tecnalia

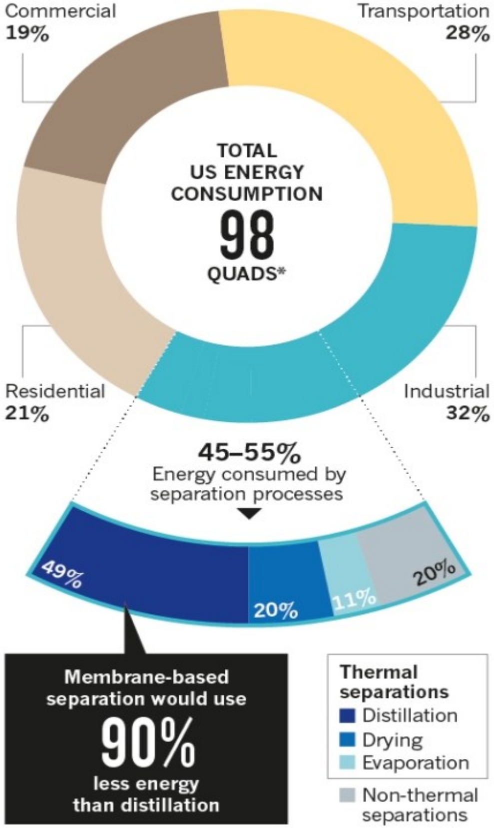
MEMBER OF BASQUE RESEARCH
& TECHNOLOGY ALLIANCE

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

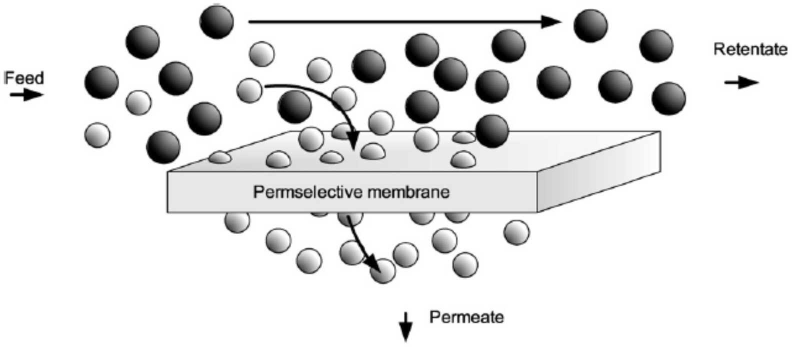
STRUCTURE

- Symmetric
- Asymmetric
  - Integral asymmetric
  - Composite

GEOMETRY

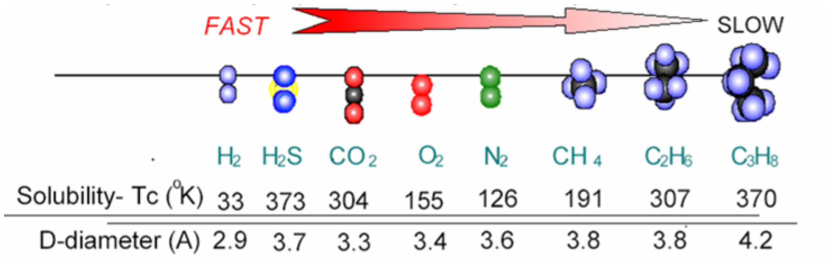
- Flat sheet
- Tubular
- Hollow fiber

POLYMERIC MEMBRANES: SOLUTION-DIFFUSION MODEL



$$P_i = S_i \cdot D_i$$

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



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

tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

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

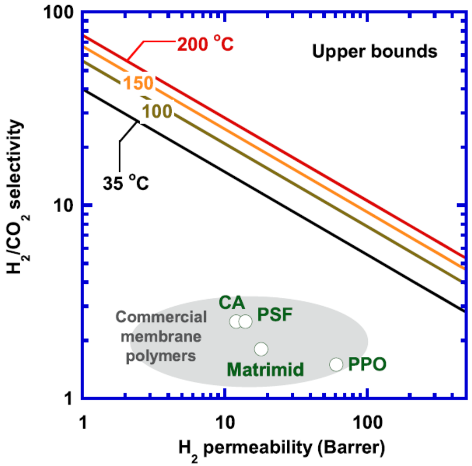
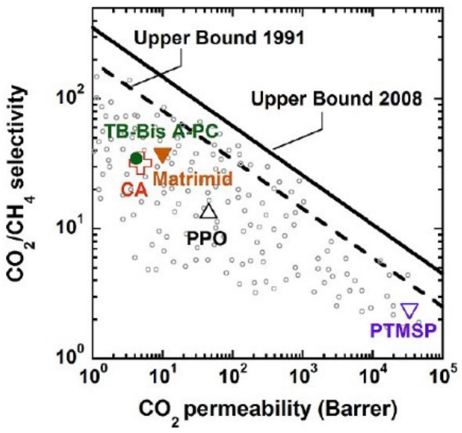
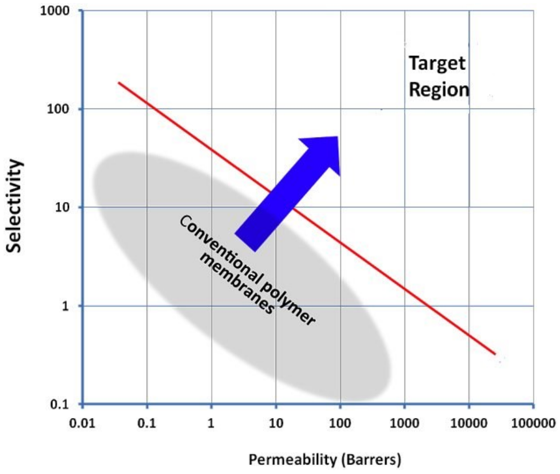


