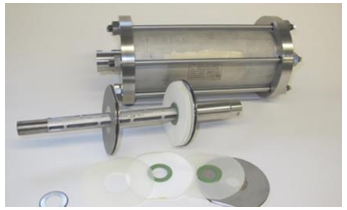
Lab. scale investigations

- Polymer synthesis
- Polymer modification
- Permeation behaviour

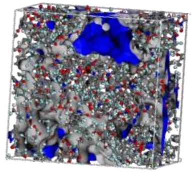
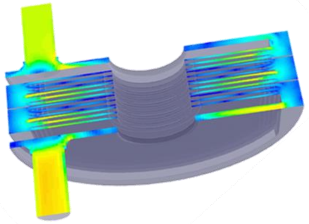
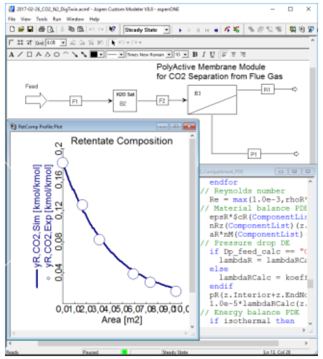

Pilot scale membrane production

Pilot plants

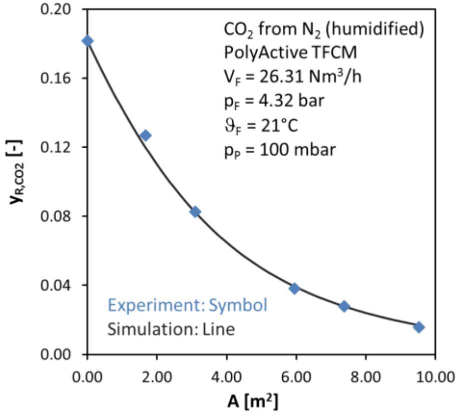

Module design

Modelling and simulation

Comp. pilot plant/simulation



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

Hereon’s role within BioCoMem project

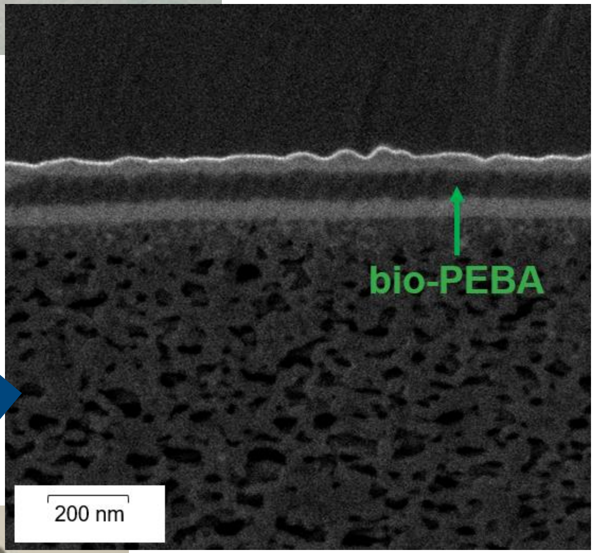
- **Objectives**:

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

  ✓ Manufacture of **membrane modules**

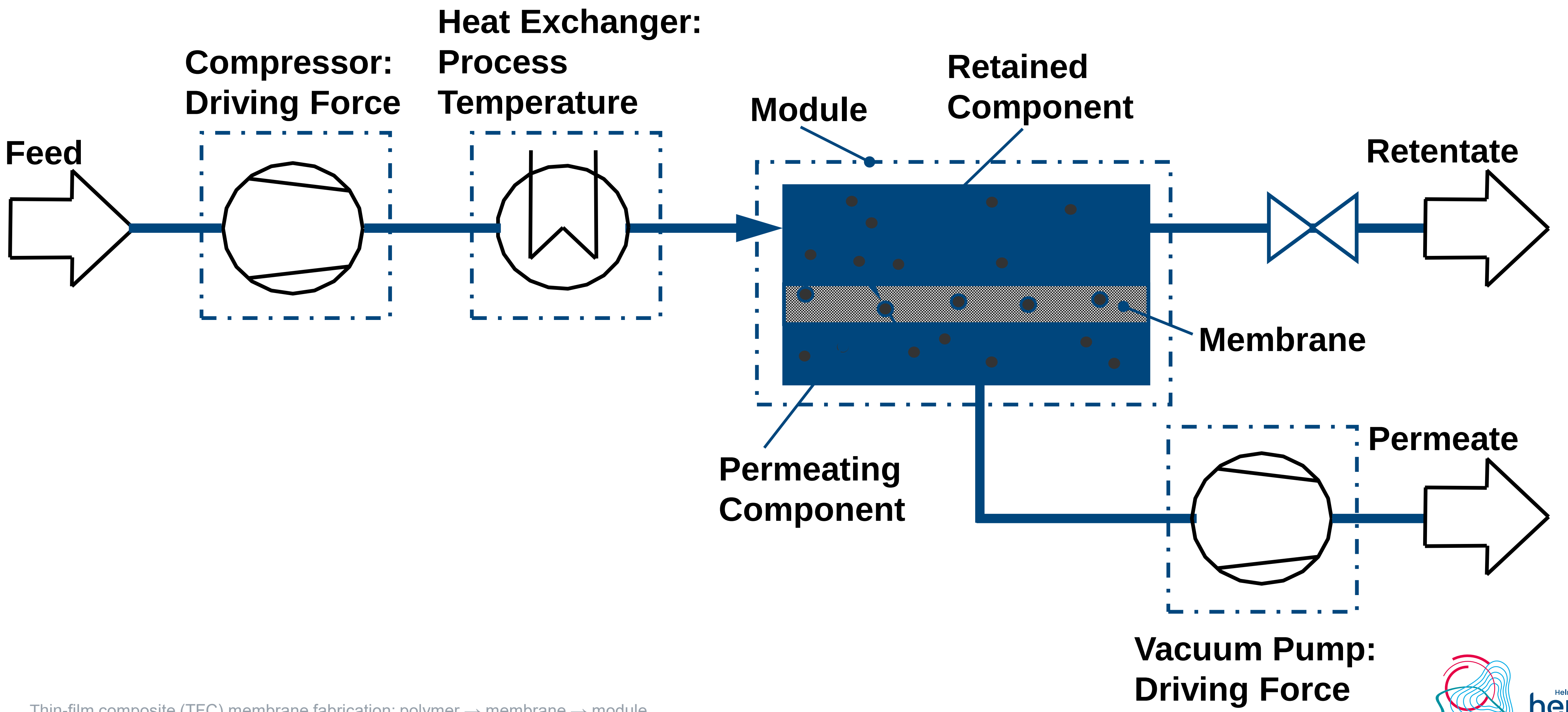
Intended applications:
CO_2 separation

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



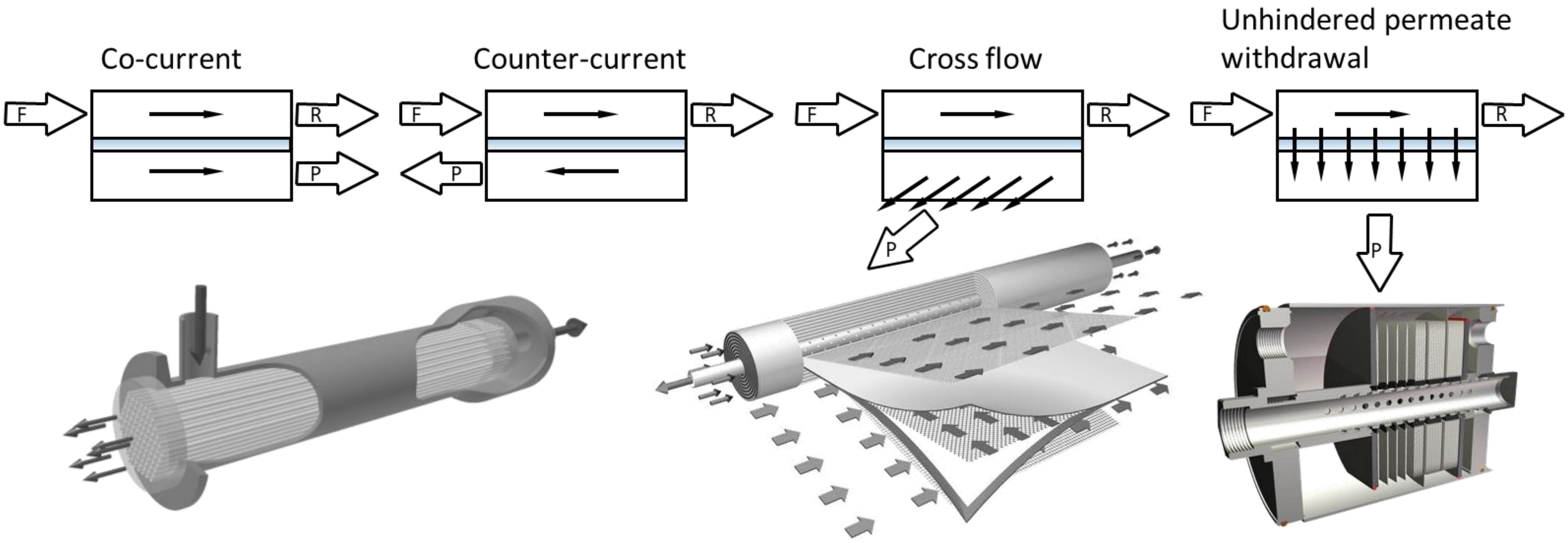
Thin-film composite (TFC) membrane fabrication: polymer → membrane → module

Membrane gas separation process



Membrane modules

Transfer membrane’s properties into process



Hollow fibre/capillary/tubular module

Spiral wound module

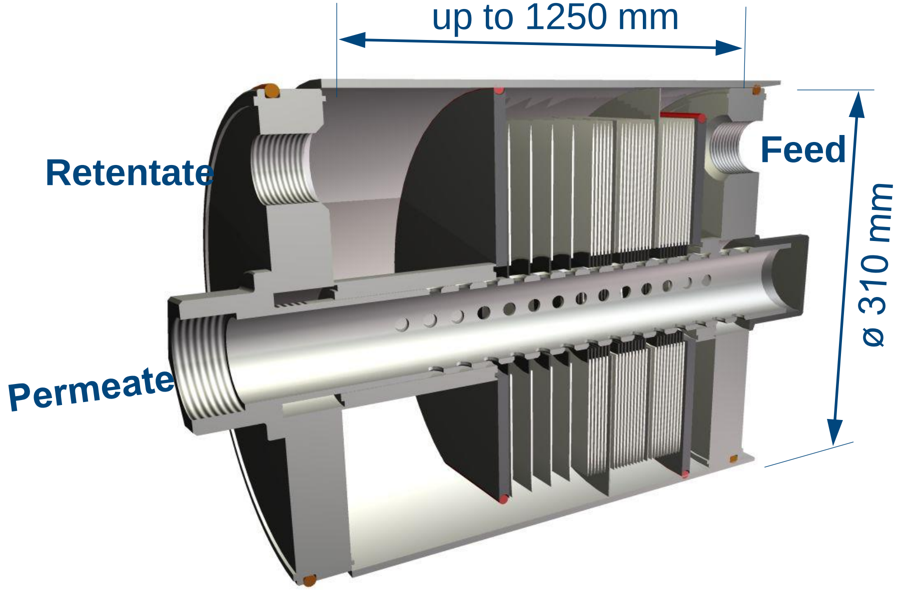
https://doi.org/10.1016/j.desal.2006.12.009

Envelope type module

Envelope type membrane modules

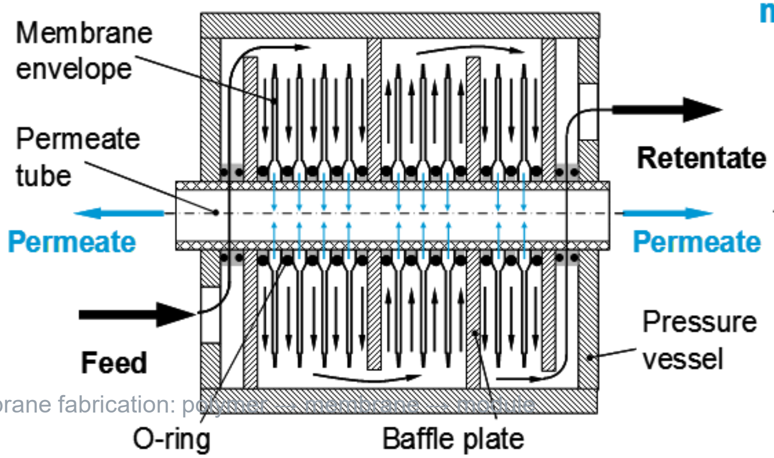
Standard module ø 300 mm

up to 75 m^2 of membrane area

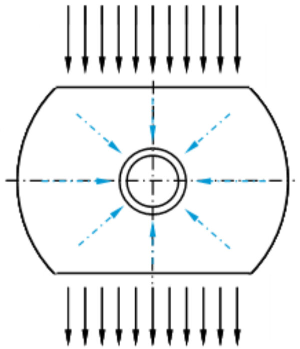


Pilot **Standard** **High pressure**

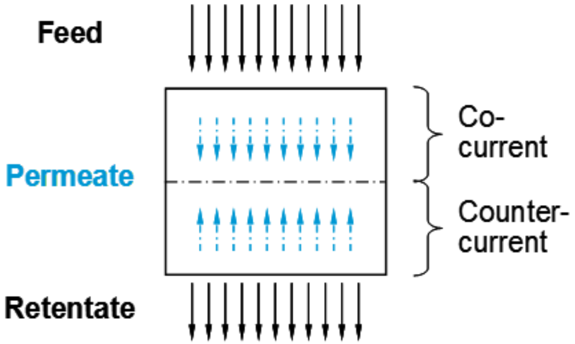
Gas flow within the module



Top view of a membrane envelope



One dimensional representation of envelope

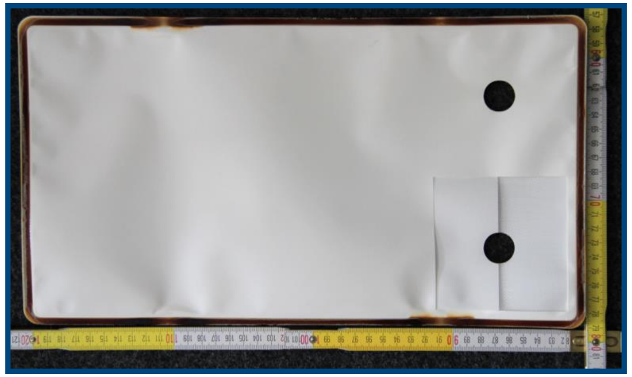


Membrane Modules: Envelope Type

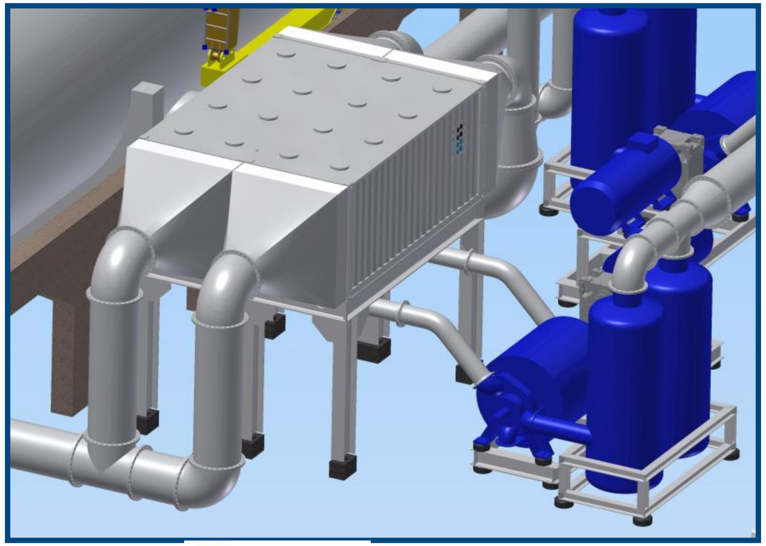
→ Standard envelope type
- ∅ 100 mm: miniplants
- $A \leq 1\ m^2$

- ∅ 310 mm: pilot / industrial
- $A \leq 70\ m^2$

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

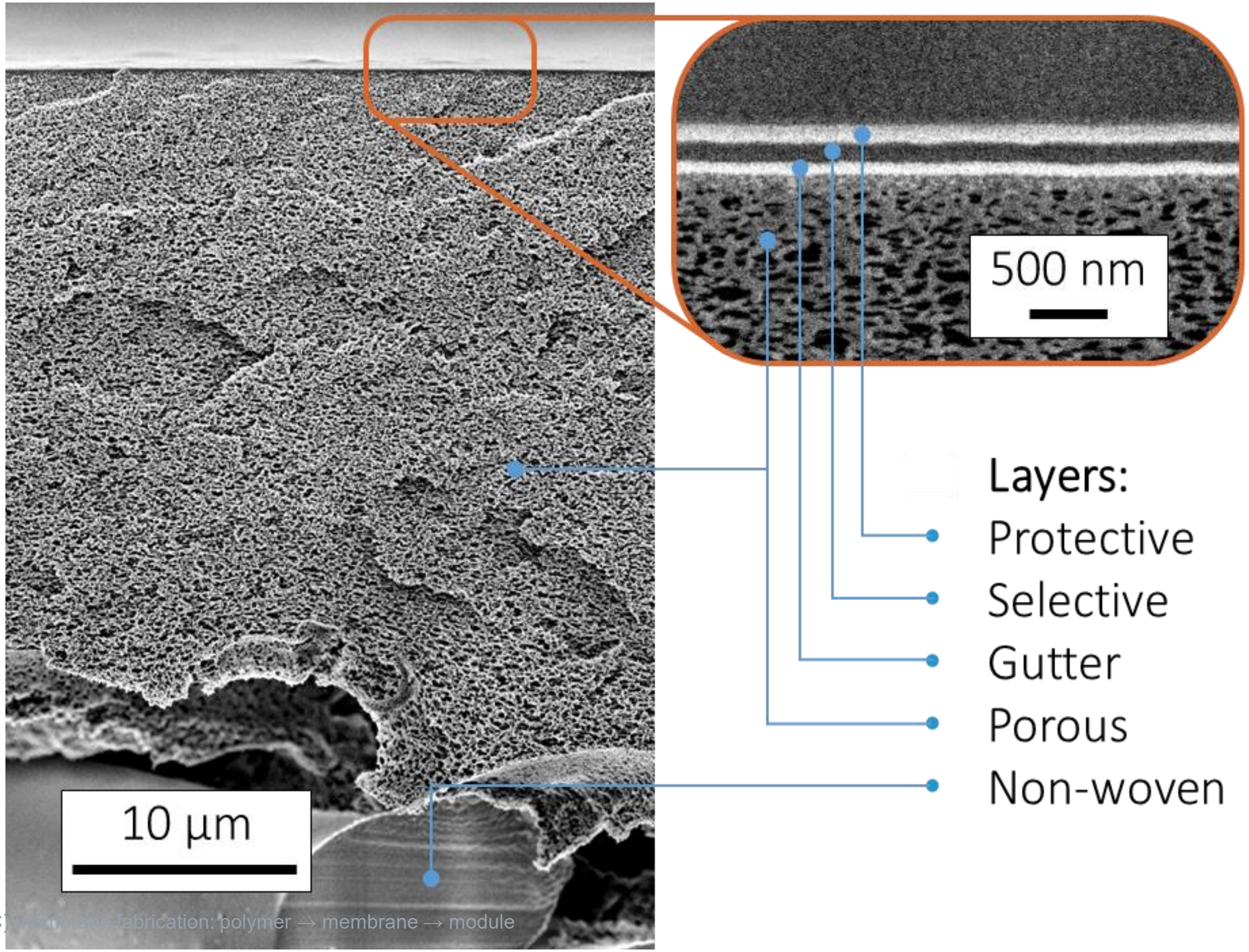


→ Scale-up concept
- Counter current flow
- 20‘ container
- Large scale applications (e.g. flue gas)
- 2.35 m × 5.89 m
- $A \leq 15\ 000\ m^2$



HELMHOLTZ ASSOCIATION Portfolio Mem-Brain

TFC membrane: multi-layer internal morphology



Layers:

Protective	δ < 100 nm
Selective	δ ≈ 50 – 200 nm
Gutter	δ ≈ 50 – 150 nm
Porous	δ ≈ 30 – 100 µm
Non-woven	δ ≈ 100 µm

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

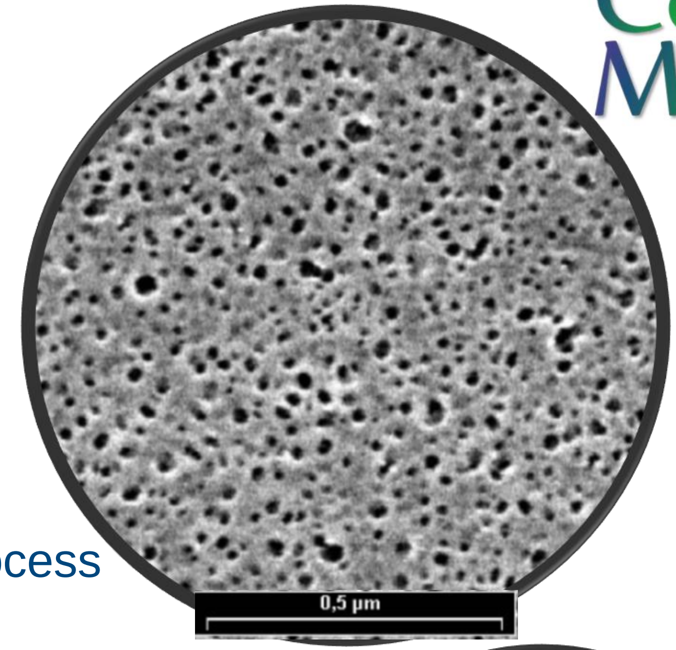
Food storage
Ethyl cellulose

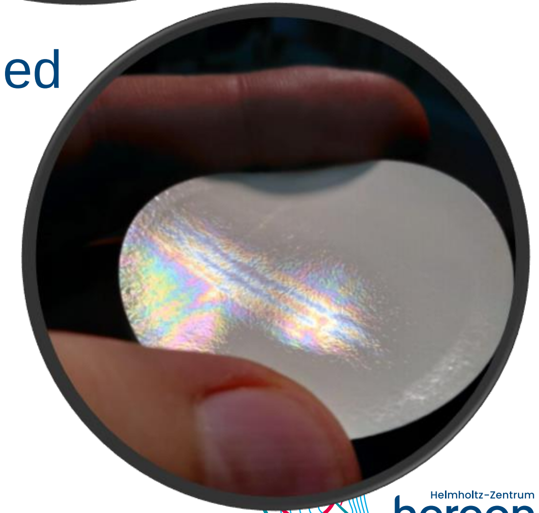
Catalytic membranes
PDMS
PIM
PEBAX®
TORLON®

High temperature separations
Polyimides
PBI

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

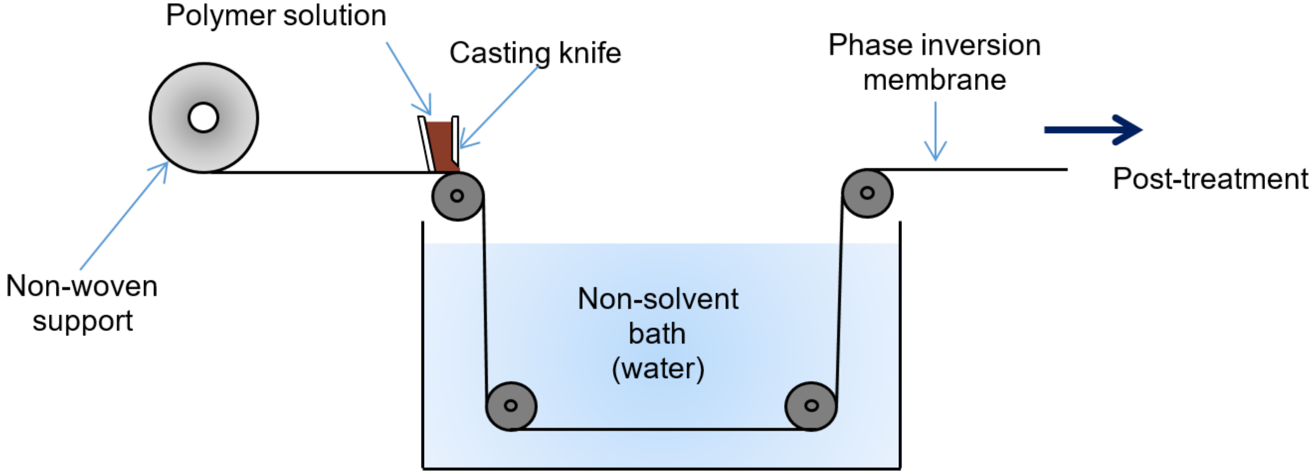
Preparation of porous support by **phase inversion**:

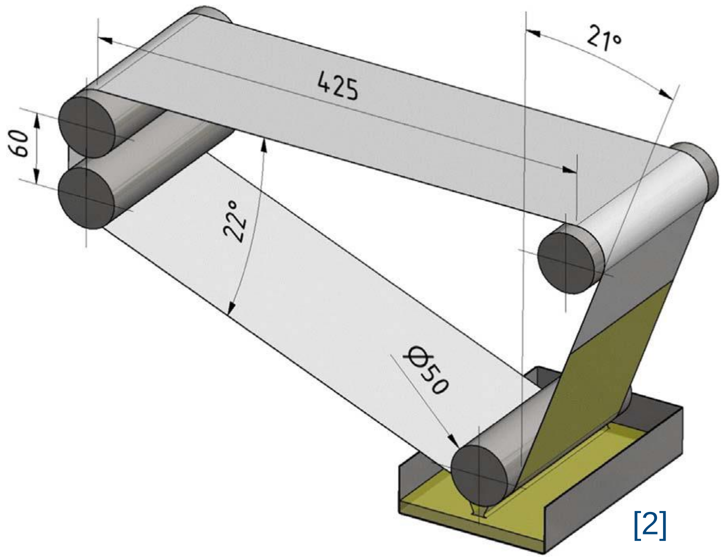
Poly(acrylonitrile) (**PAN**) on polyester (**PES**) non-woven fabric

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

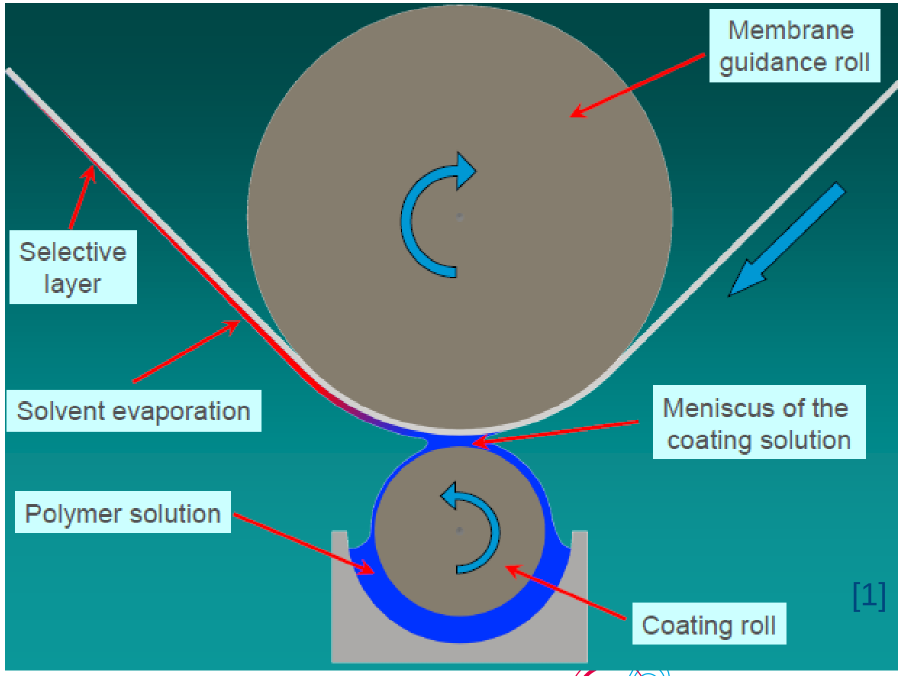
Deposition of **PEBA selective** layer by dip coating

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





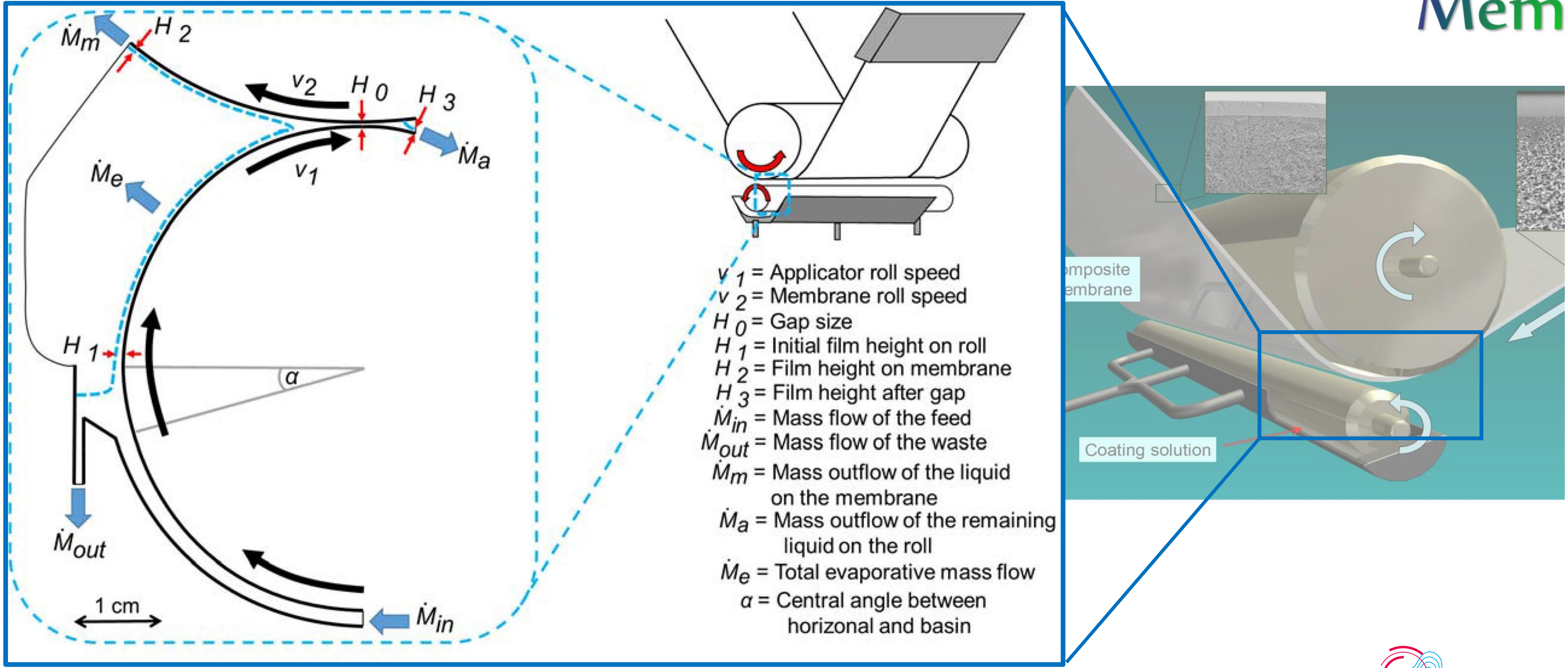
[2]



[1]

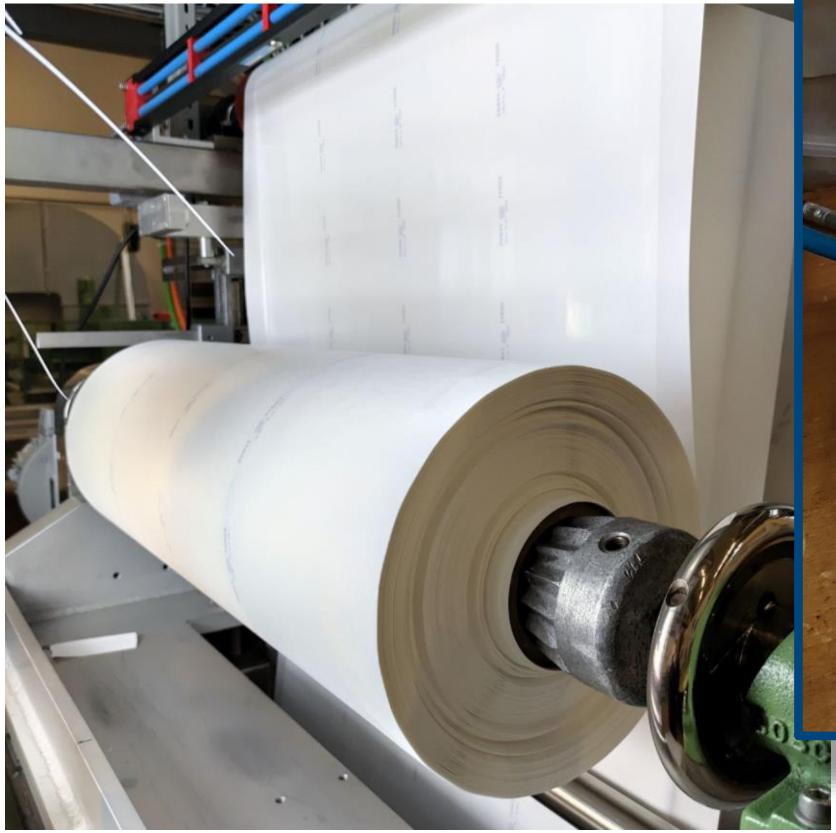
[1] Image courtesy of T. Wolff.
[2] Grünauer et al., Journal of Membrane Science, Vol. 518, 15, Pages 178-191 **(2016)**.

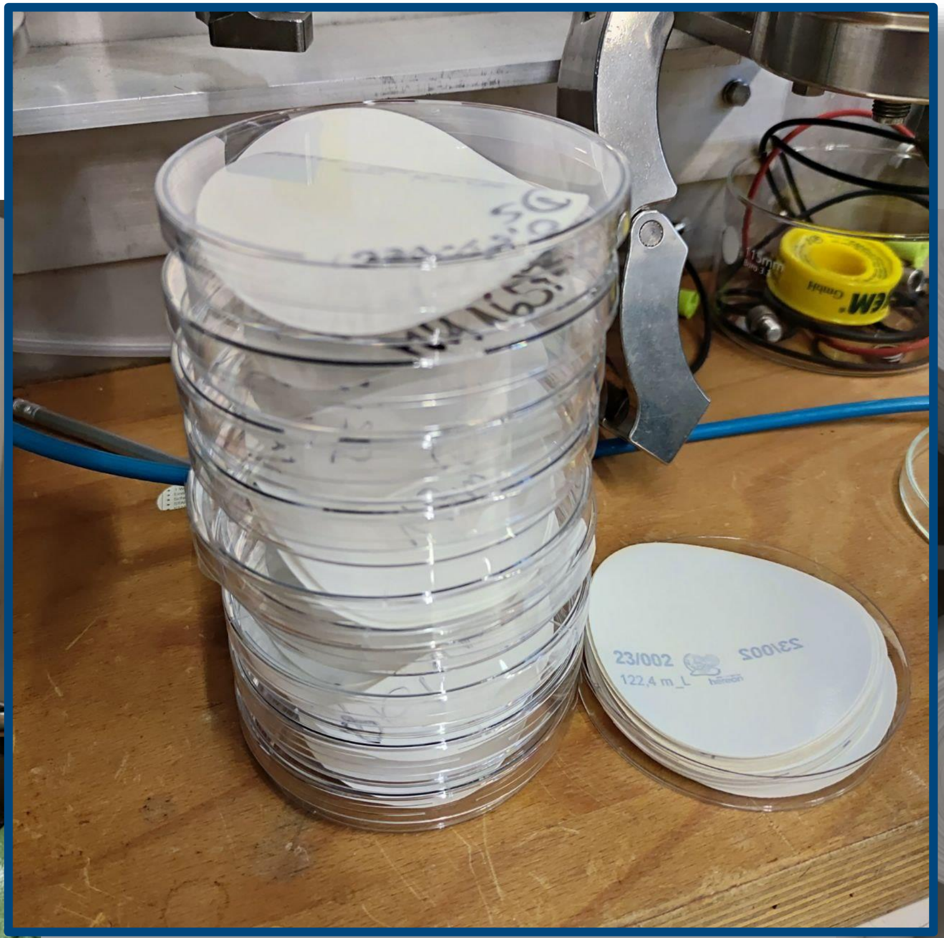
Modelling of processes occurring in solution meniscus during TFC membrane formation



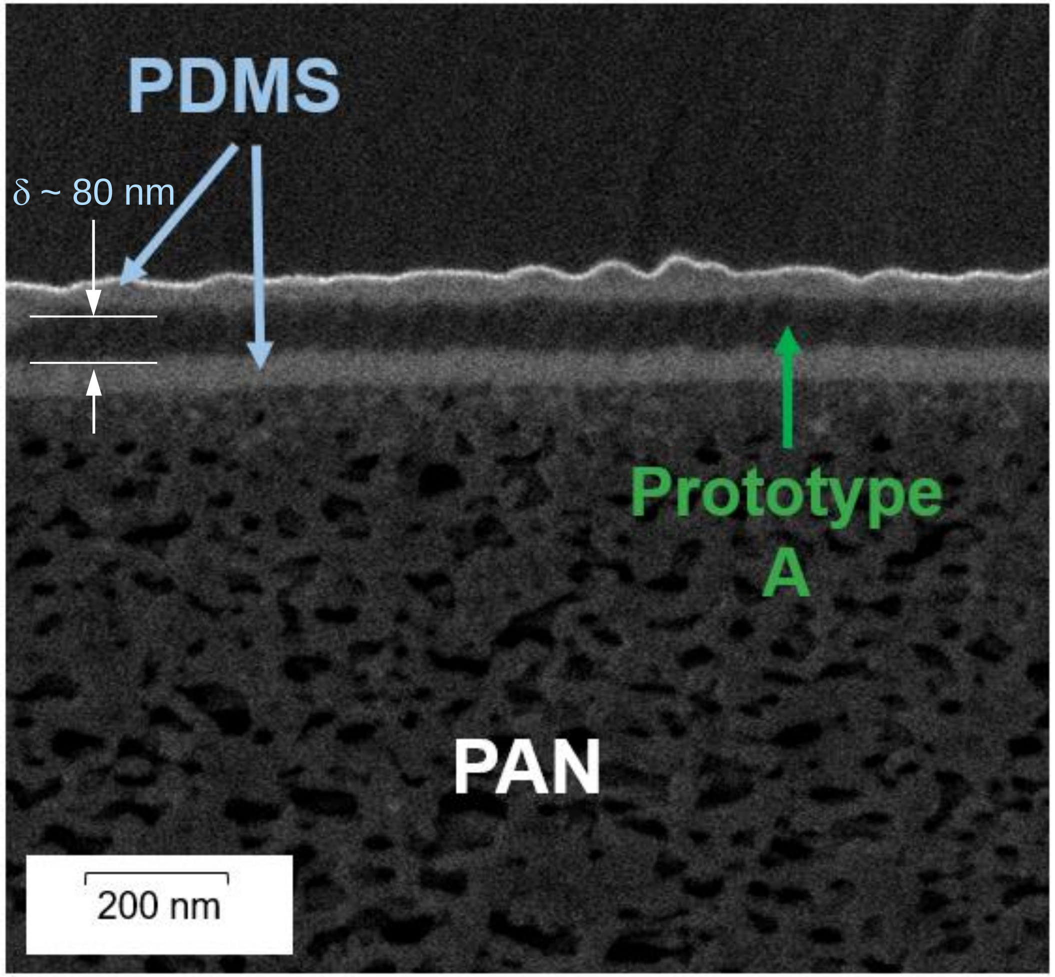
J Adv Manuf & Process, Volume: 3, Issue: 2, First published: 02 February 2021, DOI: (10.1002/amp2.10076)

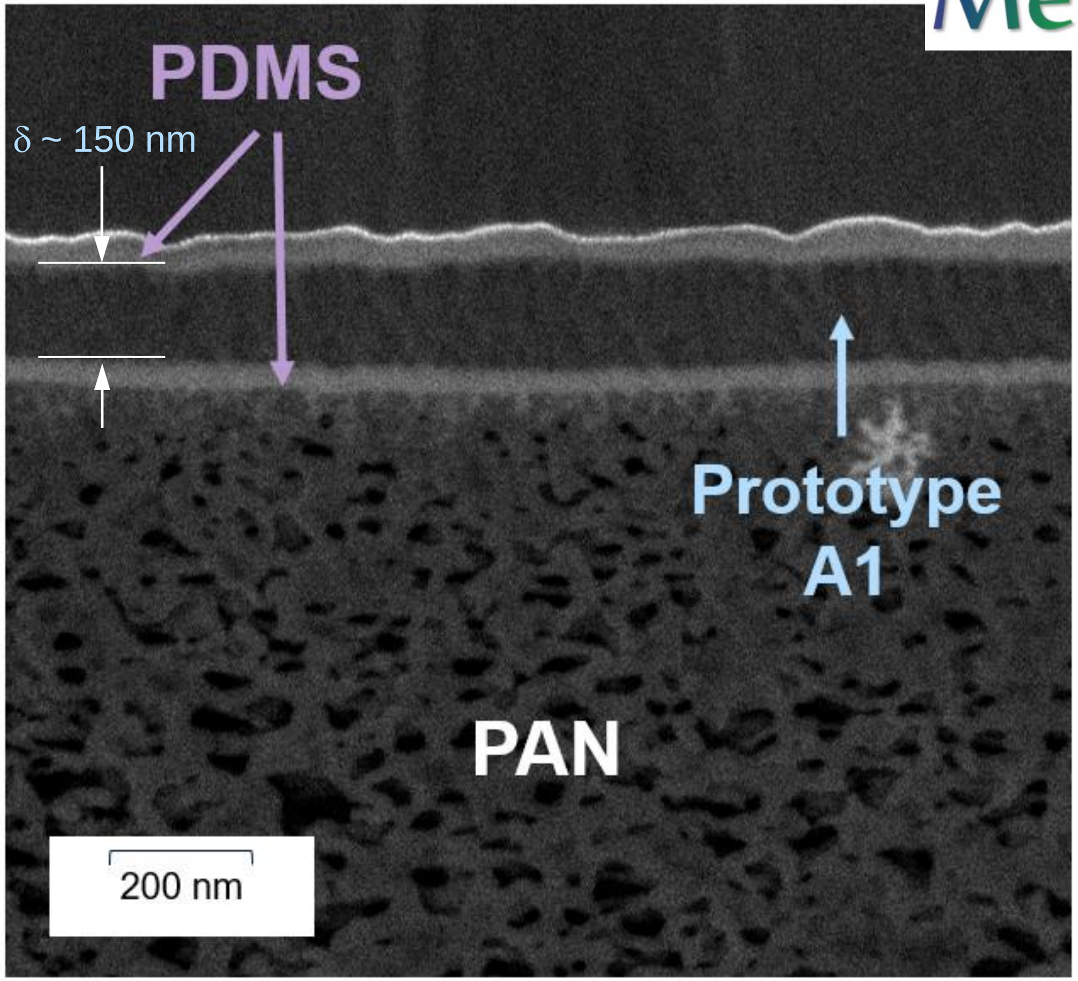
TFC membrane samples for quality control tests





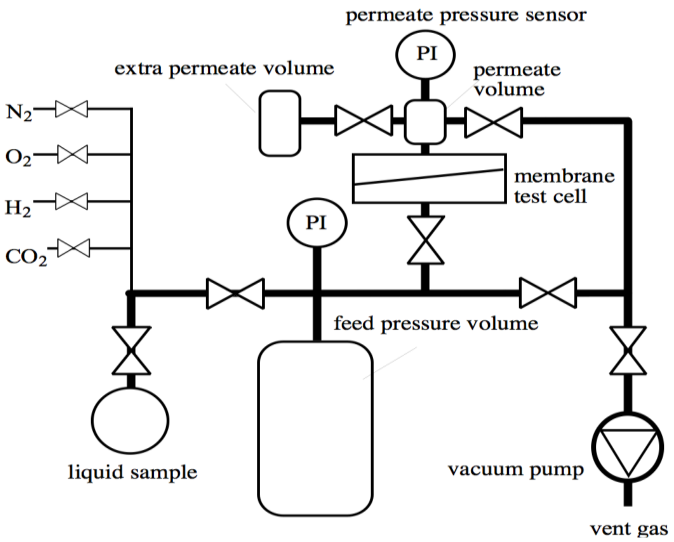
Morphological characterization of TFCMs: Bio-PEBA Prototype A and Prototype A1

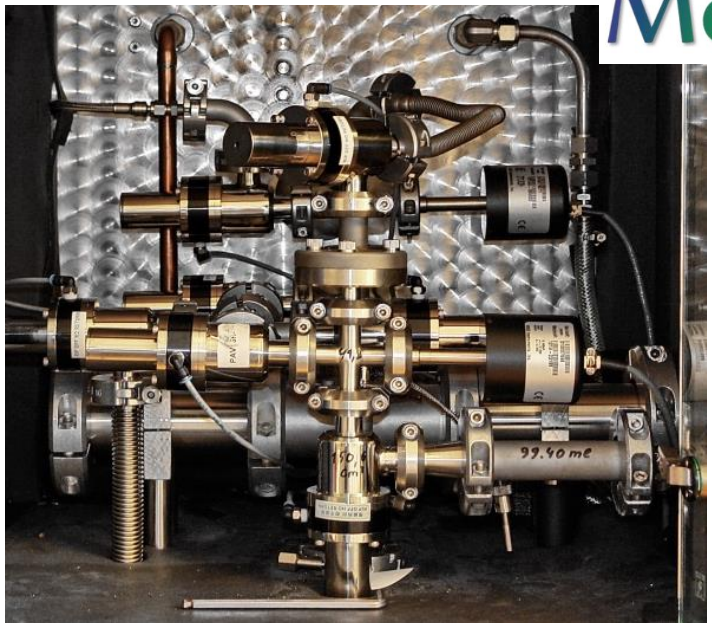


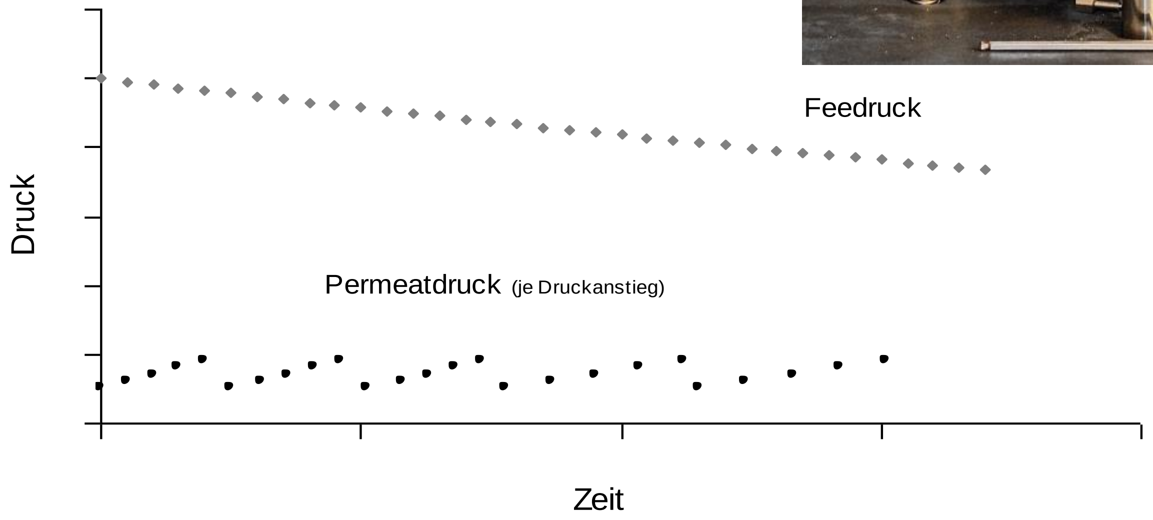


Pressure increase method for determination of single gas permeances

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



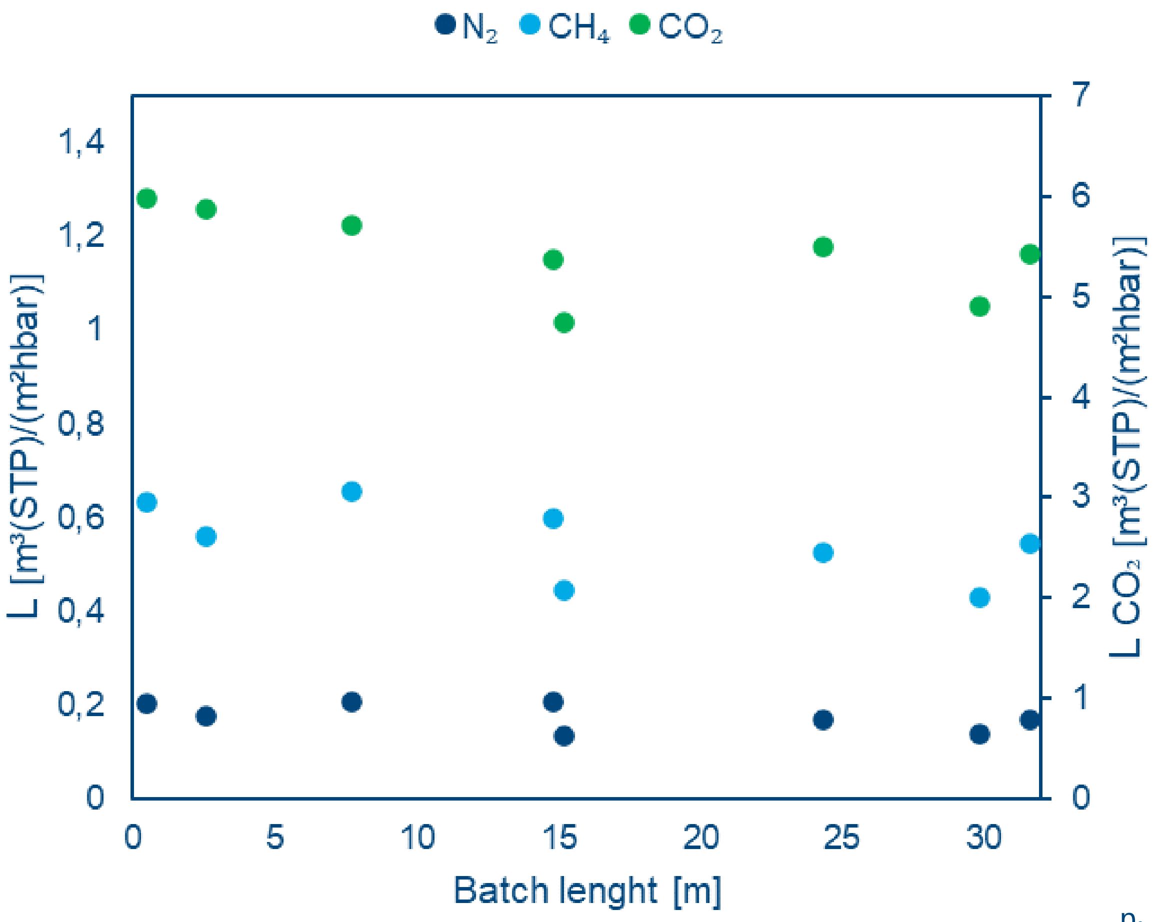


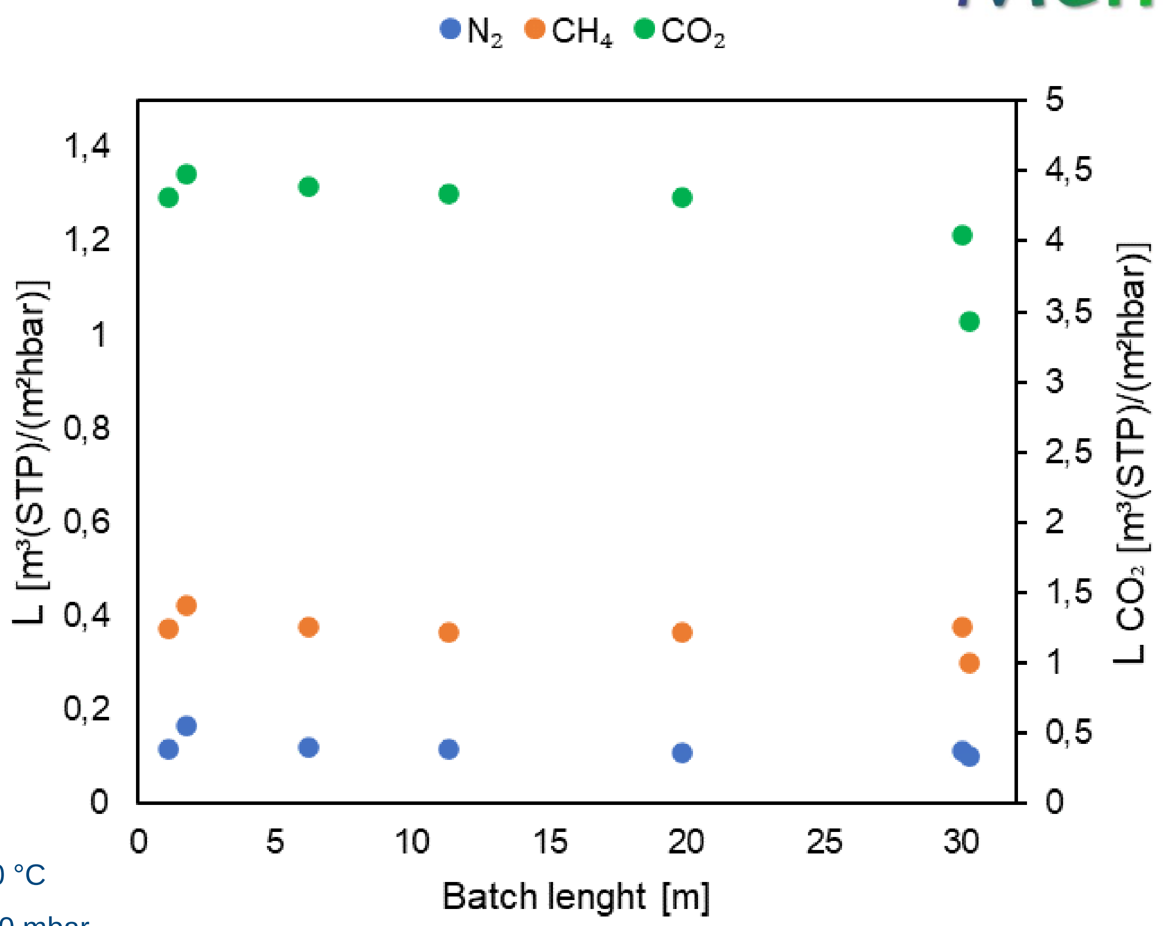


Summary of upscaled membranes

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)



