Membrane engineering for CO_2 separation by gas separation systems

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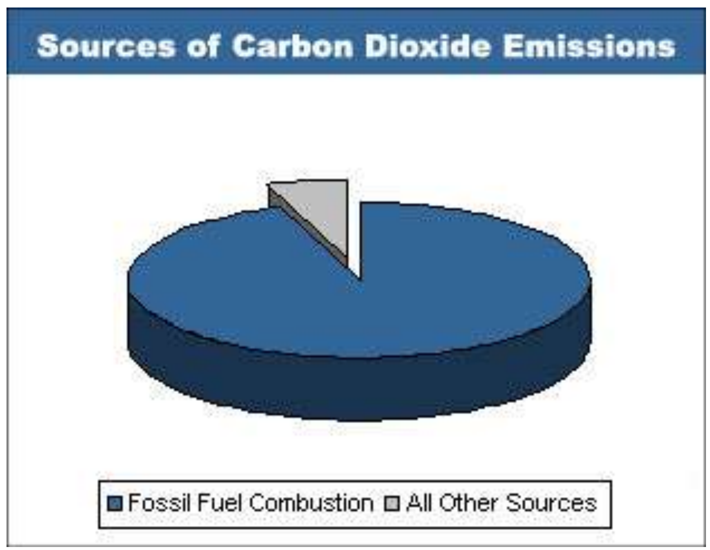
Main sources of CO_2

	Source	Separation
Flue gas streams	Power plants, coal gasification plants, Steel factory Cement factory, Transportation	CO_2/N_2
Natural Gas	Sweetening of Natural gas, etc.	CO_2/CH_4
Biogas	Various	

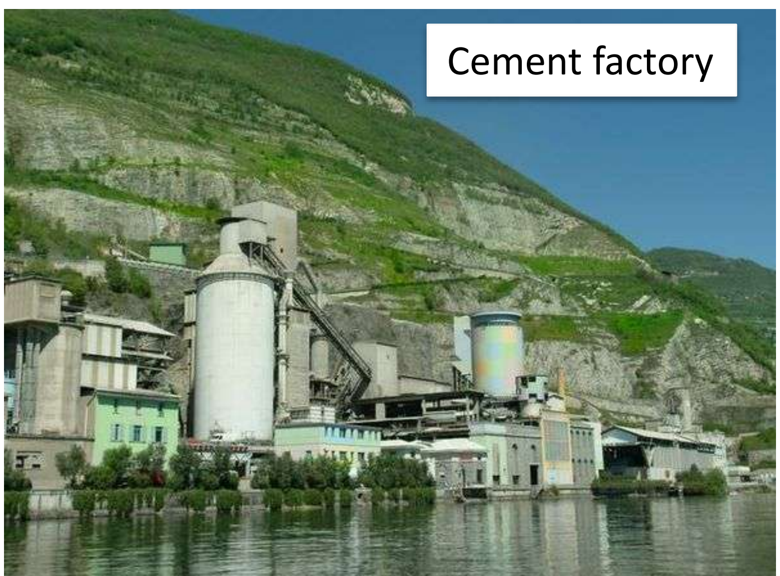


Inventory of U.S. Greenhouse Gas Emissions and Sinks (2008), EPA

Flue gas emissions from….


Power plant

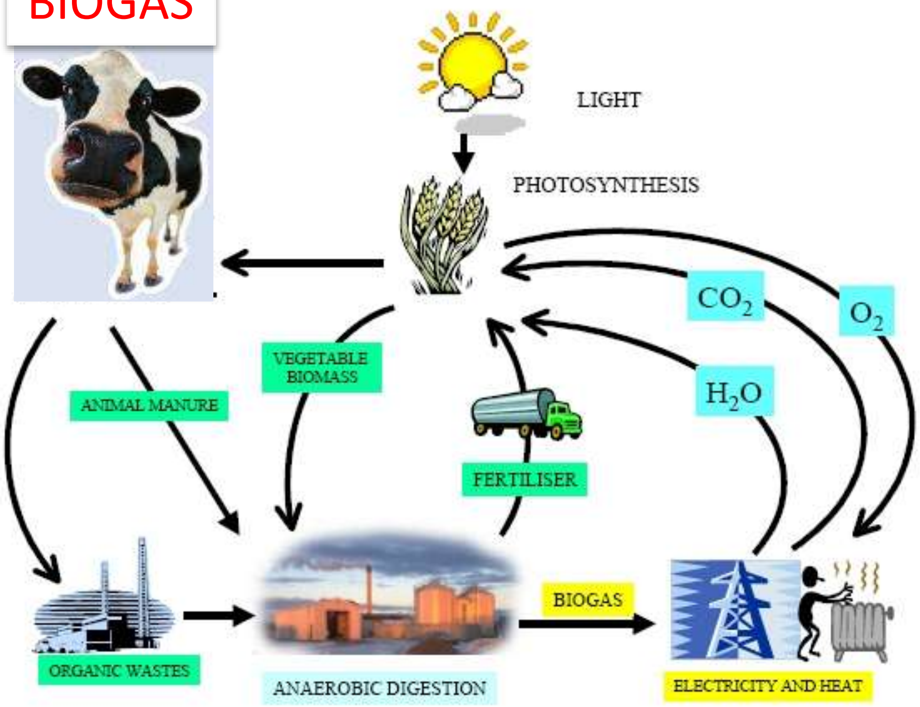

Steel factory


Cement factory


Coal gasification plant

CO_2/CH_4 mixtures from….