FIGURE 1 Upper bounds of H_2/CO_2 separation at 35, 100, 150, and 200 °C calculated using the parameters shown in Table 1.[11–13] The separation properties of commercial membrane polymers were determined at 35 °C. 1 Barrer = 10^{-10} cm^3 (STP) $cm/(cm^2\ s\ cmHg)$



CO_2/CH_4 Robeson diagram for conventional glassy polymers.

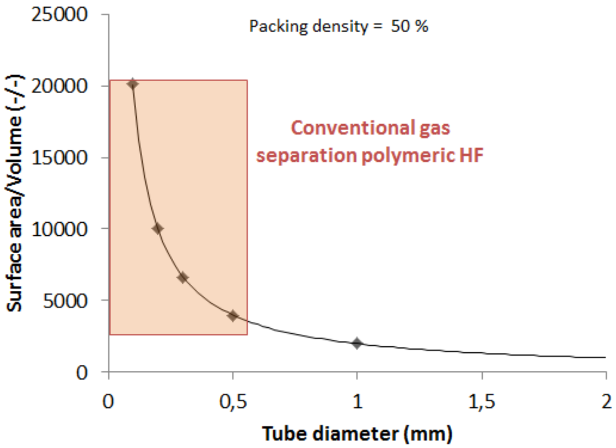


L. Hu, S. Pal, H. Nguyen, V. Bui, H. Lin, *J. Polym. Sci.* **2020**, *58*, 2467
M. Galizia, W. S. Chi, Z. P. Smith, T. C. Merkel, R. W. Baker, B. D. Freeman, *Macromolecules* **2017**, *50*, 7809

