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Istituto per la Tecnologia delle Membrane

Membrane operations for the treatment of gases

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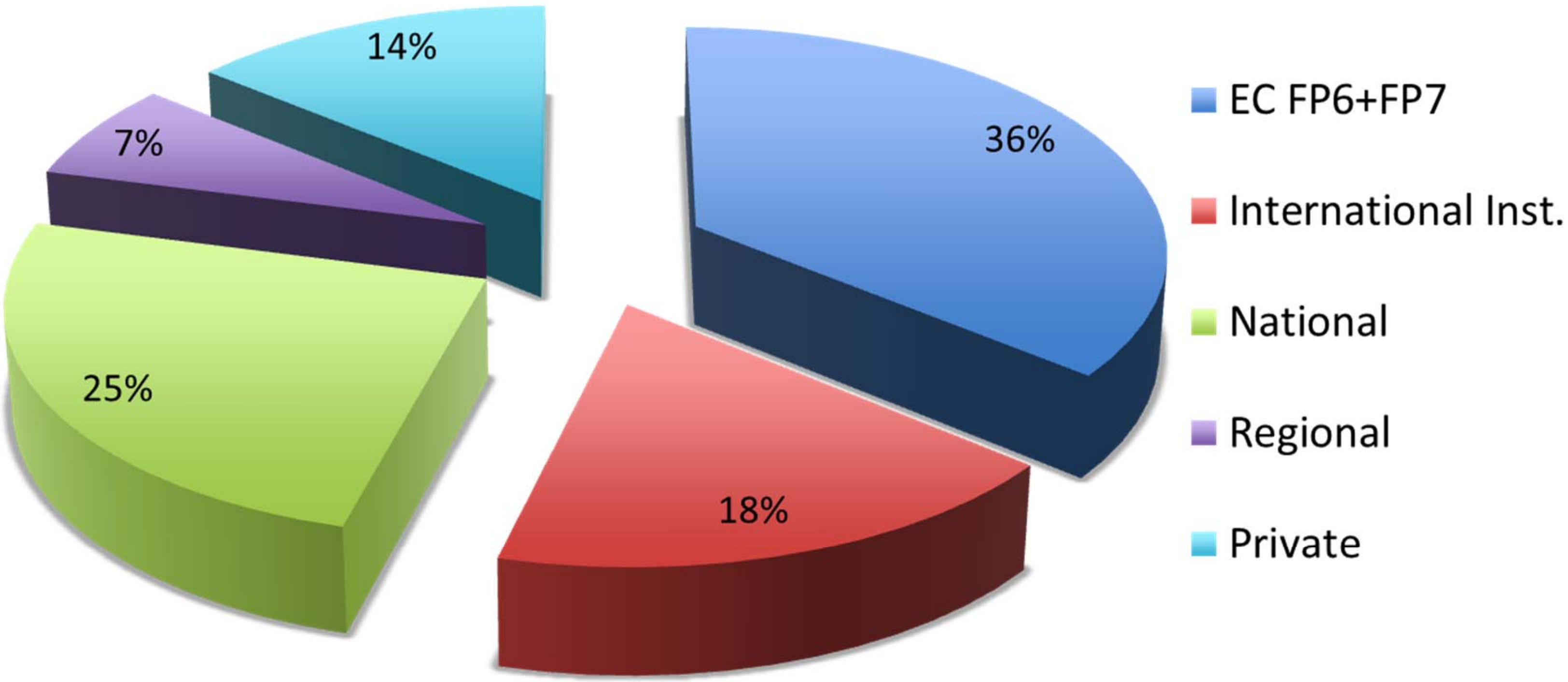
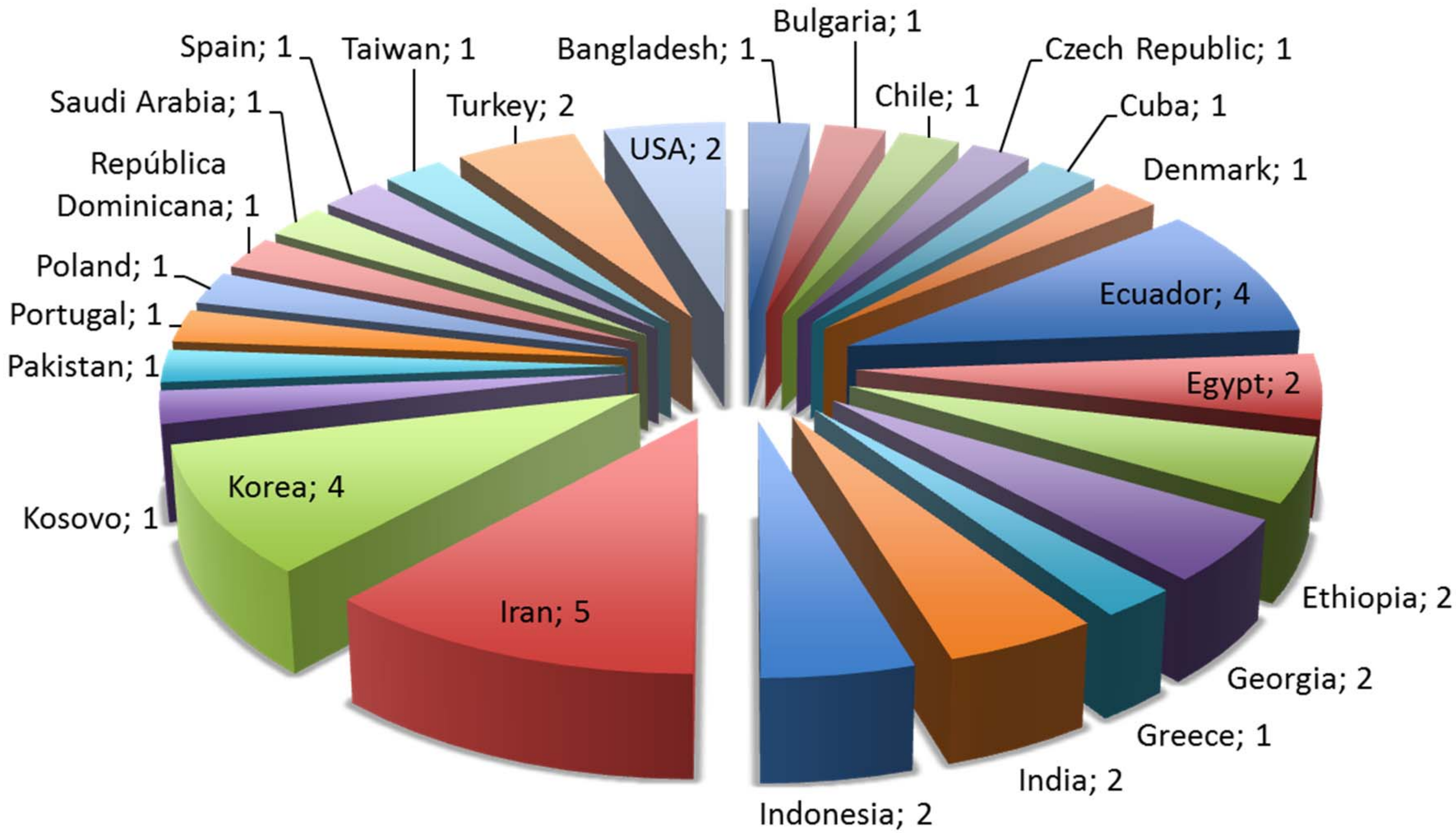
Consiglio Nazionale delle Ricerche

