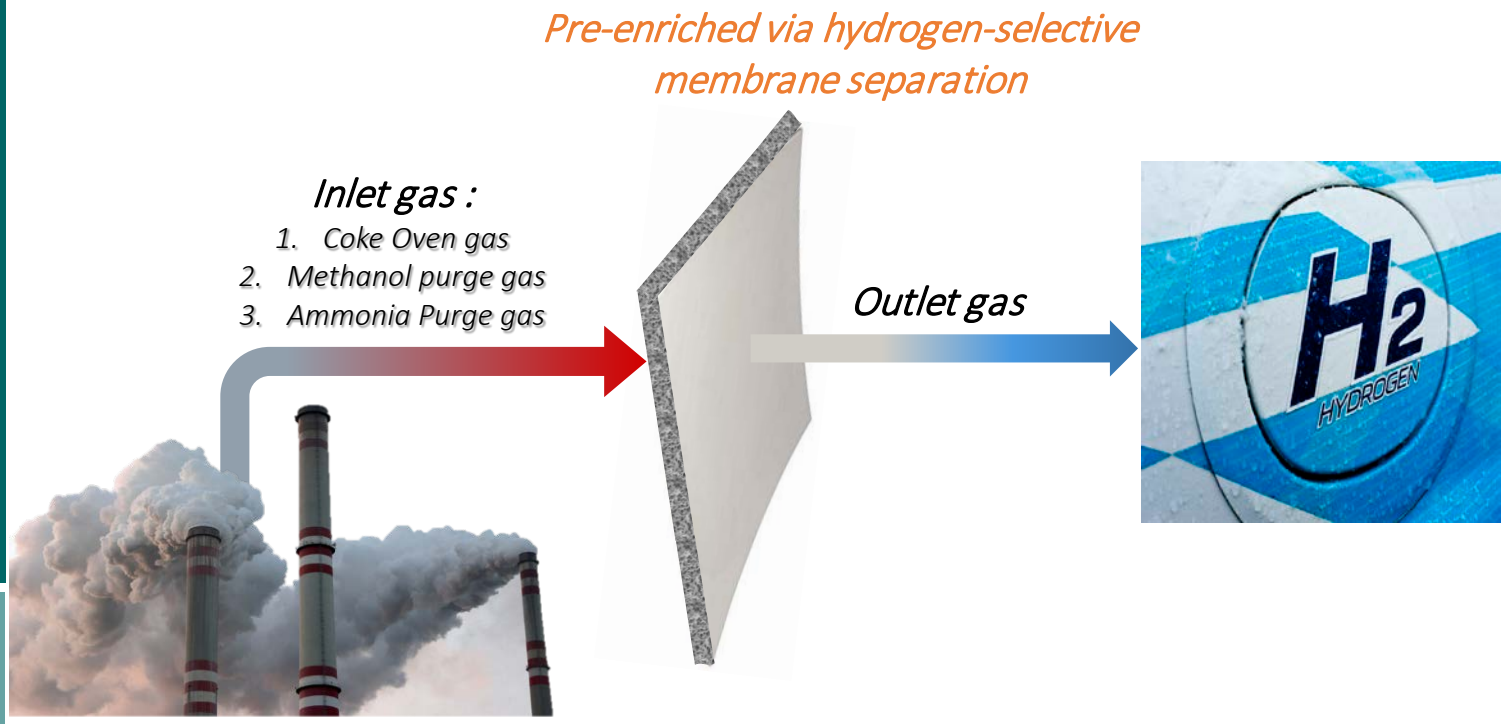
MEMBRANAS POLIMÉRICAS PARA LA SEPARACIÓN/PURIFICACIÓN DE HIDRÓGENO



Inmaculada Ortiz Uribe

13/11/2018

ANQUE-MADRID

osprocan ASP Advanced Separation Processes

UC UNIVERSIDAD DE CANTABRIA

1

- **Estado del arte de las membranas poliméricas en la separación de hidrógeno**

2

- **Oportunidad de recuperar H_2 residual**

*** Viabilidad técnico-económica de la recuperación de hidrógeno residual como combustible**

*** Viabilidad experimental de la recuperación de hidrógeno residual con membranas poliméricas**

3

Tendencias futuras

1970s Dupont primeras membranas para separación de gases HF, siendo la separación de H_2 una de las principales aplicaciones objetivo

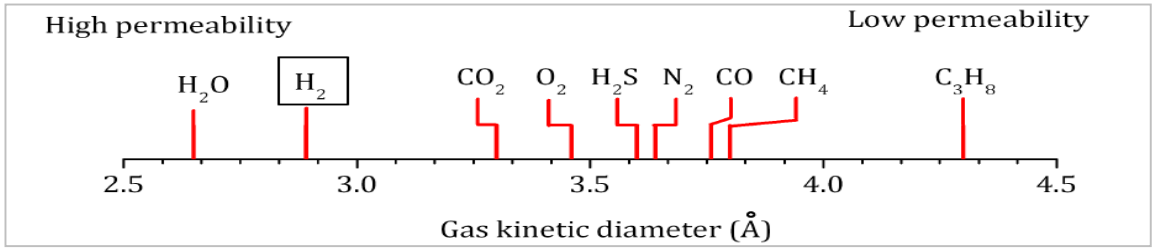
1. **Modificación de la relación H_2/CO en el gas de síntesis**
2. **Eliminación de H_2 de corrientes de hidrocarburos**
3. **Separación de los gases de purga en la fabricación de amoniaco**

Primera generación de membranas comerciales para la separación de hidrógeno

Material	**Empresa**	**H_2/N_2**	**H_2/CO**	**H_2/CH_4**
Polisulfona	Monsanto	39	23	24
Caucho de silicona				
Poliimida	Ube	35,4	30	
Acetato de celolusa	Separex	33	21	26

Organic H_2-selective membranes

COMMERCIAL MEMBRANE	MANUFACTURER	POLYMER	SELECTIVITY			
			H_2/CO_2	H_2/N_2	H_2/CH_4	H_2/CO
PRISM	Air Products/ Permea	Polysulfone – silicone rubber composite	2,50	56-80	80,00	40-56
MEDAL	Air Liquide/DuPont	Polyimide, polyamide		>200	>200	100,00
GENERON	IGS /MG	Tetrabromopolycarbonate	3,50	90,00	120,00	123,00
SEPAREX	UOP	Cellulose acetate	2,40	72-80	30-66	60-80
UBE	UBE Industries	Polyimide	3,80	88-200	100-200	50-125



Organic H_2-selective membranes

Membrane	H_2 permeability (barrer)	H_2/CO_2	Temperature (°C)	Pressure (atm)	Reference
Polybenzimidazole	0.09	9	20	3.4	Pesiri et al. (2003)
	13	20	270		
	11	3	320		
Poly(2,2′-(1,3-phenylene)-5,5′-bibenzimidazole	0.6	3.8	35	3.5	Hosseini et al. (2008)
Poly(tetrafluorochloroethylene)	0.94	4.5			Ito (1961)
Polybenzimidazole (PBI)/nano porous silicate mixed matrix	1	45	35		Choi et al. (2008)
Poly(vinyl chloride)	1.7	11			Tikhomirov et al. (1968)
Poly(vinyl chloride)	2	11	30		Nakamura (1985)
Poly(methyl methacrylate)	2.4	4	30	2.04	Orme et al. (2003)
Poly(vinylidene fluoride)	2.4	2	30	2.04	Orme et al. (2003)
Polyimide	3	2.6	90	1.9	Smaihi et al. (1999)
Cellulose acetate	3.5	0.15			Waack et al. (1955)
Poly(isobutylene)	7	1.4	30		Nakamura (1985)
Poly(vinyl benzoate)	8.7	1.6	25		Hirose et al. (1985)
DMPEK-C	10	4	30	5	Wang et al. (2000)
6FDA-Durene modified by liquid-phase PDA cross-linking	10	100	35	3.5	Chung et al. (2006)
Poly(benzyl methacrylate)	11	1.4	30	2.04	Orme et al. (2003)
PEK-C	12	4.3	30	5	Wang et al. (2000)
Poly sulfone	12	2	30	2.04	Orme et al. (2003)
Poly sulfone	14	2.5	30	5	Wang et al. (2000)
Poly vinyl acetate	15	1.2	30	2	Orme et al. (2003)
TMPEK-C	22	4.0	30	5	Wang et al. (2000)
Poly(styrene)	22	2.15	35		Yasuda and Rosengren (1970)
Poly styrene	24	2.3	30	2	Orme et al. (2003)
Matrimid	27	4	35	3.5	Hosseini et al. (2008)
6FDA-Durene modified by vapor-phase EDA cross-linking	3319[a]	10217[a]	35	3.5	Shao et al. (2009a,b)
Poly(propylene)	41	4.5	35		(1999)
Poly(butadiene)	42	0.3	30		Nakamura (1985)
IMPEK-C	43	2.2	30	5	Wang et al. (2000)
6FDA-Durene modified by liquid-phase EDA cross-linking	120	5	35	3.5	Chung et al. (2006)
6FDA-Durene	600	1	35	3.5	Chung et al. (2006)
Thermally rearranged (TR) poly(benzoxazole-co-pyrrolone	1680	3.2	25	1	Choi et al. (2010)

