Bio-based copolymers for membrane end products for gas separations

Demonstration of Biocomem membranes at TRL 4 and TRL 5

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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

$$dn = -JSdz$$

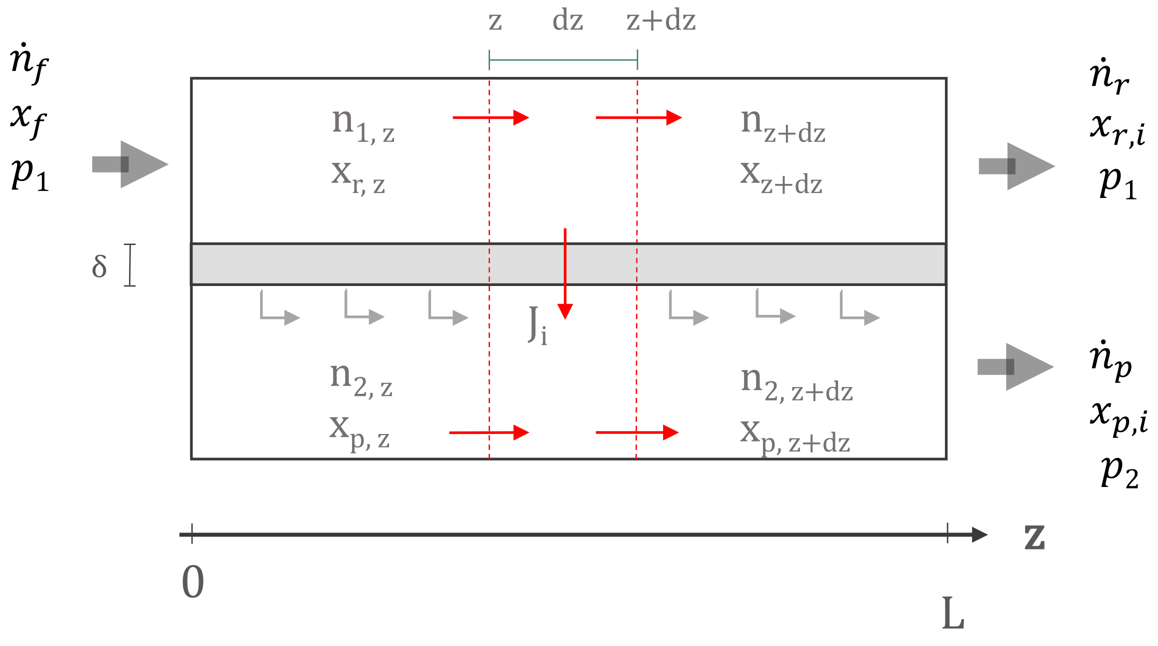
$$d(nx_{i,r}) = -J_i S dz$$

- **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**

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



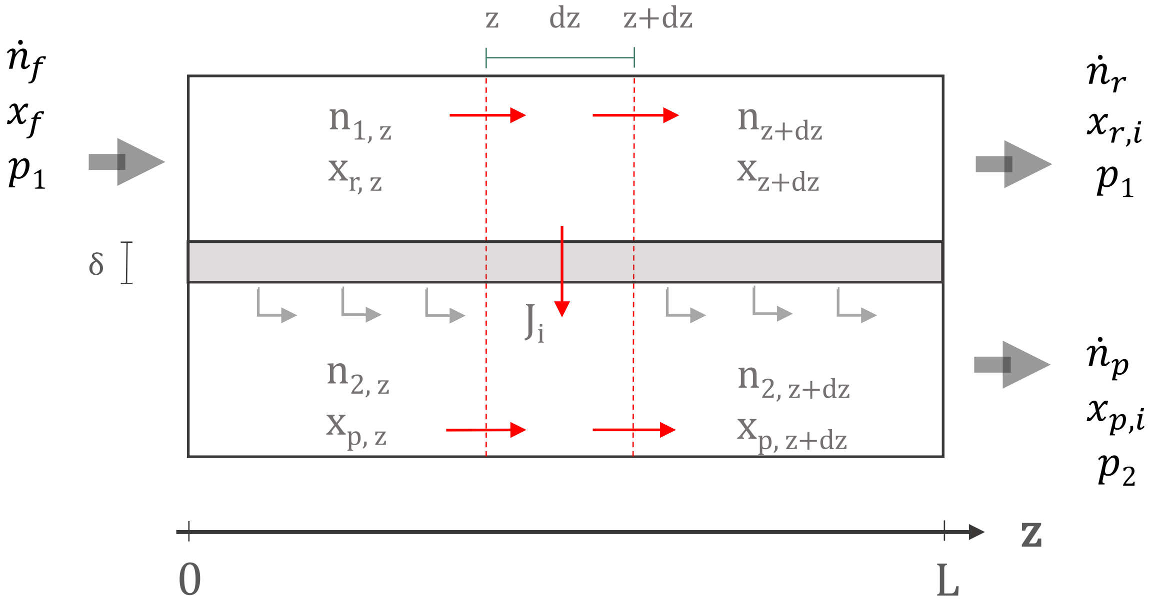
The system includes $\mathbf{2n+2}$ coupled differential equations (where $\boldsymbol{n}$ represents the number of species in the feed gas mixture).

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