Institute on Membrane Technology - CNR @ University of Calabria Campus

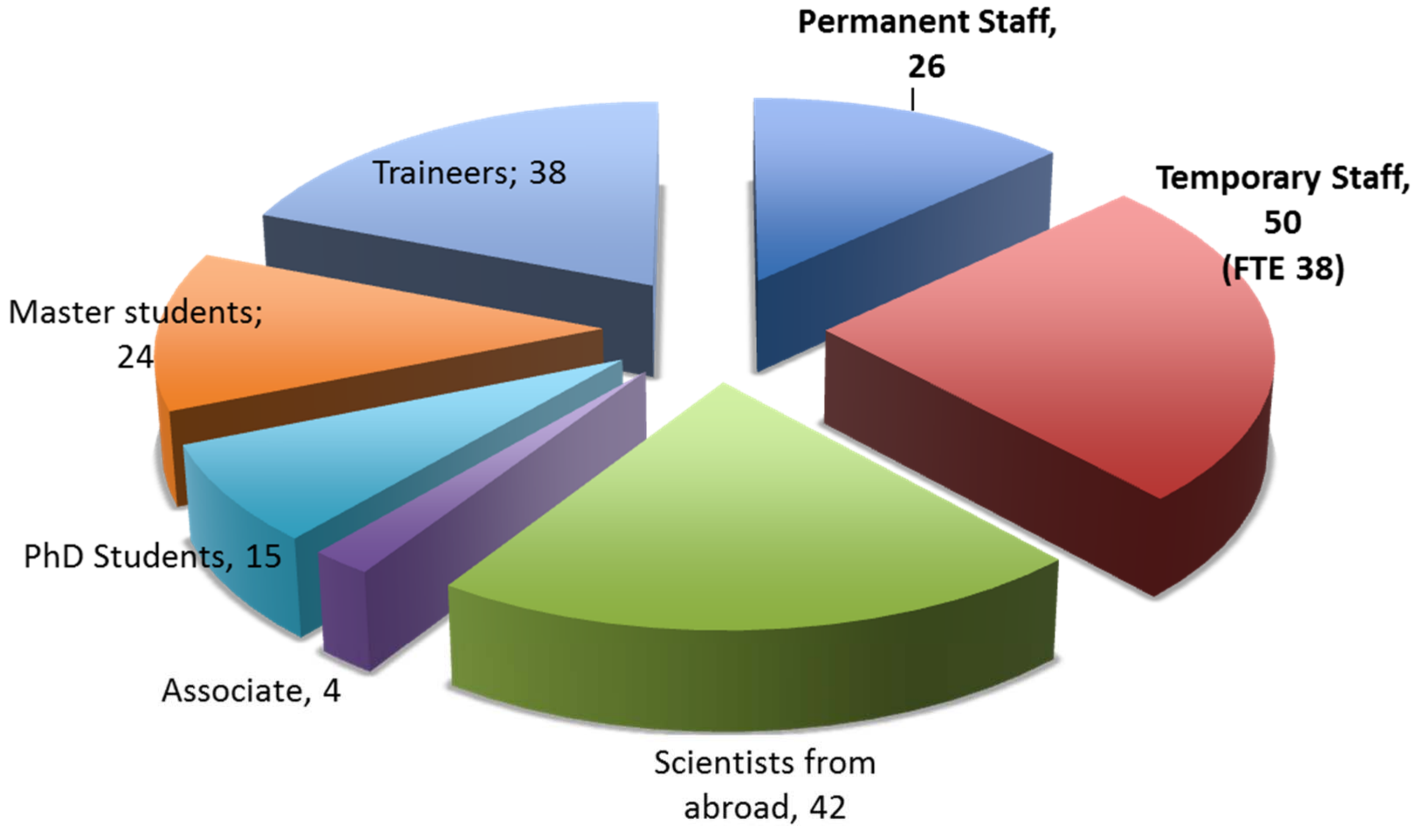
Funding Institutions



Visiting Scientists from abroad @ ITM in 2015



Total personnel



For a total of 89 FTE on an average of 5 years

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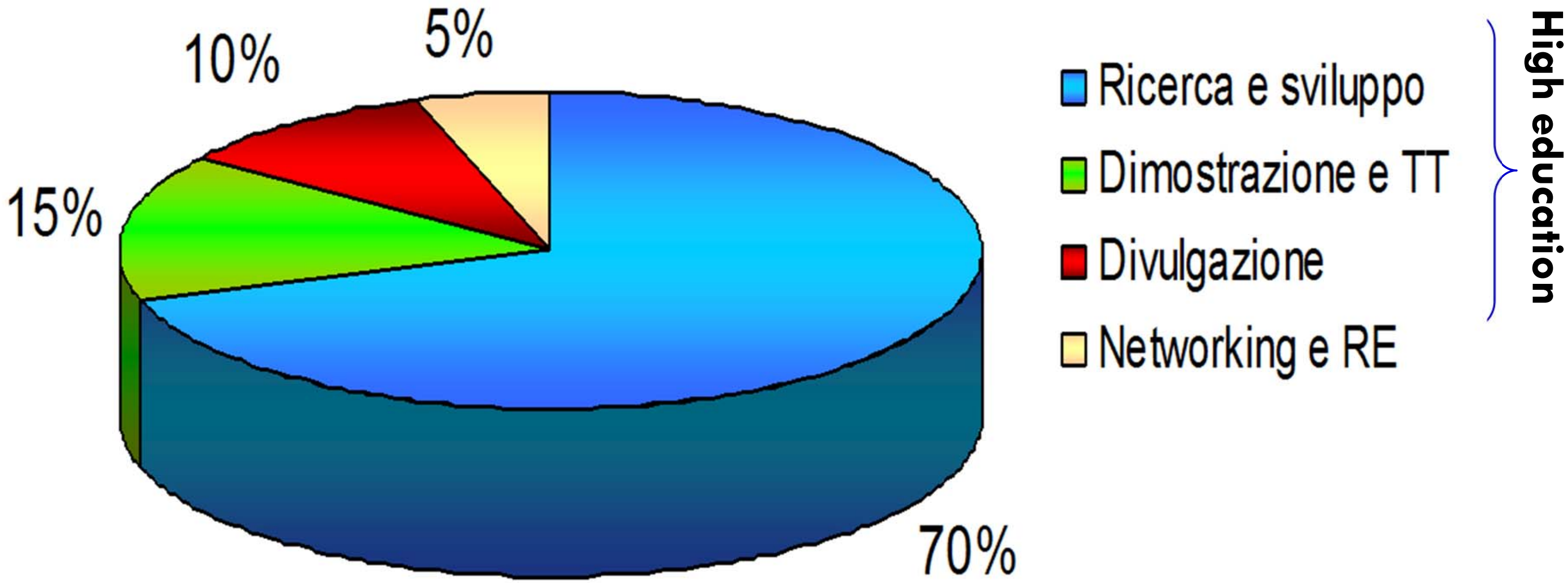
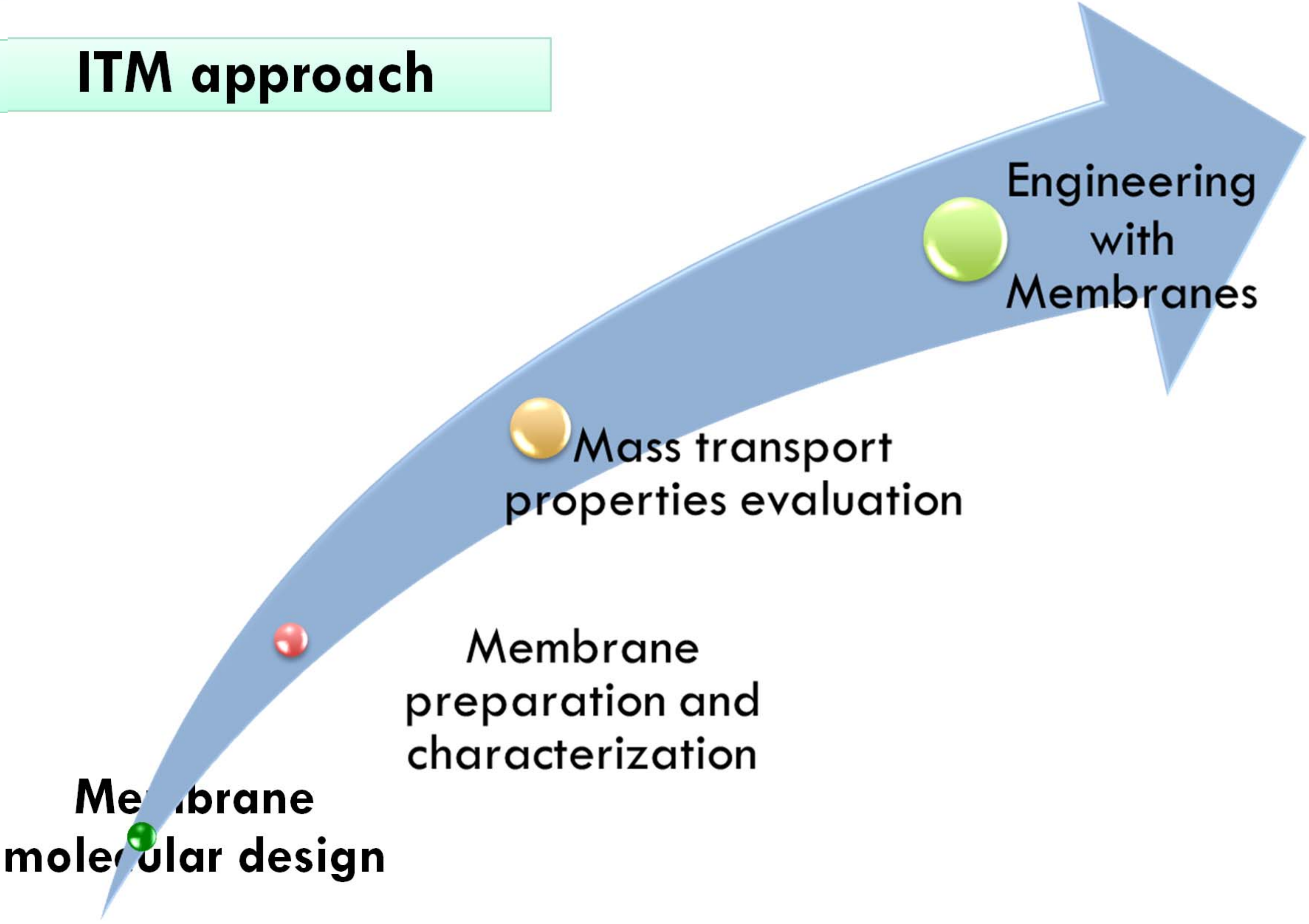
Activities distribution



