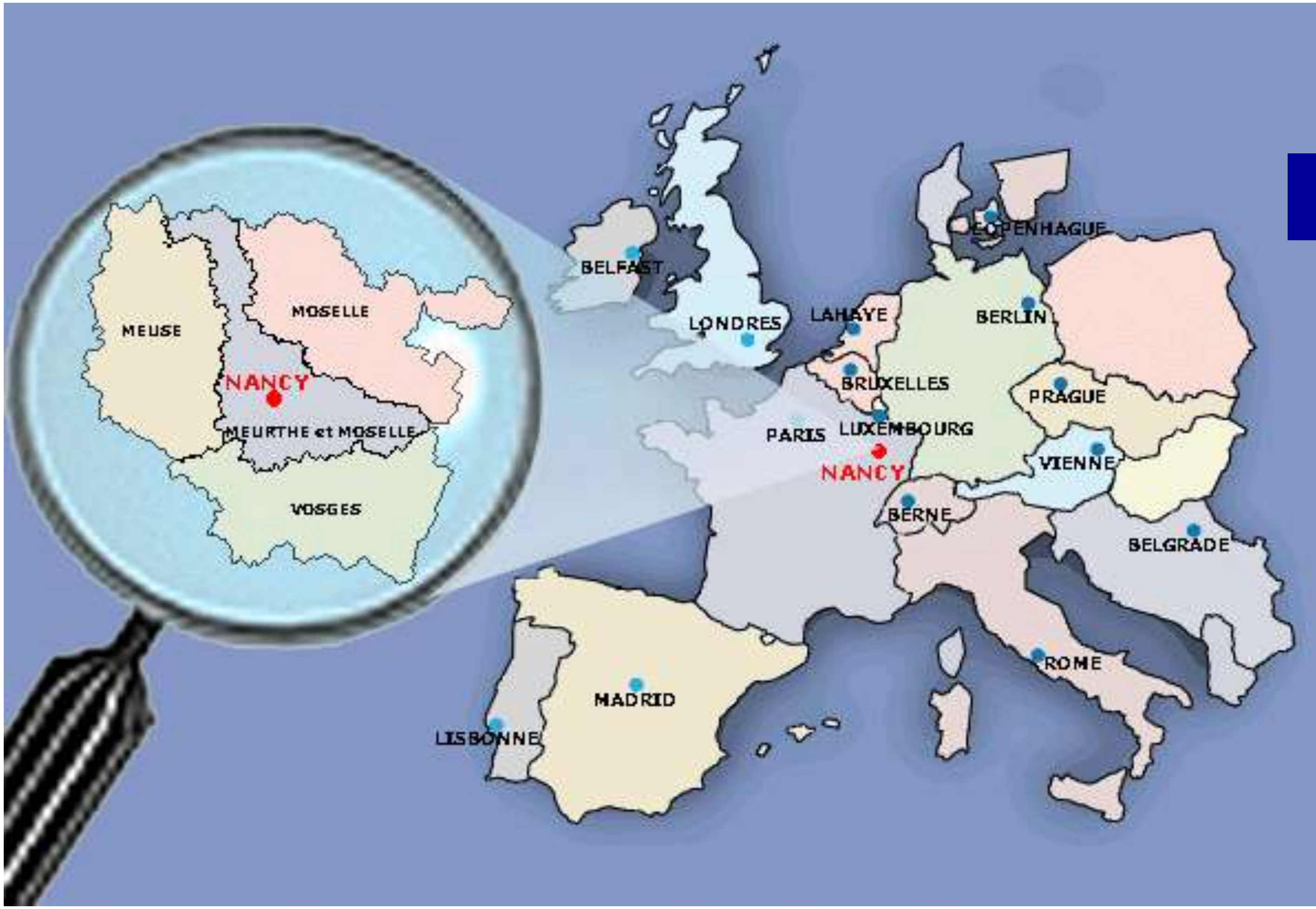
Membranes and post-combustion carbon dioxide capture

Eric FAVRE

Laboratoire Réactions & Génie des Procédés (UPR CNRS 3349)

Université de Lorraine Nancy FRANCE



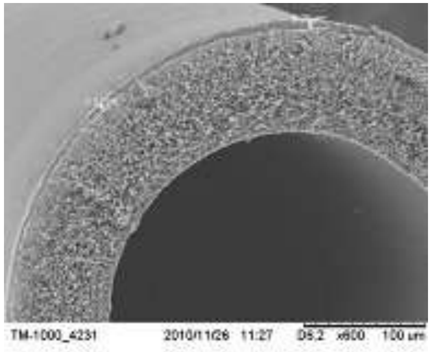
Nancy… somewhere in France

Nancy, Lorraine, France

ENSIC

LRGP

Membrane team LRGP (EMSP) Current research projects on CCS



Membrane contactors for intensified absorption processes:

High flux dense skin composite fibers (ANR Cicadi)

Pilot membrane contactor design and test (FP7 CESAR)

Membrane contactor for chilled ammonia process (ANR Amélie)

Pilot absorption unit for gas boiler plants (ANR Energicapt)

Optimization of solvent/gas absorption processes (with EDF)

Membrane gas separations:

Material synthesis Mixed Matrix Membranes (ACI Carbomem)

Membrane characterization (mass transfer, separation performances)

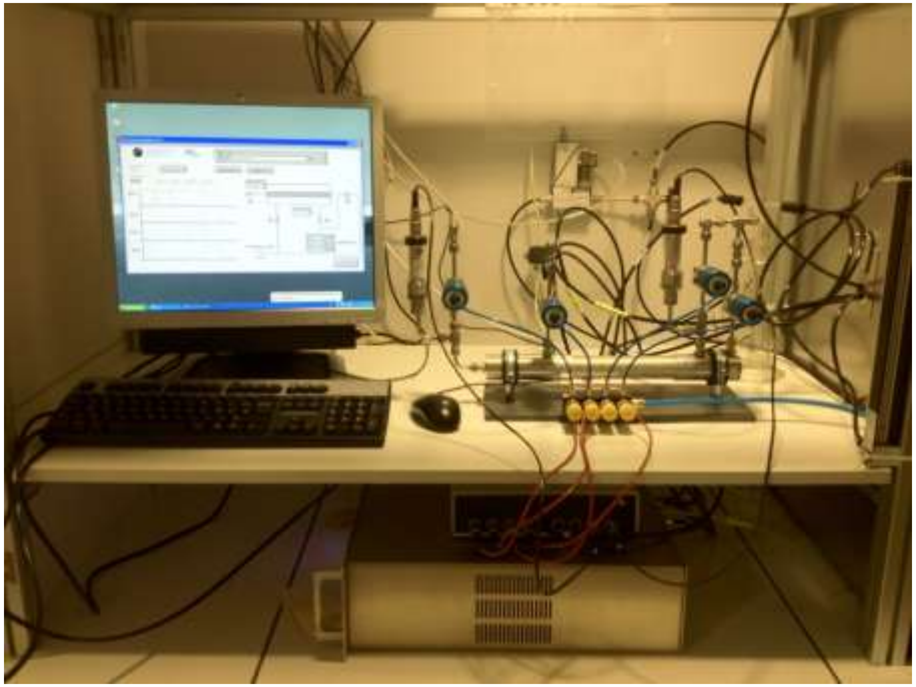
Process modelling (M3Pro software)