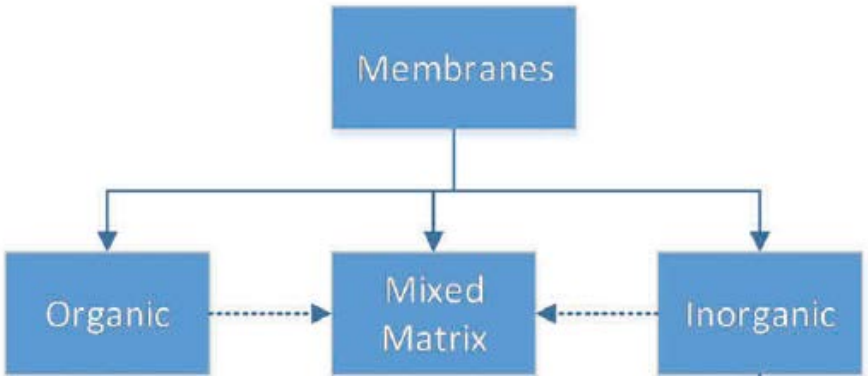
Source: Colin A. Sholes et al. (2010)

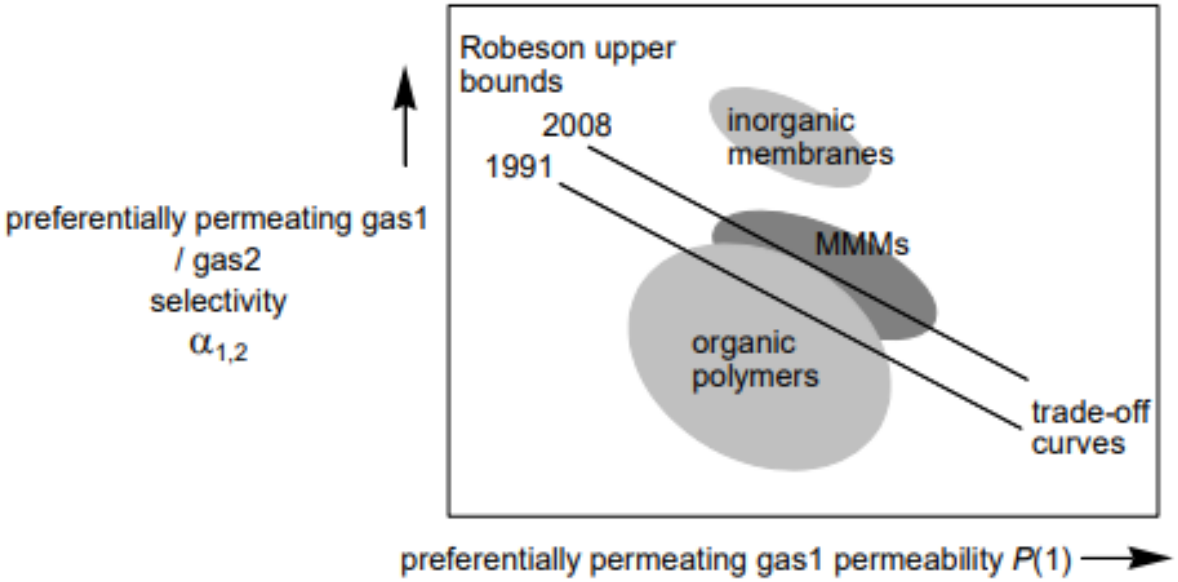
Review H_2-selective membranes

	Organic - Polymeric membranes	Inorganic- Non polymeric membranes			
	Polymer	Ceramic		Metallic	Carbon
	Dense	Dense	Microporous	Dense	Microporous
Temperature range	<90-100 °C.	600-900 °C	200-600 °C	300-600 °C	500-900 °C
H_2 selectivity	low	>1000	5-139	>1000	4-20
H_2 flux (10-3 mol/m2s) at dP=1 bar	low	6-80	60-300	60-300	10-200
Stability issues	Swelling, compaction, mechanical strength	Stability in CO2	Stability in H2O	Phase transition	Brittle, oxidising
Poisoning issues	H2S, HCl, SOx, CO2	H2S, H2O, CO2		H2S, HCl, SOx, CO2	Strong adsorbing vapours, organics
Materials	Polymers	Ceramics (mainly SrCeO3-δ, BaCeO3-δ)	Silica, alumina, zirconia, titania, zeolites	Groups III–V Metals Pd, Ta, V, Nb and alloys	Carbon Proton conducting
Transport mechanism	Solution/ diffusion	Solution/ diffusion (proton conduction)	Molecular sieving	Solution/ diffusion	Surface diffusion; molecular sieving

Source: N. W. Ockwig and T. M. Nenoff (2007)

H_2-selective membranes





Source: Colin A. Sholes et al. (2010) & Katharina Hunger et al. (2012)

Características de las membranas poliméricas:

- Menor selectividad y flujo que las membranas inorgánicas

- Mejor procesabilidad

- Menor coste

- Mayor estabilidad frente a elevadas pérdidas de carga

Implementación a Escala industrial

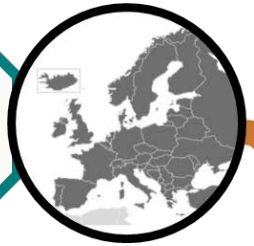
Recuperación de hidrógeno residual

(ALTERNATIVA A LA GENERACIÓN DE H_2 POR REFORMADO DE METANO/WATER-GAS SHIFT REACTION)

This research was supported by the Project "PEMFC-SUDOE" - SOE1/P1/E0293 which is co-financed by the European Regional Development Fund in the framework of the Interreg Sudoe programme.

Key figures of waste hydrogen sources

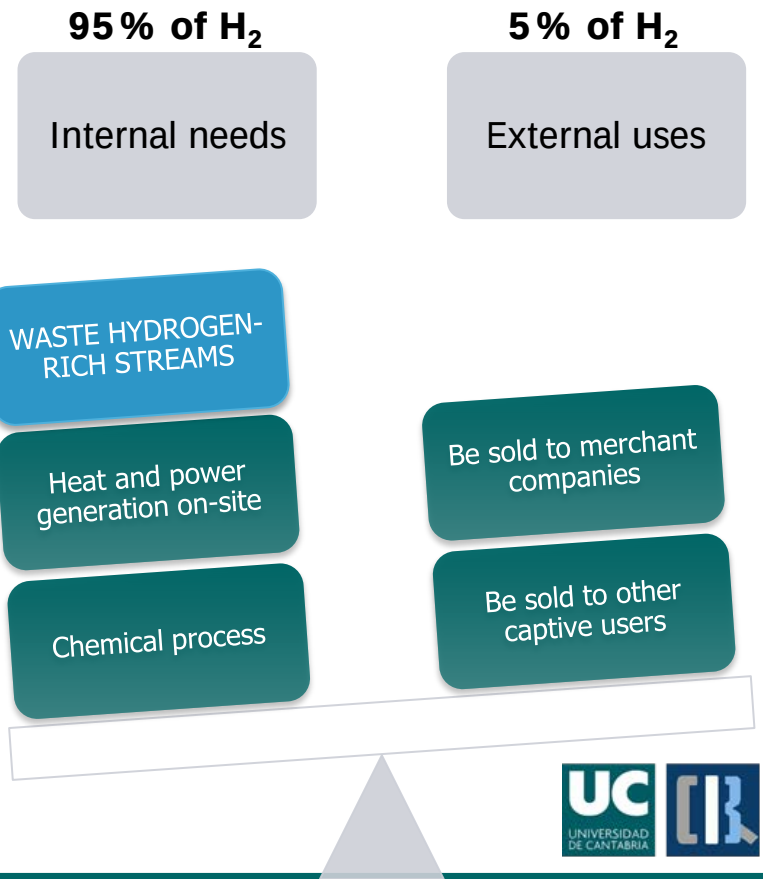
10 bn Nm^3 H_2 per year in EU



0.3 - 1 bn Nm^3 H_2 per year in the SUDOE Region

The hydrogen net balance of an industrial complex strongly depends on the generated products and the processes involved.

Likewise, surplus hydrogen could be recovered as feedstock for the **manufacture of high value products** such as ammonia or methanol, or even **fueling more efficient energy systems such as PEM fuel cells.**



Objetivo: viabilidad técnico-económica de incorporar H2 residual industrial en unaCSH