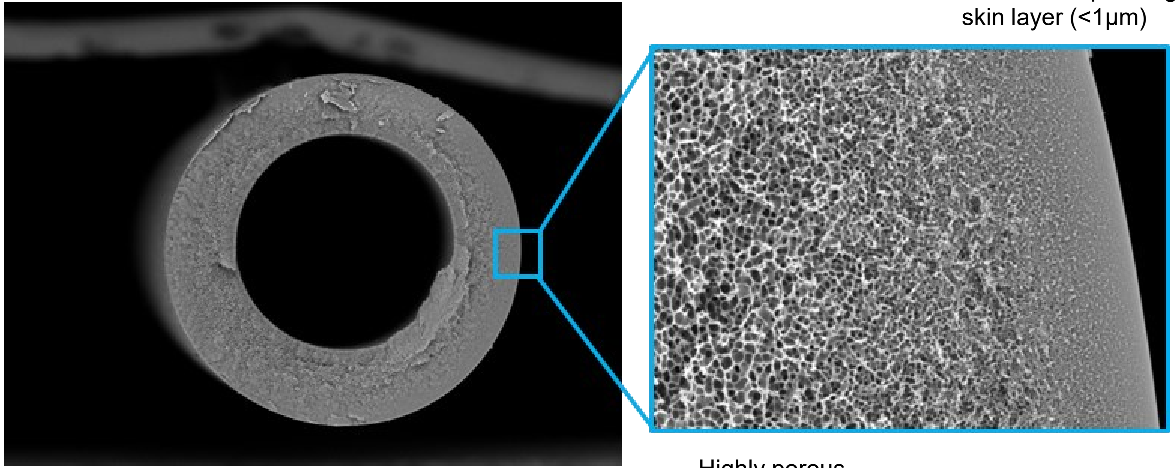
HOLLOW FIBER MEMBRANES

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



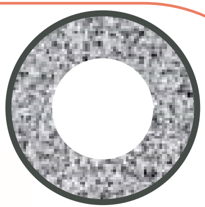
Asymmetric hollow fiber

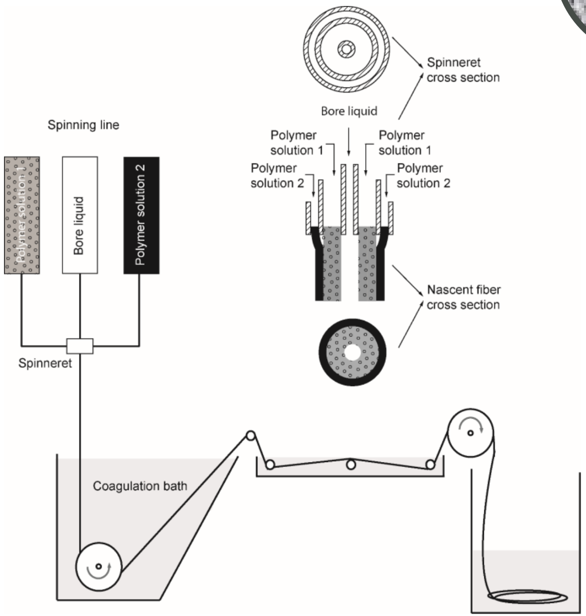


HOLLOW FIBER PREPARATION METHODS

SPINNING

Monolithic hollow fiber

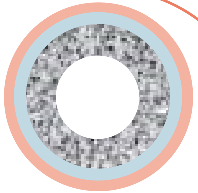


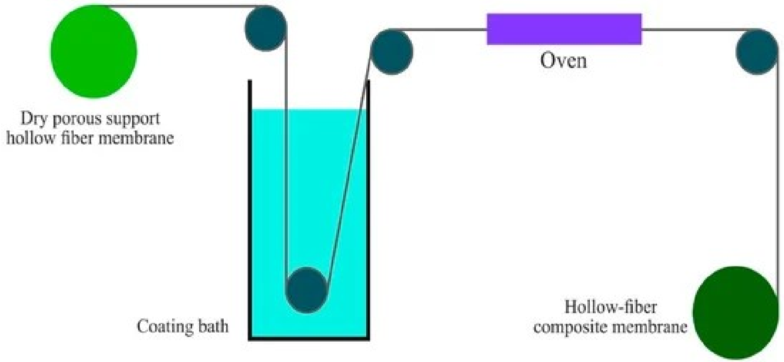


Single step process: simultaneous formation of the porous support + dense selective layer

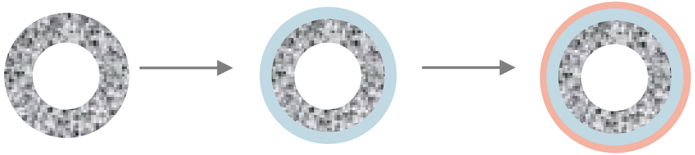
DIP COATING

Composite hollow fiber





Multiple step process



Porous support

Porous support
Gutter layer

Porous support
Gutter layer
Selective layer

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

MEMBRANE DEVELOPMENT STRATEGY

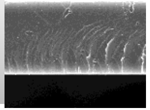
Defining target performance

↓

Material development and/or selection

↓

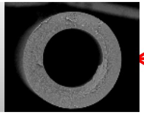
Dense film preparation and characterization



Intrinsic separation properties
Permeability and selectivity

↓ ✓

Hollow fiber preparation and characterization



Separation properties
Permeance and selectivity

↓ ✓

Possible to Scale-up, Prototype??

Example 1: “zero defects”

"zero defects"

P84 polyimide

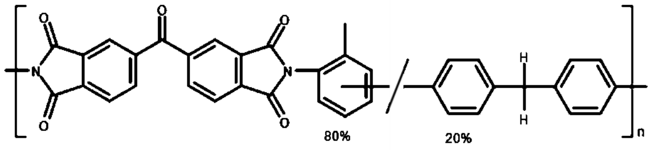
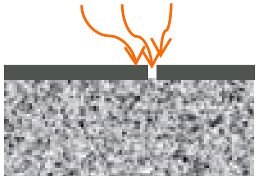
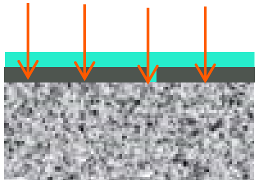


Table 2
Permeability and selectivity for P84 and Matrimid 5218 (25 °C)

	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.