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



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:

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

where:

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

$$A = S N_f L$$

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

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

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:

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

$N_f = 800$

$A = 0.38\ m^2$

$L = 0.38\ m$

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

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

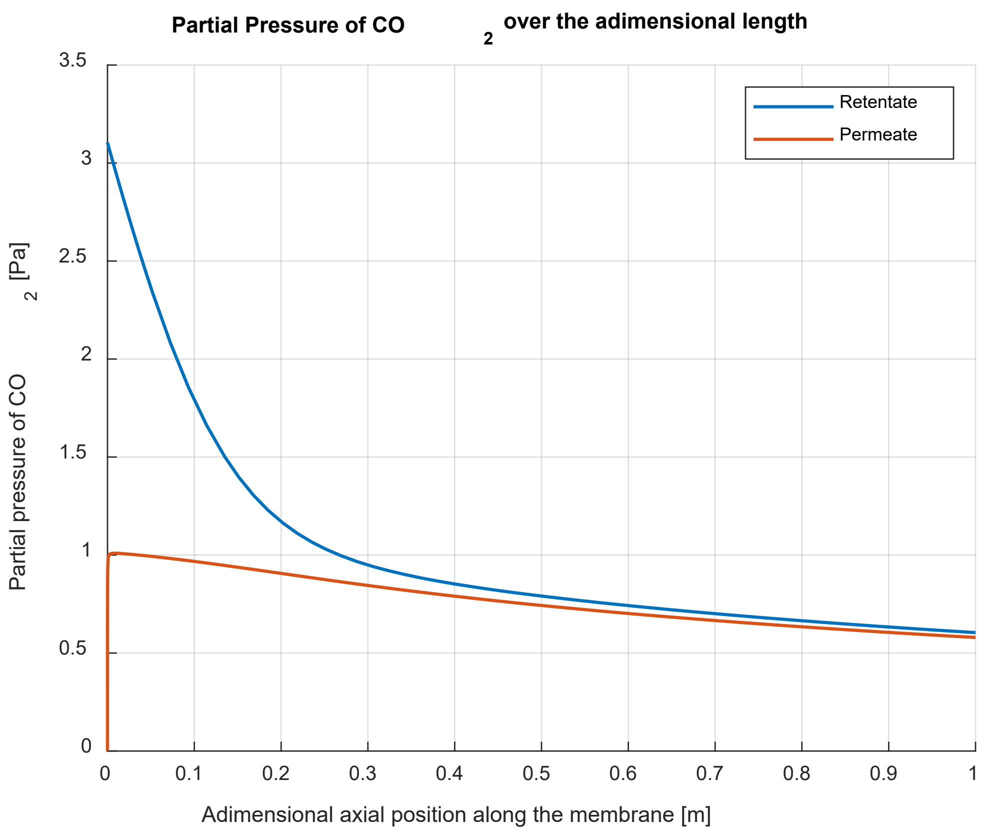
$x_{f,CH_4} = 0.645, \quad x_{f,O_2} = 0.01, \quad x_{f,CO_2} = 0.345$