BIOGAS



NATURAL GAS SWEETENING

Traditional operations for gas separation

ABSORPTION

Absorption is a process that relies on a solvent's chemical affinity with a solute to dissolve preferably one species into another. It is widely proposed for CO_2 separation where generally, monoethanolammine or a solid absorbent is used. High amount of energy consumed is for solvent(MEA) recovery (3-4 units)

ADSORPTION

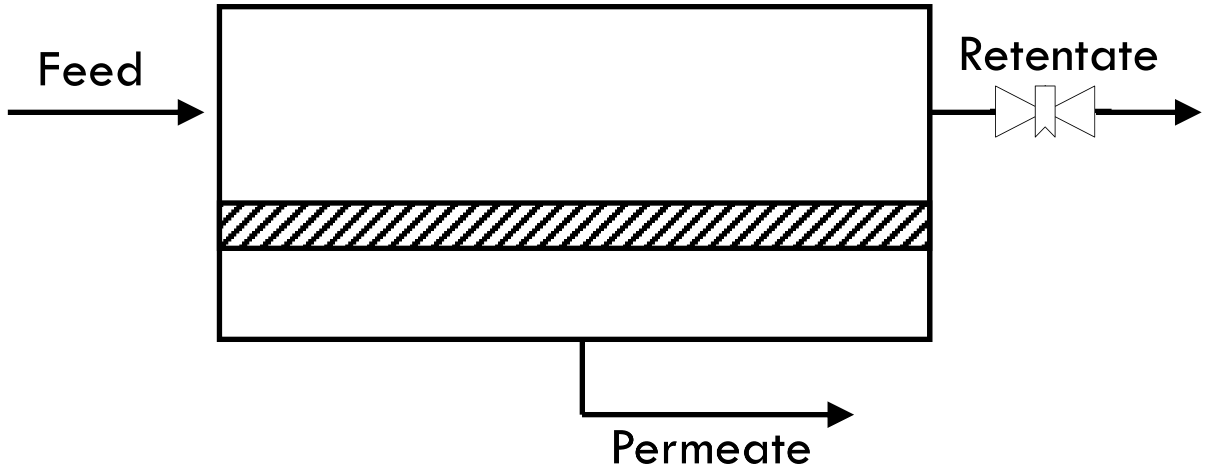
The PSA process is based on the capacity of some adsorbents (zeolites, etc.) in adsorbing such gases at high gas-phase partial pressure. Proper selection of the adsorbents is critical for both the performance of the unit and adsorbent life-time. For instance, the CO2 is adsorbed at higher partial pressure and then desorbed at lower partial pressure. High pressure is required (3-4 units).

CRYOGENIC

Low temperature separation process. The difference in boiling temperatures of the feed components affects the separation. One of the main advantages is the ability to produce separated hydrocarbon streams rich in C4+, ethane/propane, etc. One of the main drawbacks is the presence of H_2O in the gaseous stream that can strongly affect the separation performance; the gaseous stream to be treated needs to be completely dehydrated prior to be cooled. High energy intensity. Pre-treatment stages of the up-stream. (2 units)

Aaron D., Tsouris C., Separation Science and Technology, 40, (2005), 321-

Membrane-assisted Gas Separation



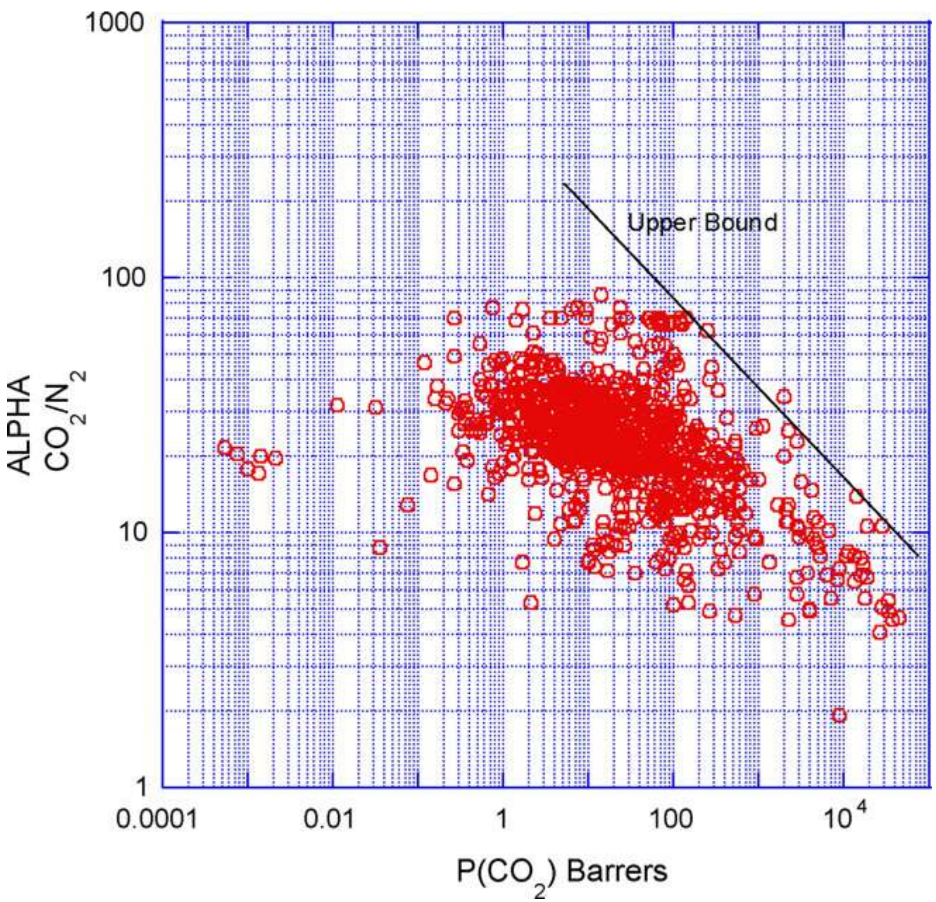
- Simplicity
- Modularity
- Equipments: reduced in size & number
- Low investment costs
- The required gas compression is much smaller than that of PSA
- Temperature not as extreme as cryogenic

- CO_2/N_2 Streams
  - No value
  - Pressure is required for separation
  - The final stream of interest is the permeate
  - Low CO_2 concentration (10-30%)

- CO_2/CH_4 Streams
  - Value due to the CH_4 content
  - Pressurised stream
  - The final stream is the retentate (high pressure)

Robeson trade-off

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



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 selective carbon, PEO, PEBAX, PEBAX+silica, PEG+Silica, PI+zeolite, PVAm (Facilitated transport membranes)	50-100
PVAm (Facilitated transport membranes)	150-300