Hybrid processes:

Oxygen enriched air combustion / membrane capture (Cocase ICEEL)

Membrane concentration / cryogenic condensation (with EDF)

Prospective & breakthrough approaches

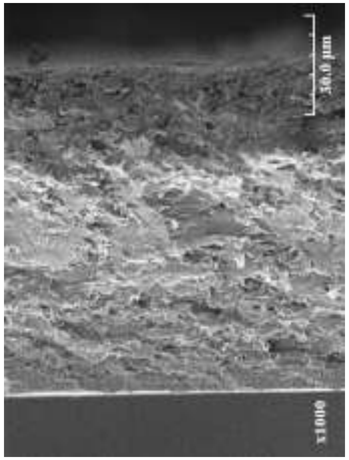


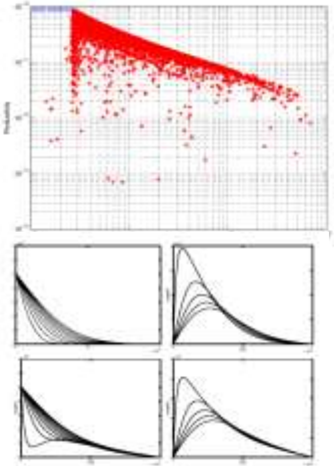
Liquid membranes (TIPS Russia)

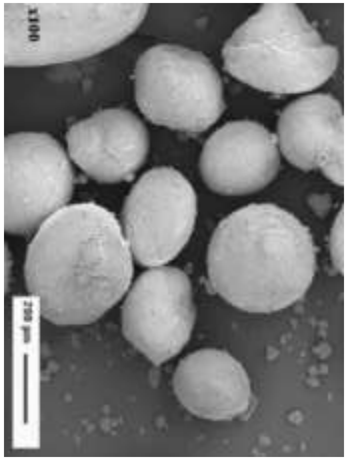
Impregnated particles (MESR)

Electrical swing adsorption (ACI Procap)

Cyclic membrane gas separations (ICEEL)