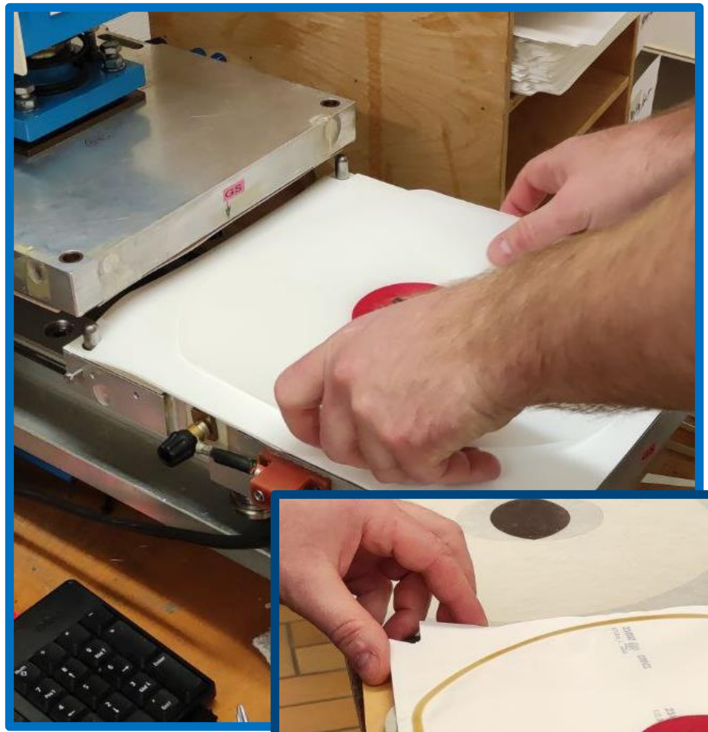


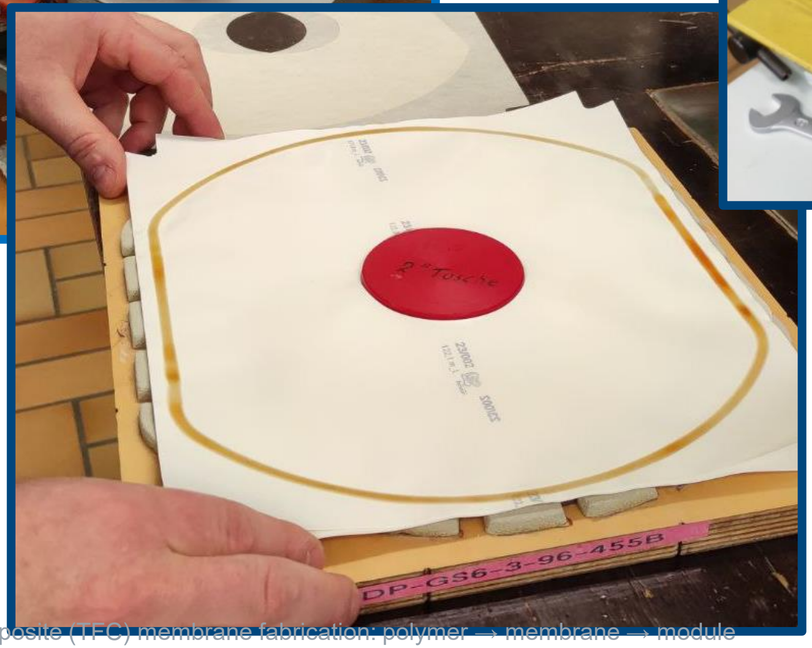
T = 30 °C

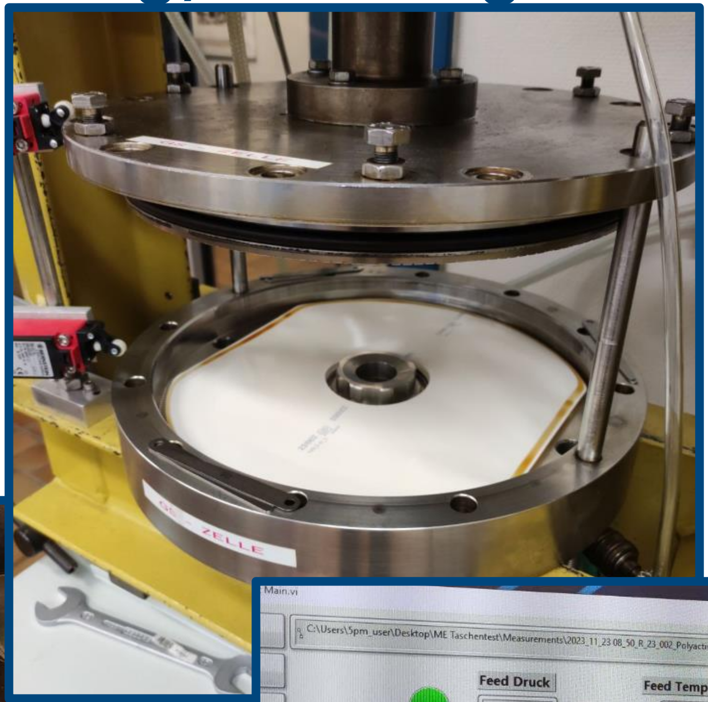
p_{feed} = 800 mbar

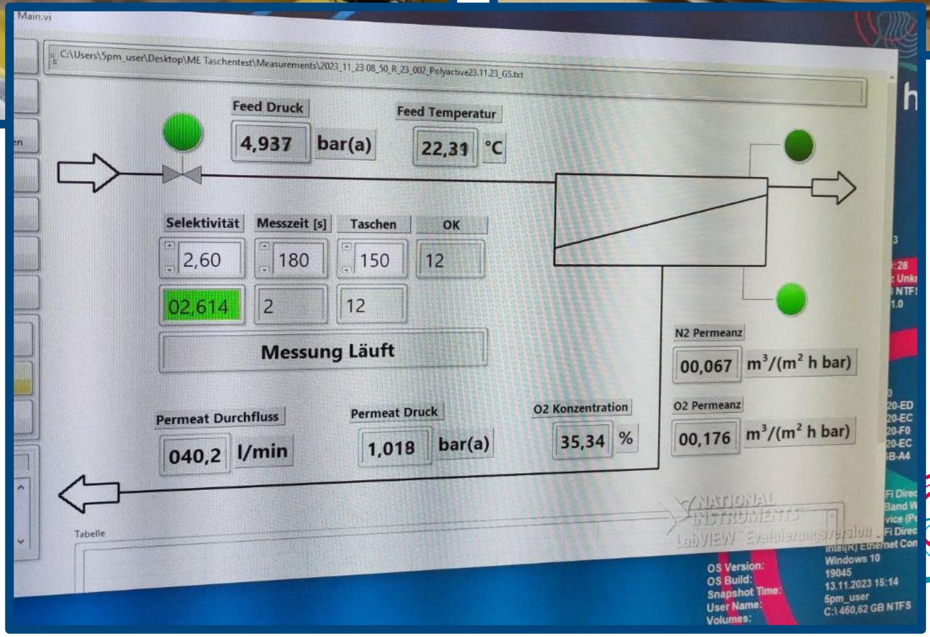
A_M = 8,3 cm^2

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



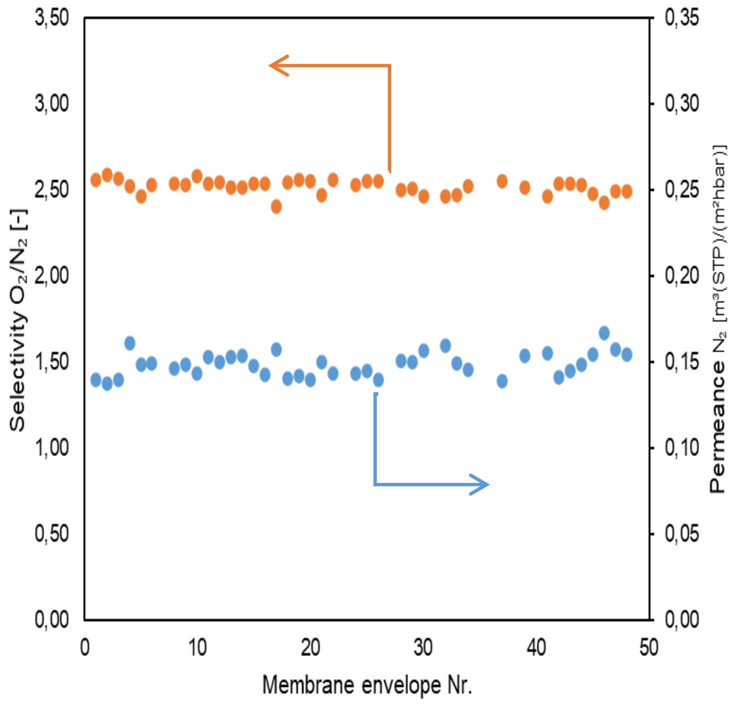




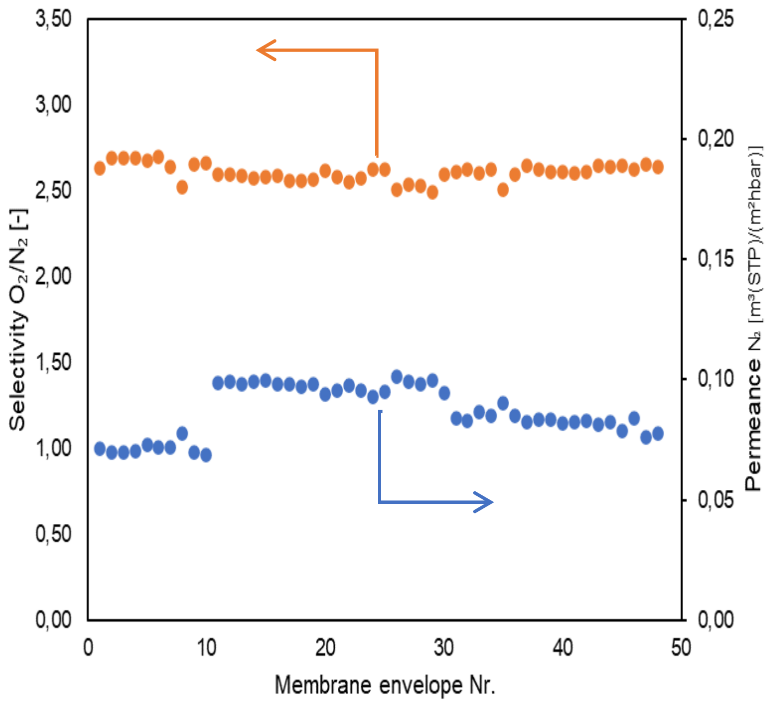


Comparison of envelope quality for different PEO based TFC membranes

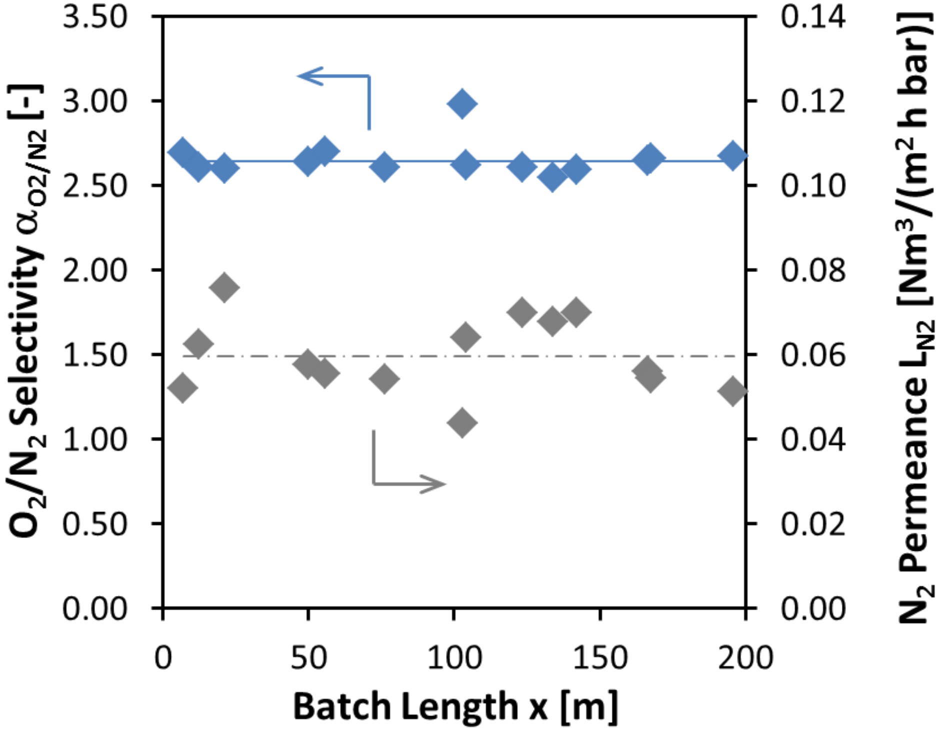
Prototype A



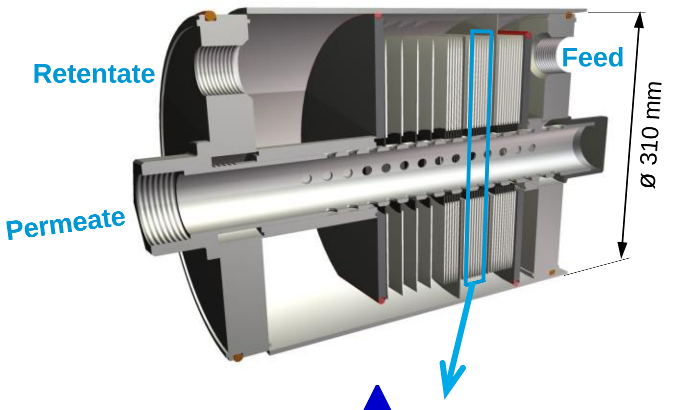
Prototype A1

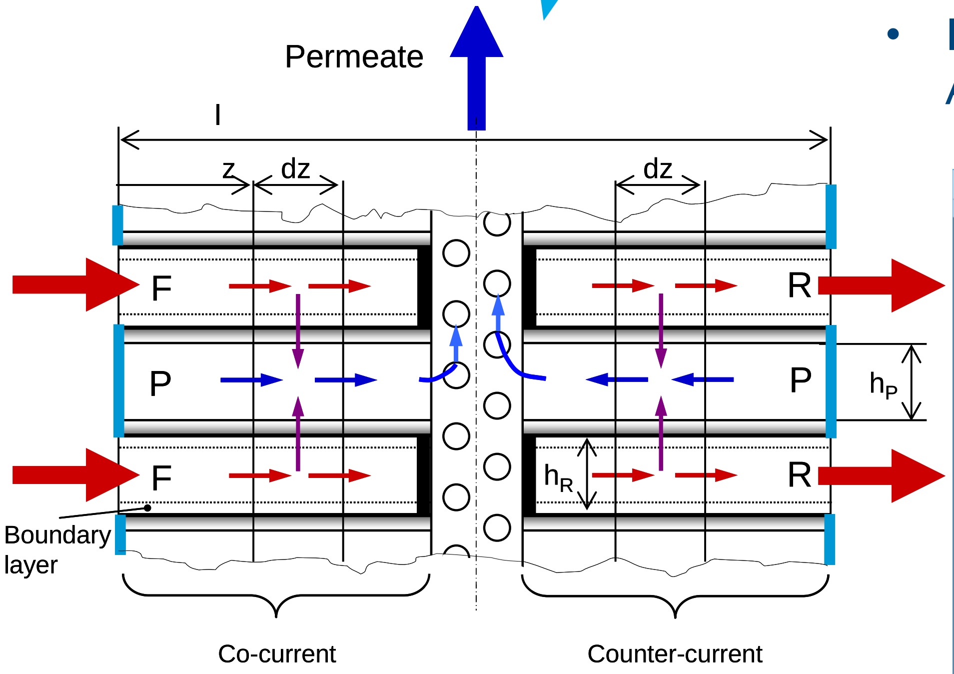


PolyActive™

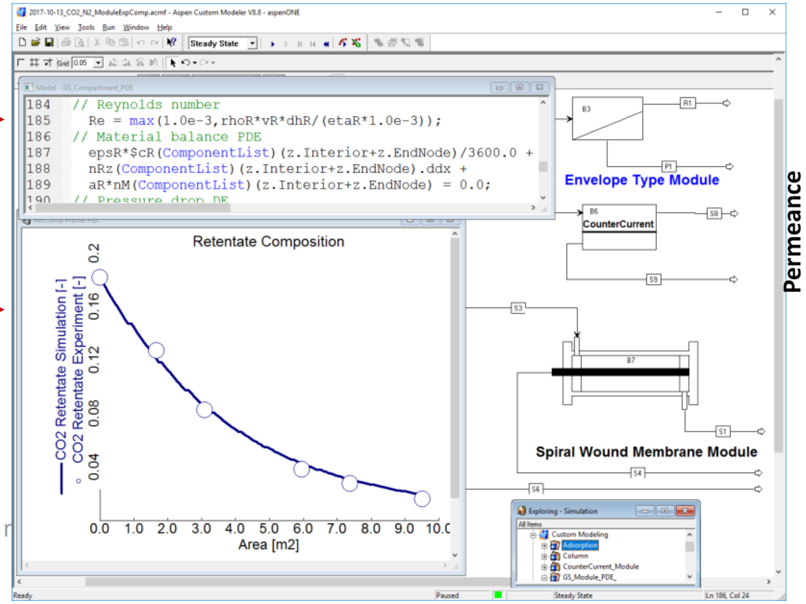


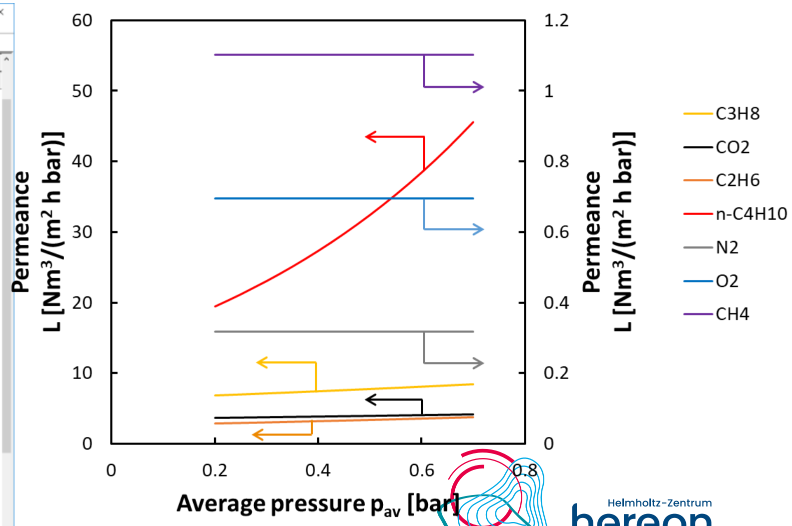
Simulation model – envelope type module





- 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

BioCoMem

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!

In case of questions please contact us:
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Torsten.Brinkmann@hereon.de

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

Bio Co Mem

BBI JU

Bio-based Industries Consortium

This project has received funding from the Bio Based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation programme, under grant agreement No 887075.

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

Helmholtz-Zentrum hereon

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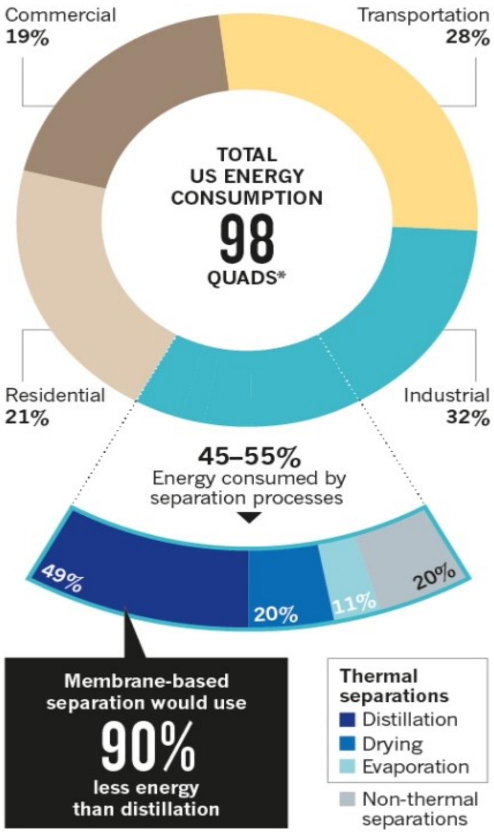
Hollow fiber membrane fabrication

Dr. Miren Etxeberria Benavides and Dr. Oana David

Membrane Technology and Process Intensification

MEMBRANE TECHNOLOGY



MEMBRANE SEPARATION

- No require a gas-liquid phase change
- Smaller separation units → small footprint
- Lack of mechanical complexity
- Operate under continuous, steady-state conditions

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GAS SEPARATION WITH MEMBRANES

APPLICATIONS

CO_2 capture	CH_4 purification	H_2 purification	Olefin / paraffin separation	Water separation

TYPE OF MEMBRANE

MATERIAL

- Inorganic
  - Metallic
  - Ceramic
  - Carbon
  - Zeolite
- Organic
  - Polymeric

STRUCTURE

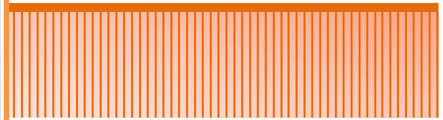
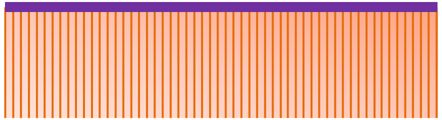
- Symmetric
- Asymmetric
  - Integral asymmetric
  - Composite

GEOMETRY

- Flat sheet
- Tubular
- Hollow fiber (< 0.5mm)

MEMEBRANE STRUCTURE AND GEOMETRY

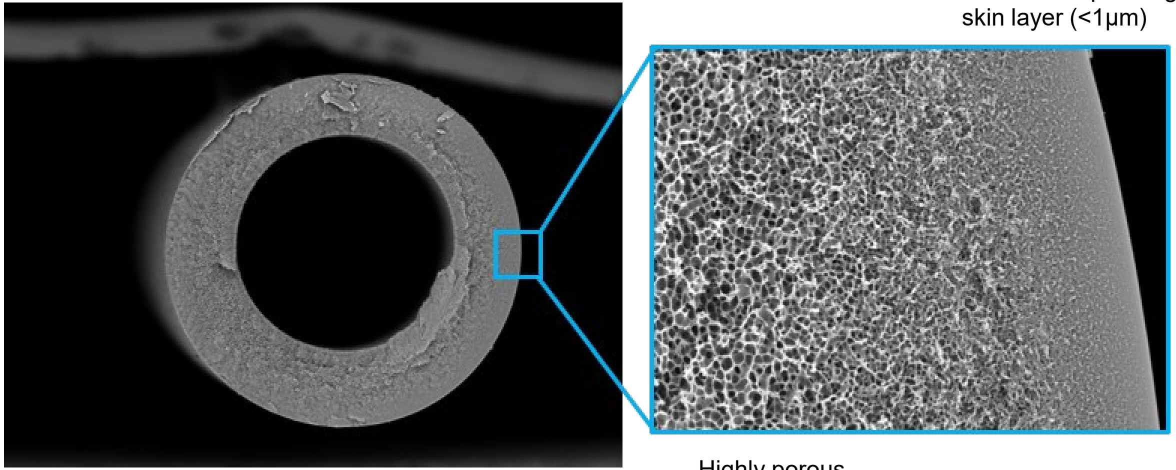
Commercial membranes

		Asymmetric	
	Homogeneous	**Monolithic**	**Composite**
Membrane structure			
Membrane processing	**Polymeric melt extrusion:** temperature phase separation **Solution film casting:** Evaporation induced phase separation	**Solution film casting or Hollow fiber spinning:** Evaporation followed by non-solvent induced phase separation	**Dip-coating:** Evaporation induced phase separation **Interfacial polymerisation**
Geometry			

$$J_i = \frac{P_i \cdot \Delta p_i}{l}$$

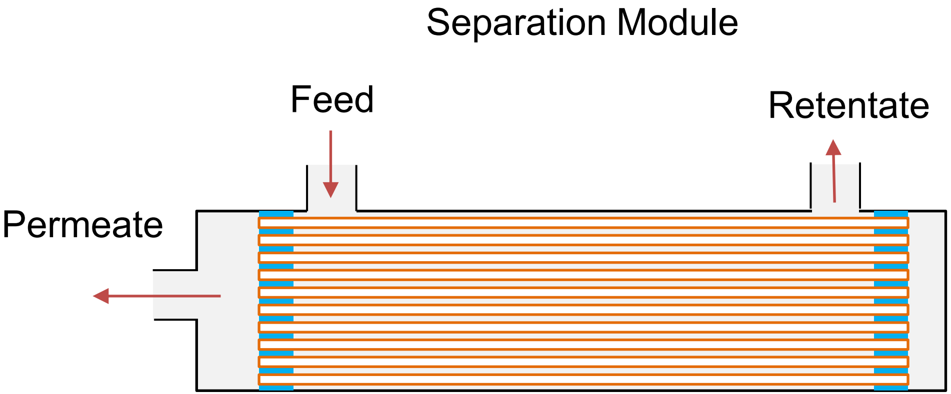
MEMEBRANE STRUCTURE AND GEOMETRY

Monolithic and asymmetric hollow fiber membrane



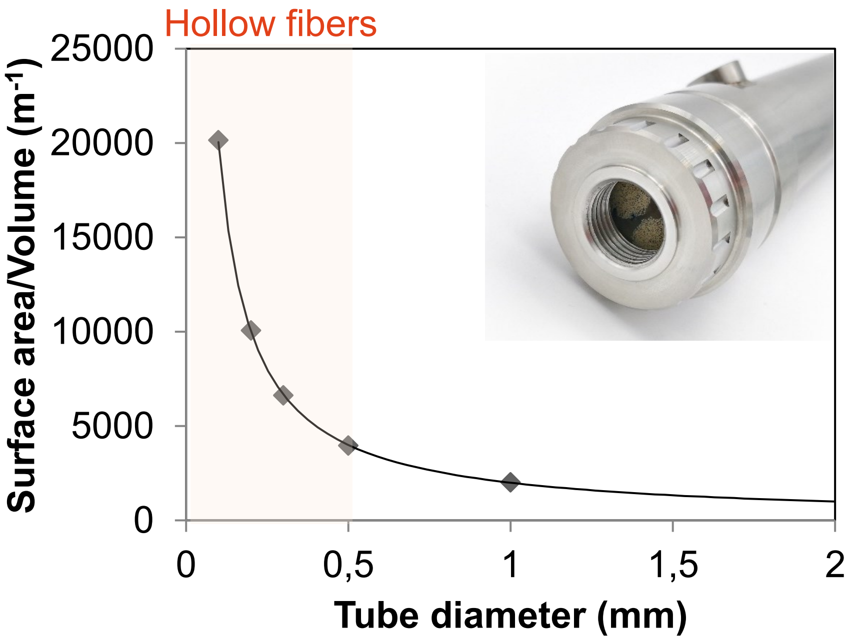
$$J_i = \frac{P_i \cdot \Delta p_i}{l}$$

HOLLOW FIBER MEMBRANES - Geometry



HOLLOW FIBER MEMBRANES - Geometry

Membrane packing density inside the permeation module = 50 %



Advantages of HF

- High packing density (over 10000 m^2/m^3), 10 times higher than plate and frame modules

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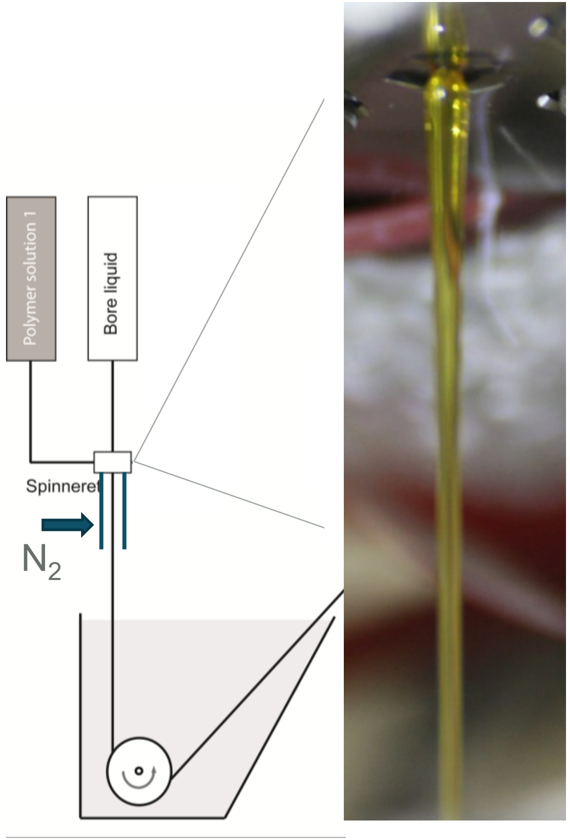
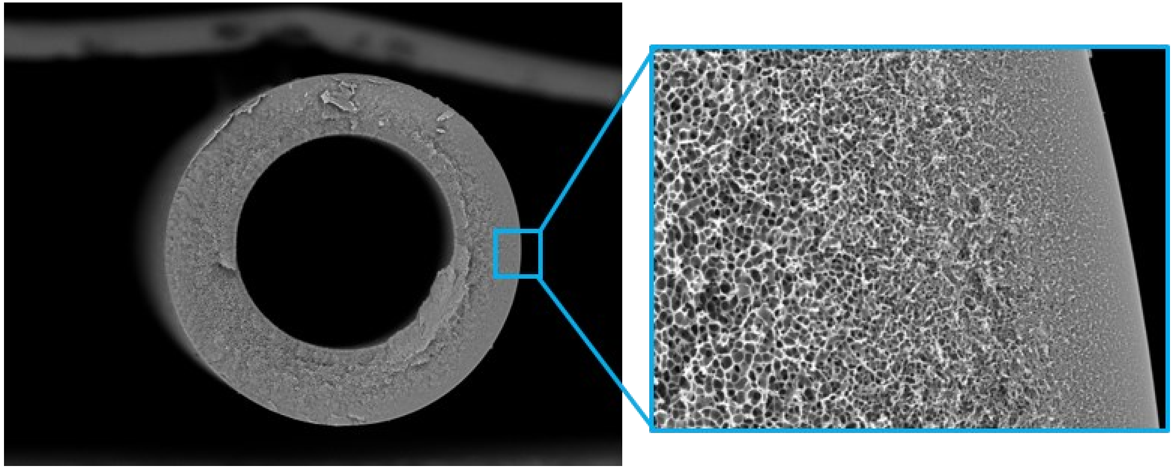
HOLLOW FIBER PREPARATION METHODS -spinning

Single step process: simultaneous formation of the porous support + dense selective layer

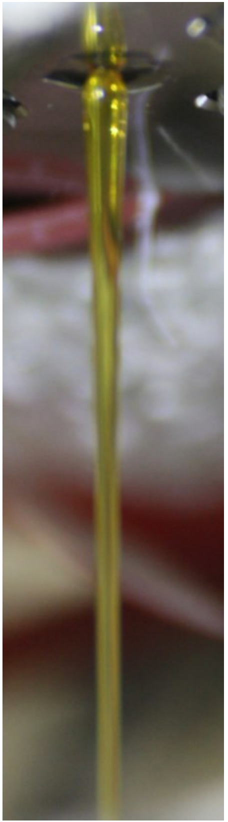




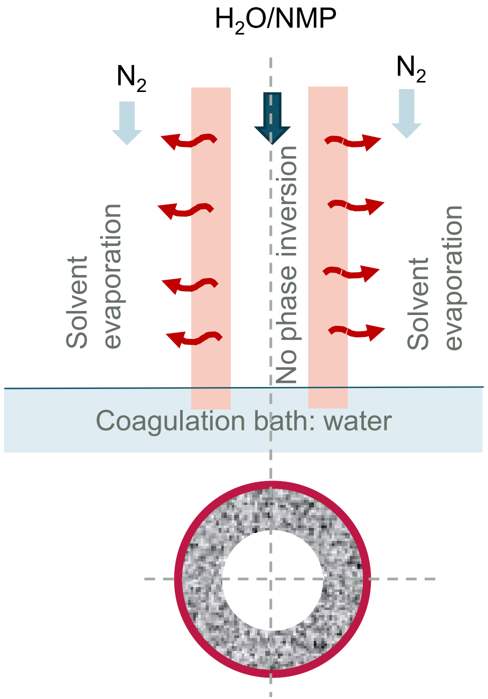
Process parameters:
Dope and bore composition and flow rate
Spinneret and coagulation bath temperature
Air gap height and atmosphere
Take up-rate
Room temperature and humidity

Membranes 2021, 11(8), 557; https://doi.org/10.3390/membranes11080557

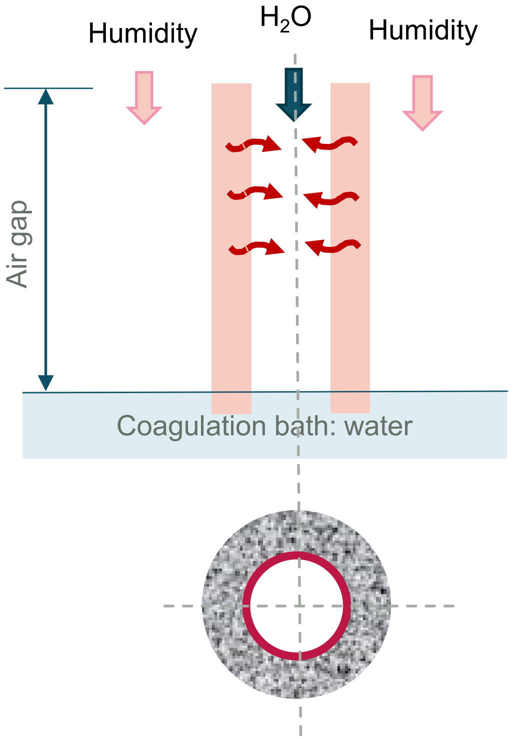
HOLLOW FIBER PREPARATION METHODS -spinning



Forming the selective layer at the outer part of the fiber:



Forming the selective layer at the inside part of the fiber:



MEMBRANE DEVELOPMENT STRATEGY

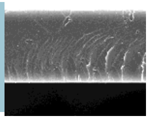
Defining target performance

↓

Material development and/or selection

↓

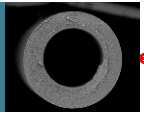
Dense film preparation and characterization



Intrinsic separation properties
Permeability and selectivity

↓

Hollow fiber preparation and characterization



Separation properties
Permeance and selectivity

↓

Possible to Scale-up, Prototype??

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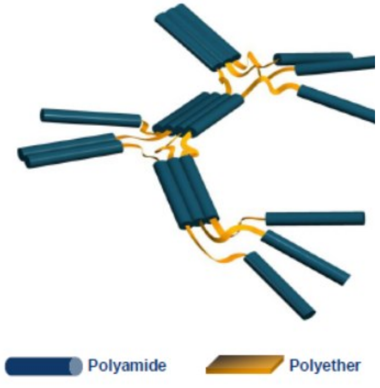
BENCHMARK

Polymeric materials used
Polyaramide
Polysulfone
Poly(phenilene oxide)
Cellulose acetate
Polyimides:
P84
PBI
6FDA-DAM
PI-Extem

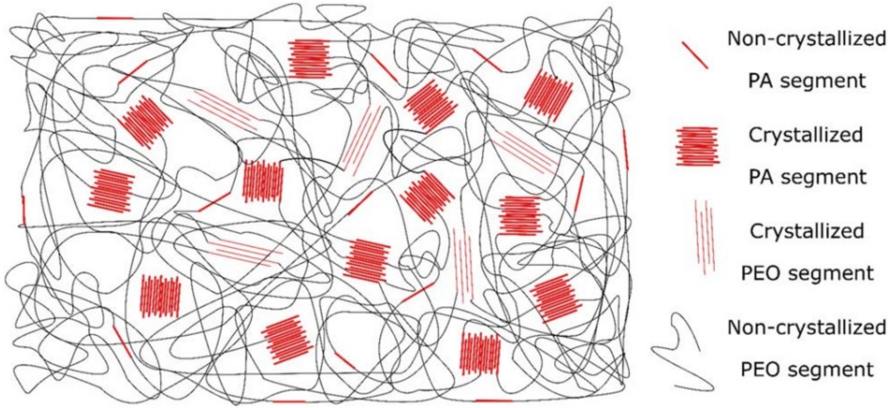
Bio-Based HF membranes

Material development and/or selection

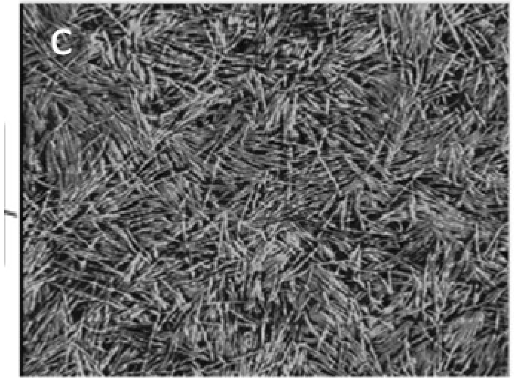
PEBA type Polymers



Arkema



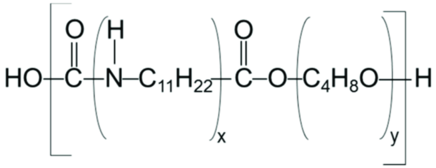
Didden, Jeroen; Thür, Raymond; Volodin, Alexander; Vankelecom, Ivo F. J. (2018), Journal of Applied Polymer Science, 46433

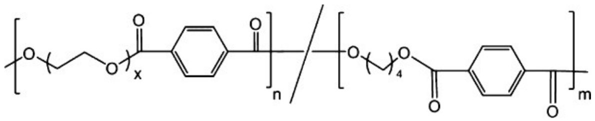


Yave, W., A. Car, and K.-V. Peinemann, J. Membr. Sci. 2010, 350: p. 124-129 (2010)

Material development and/or selection

Polymer	P (Barrer)	Permselectivity			Ref.
	CO_2	CO_2/N_2	CO_2/CH_4	CO_2/H_2	
Pebax 1657 PEO with PA6	98	53,2	16,1	9,5	1
PEBAX 2533 PTMO with PA12	234 -351	25 - 41			2
PEBAX 1074 PEO with PA12	134,74	59,61	16,16	10,28	2
Bio PEBAX PEO with PA11	311,41	45	14,07	9,35	Bioco mem





[1] S.R. Reijerkerk et al. / Journal of Membrane Science 352 (2010) 126–135
[2] H. Lin, B.D. Freeman, Gas solubility, diffusivity and permeability in poly(ethylene oxide), J. Membr. Sci. 239 (1) (2004) 105–117

BioCoMem

RESEARCH LINES

Co-polymer	Polyamide block	Polyether block	Main expected result
A **Reference bio-PEBAs**	Bio-based polyamide 11 derived from castor oil $(PA_{ref}{}^{bio})$	Fossil based polyether block $(PE_{ref}{}^{fossil})$	Composite HF Membrane
B **New bio-PEBAs Pathway 1** aromatic/cycloaliphatic polyamide-b-polyether	Bio-based polyamides derived from new building blocks $(PA_{new}{}^{bio})$	Fossil based polyether block $(PE_{ref}{}^{fossil})$	Better processability: (Monolithic HF membrane) *and* Higher gas separation performance
C **New bio-PEBAs Pathway 2** lignin-g-(polyether-b-polyamide 11)	Bio-based polyamide 11 derived from castor oil $(PA_{ref}{}^{bio})$	Bio-based polyether block derived from lignin-g-polyether $(PE_{new}{}^{bio})$	Better processability: (Monolithic HF membrane) *and* Development of PEBA type co-polymer with bio-based components in both blocks

Preliminary solubility study

	Concentration wt%							
	SOL 01	SOL 02	SOL 03	SOL 04	SOL 05	SOL 06	SOL 07	SOL COMPL.
35 B6	20	20	20	20	20	20	20	20
NMP	80	78	76	70	74	68	66	64
LiCl		2			2	2		2
PVP K30			4		4		4	4
THF				10		10	10	10

Conclusions:

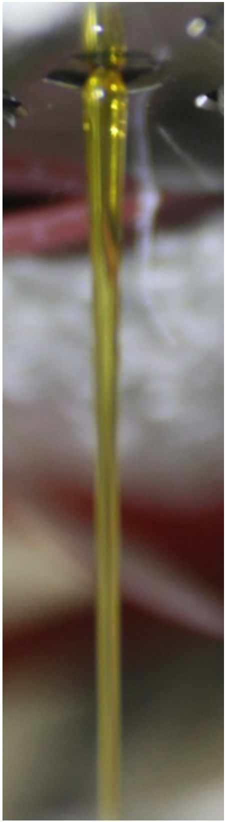
1. THF is better solvent than NMP (SOL 01 vs SOL 04).
2. Addition of PVP does not form a homogeneous blend (SOL 03, SOL 05, SOL 07 and SOL COMPL), therefore is not a viable approach.
3. At Polymer/LiCl=10, adding THF induces lower gel formation speed at RT (~2 h for SOL 02 vs ~8 h for SOL 06).

4. Gel formation could not be prevented at room temperature. Therefore, the solution should be kept at minimum 40 ºC within the spinning vessels and lines.

5. A good dope composition could be SOL 06 and SOL 04.

6. Spinning with SOL 02 instead of SOL 06 will determine a higher contribution of crystallization phenomena to phase inversion phenomena during the coagulation of the fibers.

Polymer spinning



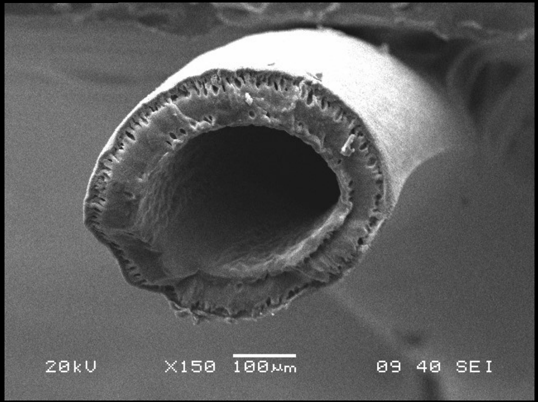
Polymer dope composition:

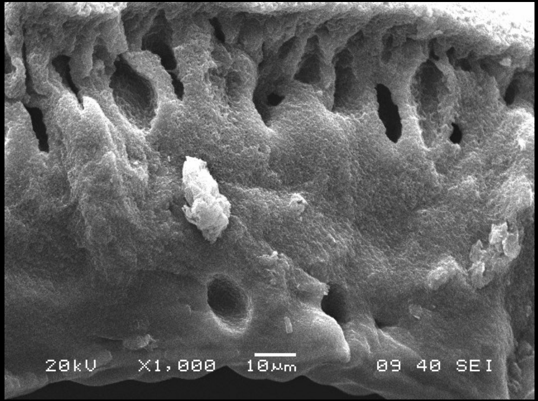
035 B5	20 and 23 wt%
LiCl	3.67 wt%
NMP	73.33 wt%

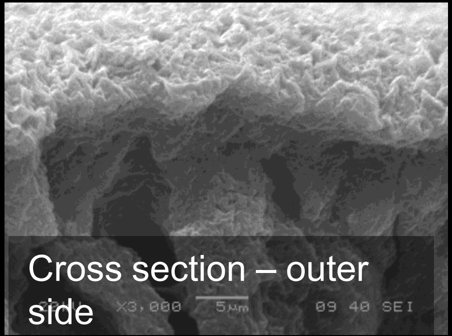
Gel at RT liquid at 40 ºC

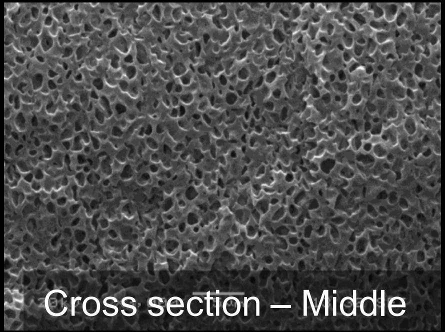
Pump temperature (ºC)	Spinneret temperature (ºC)	Bore liquid composition H_2O/NMP wt%	Air gap (cm)	Air gap environment	Hollow fiber?
50	50	100/0	26	78% RH	✓
50	50	30/70	5 - 20	N_2	✗
50	21	50/50	5, 11	N_2	✓

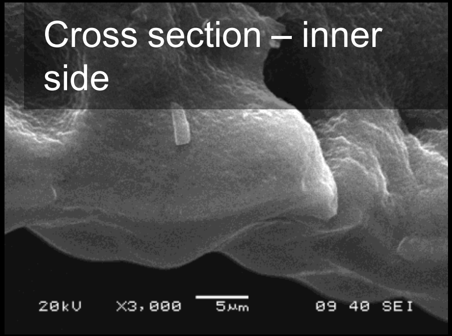
Bio Co Mem

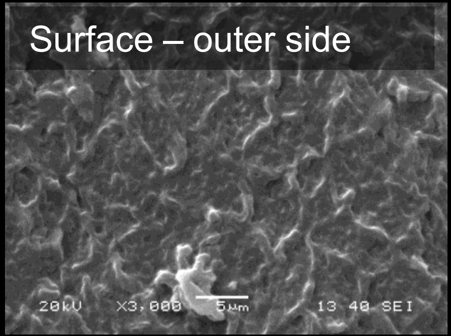

20kV X150 100µm 09 40 SEI

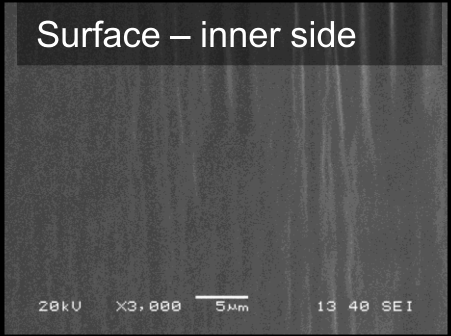

20kV X1,000 10µm 09 40 SEI


Cross section – outer side
X3,000 5µm 09 40 SEI


Cross section – Middle


Cross section – inner side
20kV X3,000 5µm 09 40 SEI


Surface – outer side
20kV X3,000 5µm 13 40 SEI


Surface – inner side
20kV X3,000 5µm 13 40 SEI

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ARKEMA

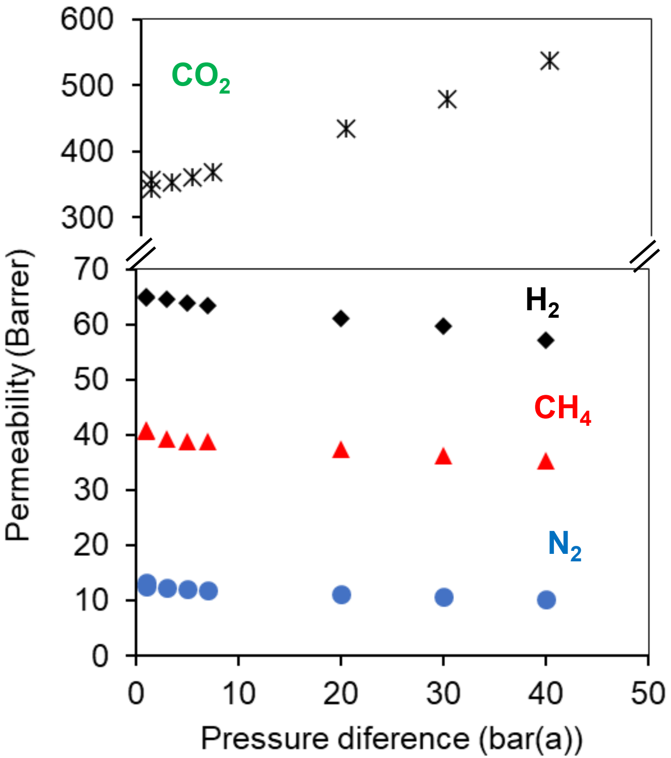
BioCoMem

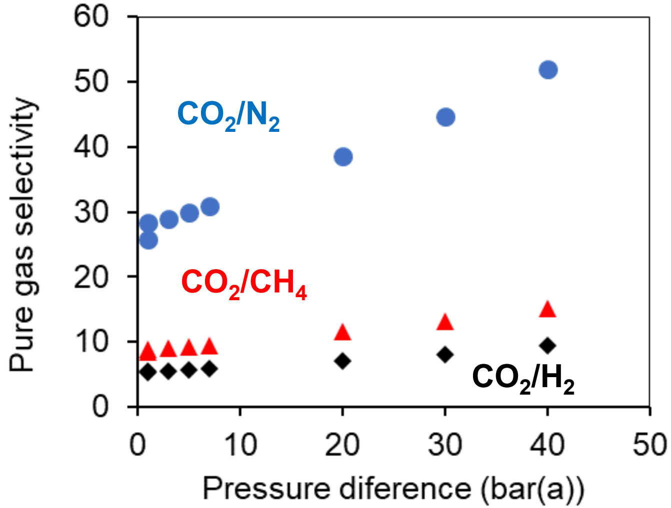
Polymer scale - up

	PA structure	T_g [°C]	T_m [°C] PEO/PA	CO_2 permeability (Barrer)	CO_2/N_2 Selectivity	CO_2/CH_4 Selectivity	CO_2/H_2 Selectivity
35 ºc and 3 bar(a) Δp	**Prototype A**	**<-50**	**25/160**	**311,41**	**45**	**14,07**	**9,35**
	MS-2021-035	<-40	16 / 80	228,8	27,5	9,2	
	Prototype B *(scaled-up)* 2021-1449TLT500	n.d	13/77	353,99	28,83	8,99	5,48
	Prototype B *(scaled-up)* 2021-1449TLT502	n.d	20/94	342,77	30,13	9,25	5,37
30 ºC, 300 mbar	Polyactive (1500PEO77PBT23)	**-49**	**27/110**	**115**	**45,6**		**n.d.**

Objective for HF membrane:
PCO2= 1000 GPU
$\alpha_{CO2/N2}$ = 30

Gas permeation Properties: 2021-1449TLT500





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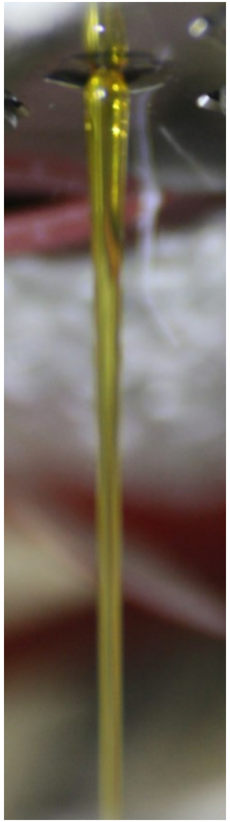
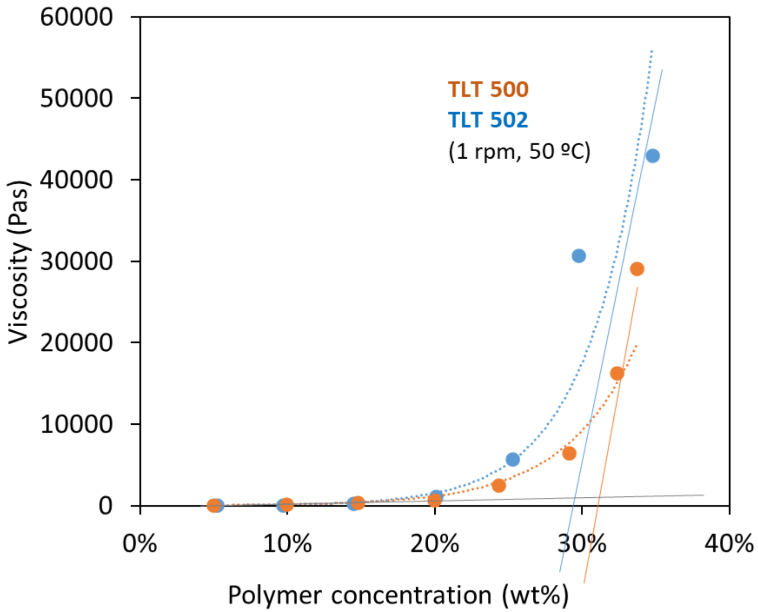
Solubility study

BioCoMem



	Conc. (wt%)					
TLT 500 or TLT 502	**5**	**10**	**15**	**20**	**25**	**30**
NMP	92,5	85	77,5	68	62,5	55
LiCl	0,5	1	1,5	2	2,5	3
THF	2,5	5	7,5	10	12,5	15

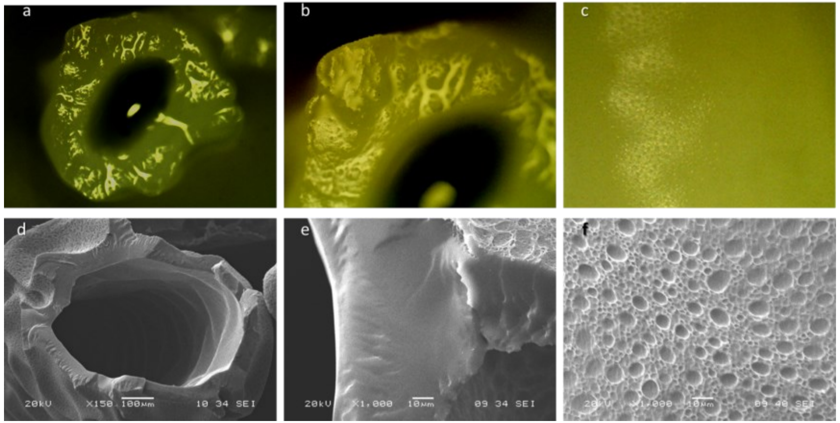


- All solutions are liquid at 40 ºC
- All solutions form a gel at room temperature.
- At RT, gel formation is 3 h for TLT 502 and takes longer time for TLT 502
- Gel formation is faster at lower concentrations (see below)

Polymer spinning

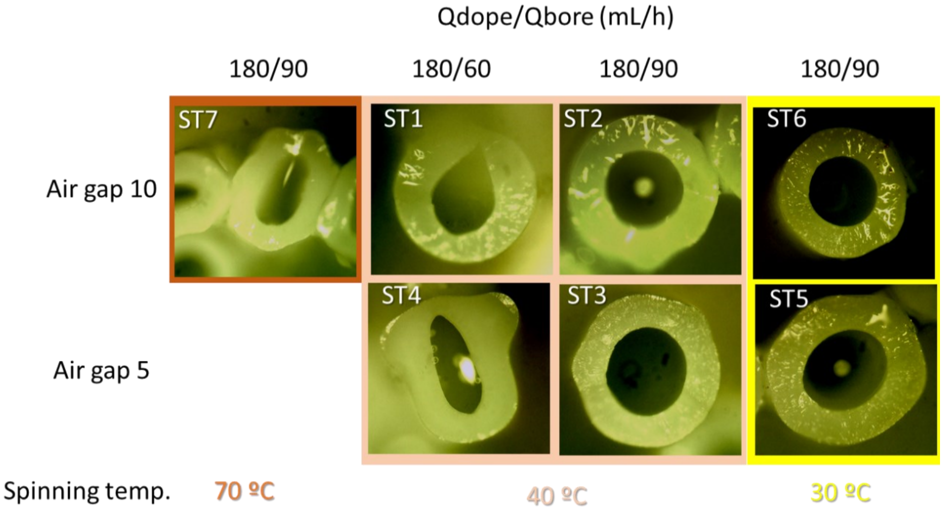
28 wt% TLT 502 ; 14 wt% THF; 2,8 wt% LiCl in NMP

Qdope/Qbore=180/90



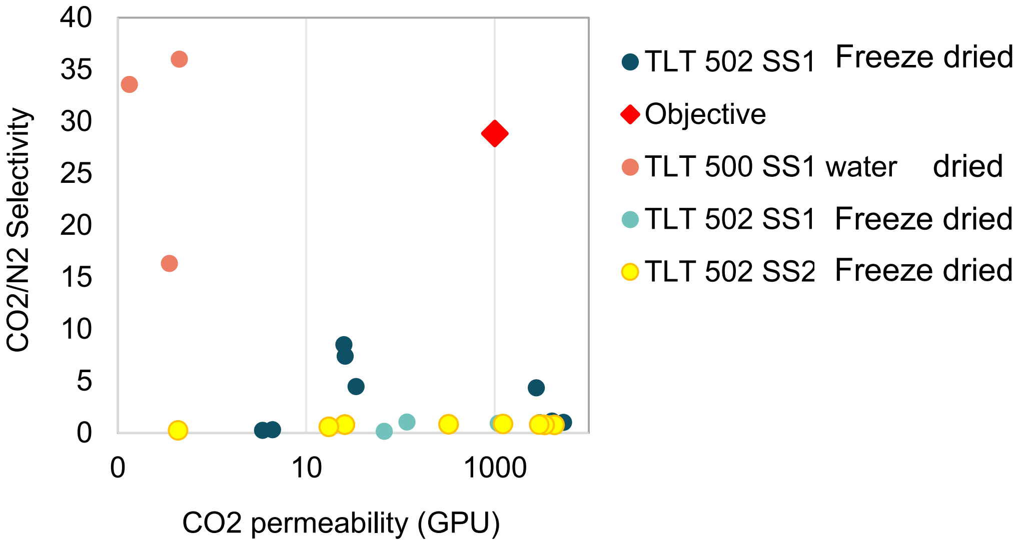
- bore liquid composition H2O/NMP=90/10 wt%,
- spinning temperature: 30 °C,
- air gap height = 50, humidity in the air gap,
- take up rate = 8 m/min.

26 wt% TLT 502; 1.3 wt% LiCl in NMP



- bore liquid composition H2O/NMP=95/5 wt%,
- take up rate = 8 m/min.