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

*TR, thermally rearranged

Simple tool for a preliminary analysis on the prospects for membranes in CO_2 capture from flue gas

Dimensionless 1D mathematical model for the multi-species steady-state permeation in no-sweep mode and co-current configuration

Feed/Retentate side

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

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

Permeate side

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

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

Flue gas composition	13% CO_2; 87% N_2
Flue gas pressure	1 bar
Selectivity	30, 50; 100; 150; 300
Pressure ratio	5; 10; 20; 50
Number of stages	1

Simple tool for a preliminary analysis on the prospects for membranes in CO_2 capture from flue gas

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.

$$\varphi_i = \frac{Q_i}{Q_i^{Feed}} \qquad \zeta = \frac{z}{L}$$

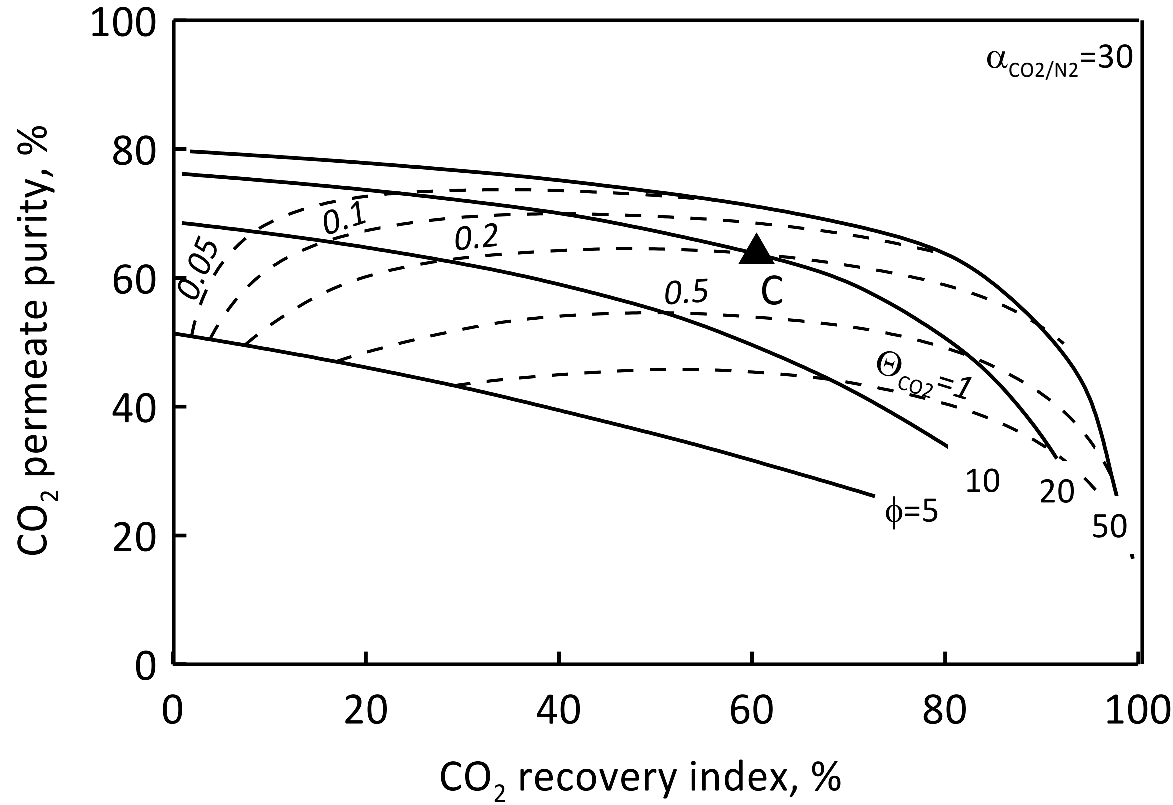
Θ_i and ϕ are the parameters affecting the performance of a one stage membrane system, the permeation number and the feed to permeate pressures ratio, respectively.

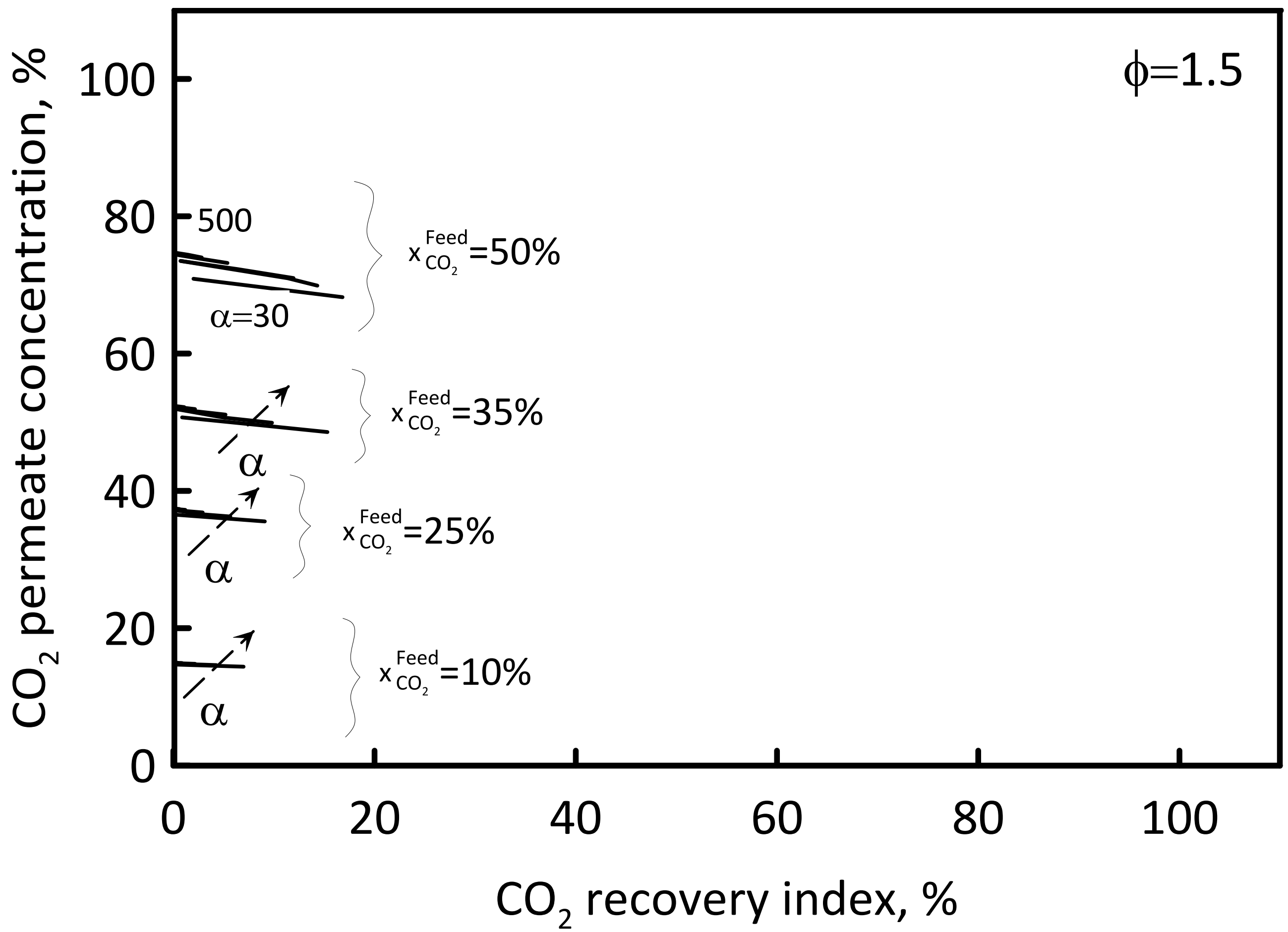
$$\boxed{\Theta_{CO_2} = \frac{Permeance_{CO_2} \; A^{Membrane} \; P^{Feed}}{x_{CO_2}^{Feed} \; Q^{Feed}}} \qquad \phi = \frac{P^{Feed}}{P^{Permeate}}$$