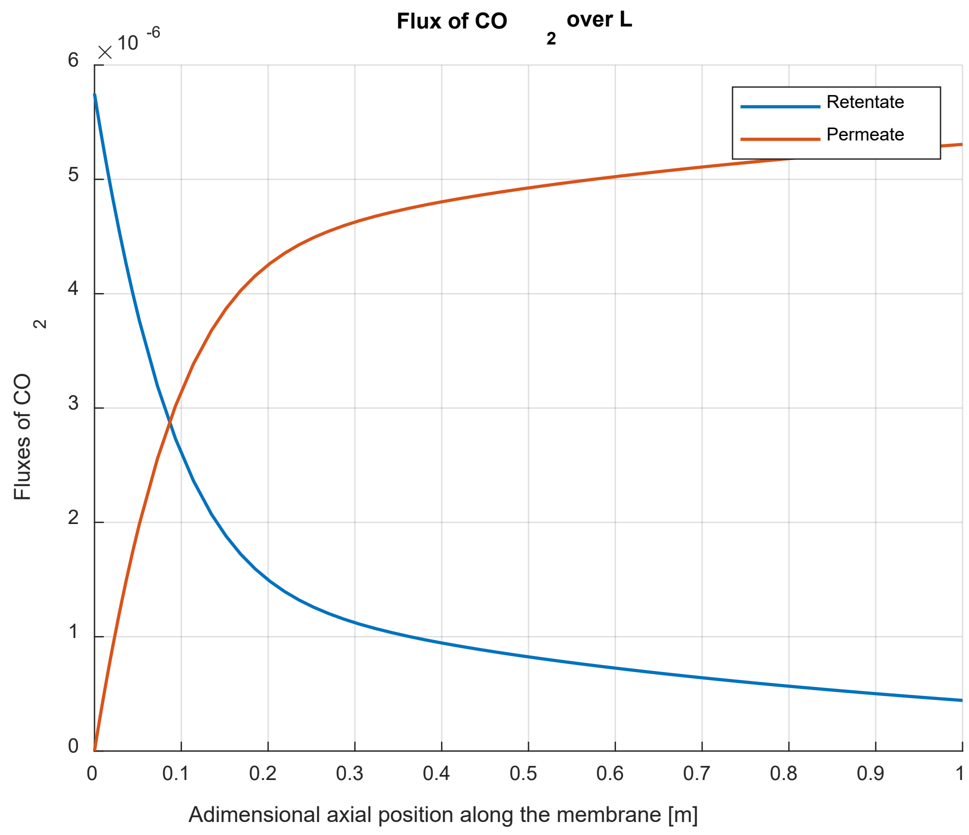
$p_1 = 9\ bar$

$p_2 = 1.1\ bar$

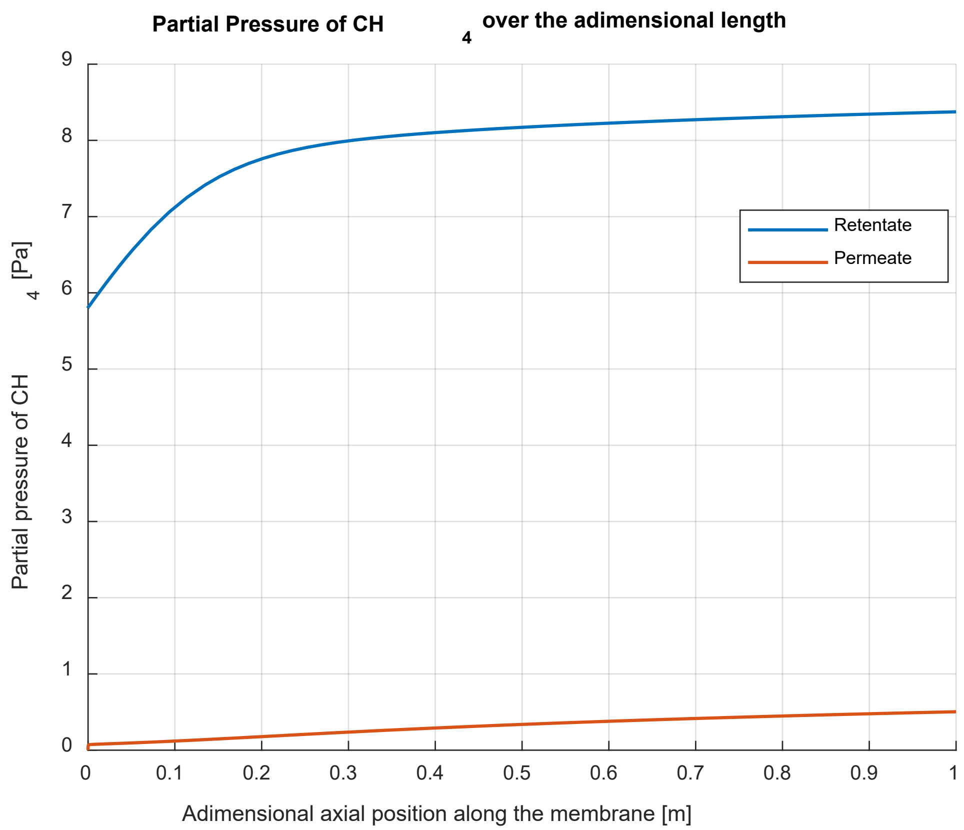
Makaruk et al., Numerical algorithm for