From material to process

ITM approach



Membrane operations for CO_2 separation

Gas separation by means of …

- Polymeric membranes
- Pd-based membranes

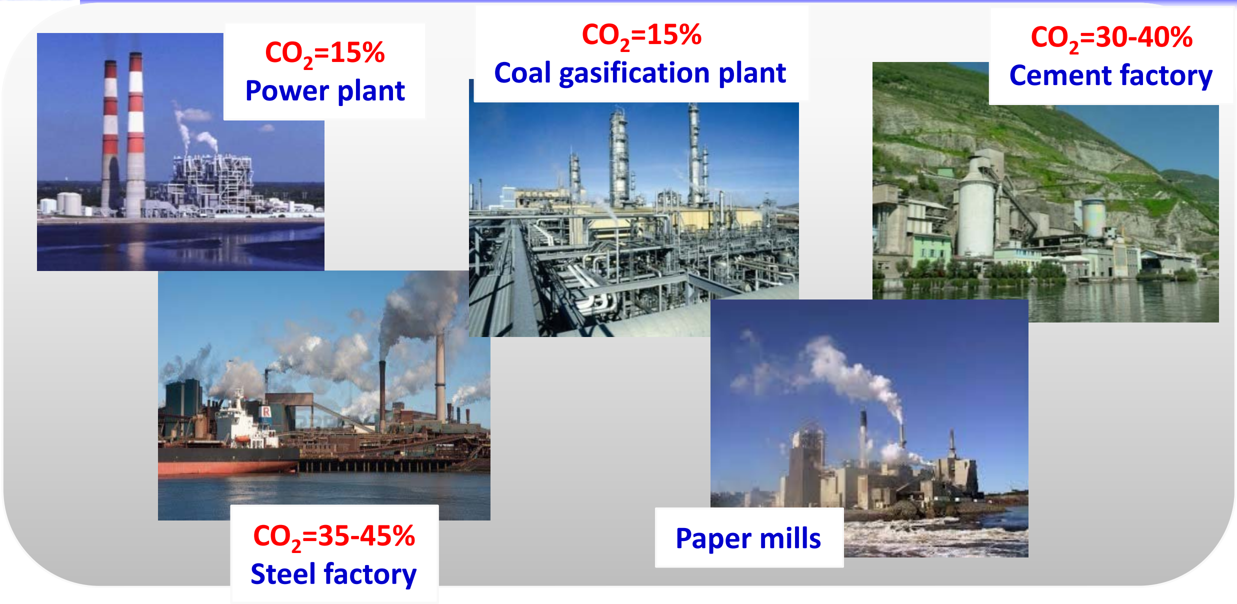
… in post-combustion capture

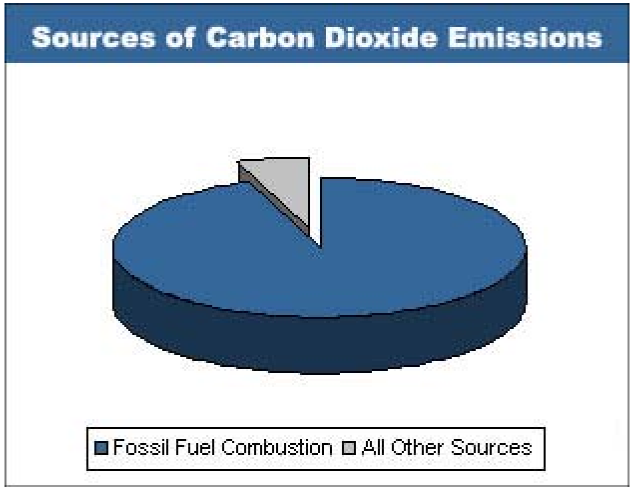
Pd-based membrane reactors for H_2 separation/production, CO_2 present as significant by-product

- Reformate hydrogen streams
- Steam methane reforming reaction
- Water gas shift process

… in pre-combustion capture

Flue gas emissions by....

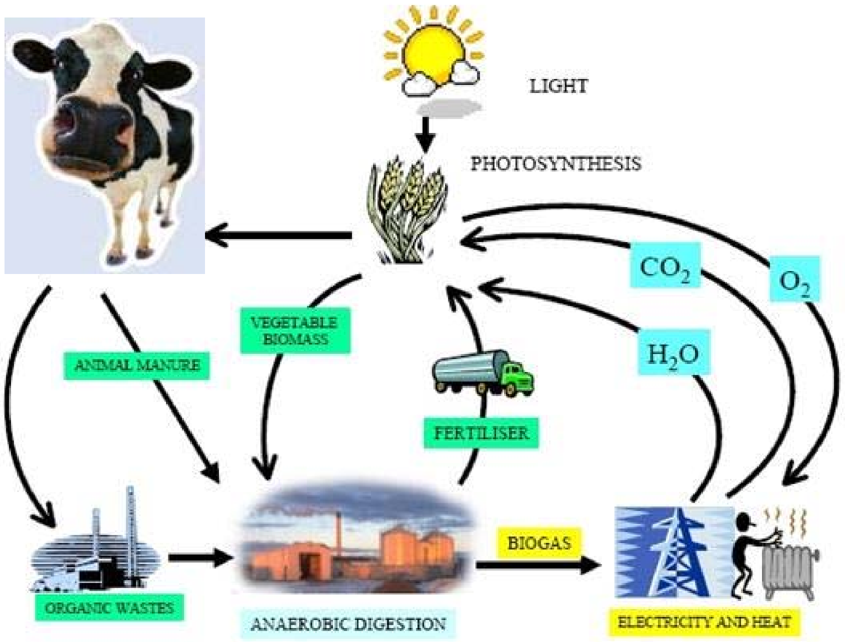




Inventory of U.S. Greenhouse Gas Emissions and Sinks (2008), EPA

CO_2/CH_4 mixtures by….

BioGAS

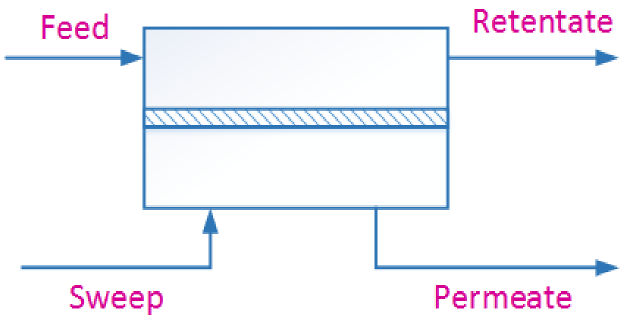


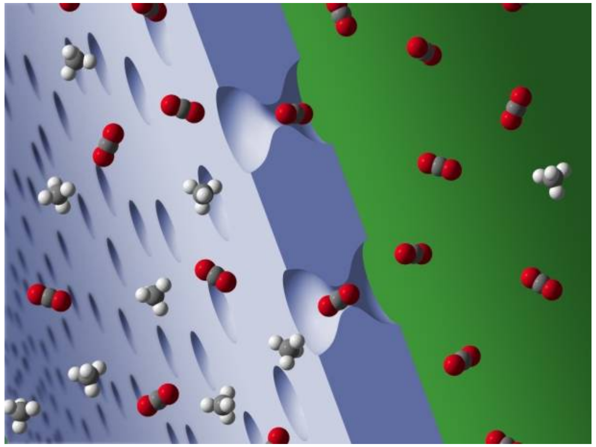
Natural GAS sweetening

Separations ...

- **CO_2/N_2** (the one focused on)
  - Involved streams have not a value
  - Pressure is required only for separation
  - The final stream is the permeate (at low pressure)
  - Low CO_2 feed concentration (10-30%)
  - Contaminants = membrane chemical stability
- **CO_2/CH_4**
  - A value product (CH_4) containing stream
  - Pressurized stream
  - The final stream is the retentate (membrahe high-side pressure)

Membrane modules





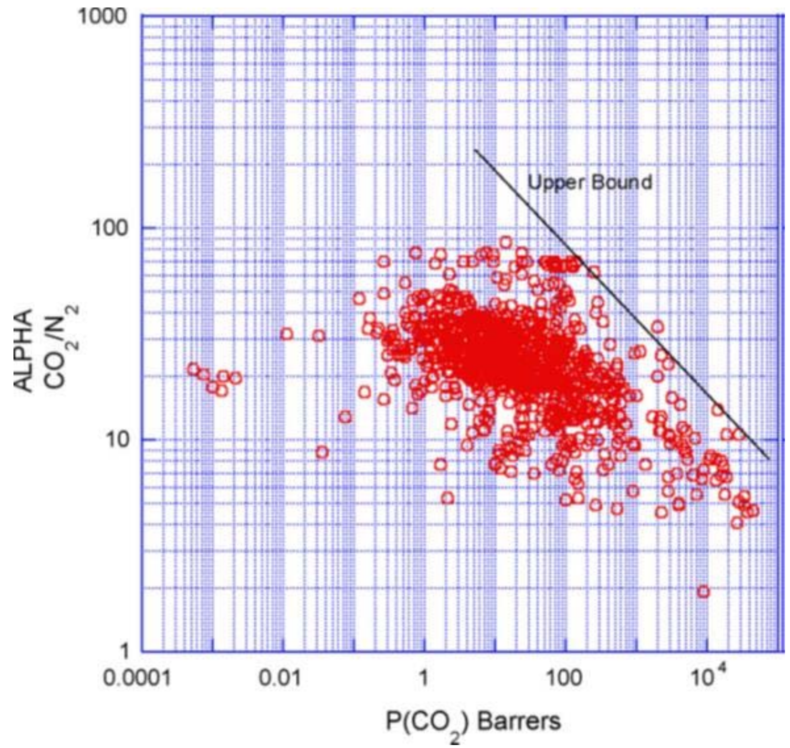
Separation design

- **CO_2 recovery**
  >80%
- **CO_2 concentration**
  >90%
- **What technology** (Absorption, adsorption, cryogenic distillation, **membrane**, …)? Depends on
  - Driving force
  - Operating conditions
  - Materials
  - Efficiency
  - Environmental friendly

Robeson's permeability/selectivity trade-off

Polymeric membranes generally undergo a trade–off limitation between permeability and selectivity: as permeability increases, selectivity decreases, and vice-versa.

$$PermatingFlux_A = \frac{Permeability_A}{membranethickness}\left(P_A^{Feed} - P_A^{Permeate}\right)$$