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.

The maps could be the starting point in the *carbon capture and storage* process design. In fact, global economic considerations on the final electricity cost and CO_2 storage technology allow the optimal performance to be univocally individuated on the maps

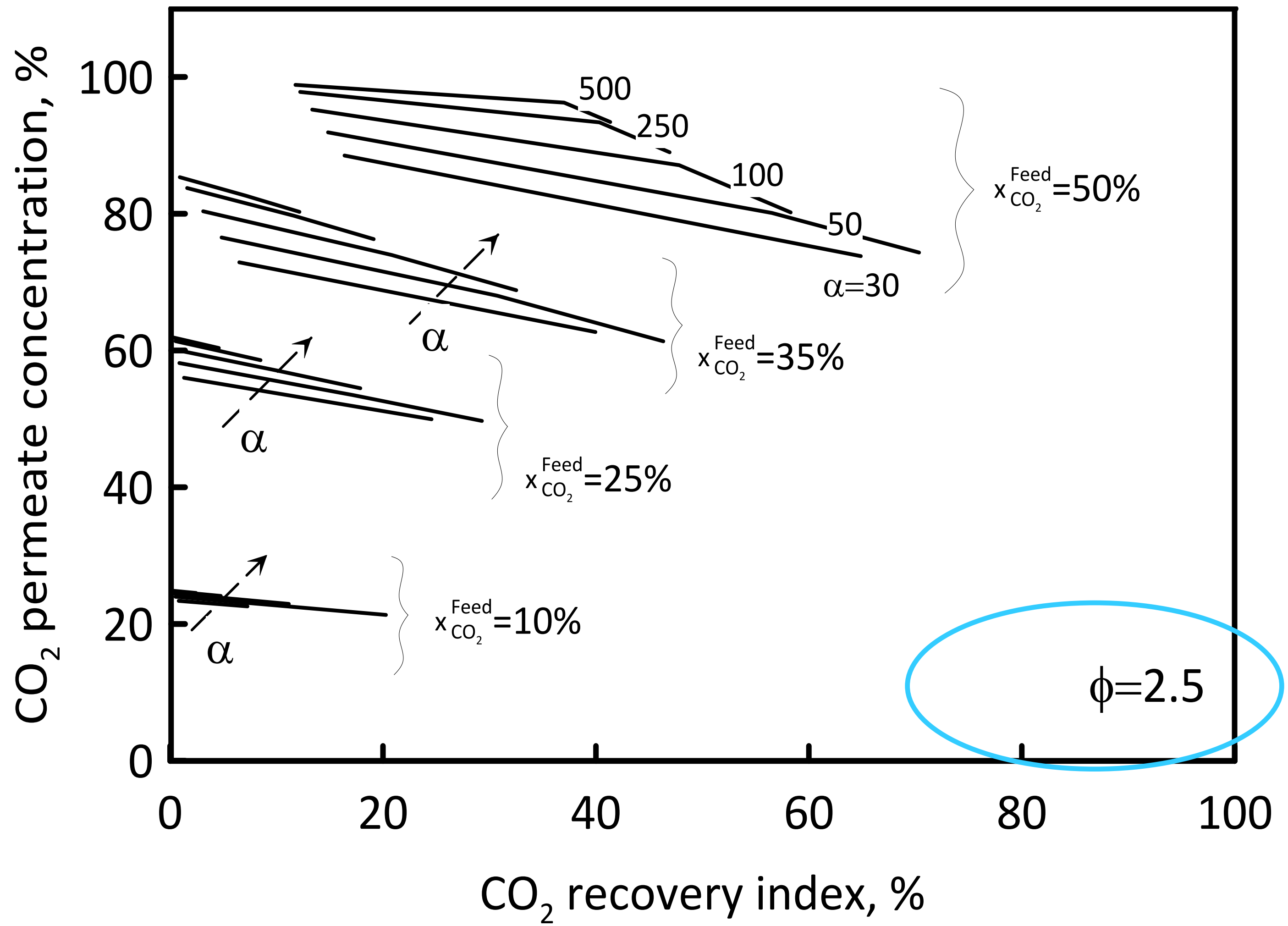
For instance, 64% CO_2 purity and 61% recovery corresponds to a system having a pressure ratio of 20 and a permeation number (Q_{CO2}) of 0.2. For a given geometry and membrane (*Permeance*$_{CO2}$) this pair of parameters can be obtained by means of infinite different couples of operating conditions