Gas permeation



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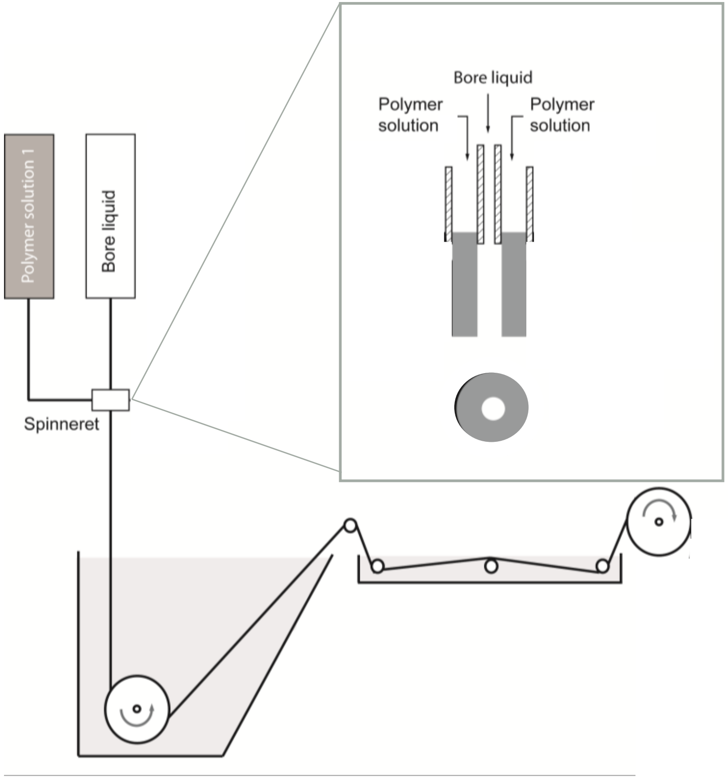
Dual layer Hollow fiber spinning

BioCoMem



PA structure	T_g [°C]	T_m [°C] PEO/PA	CO_2 permeability (Barrer)	CO_2/N_2 Selectivity	CO_2/CH_4 Selectivity	CO_2/H_2 Selectivity
Prototype A	**<-50**	**25/160**	**311,41**	**45**	**14,07**	**9,35**
MS-2021-035	<-40	16 / 80	228,8	27,5	9,2	
Prototype B *(scaled-up)* 2021-1449TLT500	n.d	13/77	353,99	28,83	8,99	5,48
Prototype B *(scaled-up)* 2021-1449TLT502	n.d	20/94	342,77	30,13	9,25	5,37
Prototype B *(scaled-up)* 2021-1449TLT549			**395,88**	**36,13**	**10,9**	**7,46**
Prototype B *(scaled-up)* 2021-1449TLT550			**106**	**21,02**	**7,16**	**2,81**
Polyactive (1500PEO77PBT23)	**-49**	**27/110**	**115**	**45,6**		**n.d.**

Objective for dual layer fiber approach:
PCO2= 400 GPU
$\alpha_{CO2/N2}$ = 30

Membranes 2021, 11(8), 557; https://doi.org/10.3390/membranes11080557

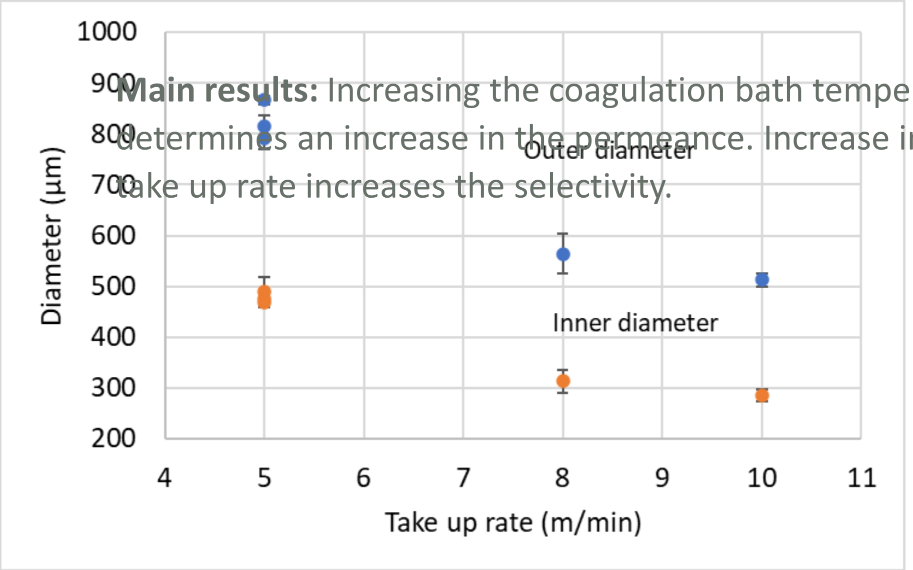
Dual layer Hollow fiber spinning

TLT 550	20,00%
NMP	72,90%
LiCl	1,10%
PEG 1500	6,00%

TLT 549	22,0%
NMP	76,4%
LiCl	1,00%
H2O	0,5%

Spinning parameters:
Outer dope flow rate = 160 mL/min
Inner dope flow rate = 20 mL/min
Bore liquid = 80/20 H2O/NMP
Spinneret Temperature = **50 ºC, 40 ºC for exp 2**
Air gap = chimney in place when air gap of 10, No N2 flow
Freeze drying

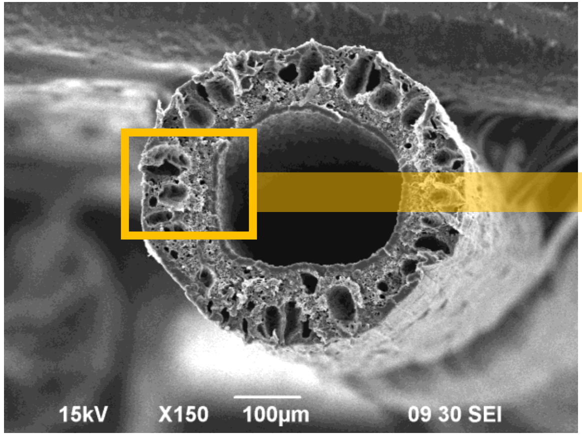
	Quench Bath Temp	Air gap height	Take up rate
	(ºC)	(cm)	(m/min)
ST1	22	10	5
ST3	21,5	1,5	5
ST4	21,5	1,5	10
ST5	39	10	5
ST6	38,8	1,5	8

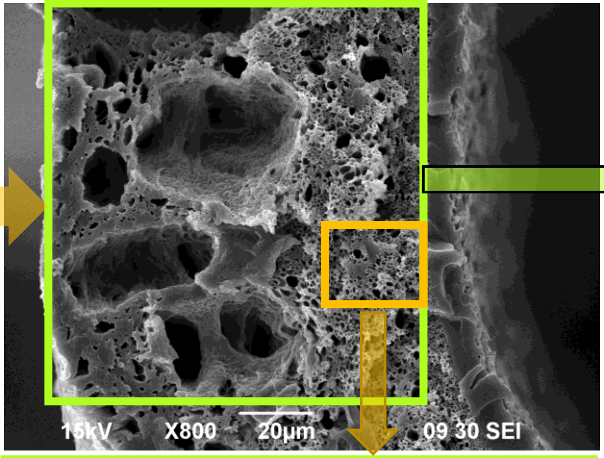


Main results: Increasing the coagulation bath temperature determines an increase in the permeance. Increase in the take up rate increases the selectivity.

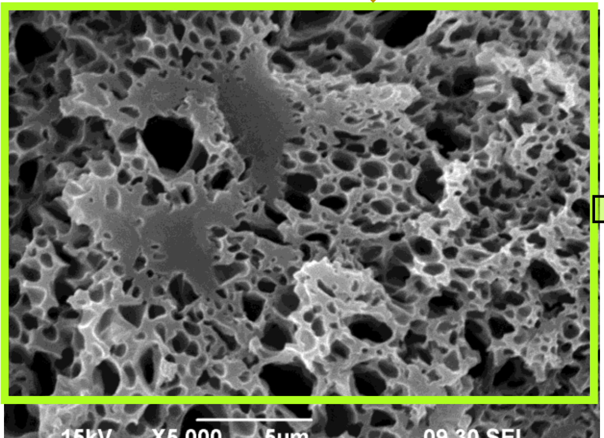
Dual layer Hollow fiber spinning

Porosity

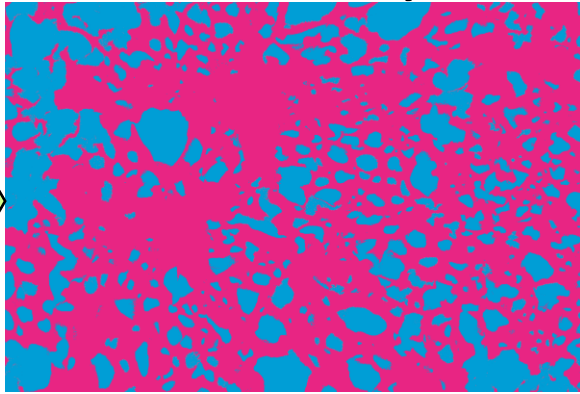




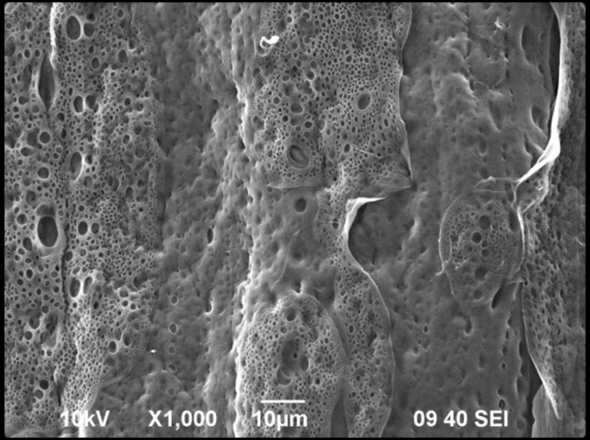
Porosity = 45 %



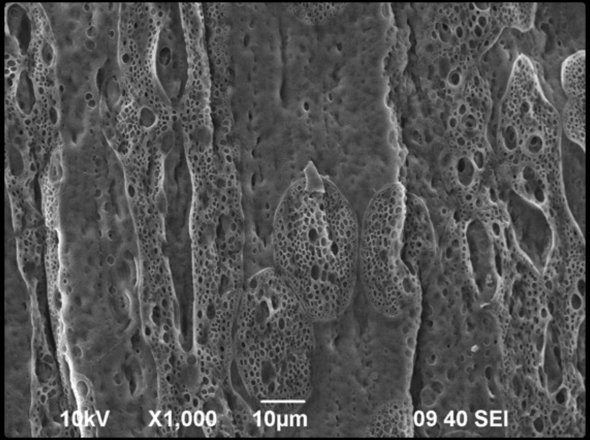
Porosity = 34 %



ST1



ST2



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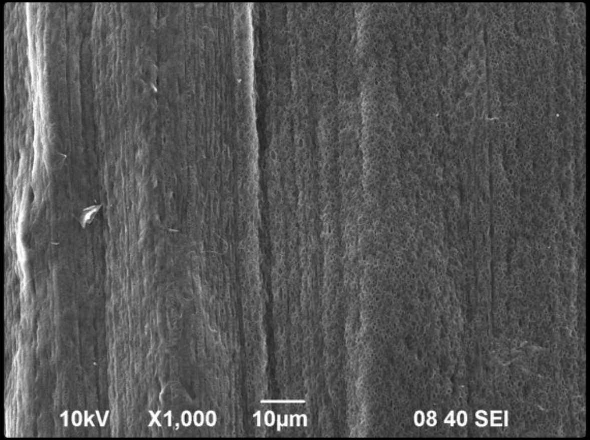
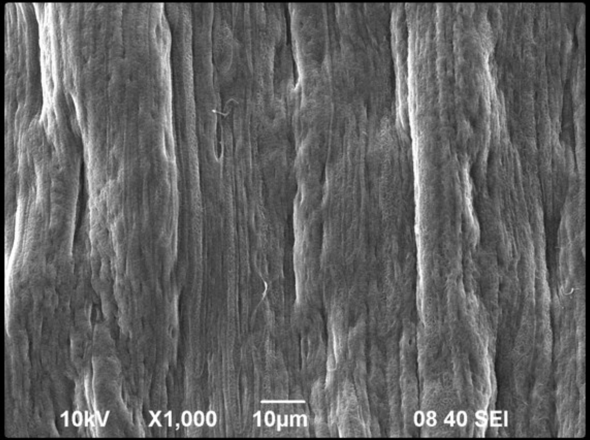
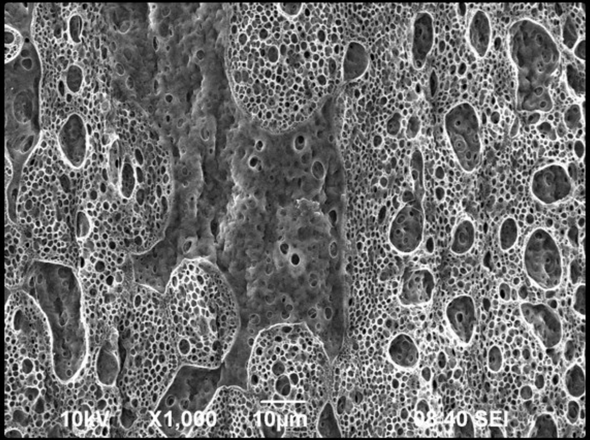


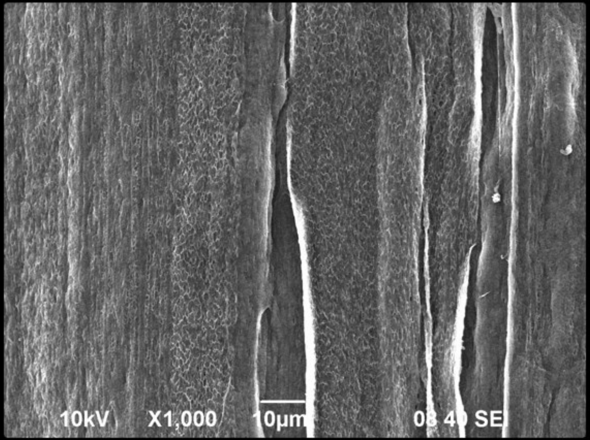
ST4

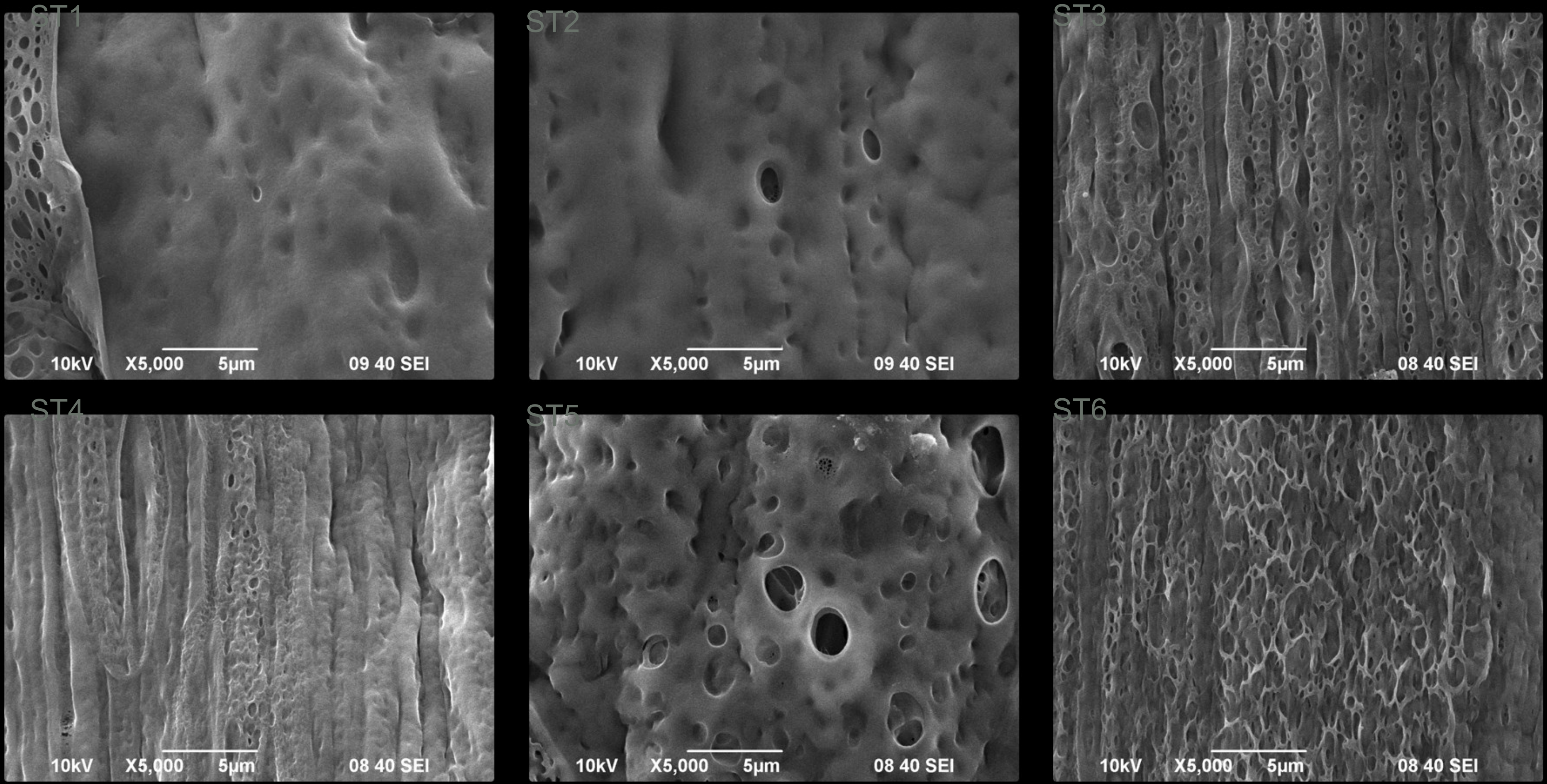


ST5



ST6




ST1
10kV X5,000 5μm 09 40 SEI
ST2
10kV X5,000 5μm 09 40 SEI
ST3
10kV X5,000 5μm 08 40 SEI
ST4
10kV X5,000 5μm 08 40 SEI
ST5
10kV X5,000 5μm 08 40 SEI
ST6
10kV X5,000 5μm 08 40 SEI

Dual layer Hollow fiber spinning

Mechanical properties: elongation

	Ultimate strength (Mpa)	±	Elongation at brake (%)	±
ST1	7,38	0,173	874%	27%
ST3	7,19	0,226	791%	10%
ST4	11,44	0,182	584%	9%
ST5	4,92	0,114	664%	5%
ST6	9,46	0,444	627%	12%

Membranes (Materials)	Young's Modulus (MPa)	Elongation at Break (%)	Ultimate Strength (MPa)	Porosity (%)
U305 (Ultem@ 1000 (PEI))	132	44	58.5	55.9
M264 (Matrimid@ 5218 (PI))	121	29	54.8	58.4
PES28 (Ultrason E6020P (PES))	72	85	5.2	46.1

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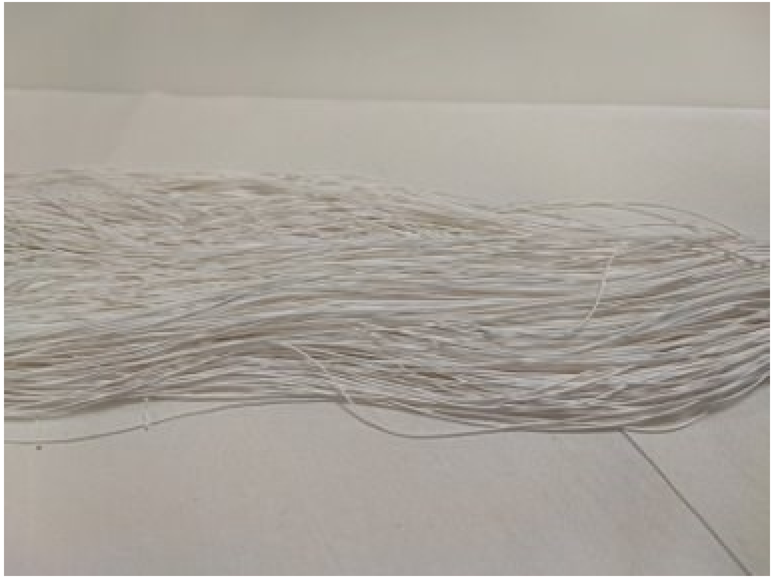
Conclusions

More optimization:
- Increase surface porosity
- Eliminate the macrovoids
- Densify the inner layer

Scale up: successful

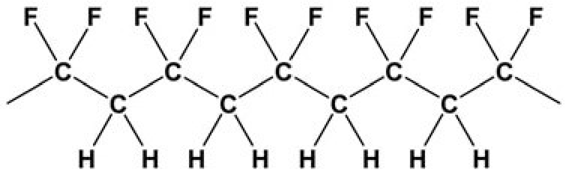


Eskerrik asko zuen arretagatik!

Thank you for your attention!

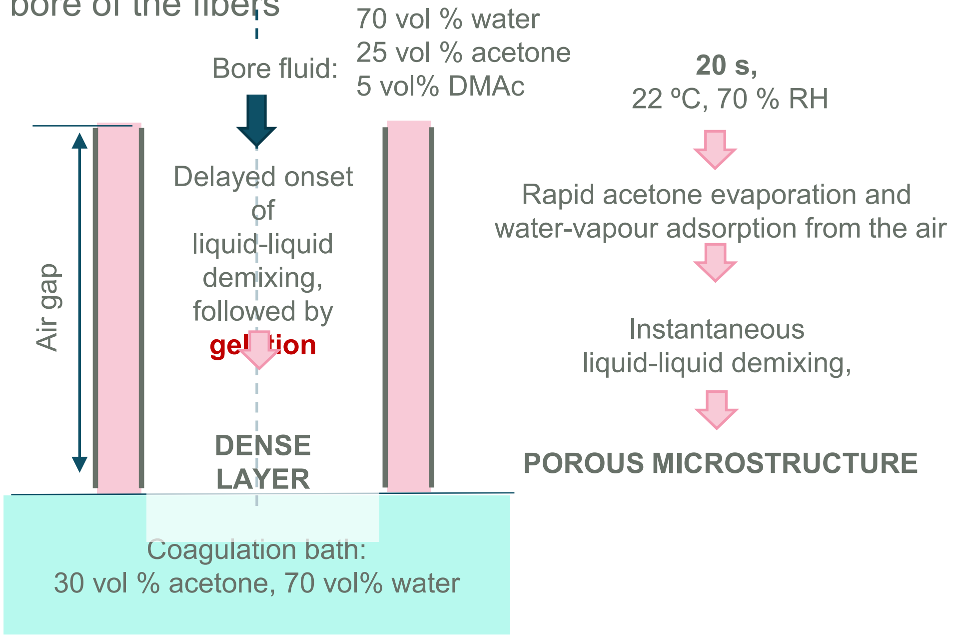
Prototype B – Polymer spinning

Literature background: Procedure for casting integral asymmetric PVDF pervaporation hollow fiber membranes with a dense layer on the inside bore of the fibers



Xc	Tm (°C)	Tc (°C)
50,7	168,3	142,1

Polymer dope composition:
25 wt% PVDF
30 wt% DMAc
45 wt% Acetone



K. Jian, P.N. Pintauro, Asymmetric PVDF hollow-fiber membranes for organic/water pervaporation separations, Journal of Membrane Science, Volume 135, Issue 1, 1997, Pages 41-53

Bio-based copolymers for membrane end products for gas separations

Membrane-based Process Design and Economics

Speaker:

Rouzbeh Ramezani

Eindhoven University of Technology

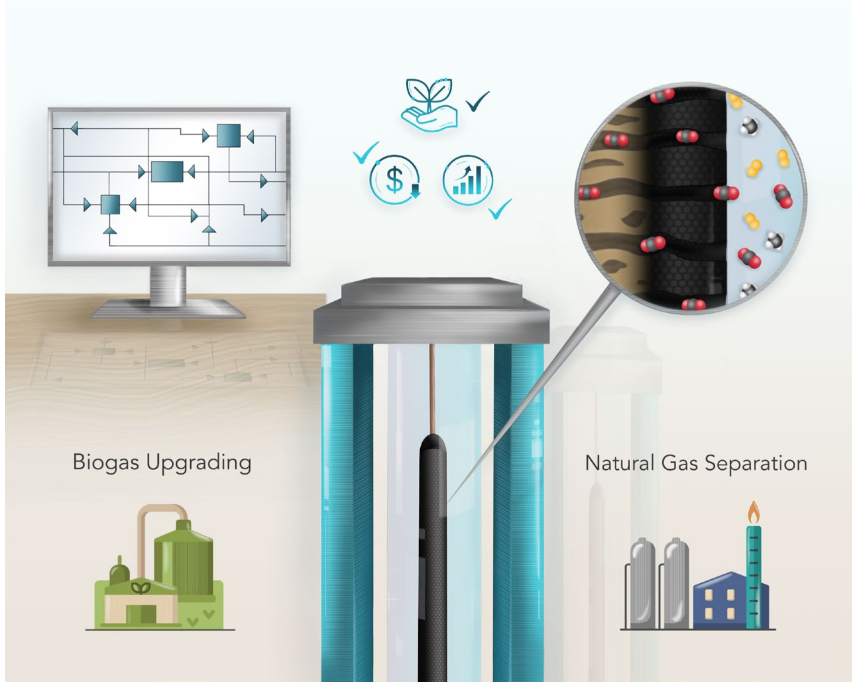
Department of Chemical Engineering and Chemistry

Sustainable Process Engineering

r.ramezani@tue.nl

Membrane-based Gas Separation

- The potential application of the membrane process in a great measure depends on the capability of membrane materials to provide high separation performance.
- Membranes suffer from a trade-off between selectivity and permeability with an upper bound.
- An optimal flowsheet of membrane-based gas separation can remarkably decrease capture cost and energy consumption.
- The development of efficient and cost-effective multi-stage membrane processes as well as improvements in membrane selectivity and permeance is of major importance.

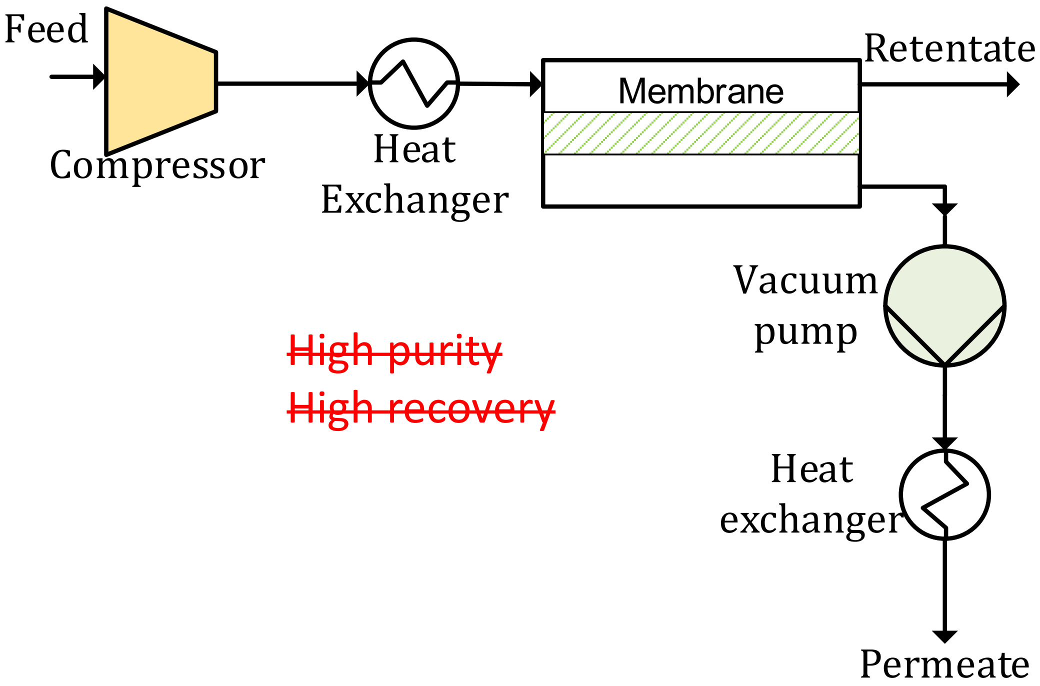


Steps of design of a membrane system

Process design is essential to provide an energy-efficient membrane technology for gas separation.

- Feed source and feed condition
- Product quality
- Select flow configuration
- Select number of stages
- Membrane type
- Optimize the membrane system

Membrane-based process design (single stage)



- The selection of the best configuration is highly related to feed quality, separation objectives and market values.
- A single-stage membrane process cannot meet high recovery and gas purity at the same time, regardless of the membrane type used.
- CO_2/N_2 selectivity must be over 200 to achieve the target separations with CO_2 recovery and purity of >90% and >95%, respectively, in a **single-stage** membrane configuration.
- Since the single-stage membrane process cannot reach the separation goal, a multi-stage membrane system needs to be implemented.

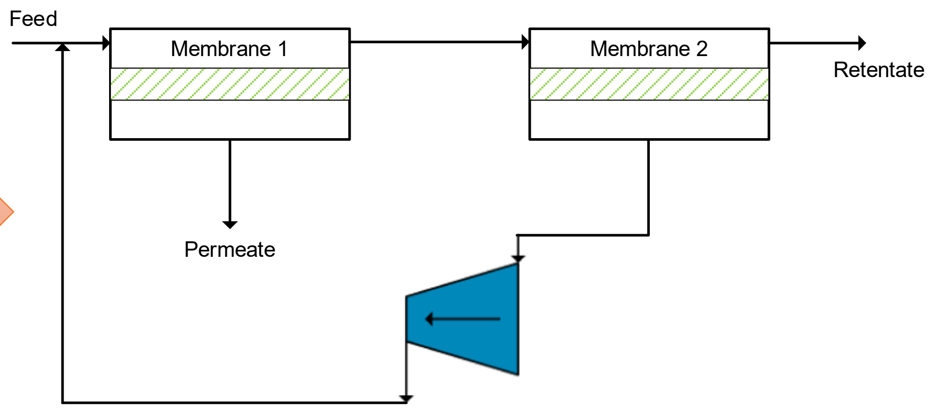
Two-stage cascade for purer retentate or permeate

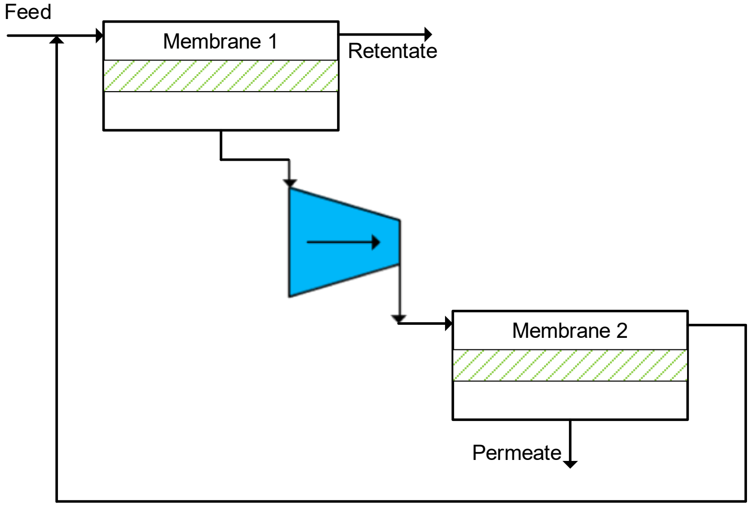
The raw gas is compressed and fed to the first membrane stage

The first stage performs a bulk separation of for example CO_2 and CH_4

The retentate of the first stage is fed to a second stage in which the final product purity is obtained.

Permeate of the second stage is recycled and mixed with the raw gas stream



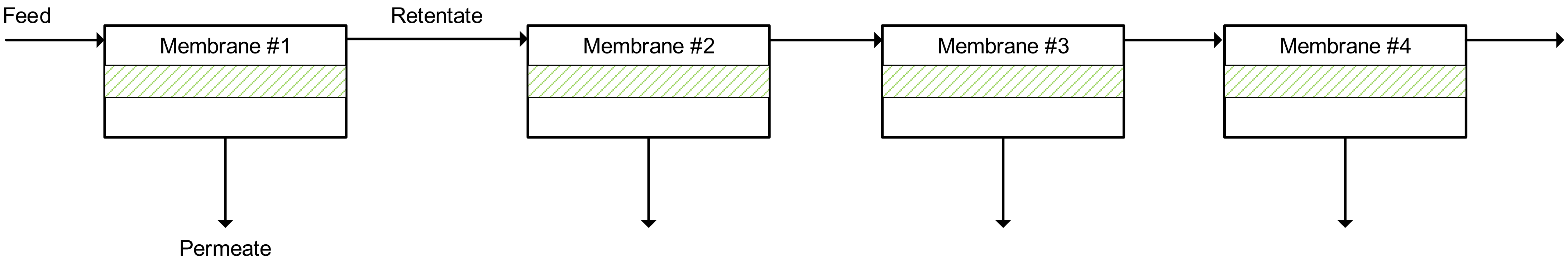


The permeate stream of the first membrane, after passing through a compressor, enters the second stage

The permeate stream of the second membrane is considered as the final product

Multi-stage membrane module

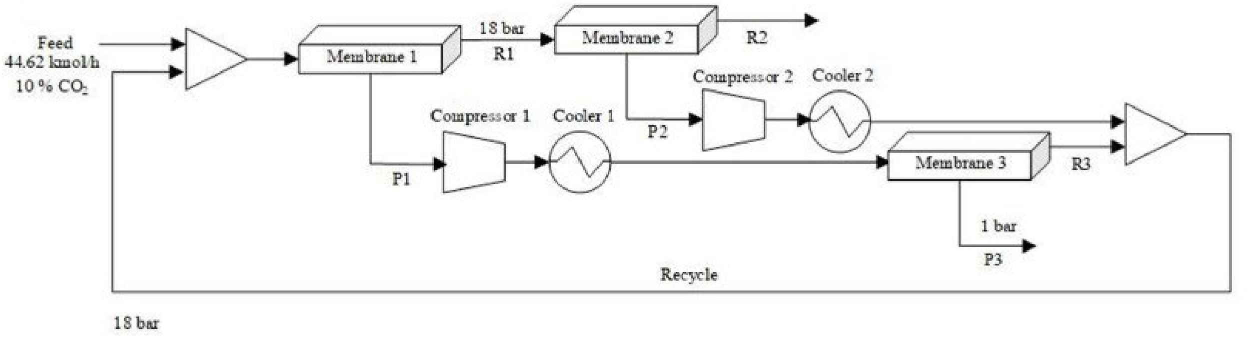
The selection of the best configuration is highly related to feed quality, separation objectives and market values.

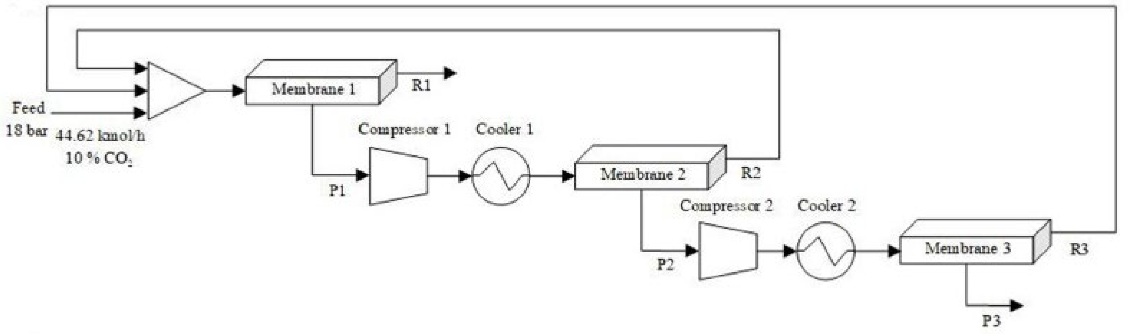


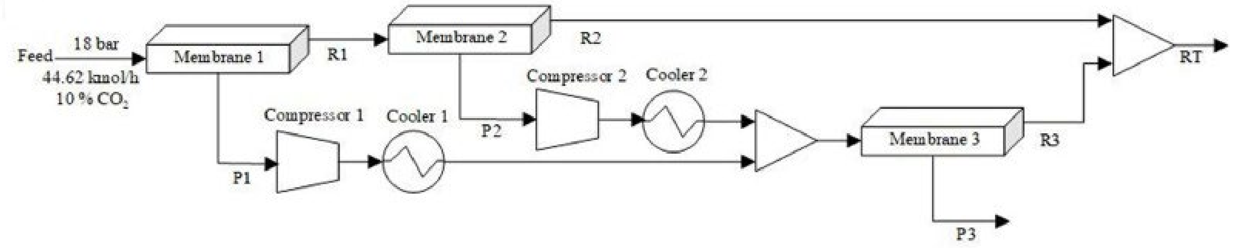
Three-stage membrane module

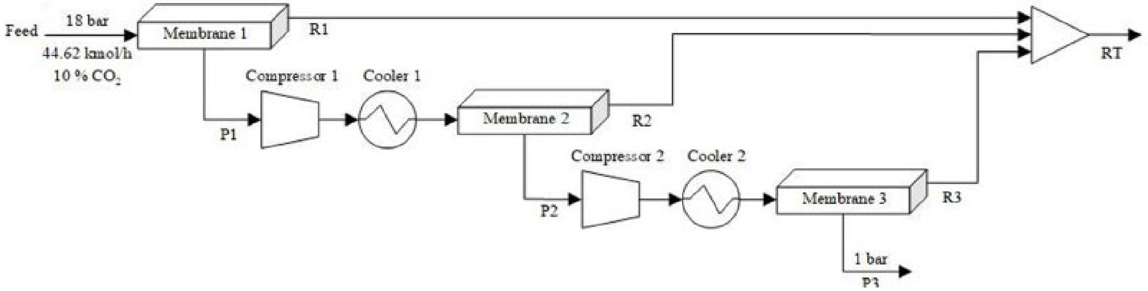
- In most of the literature's examined works, the optimization results were typically derived from heuristic design experience.

- Although using this approach does yield an optimum separation system but is in no way viable to assure whether the capture cost is a global optimum.





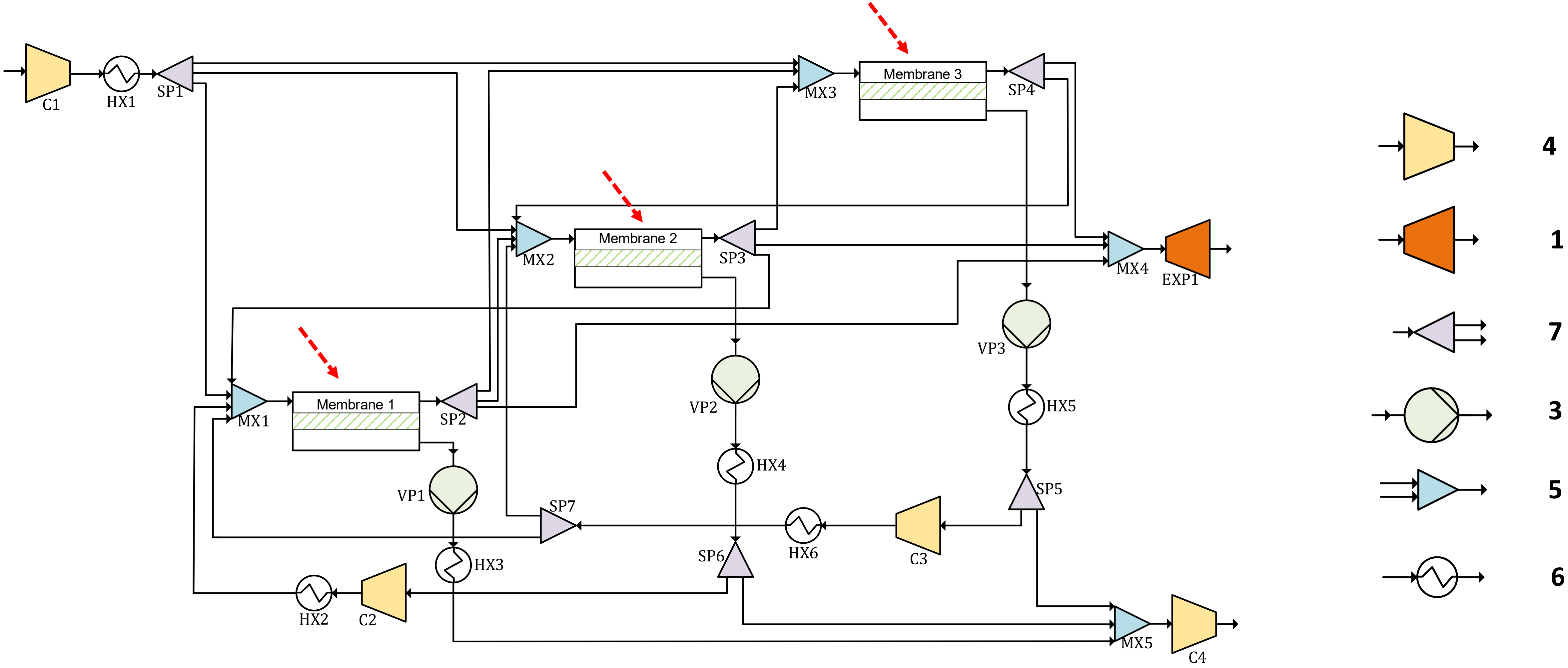




*M. Samei, A. Raisi, Chemical Engineering and Processing - Process Intensification, 170, 2022, 108676.

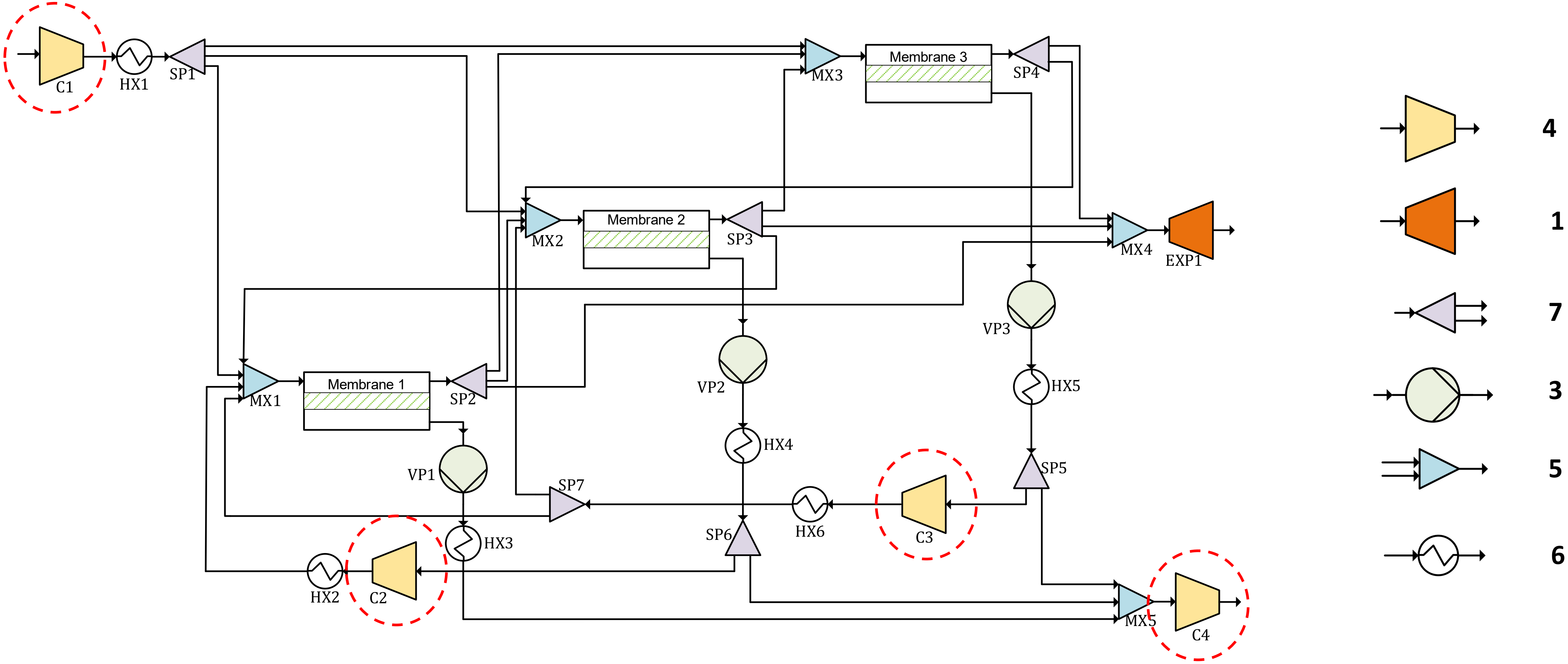
Superstructure membrane module

By applying a structural optimization approach, the most profitable process configuration including stage numbers can be determined.



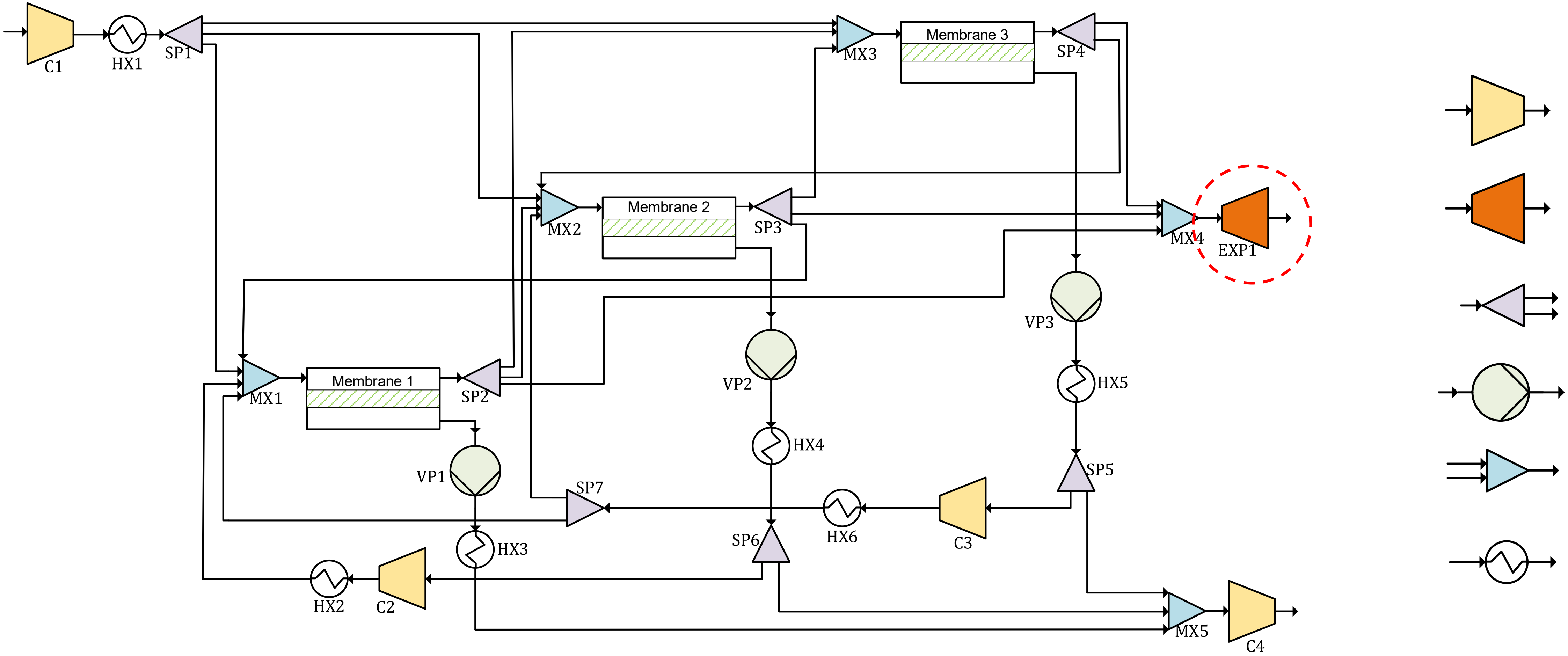
Superstructure membrane module

By applying a structural optimization approach, the most profitable process configuration including stage numbers can be determined.



Superstructure membrane module

By applying a structural optimization approach, the most profitable process configuration including stage numbers can be determined.



Superstructure membrane module

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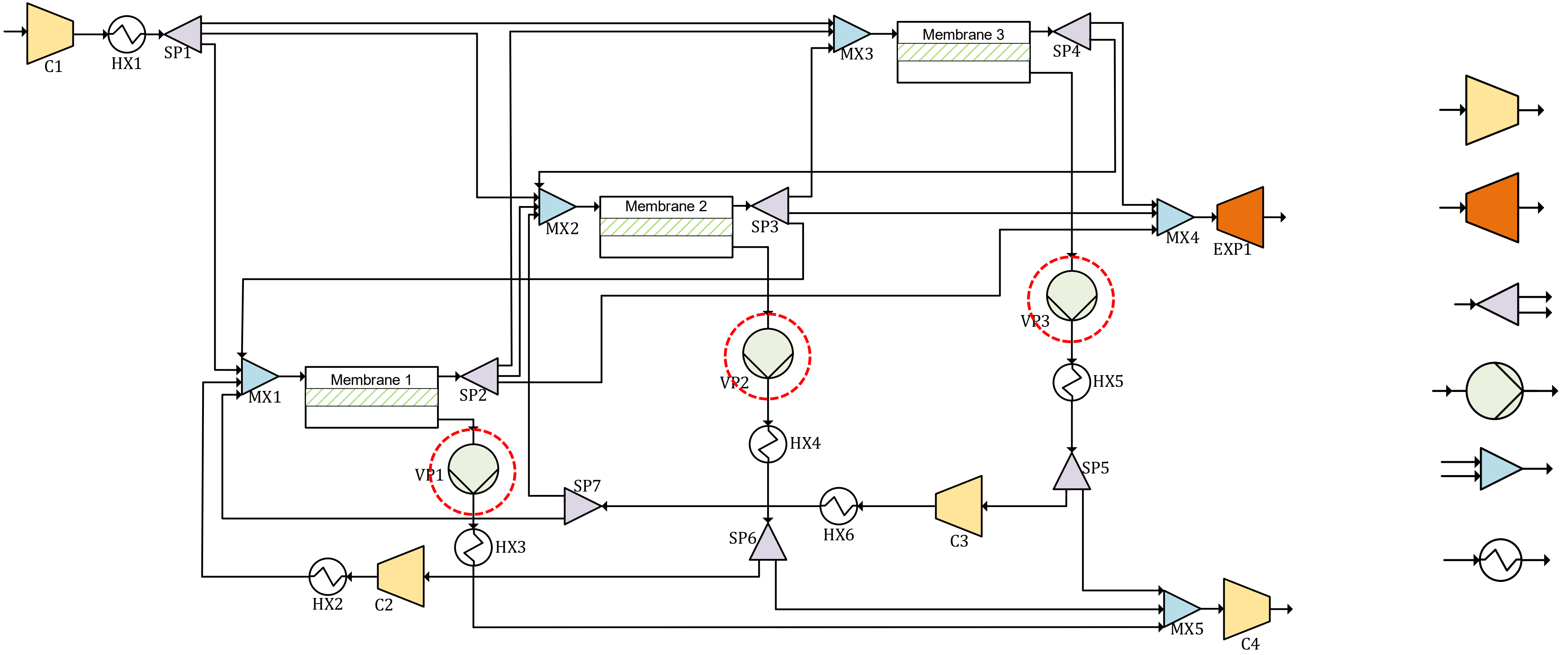
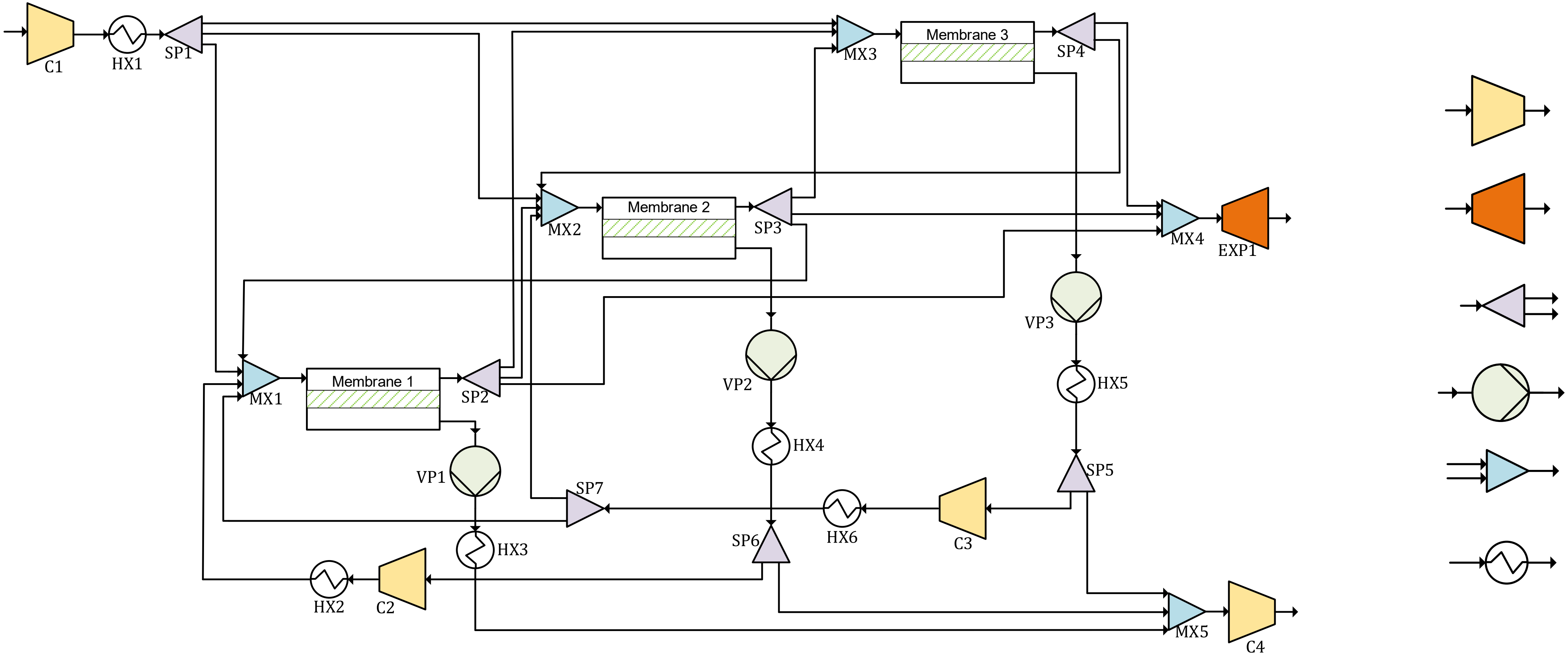


Superstructure membrane module

By applying a structural optimization approach, the most profitable process configuration including stage numbers can be determined.

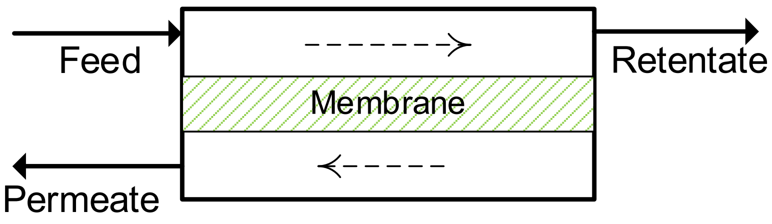


Flow arrangements in membrane modules

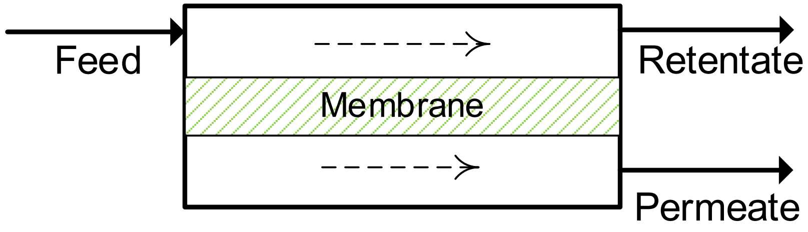
- The performance of a membrane is influenced by the way in which the permeate and retentate flow in the membrane.

- Flow arrangements of perfect mixing, co-current, counter-current, and cross flow are possible in the design of a membrane module.