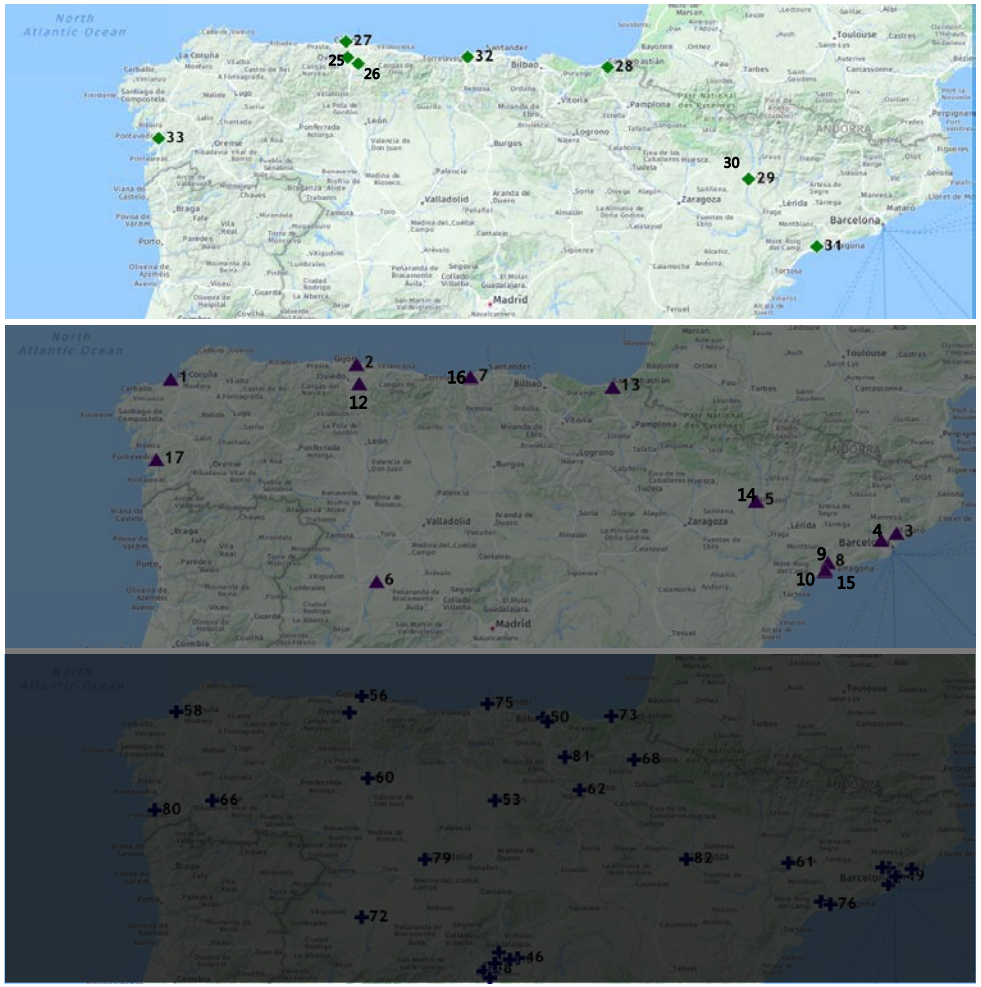
11,7 MM inhabitants & 4,1 M km2 over the period 2020-2050

Industrial waste streams with hydrogen content higher than 50%, are considered the most promising sources for hydrogen recovery using separation techniques.

Raw material	Industry	Waste streams	H_2 flowrate	Burnt off /emitted (%)	Recovered /valorized (%)
R50	Steel mills	Coke Oven Gas	209 Nm^3 of H_2 / ton of coke	3	97
	Coke plants			60 - 80	20 - 40
R99	Chlor-alkali industry	Cl_2 production	300 Nm^3 of H_2 / ton of Cl2	10	90
		HCl production	6 Nm^3 of H_2 / ton of HCl	10	90
		$NaClO_3$ production	668 Nm^3 of H_2 / ton of $NaClO_3$	10	90

Study area description: 11,7 MM inhabitants & 4,1 M km2 over the period 2020-2050

The geographic distribution of the future hydrogen market comprises a **number of stakeholders** who will be the three nodes of the hydrogen network.



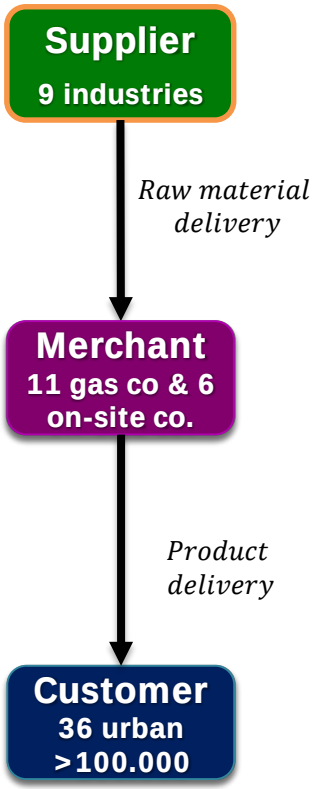
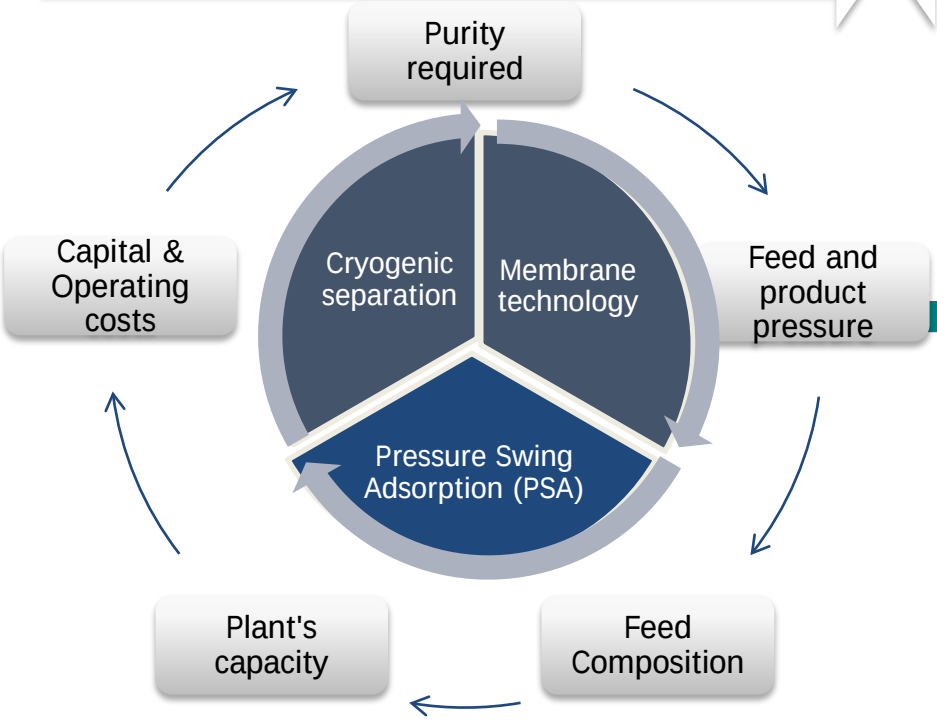


Fig. 7 Geographic breakdown studied ◆ Supplier Company i ϵ I; ▲ Merchant company j ϵ J ; ✚ Customer area k ϵ K.

Purifications techniques

Current purification technologies



H_2-fuel quality requirements

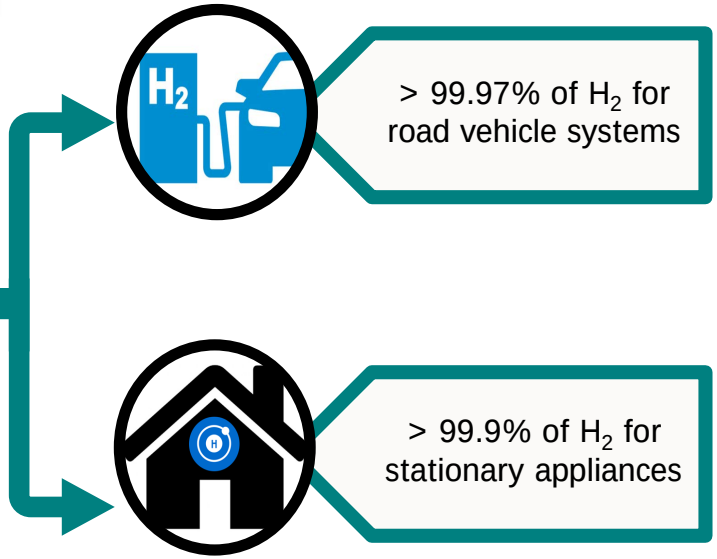


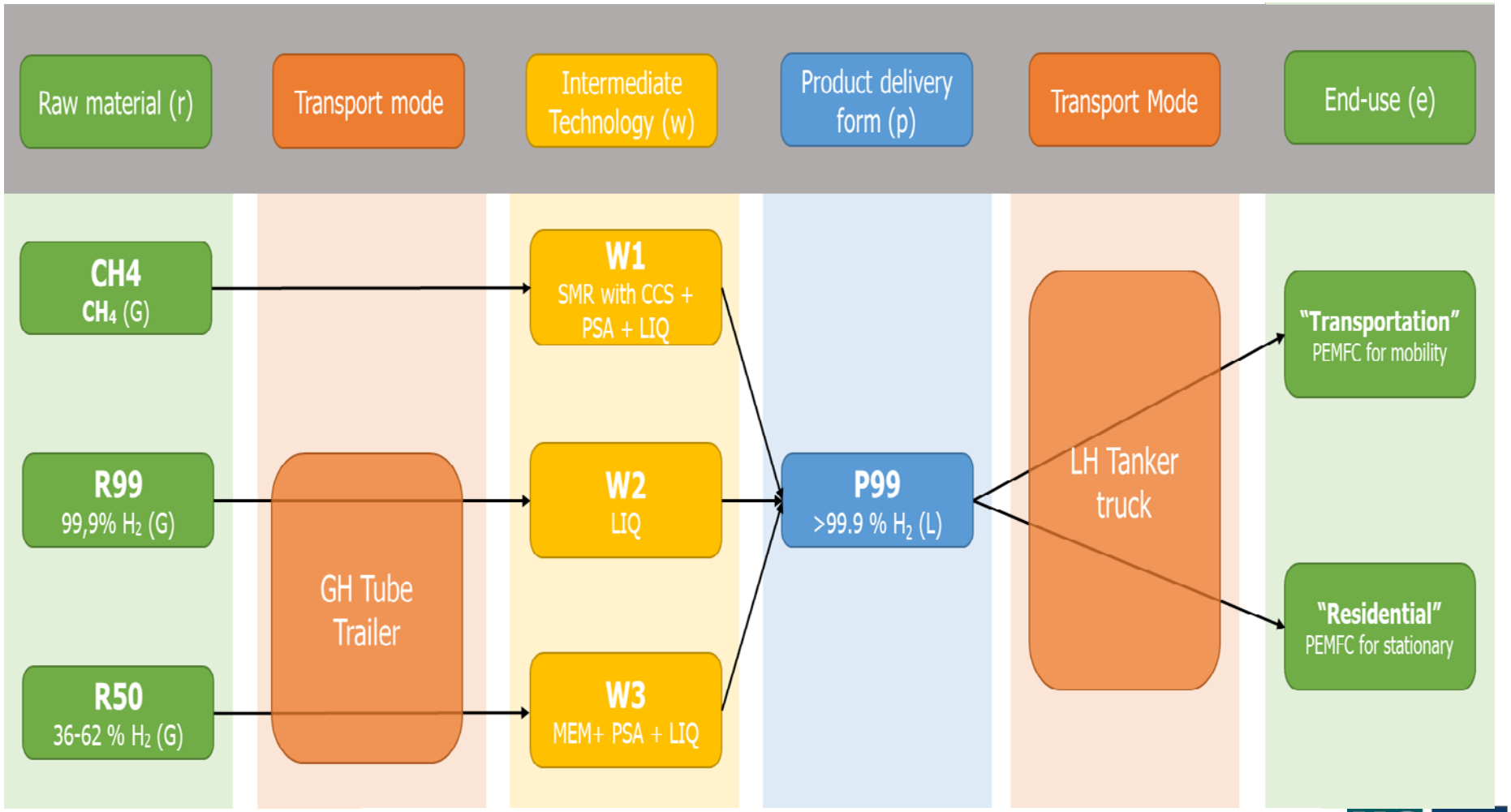
Fig. 5 International Standard ISO 14687 – Parts 2 and 3 for PEM fuel cells