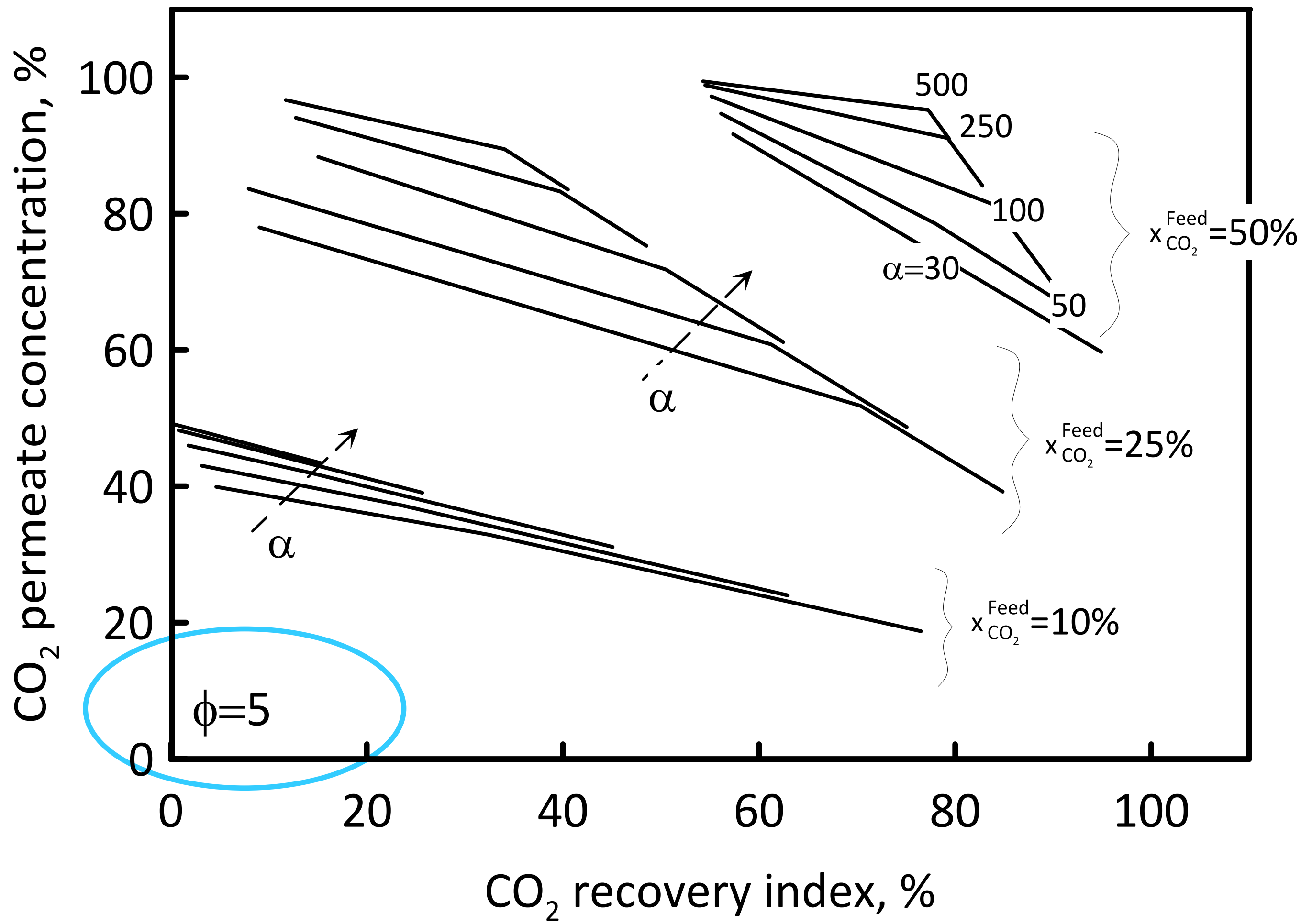


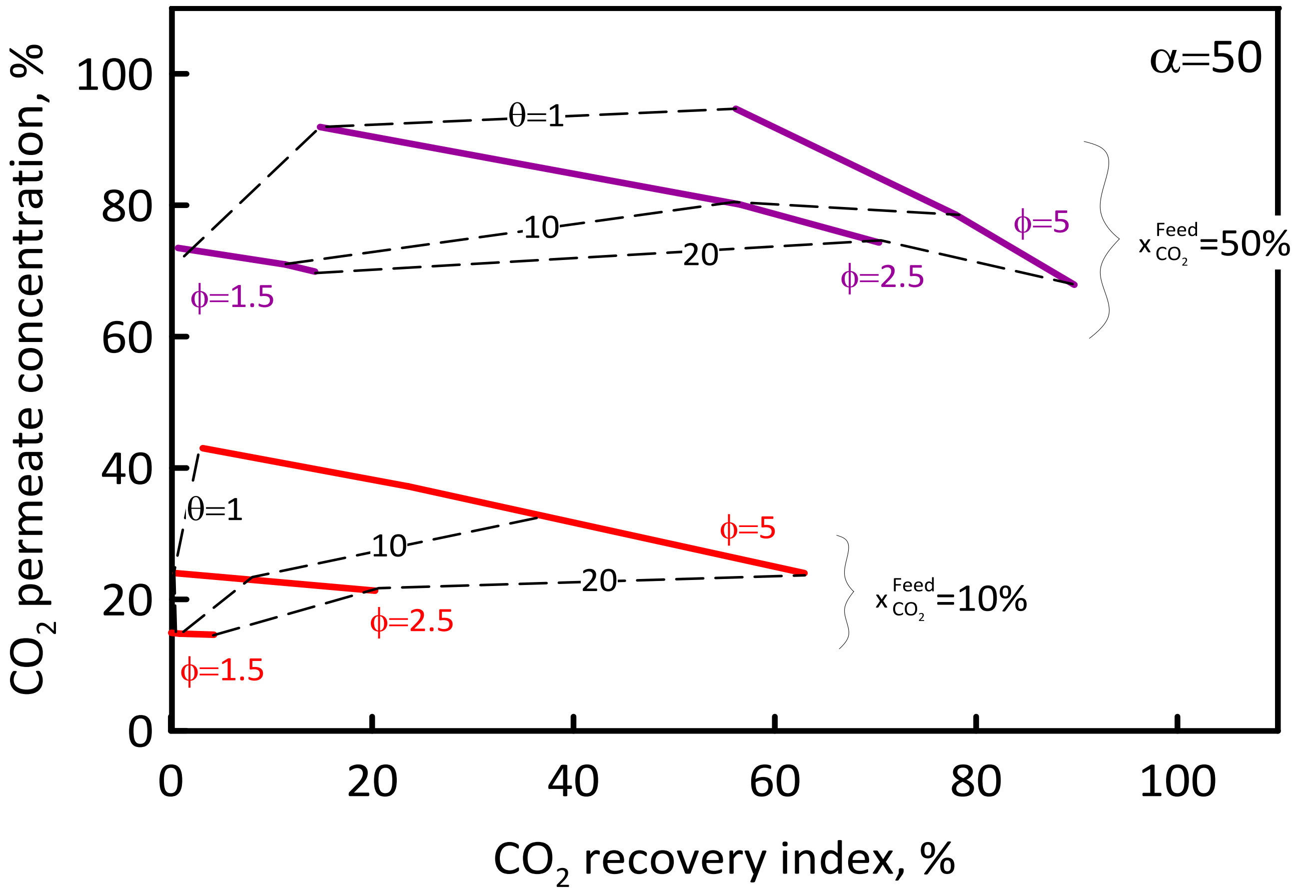
The effect of the selectivity on the performance of the membrane module is negligible at low pressure ratios.