Robeson L.M., Journal of Membrane Science, 320, (2008), p.390

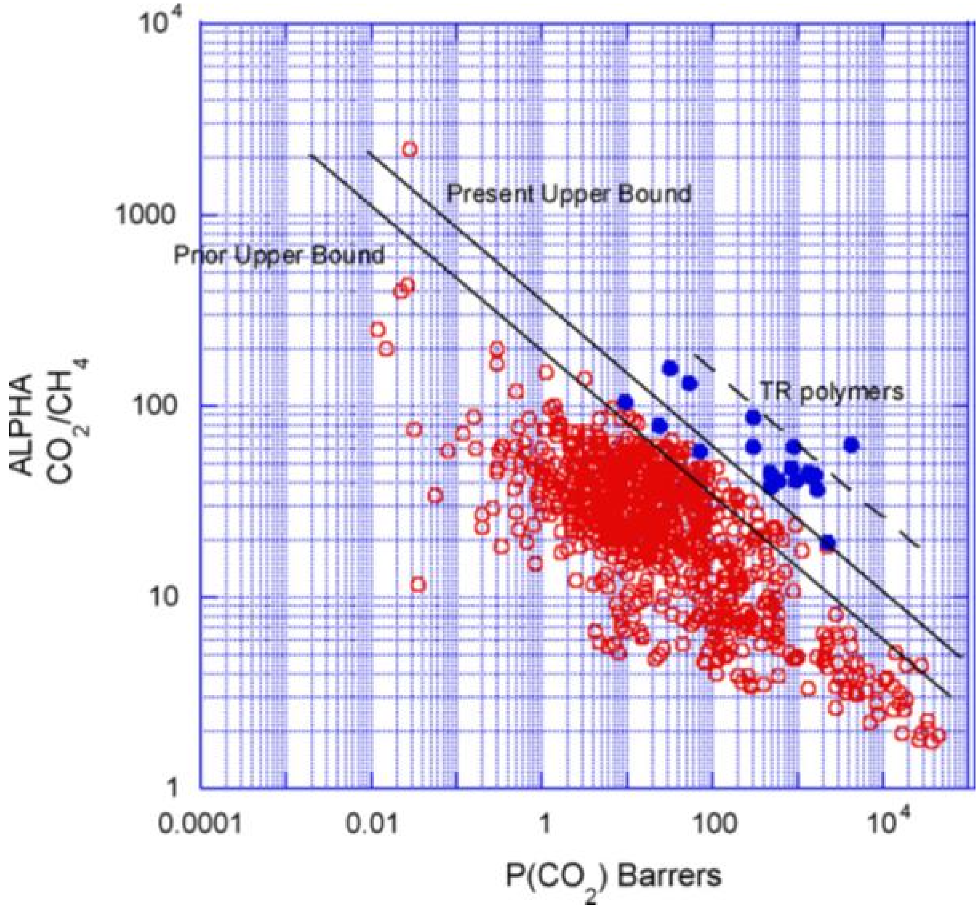
Membrane materials	CO_2/N_2 Selectivity ranges
CA, SPEEK, PSF, **TORLON, HYFLON, MATRIMID 5218**, PMMA, PPO, PEI+zeolite, CTA, PDMS modified, **TR polymers**, Polyarilates, Polycarbonates	20-30
PI modified, PEO, PES, PMEEP, PEI	30-60
Sieving carbon, PEO, **PEBAX**, PEBAX+silica, PEG+Silica, PI+zeolite, **PVAm (Facilitated transport membranes)**	50-100
PVAm (Facilitated transport membranes)	150-300

EU-NanoGloWa

PON-FotoRiduCO$_2$

Robeson trade-off

Polymeric membranes generally undergo a trade–off limitation between permeability and selectivity: as permeability increases, selectivity decreases, and vice-versa.



Robeson L.M.,
J. Membr. Science, 320, (2008), 390

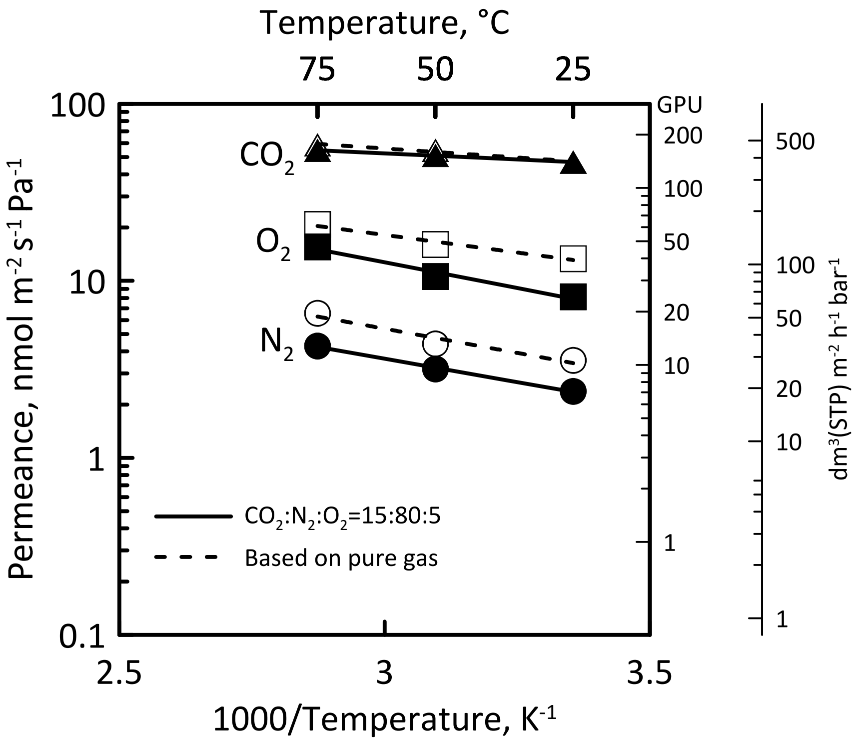
*TR, thermally re-arranged

Experimental measurements

- Temperature (room to hundred Celsius)
- Pressures ranges
  - permeate: vacuum to a few bars
  - feed: 1-10 bars (a higher pressure is possible)
- Feed composition
  - Single gas and Gas mixtures
  - Relative humidity: 0-100%
  - Other components
- Steady-state (no variation in the time)

Mixed gases CO_2:N_2:O_2=15:80:5

METT-project (MAECI)



Permeance increases from 25 to 75°C:

- 13% for CO_2
- 44% for N_2
- 47% for O_2

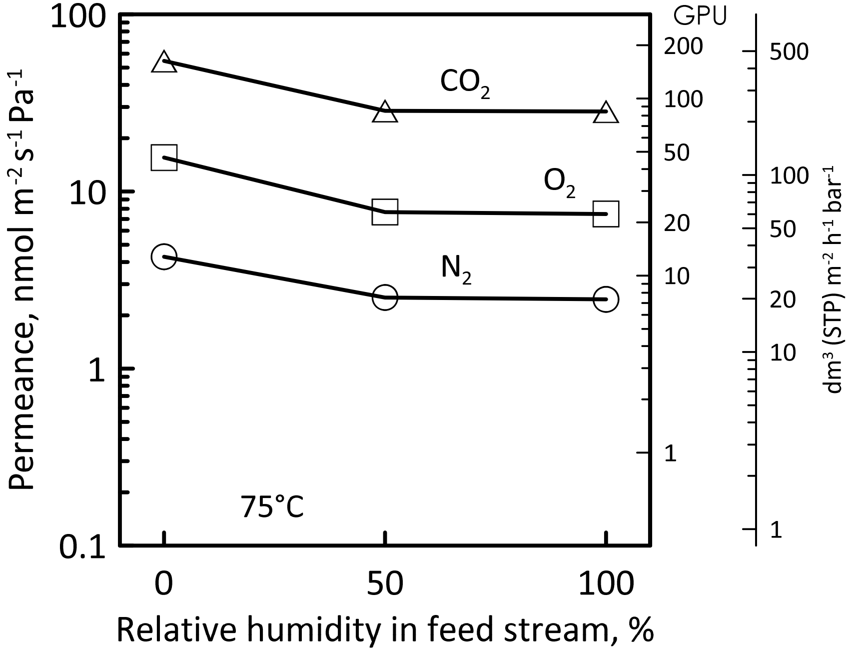
Permeance measured for single gas is higher than that measured feeding gas mixture.

Kristofer L. Gleason, Zachary P. Smith, Qiang Liu, Donald R. **Paul**, Benny D. **Freeman** [J. membrane science 475 (2015) 204-214] well describe this behavior.

Barbieri (Cersosimo et al.) “Separation of CO_2 from humidified ternary gas mixtures using thermally rearranged polymeric membranes”, J. Membr. Science, 2015, (492), 257–262, 10.1016/j.memsci.2015.05.072

Wet mixtures measurements

METT (MAECI)



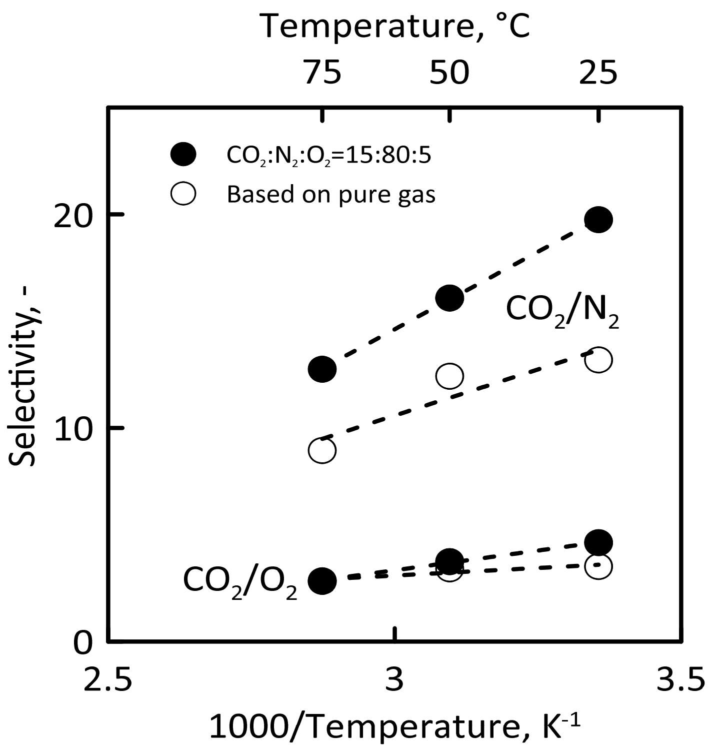
As the feed gas becomes increasingly humidified, the corresponding CO_2, N_2 and O_2 permeance decreases.
This permeance fall is owing to a competitive sorption and also declining diffusivities owing to blockage by water clusters at a higher relative humidity [Colin A. Scholes, Benny D. Freeman, Sandra E. Kentish, journal membrane science 470 (2014) 132-137].