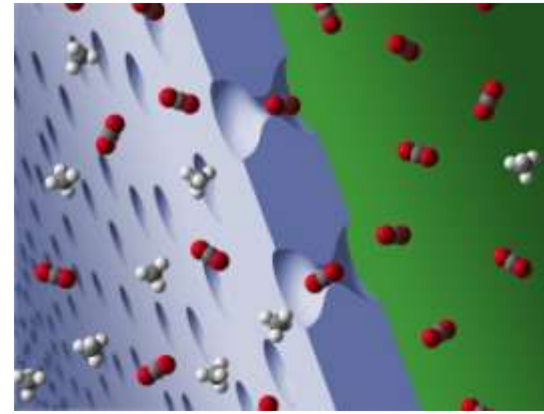




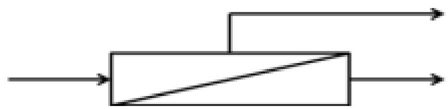


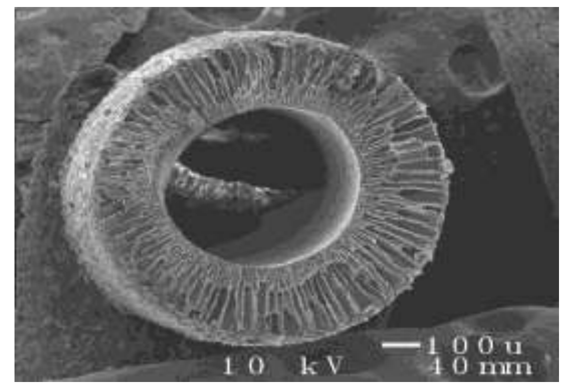
Outline

i) *Introduction*

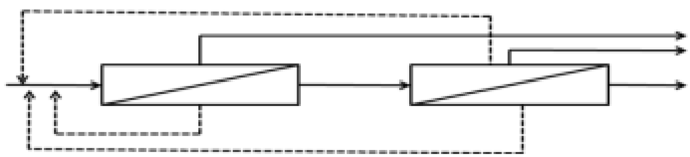


ii) *Single stage parametric sensitivity*





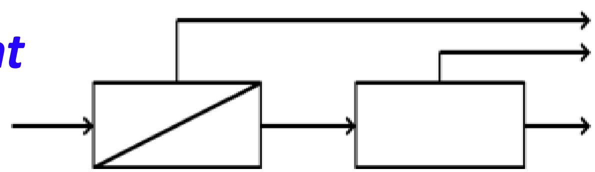
iii) *Multistage approaches*



iv) *Hybrid process:*

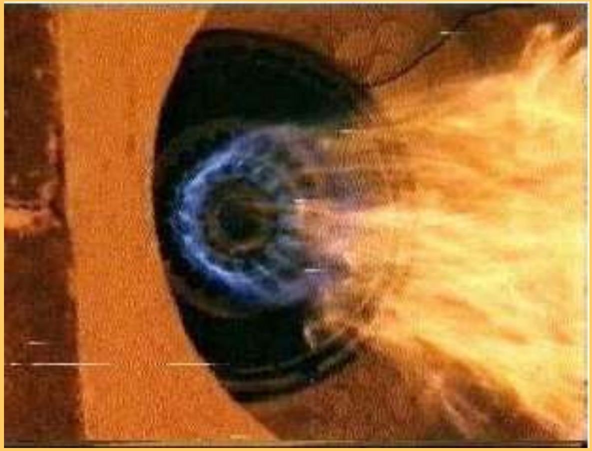
Coal power plant

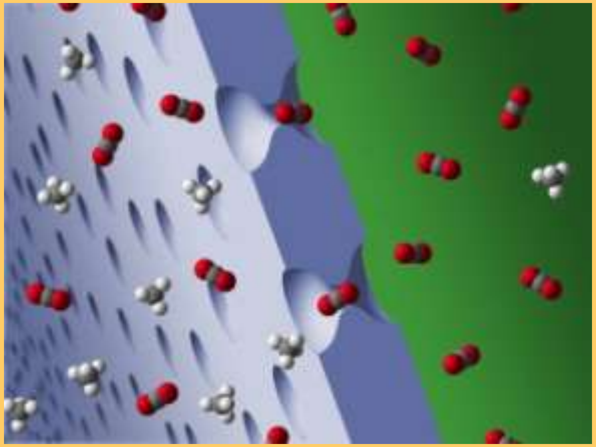
Gas turbine



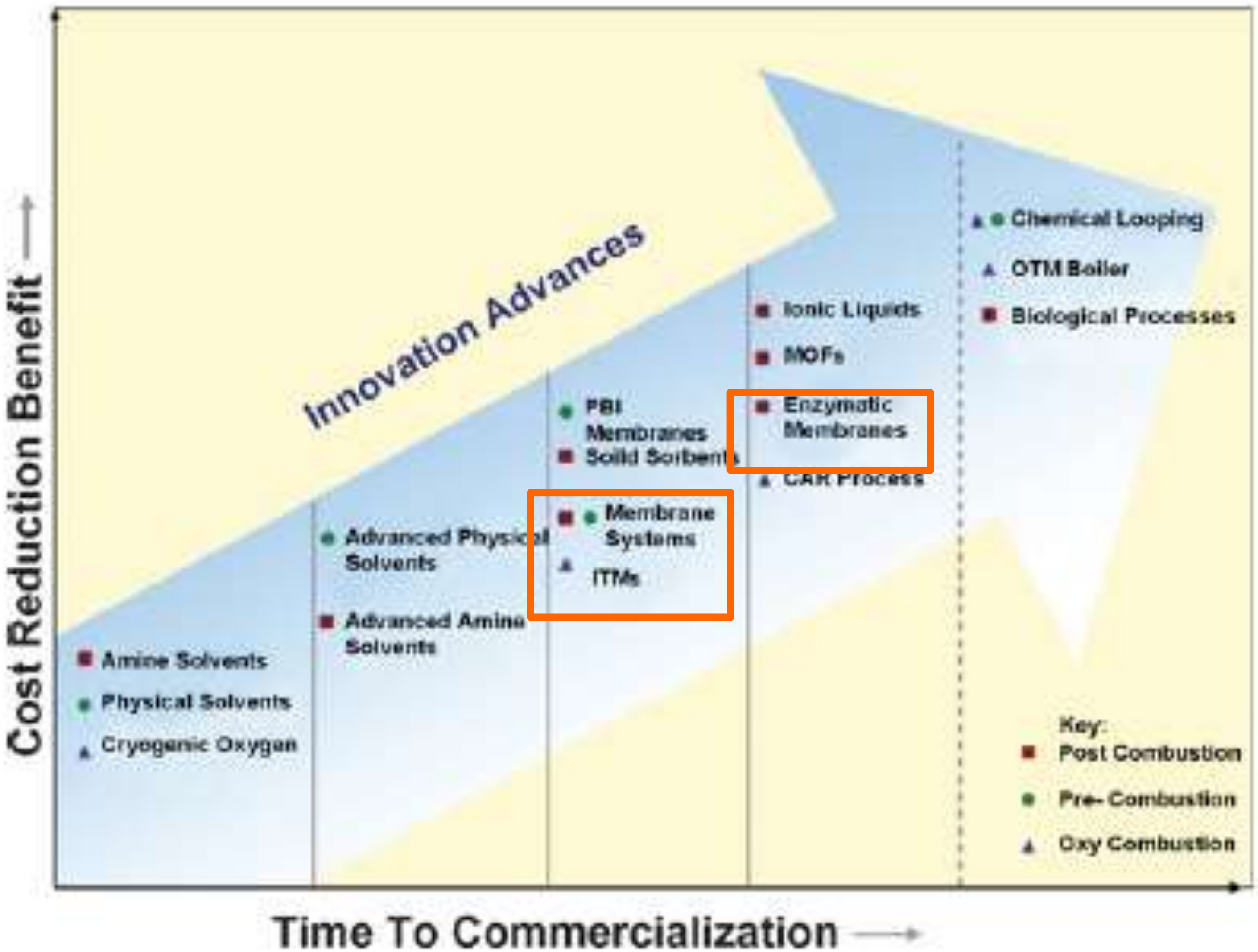
v) *Conclusion*

Introduction





Membranes: a potential 2nd generation carbon capture process

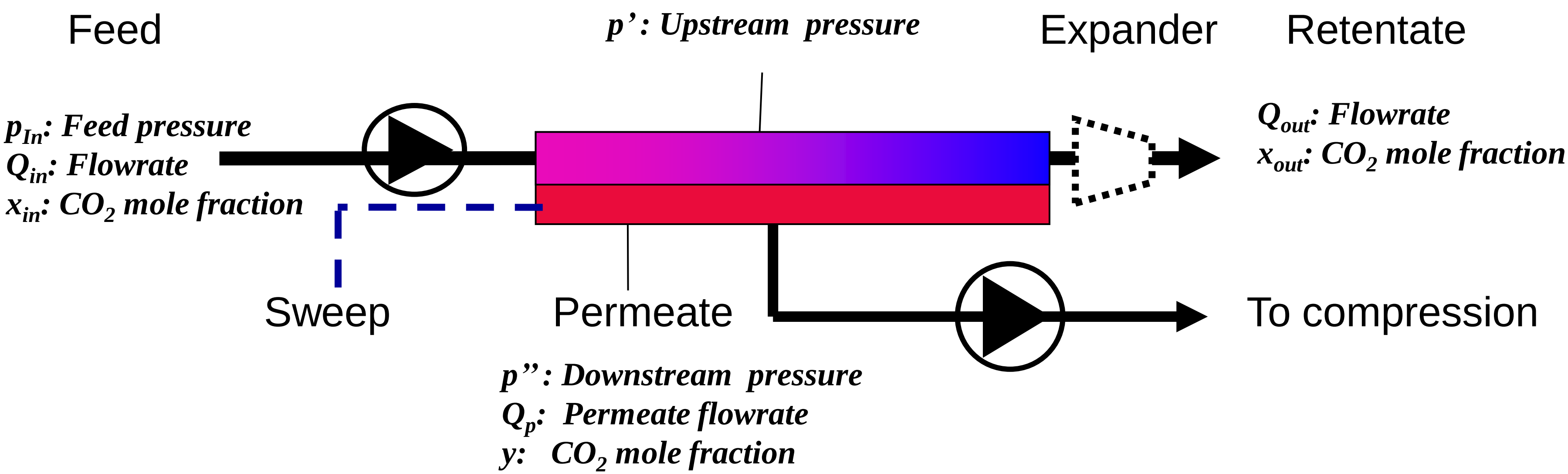


Source: Figueirao J. et al. DOE (2007) Int. J. Greenhouse Gas Control

Membranes & carbon capture strategies

Carbon capture strategy	*Target mixture*	*Conditions*	*First generation separation process*	*Possible breakthrough membrane process*
Oxycombustion	O_2/N_2	P atmospheric T ambient	Cryogeny	Ion Transfer Membranes (ITM)
Precombustion	CO_2/H_2	P up to 80 Bar T 300 – 500 C	Gas-liquid absorption in physical solvent	Membrane reactor
Postcombustion	CO_2/N_2	P atmospheric T 100 – 250 C	Gas-liquid absorption in chemical solvent (MEA)	Membrane gas separation

A classical single stage gas permeation modelling framework



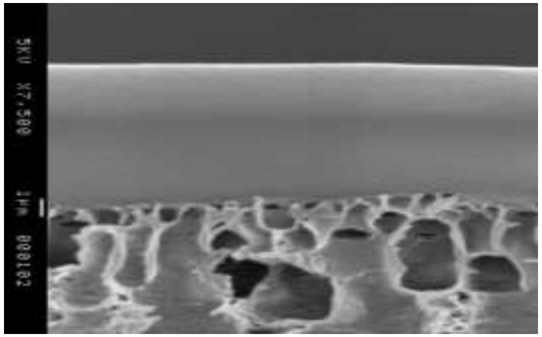
Permeability of A $\equiv P_A = D_A S_A$

where D_A = diffusion coefficient

S_A = solubility coefficient

Selectivity

$$\alpha_{A/B} = \left(\frac{P_A}{P_B}\right) = \left(\frac{S_A}{S_B}\right)\left(\frac{D_A}{D_B}\right)$$