Increasing the pressure ratio....

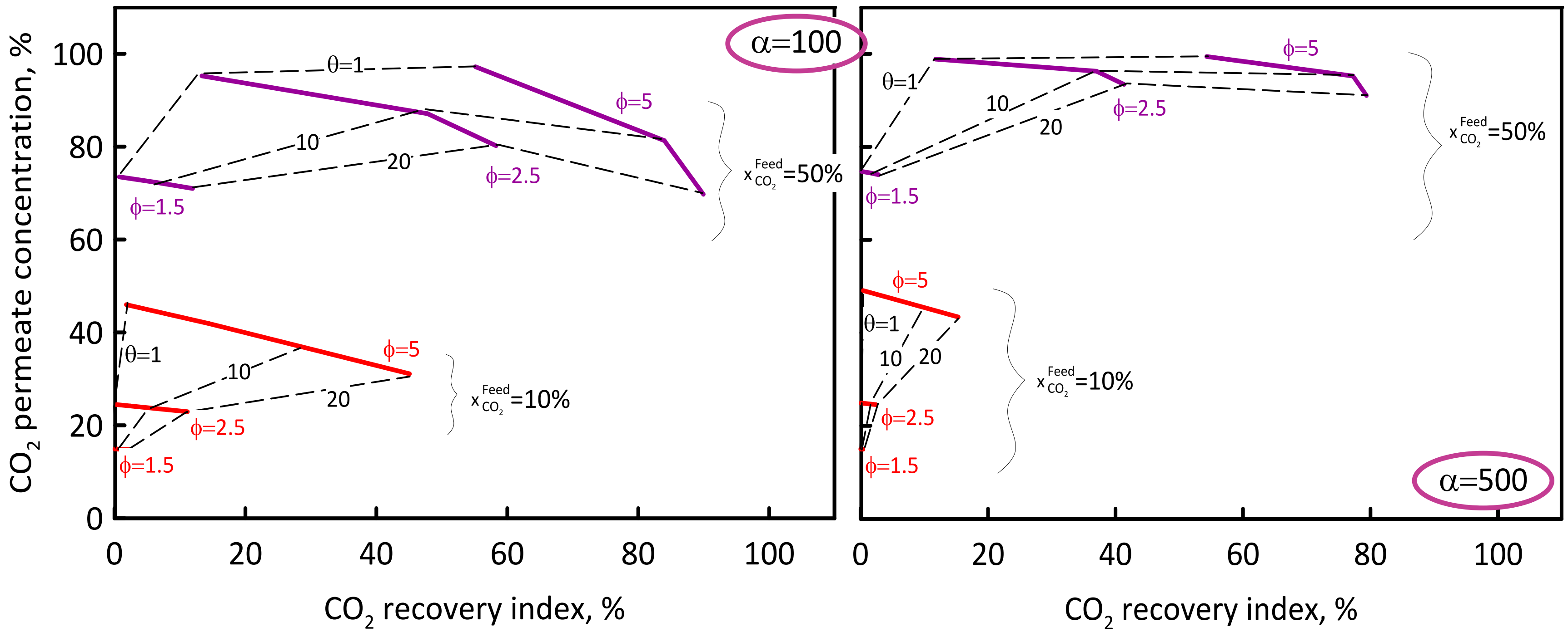


Increasing the pressure ratio….