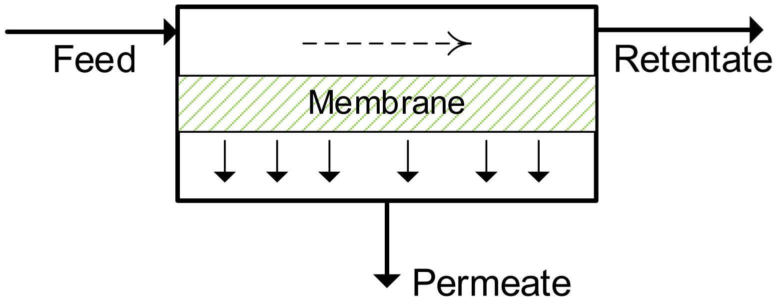
Counter-current Flow



Co-current Flow

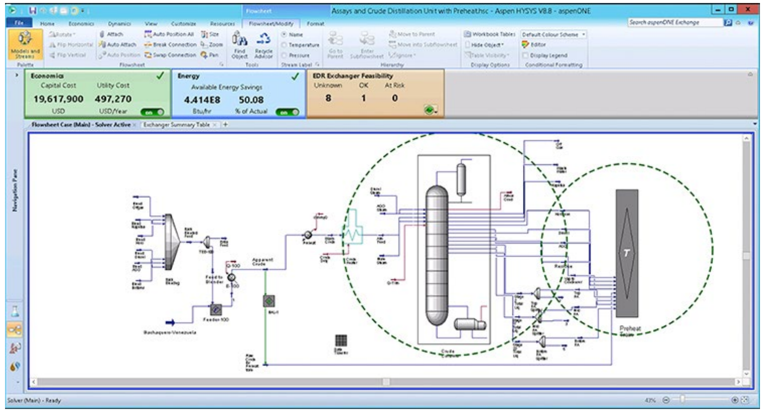


Cross Flow



Process Simulation Tools

- Process simulators have been proven to be successful in modeling, simulate, and optimize various industrial processes.



Aspen Plus **Aspen Hysys**	Can be used for batch and continuous processes for design, troubleshooting in regular operations, monitoring the plant performance through online, and real-time optimization.
gPROMS	An advanced equation oriented process modeling software, which can be used to model, analyze, and optimize in an easy-to-use process flow-sheeting environment.
PRO/II	A steady-state simulator which has an in-built membrane unit operation to simulate crossflow symmetric membranes for gas separations.
ProMax	A multifaceted process simulation software which it is designed to optimize gas processing, refining, and chemical facilities.
SuperPro Designer	A flowsheet driven simulator for batch, continuous as well as combination processes, that perform material and energy balances, equipment sizing, and costing.
Aspen Custom Modeler	Provides the capability to create unique process and equipment simulation models by describing the equations which can be exported into Aspen Plus/Hysys.

Implementation of Membrane model in Aspen Custom Modeler

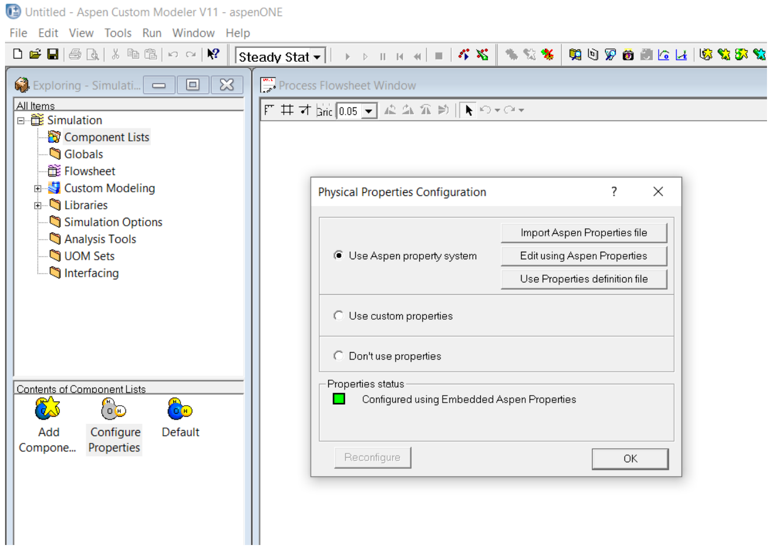
- The developed mass transfer model for the gas separation membrane process is coded.

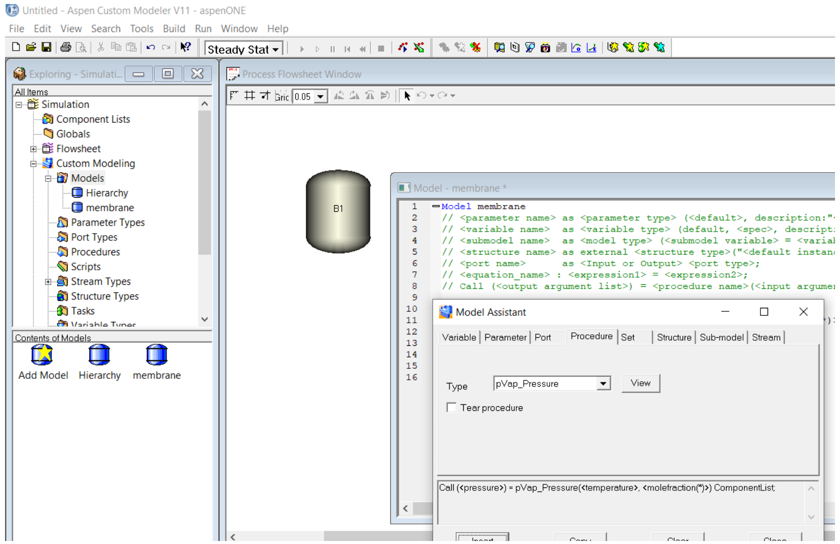
- The model for membrane gas separation can be implemented and solved in ACM, which can be added to Aspen Plus.

- To implement the membrane model in ACM, all chemicals are defined from the component list in the Aspen Properties User Interface program.

- Fixed variables or inputs (feed temperature, pressure, composition and membrane area) are defined, and the process parameters (for example, permeance) and variables are declared.

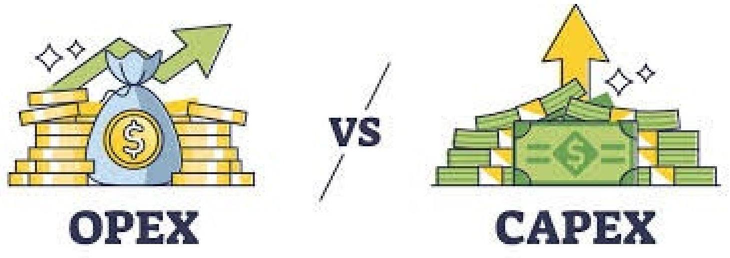
- The model has one port for feed stream and two ports as permeate and retentate streams.





Economic model

- To find the best configuration of the multi-stage gas membrane process, the cost analysis was conducted for:
  Post-combustion
  Natural gas sweetening
  Biogas upgrading



- The aim is to minimize the cost of separation while satisfying the separation targets.

- The economic analysis of the superstructure membrane process was performed by calculating the capital cost, annual operating and maintenance, and energy cost.

- **Capital cost** is associated with membrane area and membrane module skids as well as the contribution of major components such as compression, expander and vacuum pumps.

- **Operational cost** is a sum of electricity cost, and operation and maintenance costs. Operation and maintenance of the vacuum pumps, expander and compressors is estimated at 3.6% of their capital cost and 1% for the membrane and the membrane frame.

Economic model

Description		
Membrane module cost	C_m	$/m^2
Compressor unit cost	C_c	$/kW
Expander unit cost	C_{ex}	$/kW
Vacuum pump unit cost	C_v	$/kW
Efficiency of pressure units	η	-
Installation factor	f_{in}	-
Electricity cost	C_e	$/kWh^{-1}
Operation time per year	t_{op}	h/yr
Depreciation factor (25 years)	DF	-
Membrane depreciation factor (5 years)	DF_m	-
Membrane frame cost	$I_{m,fram} = 0.238 \times 10^6 \times \left(\frac{A_{t,mem}}{2000}\right)^{0.7} \left(\frac{P_t}{55}\right)^{0.88}$	$
Compressor cost	$CC = C_c \times W_c \times f_{in}$	$
Expander cost	$CE = C_{ex} \times W_{ex} \times f_{in}$	$
Vacuum pump cost	$CV = C_v \times W_{vp} \times f_{in}$	$
Total capital cost	$TCC = DF_m(C_m \times A_{t,m}) + DF(I_{m,fram} + CC + CE + CV)$	$/y
Operating and maintenance cost	$OMC = 0.01(C_m A_{t,m} + I_{m,fram}) + 0.036(CC + CE + CV)$	$/y
Energy cost	$EC = C_e \times t_{op} \times \sum W$	$/y
Total operational cost	$VOM = OMC + EC$	$/y
Gas processing cost	$\boxed{GPC = \frac{TCC+VOM}{annual\ separated\ CO_2}}$	$/tonne CO_2

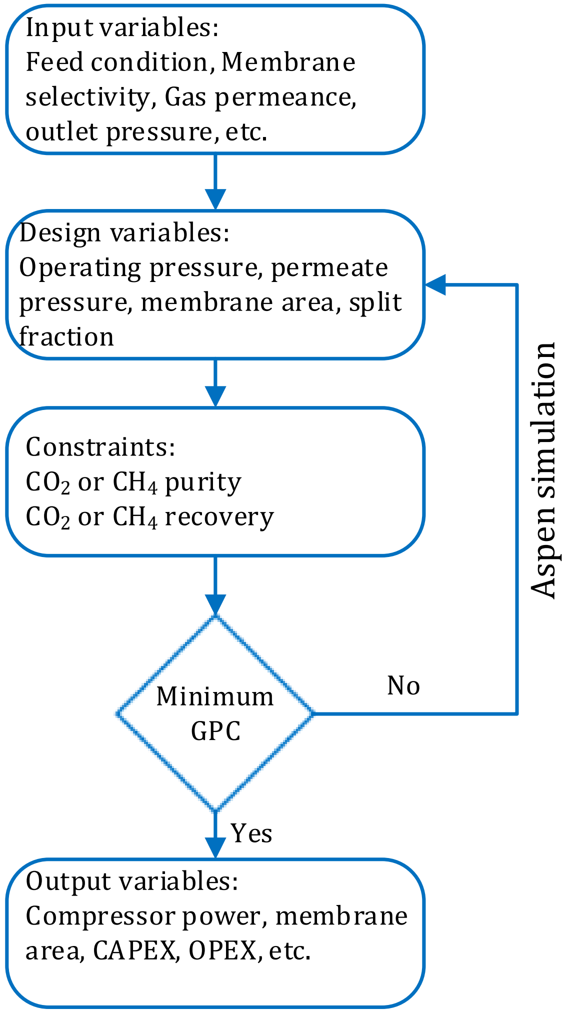
Optimization strategy

- Input variables: Feed conditions, Membrane selectivity and gas permeance, target pressure, product specification

- Targets: CO_2 or CH_4 recovery and purity, minimum GPC

- Decision variables: Membrane area of each stage, retentate pressure, permeate pressure of each stage, split fractions

- ✓ Output variables: Compressor power, membrane area, CAPEX, OPEX, GPC, number of stages



1. Post-combustion CO_2 capture

Post-combustion CO_2 capture should meet conditions of low energy consumption, small footprint, high CO_2 purity (≥ 90%) and recovery (≥ 90%), no adverse environmental impact, and minimal gas processing costs.

The flue gas produced from coal combustion has low CO_2 composition and a high-volume flow rate. For example, a 500 MW coal-fired power plant emits approximately 426 tons of CO_2 per hour

TFCM	Permeance (GPU)		Selectivity
	N_2	CO_2	CO_2/N_2
Prototype A	65	2027	31.0
Prototype A1	46	1598	34.4

Feed characteristic	
Feed flow rate	80,000 kmol/hr
Feed temperature	308.15 K
Feed pressure	1 bar
Feed composition	14 % CO_2 86 % N_2
CO_2 emission	505 tons/hr
Output targets	
CO_2 recovery	90 % and 95 %
CO_2 purity	95 % and 98 %
Product pressure	76 bar

1. Post-combustion CO_2 capture

Prototype A1

CO_2/N_2 selectivity=34.4

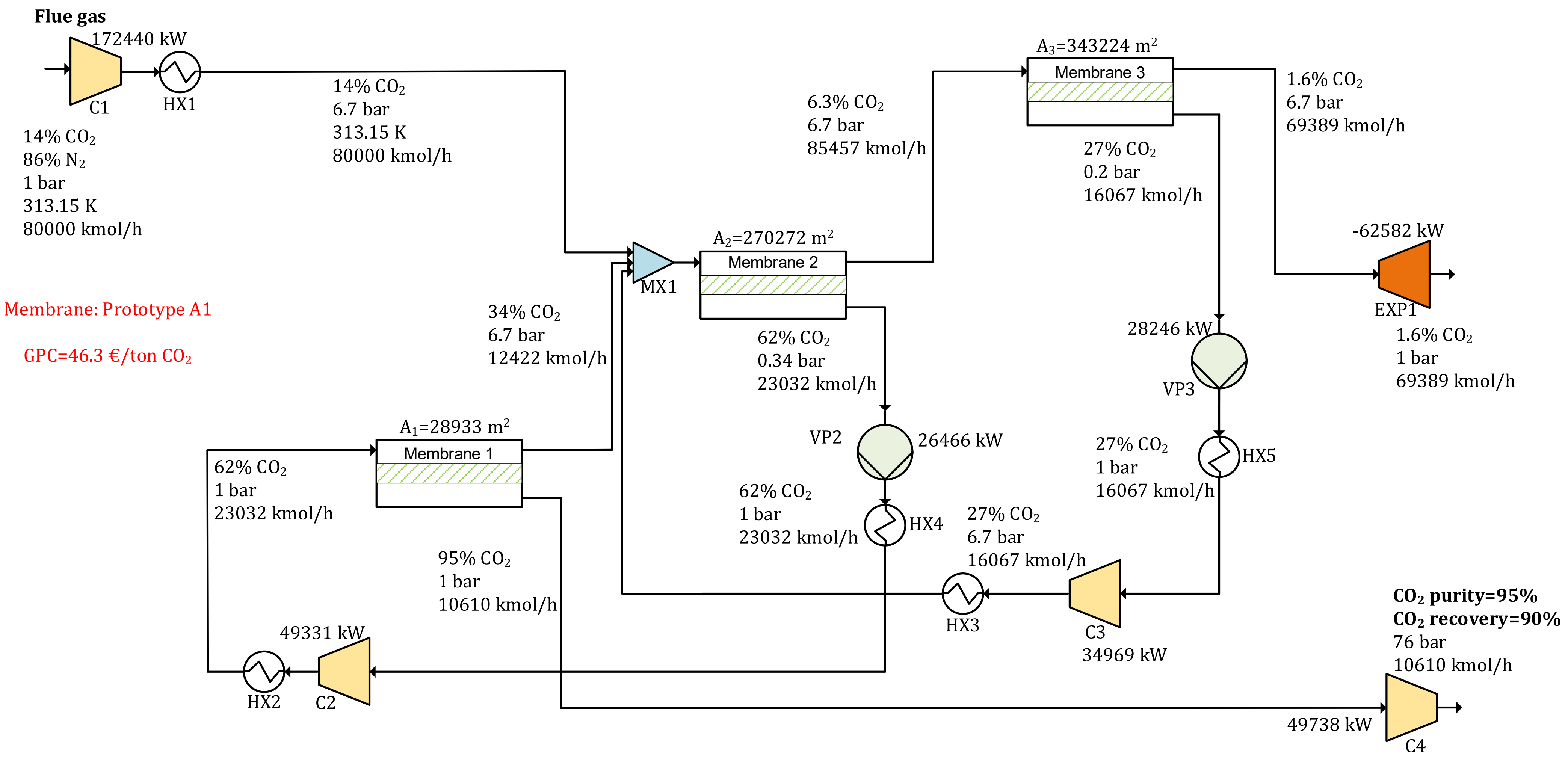
CO_2 purity= 95 %

CO_2 recovery=90 %

Area= 642430 m²

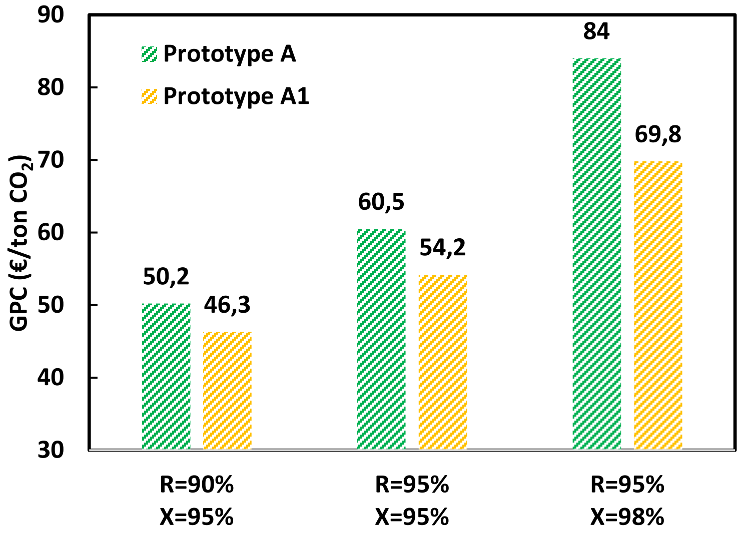
GPC= 46.3 €/tonCO_2

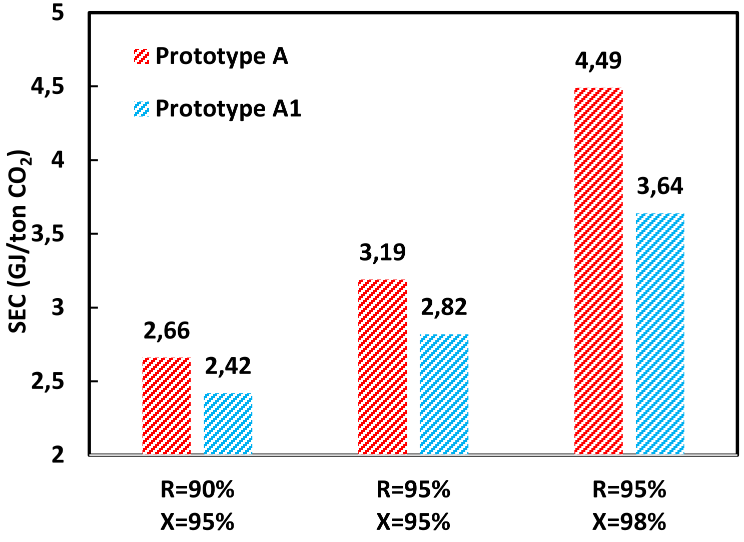
SEC= 2.4 GJ/tonCO_2



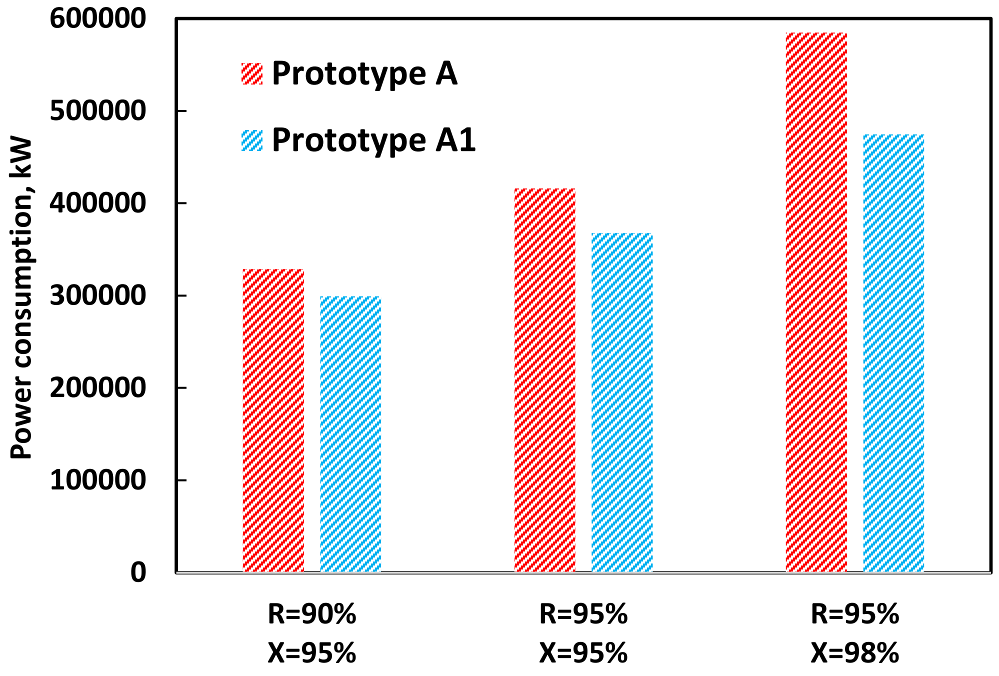
1. Post-combustion CO_2 capture

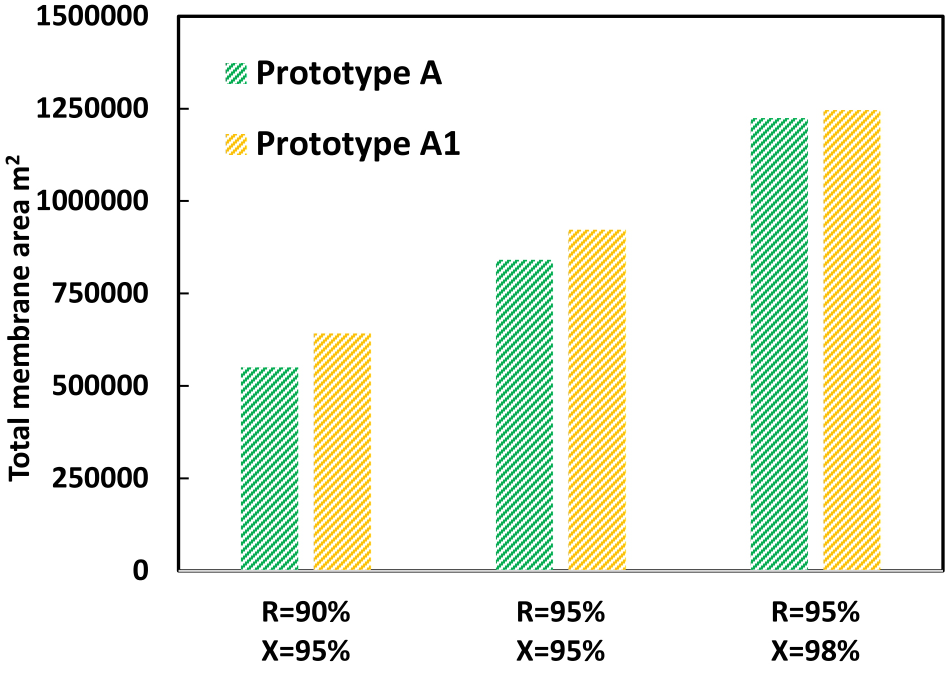
	Prototype A			Prototype A1		
CO_2 permeance	2027	2027	2027	1598	1598	1598
N_2 permeance	65	65	65	46	46	46
CO_2/N_2 selectivity	31	31	31	34.4	34.4	34.4
CO_2 recovery	90%	95%	95%	90%	95%	95%
CO_2 purity	95%	95%	98%	95%	95%	98%
Stages	3	3	3	3	3	3
CAPEX, *€/yr*	37×10^6	49×10^6	68×10^6	36×10^6	45×10^6	59×10^6
OPEX, *€/yr*	140×10^6	177×10^6	249×10^6	128×10^6	157×10^6	202×10^6
Power, *kW*	328,841	415,899	584,585	299,364	367,919	474,508
Membrane area, *m^2*	550,268	841,188	1,224,300	642,430	922,526	1,245,790
SEC, *$GJ/tonCO_2$*	2.66	3.19	4.49	2.42	2.82	3.64
GPC, *$€/tonCO_2$*	50.2	60.5	84	46.3	54.2	69.8



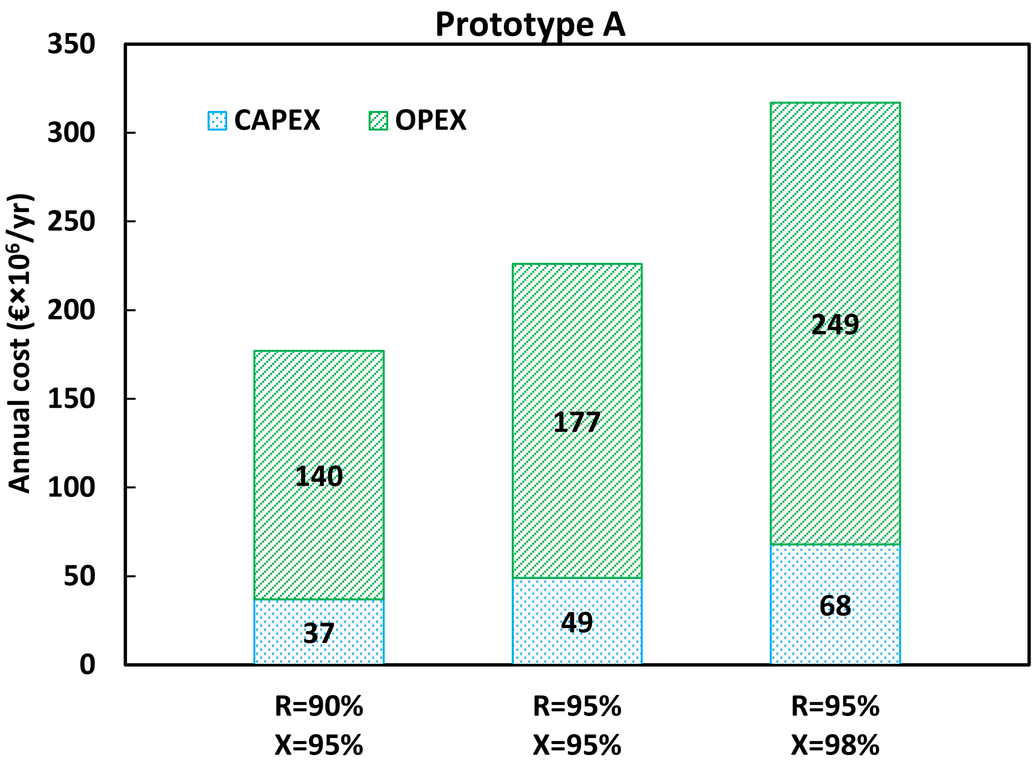


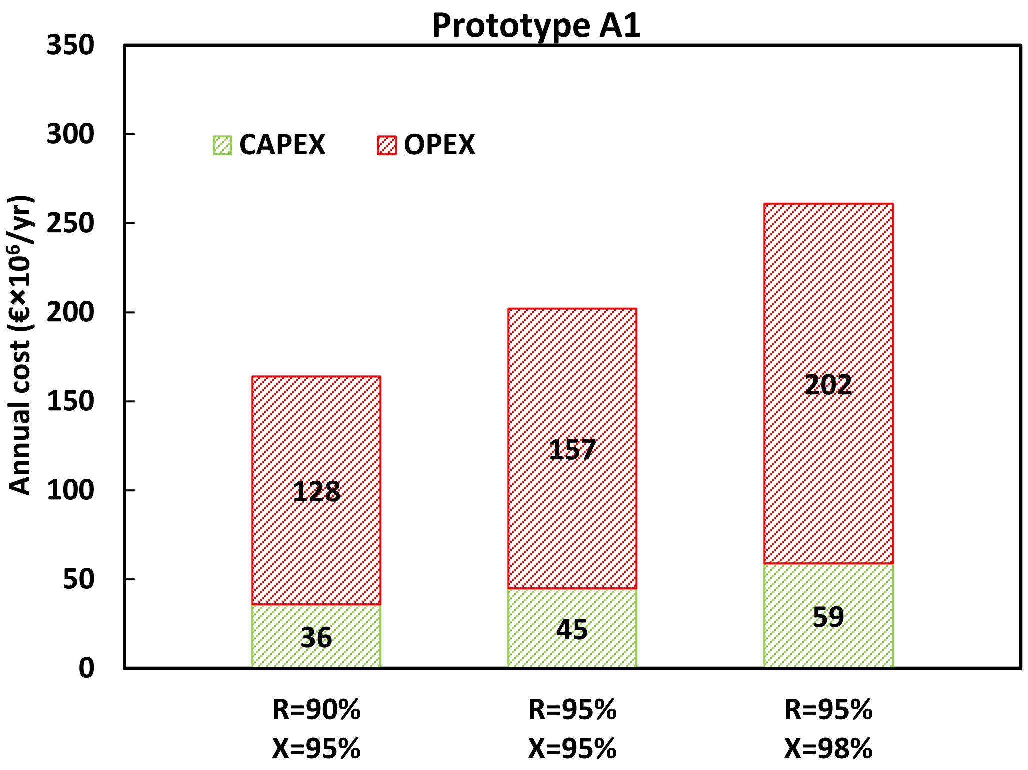
1. Post-combustion CO_2 capture





1. Post-combustion CO_2 capture





R=CO_2 recovery
X=CO_2 purity

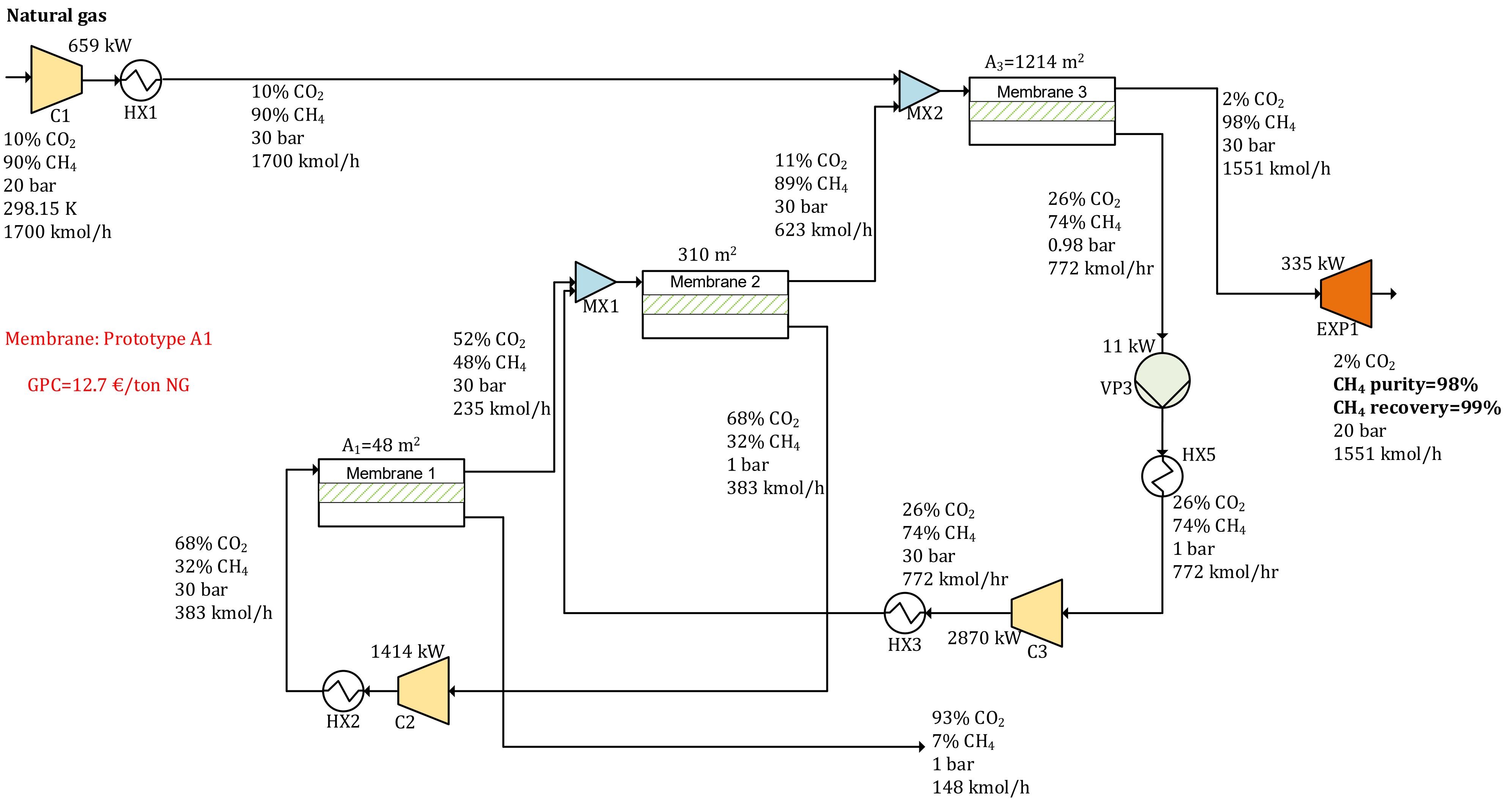
2. Natural gas separation

- Every year, the world uses close to 3.9 trillion cubic meters of natural gas.
- CO_2 separation from natural gas is critical as the presence of CO_2 adversely affects the produced gas quality, and can form acids in the presence of water that corrodes the pipelines and equipment.
- CO_2 content in natural gas needs to be decreased to below 3%.

TFCM	Permeance (GPU)		Selectivity
	CH_4	CO_2	CO_2/CH_4
Prototype A	204	2027	9.9
Prototype A1	142	1598	11.2

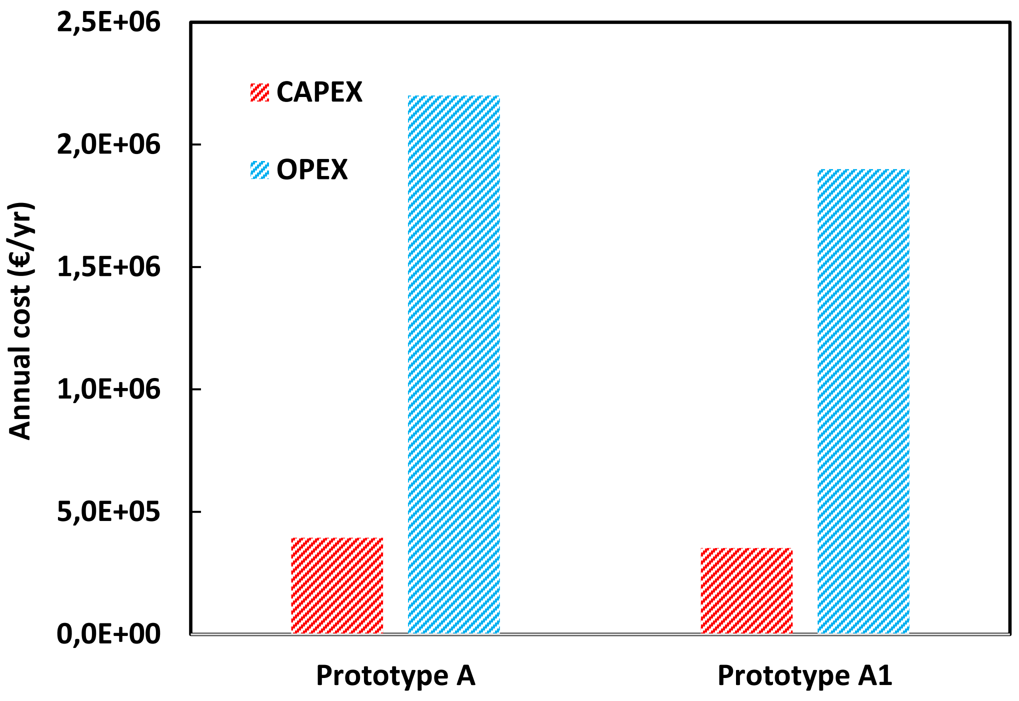
Feed gas characteristic	Feed flow rate	1700 kmol/hr
	Feed temperature	298.15 K
	Feed pressure	20 bar
	Feed composition	10 % CO_2 90 % CH_4
Output targets	CH_4 recovery	99 %
	CH_4 purity	98 %
	Product pressure	20 bar

2. Natural gas separation



2. Natural gas separation

	Prototype A	Prototype A1
CO_2 permeance	2027	1598
CH_4 permeance	204	142
CO_2/CH_4 selectivity	9.9	11.2
CH_4 recovery	99 %	99 %
CH_4 purity	98 %	98 %
Stages	3	3
CAPEX, €/yr	394000	352031
OPEX, €/yr	2.2×10^6	1.9×10^6
Power	5338 kW	4622 kW
Membrane area	1348 m^2	1574 m^2
GPC	15.0 €/ton NG	12.7 €/ton NG



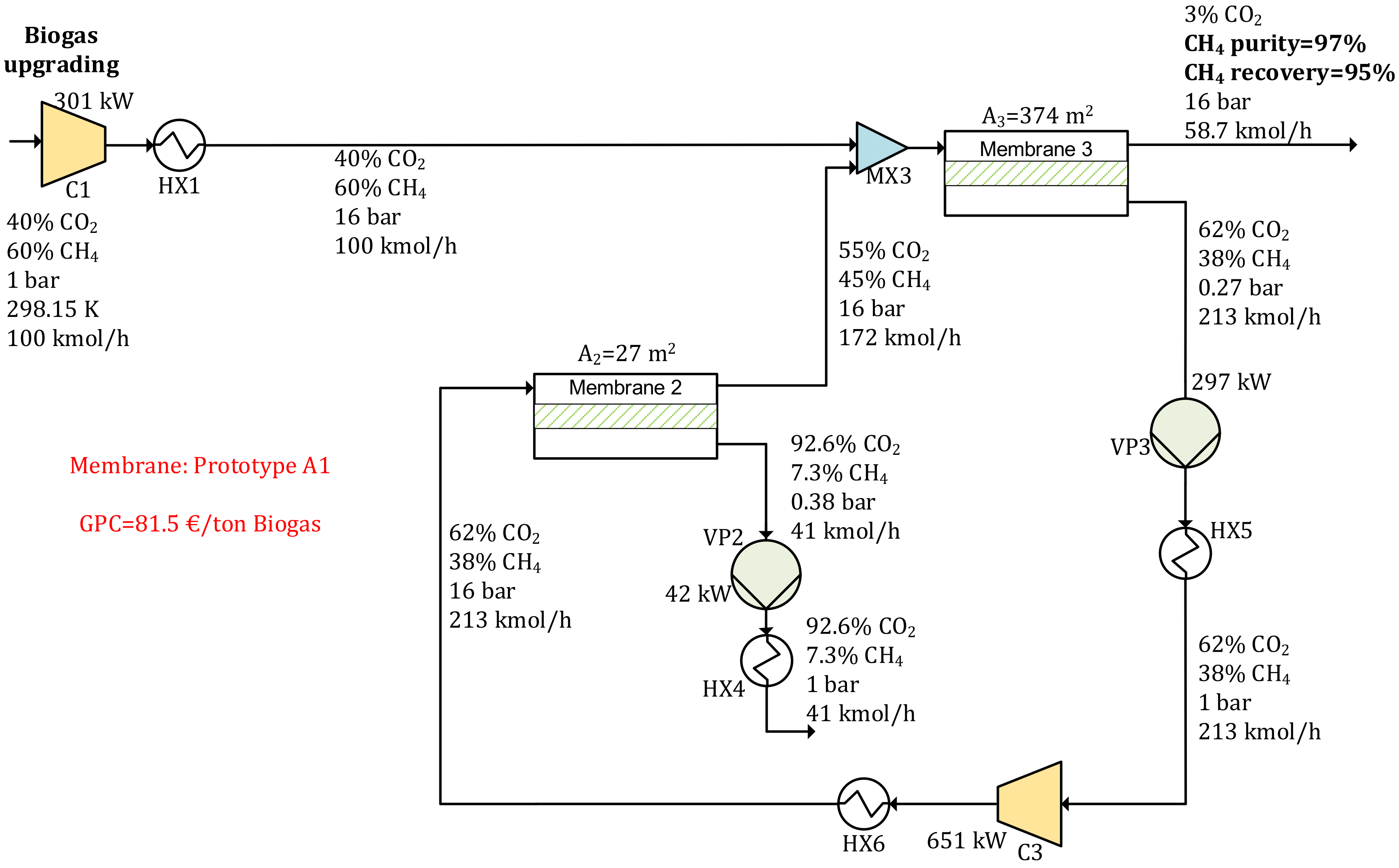
3. Biogas Upgrading

- Biogas is a potential alternative to the world's unquenchable demand for energy and concurrently reduces waste and greenhouse gas emissions.
- CO_2 is the non-combustible portion of biogas.
- CO_2 has to be removed from CH_4 to enhance the heating value of the product gas.
- CH_4 mole fraction in the raw gas of 60% has to be increased to more than 90% in order to meet the natural gas grid requirements.
- CH_4 purity and recovery are the most important technical parameters in determining an optimal module arrangement to ensure a low CH_4 loss.

Feed gas characteristic	Feed flow rate	100 kmol/hr
	Feed temperature	298.15 K
	Feed pressure	1 bar
	Feed composition	40 % CO_2 60 % CH_4
Output targets	CH_4 recovery	95 %
	CH_4 purity	97 %
	Product pressure	16 bar

TFCM	Permeance (GPU)		Selectivity
	CH_4	CO_2	CO_2/CH_4
Prototype A	204	2027	9.9
Prototype A1	142	1598	11.2

3. Biogas Upgrading

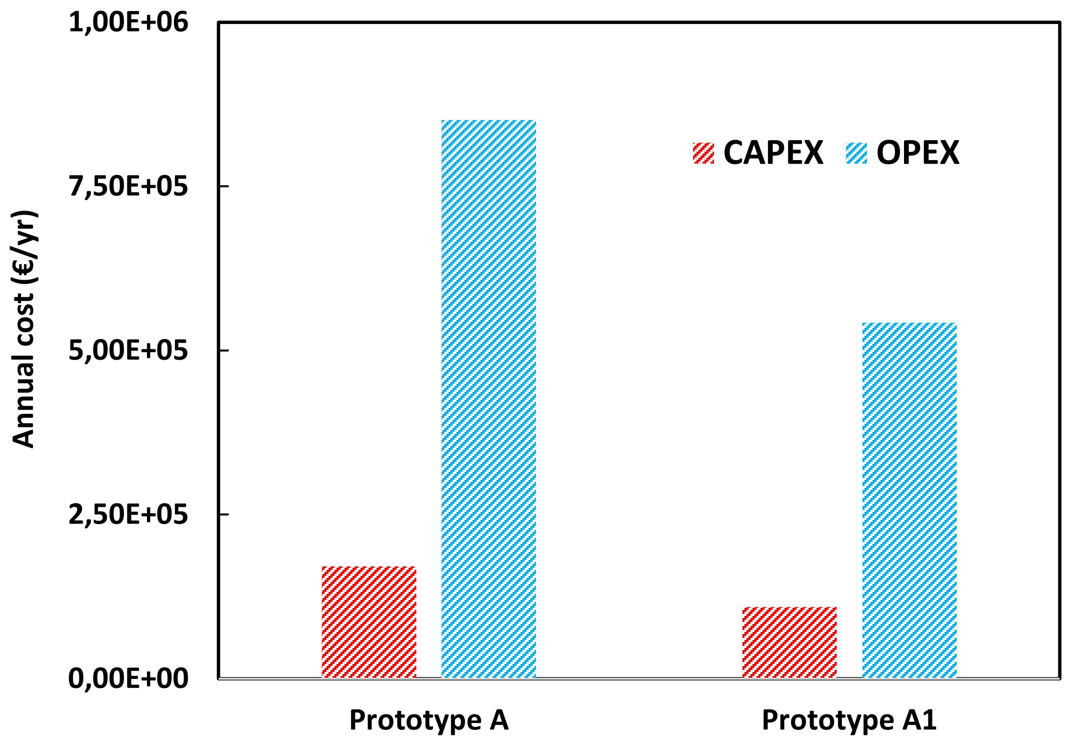


Membrane: Prototype A1

GPC=81.5 €/ton Biogas

3. Biogas Upgrading

	Prototype A	Prototype A1
CO_2 permeance	2027	1598
CH_4 permeance	204	142
CO_2/CH_4 selectivity	9.9	11.2
CH_4 recovery	95%	95%
CH_4 purity	97 %	97 %
Stages	2	2
CAPEX, €/yr	171019	109147
OPEX, €/yr	850959	542137
Power	2036 kW	1298 kW
Membrane area	490 m^2	402 m^2
GPC, €/ton Biogas	128.8	81.5



Conclusion

- The proposed superstructure is beneficial for further reduction of the cost associated with membrane CO_2 capture process and can be successfully applied for various applications.
- The membrane selectivity plays a key role on final gas separation cost.
- Three-stage structure with two recycle streams and two vacuum pumps is the most profitable layout for post-combustion CO_2 capture.
- The gas separation costs increased from about 46 to 70 €/ton CO_2 and specific energy consumption increased from 2.4 to 3.6 GJ/ton CO_2, when product targets increased from 90% recovery and 95% purity to 95% recovery and 98% purity.
- A two-stage process with one recycle stream is able of upgrading biogas to meet the separation targets of 95% recovery and 97% CH_4 purity.
- The optimal configuration for a 99% CH_4 recovery and 98% CH_4 purity in natural gas included three membrane stages with two permeate recycles and one vacuum pump at 12.7 €/ton NG.

Bio-based copolymers for membrane end products for gas separations

Bio-based Industries
Consortium

This project has received funding from the Bio Based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation programme, under grant agreement No 887075.

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

Bio-based copolymers for membrane end products for gas separations

Demonstration of Biocomem membranes at TRL 4 and TRL 5

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Sustainable Process Engineering

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Outlook

- Introduction
- Membrane module modeling
- Setup description for TRL4 demonstration
- Aging tests composition
    i. Procedure for the assessment of the influence of pollutants over the membrane
- Setup description and results TRL5 (DMT)

Introduction

- Currently, chemical separations play a major part in energy use in process industry.

- BIOCOMEM´s first goal is to produce at pilot scale new bio-based PEBA co-polymers, each specially designed to bring added value for three CO2 separation market sectors:
  - Post Combustion flue gas treatment,
  - Natural Gas Sweetening,
  - Biogas Upgrading.

- Another goal is to validate at pilot scale in an industrially relevant environment (TRL 5) three production processes, to manufacture gas separation hollow fiber membranes that meet performance requirements in application using PEBA type co-polymers eith bio-based origin.

ODE System Equations

- **Finite material balance** between *z = 0* and *z = L*

$$n_f = n_r + n_p$$

$$n_f \cdot x_{i,f} = n_r \cdot x_{i,r} + n_p \cdot x_{i,p}, \qquad \forall\, i = 1, \dots, N_c$$

- **Differential material balance,** retentate side

$$dn = -JSdz$$

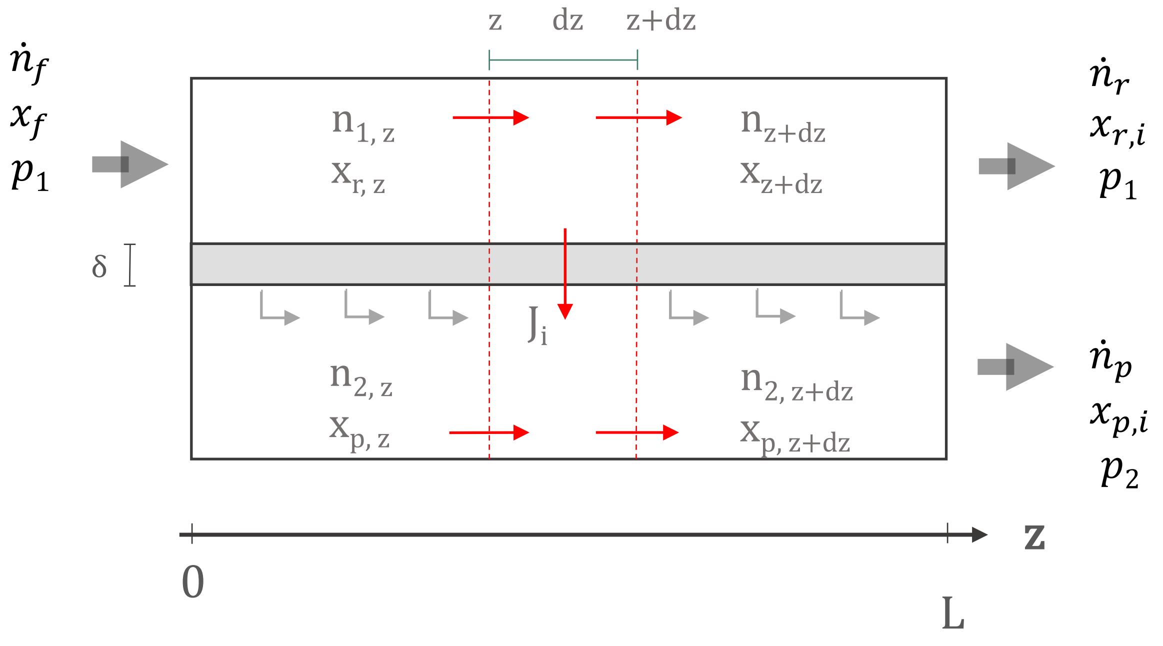
$$d(nx_{i,r}) = -J_i S dz$$

- **Constitutive Flux Equations**

$$J_i = -\frac{P_i}{\delta} \cdot (p_1 \cdot x_{i,r} - p_2 \cdot x_{i,p}), \qquad \forall\, i = 1, \dots, N_c$$

- **Composition Equations**

$$\sum_{i=1}^{N_c} x_{i,f} = \sum_{i=1}^{N_c} x_{i,r} = \sum_{i=1}^{N_c} x_{i,p} = 1$$



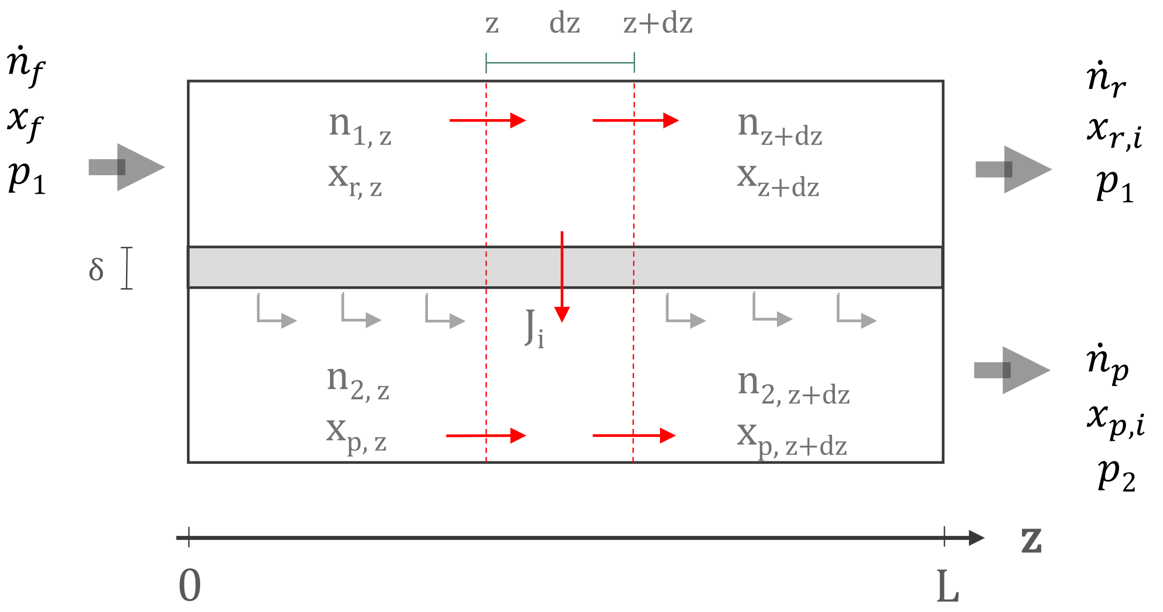
The system includes $\mathbf{2n+2}$ coupled differential equations (where $\boldsymbol{n}$ represents the number of species in the feed gas mixture).