Membrane separation & CCS: a simplified overview

Feed composition x
Capture ratio R
Purity y

Selectivity challenge α

Operating Conditions (P, T)

Energy GJ_{th}/ton

Feed flow rate vs outlet performances

Productivity Maximal flux

Energy cost

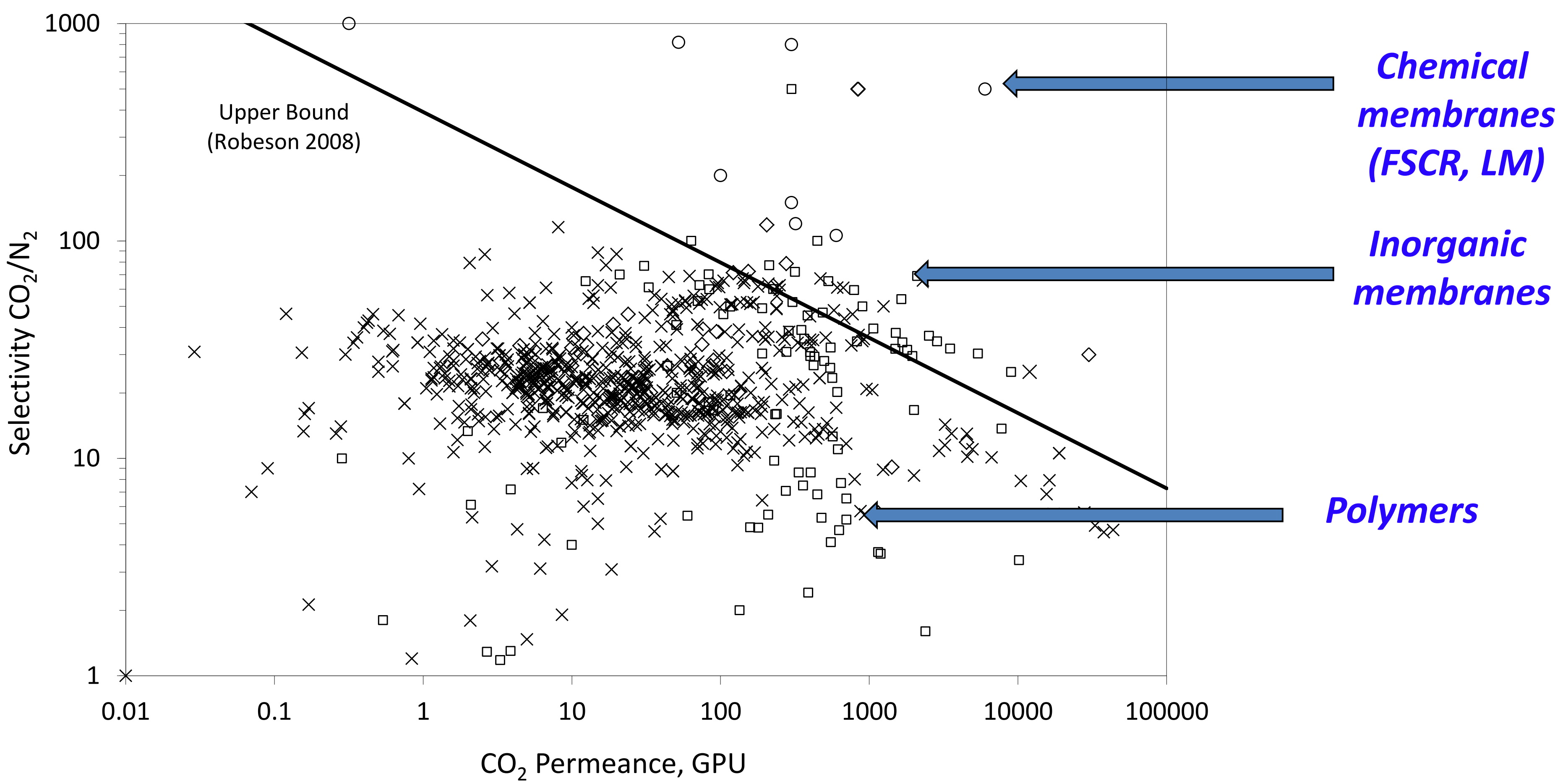
OPEX

CAPEX

Membrane cost (€/m^2)

Overall Capture Cost

Materials challenge of gas separation membranes



Favre, E. (2007) Carbon dioxide recovery from post combustion processes: Can gas permeation membranes compete with absorption? *Journal of Membrane Science,* 294, 50-59

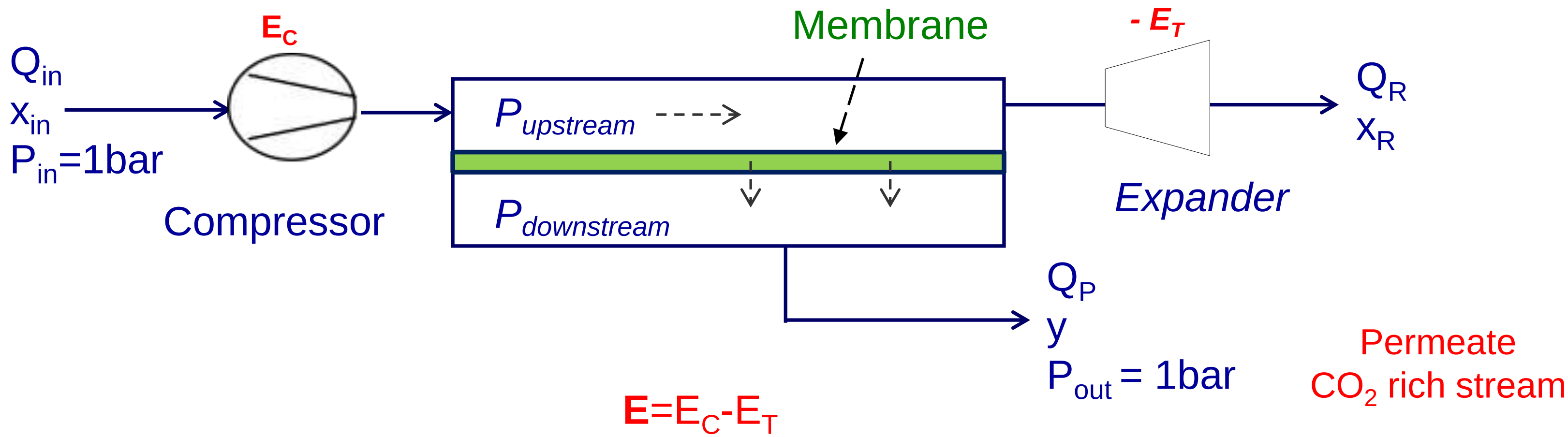
Materials performances for post-combustion carbon capture