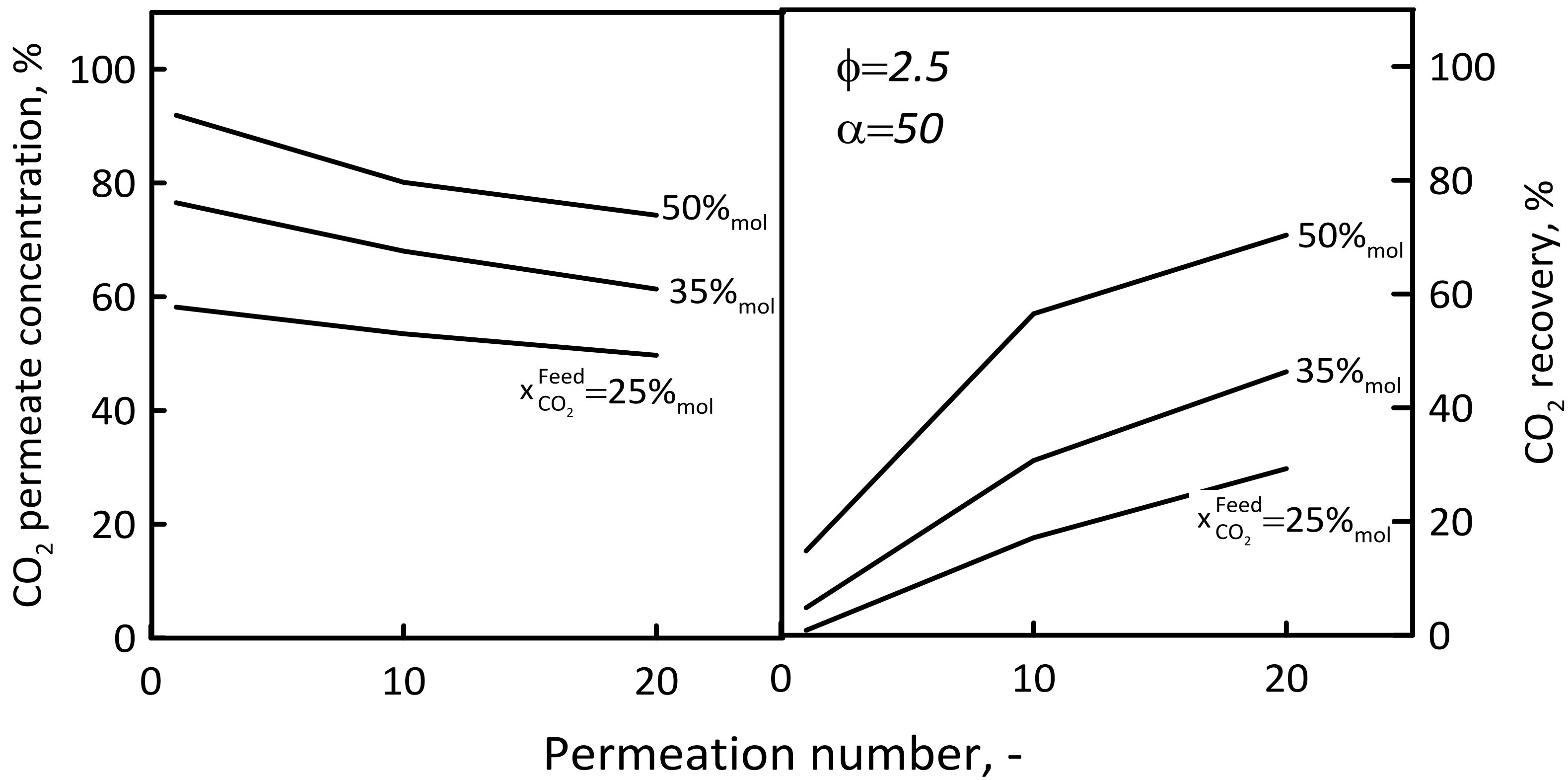




The low concentration of CO_2 in the feed does not allow to achieve high purity streams in the permeate, even increasing the pressure ratio. More separation stages are necessary.