Input parameters providing for the boundary conditions for the differential equations include:

- feed conditions: $\boldsymbol{n_f, x_{i,f}, p_f}$
- the geometrical features of the membrane

ODE System Equations

$$
\begin{cases}
\dfrac{dn_1}{dz} = -\displaystyle\sum_{i=1}^{n} J_i(p_1, p_2, x_{i,r}, x_{i,p}) \cdot SN_f \\[2ex]
\dfrac{dx_{i,r}}{dz} = \dfrac{x_i \sum_{i=1}^{n} J_i(p_1, p_2, x_{i,r}, x_{i,p}) \; - J_i(p_1, p_2, x_{i,r}, x_{i,p})}{n_1} \cdot SN_f \\[2ex]
\dfrac{dn_2}{dz} = +\displaystyle\sum_{i=1}^{n} J_i(p_1, p_2, x_{i,r}, x_{i,p}) \cdot SN_f \\[2ex]
\dfrac{dx_{i,p}}{dz} = \dfrac{J_i(p_1, p_2, x_{i,i}, x_{i,p}) - y_i \sum_{i=1}^{n} J_i(p_1, p_2, x_{i,r}, x_{i,p})}{n_2} \cdot SN_f
\end{cases}
$$



where:

- $\dot{n}_f$ feed molar flow rate
- $\dot{n}_{r/p,i}$ retentate/permeate flow rates
- $x_{r/p,i}$ retentate/permeate molar fraction of *i*
- J_i local transmembrane molar flux of *i*
- p_1 retentate pressure
- p_2 permeate pressure
- S geometrical factor *(e.g. πD – hollow fibers)*
- N_f number of fibers

Initial conditions (z = 0):

- $n_1 = \dot{n}_f$
- $x_i = x_{i,f}$
- $n_2 = 0$

Dimensionless Analysis

Introducing the following adimensional parameters:

- $\mathbf{r_p} = \frac{p_2}{p_1}$
- $\boldsymbol{\gamma_i} = \frac{P_i}{P_1} = \frac{\Pi_i}{\Pi_1}$
- $\boldsymbol{\bar{n}_1} = \frac{n_1}{n_f}$
- $\boldsymbol{\bar{A}} = \frac{AP_1p_1}{\delta n_f}$
- $\boldsymbol{\zeta} = \frac{Sdz}{SL}$

where:

$$\Pi_1 = \frac{P_1}{\delta}$$

$$A = SN_fL$$

$$\frac{1}{\frac{P_1}{\delta}} \cdot \frac{n_f}{n_f} \cdot \frac{1}{p_1} \cdot \frac{d(n_1)}{dA} = -\sum_i^{N_c} \frac{P_i}{\delta} \cdot \left(p_1 \cdot x_{i,r} - p_2 \cdot x_{i,p}\right) \cdot \frac{1}{p_1} \cdot \frac{\delta}{P_1}$$

$$\frac{d\boldsymbol{\bar{n}_1}}{d\boldsymbol{\zeta}} = -\sum_i^{N_c} \boldsymbol{\gamma_i} \cdot \left(x_{i,r} - \boldsymbol{r_p} \cdot x_{i,p}\right) \cdot \boldsymbol{\bar{A}}$$

Permeate pressure drop

Hagen-Poiseuille Law

$$dp = \frac{-256RT\boldsymbol{\mu}q_2}{\pi D_i^4 Np}$$

Perry's Chemical

$$\mu_i = \frac{C_1 \cdot T^{C_2}}{1 + \frac{C_3}{T} + \frac{C_4}{T^2}}$$

Wilke

$$\mu_{mix} = \sum_{i=1}^{n} \frac{\mu_i}{1 + \frac{1}{x_i}\sum_{\substack{j=1 \\ j\neq i}}^{n} x_j \phi_{ij}}$$

$$\phi_{ij} = \sum_{i=1}^{n} \frac{\mu_i}{1 + \frac{1}{x_i}\sum_{\substack{j=1 \\ j\neq i}}^{n} x_j \phi_{ij}}$$

Components	CO_2	O_2	CO	H_2	CH_4	N_2	C_2H_6	$\boldsymbol{\mu \times 10^6}$ $g/(cm \cdot s)$ μ_{calc}	μ_{exp}
	6,2	10,7				83,1		175	179,3
$\boldsymbol{x_i}$ (%)	10,6		29,8	3,9	0,3	55,4		171,3	174,3
	2,5	0,8	14,9	53,0	18,1	9,1	1,6	126,05	135,5

Wilke, A Viscosity Equation for Gas Mixtures J. Chem. Phys. 18, 517 (1950); https://doi.org/10.1063/1.1747673

Biogas Upgrading case

Input data:

$\dot{n}_f = 1 - 15\ l_{STP}/min$

$N_f = 800$

$A = 0.38\ m^2$

$L = 0.38\ m$

$D = 3.9789 \cdot 10^{-4}\ m$

$\Pi_{CO_2} = 5.91 \cdot 10^{-5}, \quad \Pi_{O_2} = 1{,}36 \cdot 10^{-5}, \Pi_{CH_4} = 1.59 \cdot 10^{-6}$

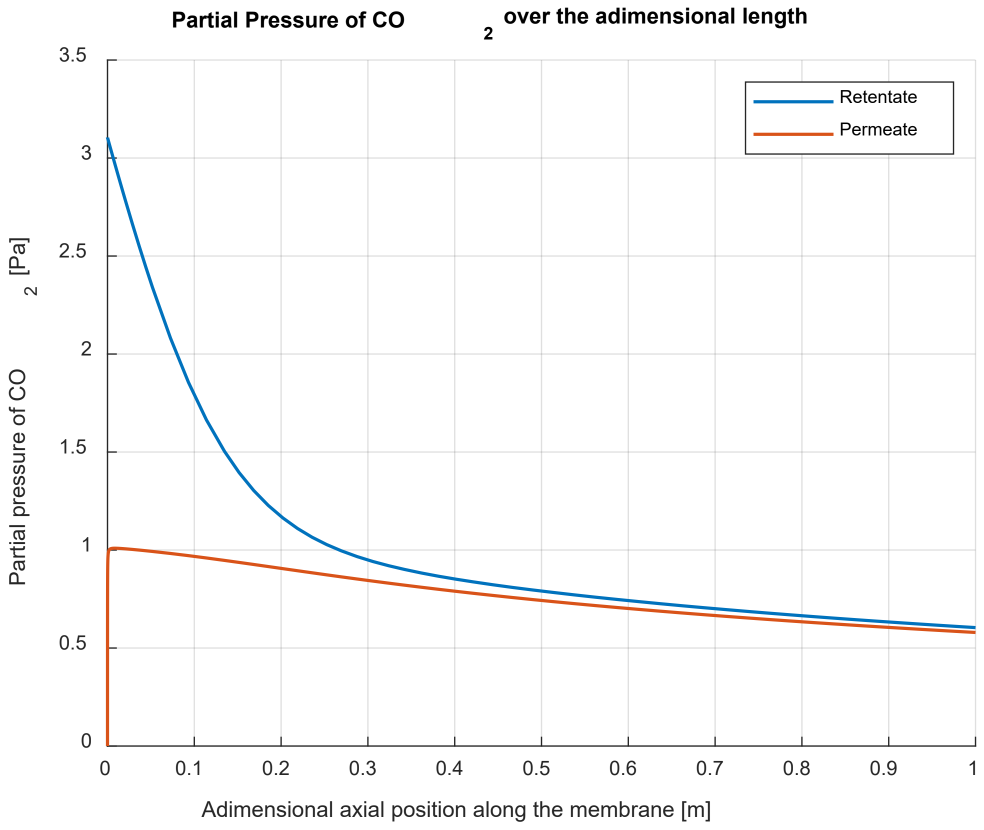
$x_{f,CH_4} = 0.645, \quad x_{f,O_2} = 0.01, \quad x_{f,CO_2} = 0.345$

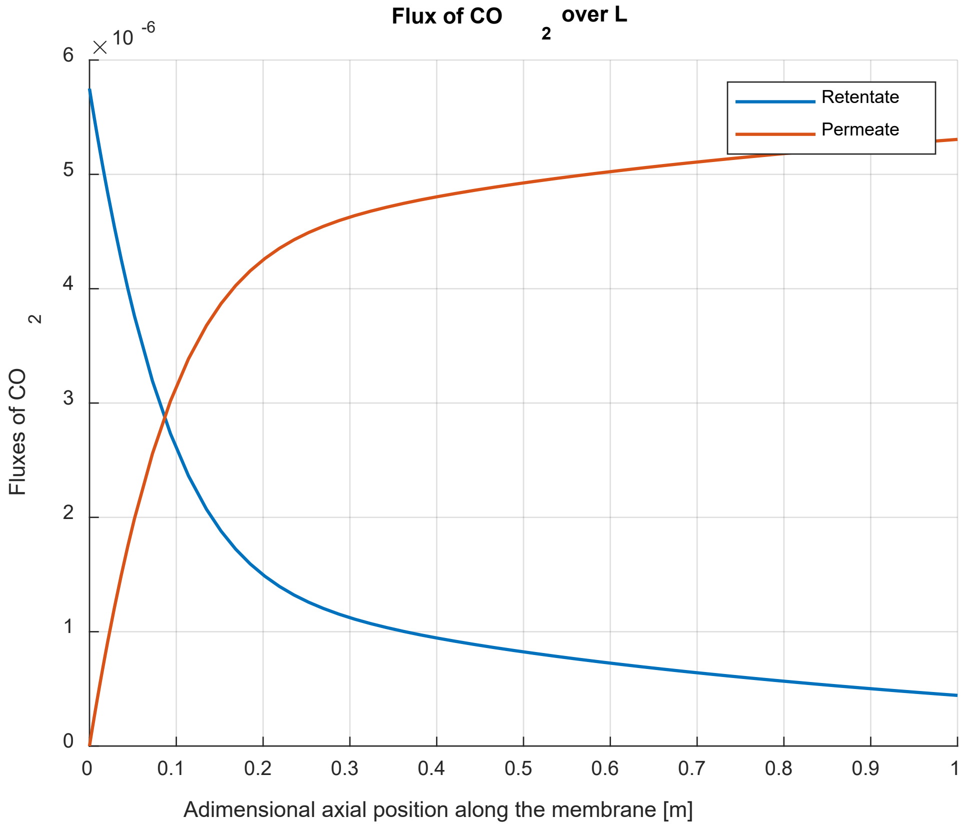
$p_1 = 9\ bar$

$p_2 = 1.1\ bar$

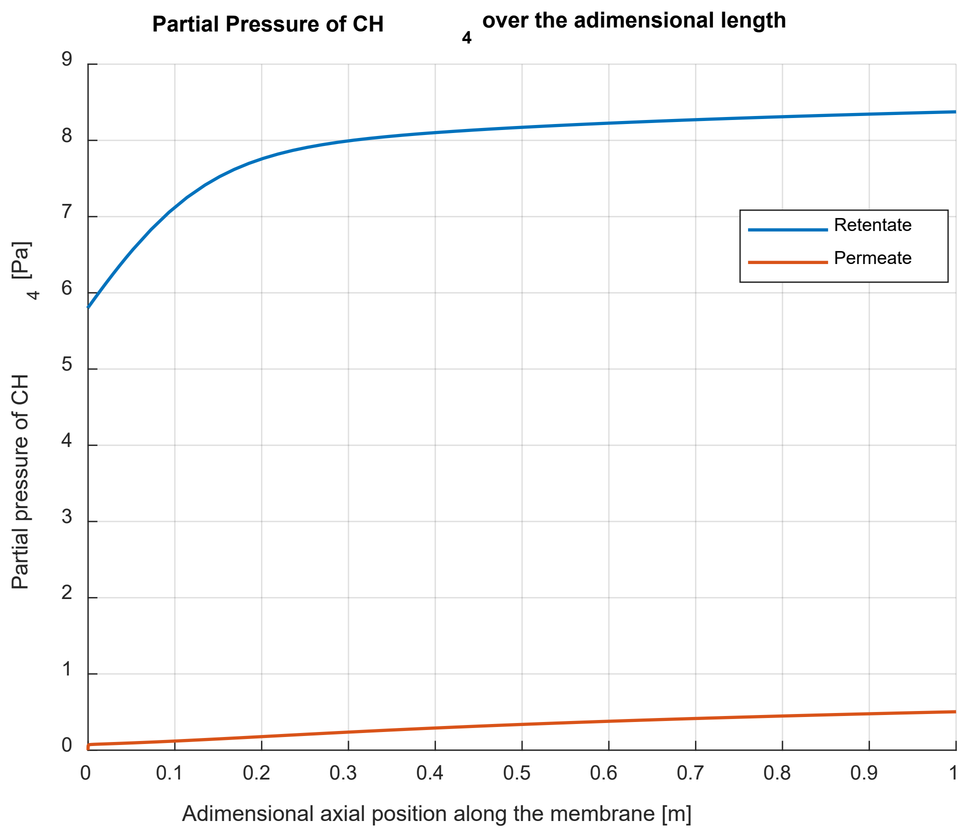
Makaruk et al., Numerical algorithm for modelling multicomponent multipermeator systems, (2009)

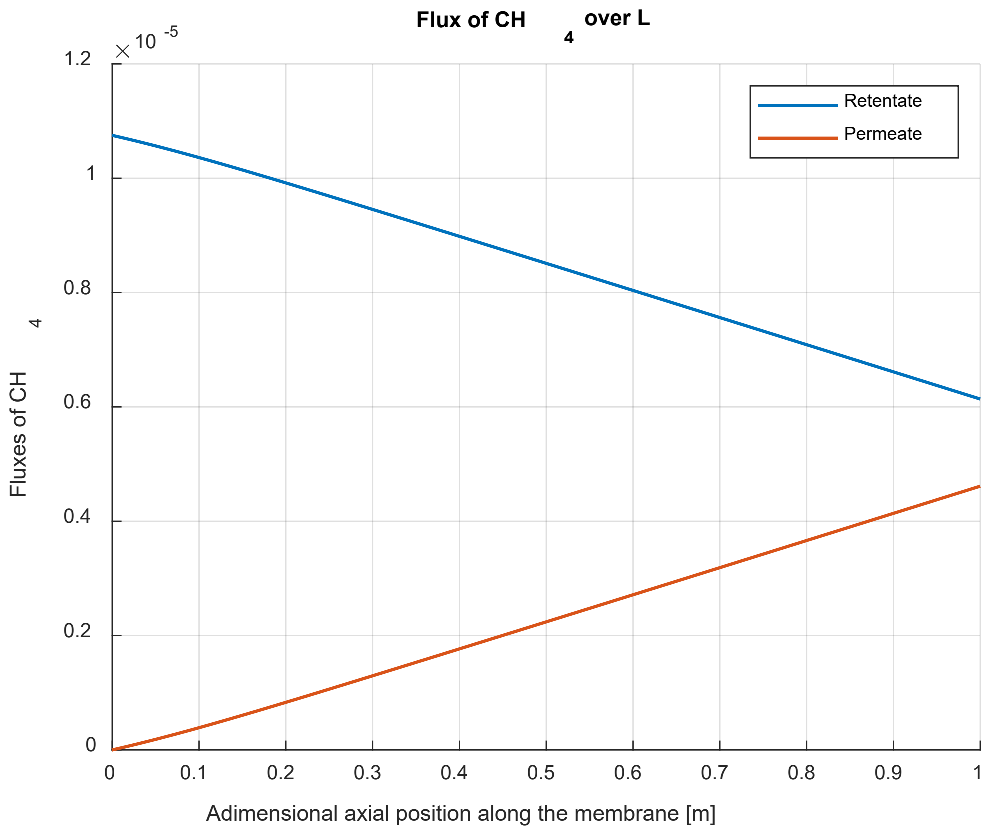
Partial Pressure and Retentate/Permeate Flux (CO_2)



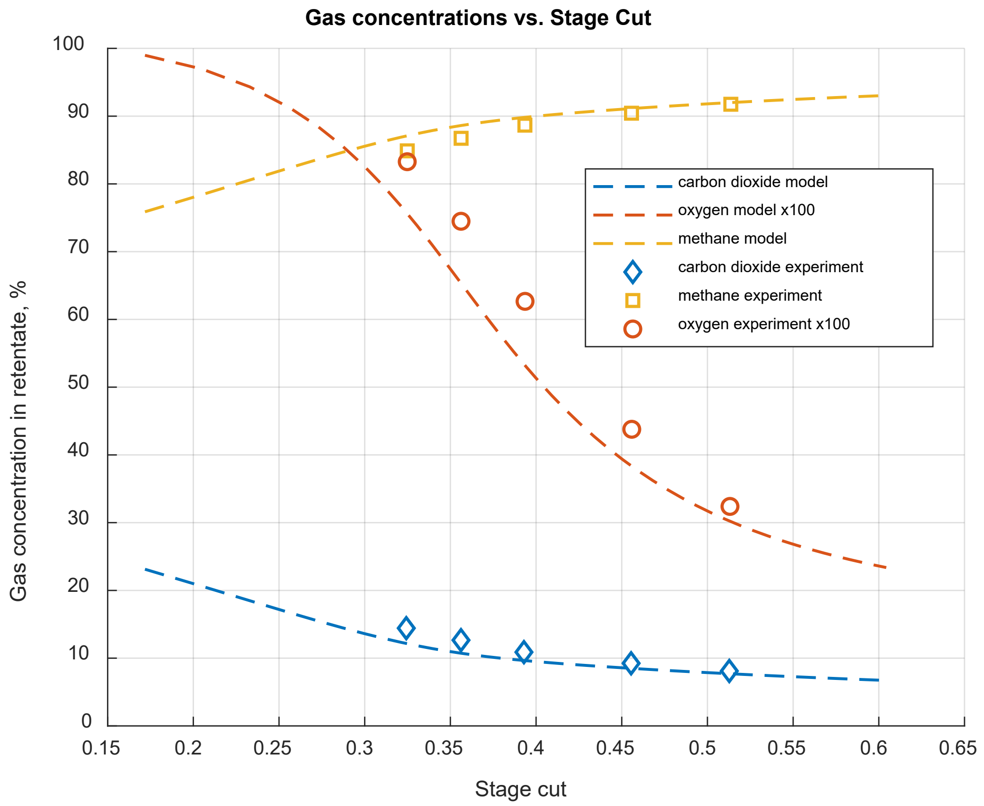


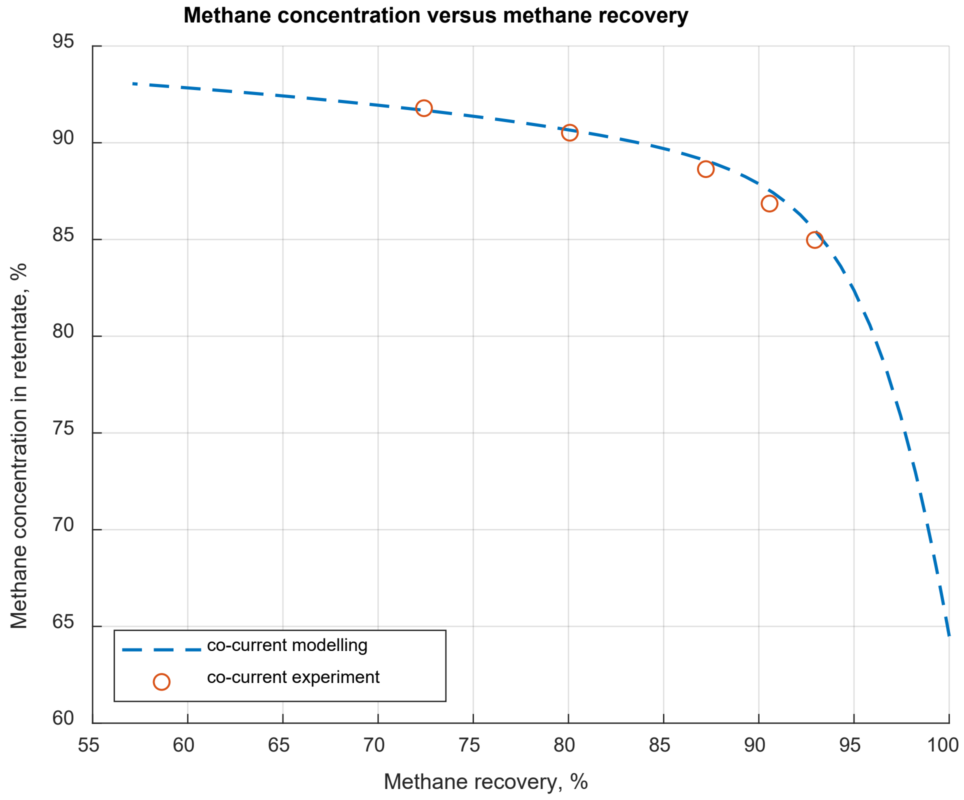
Partial Pressure and Retentate/Permeate Flux (CH_4)





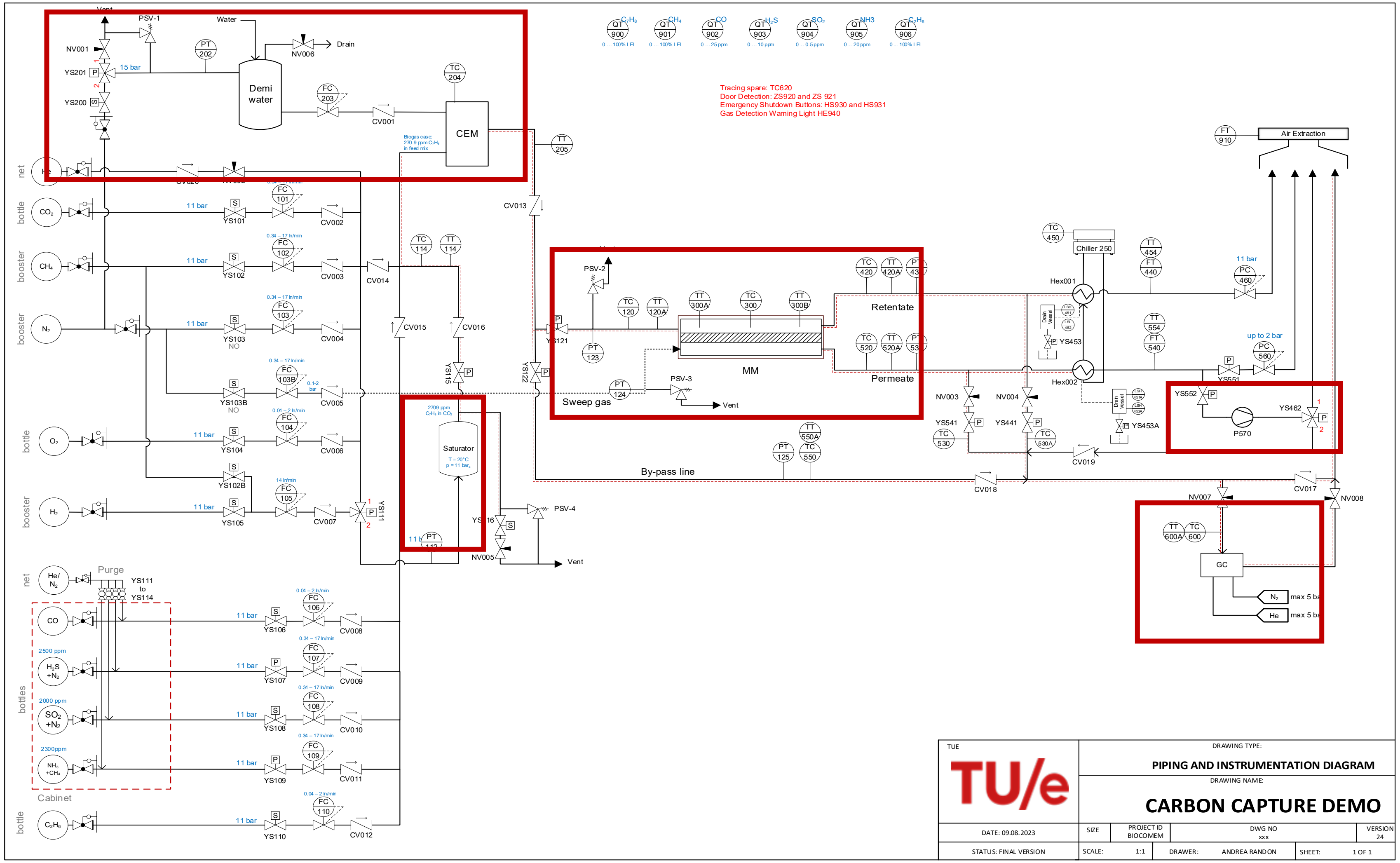
Model Validation





Makaruk et al., Numerical algorithm for modelling multicomponent multipermeator systems, (2009)

TRL4 Lab scale Setup



Subsystems

1. Feed system
2. Water Vapor Saturation (CEM)
3. Membrane separator
4. GC sampling
5. Vacuum
6. Thermosaturator (C_7H_8 feeding)

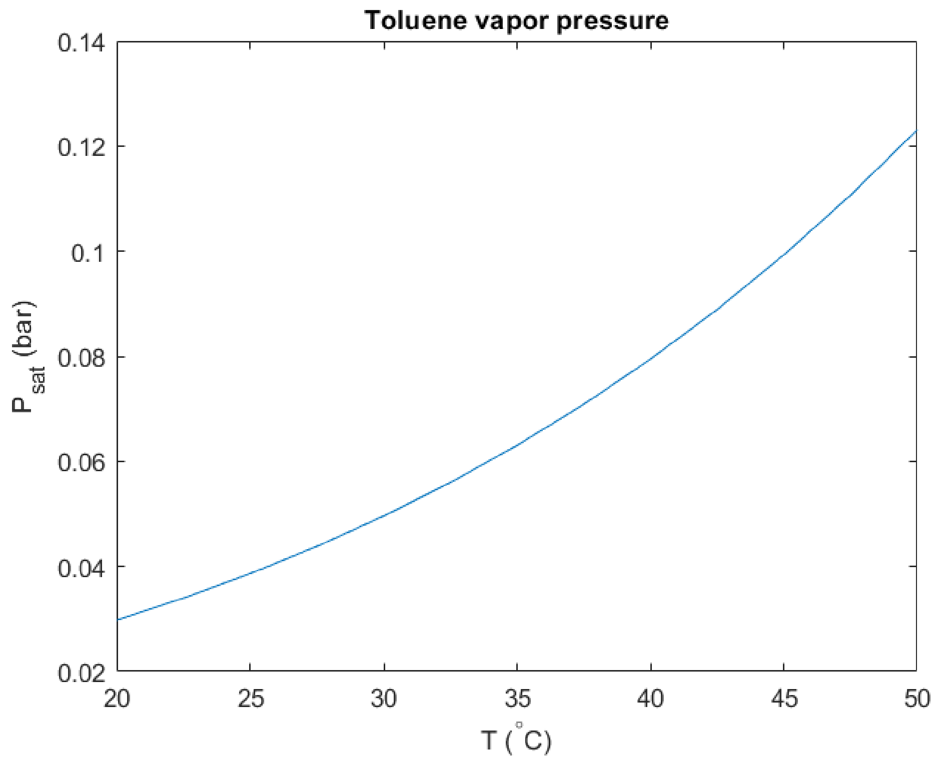
Feeding toluene

- Toluene will be fed by means of a thermal saturator. Inside the thermal saturator there will be liquid toluene in equilibrium with its vapor at ambient temperature.

T (°C)	$P_{sat}(T)$	$x_{tol} = P_{sat}/P$	%mol	ppm
20	0.0298	0.0027091	0.27091	2709.091

- The vapor pressure in function of the temperature of toluene has been calculated making use of the Antoine Law as it is shown on the right picture.

- Thus, a flow rate of CH_4 will be fed through it, taking away the amount of vapors needed to achieve a composition suitable for accelerated aging tests



Aging Tests

In the framework of the BIOCOMEM project three different applications are simulated.

1. Natural Gas Sweetening
2. Post-Combustion Capture
3. Biogas Upgrading

Natural Gas Sweetening

Component	%mol	ppm
CH_4	83,64	835400
CO_2	1,68	16800
N_2	10,21	102100
C_2H_6	4,47	44700

Post Combustion CO_2 capture

Component	%mol	ppm
N_2	56,5	565000
CO_2	17,8	178000
O_2	7,5	75000
$H_2O_{(v)}$	Satur.	Satur.
CO	1470 mg/Nm^3	1176,31
SO_2	1000 mg/Nm^3	349,84

Biogas Upgrading

Component	%mol	ppm
CH_4	57,89	578900
CO_2	37,89	378900
$H_2O_{(v)}$	Satur.	Satur.
H_2S	100 mg/Nm^3	65,79
NH_3		287
N_2	3,15	31500
O_2	1,05	10500
C_7H_8	1000 mg/Nm^3	243,63

Procedure for the membrane degradation assessment

i. Check the membrane performance with the synthetic clean gas to measure the initial membrane performance.

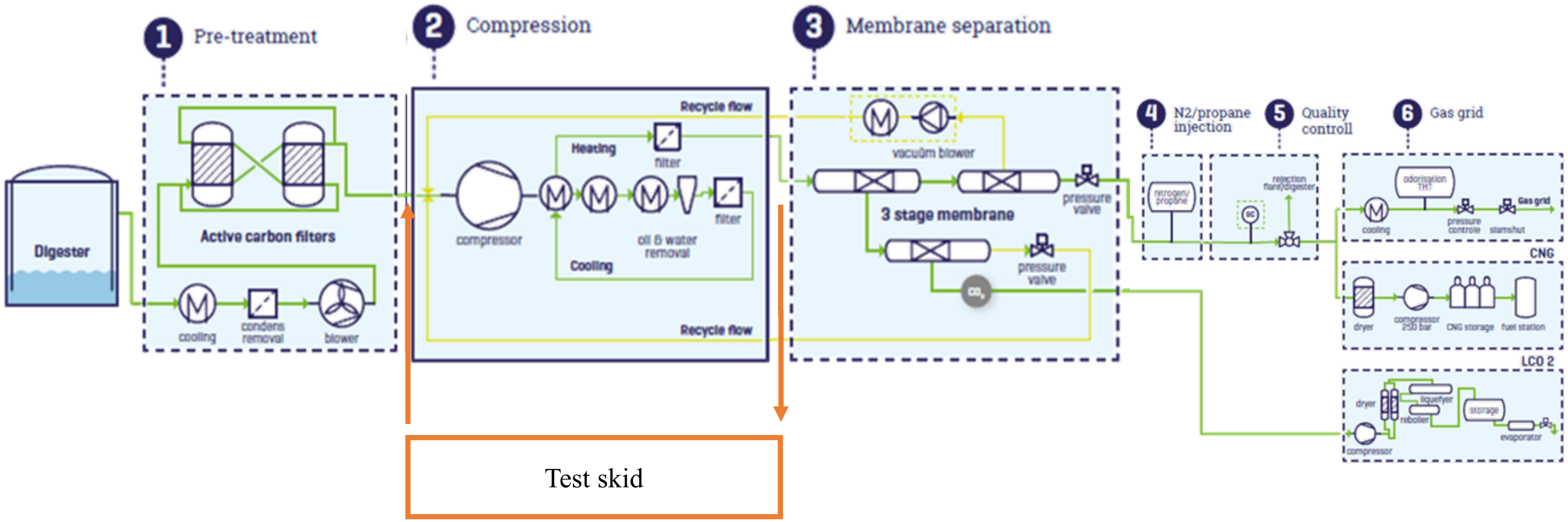
ii. Run the aging tests with the real gas composition and the pollutants at a concentration defined below. The cycle will be operated until the loss of performances of the membrane.

iii. A synthetic clean gas cycle to assess the possibility to clean the membrane and recover the initial properties.

A representative test condition from the permeation tests is chosen for each application, and it is used as performance reference to assess the degradation/stability of the membrane in time.

Prototype demonstration at TRL 5

Testing facility in full-scale biogas upgrading unit located in NL



- Pretreated real gas (~ 55% CH_4, 45% CO_2, O_2, N_2)
- Flow 2 - 5 Nm^3/h, pressure 1 - 14 bar
- Controlling and/or measuring inlet and outlet flow, composition, pressure and temperatures
- Performance (permeance, selectivity) and aging test

Test Skid Setup

BioCoMem

Performance test

Performance close to the simulations. Deviations due to inlet conditions and real gas effects

Table 1. Membrane performance in the field and in the simulations

Performance		Field			Simulation		
Stream		Feed	Retentate	Permeate	Feed	Retentate	Permeate
Flow	*Nm³/h (wet)*	3,00	0,69	2,31	3,00	1,05	1,95
P	*bar (a)*	6,01	6,00	2,20	6,00	5,99	2,20
T	*°C*	22,7	22,7		25	25	
CH_4	*vol %*	56,20%	80,60%	44,70%	56,20%	82,43%	42,11%
CO_2	*vol %*	43,70%	19,20%	55,21%	43,70%	15,93%	58,61%
N_2 [vol%]	*vol %*	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%
O_2 [vol%]	*vol %*	0,10%	0,20%	0,09%	1,00%	1,64%	0,66%

Estimated performances	Sep. capacity *GPU.m²*	Permeance *GPU*	Selectivity -	Sep. capacity *GPU.m²*	Permeance *GPU*	Selectivity -
CH_4	123	**279**	1,0	94	**214**	1,0
CO_2	701	**1593**	**5,7**	849	**1929**	**9,0**
N_2	790	1794	6,4	27	62	0,3
O_2	110	249	0,9	73	167	0,8

- $$SC_i = \frac{F_p y_{p,i}}{N_m \cdot \left(\frac{P_f y_{f,i} + P_r y_{r,i}}{2} - P_p y_{p,i}\right)}$$
- $$\alpha_{i/j} = \frac{SC_i}{SC_j}$$
- $$P_i = \frac{SC_i}{A_m}$$

dmt Environmental Technology

Degradation test prototype A

The degradation test for a total of > 240 h per membrane.
- Flow: 5 Nm^3/h @6 bara.

Table 1. Average performance data before and after 240h exposure test

Time	Feed flow	Retentate P	Retentate CO_2	Permeate CH_4	Retentate Split	Permeate CH_4	Permeate CO_2	Selectivity (CO_2/CH_4)
	Nm^3/h	*bara*	*vol%*	*vol%*	*%*	*GPU*	*GPU*	-
Before exposure	5	6	28%	37%	48%	272	1768	6,50
After 240h exposure			30%	36%	55%	237	1310	5,55
		Deviations (Relative):	**6%**	**-2%**	**15%**	**-13%**	**-26%**	**-15%**

The results at the beginning and at the end of the demonstration have deviations concerning the flow split between permeate and retentate, the performance of CH_4 and CO_2 and consequently the selectivity.

Thank you

Demonstration of Biocomem membranes at TRL 4 and TRL 5

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This project has received funding from the European Union's Horizon 2020 Research and Innovation Program under grant agreement No 887075 (BIOCOMEM).

From polymer to membrane: development of thin-film composite membranes

BioCoMem

Angeles Ramirez-Kantun, M.Sc.
Dr. Sergey Shishatskiy

26.06.2023

Institute of Membrane Research

Helmholtz-Zentrum hereon

1

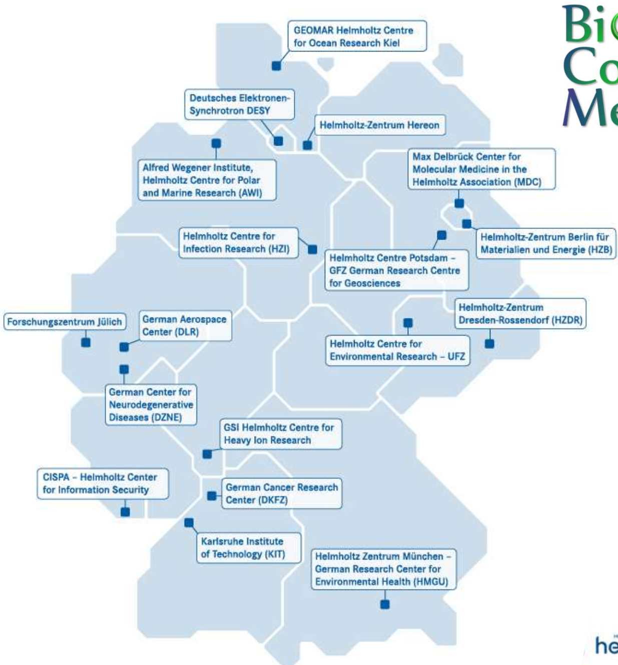
Helmholtz Association
18 Centers and their Funding

HELMHOLTZ
SPITZENFORSCHUNG FÜR GROSSE HERAUSFORDERUNGEN

Total Budget 4.8B €

70% Federal/State | 30% Third Party

90% Federal | 10% State



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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

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3

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

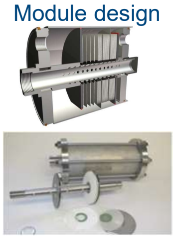
Lab. scale investigations

- Polymer synthesis
- Polymer modification
- Permeation behaviour

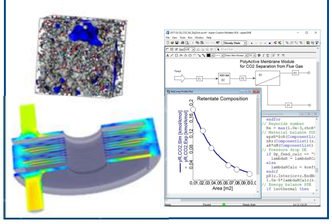
Pilot scale membrane production

Pilot plants

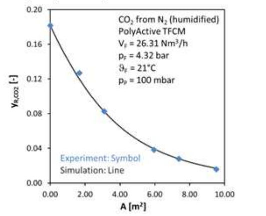
Module design



Modelling and simulation



Comp. pilot plant/simulation



BioCoMem

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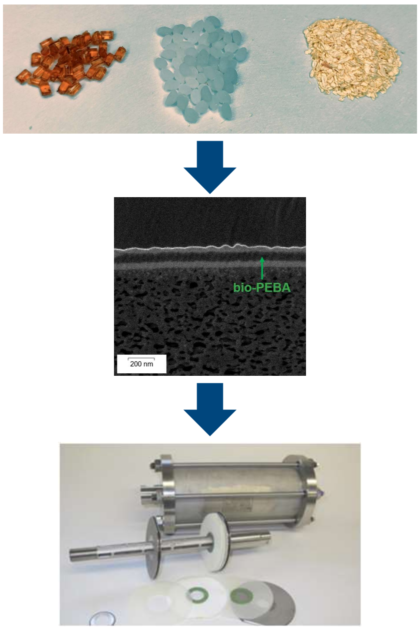
4

Hereon's role within BioCoMem project

- **Objectives**:
  - ✓ Development of thin-film composite membranes (**TFCMs**) with **bio-based polyether-block-amide (PEBA) copolymers** as **selective layer** materials
  - ✓ Manufacture of **membrane modules**
  - ✓ Intended application → **CO_2 separations**:
    - Post-combustion flue gas treatment
    - Natural gas upgrading
    - Biogas upgrading



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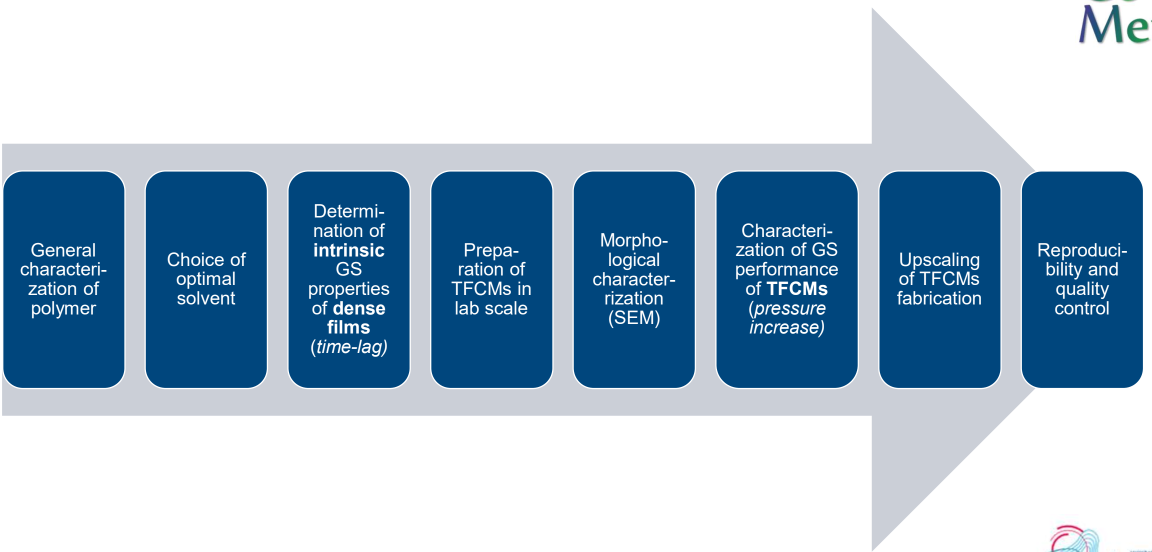
Methodology for the development of a TFCM



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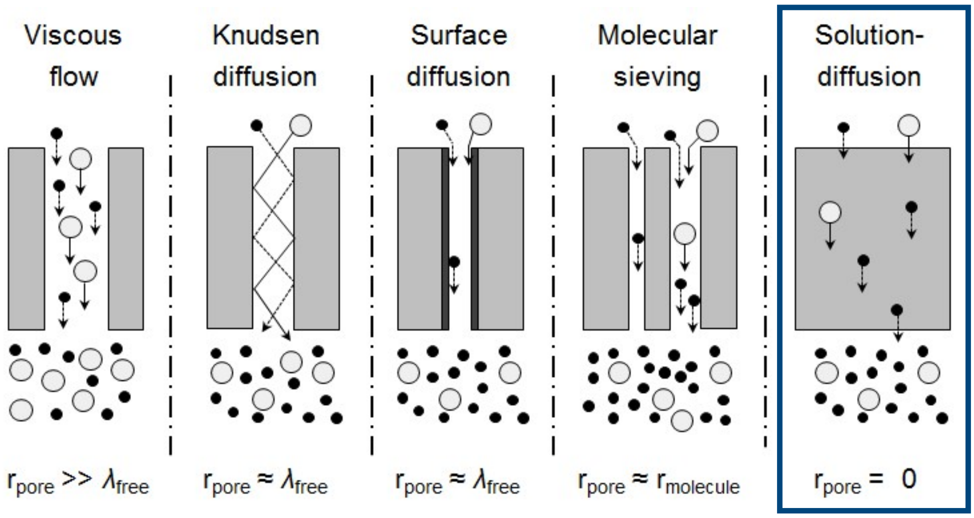
Gas separation membranes: transport mechanisms



λ_{free}: mean free path of molecule

Solution-diffusion mechanism of transport in polymers

Gas permeation through a nonporous polymer membrane is usually described using a solution–diffusion model

$P_i = D_i S_i$ Equation postulated by Graham (1866) $1\ Barrer = 1 \cdot 10^{-10} \frac{cm^3(STP) \cdot cm}{cm^2 \cdot s \cdot cmHg}$

$$P_i = P_{i0} e^{-E_{P_i}/(RT)} \quad [cm^3(STP) cm\ cm^{-2}\ s^{-1} cmHg^{-1}]$$

$$D_i = D_{i0} e^{-E_{D_i}/(RT)} \quad [cm^2\ s^{-1}]$$

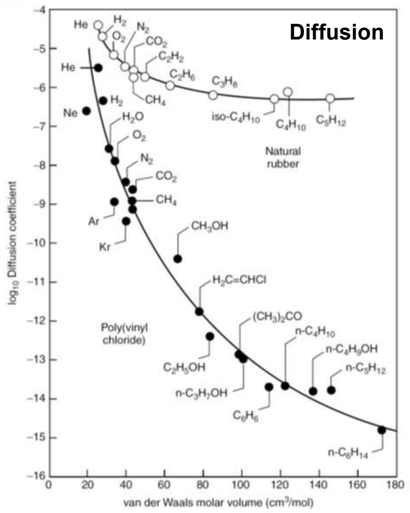
$$S_i = S_{i0} e^{-\Delta H_{S_i}/(RT)} \quad [cm^3(STP)\ cm^{-3}\ cmHg^{-1}]$$

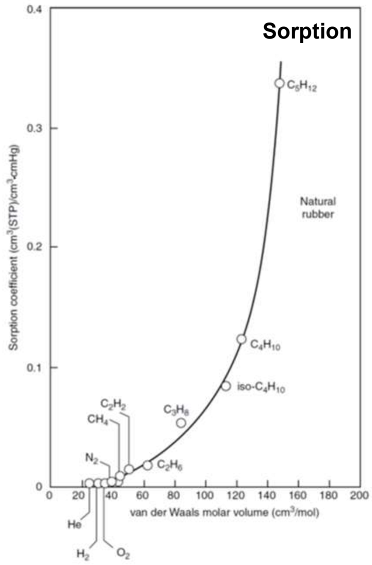
P_{i0}, D_{i0}, S_{i0} → Pre-exponential factors
E_{Pi}, E_{Di} → Activation energies
ΔH_{Si} → Enthalpy of solution of the penetrant *i*

Ideal Selectivity: $\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i}{D_j} \cdot \frac{S_i}{S_j}$

Example:
Permeability coefficient for polymer P_{gasX} = 100 Barrer and **selective layer thickness** = 100 nm
→ membrane **Permeance** L_{gasX} = 2.736 m^3(STP) m^{-2} h^{-1} bar^{-1} = 1000 GPU

Gas diffusion and sorption in polymers depend on penetrating molecule nature and size





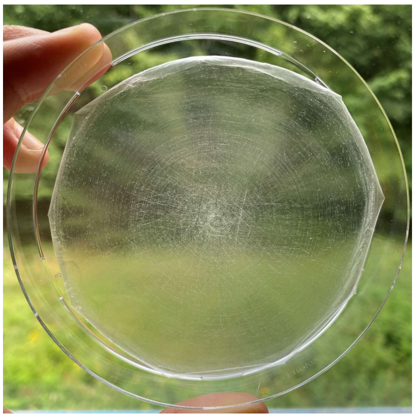
F. Gruen, *Experimenta* **3**, 490 (1947)
G.J. van Amerongen, *J. Appl. Phys.* **17**, 972 (1946)

9

9

Preparation of polymer dense films via solution casting

- Preparation of polymer solution in chosen solvent
- Filtering of homogeneous solutions
- Pouring of solutions in leveled Teflon® molds
- Drying solvent out under slow N_2 flow
- Drying film under vacuum
- Weight, density, thickness determination

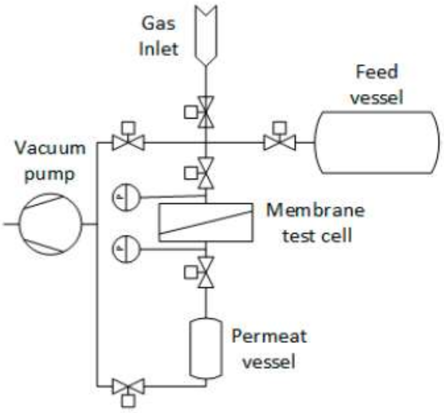


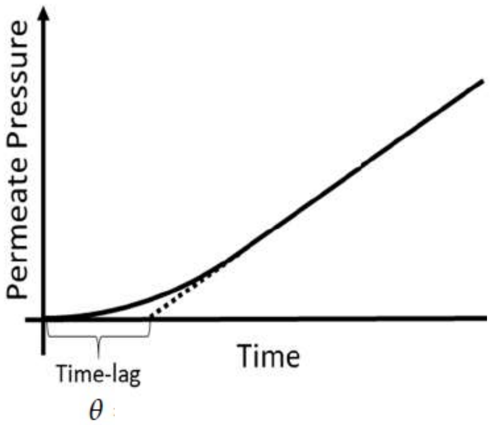
10 From polymer to membrane: development of thin-film composite membranes

10

Determination of intrinsic gas transport parameters: the „time-lag“ method

- Constant volume, variable pressure measurement principle
- Feed/permeate pressure ratio >100 ensures correct diffusion coefficient determination (±3%)
- Permeate volume calibration accuracy of ±0.5% for permeability and solubility determination with accuracy of at least ±3%





$$\theta = \frac{l^2}{6D_{eff,i}}$$

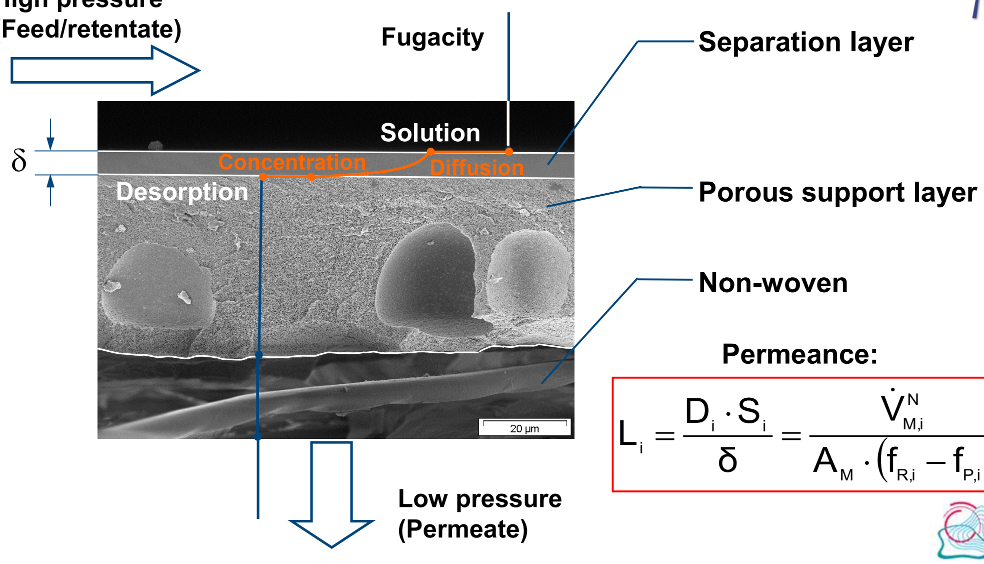
$$P_{eff,i} = \frac{N_i l}{A_m \Delta p_i}$$

$$P_{eff,i} = D_{eff,i} S_{eff,i}$$

* Weigelt et al. (2018).

11 From polymer to membrane: development of thin-film composite membranes

Solution-diffusion mechanism and practical membranes: battle against the selective layer thickness

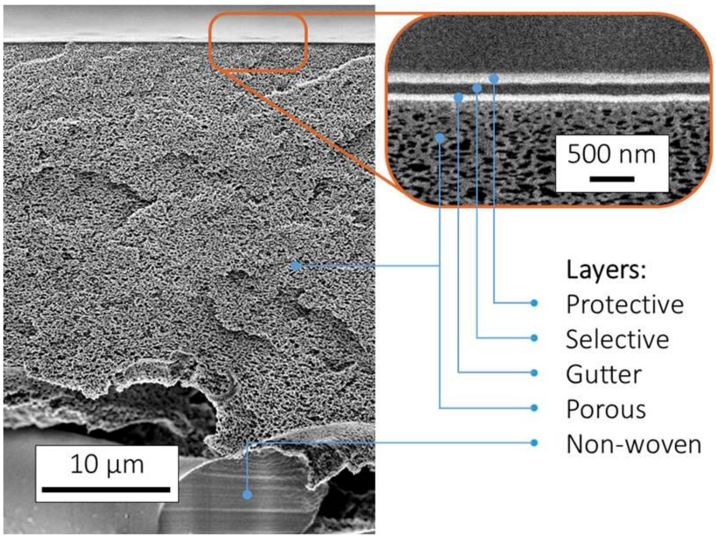


Permeance:

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

12

TFCM: main components



Layers:

Protective	δ < 100 nm
Selective	δ ≈ 50 – 200 nm
Gutter	δ ≈ 50 – 150 nm
Porous	δ ≈ 30 – 100 µm
Non-woven	δ ≈ 100 µm

13 From polymer to membrane: development of thin-film composite membranes

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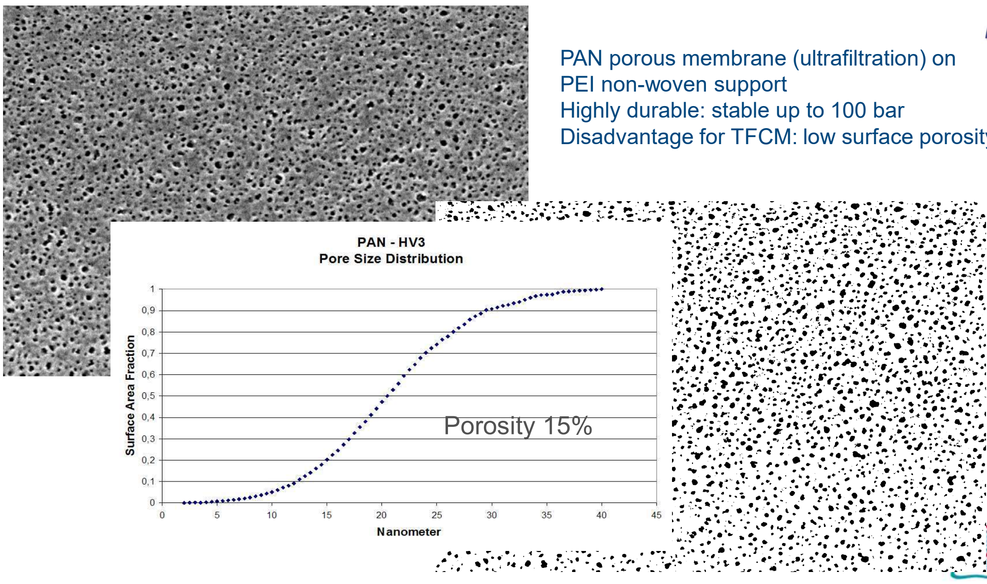
TFCM: surface of porous support

PAN porous membrane (ultrafiltration) on
PEI non-woven support
Highly durable: stable up to 100 bar
Disadvantage for TFCM: low surface porosity



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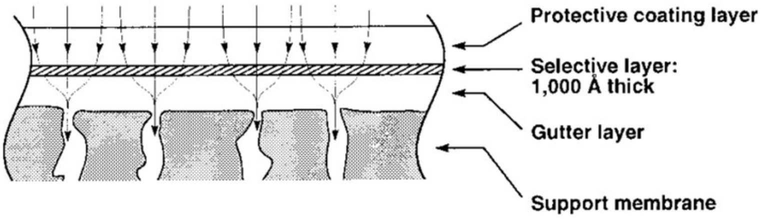
PDMS gutter layer membrane: basis of a good TFCM

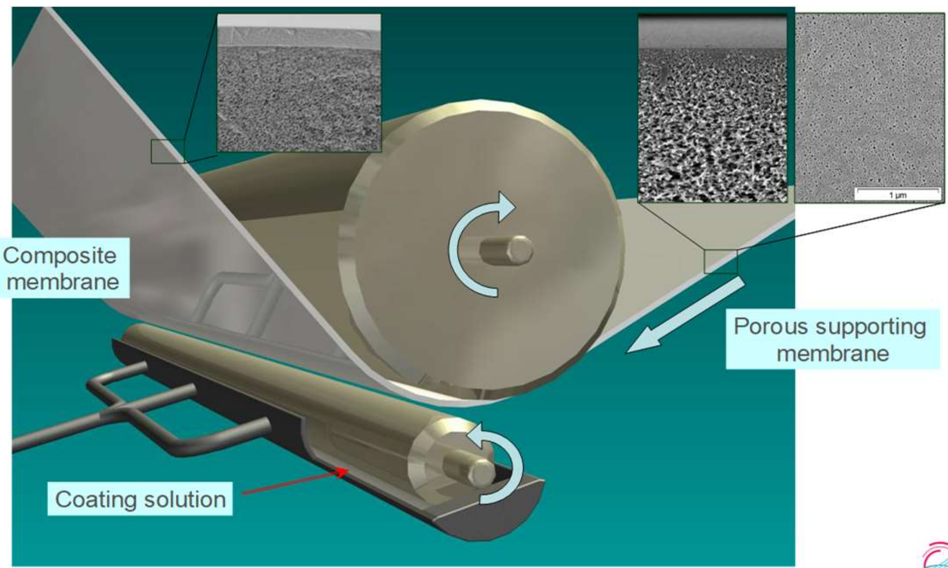
Properties:
- **< 150 nm thickness**
- **N_2 - permeance 2.5 $Nm^3m^{-2}h^{-1}bar^{-1}$**
- **highly cross-linked**
- **solvent resistant**
- **good adhesion due to additives**



I. Cabasso, K.A. Lundy, 1986
R.W. Baker, Ind. Eng. Chem. Res. 41 (2002) 1393–1411.

16

TFCM production: deposition of selective layer



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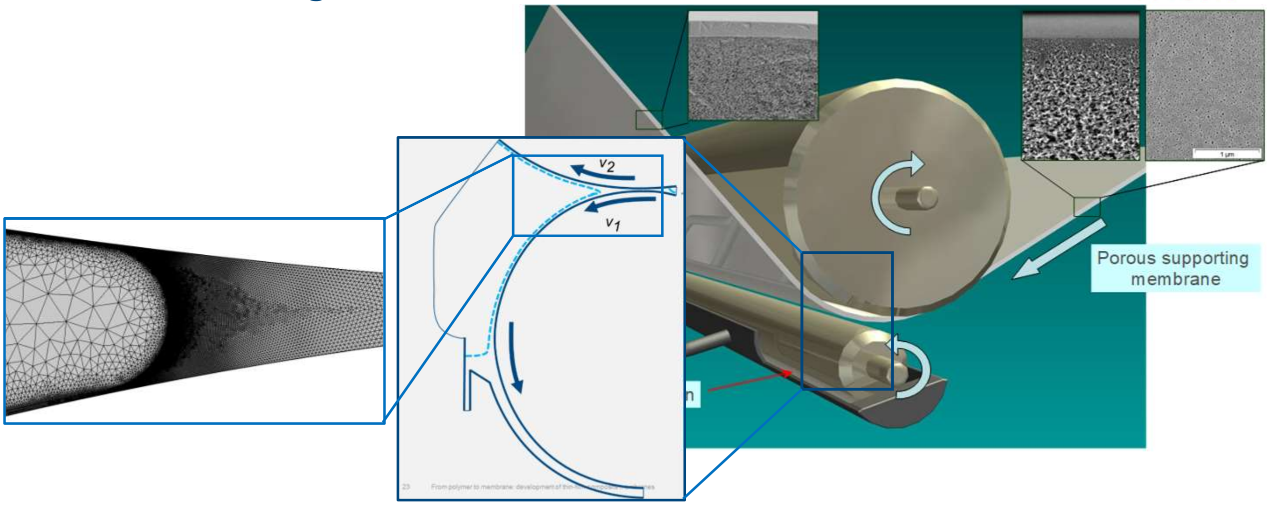
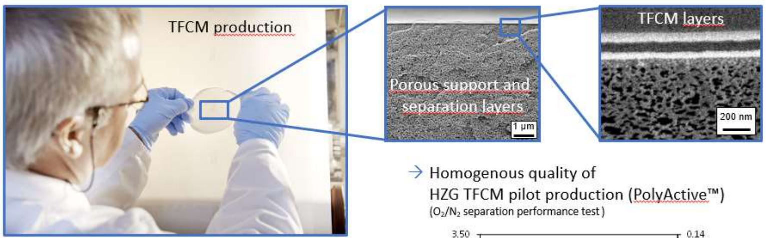
Mathematical modelling of processes occurring in meniscus during TFCM formation



F. Brennecke *et al.*, JMS, 2022

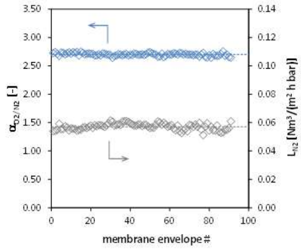
Asymetric membrane preparation methods

Pilot scale membrane coating facility for thin-film composite membranes (TFCM)



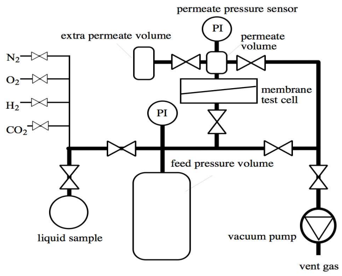
→ Superior properties can be transferred to 100 m² scale

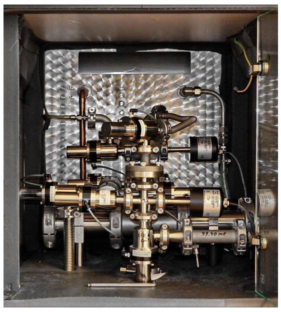
→ Homogenous quality of HZG TFCM pilot production (PolyActive™)
(O_2/N_2 separation performance test)

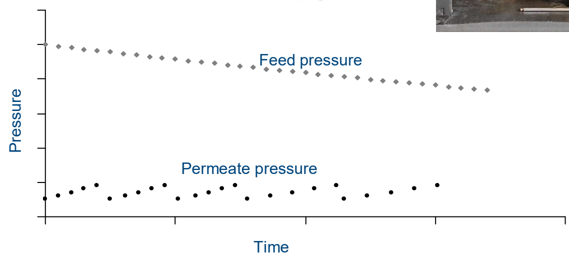


Pressure increase method for determining permeances

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







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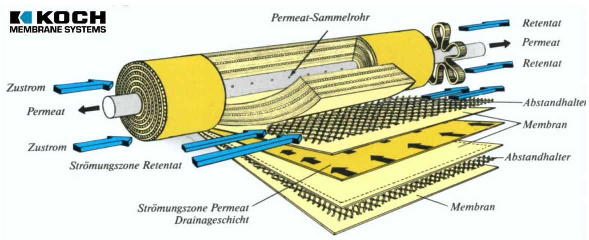
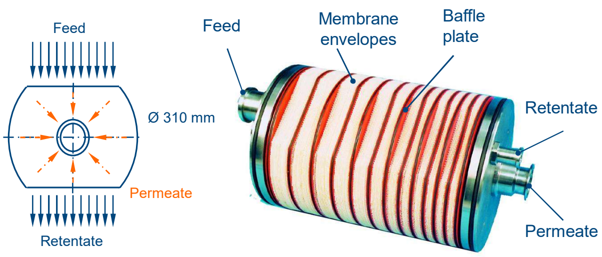
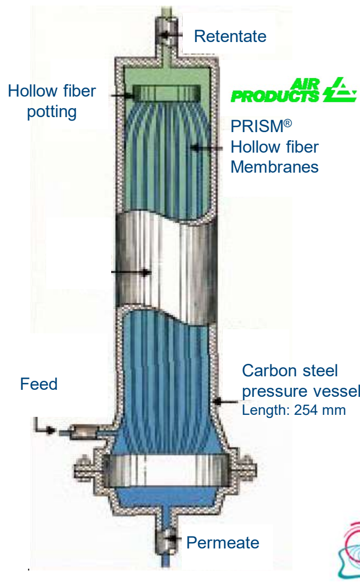
Membrane module design





Hereon's Envelope Type Module



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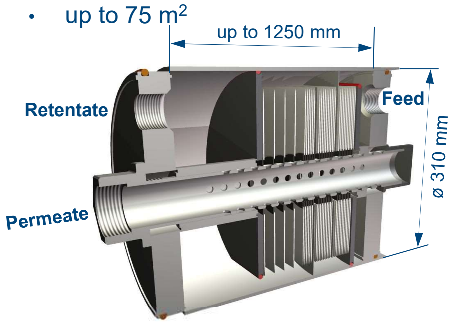
Envelope type membrane modules

Bio Co Mem

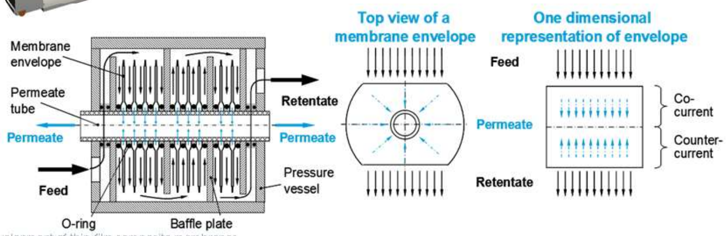
Standard module

- up to 75 m^2



Pilot Standard High pressure

Model



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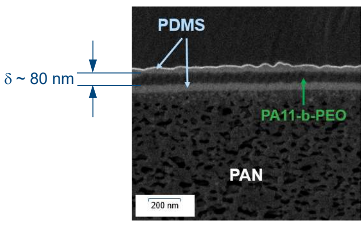
PA11-*b*-PEO TFCM

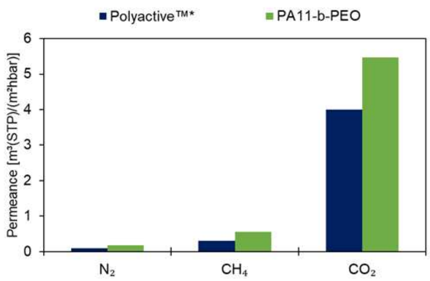
Bio Co Mem

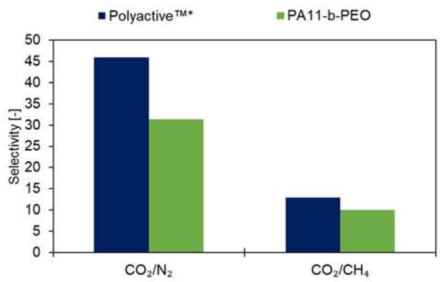
Membrane cross-section



Membrane envelopes

Membrane module





CO_2 transport in bio-PEBA at 30°C	
P [Barrer]	165
L [GPU]	2000

[*] Brinkmann et al., Engineering, Vol. 3, Issue 4, Pages 485-493 **(2017)**

hereon

Summary

→ TFCMs can be produced from both glassy and rubbery polymers, offering the possibility to use the same supports for various selective layers and thus utilize previously developed technological solutions of membrane packing into the membrane module

→ Multilayer membrane design gives developer flexibility in a material choice. Each layer is serving a specific task: mechanical stability, permeate drainage, smooth support, selectivity, protection

→ TFCMs require extremely small amount of selective material per m^2 of membrane opening the way for experimental polymers and other materials into the practical applications

→ The Institute of Membrane Research of Helmholtz-Zentrum Hereon has extensive experience in membrane technology from selective polymer synthesis to pilot scale separation process design

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Thank you for your attention!