Membrane type	*Material and/or carrier*	*CO_2/N_2 selectivity*	*CO_2 permeability (Barrer) or permeance (GPU)*
Gas separation membrane (dense polymers)	PEO-PBT PEG/Pebax© PEG-DME/ Pebax© PEGDA/PEGMEA **Polaris™**	70 47 43 41 **50**	120 Barrer 151 Barrer 600 Barrer 570 Barrer **1000 GPU**
Fixed Site Carrier Membrane (FSCM)	PAAM-PVA / PS PVAm/PVA PEI / PVA PDMA/PS PDMAMA	80 145 230 53 80	24 GPU 212 GPU 1 GPU 30 GPU 5 GPU
Liquid Membrane (LM)	PVAm-PVA/PS PVAm/PVA Amines/PVA Carbonic anhydrase Amines / PVA	90 90 500 250 493	22 GPU 15 GPU 250 GPU 80 GPU 693 Barrer

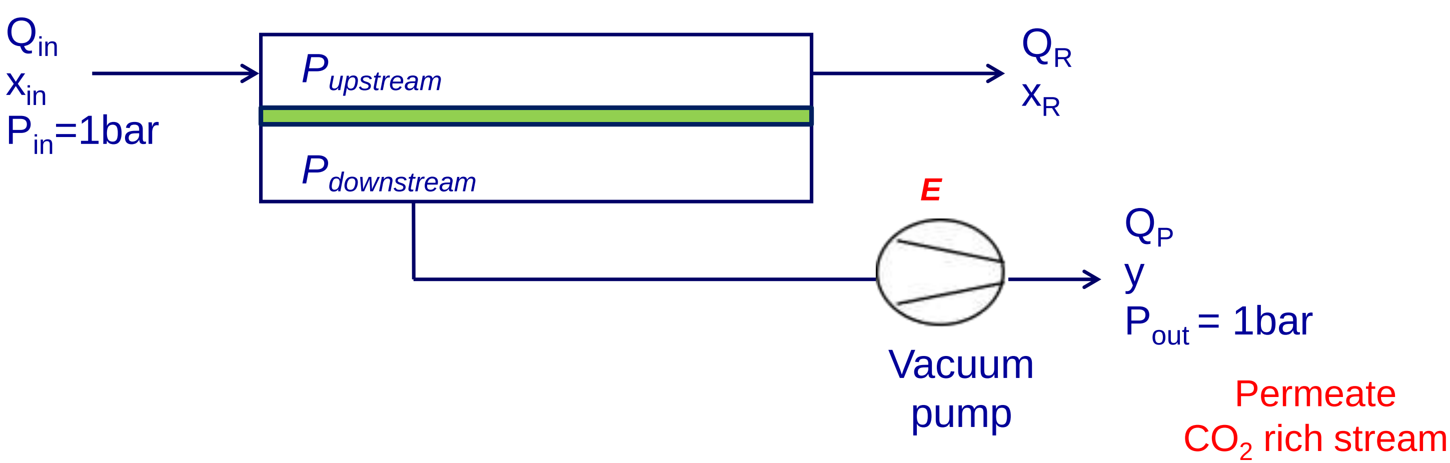
Baseline case for simulations

Single stage simulations: Process alternatives

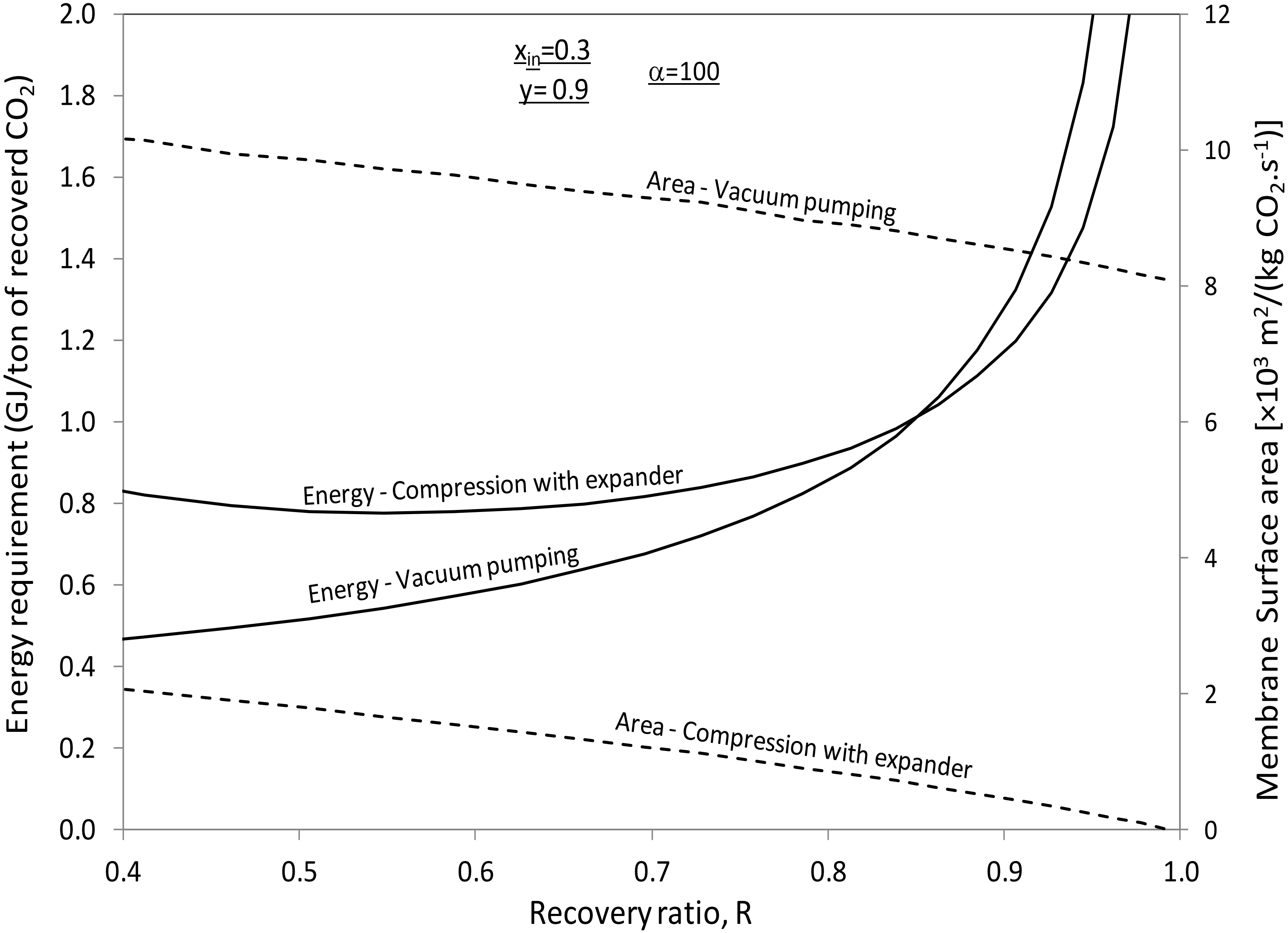
Feed compression with ERS on the retentate