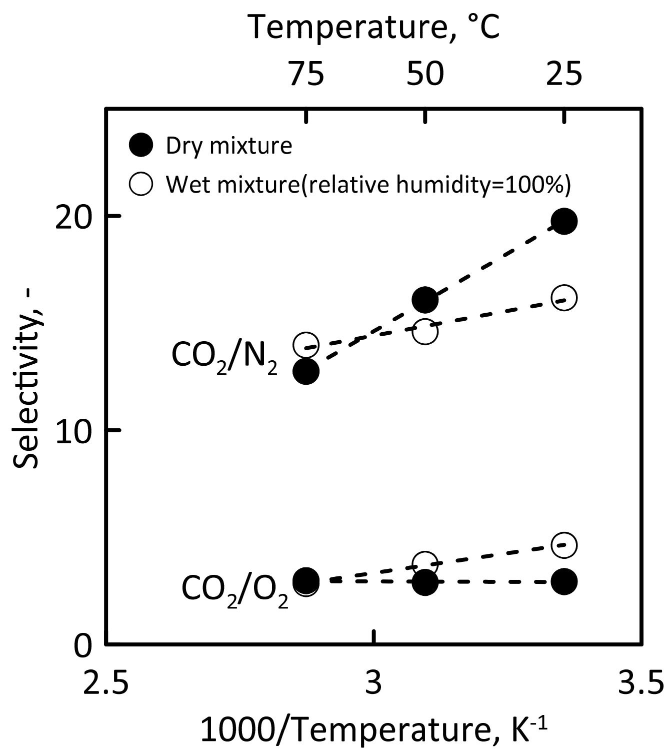
Barbieri (Cersosimo et al.) “Separation of CO_2 from humidified ternary gas mixtures using thermally rearranged polymeric membranes”, J. Membr. Science, 2015, (492), 257–262, 10.1016/j.memsci.2015.05.072

Wet and dry mixtures measurements

CO_2/N_2 actual selectivity is higher of that based on pure gases

The selectivity is lower and it decreases as a function of the temperature





METT (MAECI)

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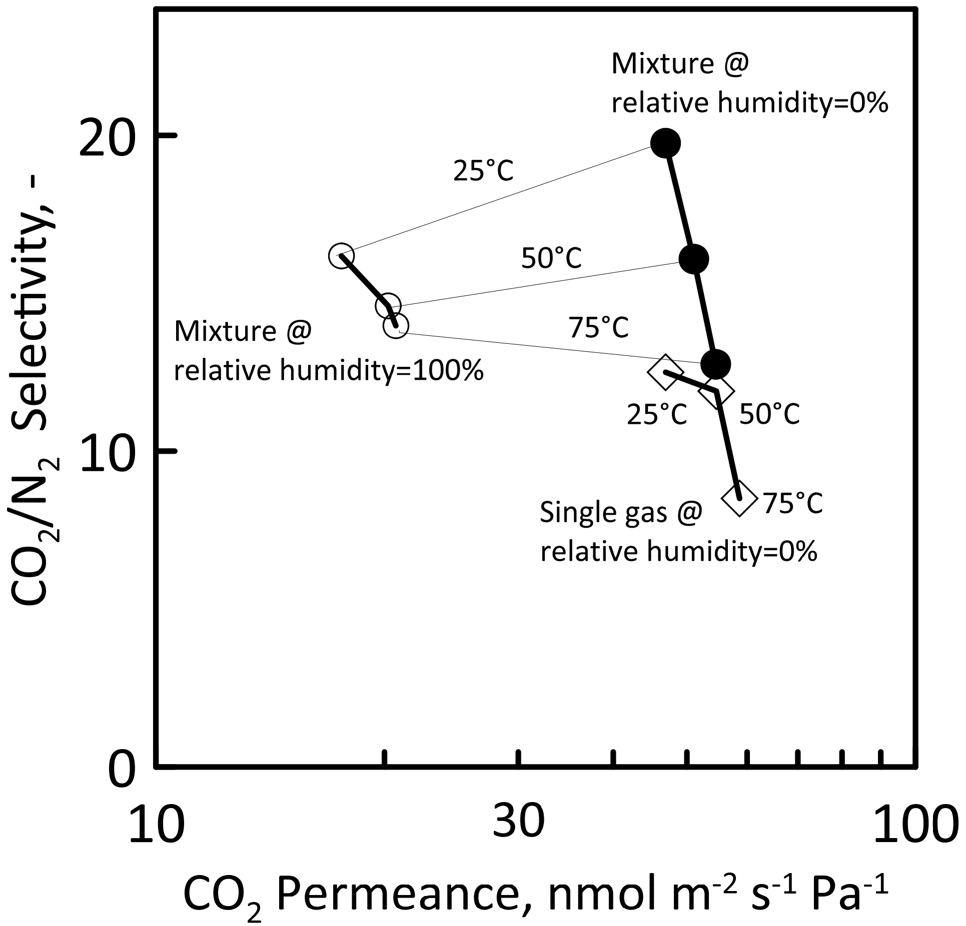
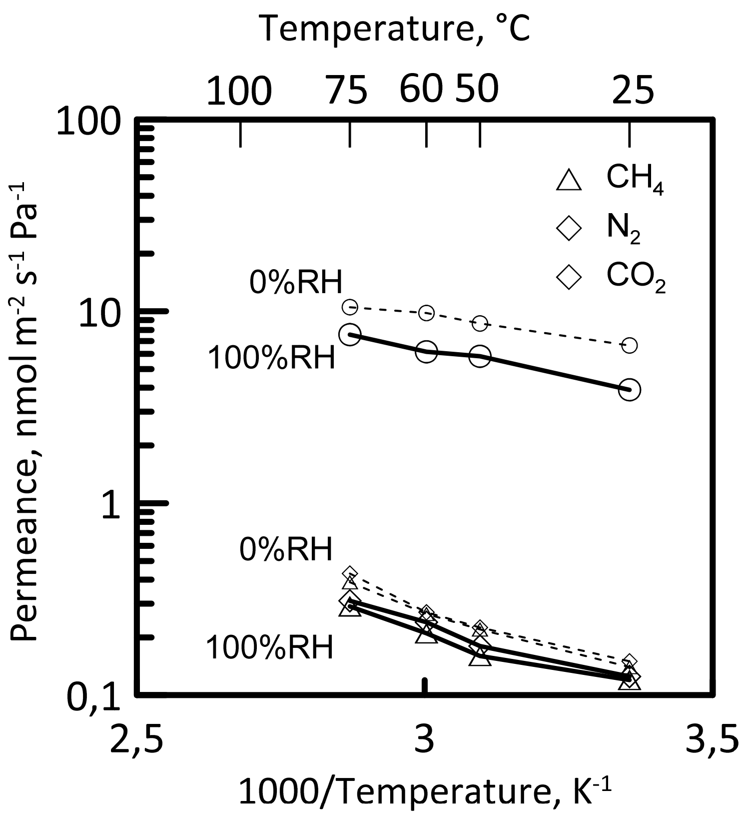
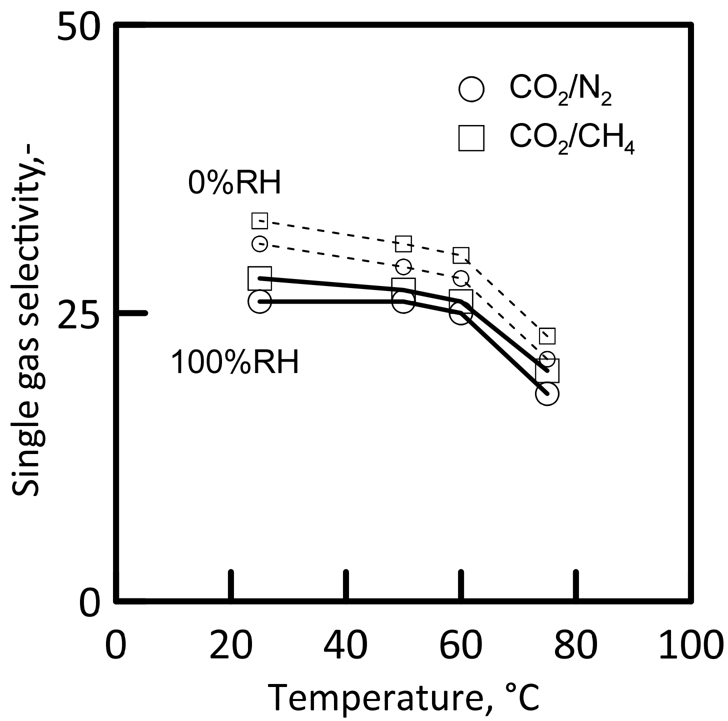


Consiglio Nazionale delle Ricerche

Barbieri (Cersosimo et al.) “Separation of CO_2 from humidified ternary gas mixtures using thermally rearranged polymeric membranes”
J. Membr. Science, 2015, (492), 257–262, 10.1016/j.memsci.2015.05.072