modelling multicomponent multipermeator systems, (2009)

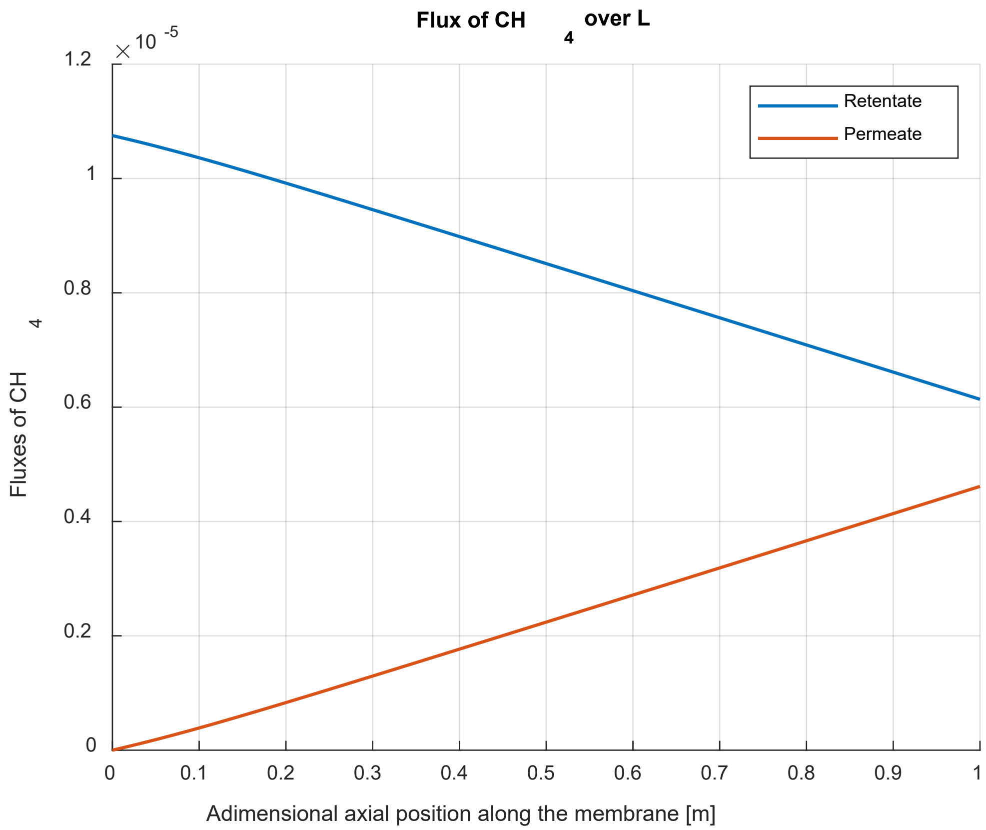
Partial Pressure and Retentate/Permeate Flux (CO_2)