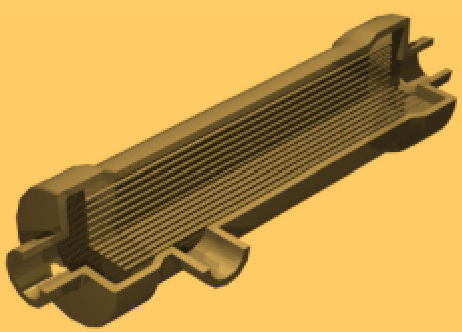
Permeate vacuum pumping



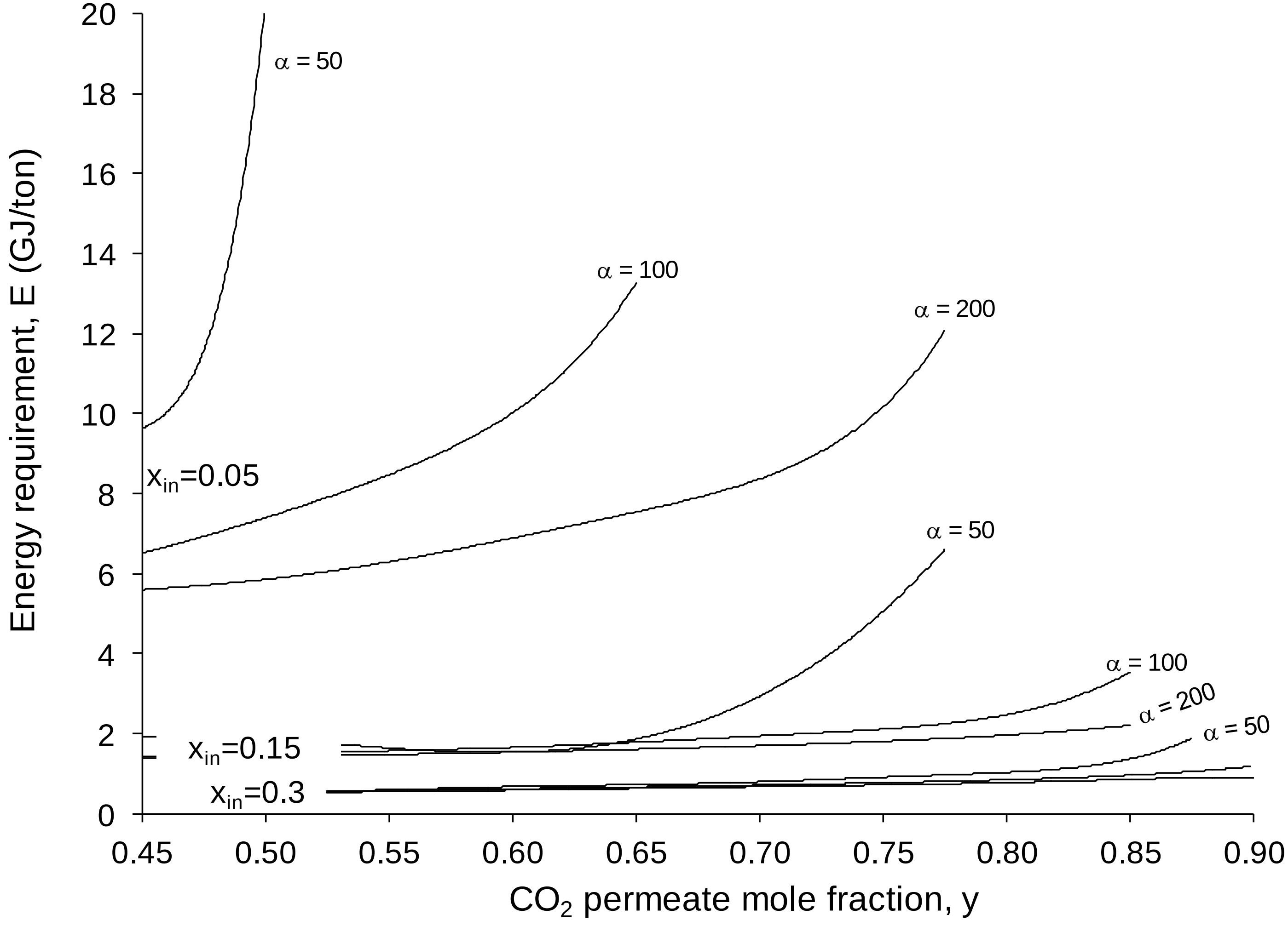
The feed compression / vacuum pumping dilemma



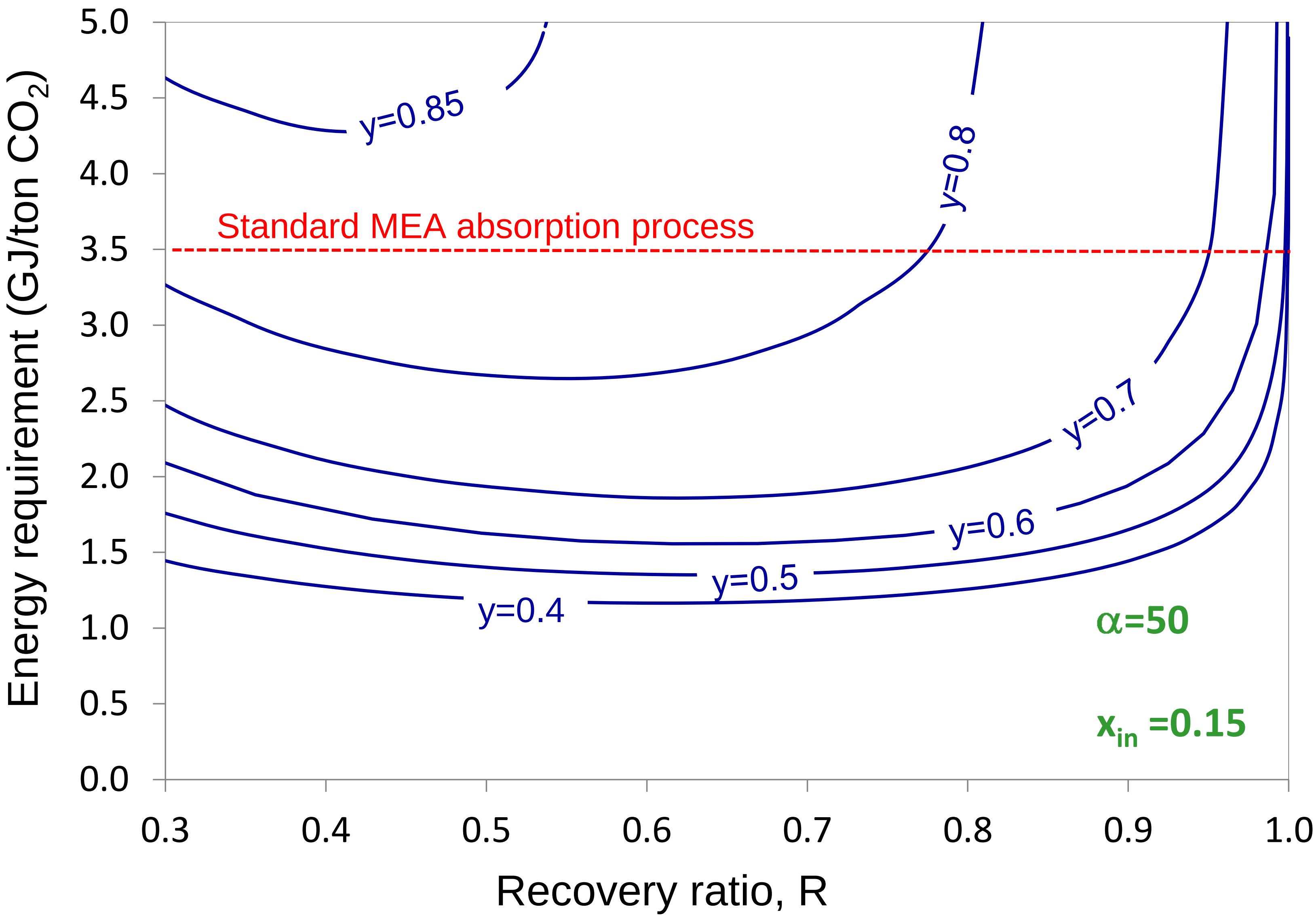
Parametric study of a single stage gas permeation module