membranes MDPI

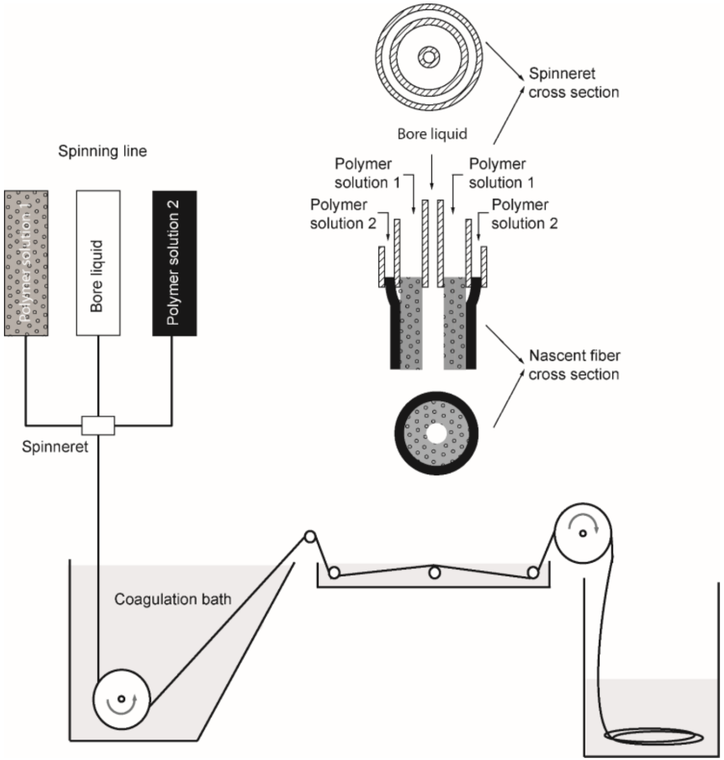
Article

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

Dope composition: key parameter

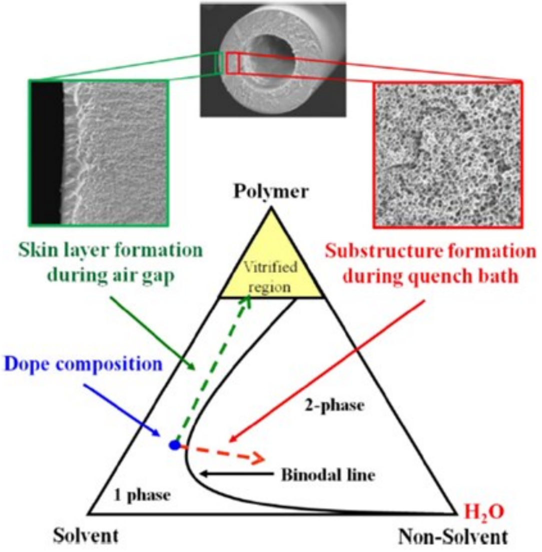


Figure. Gas separation asymmetric hollow fiber formation process represented in a ternary phase diagram

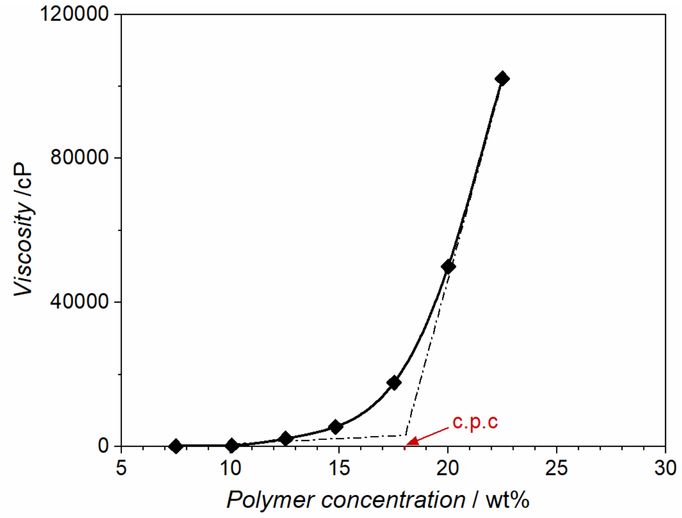


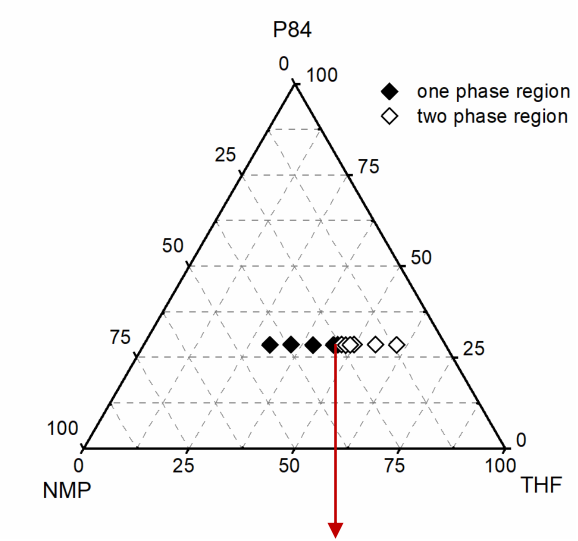
Figure 1.6. Typical viscosity versus polymer concentration curve and the determination of the critical polymer concentration, c.p.c.

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

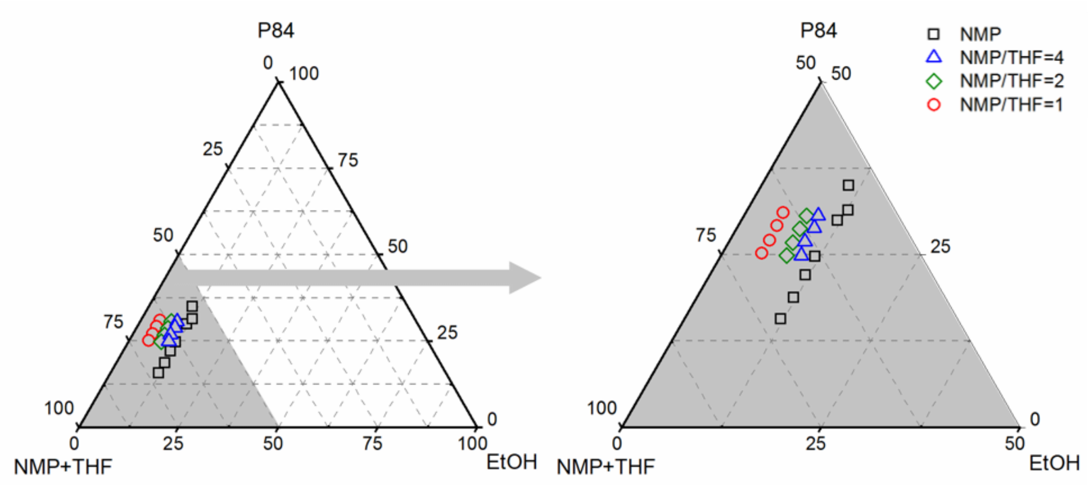
“zero defects”