Experimental analysis



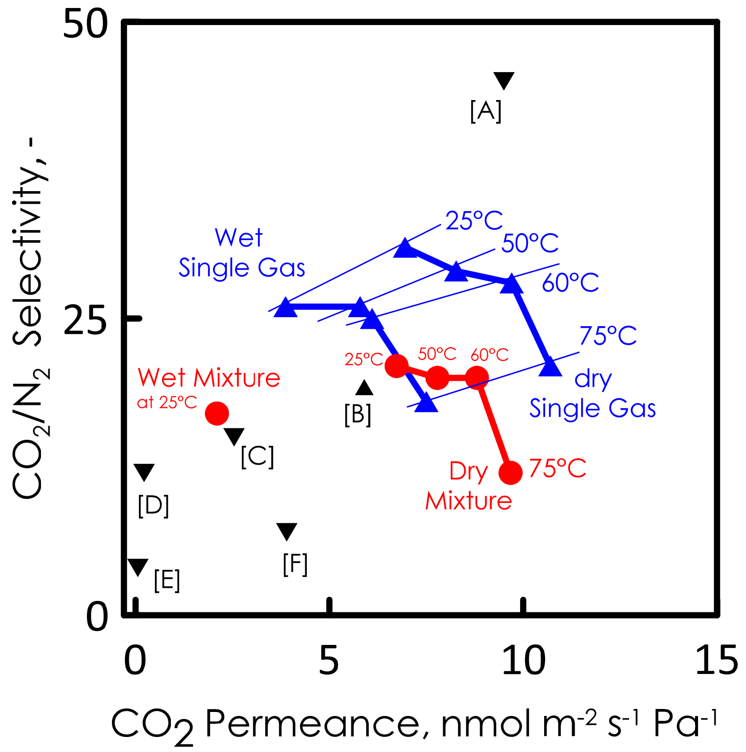


PON-FotoRiduCO$_2$

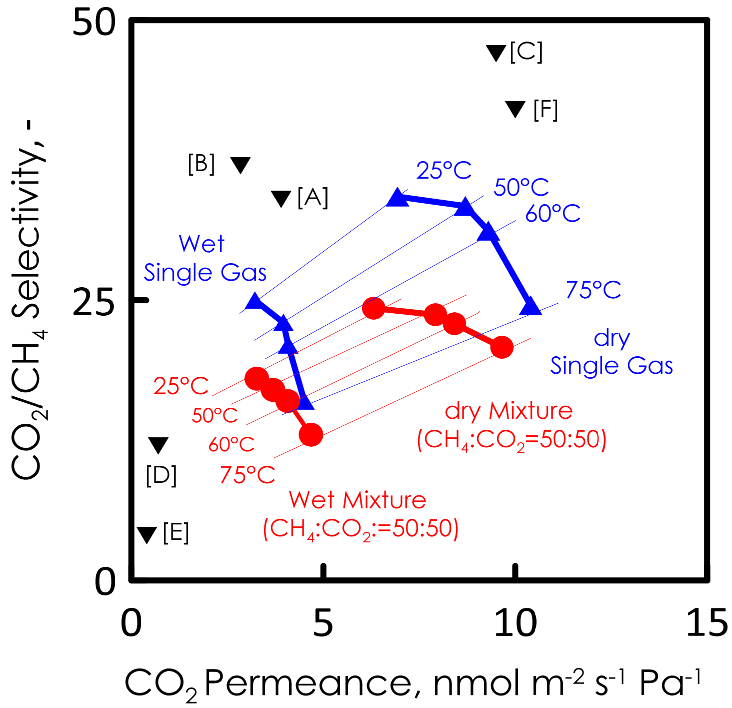
F. Falbo, F. Tasselli, A. Brunetti, E. Drioli, G. Barbieri, "CO_2 separation through hollow fiber polyimide membranes", Brazilian Journal of Chemical Engineering 2014 31 1023 – 1034. http://dx.doi.org/10.1590/0104-6632.20140314s00003031.

Membrane gas transport properties

PON-FotoRiduCO$_2$



Falbo F.; Tasselli F.; Brunetti A.; Drioli E.; Barbieri G. Brazilian Journal of Chemical Engineering, vol 31 n°4, pp 1023-1034 (2014)

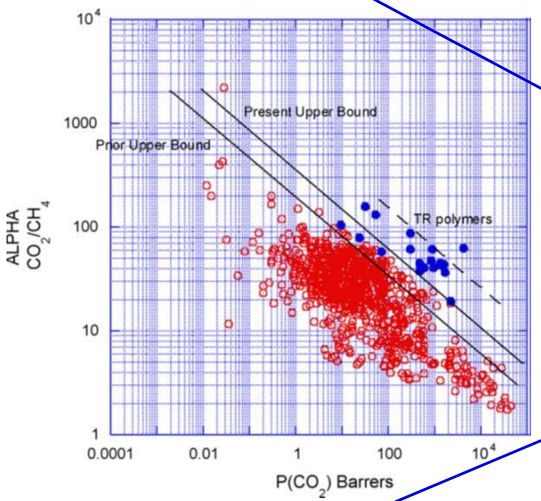


Falbo F.; Brunetti A.; Barbieri G.; Drioli E.; Tasselli F. Applied Petrochemical Research (2015), *submitted*

from Robeson's permeability/selectivity trade-off

to modelling analysis

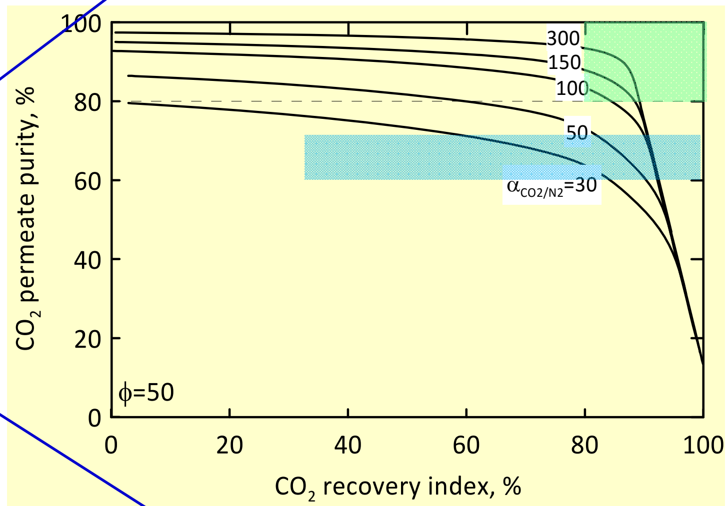
$$PermatingFlux_A = \frac{Permeability_A}{membranethickness}\left(P_A^{Feed} - P_A^{Permeate}\right)$$



Materials properties

Permeance & selectivity

Separation Performance Maps



Tool (simple) for analysing the CO_2 membrane separations (from flue gas, etc.)

1D (dimensionless) mathematical model for the multi-species permeation in steady-state and co-current configuration (no sweep)

Feed/Retentate side

$$\frac{d\varphi_{CO_2}^{Retentate}}{d\zeta} = -\Theta_{CO_2}\left(\phi\ x_{CO_2}^{Retentate} - x_{CO_2}^{Permeate}\right)$$

$$\frac{d\varphi_{N_2}^{Retentate}}{d\zeta} = -\frac{x_{CO_2}^{Feed}}{x_{N_2}^{Feed}}\frac{1}{\alpha_{CO_2/N_2}}\ \Theta_{CO_2}\left(\phi\ x_{N_2}^{Retentate} - x_{N_2}^{Permeate}\right)$$

Permeate side

$$\varphi_{CO_2}^{Permeate}(\zeta) = \varphi_{CO_2}^{Feed} - \varphi_{CO_2}^{Retentate}(\zeta) \qquad \varphi_{N_2}^{Permeate}(\zeta) = \varphi_{N_2}^{Feed} - \varphi_{N_2}^{Retentate}(\zeta)$$

Brunetti A., Scura F., Barbieri G., Drioli E., *Journal of Membrane Science*, 359 (2010) 115–125

In the equations φ_{CO2}, φ_{N2} are the dimensionless molar flow rate, for CO_2 and N_2, respectively and ζ is the dimensionless module length.