In case of questions please contact us:
Angeles.Ramirez@hereon.de
Sergey.Shishatskiy@hereon.de

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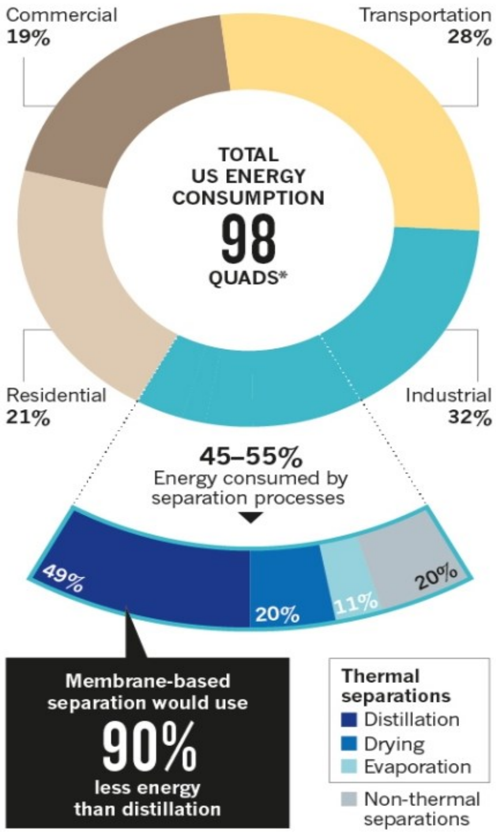
Hollow fiber polymeric membrane: preparation and scaleup.

Dr. Miren Etxeberria Benavides and Dr. Oana David

Membrane Technology and Process Intensification

MEMBRANE TECHNOLOGY



MEMBRANE SEPARATION

- No require a gas-liquid phase change
- Smaller separation units → small footprint
- Lack of mechanical complexity
- Operate under continuous, steady-state conditions

MEMBRANE TECHNOLOGY

APPLICATIONS

- CO_2 capture
- CH_4 purification
- H_2 purification
- Olefin / paraffin separation
- Water separation

MEMBRANE CLASSIFICATION

MATERIAL

- Inorganic
  - Metallic
  - Ceramic
  - Carbon
  - Zeolite
- Organic
  - Polymeric

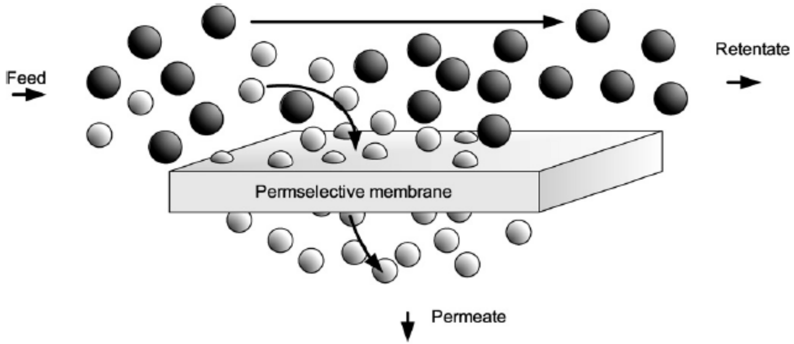
STRUCTURE

- Symmetric
- Asymmetric
  - Integral asymmetric
  - Composite

GEOMETRY

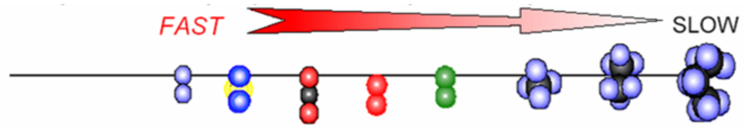
- Flat sheet
- Tubular
- Hollow fiber

POLYMERIC MEMBRANES: SOLUTION-DIFFUSION MODEL



$$P_i = S_i \cdot D_i$$

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \cdot \frac{D_i}{D_j}$$



	H_2	H_2S	CO_2	O_2	N_2	CH_4	C_2H_6	C_3H_8
Solubility- Tc (°K)	33	373	304	155	126	191	307	370
D-diameter (A)	2.9	3.7	3.3	3.4	3.6	3.8	3.8	4.2

Permeability (intrinsic property)

$$P_i = \frac{F_i \cdot l}{\Delta p_i \cdot A}$$

$$Barrer = 10^{-10} \frac{cm^3 STP\ cm}{s \cdot cm^2 \cdot cmHg}$$

Permeance (membrane property)

$$\frac{P_i}{l} = \frac{F_i}{\Delta p_i \cdot A}$$

$$GPU = 10^{-6} \frac{cm^3 STP}{s \cdot cm^2 \cdot cmHg}$$

COMMERCIAL POLYMERIC MEMBRANES

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Table 1. Current Big Four Commercial Gas Separation Membrane Applications

application	separation performed	selective layer polymer	approximate market size
hydrogen recovery	H_2/N_2, H_2/CH_4, H_2/CO	polysulfone, polyimides	$200 million/year
N_2 production	O_2/N_2	polyimides, polysulfone, polyphenylene oxide, substituted polycarbonates	$800 million/year
natural gas treatment	CO_2/CH_4, H_2S/CH_4, He/CH_4	cellulose acetates, polyimides	$300 million/year
vapor recovery	C_3H_6/N_2, C_2H_4/N_2, C_2H_4/Ar, C_{3+}/CH_4, CH_4/N_2, gasoline/air	silicone rubber	$100 million/year

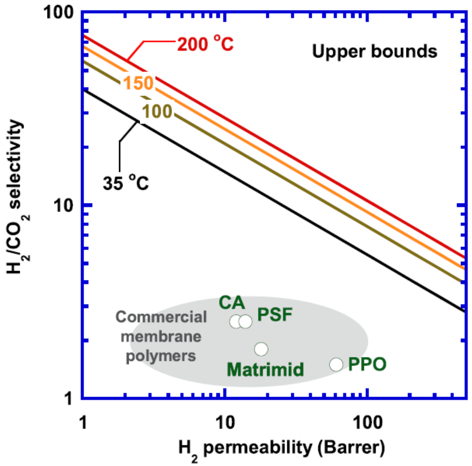
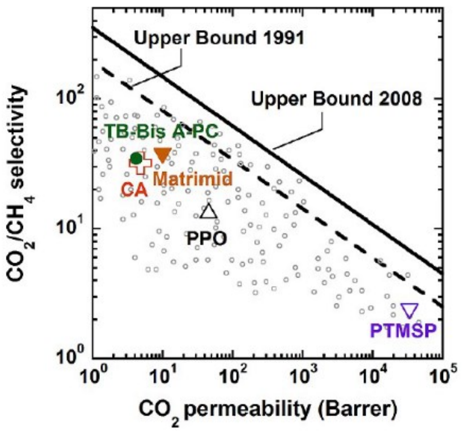
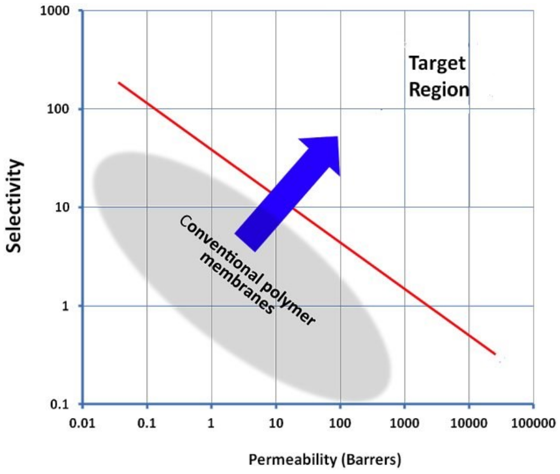


FIGURE 1 Upper bounds of H_2/CO_2 separation at 35, 100, 150, and 200 °C calculated using the parameters shown in Table 1.[11–13] The separation properties of commercial membrane polymers were determined at 35 °C. 1 Barrer = 10^{-10} cm^3 (STP) $cm/(cm^2\ s\ cmHg)$



CO_2/CH_4 Robeson diagram for conventional glassy polymers.

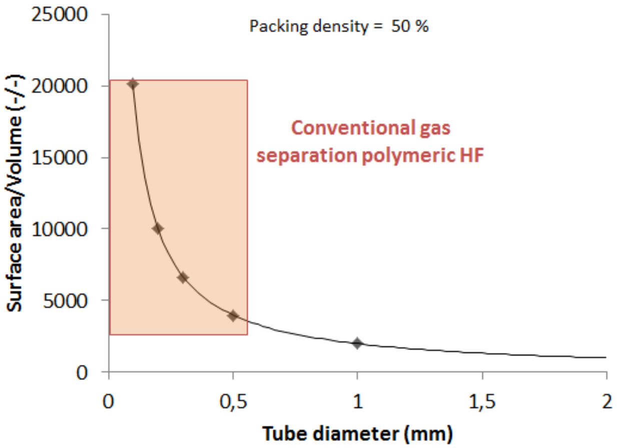


L. Hu, S. Pal, H. Nguyen, V. Bui, H. Lin, *J. Polym. Sci.* **2020**, *58*, 2467
M. Galizia, W. S. Chi, Z. P. Smith, T. C. Merkel, R. W. Baker, B. D. Freeman, *Macromolecules* **2017**, *50*, 7809

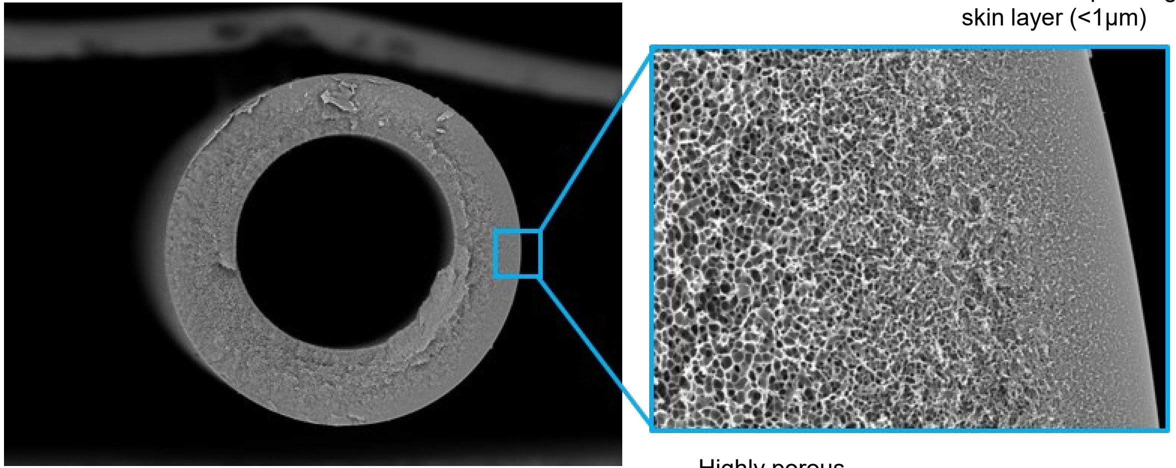
HOLLOW FIBER MEMBRANES

Advantages of HF

- High packing density (over 10000 m^2/m^3), 10 times higher than plate and frame modules
- Can handle very high transmembrane pressure differences (up to 70 bar)
- 5 to 20 times lower fabrication costs



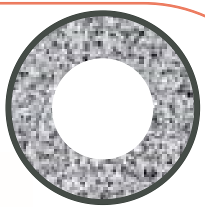
Asymmetric hollow fiber

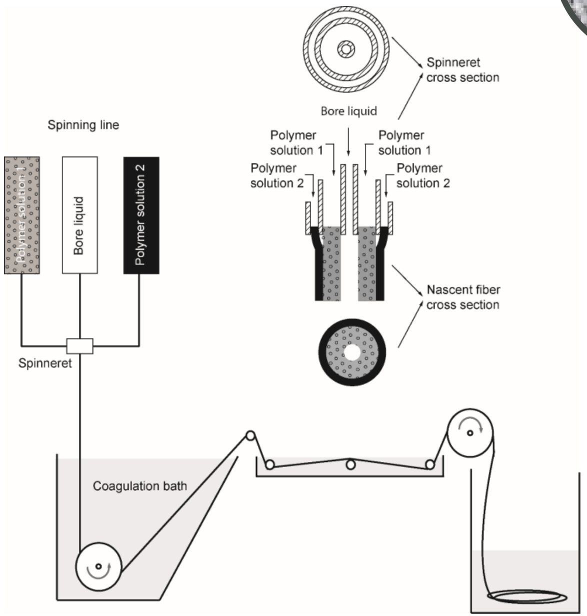


HOLLOW FIBER PREPARATION METHODS

SPINNING

Monolithic hollow fiber

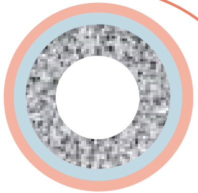


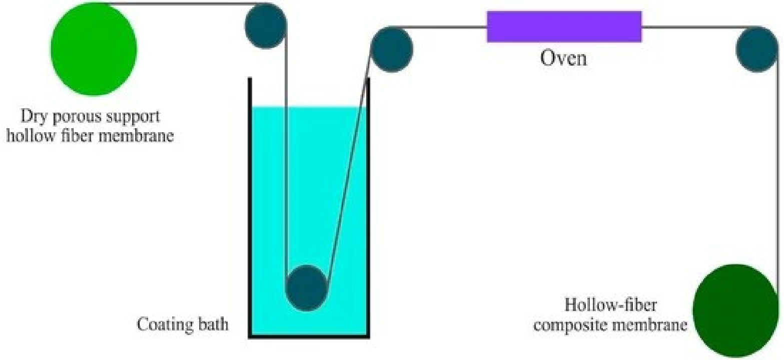


Single step process: simultaneous formation of the porous support + dense selective layer

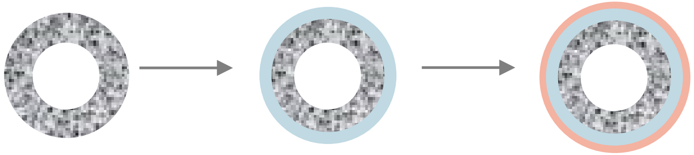
DIP COATING

Composite hollow fiber





Multiple step process



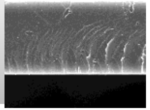
Membranes 2021, 11(8), 557; https://doi.org/10.3390/membranes11080557

MEMBRANE DEVELOPMENT STRATEGY

Defining target performance

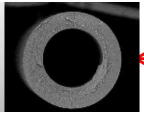
Material development and/or selection

Dense film preparation and characterization



Intrinsic separation properties
Permeability and selectivity

Hollow fiber preparation and characterization



Separation properties
Permeance and selectivity

Possible to Scale-up, Prototype??

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Example 1: “zero defects”

"zero defects"

P84 polyimide

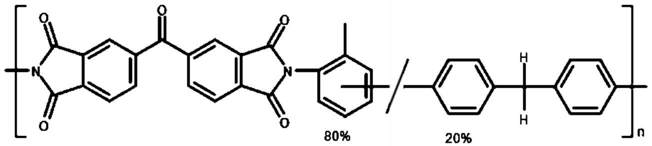


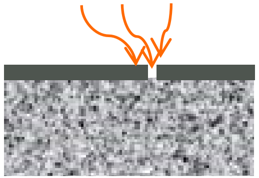
Table 2
Permeability and selectivity for P84 and Matrimid 5218 (25 °C)

	P_{He} (barrer)	P_{He}/P_{N_2}	P_{CO_2} (barrer)	P_{CO_2}/P_{N_2}	P_{O_2} (barrer)	P_{O_2}/P_{N_2}
P84	7.2	292	0.99	40.2	0.24	10.0
Matrimid 5218	22.5	122	8.7	37.8	1.32	7.2

J. N. Barsema, G. C. Kapantaidakis, N. F. A. van der Vegt, G. H. Koops, M. Wessling, *J. Memb. Sci.* **2003**, *216*, 195.

Selective layer (defective)

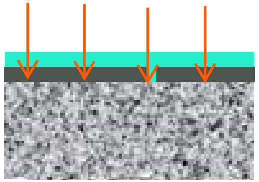
Porous support



Protective layer

Selective layer (defective)

Porous support



membranes

MDPI

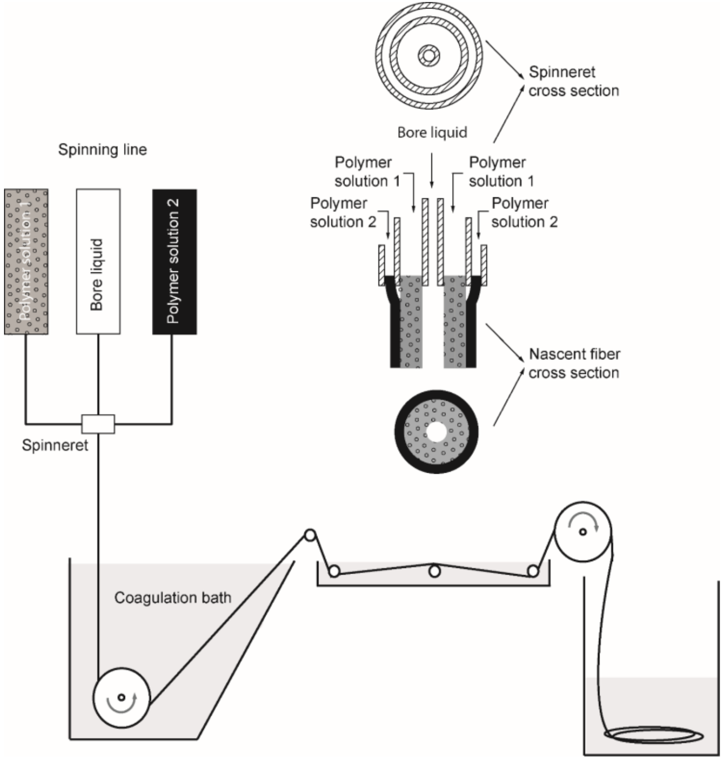
Article

Fabrication of Defect-Free P84® Polyimide Hollow Fiber for Gas Separation: Pathway to Formation of Optimized Structure

Miren Etxeberria-Benavides [1,2,*], Oguz Karvan [1,3], Freek Kapteijn [2], Jorge Gascon [2,4] and Oana David [1,*]

Development of **defect-free as-spun ultrathin** P84® asymmetric hollow fiber membranes that **do not require a silicone rubber coating post-treatment step**

“zero defects”



Process parameters

Dope Composition

Dope Flow rate

Bore Composition

Bore Flow Rate

Spinning Temp

Coagulation Bath Temp

Air Gap height

Take-up rate

Room T

Humidity

"zero defects"

Dope composition: key parameter

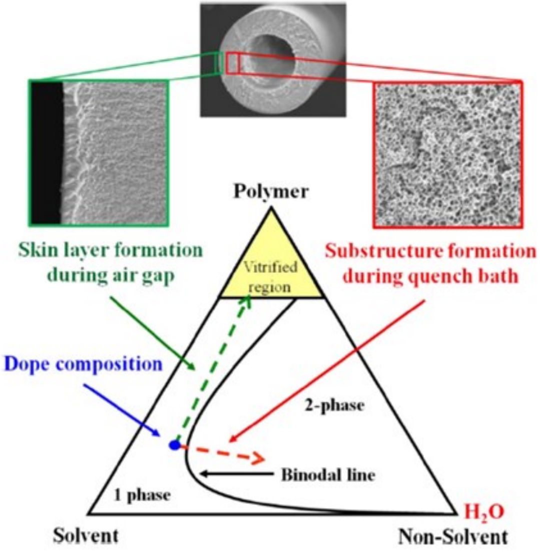


Figure. Gas separation asymmetric hollow fiber formation process represented in a ternary phase diagram

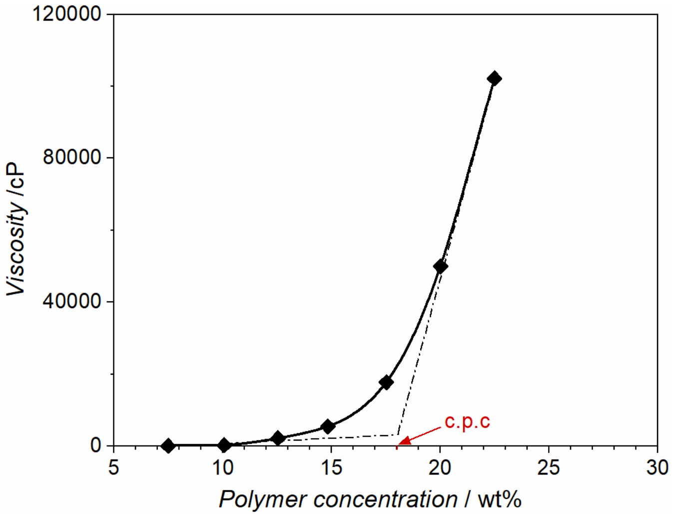


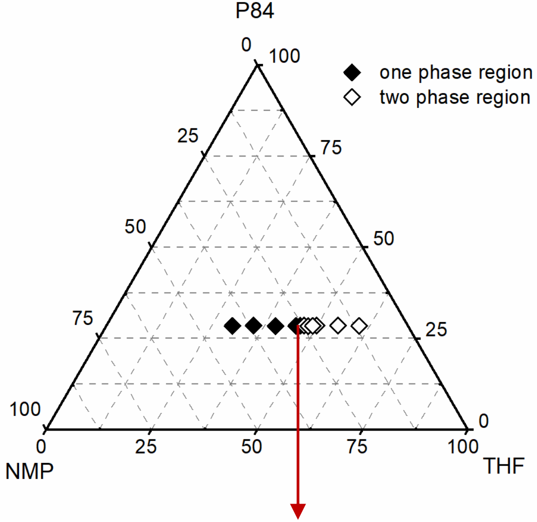
Figure 1.6. Typical viscosity versus polymer concentration curve and the determination of the critical polymer concentration, c.p.c.

L. Xu, C. Zhang, M. Rungta, W. Qiu, J. Liu, W. J. Koros, *J. Memb. Sci.* **2014**, *459*, 223.

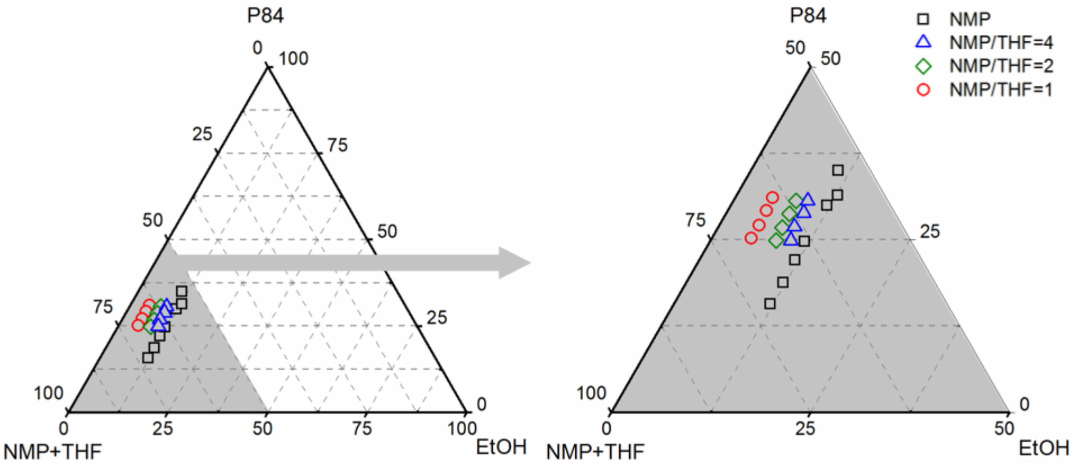
“zero defects”

Dope composition

- N-methyl-2-pyrrolidone (NMP) — Solvent
- Tetrahydrofuran (THF) — Solvent
- Ethanol (EtOH) — Non-solvent



NMP/THF ratio = 0.52



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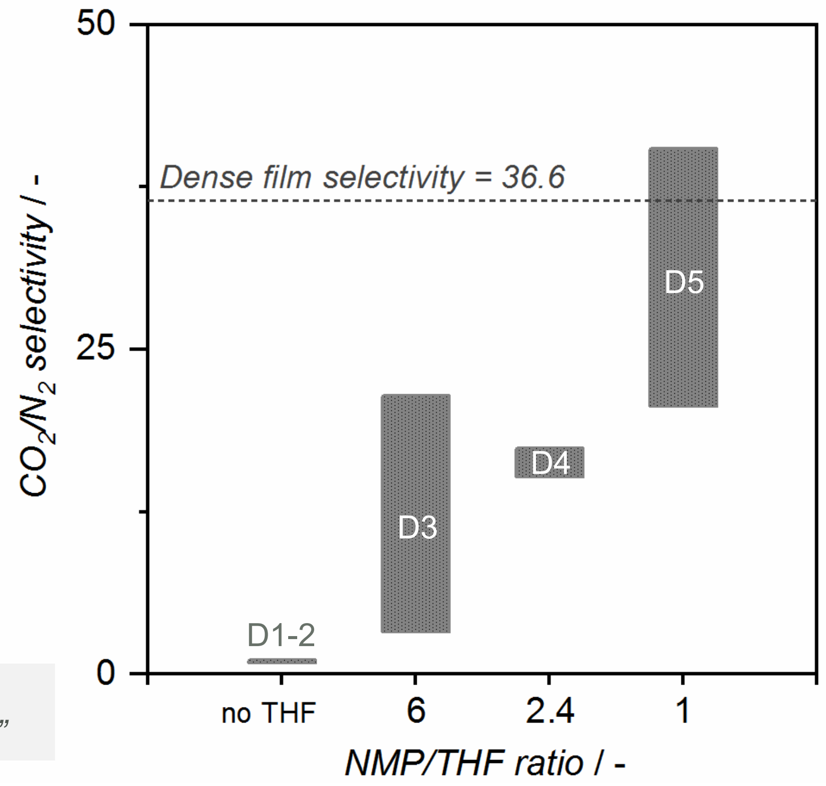
"zero defects"

Dope composition

Spinning session	D1	D2	D3	D4	D5
wt% P84®	28.5	28.5	28.5	28	28.5
wt% NMP	64.5	62.5	58.7	46.9	35.2
wt% THF	-	-	9.8	19.1	35.3
wt% EtOH	7	9	3	6	1*
NMP/THF ratio	**-**	**-**	**6**	**2.4**	**1**

"Asymmetric membranes are defined to be "defect-free" if the ideal selectivity is greater than 80% of the intrinsic selectivity of dense films"



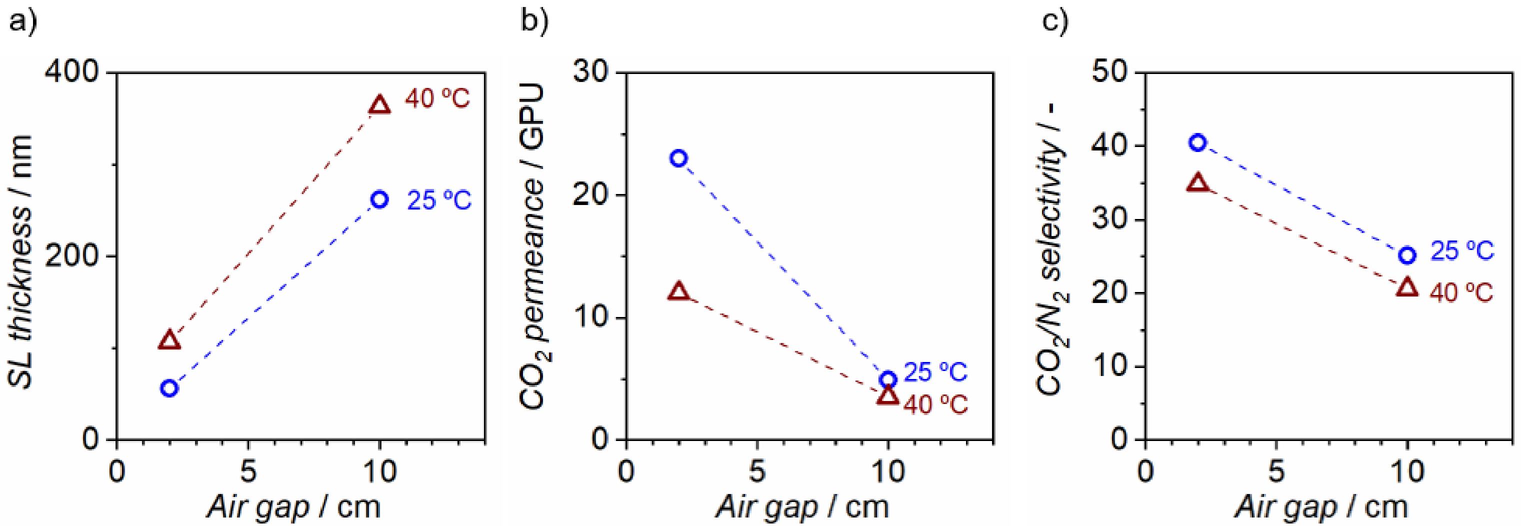
"zero defects"

Spinning sesión D05

Spinning parameters influence:

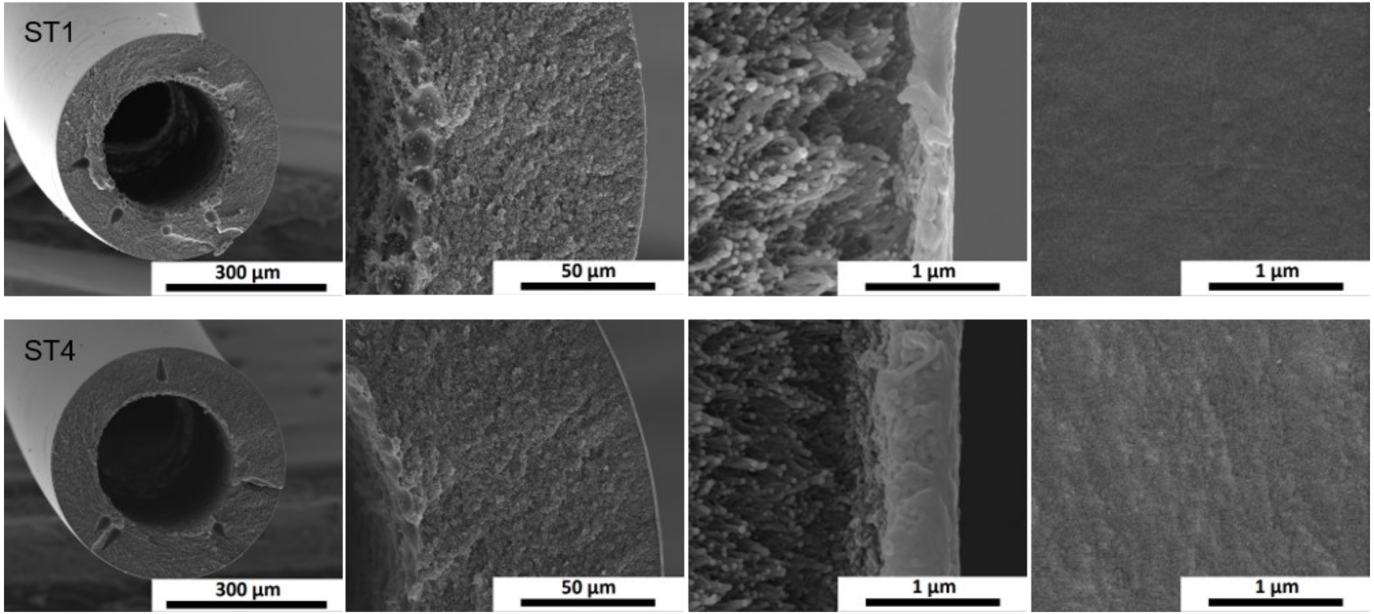
- Spinneret temperature (25-40ºC)
- Air gap height (2-10 cm)

Separation performace for single gas permeation at 35°C and 7 bar transmembrane pressure



“zero defects”

Cross section | Fiber wall | Selective layer | Outer surface



- Spinneret temperatura: 25ºC
- Air gap height: 2 cm

- Spinneret temperatura: 40ºC
- Air gap height: 10 cm

Barsema et al. (at 25ºC)

2.2 GPU CO_2

46.8 CO_2/N_2

500 nm (selective layer thickness)

PDMS coated

TECNALIA (at 35ºC)

23 GPU CO_2

40.4 CO_2/N_2

56 nm (selective layer thickness)

With out PDMS coating

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Example 2: “Bio-Based HF membranes”

RESEARCH LINES

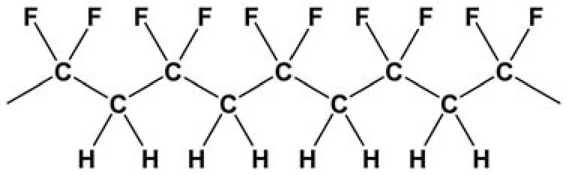
Co-polymer	Polyamide block	Polyether block	Main expected result
A **Reference bio-PEBAs**	Bio-based polyamide 11 derived from castor oil $(PA_{ref}{}^{bio})$	Fossil based polyether block $(PE_{ref}{}^{fossil})$	Composite HF Membrane
B **New bio-PEBAs Pathway 1** aromatic/cycloaliphatic polyamide-b-polyether	Bio-based polyamides derived from new building blocks $(PA_{new}{}^{bio})$	Fossil based polyether block $(PE_{ref}{}^{fossil})$	Better processability: (Monolithic HF membrane) *and* Higher gas separation performance
C **New bio-PEBAs Pathway 2** lignin-g-(polyether-b-polyamide 11)	Bio-based polyamide 11 derived from castor oil $(PA_{ref}{}^{bio})$	Bio-based polyether block derived from lignin-g-polyether $(PE_{new}{}^{bio})$	Better processability: (Monolithic HF membrane) *and* Development of PEBA type co-polymer with bio-based components in both blocks

Prototype B – Polymer Properties

Co-Polymer	T_g [°C]	T_m [°C] PEO/PA	CO_2 permeability (Barrer)	CO_2/N_2 Selectivity	CO_2/CH_4 Selectivity
1	-45	n.d. / 30	20,87	22,5	n.d.
2	-45	n.d. / 37	150	12,6	n.d.
3	<-40	31 / 102	139,4	24,3	8,0
4	<-40	40 / 98	47,5	23,76	8,4
5	**<-40**	**16 / 80**	**237,0**	**30,1**	**9,9**
6	n.d.	53 / n.d.	40,1	25,5	8,8

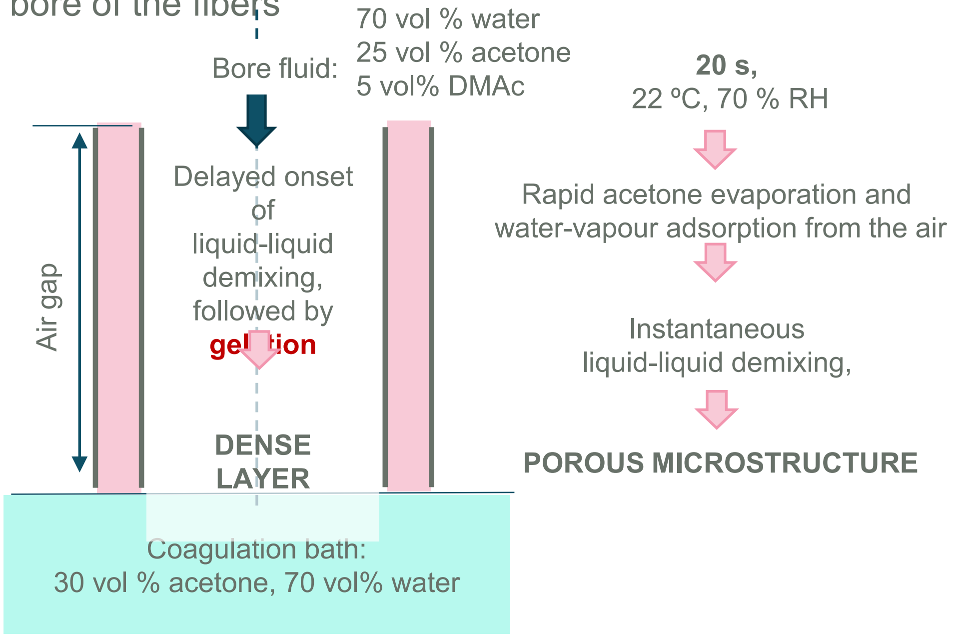
Prototype B – Polymer spinning

Literature background: Procedure for casting integral asymmetric PVDF pervaporation hollow fiber membranes with a dense layer on the inside bore of the fibers



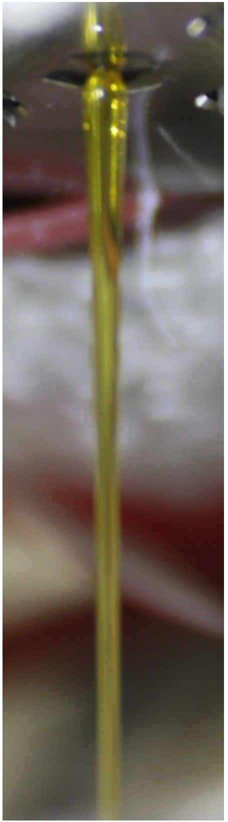
Xc	Tm (°C)	Tc (°C)
50,7	168,3	142,1

Polymer dope composition:
25 wt% PVDF
30 wt% DMAc
45 wt% Acetone

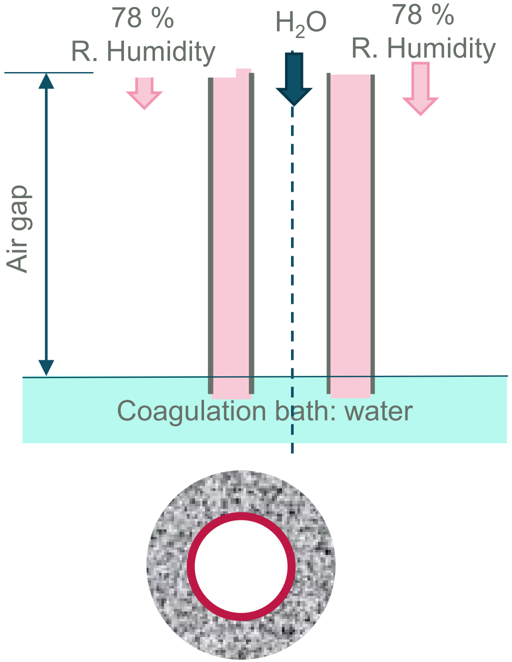


K. Jian, P.N. Pintauro, Asymmetric PVDF hollow-fiber membranes for organic/water pervaporation separations, Journal of Membrane Science, Volume 135, Issue 1, 1997, Pages 41-53

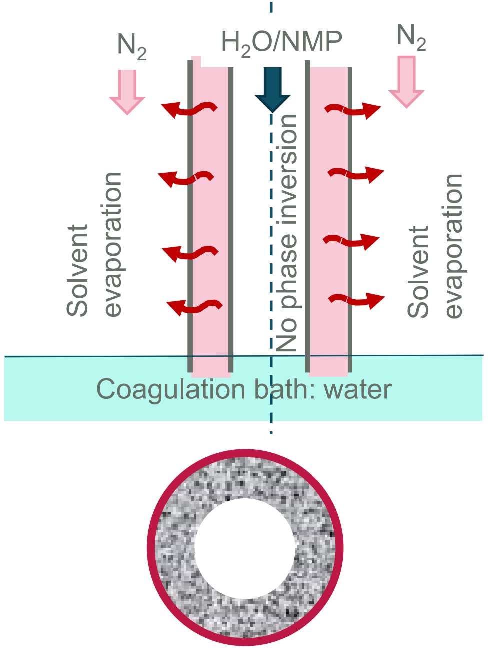
Prototype B – Polymer spinning



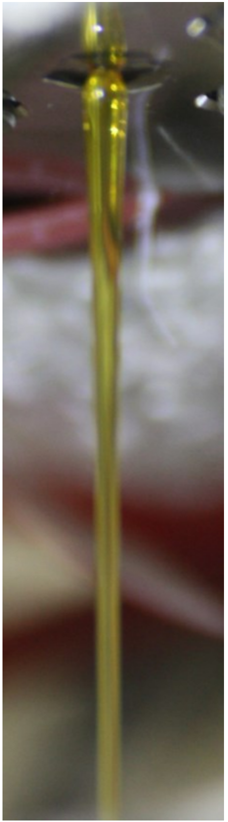
Forming the selective layer at the **inside** part of the fiber:



Forming the selective layer at the **outer part** of the fiber:



Prototype B – Polymer spinning



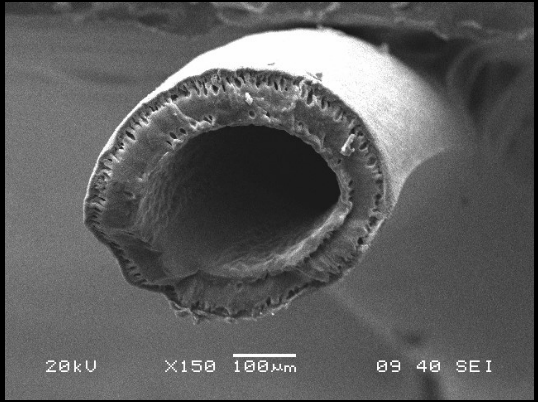
Polymer dope composition:

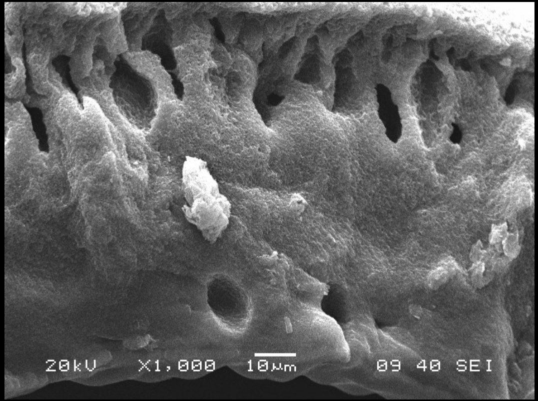
MS-2021-035	20 and 23 wt%
LiCl	3.67 wt%
NMP	73.33 wt%

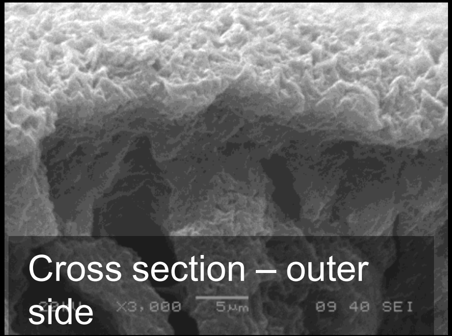
Gel at RT liquid at 40 ºC

Pump temperature (ºC)	Spinneret temperature (ºC)	Bore liquid composition H_2O/NMP wt%	Air gap (cm)	Air gap environment	Hollow fiber?
50	50	100/0	26	78% RH	✓
50	50	30/70	5 - 20	N_2	✗
50	21	50/50	5, 11	N_2	✓

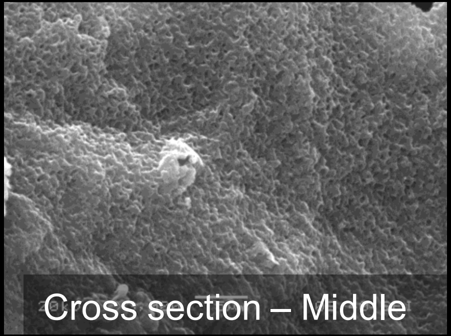
BioCoMem

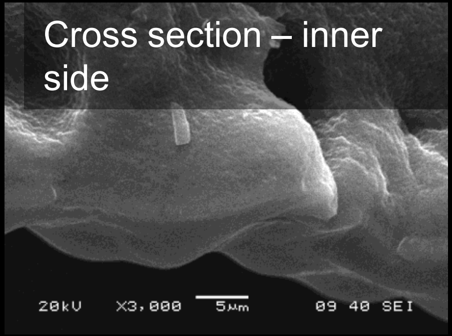




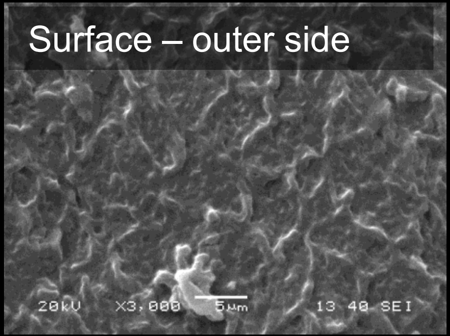


Cross section – outer side

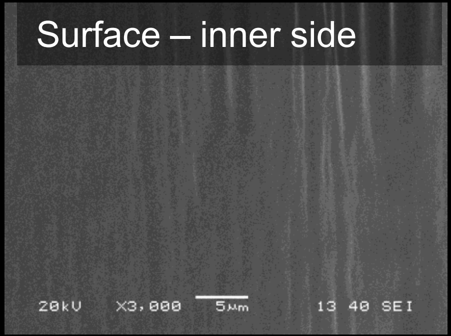

Cross section – Middle



Cross section – inner side



Surface – outer side



Surface – inner side

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Eskerrik asko zuen arretagatik!

Thank you for your attention!

Bio-based copolymers for membrane end products for gas separations

Membrane based Process Design and Economics

Contact:

Rouzbeh Ramezani

Eindhoven University of Technology

Department of Chemical Engineering and Chemistry

Sustainable Process Engineering

r.ramezani@tue.nl

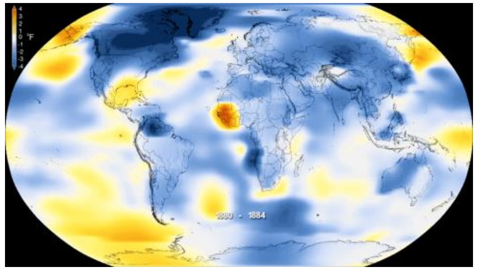
Webinar: Bio-based Membranes for CO_2 separation - 26th June 2023

CO_2 capture

- Concentration of carbon dioxide in atmosphere is rising sharply, and it is accelerating the global warming and climate change.

- CCS is a combination of technologies designed to prevent the release of CO_2 generated through conventional power generation and industrial production processes by injecting the CO_2 in suitable underground storage reservoirs.

- It is estimated that up to 90% of carbon emissions from the industrial use of fossil fuels could be captured by CCS.



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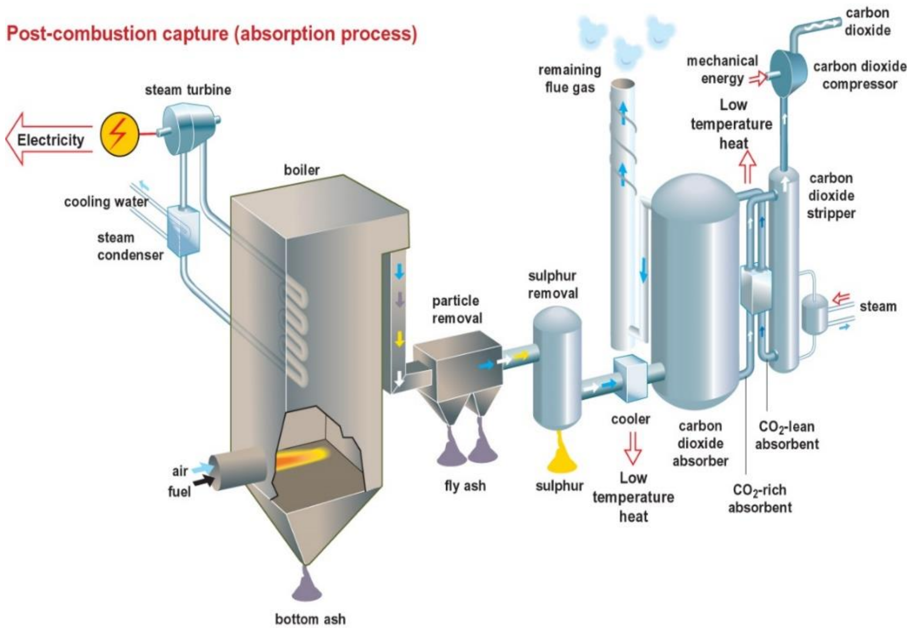
Carbon capture project explores liquid CO_2 carrier design (rivieramm.com)

CO_2 capture technologies

- Different technologies are available for removing CO_2 from different streams, e.g., cryogenic, adsorption, chemical absorption, membrane separation, and carbon fuel cells.
- The choice of technology depends on the specific application, process conditions, and economic factors.
- Absorption is a mature technology that is widely used in industrial applications, but it can be energy-intensive and requires significant space and capital investment.



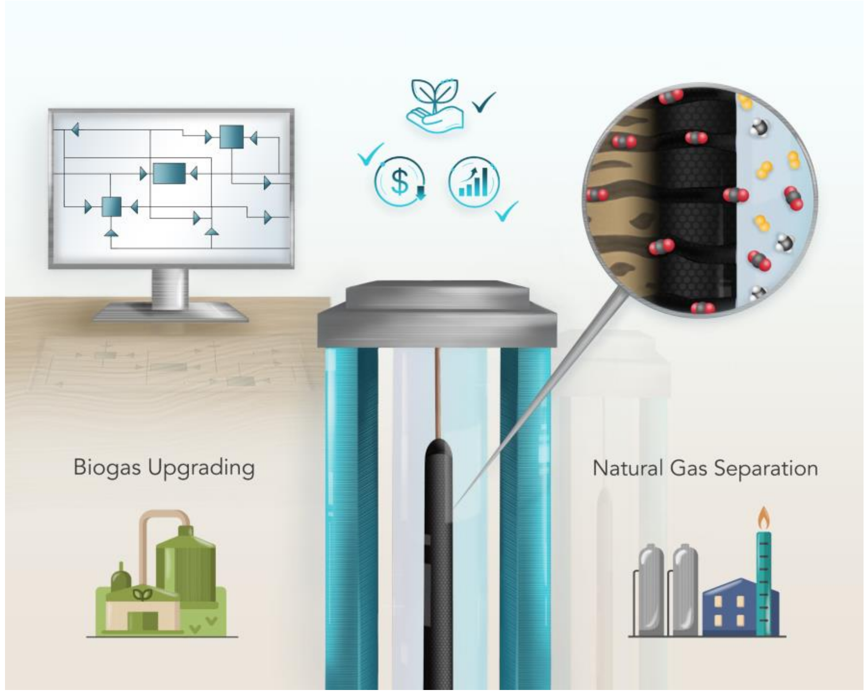
Challenge of the integration of CO_2 capture in the refining sector.

Membrane Gas Separation

- Has great potential for CO_2 capture due to its advantages such as avoiding chemical use, being simple to operate, energy-efficient, and suitable for intermittent and continuous operations.

- The potential application of the membrane process in a great measure depends on the capability of membrane materials to provide high separation performance.

- Membranes suffer from a trade-off between selectivity and permeability with an upper bound.



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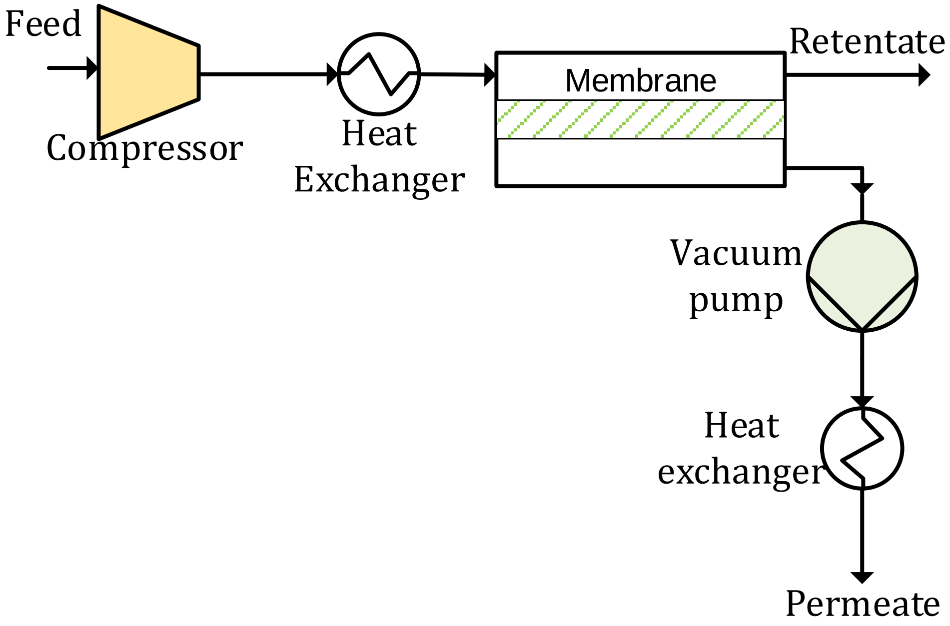
Steps of design of a membrane system

Process design is essential to provide an energy-efficient membrane technology for gas separation.