Dope composition

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



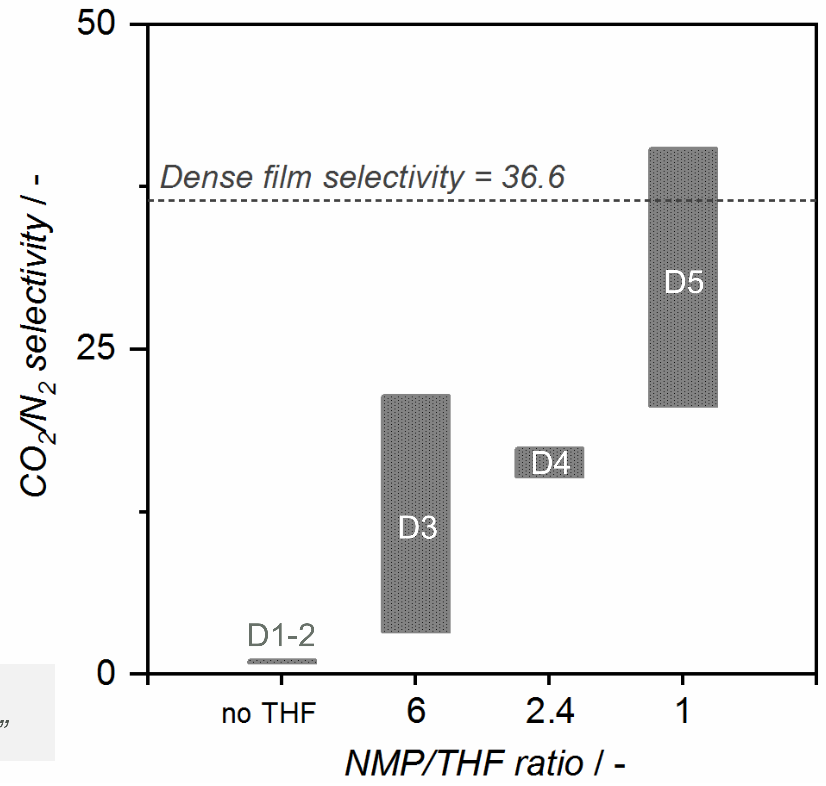
NMP/THF ratio = 0.52



"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"

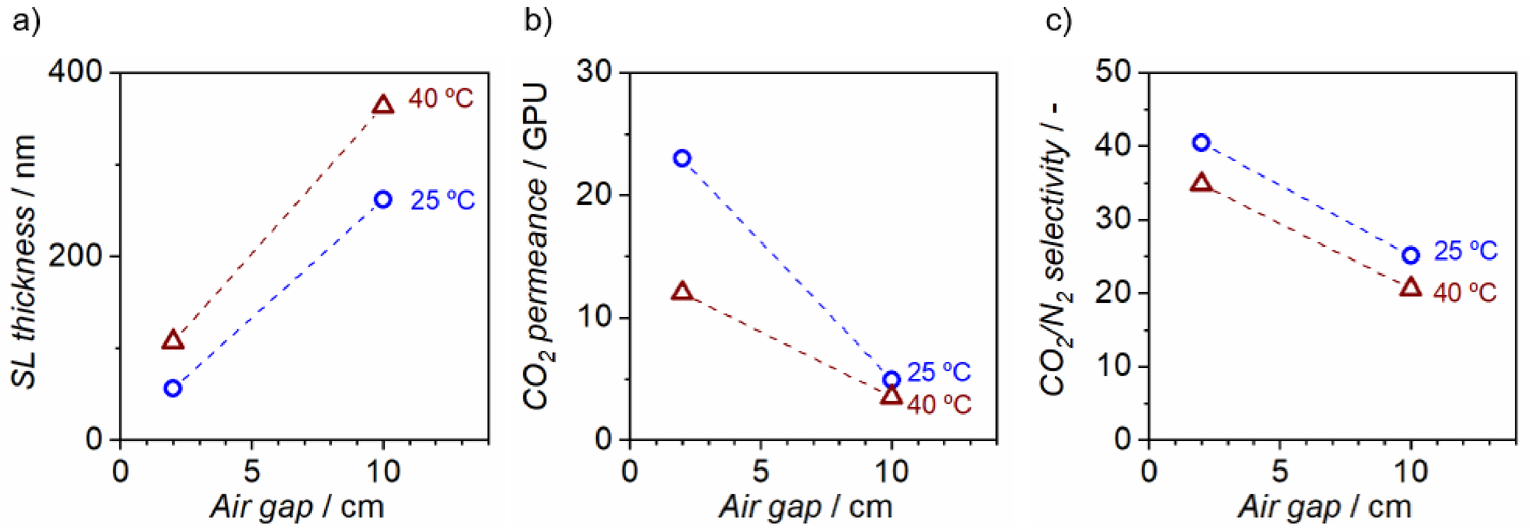
"zero defects"