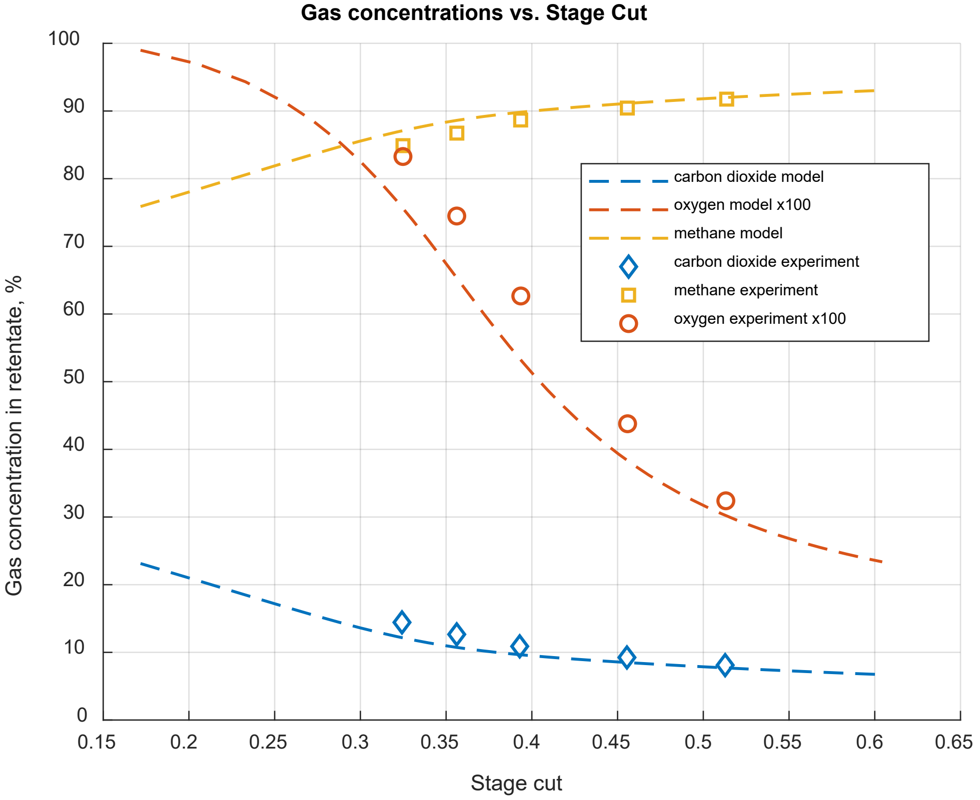


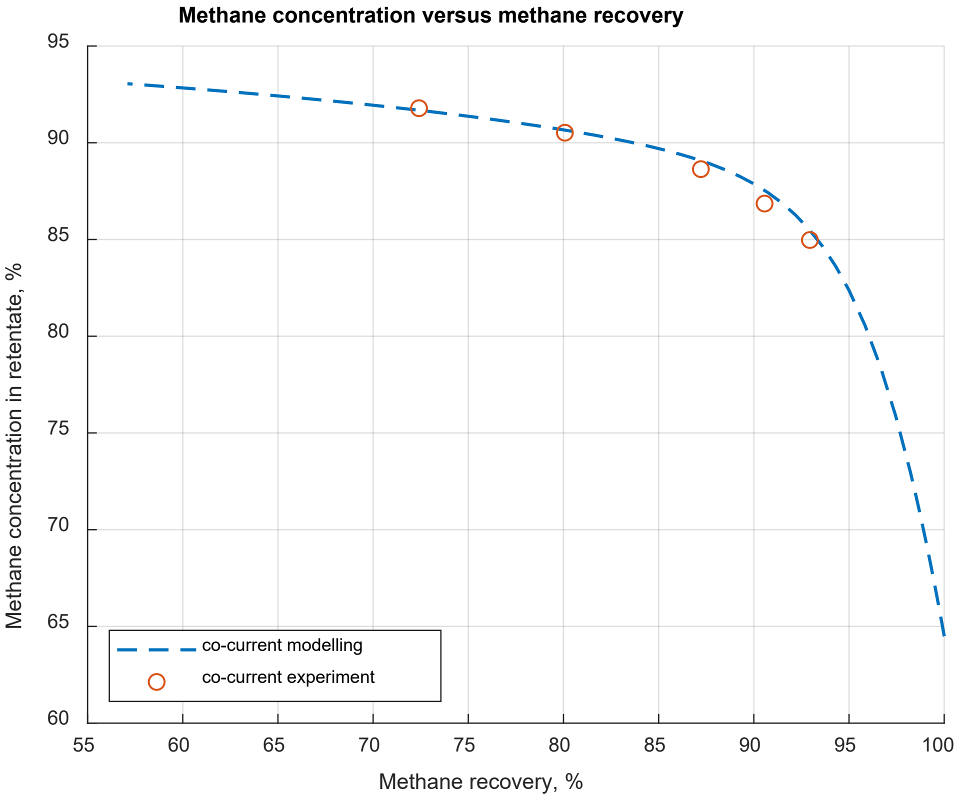
Partial Pressure and Retentate/Permeate Flux (CH_4)