State-of-art technology to obtain hydrogen at fuel cell quality

Methods	Means Media	Operating conditions		H2 concentration (%v/v)		H2 recovery (%)
		T (ºC)	P (bar)	Feed	Product	
Cryogenic	Cooling agents	- 183	20 - 50	30 - 90	90 - 98	95
PSA	Adsorbents	RT	20 - 150	60 - 90	> 99.9	70 - 90
PSA	Adsorbents	RT	10 - 40	50 -80	> 99.999	70 - 85
Polymer Membrane	Polyamide Polysulfone	0 - 100	20 - 200	60 - 95	85 - 99	85 - 95

Hydrogen supply chain (HSC)

- Technology selection and operation;
- hydrogen demand forecast;
- geographical information
- capital investment models,
- economy models



Structure of the waste gaseous streams-based HSC

Problem statement

Given:

- **Amounts and qualities** of the main industrial hydrogen-rich gaseous mixtures.
- **Locations of the key stakeholders.**
- **Hydrogen demand** forecast (2020-2050)
- **Transportation modes**, capacities, distances and cost
- **Production technologies** and conversion factors
- **Investment and operating costs**

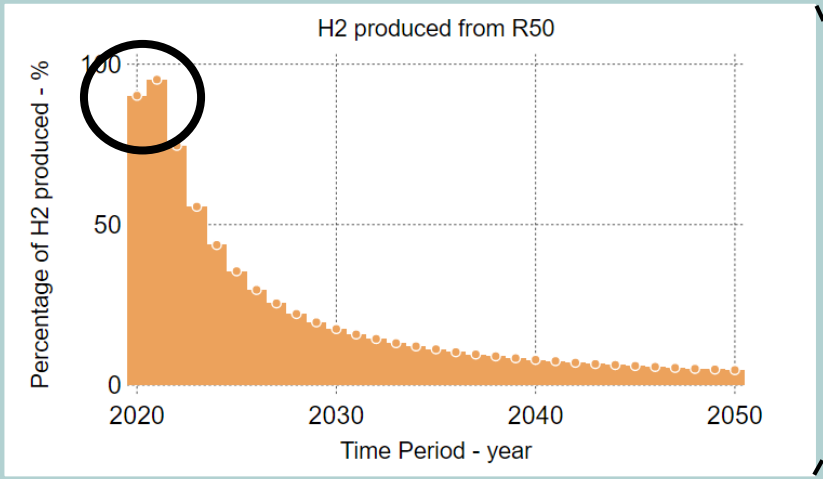
Maximize the Net Present Value (NPV)

Determine:

- **Optimal investment plan for all the merchants** considered.
- **Location, type, scale and number of intermediate technologies**, as well as production rates.
- **Sourcing and supply routes for the raw materials and products** considered.
- **Connexions between the stakeholders**.

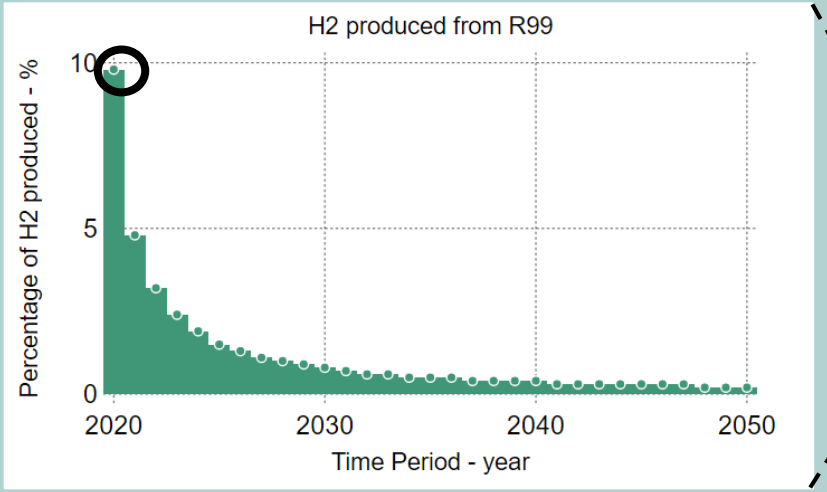
Methodology based on: A. Almansoori and N. Shah, "Design and operation of a future hydrogen supply chain: Multi-period model," Int. J. Hydrogen Energy, vol. 34, no. 19, 2009.

Surplus hydrogen flowrates



R50

Period	TotalFlow	TotalDemand	Percent
2020	8057	8936	90.2
2030	21173	120823	17.5
2040	21500	271489	7.9
2050	21500	458774	4.7

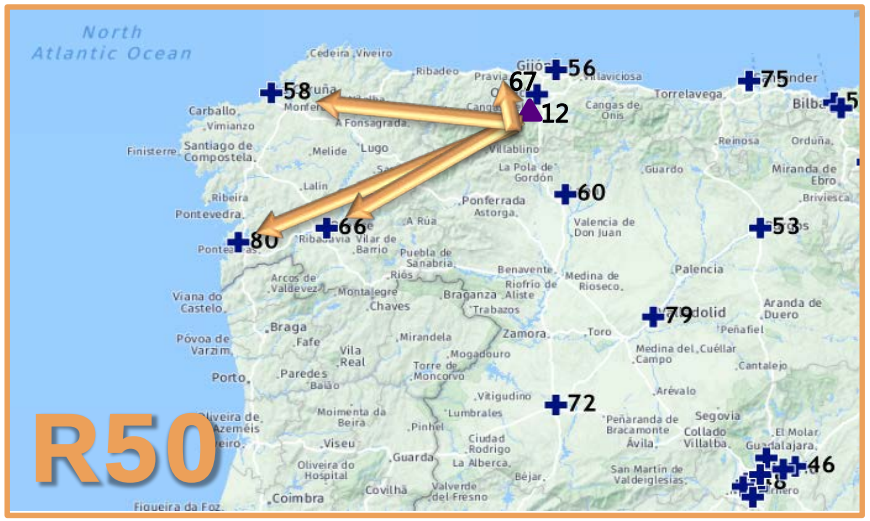


R99

Period	TotalFlow	TotalDemand	Percent
2020	879	8936	9.8
2030	920	120823	0.8
2040	960	271489	0.4
2050	1025	458774	0.2

Fig. 12 Hydrogen produced from raw materials R50 and R99 by year (tons H_2/year)

Surplus hydrogen flowrates



Merchant (j=12) located in Asturias **may fulfil hydrogen demand by more than 90%** in Gijón (k=56), La Coruña (k=58), Orense (k=66), Oviedo (k=67) and Vigo (k=80).

Merchant (j=14) located in Huesca may **fulfil hydrogen demand by more than 3%** in Logroño (k=62) and Zaragoza (k=82). Merchant (j=16) located in Santander may fulfil hydrogen demand by **more than 4%** in Baracaldo (k=50) and Santander (k=75).