Spinning sesión D05

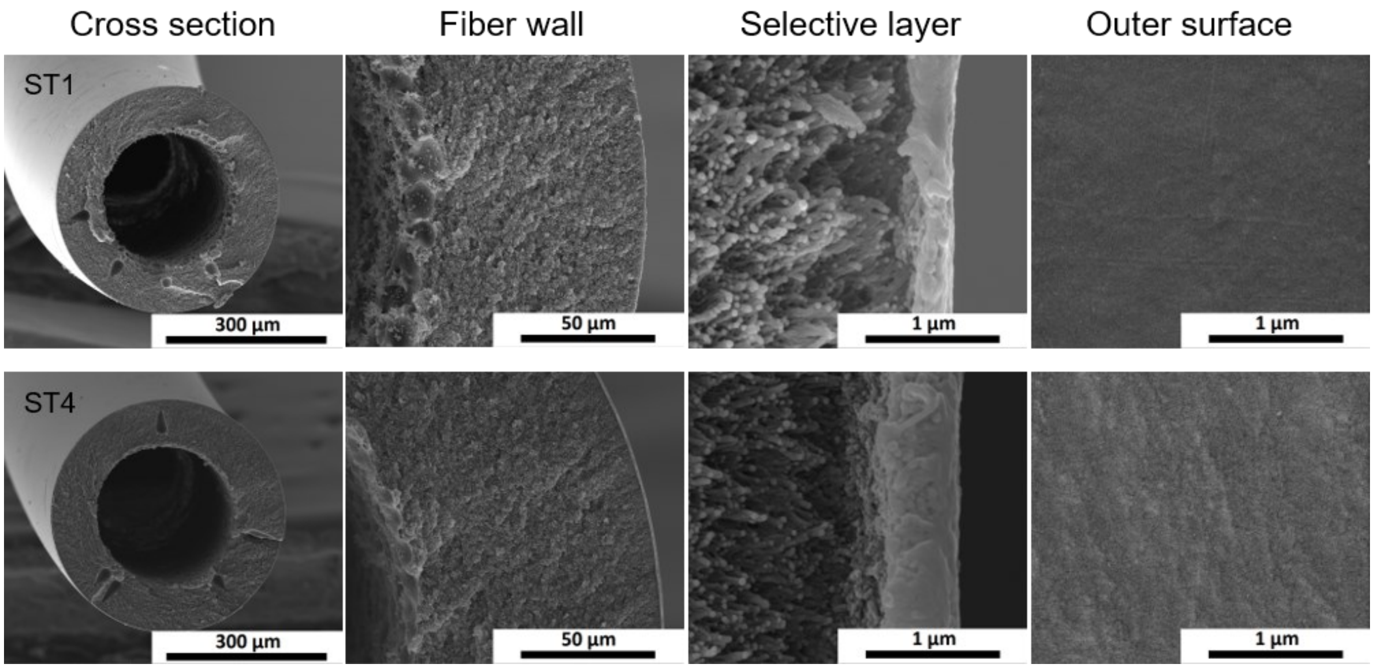
Spinning parameters influence:

- 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”



- 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

MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Example 2: “Bio-Based HF membranes”

RESEARCH LINES

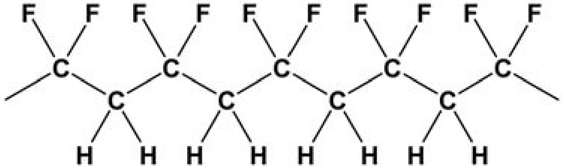
Co-polymer	Polyamide block	Polyether block	Main expected result
A **Reference bio-PEBAs**	Bio-based polyamide 11 derived from castor oil (PA_{ref}^{bio})	Fossil based polyether block (PE_{ref}^{fossil})	Composite HF Membrane
B **New bio-PEBAs Pathway 1** aromatic/cycloaliphatic polyamide-b-polyether	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