$$\varphi_i = \frac{Q_i}{Q_i^{Feed}}$$

$$\zeta = \frac{z}{L}$$

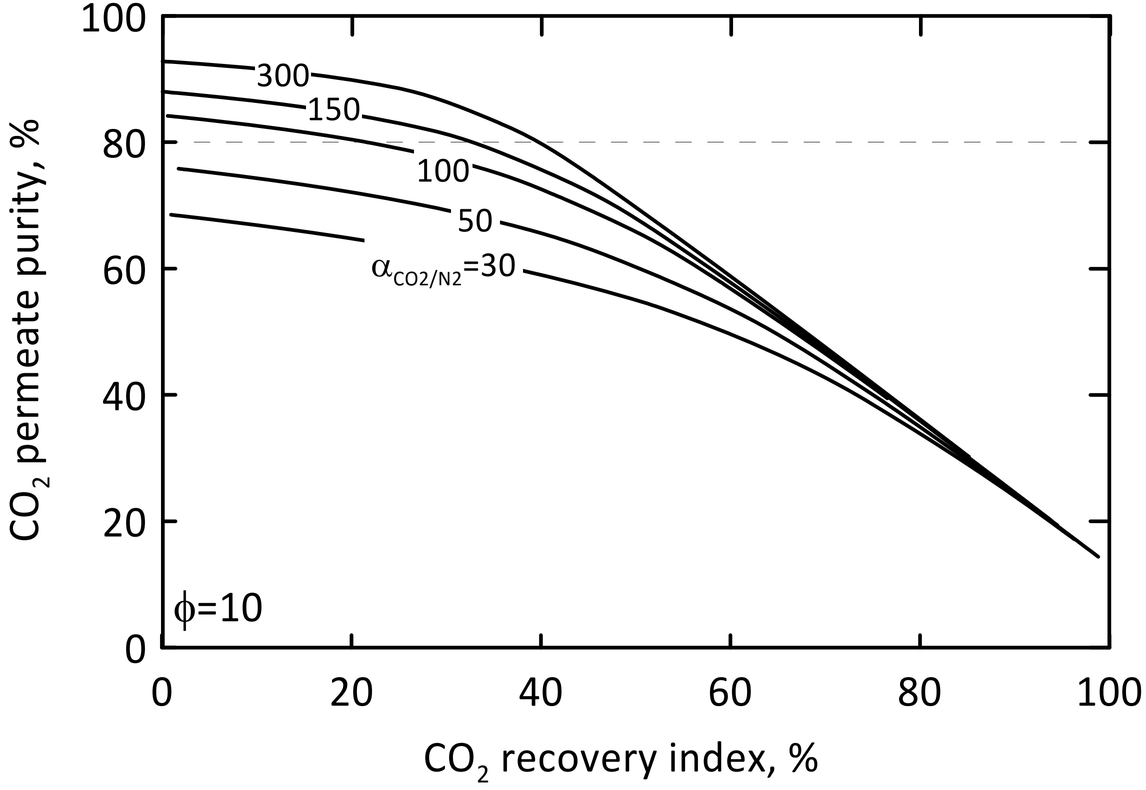
Θ_i and ϕ are the parameters affecting the performance of a one stage membrane system, the permeation number and the feed to permeate pressures ratio, respectively.

$$\Theta_{CO_2} = \frac{Permeance_{CO_2} \; A^{Membrane} \; P^{Feed}}{x_{CO_2}^{Feed} \; Q^{Feed}}$$

$$\phi = \frac{P^{Feed}}{P^{Permeate}}$$

Θ_i expresses a comparison between the two main mass transport mechanisms involved: the permeating one through the membrane and the convective flux of the feed stream.

Separation analysis by Mathematical Modelling



$$\phi = \frac{P^{Feed}}{P^{Permeate}}$$

Brunetti A.; Scura F.; Barbieri G.; Drioli E.; "Membrane technologies for CO_2 separation", *J. Membr. Sci.*, 2010, 359, 115-125; dx.doi.org/10.1016/j.memsci.2009.11.040

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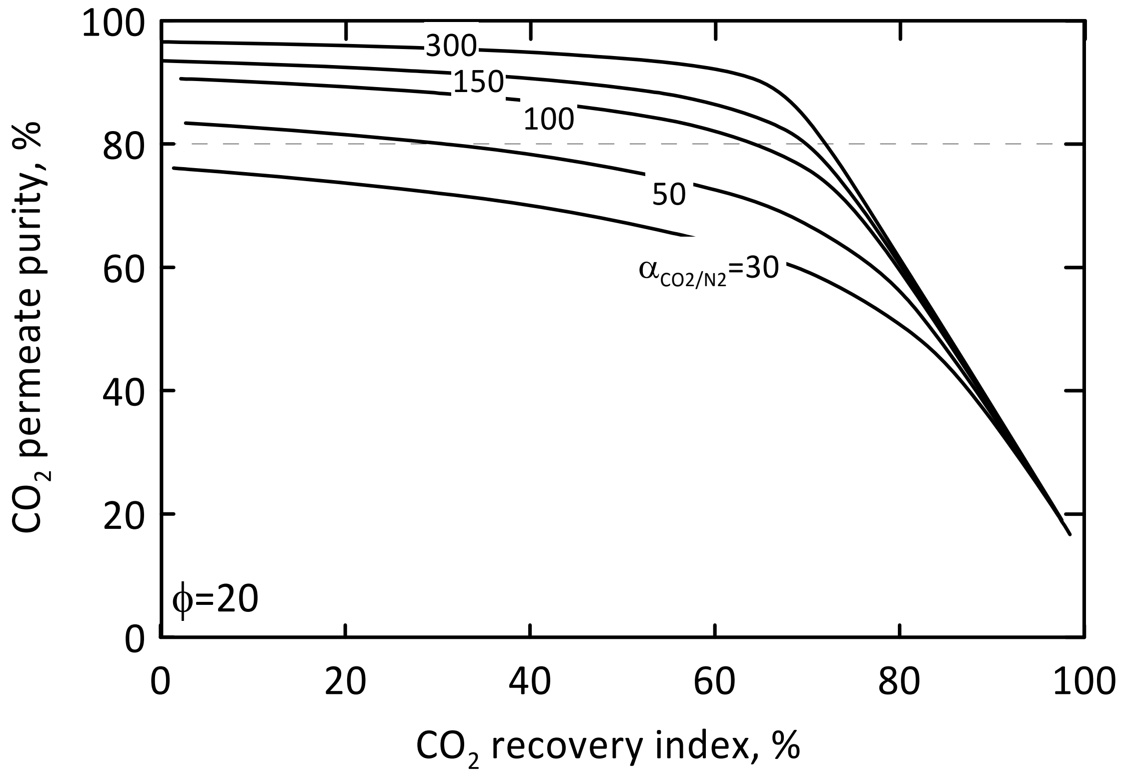

$$\phi = \frac{P^{Feed}}{P^{Permeate}}$$

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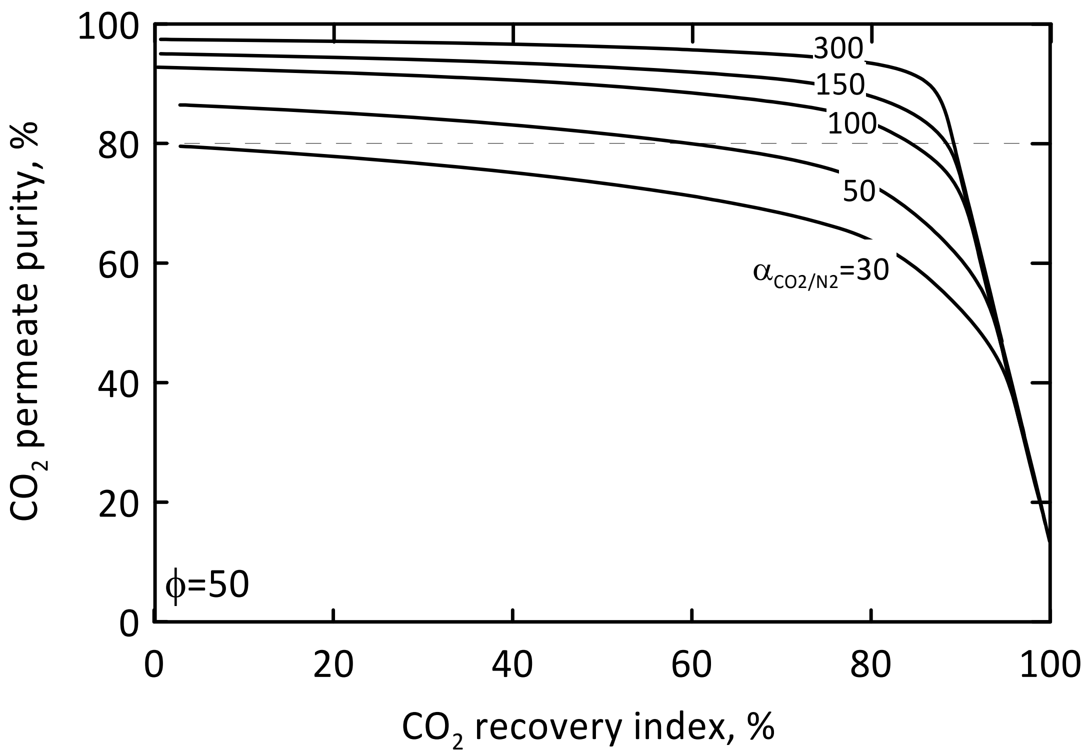