Total hydrogen consumed by ✚ Customer area k ϵ K, produced from R50 and R99 at ▲ Merchant company j ϵ J

M. Yañez, A. Ortiz, B. Brunau, I. Grosmann, M.I. Ortiz, ***Contribution of upcycling surplus hydrogen to design a sustainable supply chain: the case study of northern Spain***, Applied Energy, 2018

Recuperación de hidrógeno residual

Viabilidad experimental con membranas comerciales

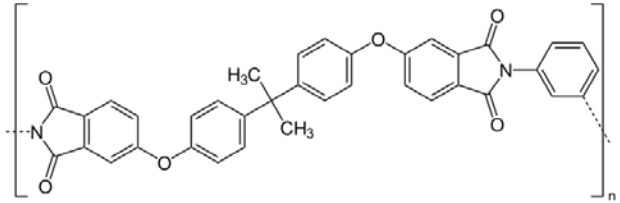
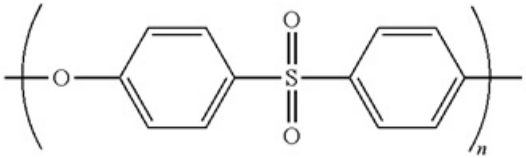
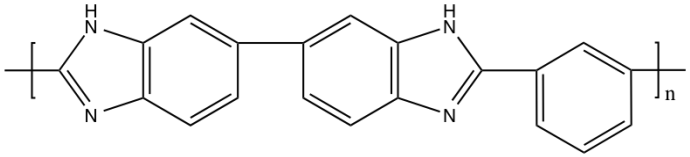
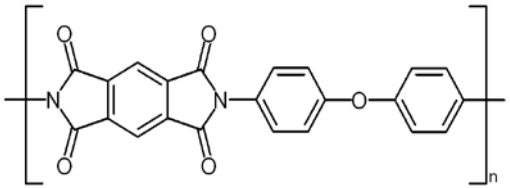
This research was supported by the Project "PEMFC-SUDOE" - SOE1/P1/E0293 which is co-financed by the European Regional Development Fund in the framework of the Interreg Sudoe programme.

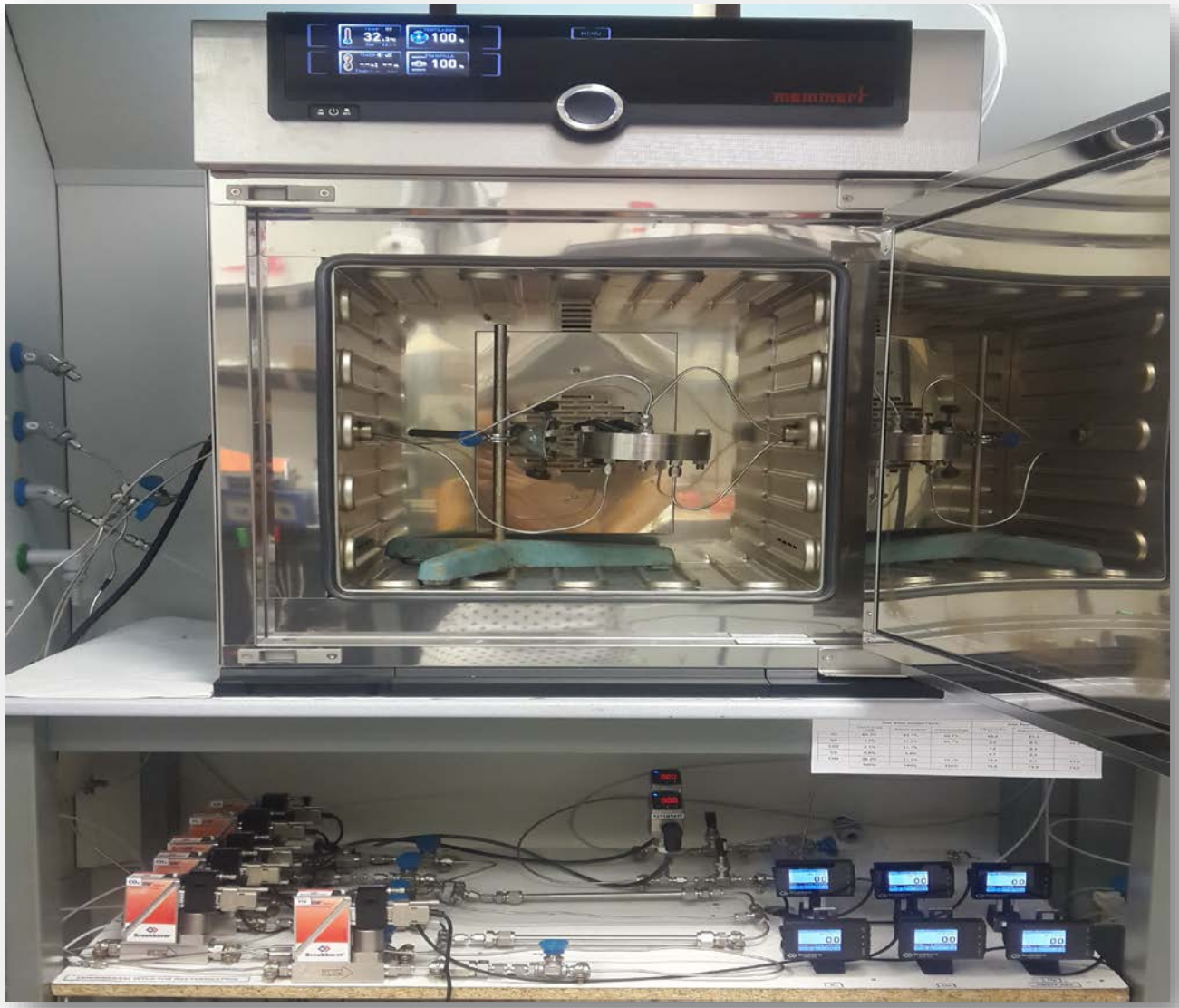
Waste gas streams studied

	Inlet Molar fraction (%v/v)		
	Coke Oven Gas (COG)	**Methanol purge gas**	**Ammonia purge gas**
H2	**60.2**	**63.1**	**58.6**
N2	**4.7**	**11.3**	**25.7**
CO2	**2.1**	**11.1**	**-**
CO	**6.8**	**3.4**	**-**
CH4	**26.2**	**11.2**	**15.7**
T (ºC)	**25**	**40**	**15**
P (bar)	**1**	**68**	**150-200**
Ratio available	5-108 kg $COG_{recoverable}$/ t coke	43 kg $MPG_{recoverable}$/ t CH3OH	84 kg $APG_{recoverable}$/ t NH3

Sources: Y. Alqaheem et al. (2017) & Solten et al. (2016), Arezoo Sadat Emrani (2011)

1.3. Commercial membranes studied

ID	Name	Acronym	Tg (K)	ρ(g/cm3)	δ (µm)	Chemical structure
1	Polyetherimide (ULTEM 1000B)	PEI	490	1.27	25 50 75	
2	Polyethesulfone (Ultrason E)	PES	489	1.37	25	
3	Polybenzimidazole (m-PBI)	PBI	427	1.30	55	
4	Polyimide (Kapton®)	PI	633	1.42	25	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Average permeability values for each membrane

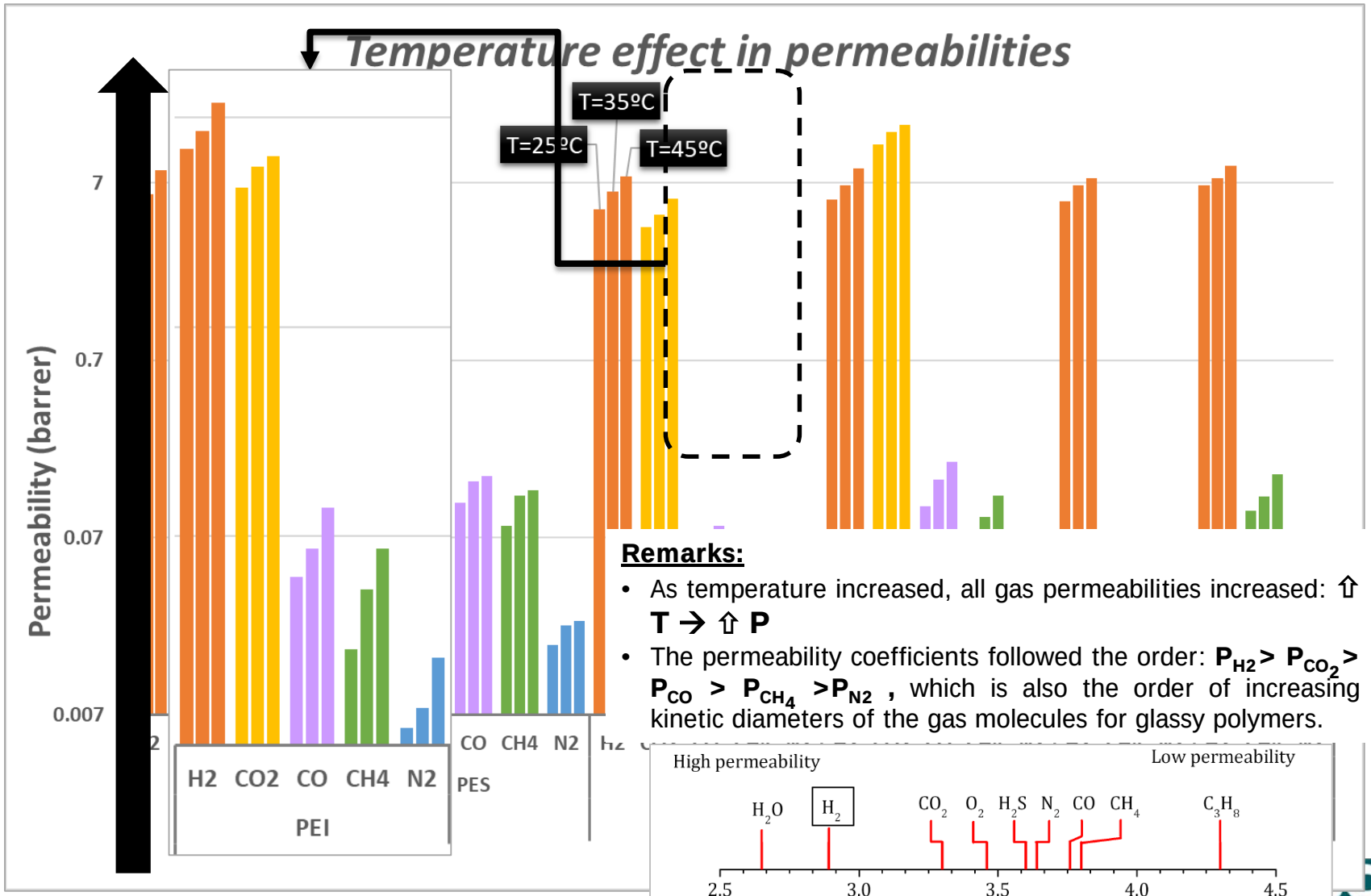
Membrane Type	Inlet gas	PERMEABILITY, barrer				
		H2	N2	CH4	CO	CO2
PEI Ultem 25 µm	Pure gases (30ºC)	7.80	0.05	0.04	-	1.32
	COG	6.2 ± 1.2	0.01 ± 0	0.04 ± 0.02	0.06 ± 0.02	3.7 ± 0.6
	MPG	6.2 ± 1	0.01 ± 0	0.03 ± 0.01	0.06 ± 0.01	4.5 ± 0.7
	APG	6.5 ± 0.8	0.01 ± 0	0.03 ± 0.01	-	-
PES Ultrason 25 µm	Pure gases (30ºC)	8.96	0.13	0.11	-	3.38
	COG	6.7 ± 0.6	0.02 ± 0	0.11 ± 0.02	0.14 ± 0.02	9.9 ± 0.2
	MPG	6.8 ± 1	0.02 ± 0.01	0.09 ± 0.02	0.14 ± 0.03	12.6 ± 1.6
	APG	7.5 ± 0.8	0.03 ± 0.01	0.12 ± 0.02	-	-