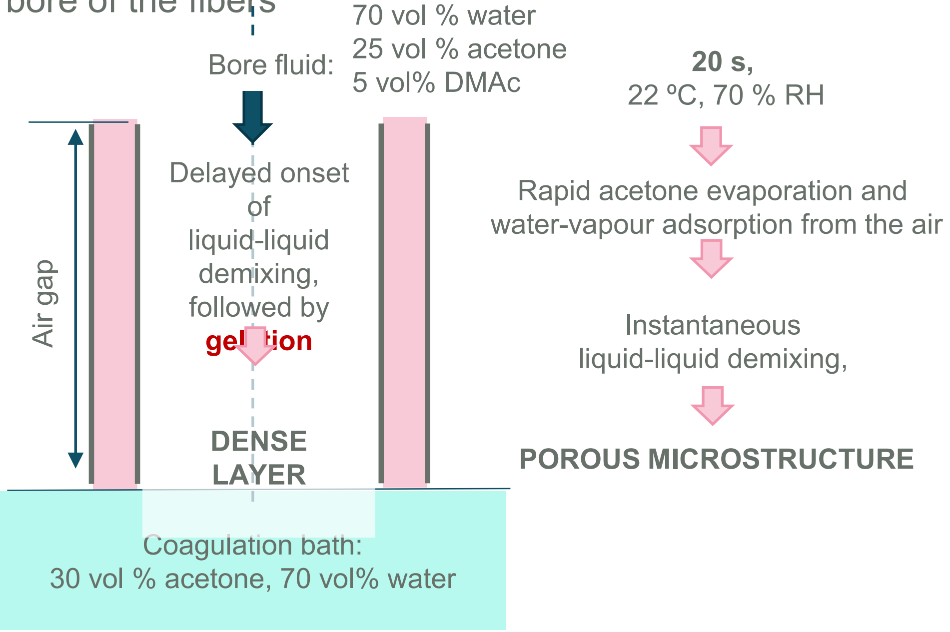
Prototype B – Polymer spinning

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



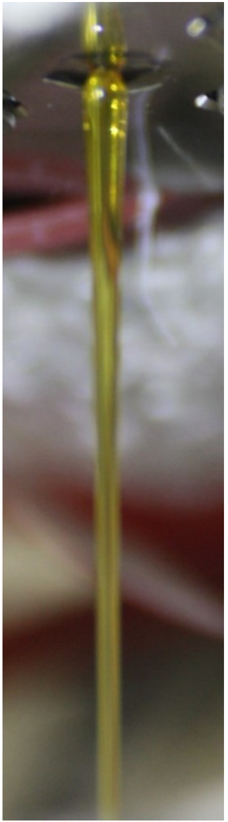
Xc	Tm (°C)	Tc (°C)
50,7	168,3	142,1

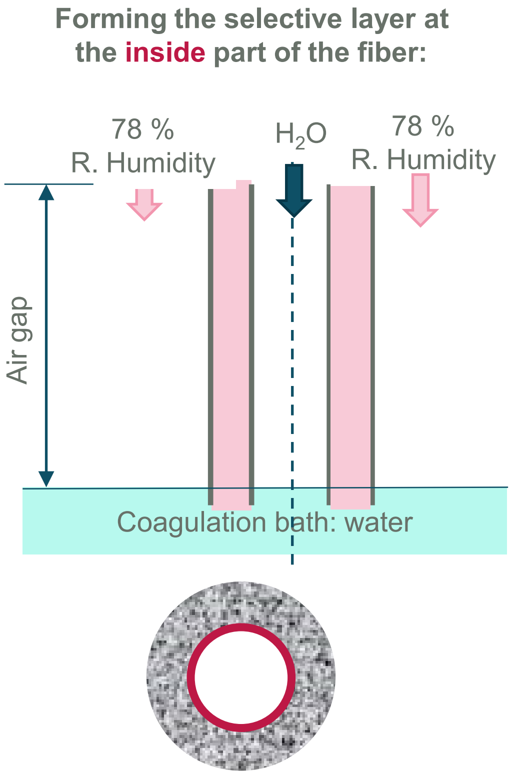
Polymer dope composition:
25 wt% PVDF
30 wt% DMAc
45 wt% Acetone

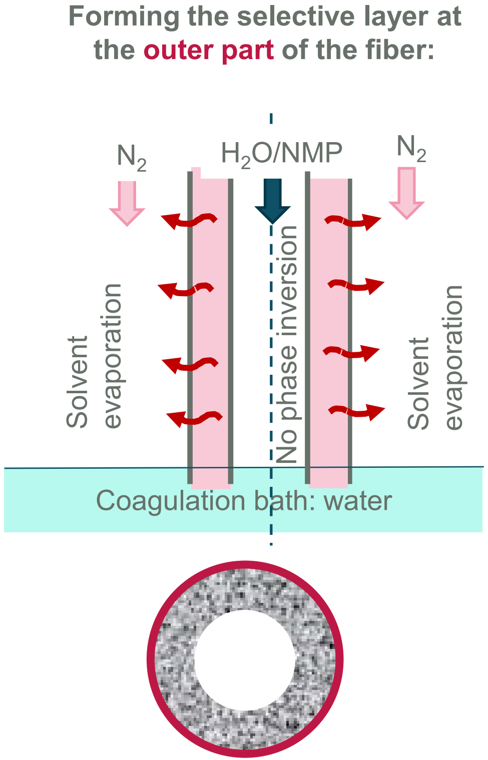


K. Jian, P.N. Pintauro, Asymmetric PVDF hollow-fiber membranes for organic/water pervaporation separations, Journal of Membrane Science, Volume 135, Issue 1, 1997, Pages 41-53