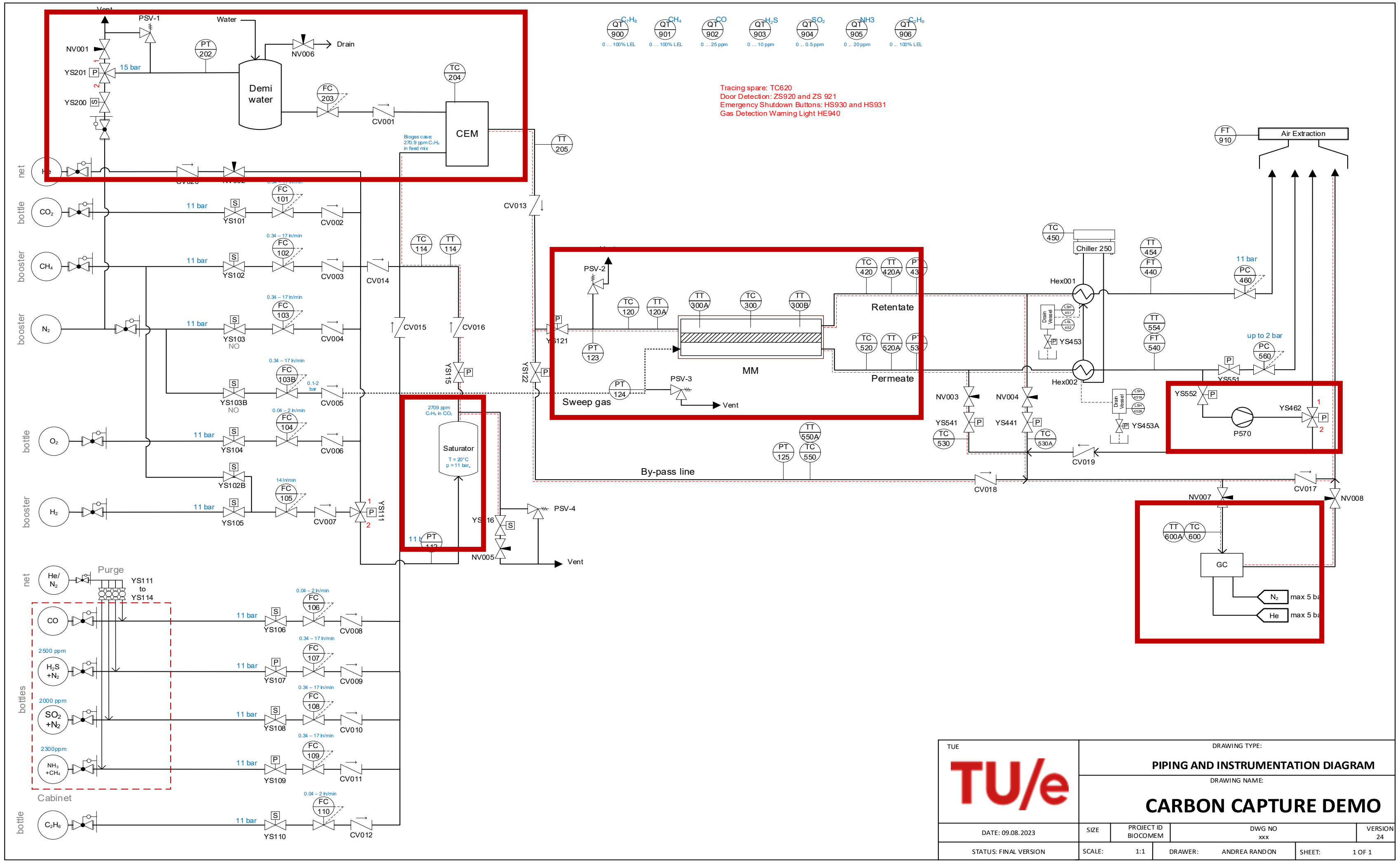
Model Validation





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)