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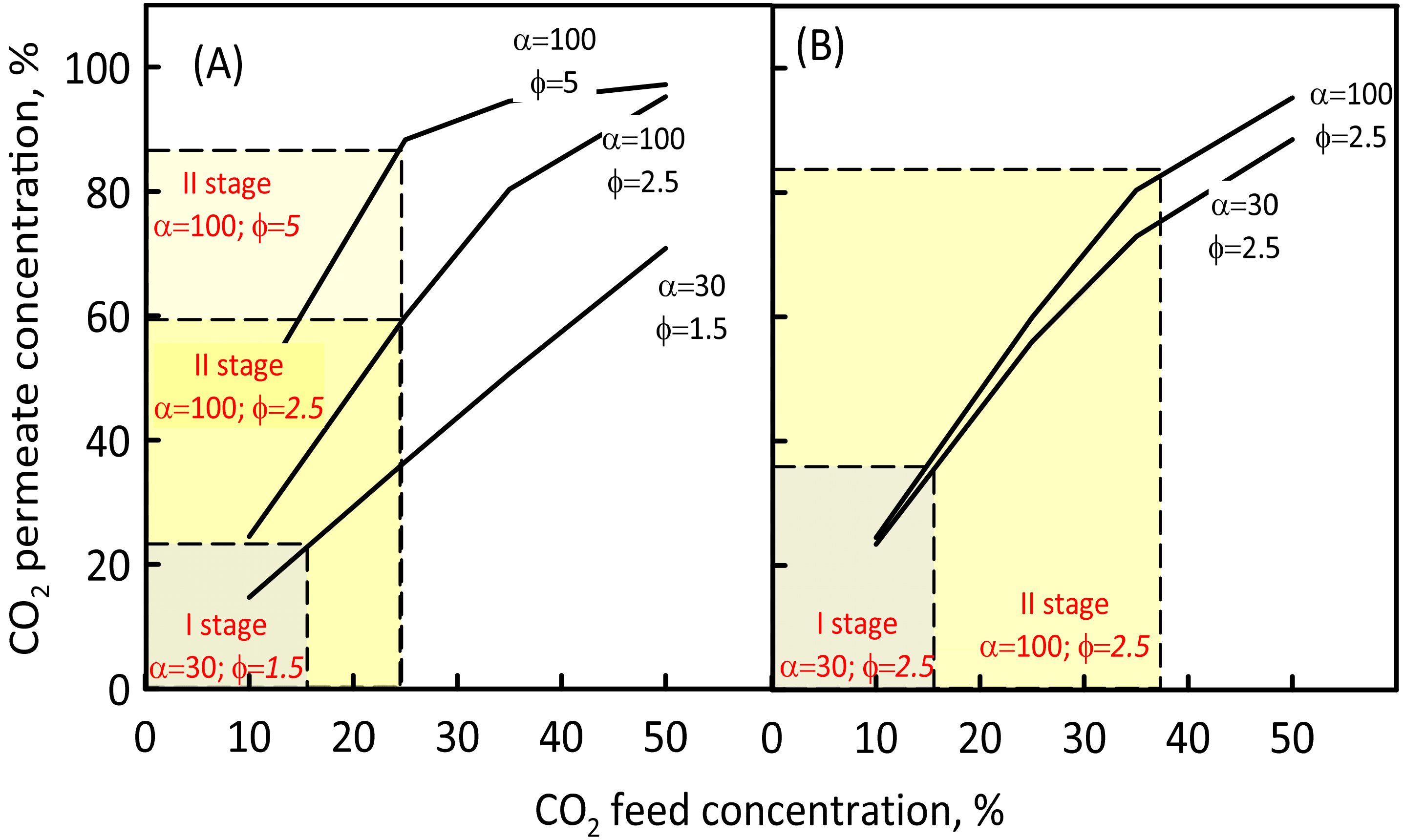
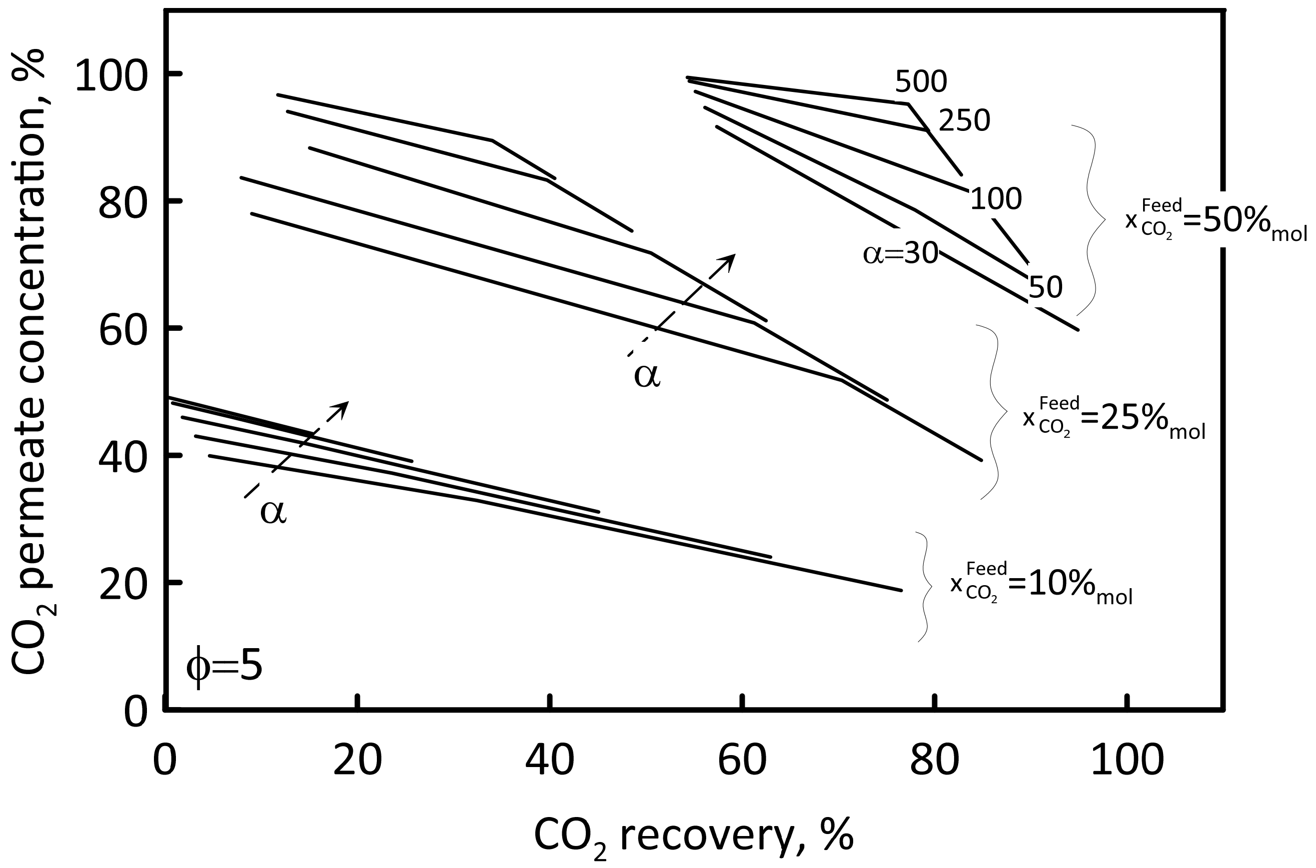


CO_2 permeate concentration as function of CO_2 feed concentration at different selectivities for a multistage configuration

Brunetti A.; Drioli E.; Lee Y.M.; Barbieri G.; "Engineering evaluation of CO_2 separation by membrane gas separation systems", *J. Membr. Sci.*, 2014, 454, 305-315; http://dx.doi.org/10.1016/j.memsci.2013.12.037



- CO_2 permeate concentration as function of CO_2 recovery at various selectivities and CO_2 feed concentrations. **Pressure ratio=5**

Brunetti A.; Drioli E.; Lee Y.M.; Barbieri G.; "Engineering evaluation of CO_2 separation by membrane gas separation systems", *J. Membr. Sci.*, 2014, 454, 305-315; http://dx.doi.org/10.1016/j.memsci.2013.12.037

Guidelines for sustainable separations

Comparison among some important design parameters

	Membrane System	Absorption	Adsorption	Cryogenic
Operating flexibility	High (% CO_2>20%) Low (% CO_2<20%)	Moderate	High	Low
Response to variations	Instantaneous	Rapid (5-15 minutes)	Rapid (5-15 minutes)	Slow
Start up after the variations	Extremely short (10 minutes)	1 h	1 h	8-24 h
Turndown	down to 10%	down to 30%	down to 30%	down to 30-50%
Reliability	100%	Moderate	Moderate	Limited
Control requirement	Low	high	high	high
Ease of expansion	Very high (modularity)	Moderate	Moderate	Very low

Brunetti A.; Scura F.; Barbieri G.; Drioli E.; "Membrane technologies for CO_2 separation", *J. Membr. Sci.*, 2010, 359, 115-125; dx.doi.org/10.1016/j.memsci.2009.11.040

Concluding remarks

Membranes and membrane operations are good candidate for sustainable chemistry and processes

- no solvents are required
- Less energy intensive processes

Membrane engineering, together with material science, has a crucial role for the application of membrane operations in CO_2 separation. This means …

- integrated process design
- optimization of operating conditions
- process intensification

Contest

Some projects on this activity line

- ✓ **MAECI**, "METT - New highly innovative membrane operations for CO_2 separation (capture) at medium and high temperature: Experimental preparation and characterization, theoretical study on elementary transport mechanisms and separation design"
  Bilateral agreement between MAECI (Italy) and MOST (South Korea).
- ✓ **MIUR**, Ricerca e competitività 2007-2013, PON 01_02257 "FotoRiduCO$_2$ - Photoconversion of CO_2 to methanol fuel", ("Studio e sperimentazione di sistemi di foto conversione con luce solare di CO_2 in metanolo, da utilizzare come combustibile")
- ✓ **EU**, "NanoGlowa – Nanomembranes against Global Warming" FP6/NMP3-CT-2007-026735
- ✓ **ItalCementi S.p.A.; ENEL Produzione S.p.A.**
- ✓ **CNR**-CSIR(India) bilateral agreement

Some other activities

Central testing lab in EU co-funded projects

Hydrogen production, upgrading and purification

- ✓ CNR-KOSEF, CNR-SRNSF and MAE/MAECI-MOST bilateral agreements, EU-GRACE, EU-HydroFueler, EU-DEMACMER, FIRB-CAMERE, …

Membrane reactors for petrochemical processes

- ✓ King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia

Fuel Cells

- ✓ "LoLiPEM: Long-life PEM-FCH &CHP systems at temperatures higher than 100°C" GA 245339. EC-FP7/FCH JU (coordination)
- ✓ HYPOD (Advanced Devices Spa)

Water capture

- ✓ "EU-CapWa – Capture of evaporated Water" 2010-2013 – Co-funded by EU (GA 246074)

Innovative membrane utilizzation

- ✓ "OMPA - Osmotic Pressure Actuator". Funded by The Norway Research Council, through Statoil

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Grazie per la vostra cortese attenzione

Thank you for your attention

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