Remarks:

- Independent of the synthetic waste gas stream under study, **gas permeabilities using PES Ultrason membrane are higher than in the case of using PEI Ultem, but selectivity follows the opposite trend**

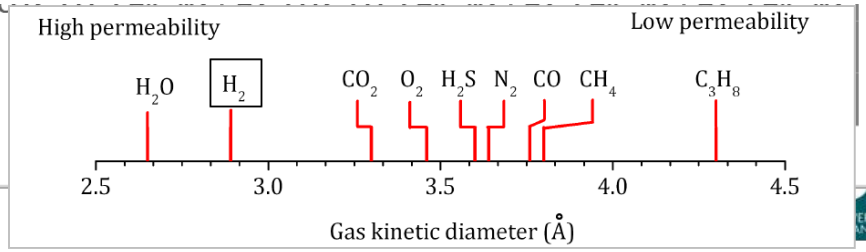
V. Abetz et al. (2006) & Y. Li et al (2008)

Analysis of the Temperature influence

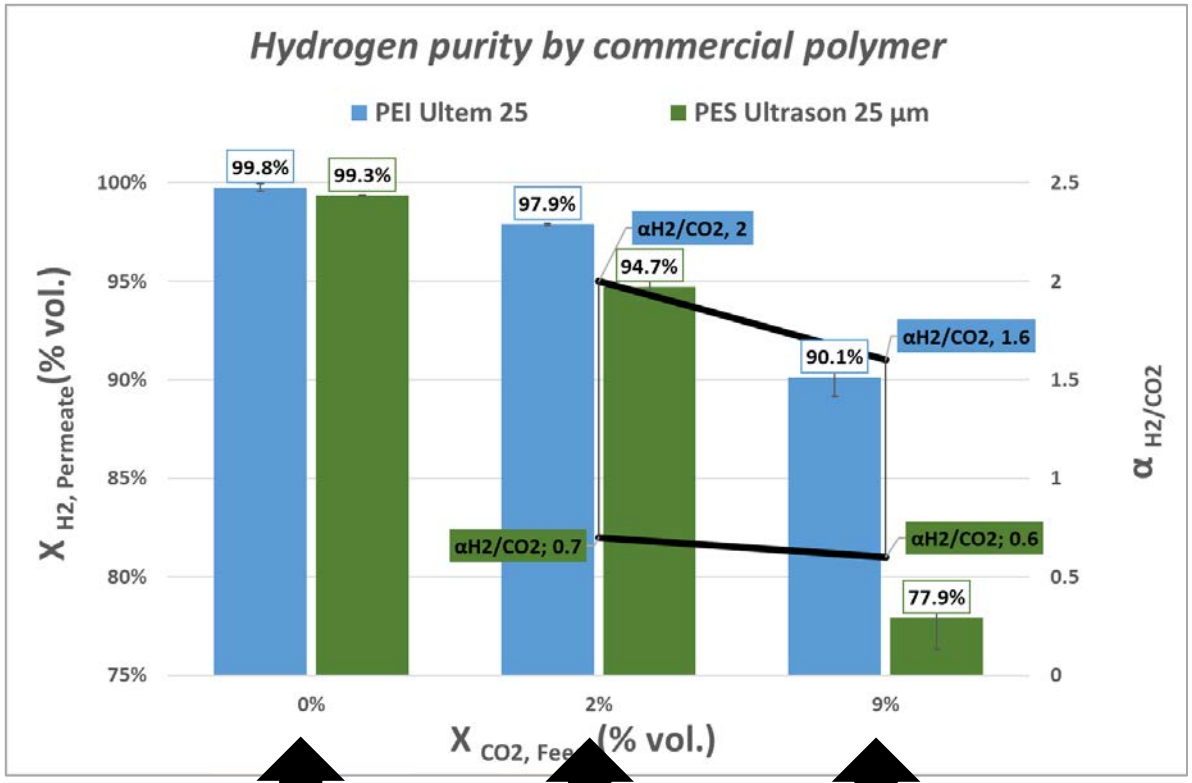


Remarks:

- As temperature increased, all gas permeabilities increased: ⇧ **T → ⇧ P**
- The permeability coefficients followed the order: $P_{H2} > P_{CO_2} > P_{CO} > P_{CH_4} > P_{N2}$, which is also the order of increasing kinetic diameters of the gas molecules for glassy polymers.



Gas product purity

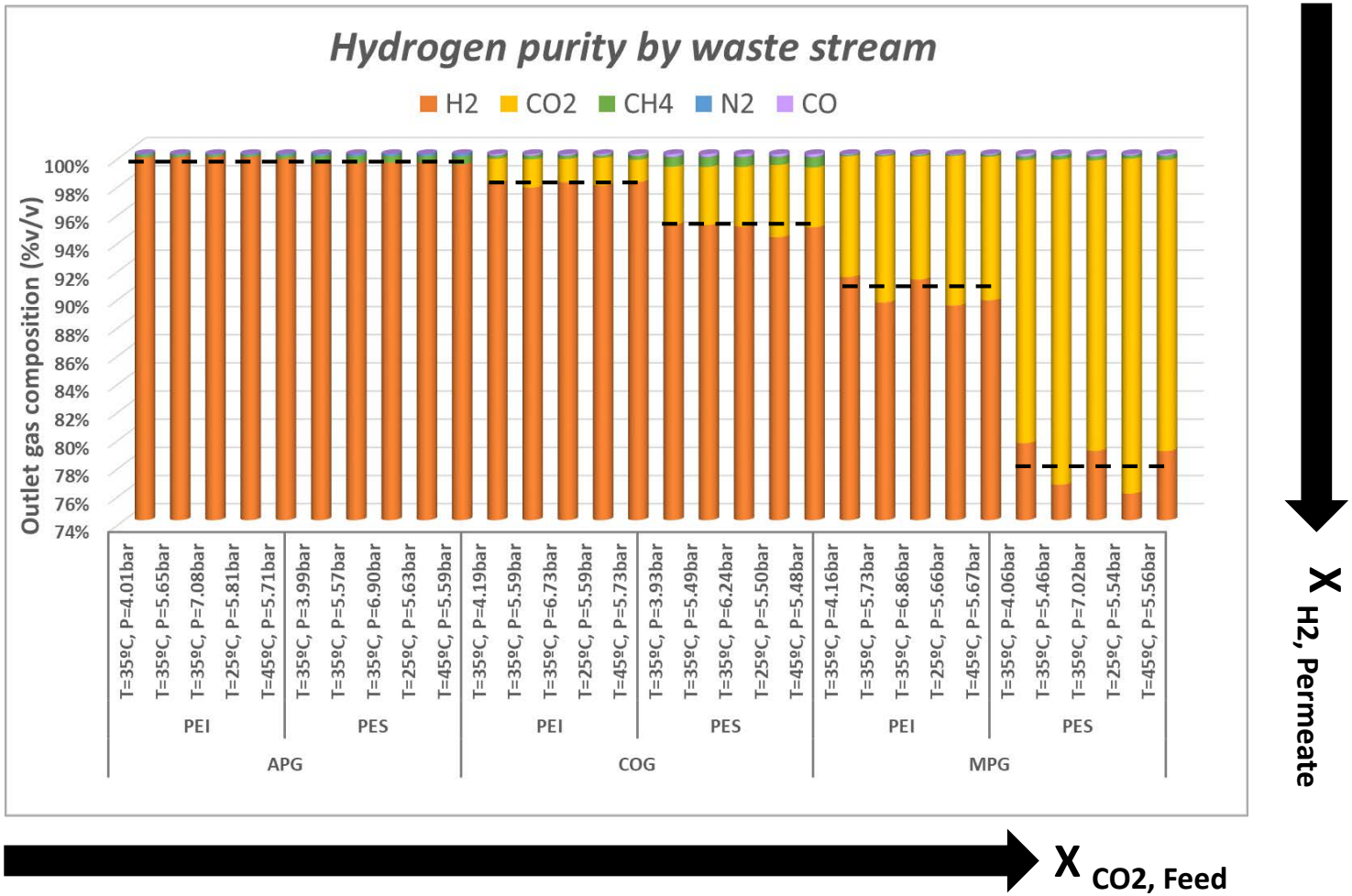


APG COG MPG

Remarks:

- Hydrogen recovery degree may achieve up to **99.8 ± 0.1 vol. H_2 from APG**, **97.9 ± 0.2 from COG** and **90.1 ± 1 from MPG** using PEI Ultem membrane. However, these product purities drops using PES Ultrason membrane up to **99.3 ± 0.1 vol. H_2 from APG**, **94.7 ± 0.4 from COG** and **77.9 ± 1.6 from MPG.**
- Purities obtained follow the order: **$x_{H2, PERM}$ from APG > $x_{H2, PERM}$ from COG > $x_{H2, PERM}$ from MPG.**
- As might be expected because of permeability and selectivity values obtained, **hydrogen purities obtained using PES Ultrason membrane are lower than in the case of using PEI Ultem membrane.**

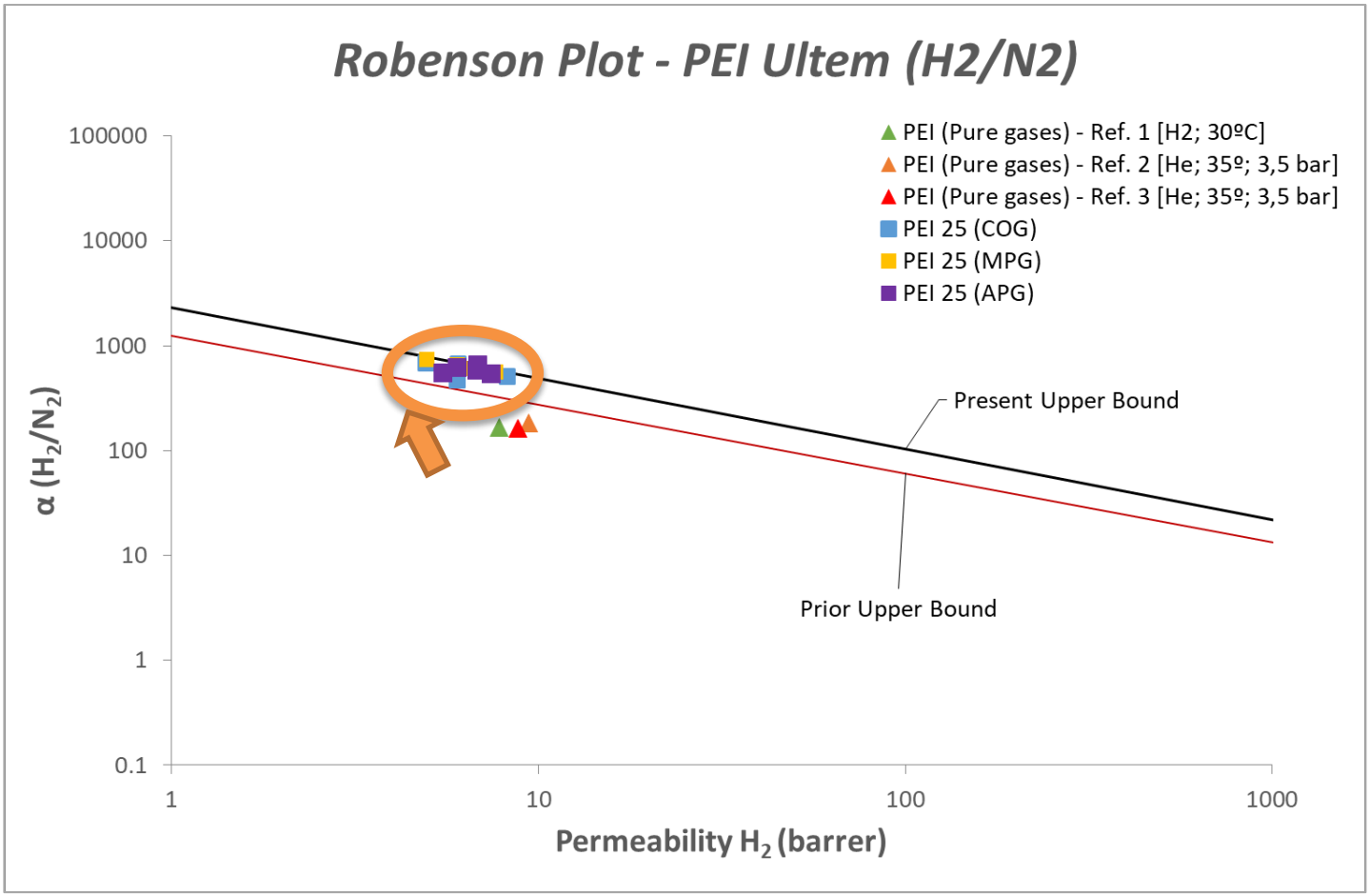
Gas product purity



Remarks:

- **Hydrogen purity is strongly affected by the CO_2 feed concentration** however the results showed that hydrogen purity remains almost constant to temperature and pressure changes.

Robeson Plots: PEI Ultem

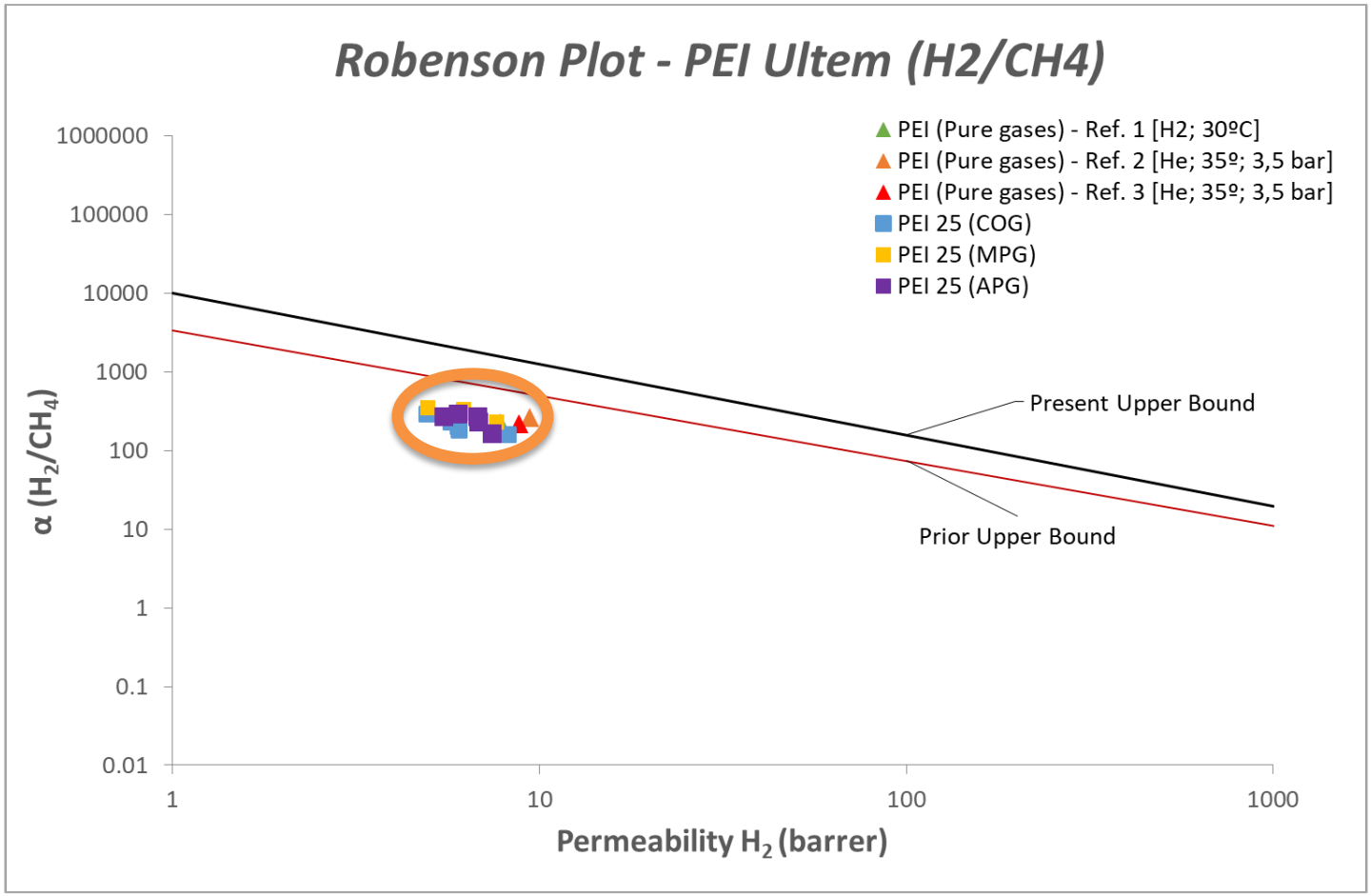


[1] V. Abetz et al., "Developments in membrane research: From material via process design to industrial application," Advanced Engineering Materials, vol. 8, no. 5. pp. 328–358, 2006.