Strong parametric sensitivity on feed composition

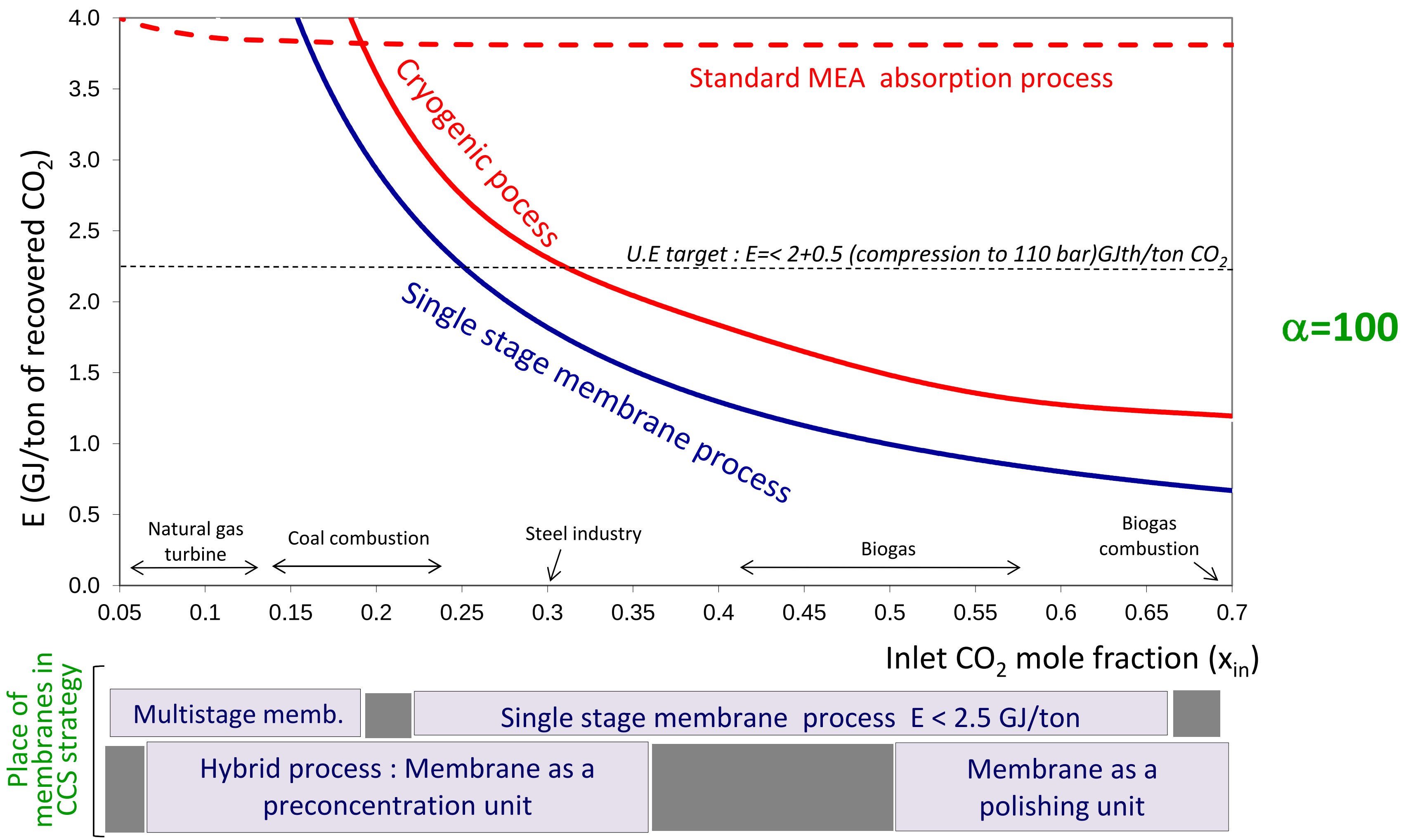


Tackling the capture ratio / purity challenge



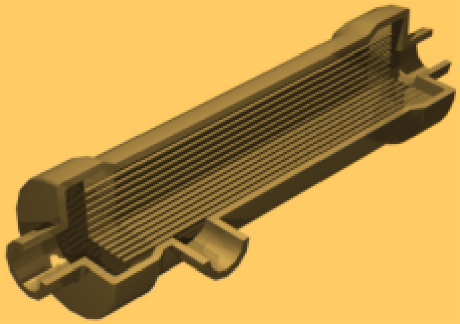
B. Belaissaoui , D. Willson , E. Favre, Chemical Engineering Journal, 211-212 (2012) 122-132