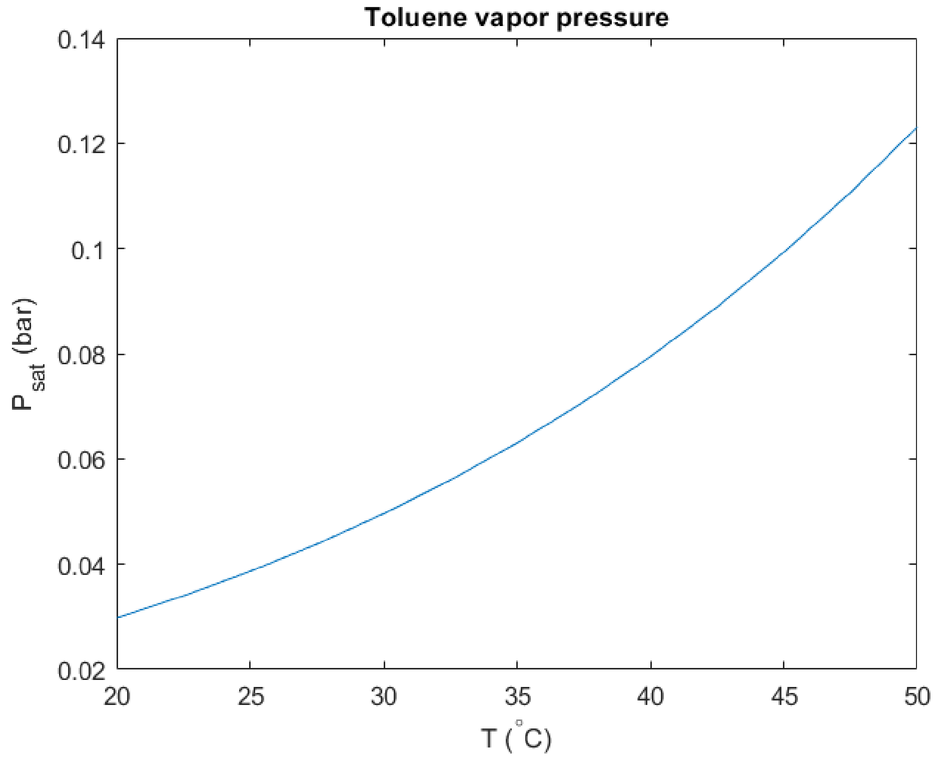
Feeding toluene

- 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.

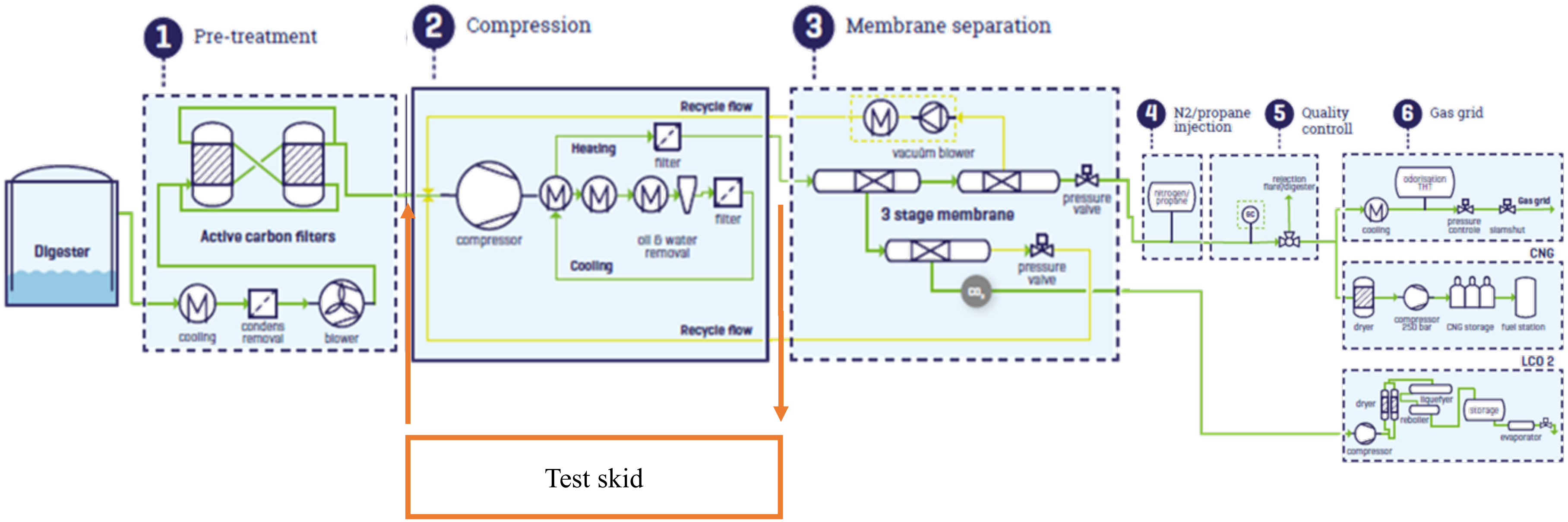
ii. Run the aging tests with the real gas composition and the pollutants at a concentration defined below. The cycle will be operated until the loss of performances of the membrane.

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

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

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

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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