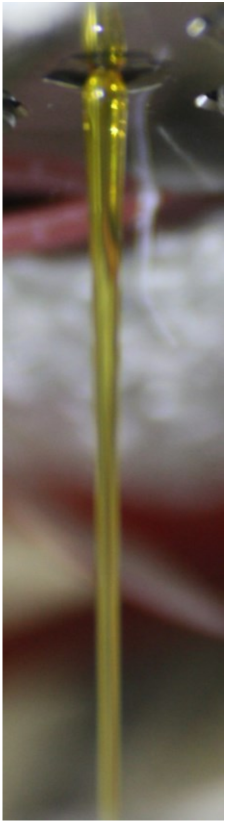
Prototype B – Polymer spinning







Prototype B – Polymer spinning



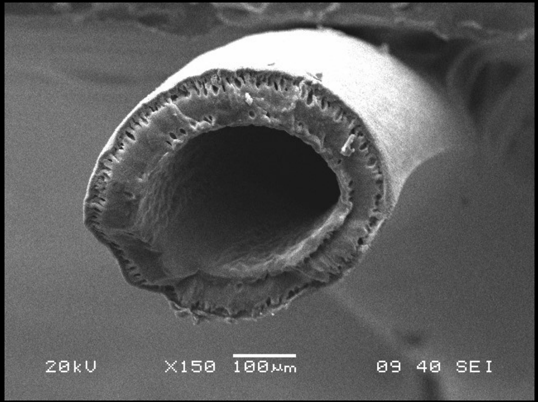
Polymer dope composition:

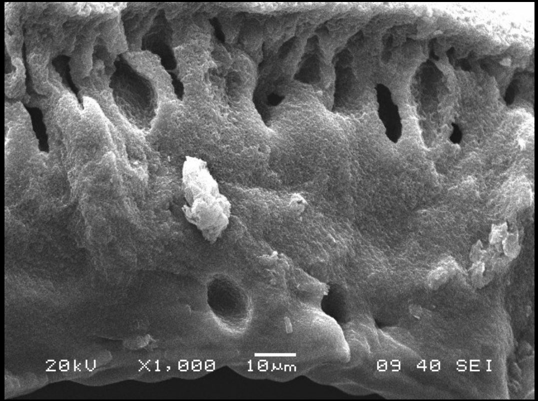
MS-2021-035	20 and 23 wt%
LiCl	3.67 wt%
NMP	73.33 wt%

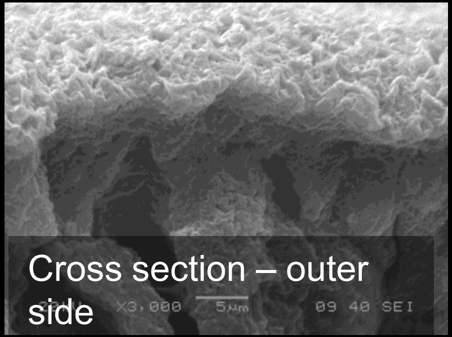
Gel at RT liquid at 40 ºC

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	✓

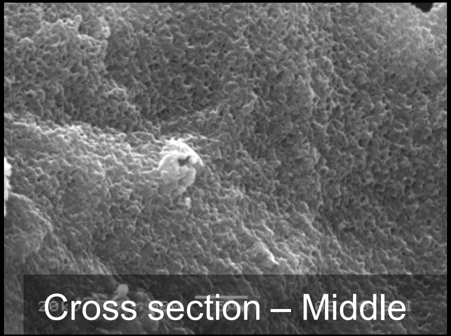
BioCoMem

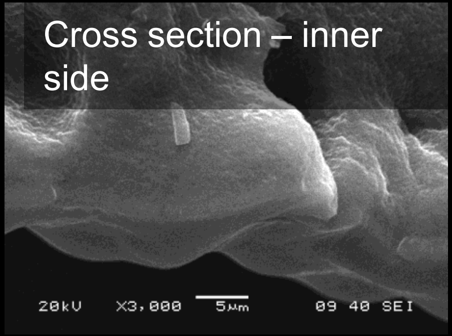




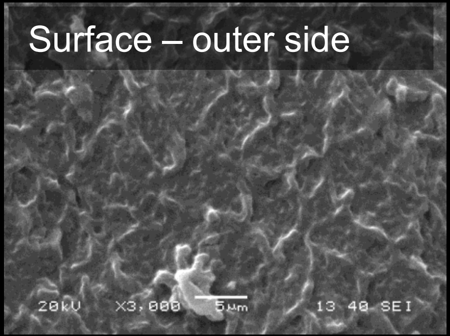


Cross section – outer side

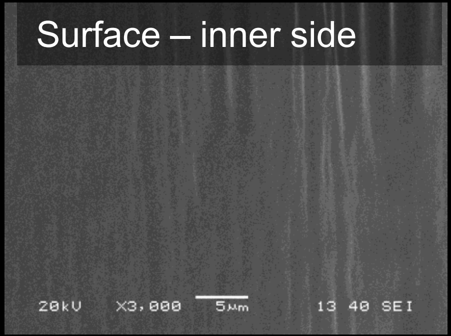

Cross section – Middle



Cross section – inner side



Surface – outer side



Surface – inner side

tecnalia
MEMBER OF BASQUE RESEARCH
& TECHNOLOGY ALLIANCE

Eskerrik asko zuen arretagatik!

Thank you for your attention!