- Feed source and feed condition
- Product quality
- Select flow configuration
- Select number of stages
- Membrane type
- Optimize the membrane system

Membrane-based process design



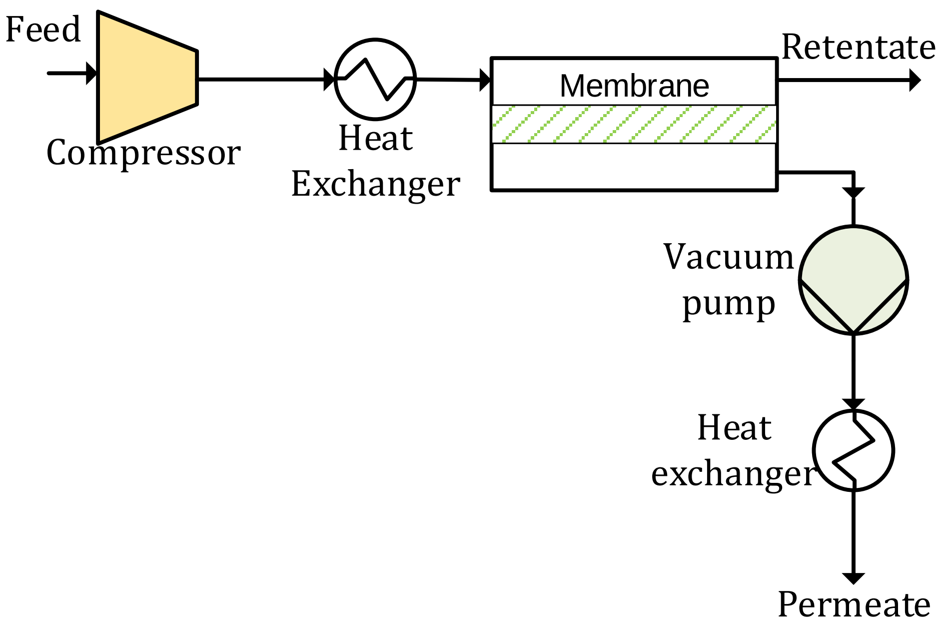
- In case of a post-combustion CO_2 capture, flue gas with atmospheric pressure is fed to a compressor to provide the required driving force for the gas separation.
- The driving force for CO_2 permeation in a membrane-based gas separation is the difference in the partial pressure of the feed and permeate side.
- The permeate stream exits the membrane at a lower pressure than the feed stream and enters either a vacuum pump or a compressor.
- The permeate stream is enriched from CO_2 while the retentate stream is enriched from N_2.

Membrane-based process design

- A single-stage membrane process cannot meet high recovery and gas purity at the same time, regardless of the membrane type used.

- CO_2/N_2 selectivity must be over 200 to achieve the target separations with CO_2 recovery and purity of >90% and >95%, respectively, in a **single-stage** membrane configuration.

- Since the single-stage membrane process cannot reach the separation goal, a multi-stage membrane system needs to be implemented.

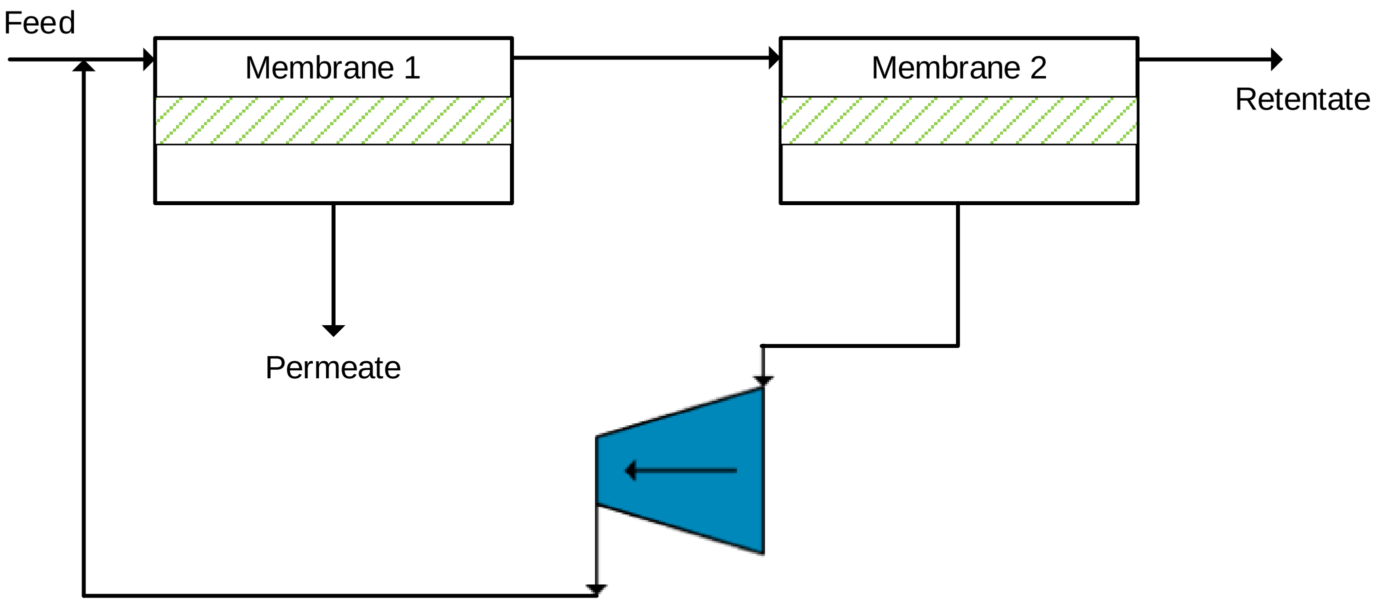


~~High purity~~
~~High recovery~~

Engineering evaluation of CO_2 separation by membrane gas separation systems, J Memb Sci. 454 (2014).

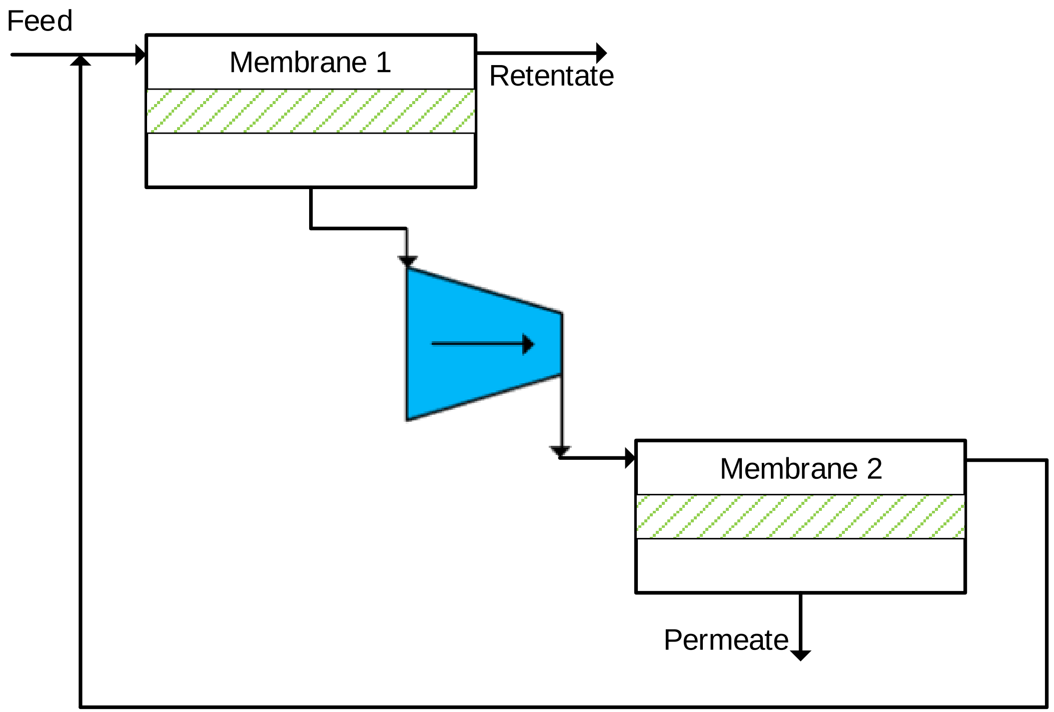
Two-stage cascade for purer retentate

- The raw gas is compressed and fed to the first membrane stage.
- The first stage performs a bulk separation of for example CO_2 and CH_4
- The retentate of the first stage is fed to a second stage in which the final product purity is obtained.
- The permeate of the second stage is recycled and mixed with the raw gas stream to enhance the CH_4 recovery.



Two-stage cascade for purer permeate

- The permeate stream of the first membrane unit, after passing through a compressor and a cooler, enters the second stage
- The permeate stream of the second membrane unit is considered as the final product.
- The product purity and recovery of this configuration are higher than those of the previous configuration.
- The combination of similar membranes or/and different membranes in the two-stage process results in good separation performance as product purity reaches the desired values.



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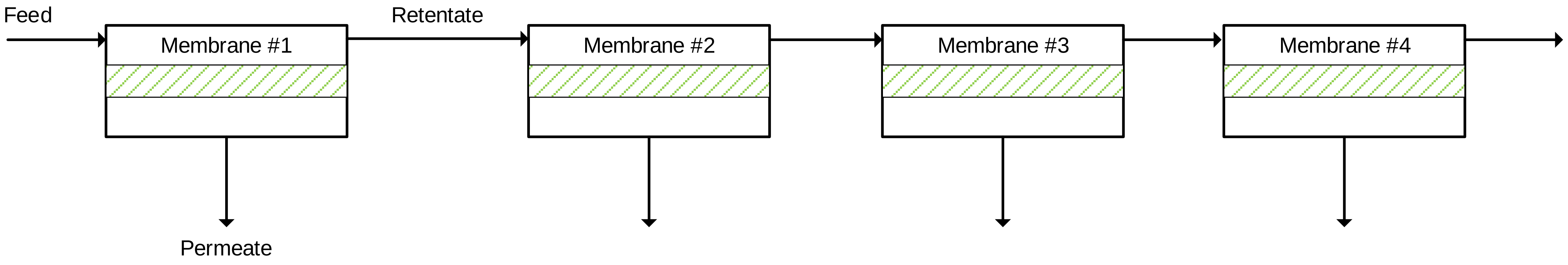
Multi-stage membrane module

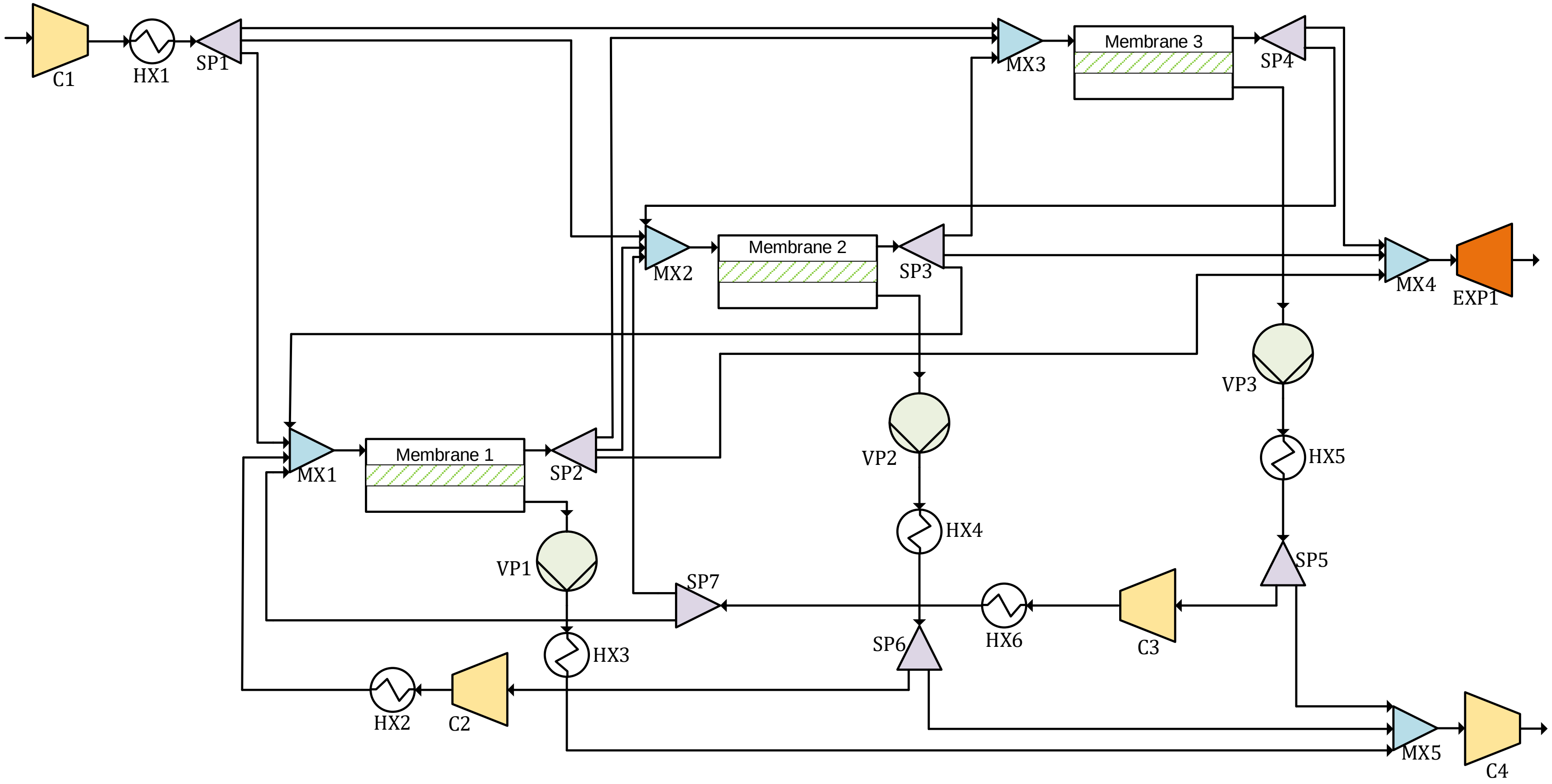
The selection of the best configuration is highly related to feed quality, separation objectives and market values.

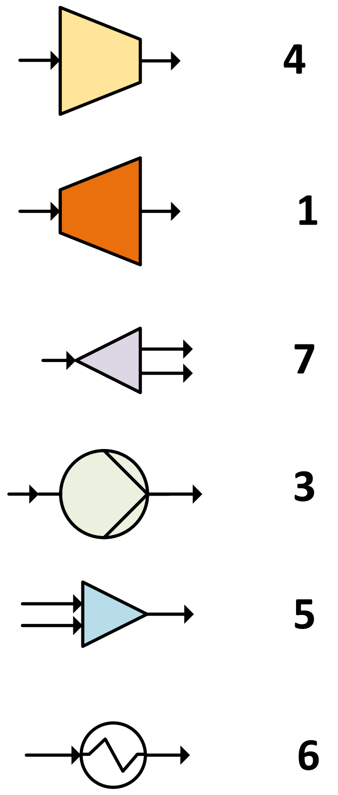


BioCoMem

Multi-stage membrane module

By applying a structural optimization approach, the most profitable process configuration including stage numbers can be determined.





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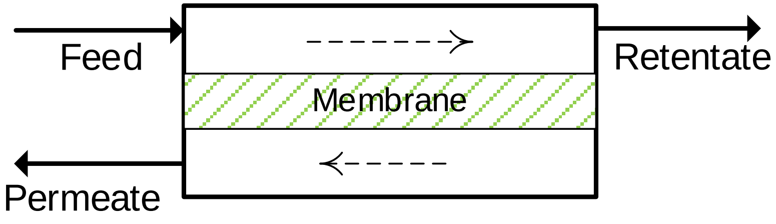
The main objective in the optimization of the multi-stage membrane design was to minimize GPC while achieving the product target purity and recovery.

Flow arrangements in membrane modules

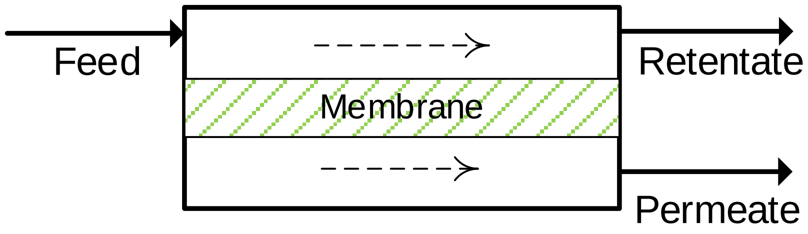
- The performance of a membrane is influenced by the way in which the permeate and retentate flow in the membrane.

- Flow arrangements of perfect mixing, co-current, counter-current, and cross flow are possible in the design of a membrane module.

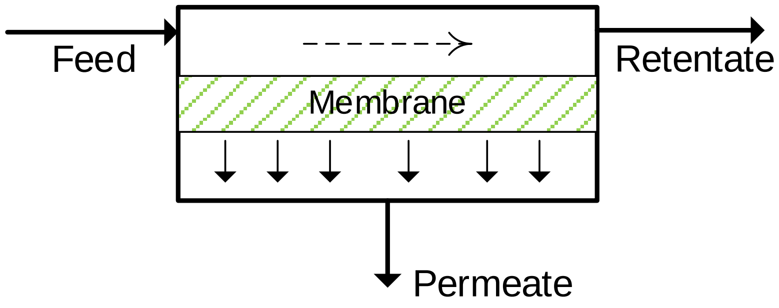
Counter-current Flow



Co-current Flow

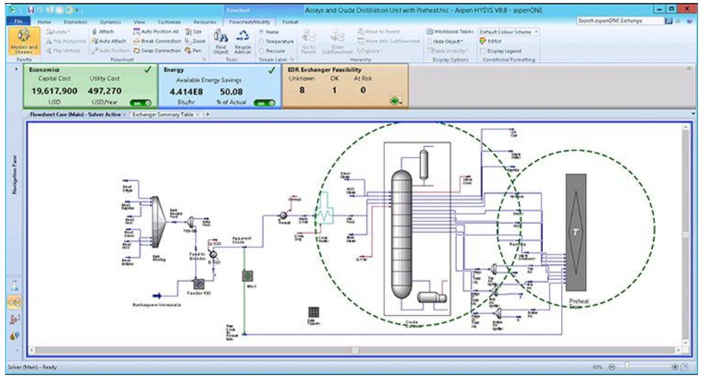


Cross Flow



Process Simulation Tools

Process simulators have been proven to be successful in modeling, simulate, and optimize various industrial processes.



Aspen Plus **Aspen Hysys**	Can be used for batch and continuous processes for design, troubleshooting in regular operations, monitoring the plant performance through online, and real-time optimization.
gPROMS	An advanced equation oriented process modeling software, which can be used to model, analyze, and optimize in an easy-to-use process flow-sheeting environment.
PRO/II	A steady-state simulator which has an in-built membrane unit operation to simulate crossflow symmetric membranes for gas separations.
ProMax	A multifaceted process simulation software which it is designed to optimize gas processing, refining, and chemical facilities.
SuperPro Designer	A flowsheet driven simulator for batch, continuous as well as combination processes, that perform material and energy balances, equipment sizing, and costing.
Aspen Custom Modeler	Provides the capability to create unique process and equipment simulation models by describing the equations which can be exported into Aspen Plus/Hysys.

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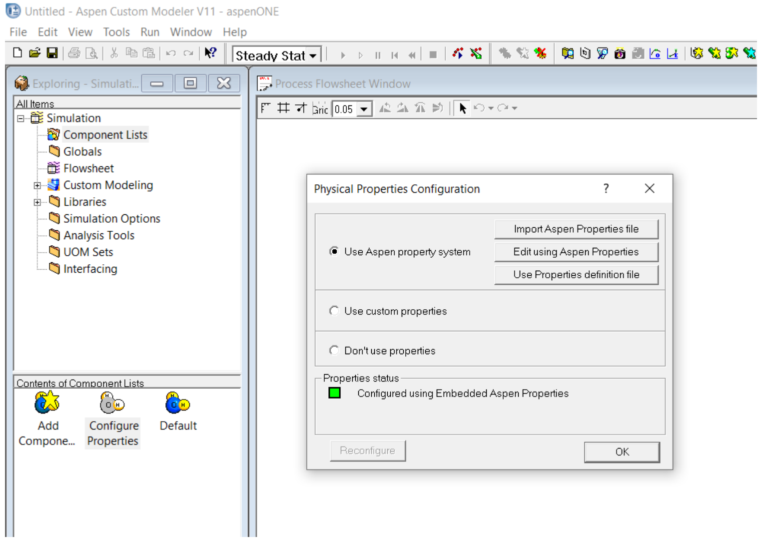
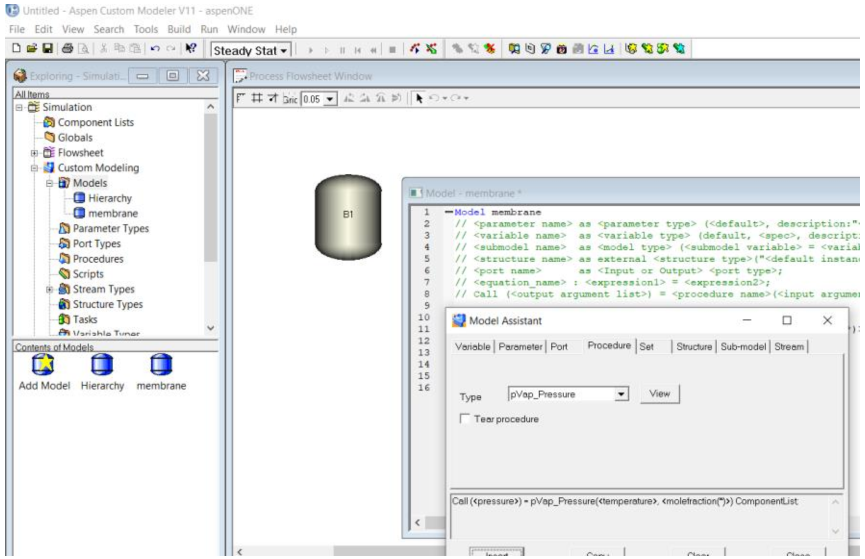
Implementation of Membrane model in Aspen Custom Modeler (ACM)

- Some process models like membrane separation are <u>not available in Aspen Plus</u>.
- The developed mass transfer model for the gas separation membrane process is coded by MATLAB.
- The model for membrane gas separation can be implemented and solved in ACM, which can be added to Aspen Plus.
- To implement the membrane model in ACM, all chemicals are defined from the component list in the Aspen Properties User Interface program.
- Fixed variables or inputs (feed temperature, pressure, composition and membrane area) are defined, and the process parameters (for example, permeance) and variables are declared.
- The model has one port for feed stream and two ports as permeate and retentate streams.





R. Kancherla et al., Computers & Chemical Engineering, 148 (2021) 107258.

Economic model

- In order to find the best configuration of the multi-stage gas membrane process, the cost analysis was conducted for:
  - Post-combustion
  - Natural gas sweetening
  - Biogas upgrading
- The aim was to minimize the cost of separation while satisfying the separation targets.
- The economic analysis of the superstructure membrane process was performed by calculating the capital cost, annual operating and maintenance, and energy cost.
- Capital cost is associated with membrane area and membrane module skids as well as the contribution of major components such as compression, expander and vacuum pumps.
- Operational cost is a sum of electricity cost, and operation and maintenance costs. Operation and maintenance of the vacuum pumps, expander and compressors is estimated at 3.6% of their capital cost and 1% for the membrane and the membrane frame.

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Economic model

Description		
Membrane module cost	C_m	$\$/m^2$
Compressor unit cost	C_c	\$/kW
Expander unit cost	C_{ex}	\$/kW
Vacuum pump unit cost	C_v	\$/kW
Efficiency of pressure units	η	-
Installation factor	f_{in}	-
Electricity cost	C_e	$\$/kWh^{-1}$
Operation time per year	t_{op}	h/yr
Depreciation factor (25 years)	DF	-
Membrane depreciation factor (5 years)	DF_m	-
Membrane frame cost	$I_{m,fram} = 0.238 \times 10^6 \times \left(\frac{A_{t,mem}}{2000}\right)^{0.7} \left(\frac{P_t}{55}\right)^{0.88}$	\$
Compressor cost	$CC = C_c \times W_c \times f_{in}$	\$
Expander cost	$CE = C_{ex} \times W_{ex} \times f_{in}$	\$
Vacuum pump cost	$CV = C_v \times W_{vp} \times f_{in}$	\$
Total capital cost	$TCC = DF_m(C_m \times A_{t,m}) + DF(I_{m,fram} + CC + CE + CV)$	\$/y
Operating and maintenance cost	$OMC = 0.01(C_m A_{t,m} + I_{m,fram}) + 0.036(CC + CE + CV)$	\$/y
Energy cost	$EC = C_e \times t_{op} \times \sum W$	\$/y
Total operational cost	$VOM = OMC + EC$	\$/y
Gas processing cost	$GPC = \frac{TCC+VOM}{annual\ separated\ CO_2}$	\$/tonne CO_2

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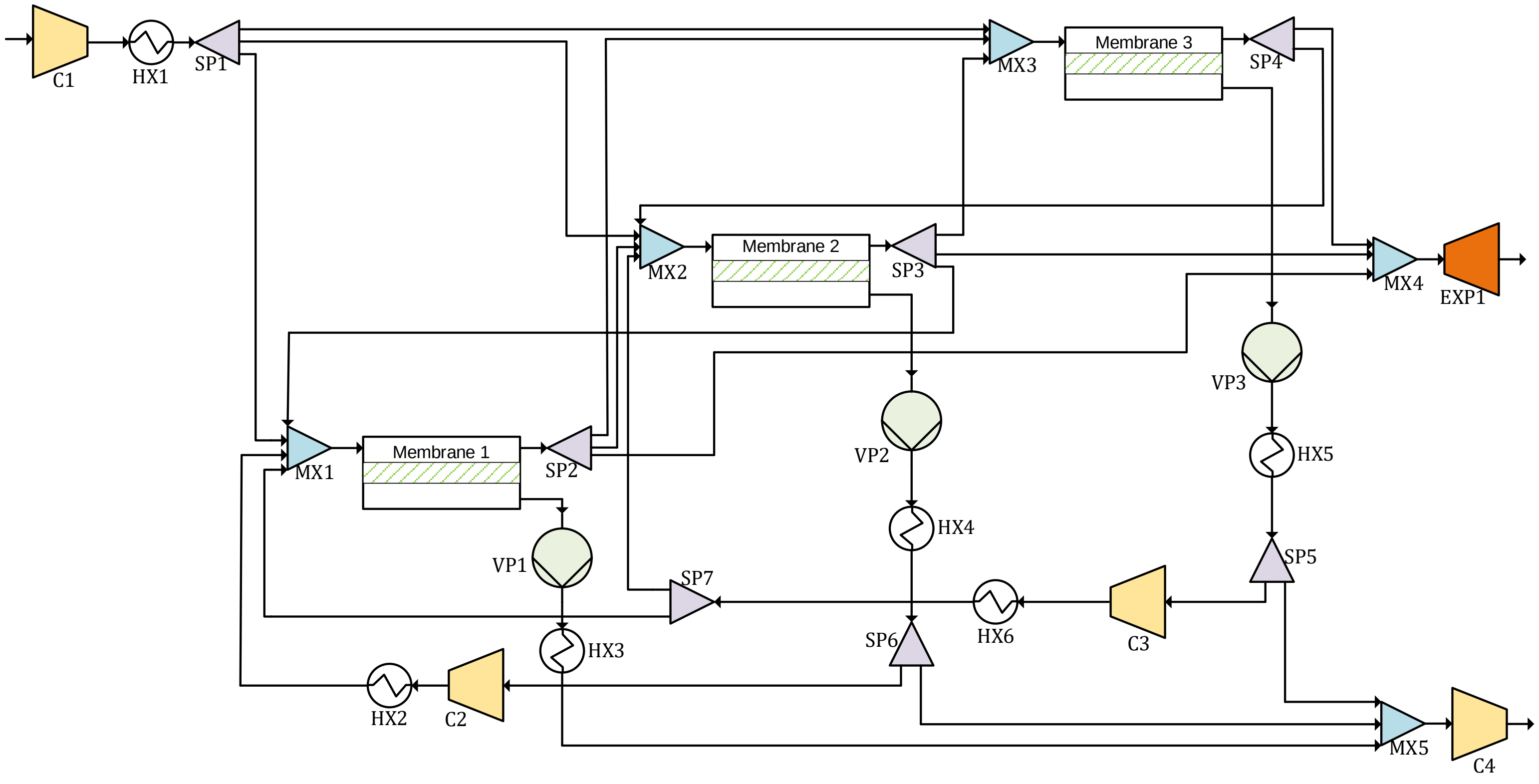
Energy Convers Manag. 246 (2021) 114633.
J Memb Sci. 598 (2020) 117796.

Optimization



- A structural optimization approach was applied to determine the most efficient membrane strategy from the point of view of gas separation cost.

- Membrane area of each stage
- Retentate pressure
- Permeate pressure of each stage
- Split fractions

Optimization

Input variables

- Feed conditions
- Membrane selectivity
- Gas permeance
- Target pressure

CO_2 or CH_4 purity
CO_2 or CH_4 recovery
Minimum GPC

Output variables

- ✓ Compressor power
- ✓ Membrane area
- ✓ CAPEX
- ✓ OPEX
- ✓ GPC
- ✓ Number of stages

Biogas Upgrading

- Biogas is a potential alternative to the world's unquenchable demand for energy and concurrently reduces waste and greenhouse gas emissions.
- CO_2 is the non-combustible portion of biogas.
- CO_2 has to be removed from CH_4 to enhance the heating value of the product gas.
- CH_4 mole fraction in the raw gas of 60% has to be increased to more than 90% in order to meet the natural gas grid requirements.
- CH_4 purity and recovery are the most important technical parameters in determining an optimal module arrangement in order to ensure a low CH_4 loss.

Feed gas characteristic	Feed flow rate	44 kmol/hr
	Feed temperature	298.15 K
	Feed pressure	1 bar
	Feed composition	40 % CO_2
		60 % CH_4
Output targets	CH_4 recovery	90 %
	CH_4 purity	95 %
	Product pressure	16 bar

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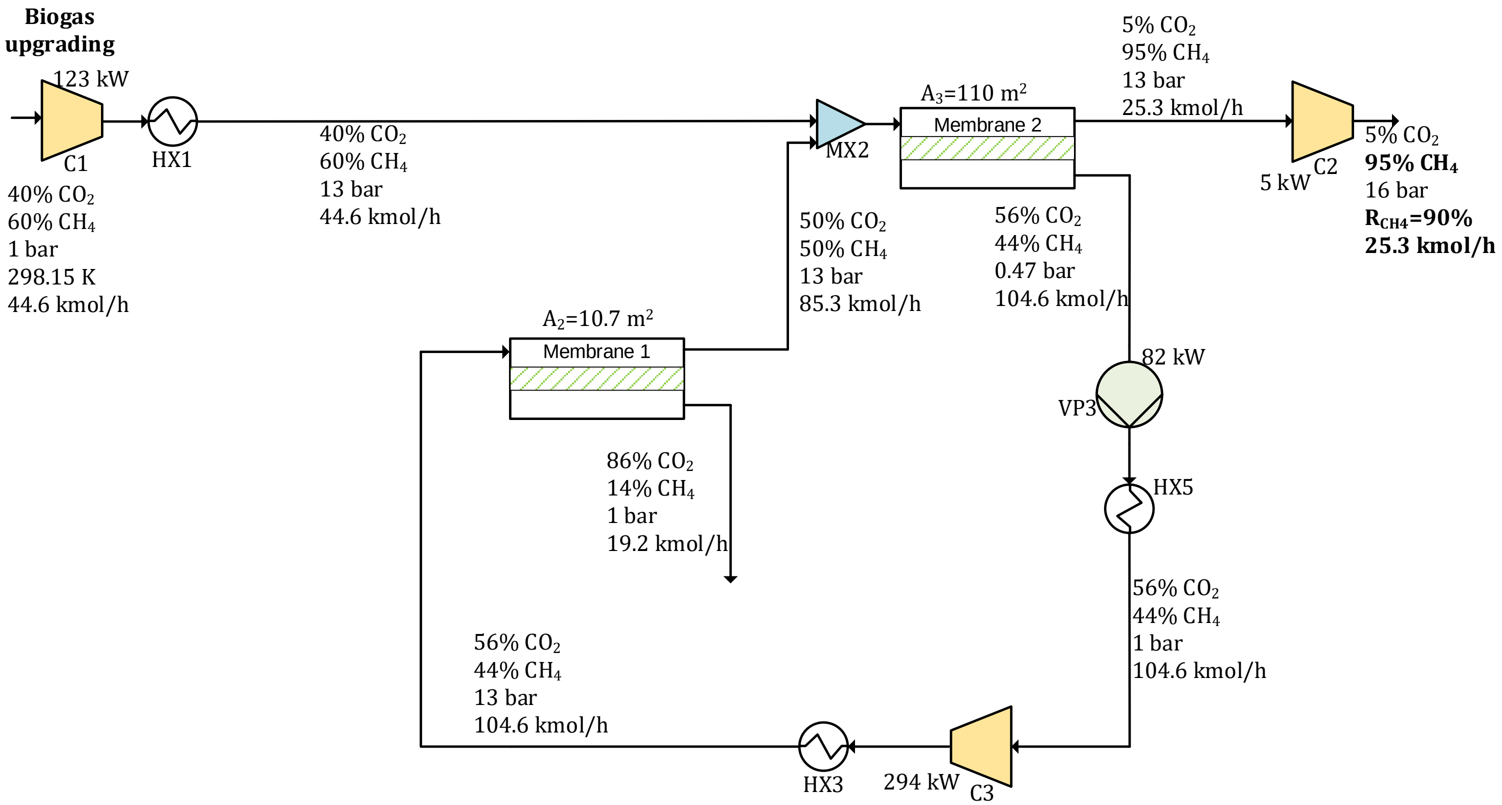
Biogas Upgrading



Variable	Biogas upgrading
CO_2/CH_4 selectivity	7.9
Methane recovery	90 %
Methane purity	95 %
Number of membrane stages	2
TCC	38899 €/yr
OMC	21225 €/yr
EC	202364 €/yr
Total power	505 kW
Power recovered in expander	-
Total net power	505 kW
Total membrane area	121 m^2
Operating pressure	13 bar
GPC	69.8 €/ton product

Natural gas separation

- CO_2 separation from natural gas is critical as the presence of CO_2 adversely affects the produced gas quality, and can form acids in the presence of water that corrodes the pipelines and equipment.

- To satisfy the legal requirements and gas grid specifications, CO_2 content in natural gas needs to be decreased to below 2%.

Feed gas characteristic	Feed flow rate	1700 kmol/hr
	Feed temperature	298.15 K
	Feed pressure	20 bar
	Feed composition	10 % CO_2
		90 % CH_4
Output targets	CH_4 recovery	98 %
	CH_4 purity	97.5 %
	Product pressure	20 bar

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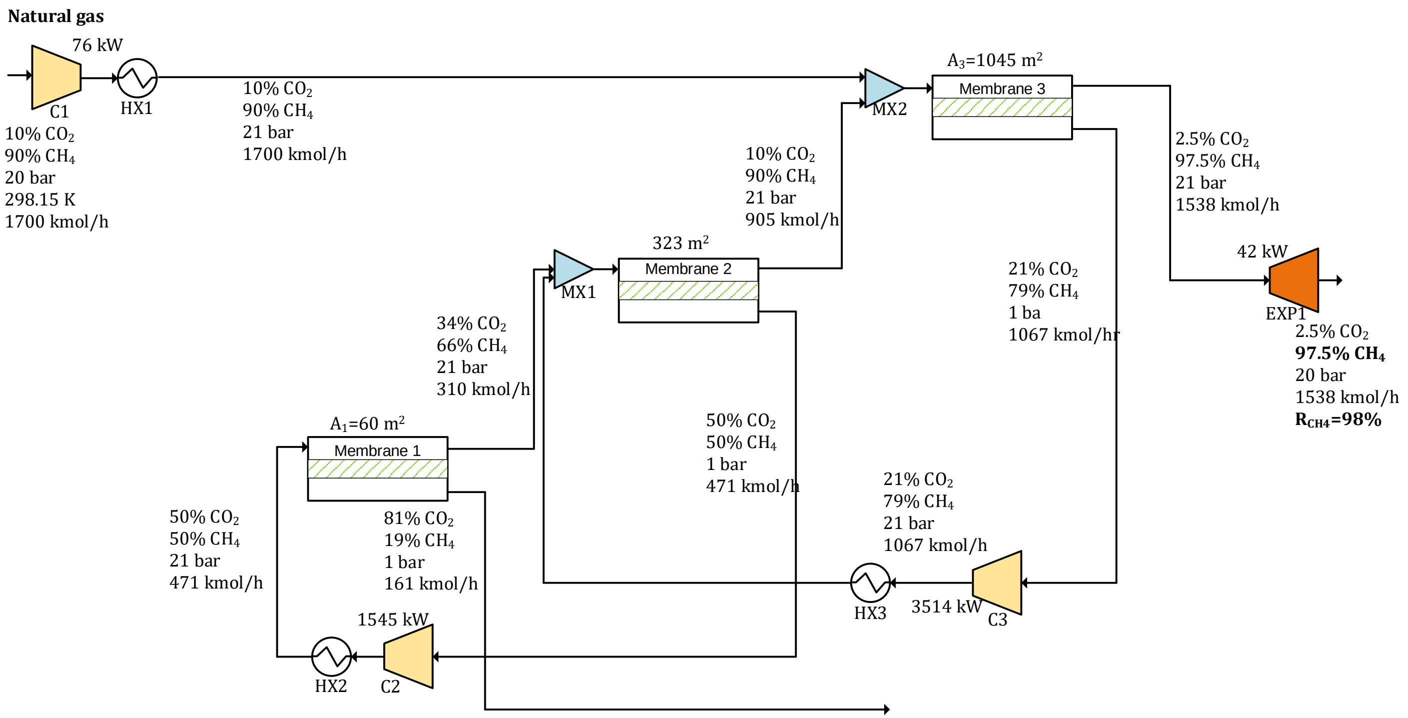
Natural gas separation



Variable	Natural gas
CO_2/CH_4 selectivity	7.9
Methane recovery	98 %
Methane purity	97.5 %
Number of membrane stages	3
TCC	345096 €/yr
OMC	186372 €/yr
EC	2.03×10^6 €/yr
Total power	5096 kW
Power recovered in expander	42 kW
Total net power	5054 Kw
Total membrane area	1428 m^2
Operating pressure	21 bar
GPC	17.4 €/ton NG

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Post-combustion CO_2 capture

The multi-stage membrane process is investigated in terms of

- capture cost
- energy consumption
- membrane area

The effects of membrane selectivity, CO_2 recovery and CO_2 purity on gas separation cost, CAPEX, OPEX and power consumption were examined.

Feed characteristic	Feed flow rate	2000 kmol/hr
	Feed temperature	308.15 K
	Feed pressure	1 bar
	Feed composition	14 % CO_2, 86 % N_2
	CO_2 emission	13 tons/hr
Output targets	CO_2 recovery	90 % and 95 %
	CO_2 purity	95 % and 98 %
	Product pressure	76 bar

EINDHOVEN UNIVERSITY OF TECHNOLOGY

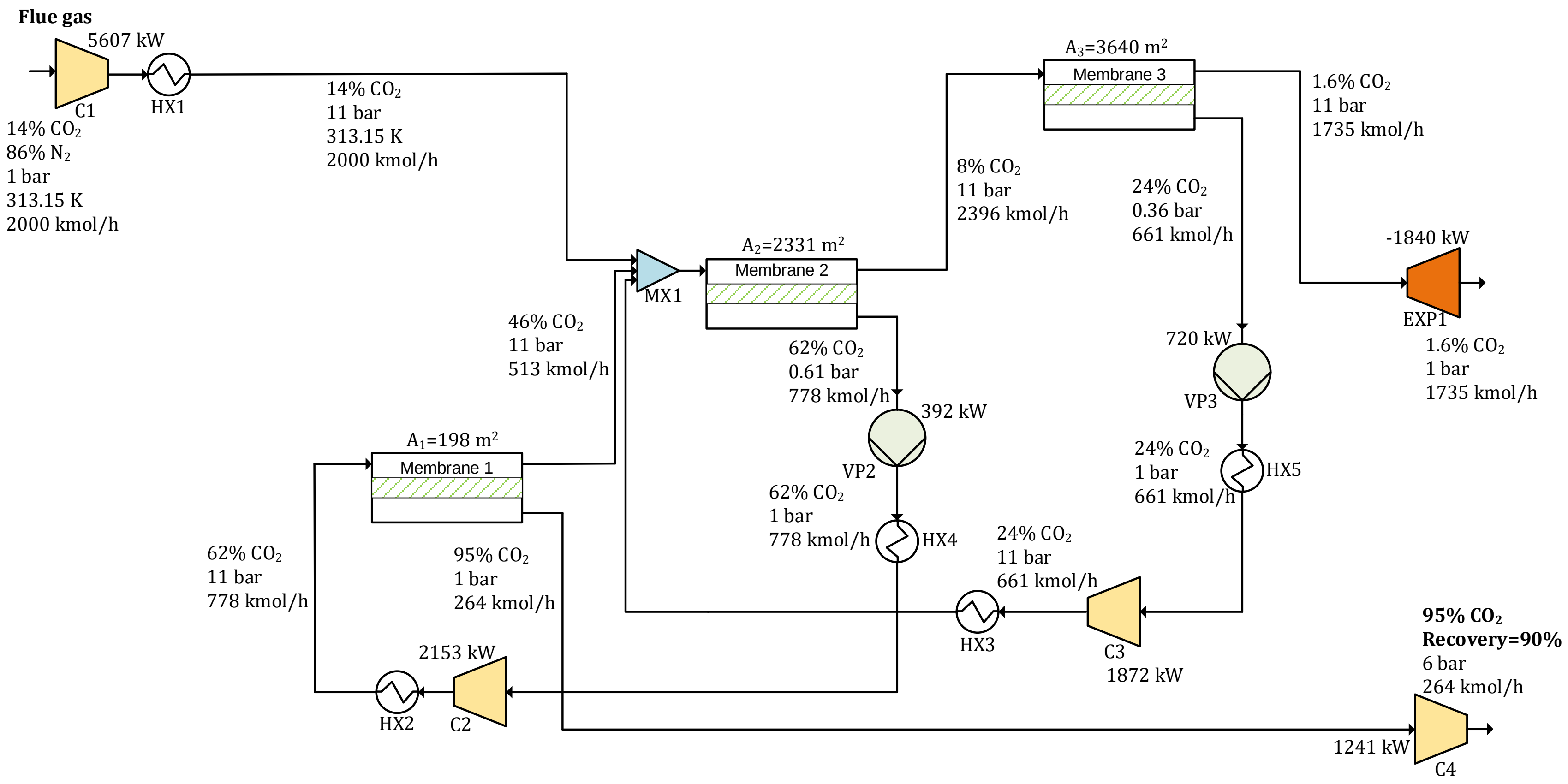
Post-combustion CO_2 capture

Optimal configuration from a capture cost point of view for CO_2 capture from flue gas with 90% CO_2 recovery and 95% purity.

Area=6170 m^2

GPC=59.6 €/ton CO_2

SEC=3.3 GJ/tonCO_2

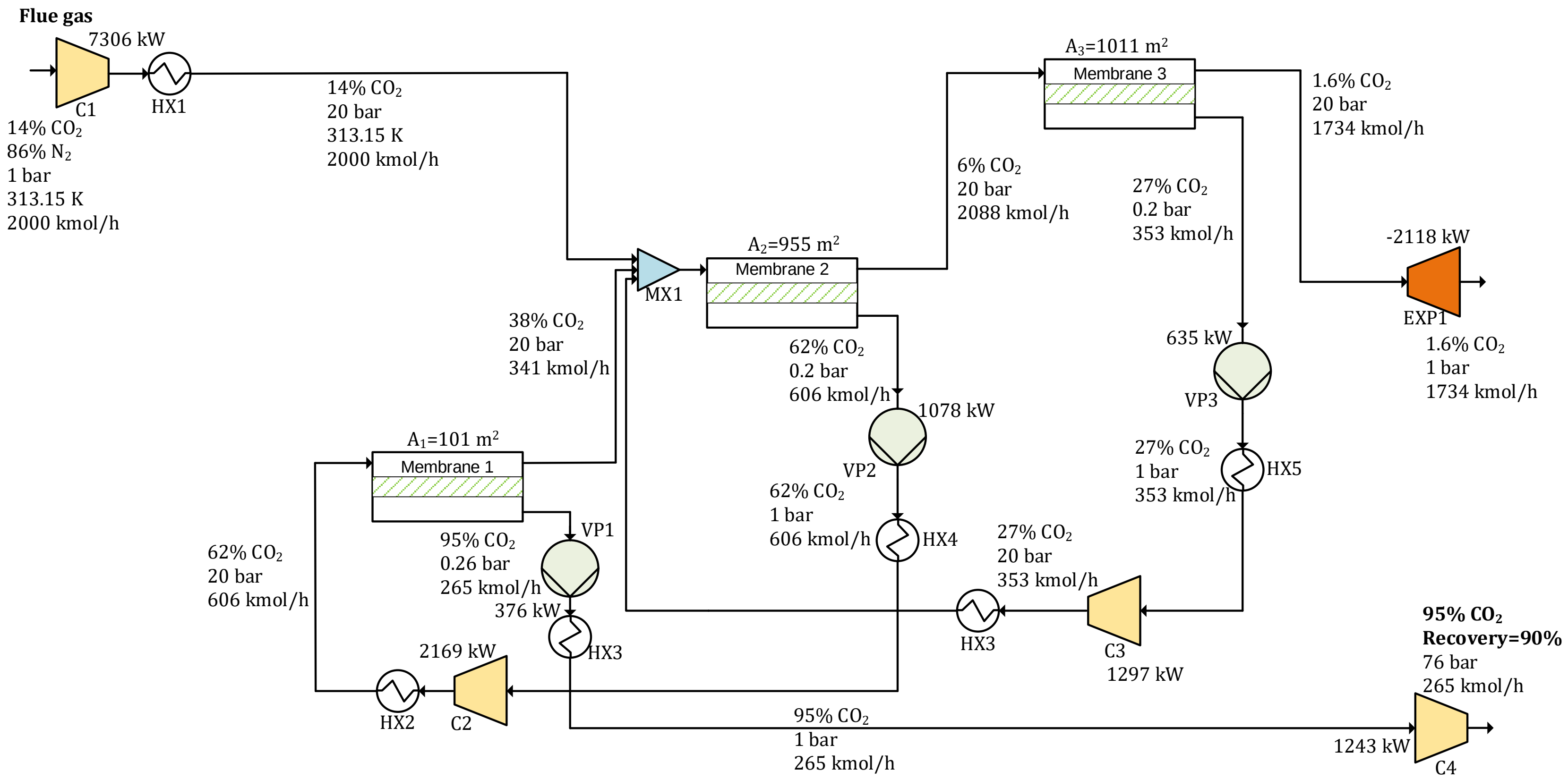


Post-combustion CO_2 capture

Optimal configuration from a membrane area point of view for CO_2 capture from flue gas with 90% CO_2 recovery and 95% purity.

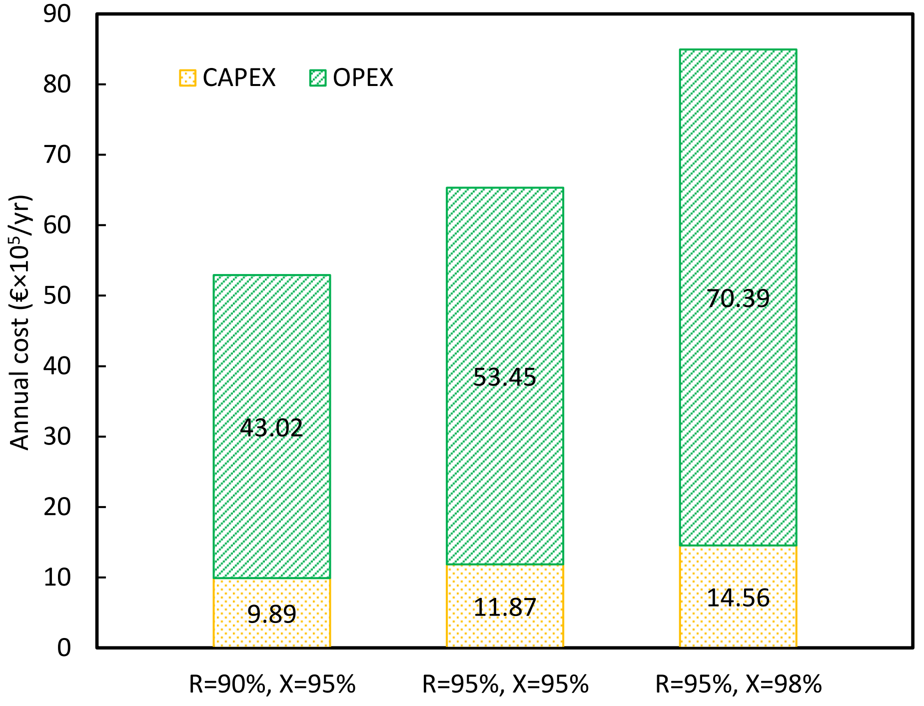
Area=2067 m^2

GPC=70 €/ton CO_2

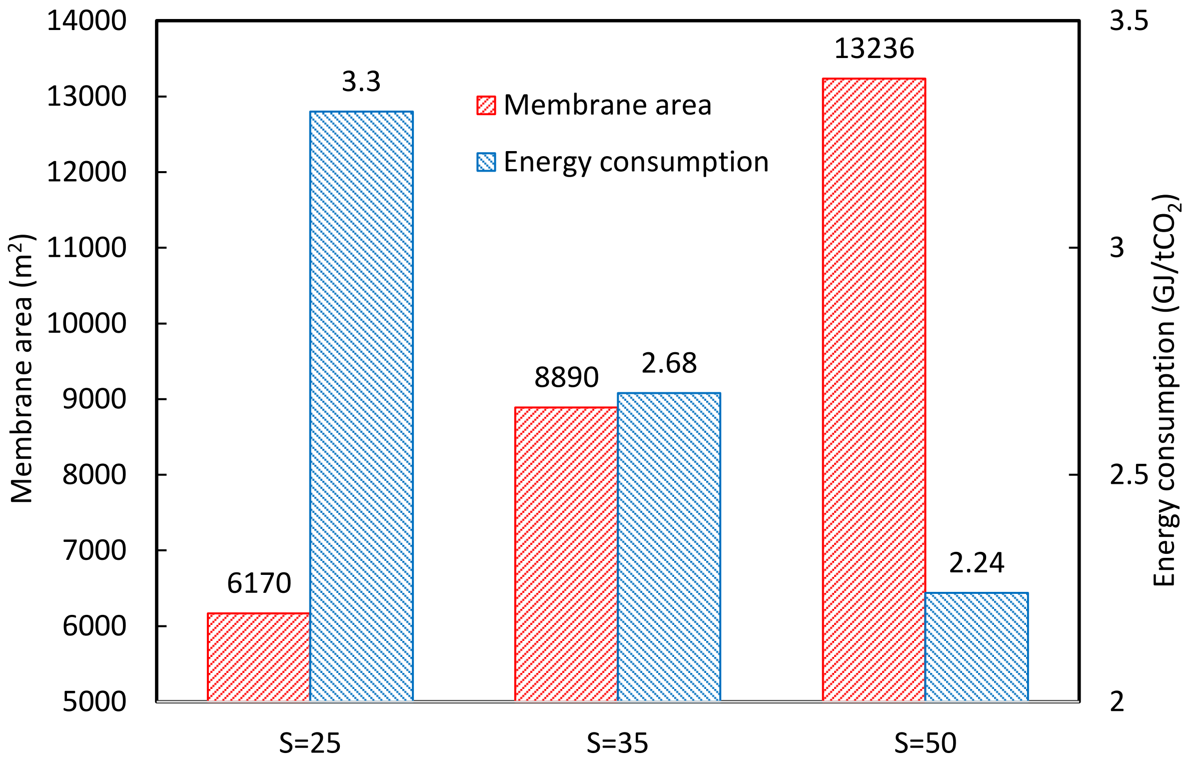


Post-combustion CO_2 capture

CO_2 recovery	90%	95%	95%
CO_2 purity	95%	95%	98%
Number of membrane stages	3	3	3
TCC	989581 €/yr	$1.18*10^6$ €/yr	$1.45*10^6$ €/yr
VOM	$4.30*10^6$ €/yr	$5.34*10^6$ €/yr	$7.04*10^6$ €/yr
Total net power	10158 kW	12661 kW	16793 kW
Power recovered in expander	1840 kW	1954 kW	2107 kW
Total membrane area	6170 m^2	5928 m^2	4910 m^2
SEC (GJ/ton CO_2)	3.30	3.9	5.16
GPC (€/ton CO_2)	59.6	69.8	90.7



Post-combustion CO_2 capture



Improving the membrane selectivity from 25 to 50 reduces the gas processing cost by 28%, from about 59 €/tonCO_2 to 42 €/tonCO_2.

Bio-based copolymers for membrane end products for gas separations

Thank you

Membrane based Process Design and Economics

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Sustainable Process Engineering

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LCA:
Life Cycle Assessment, Action, Accountability

From measurement to management: Use of the LCA framework in the context of biobased solutions

Stefan Frehland, Senior Sustainability Consultant - Quantis

26/06/2023

Agenda

01 Introduction & Context

02 What is Life Cycle Assessment, why is important and how can it be used

03 The LCA framework: how to approach it right

04 Biobased solutions in context

05 Key takeaways

Speakers

Stefan Frehland

Quantis
Senior Sustainability Consultant

Link

Quantis

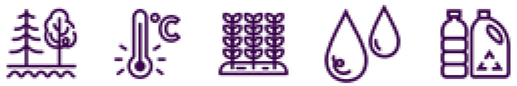
Environmental sustainability consultancy that works with brands across the globe to **drive sustainable transformation** and **align business with planetary boundaries**

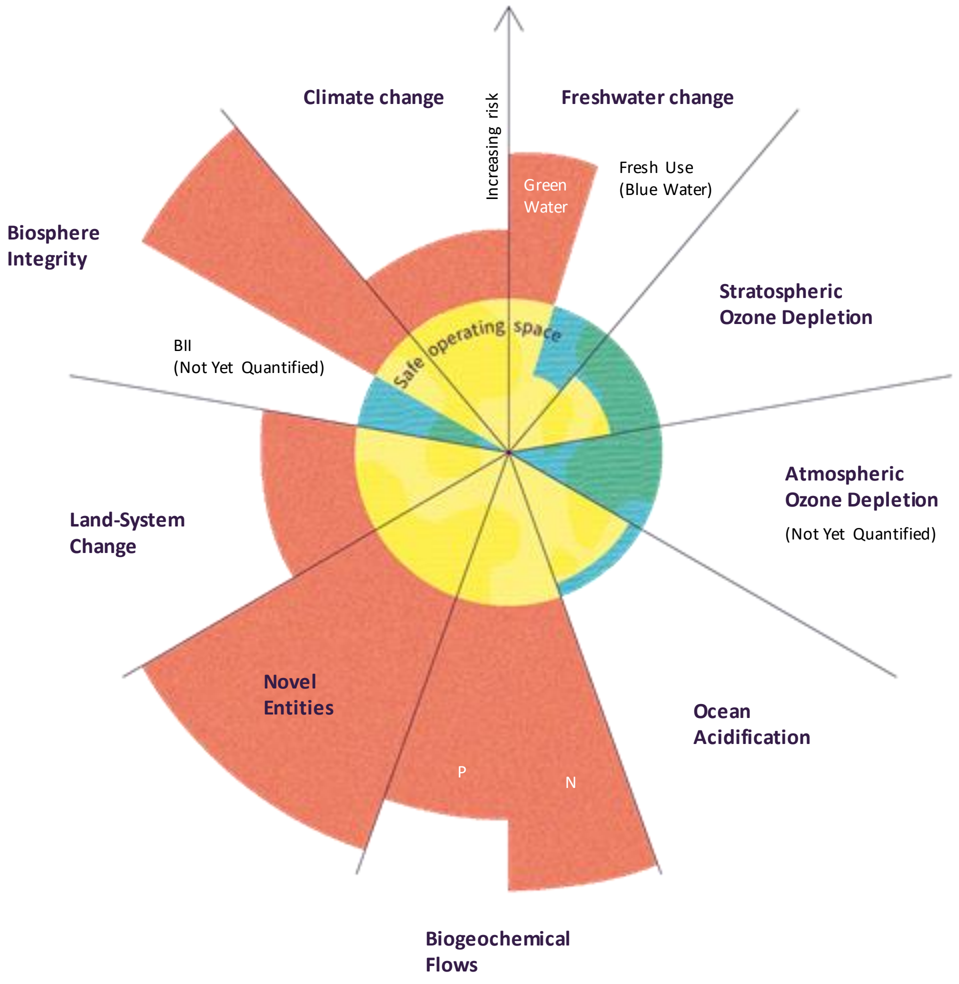
Aligning business with planetary boundaries

Scientific models such as the Planetary Boundaries define the operating spaces within which we must stay to maintain life as we know it on our planet.