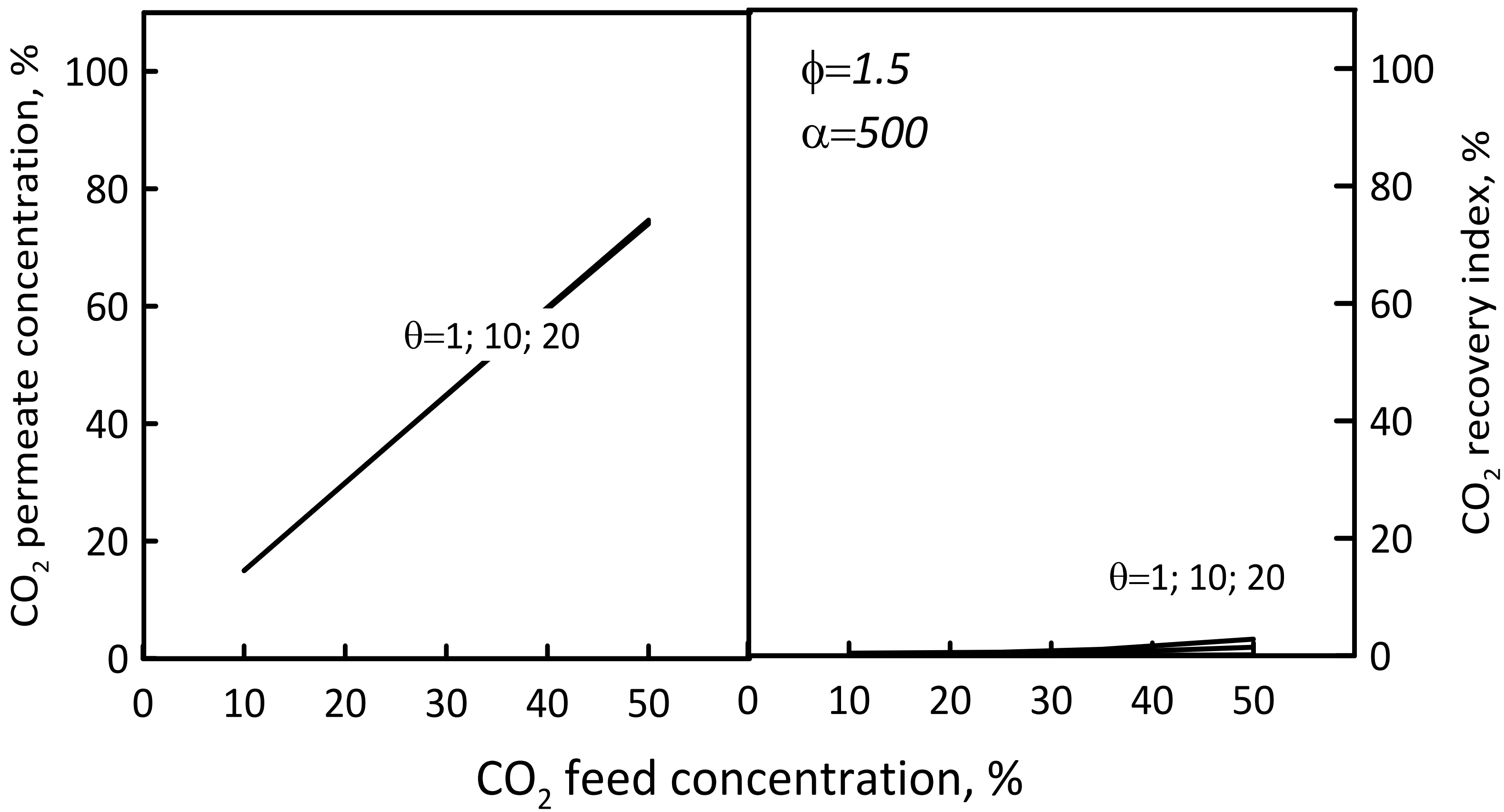


Also at higher selectivity, the low concentration of CO_2 in the feed does not allow achieving high purity streams in the permeate, even increasing the pressure ratio.



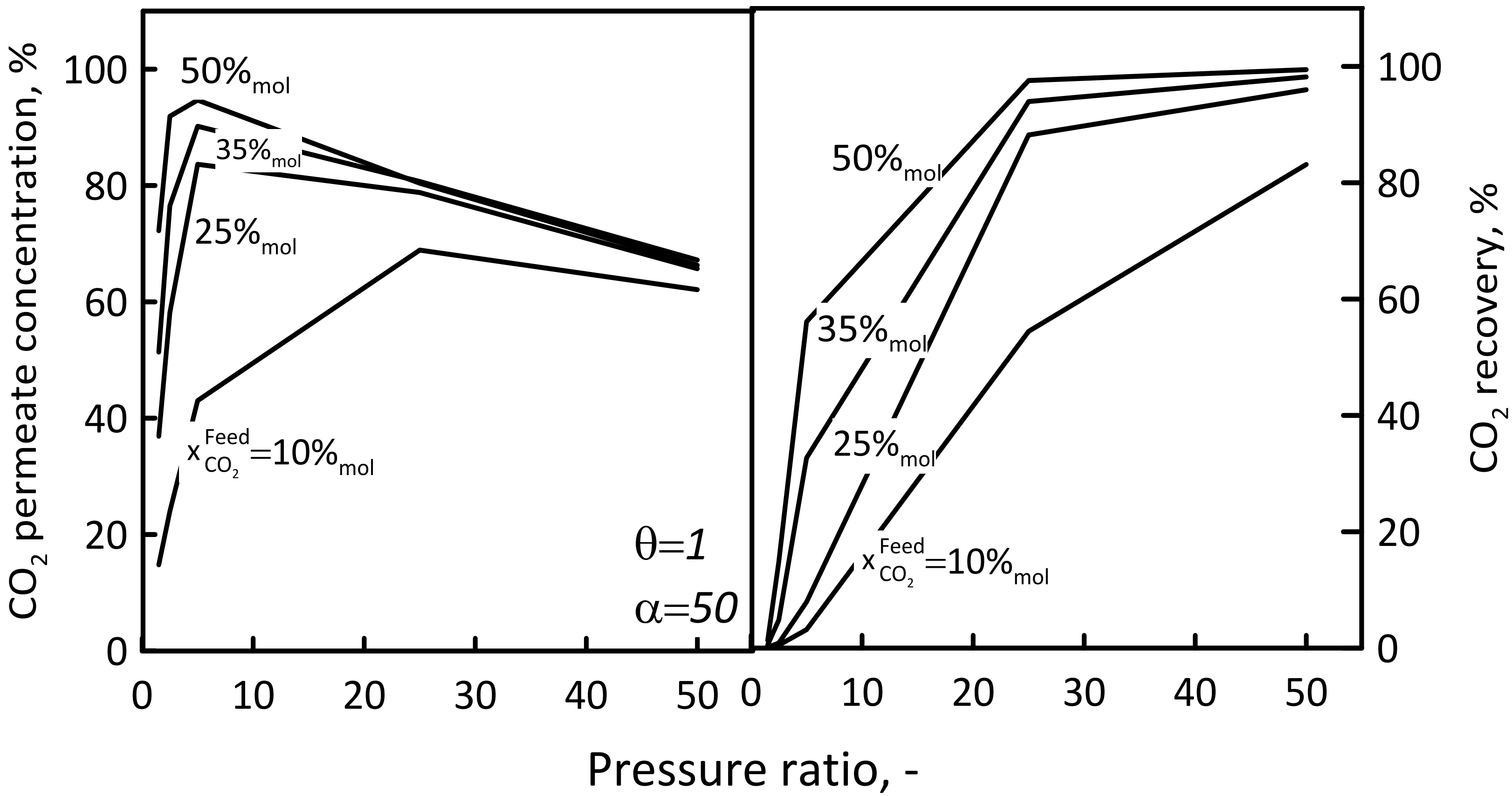
Another limiting parameter for the module performance is the membrane area (Permeation number). For a set feed flow rate, a set membrane type and defined pressure ratio, a low Θ indicates low recovery and high permeate purity, and viceversa.

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



•**The low feed pressure ratio strongly affects the performance of the membrane module even at a high selectivity of the membrane.**

•**Also the variation of θ does not affect the module performance.**



For a high value of selectivity, the double of the pressure ratio implies a recovery 2-3 times higher and also improvements in the CO_2 purity.

Final remarks…..

- Membrane engineering, together with material science, has a crucial role for the real application of membrane technology in CO_2 separation, that means integrated process design and optimization of the operating conditions are really important

- In addition to the feed conditions, the main variables affecting the performance of the membrane module are the feed pressure ratio and the permeation number.

- The low concentration of CO_2 in the feed does not allow achieving high-purity streams in the permeate, even increasing the pressure ratio. More separation stages are necessary.

- The effect of the selectivity on the performance of the membrane module is negligible at low pressure ratios but it is important at higher values of driving force

- Another limiting parameter for the module performance is the permeation number. For set feed flow rate, membrane type and pressure ratio, a low θ profides low recovery and high permeate purity.

Thank you for your attention

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