[2] J. Xia, S. Liu, P. K. Pallathadka, M. L. Chng, and T. S. Chung, "Structural determination of extem XH 1015 and its gas permeability comparison with polysulfone and ultem via molecular simulation," Ind. Eng. Chem. Res., vol. 49, no. 23, pp. 12014–12021, 2010.

[3] L. Hao, P. Li, and T. S. Chung, "PIM-1 as an organic filler to enhance the gas separation performance of Ultem polyetherimide," J. Memb. Sci., vol. 453, pp. 614–623, 2014.

Robeson Plots: PEI Ultem



[1] V. Abetz et al., "Developments in membrane research: From material via process design to industrial application," Advanced Engineering Materials, vol. 8, no. 5. pp. 328–358, 2006.

[2] J. Xia, S. Liu, P. K. Pallathadka, M. L. Chng, and T. S. Chung, "Structural determination of extem XH 1015 and its gas permeability comparison with polysulfone and ultem via molecular simulation," Ind. Eng. Chem. Res., vol. 49, no. 23, pp. 12014–12021, 2010.

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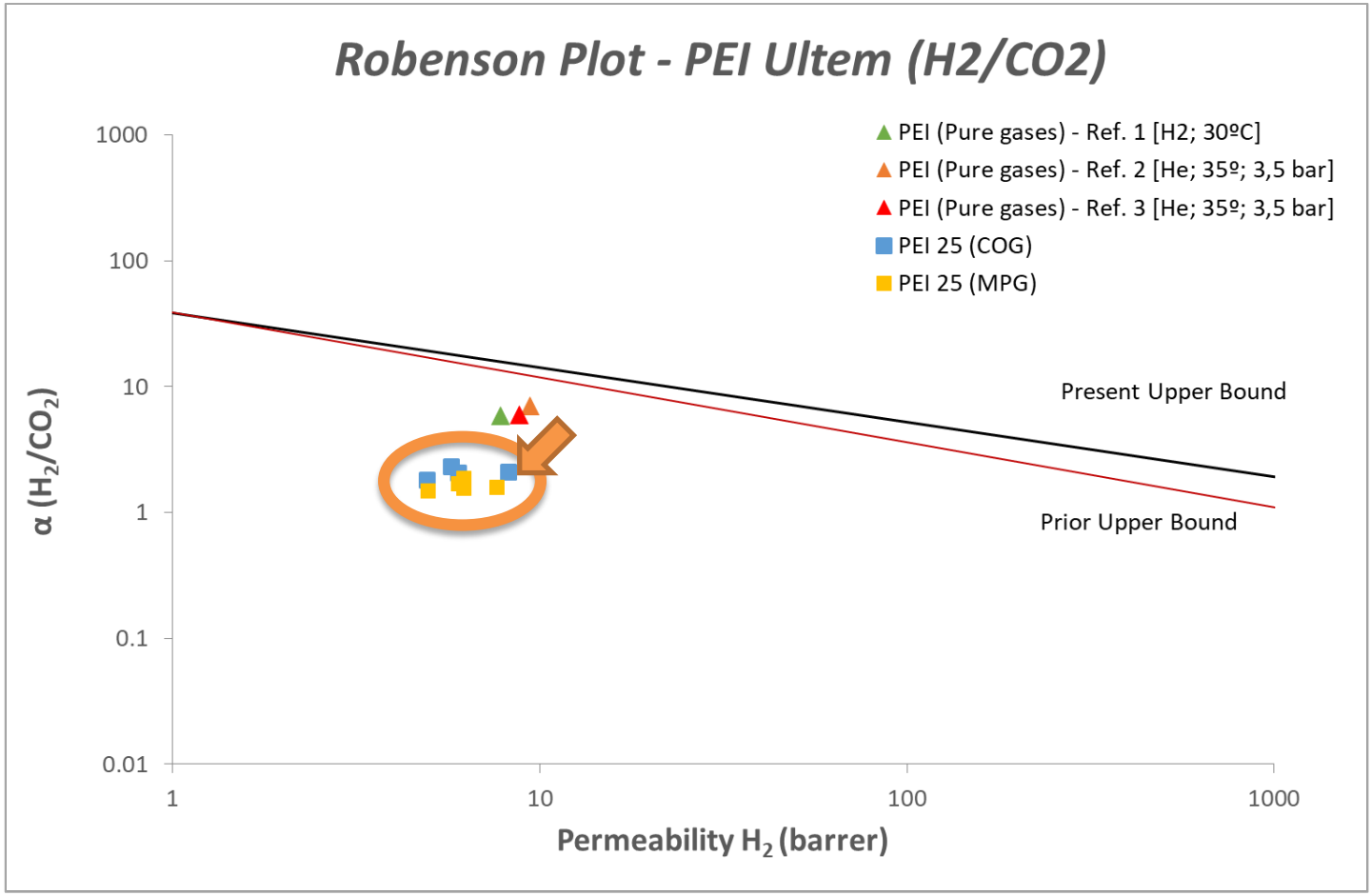

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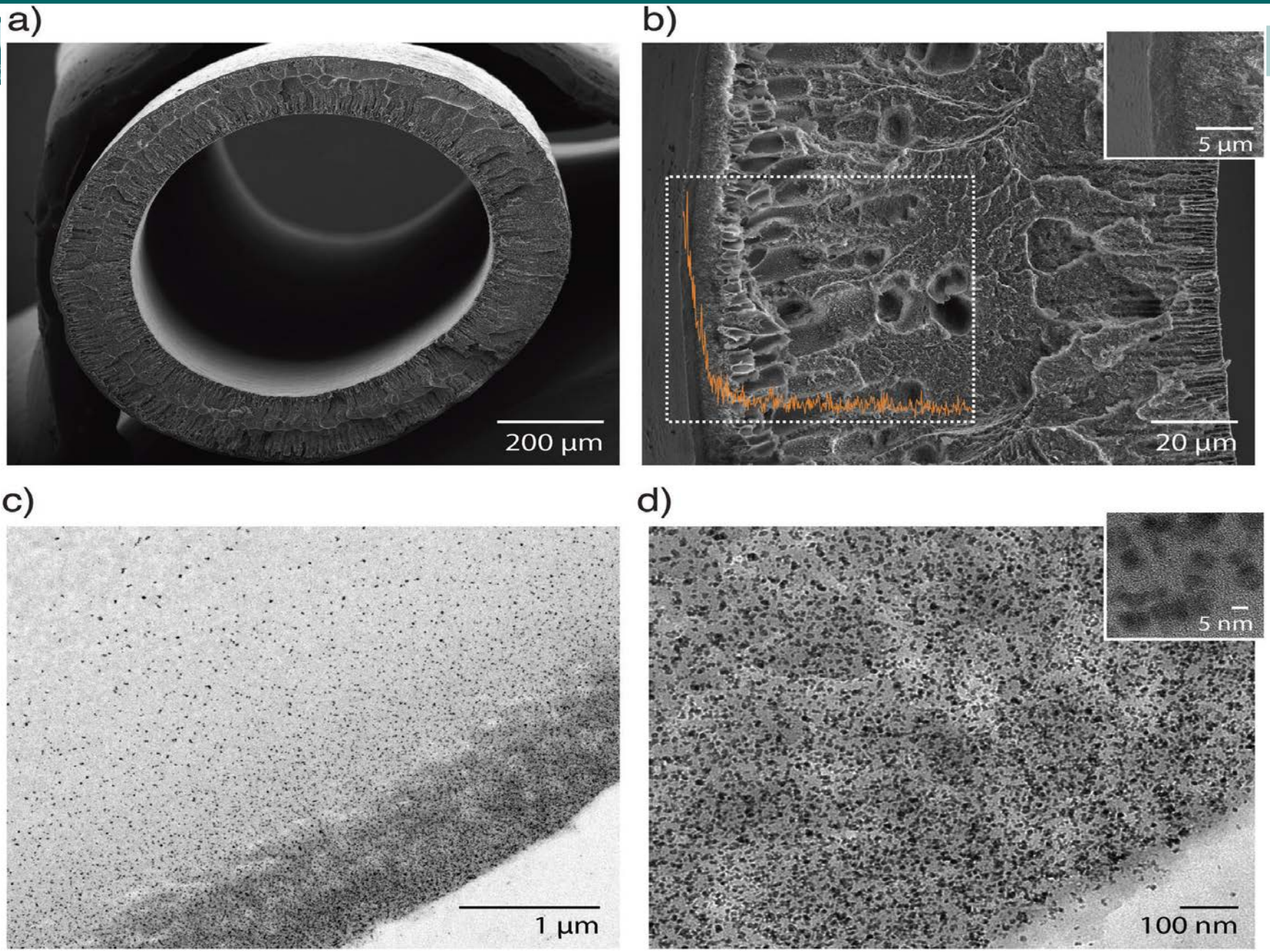
Mejoras en investigación

Fabricación de membranas poliméricas incorporando Pd: PBI-NPsPd

<u>Resultados</u>: Mejora la inestabilidad mecánica asociada al Pd y la baja permeabilidad del PBI (polímero resistente a la plastificación).

Incremento en la permeanza del hidrógeno en 3 órdenes de magnitud respecto del PBI y la selectividad H_2/CO_2 2 órdenes de magnitud.

Villalobos et al, Adv. Energ. Mater. 2018


a)
200 µm
b)
5 µm
20 µm
c)
1 µm
d)
5 nm
100 nm

¡Gracias por la atención!

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