We have already crossed the line on many boundaries.

Biodiversity, climate, land + agriculture, water and plastic pollution: Our 5 environmental expertise areas work with clients to measure your contributions and own limits, set reduction goals and chart a roadmap to get business in-line with the planet's limits:



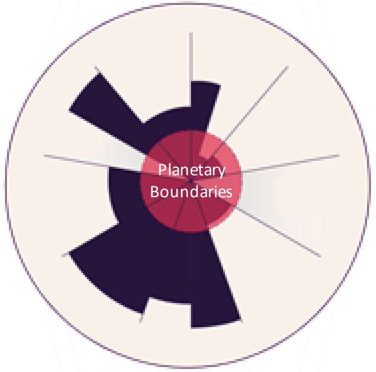


SOURCE: www.stockholmresilience.org, Rockström, J., W. Steffen, K. Noone, Å. Persson, et.al. 2009

Our 5 environmental expertise areas

Climate
Align your business + value chain to a 1.5°C world

Biodiversity
Understand the impacts of your business on nature



Water
Become a steward of shared water resources at basin level

Land + agriculture
Use the power of nature to create healthier ecosystems

Plastic pollution
Know your plastic hotspots and design for circularity

Quantis

Our Team

Our dynamic and visionary team of smart, passionate individuals — from engineers and environmental scientists to business strategists and communications experts — are committed to building a future that works for people, planet and business.

250+
Sustainability champions

5000+
Client projects

15+
Years of experience

Quantis

We guide you through a three-phased Sustainability Transformation Journey

Assess

Gather the best available data, metrics & insights

Identify opportunities for improvement

Plan

Define your ambition and strategic framework to guide the transformation

Set the goals and outline the roadmaps for actions

Transform

Put the transformation plan into action

Engage with stakeholders and activate across the supply chain and portfolio

01

Introduction & Context

1 LCA >> Life Cycle Assessment

LCA is the science-based tool that will help you measure product footprint and environmental hotspots across different categories

2 LCA >> Life Cycle Actions

LCA metrics are the ones to guide your environmental actions, enabling the Brand to focus on priorities, when it comes to environmental sustainability

3 LCA >> Life Cycle Accountability

LCA to correctly communicate with all stakeholders, adhere to new and more stringent regulatory frameworks and avoid reputational risks

01

What is LCA, why is important and how can it be used

"

Eco-design is defined as the integration of environmental perspective into products' and services' design and development.

"

Quantis

LCA - Life Cycle Assessment, Action, Accountability

LCA is the compass that guides you through your sustainability transformation process

ASSESSMENT	ACTION	ACCOUNTABILITY
See the full picture, get the facts right	**Focus on the right thing**	**Take ownership and communicate**
Identify environmental issues along the **value chain (hotspots)**	Identify **improvement** possibilities and **priority actions**	Manage **risk**
Compare alternatives	Define the **strategy**, set **goals** and measure **progress**	**Communicate** and **facilitate conversations** with stakeholders
Avoid **shifting the burden**		

03

LCA in Action: how to approach it right

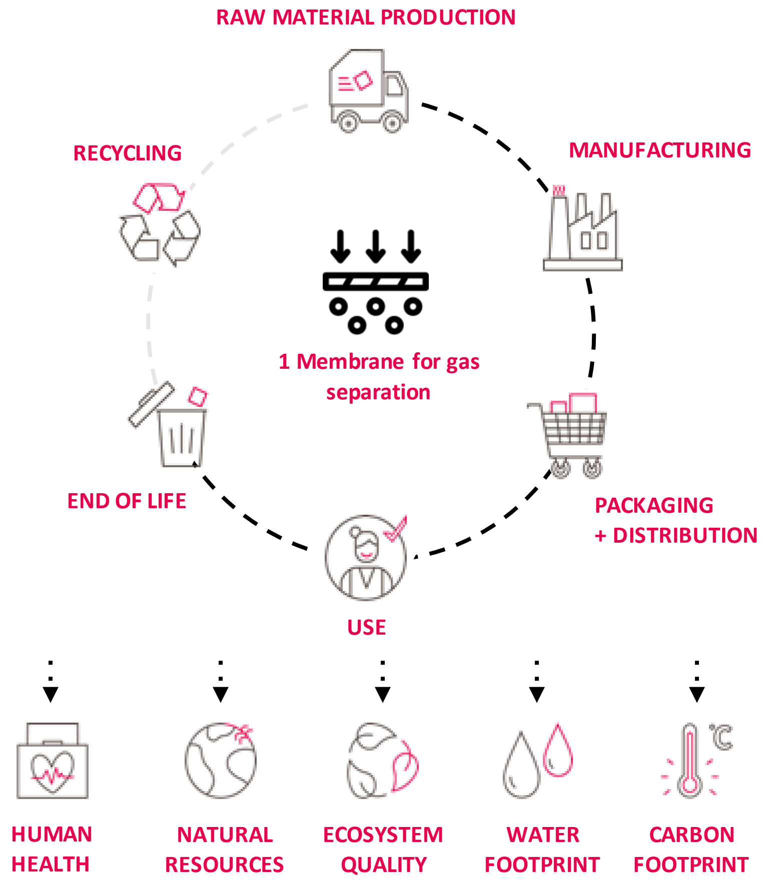
THE LCA APPROACH

Life Cycle Assessment is recognized as the leading methodology for environmental impact evaluation. The main strengths of this tool are the following:

Metrics-based approach, allowing impact evaluations and/or comparisons to be made on a quantified and credible scientific basis.

Life-cycle oriented, allowing users to consider various product stages, to highlight potential 'burden shifting', or unintended consequences.

Multi-criteria: we are aligned with the PEF guidance, and cover a multiplicity of indicators in the assessment (including water use, ecotoxicity, ozone depletion, etc.)



LCA IS A GOOD DECISION MAKING TOOL

- Identify environmental issues along the **value chain (hotspots)**
- Identify **improvement** possibilities and production **optimization**
- **Compare** alternatives
- Set **goals** and measure **progress**
- **Benchmark** performance
- Manage **risk**
- **Communicate**

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The LCA framework you need to know

Get the right picture:

- Define your **system**, **data requirements** and **assumptions** to fill potential gaps

Select the right tools and databases

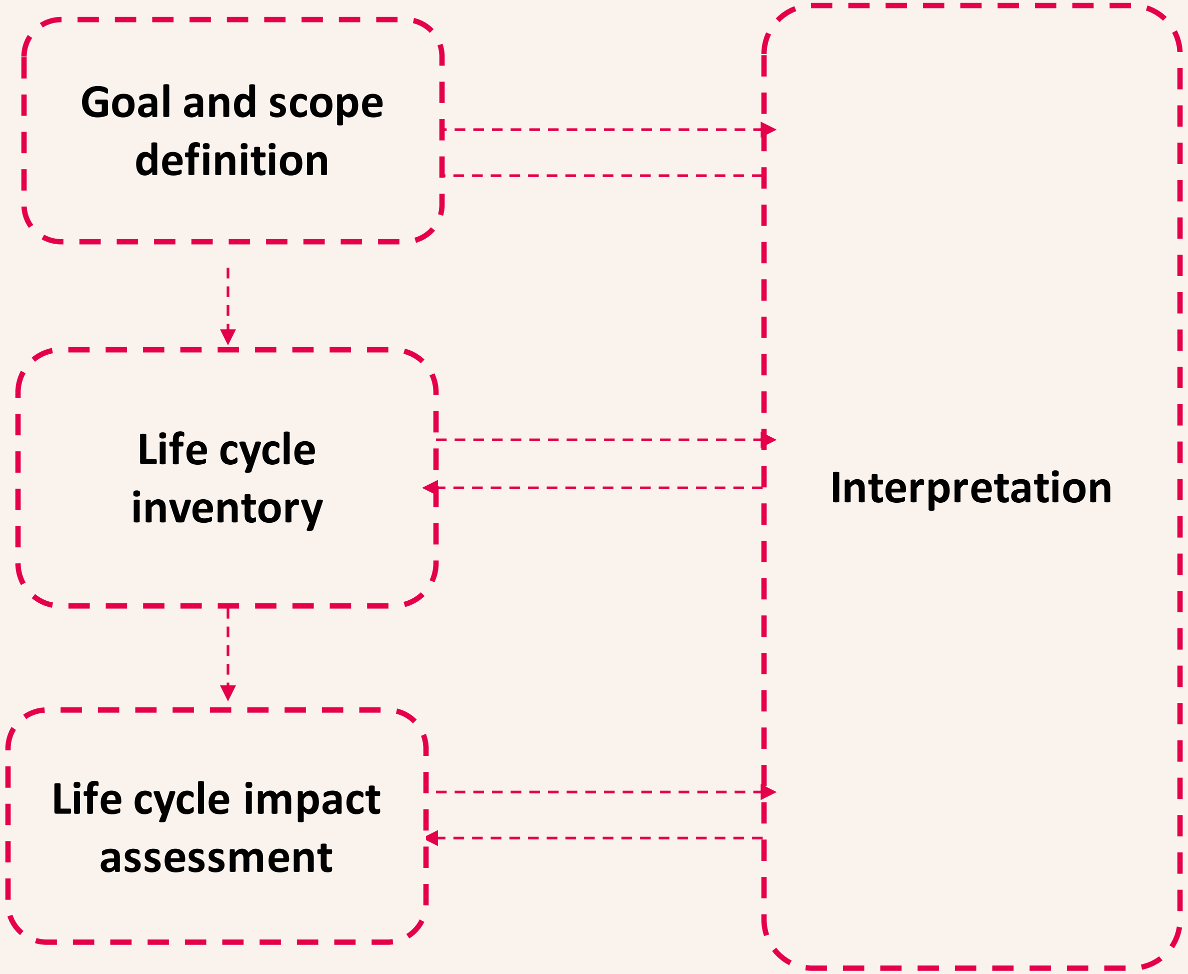
- To complement available and collected primary data, background databases can fill the gaps (secondary data)

Consider the right impact indicators for your context:

- Select the impact indicators for the assessment based on your context
- Avoid **tradeoffs** by using a multi-indicator approach

ISO NORMS 14 040 + 14 044 (2006) FOR LCA

International Organization for Standardization



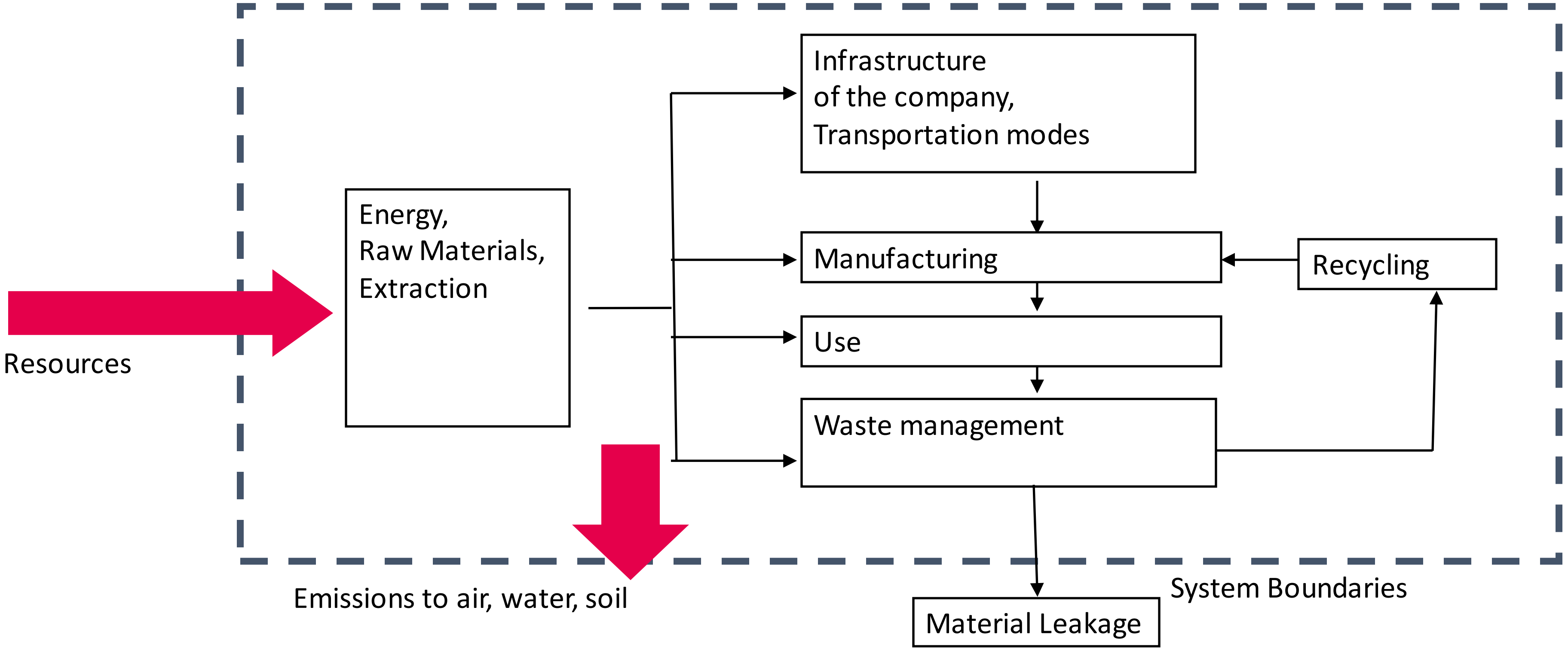

*"All the really important mistakes
are made on the first day."*

GOAL AND SCOPE

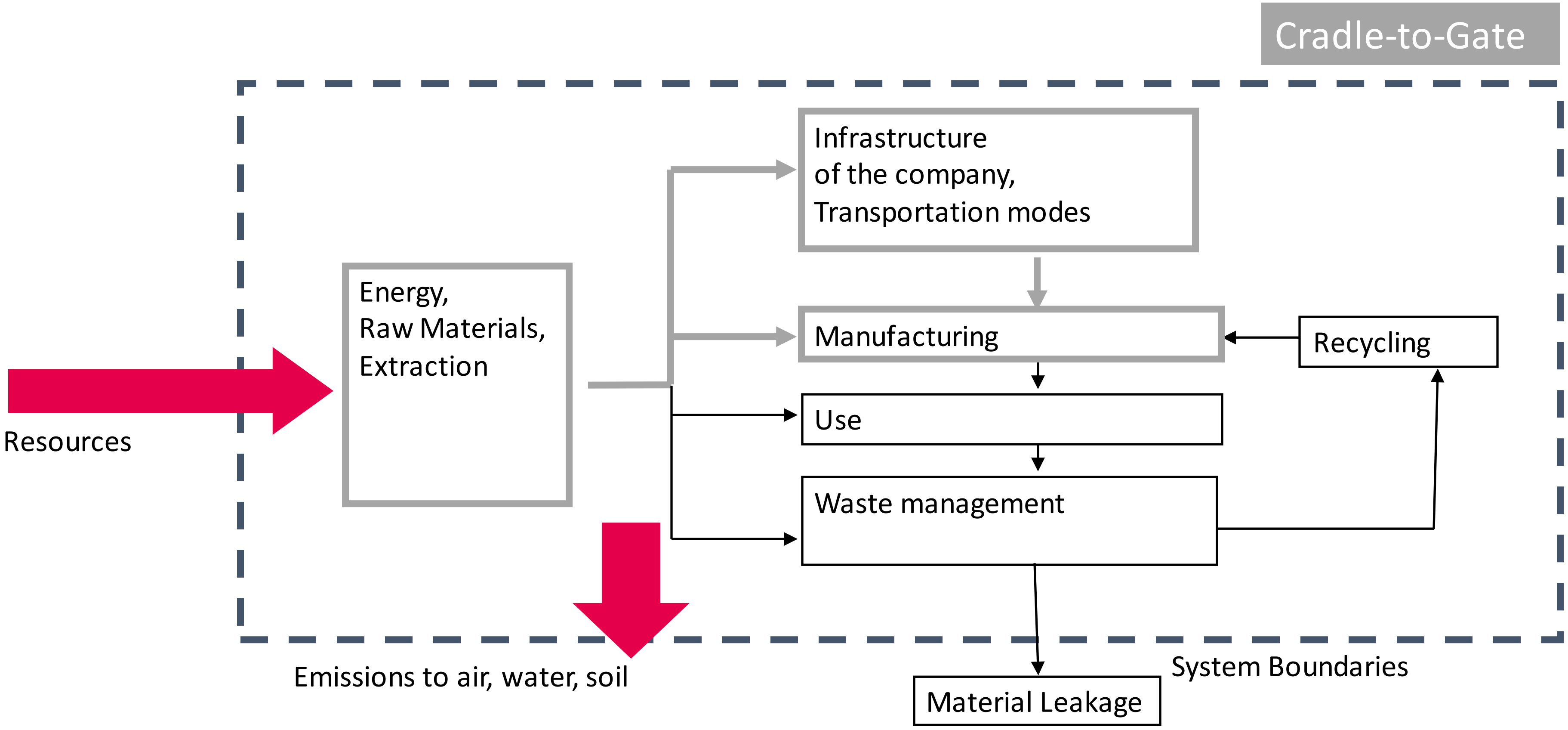
The scope includes the following items:

- **Product system** to be studied
- **Functions** of the product system or, in the case of comparative studies, the systems
- **Functional Unit (FU)** and **reference flow**
- System **boundaries**
- **Allocation** procedures
- **Impact categories** selected and methodology of impact assessment
- Data requirements; **assumptions; limitations**
- Initial data quality requirements
- **Type of critical review, if any**
- Type and format of the report required for the study

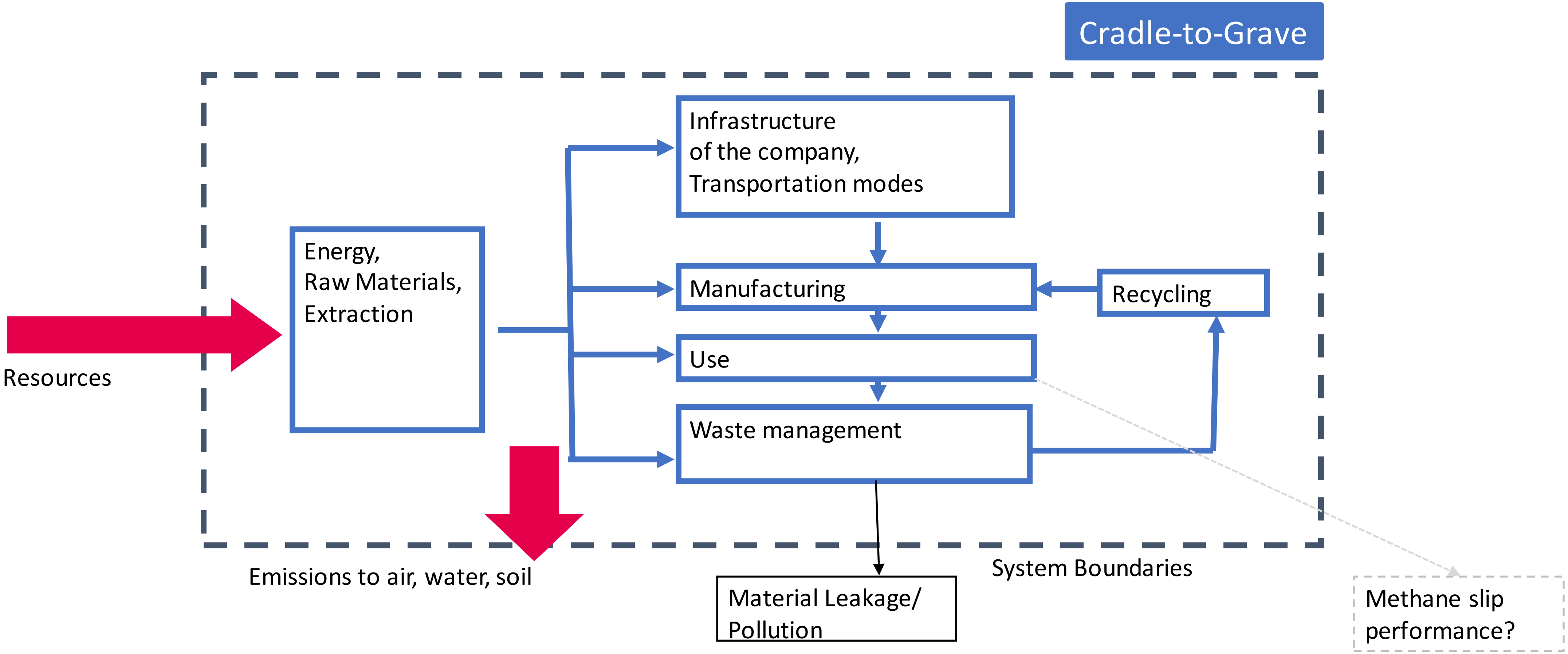
SYSTEM BOUNDARIES



SYSTEM BOUNDARIES



SYSTEM BOUNDARIES

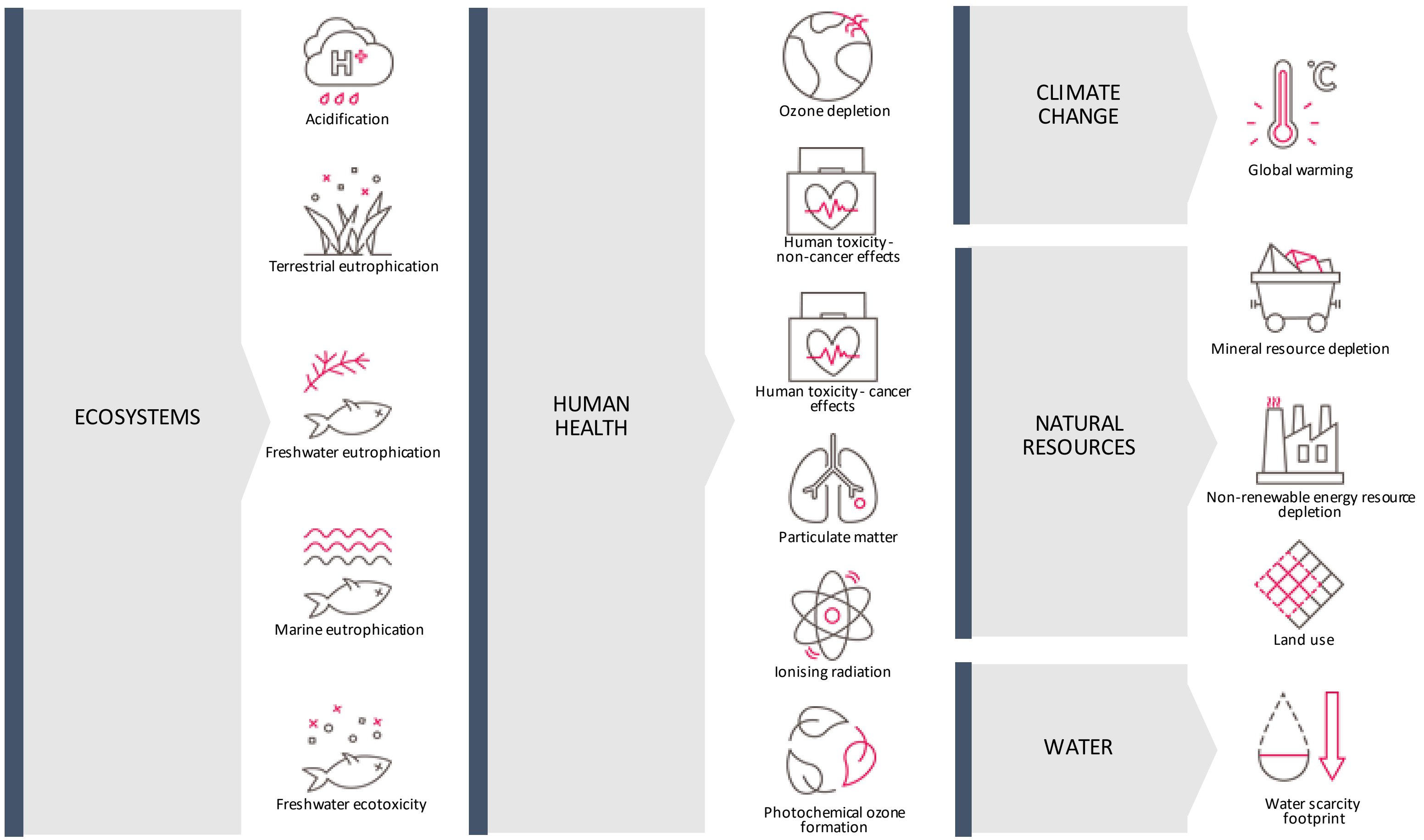


- Cradle-to-Cradle: Regenerative design, turning waste into product (=no more waste)
- Gate-to-Gate: Gate-to-gate is a partial LCA looking at only one value-added process in the entire production chain

IMPACT ASSESSMENT, ENVIRONMENTAL FOOTPRINT (EF) METHOD

Choice of LCIA method depends on

- Type of indicator desired; mid-point, end-point, single score…
- Single score helps to see if a big contributor is missing
- Subject of the project; characterization factors of an indicator.
- EF3.1 LCIA method is recommended if the sector of interest is covered by the methodology



Keep in mind…

- LCA evaluates potential impacts and produces relative results
- LCA provides a hot spot view but depending on the context, it needs to be complemented by other additional insights
- LCA is not risk assessment
- There is uncertainty associated with data and results

LCA - Assessment, action, accountability

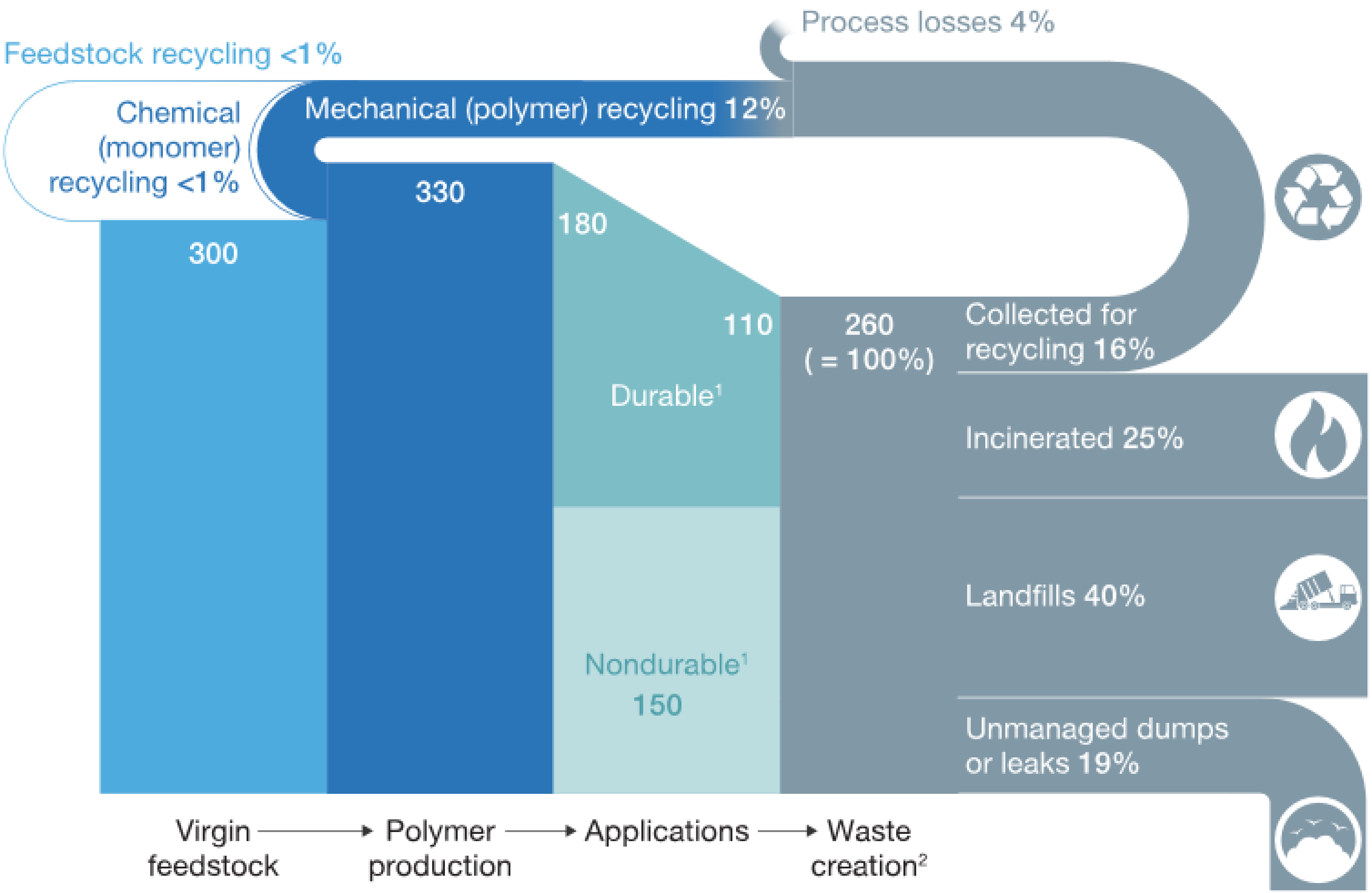
LCA is not a treasure map …

it is our compass to sustainability

04

Biobased solutions in context

PLASTICS: FROM A LINEAR MODEL



Global polymer flows 2016 (*McKinsey*)

MAIN CONCERNS:

- Contribution to climate change
- Plastic leakage and pollution

PLASTICS: A NEW PARADIGM

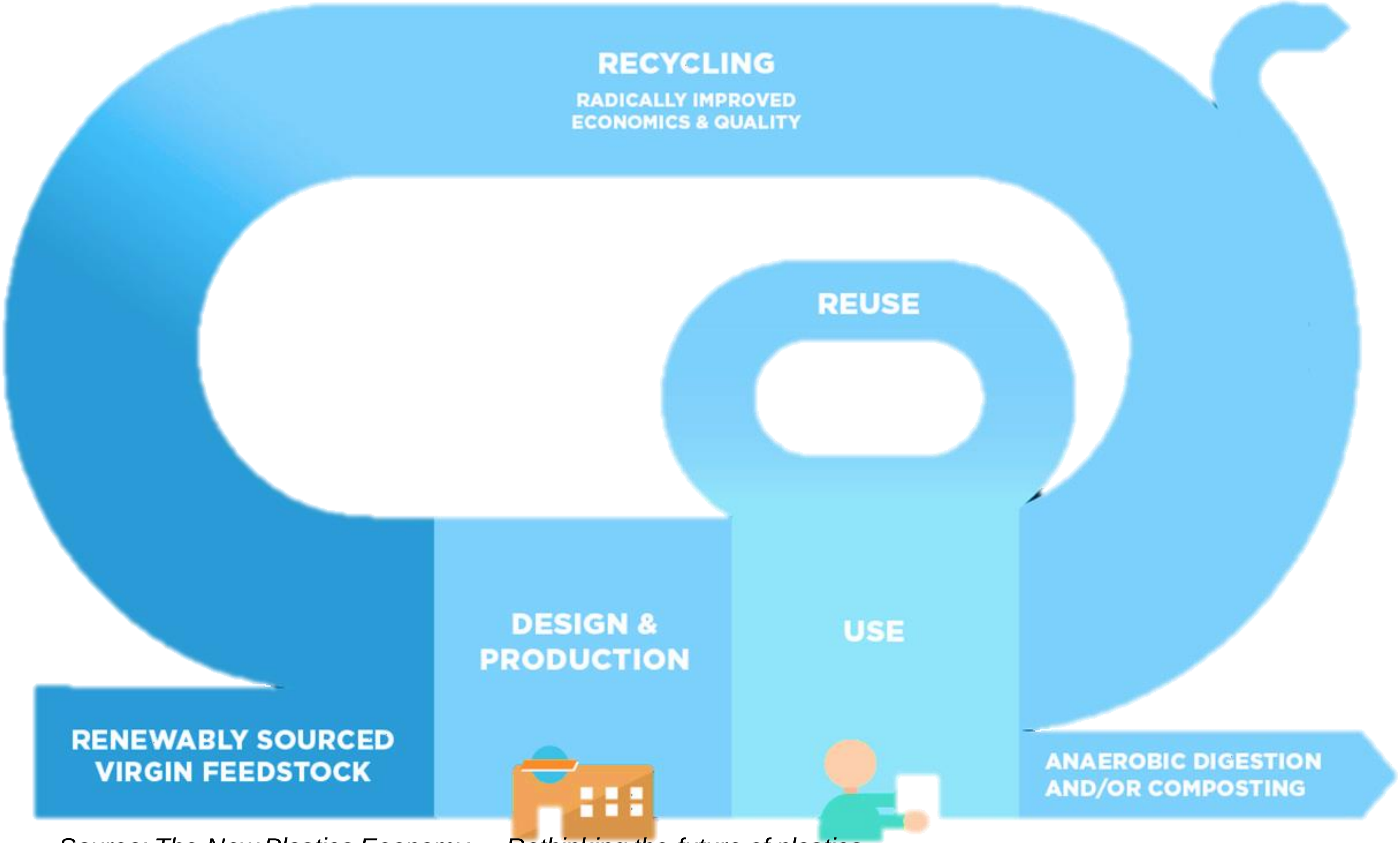
- Plastic is not the problem. The problem is the way we use use & dispose plastic
- We need to rethink the future of plastics

SPECIFIC ACTIONS

- Create an effective after-use economy
- Reduce the plastic leakage into the environment
- **Decouple plastic from fossil feedstocks**
- **Biobased plastic as a source to “close the loop”**

Source: *The New Plastics Economy — Rethinking the future of plastics*

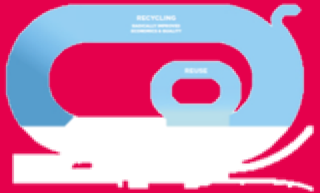
PLASTICS: TO A CIRCULAR MODEL



Source: *The New Plastics Economy — Rethinking the future of plastics*

Solutions

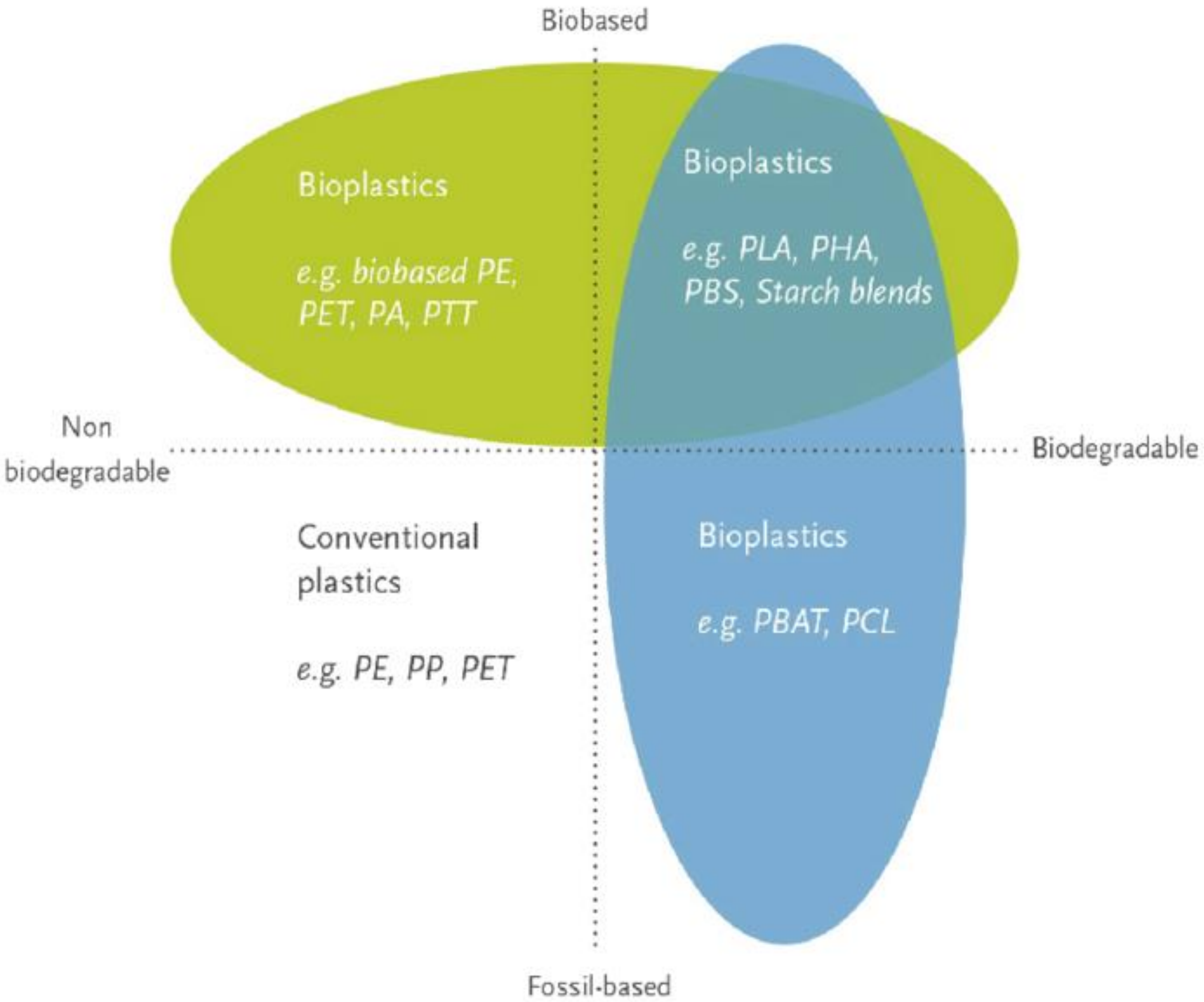
RECYCLED
"Re-circulating" the feedstock



BIOBASED
Renewable feedstocks

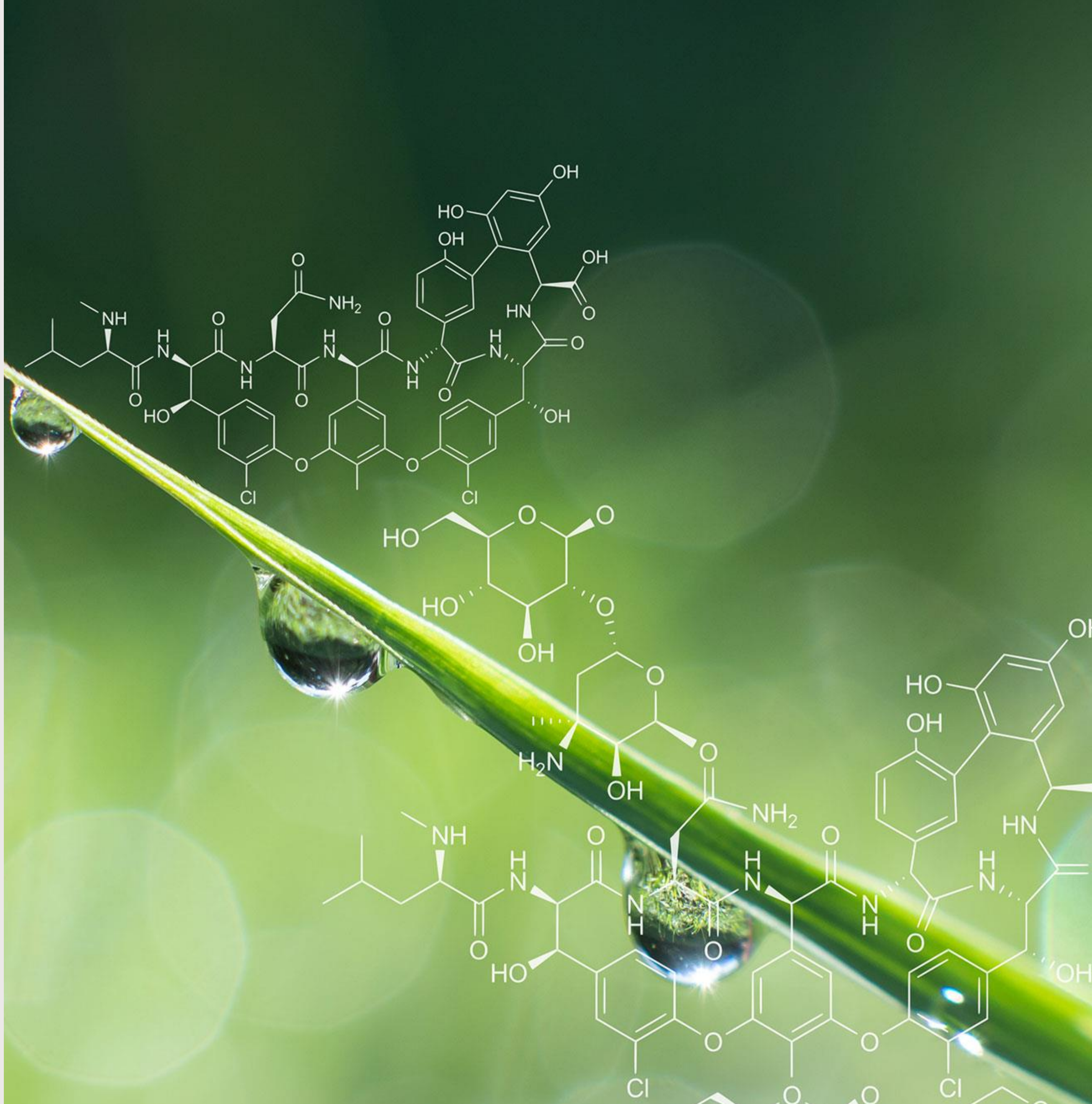
BIODEGRADABLE/COMPOSTABLE
Degrade in «natural» environment

BIOBASED
≠
BIODEGRADABLE

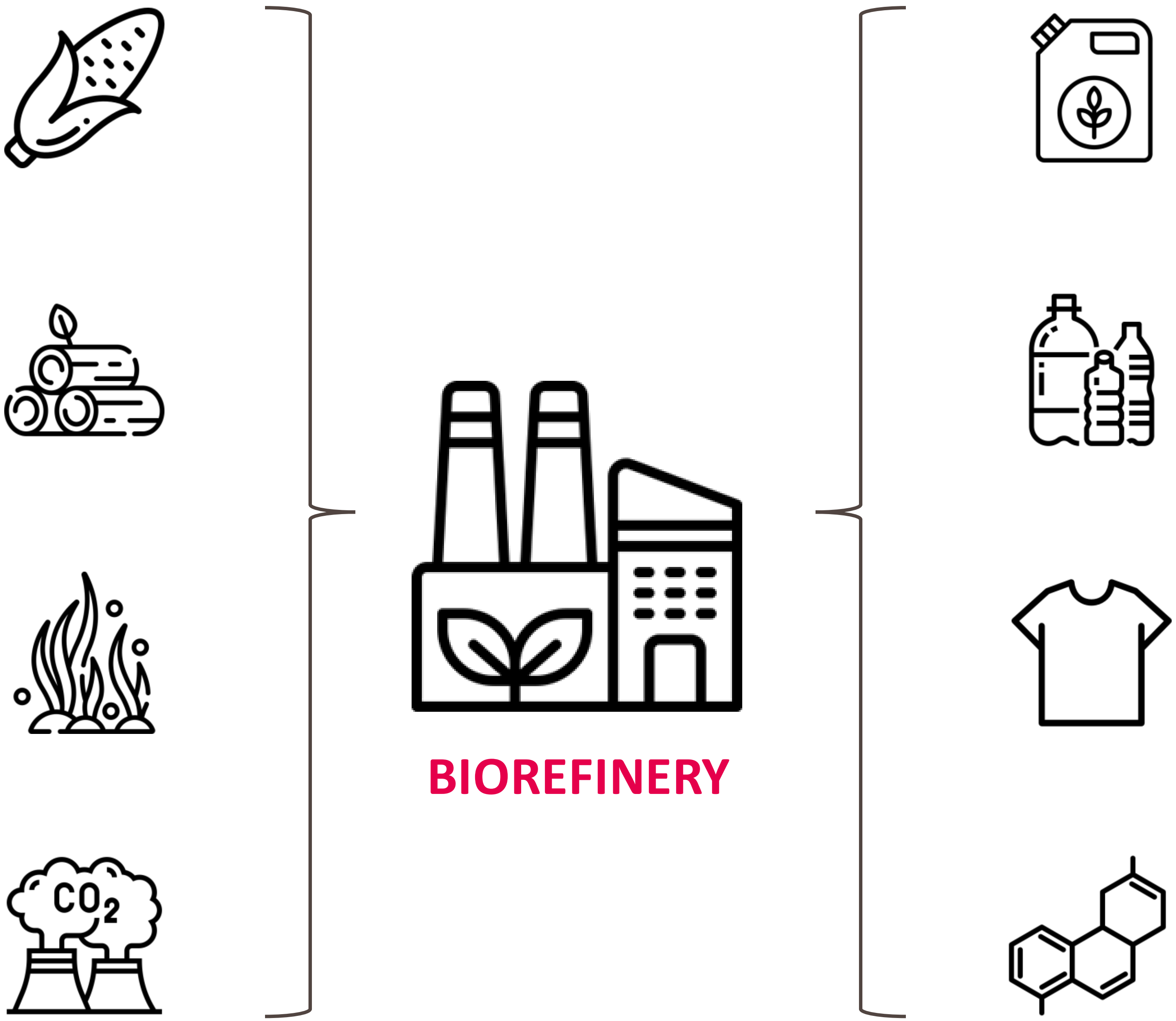


COMPOSTABLE

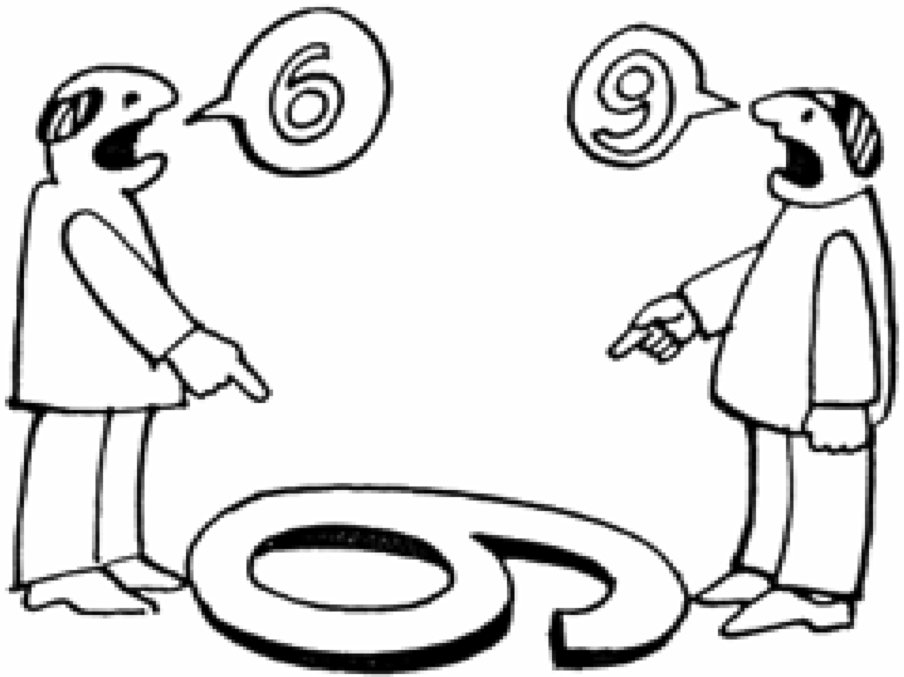
DROP-IN
VS
INNOVATIVE



BIOBASED FEEDSTOCKS



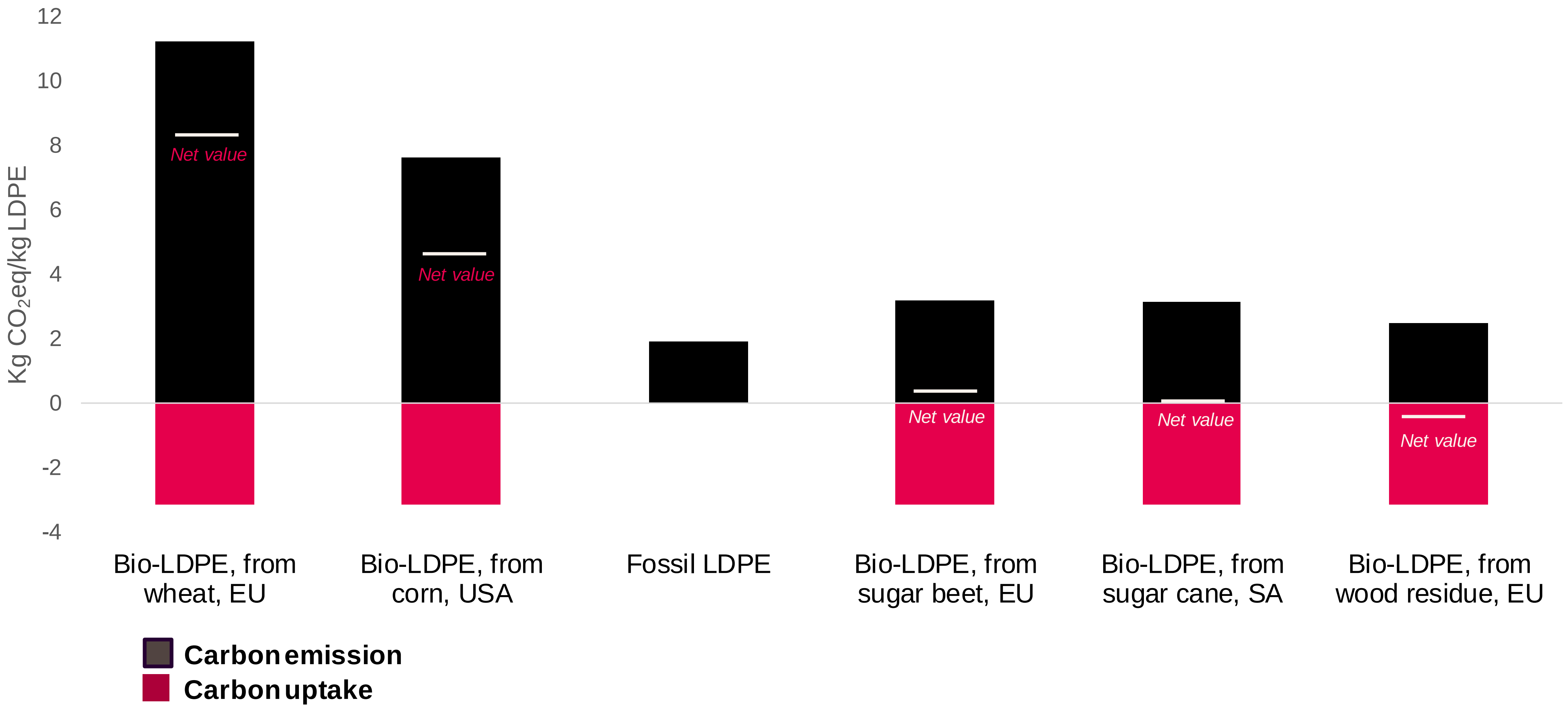
BIOBASED PLASTICS: YES OR NO?



Feedstock plays a key role

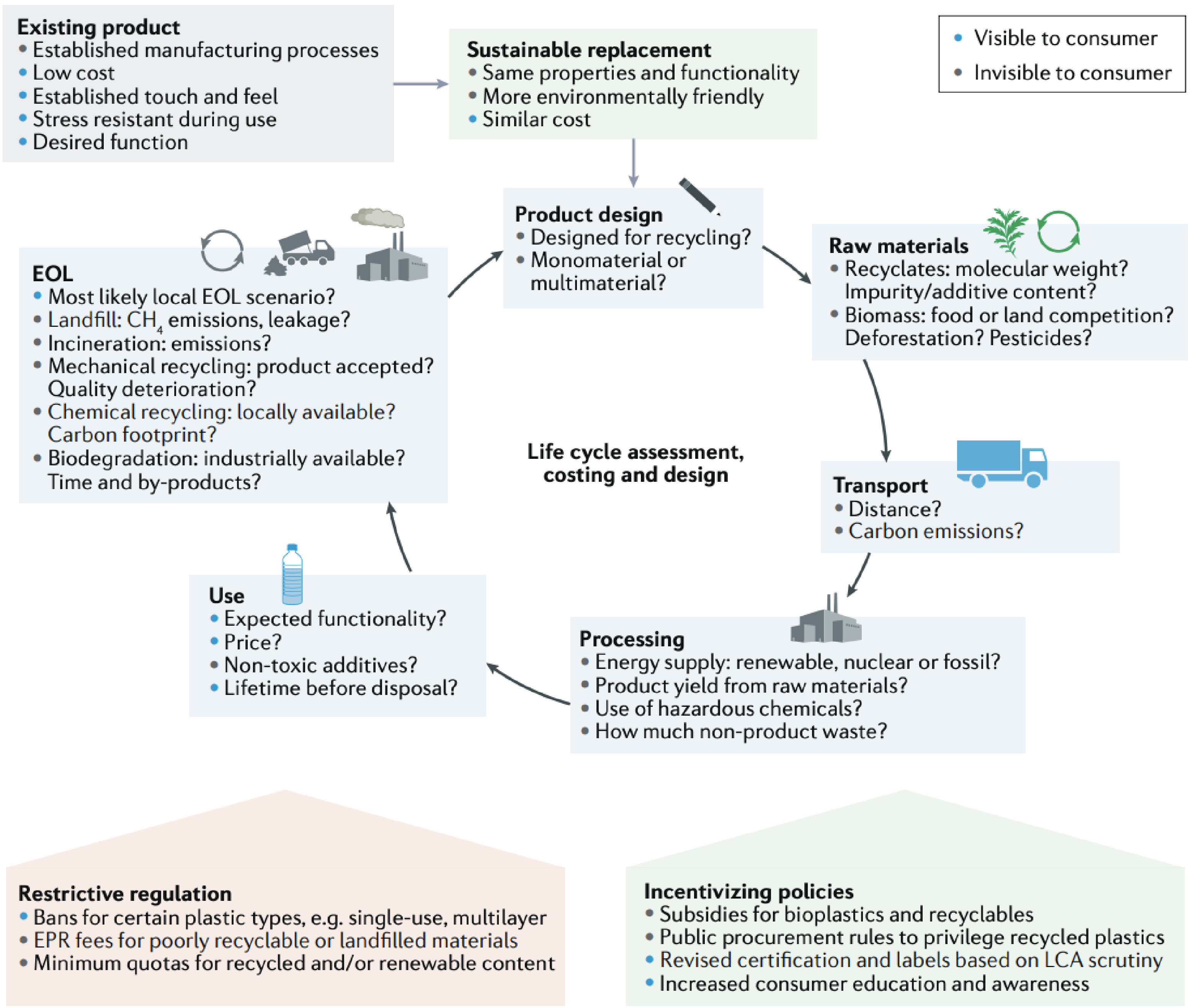
CLIMATE CHANGE
kg CO_2-eq / kg LDPE

Cradle-to-gate analysis



Implementation Framework –

Switching to biobased materials



source: Rosenboom, Jan-Georg, Robert Langer, and Giovanni Traverso. "Bioplastics for a circular economy." *Nature Reviews Materials* 7.2 (2022): 117-137.

Key takeaways

What are the 3 key things about LCA to walk away with?

1 LCA is your sustainability compass.

It's not about the number itself. LCAs can show you the right way forward in your sustainability journey
.

2 Strive for progress over perfection.

Sustainability is a journey and an extremely complicated matter. Be aware about what you don't know, focus on transforming the hotspots of your value chain and let LCAs monitor your actions.

3 Go beyond the carbon tunnel vision.

By adopting a multi-indicator approach, LCAs can thoroughly show the impact of your business on the environment, pointing you towards the right decisions and stopping you from just shifting the burden.

What are the 3 key things about biobased solutions to walk away with?

1 Biobased does not necessarily mean more sustainable

Biobased products can clearly be an improvement over petroleum products with respect to climate change; however, not all bio-based resources generates the same environmental outcome (e.g. 1st vs. 2nd gen feedstock).

2 Understand & capture ecosystem trade-offs

One metric ton (t) of biobased polymers can save, relative to conventional alternative, 55 ± 34 gigajoules of primary energy and 3 ± 1 t carbon dioxide equivalents of greenhouse gases. However, biobased materials may increase eutrophication by 5 ± 7 kilograms (kg) phosphate equivalents/t and stratospheric ozone depletion by 1.9 ± 1.8 kg nitrous oxide equivalents/t.

3 Define an implementation framework

Transitioning to sustainable plastic replacements requires companies to balance functionality, cost, and environmental considerations, while complying with regulations and certification rules.

Thank you

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