A tentative process selection map

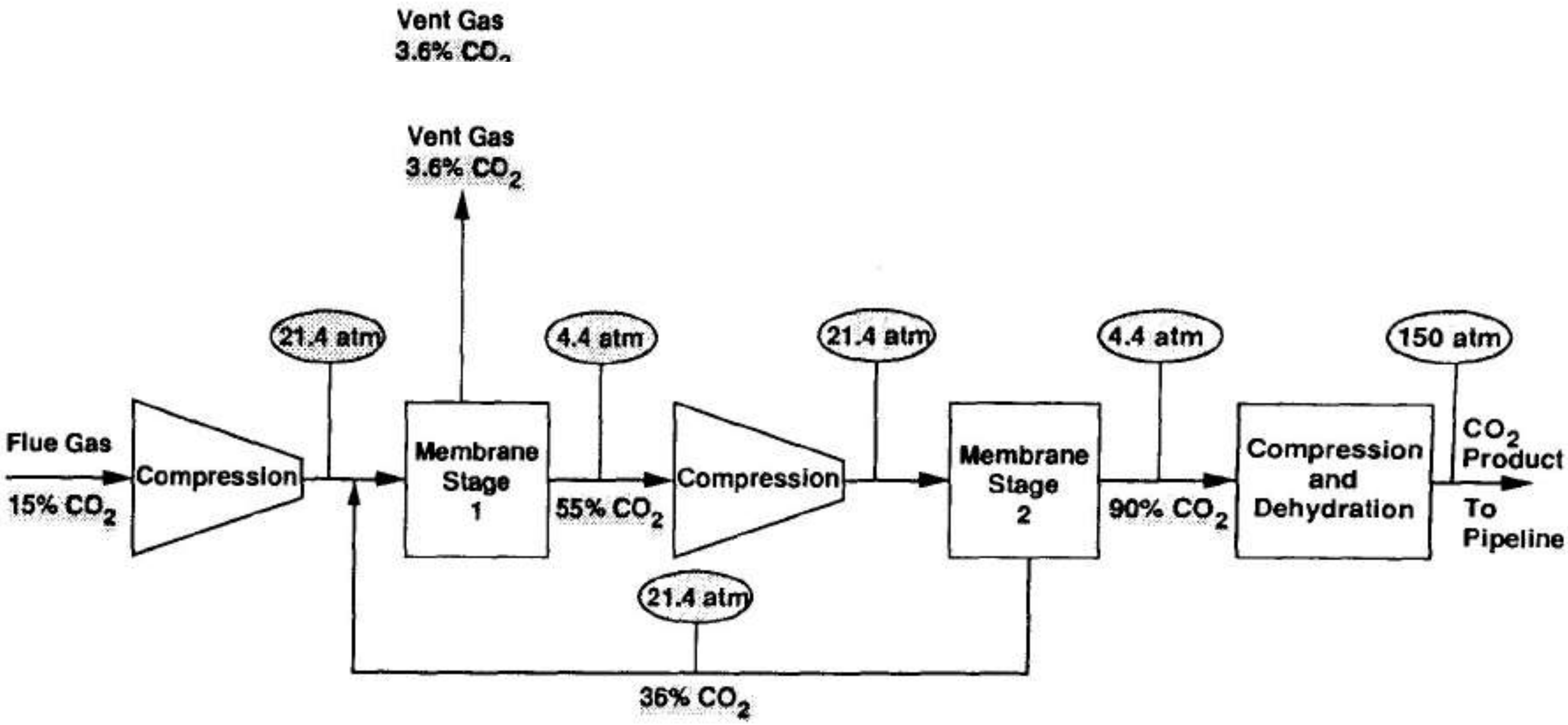


B. Belaissaoui , D. Willson , E. Favre, Chemical Engineering Journal, 211-212 (2012) 122-132

Multistage gas permeation modules for carbon capture



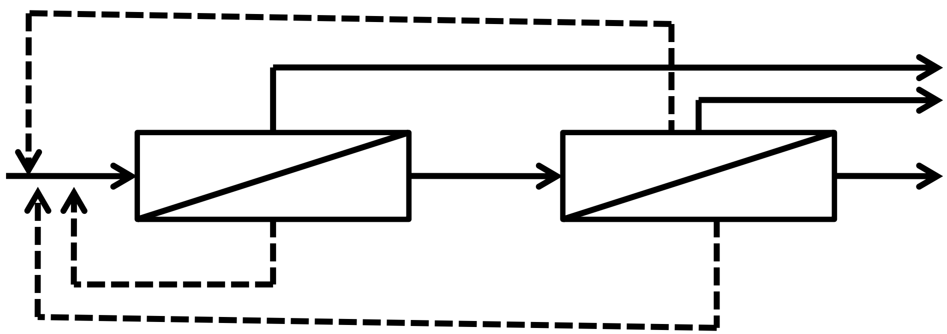
First two stages membrane gas separation process



CO_2 recovery 80%, CO_2 purity 90%
Energy requirement 50-75 % of combustion energy of coal
(MEA 47-79 %)

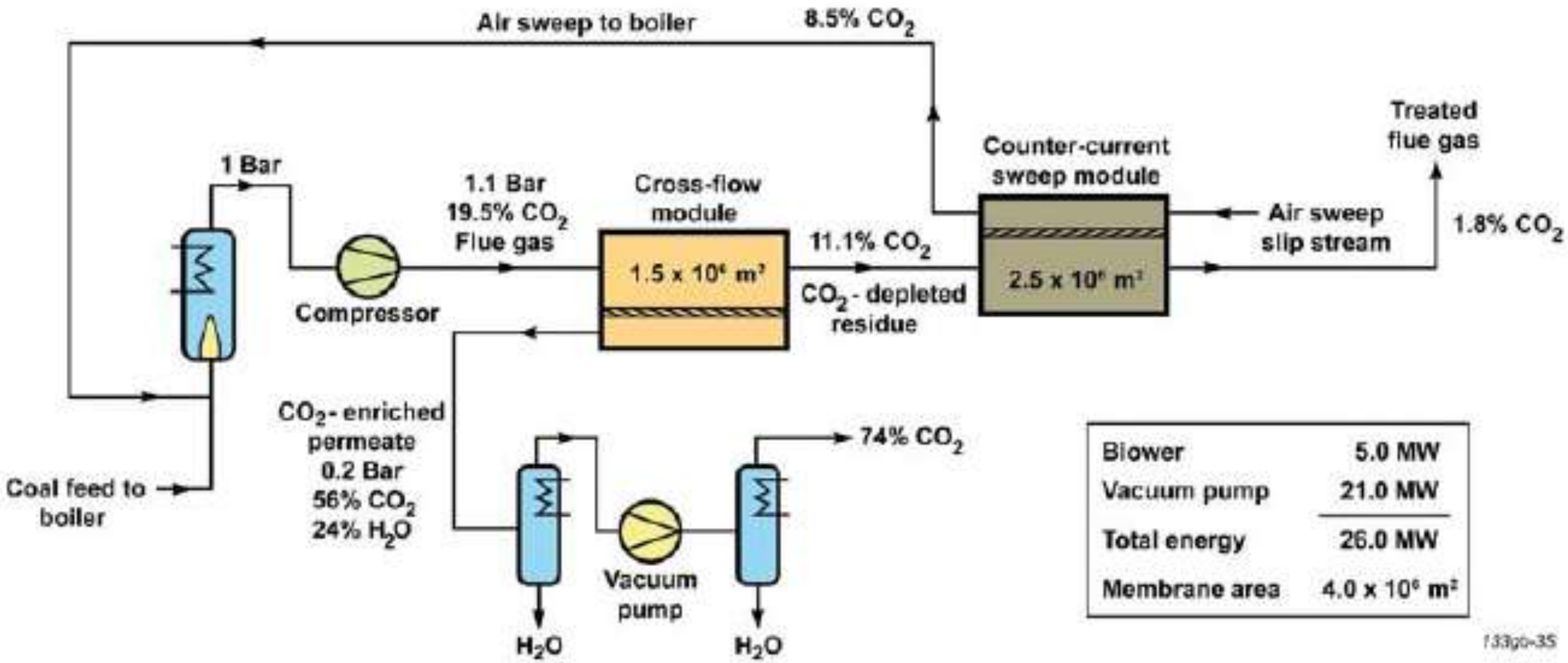
Herzog et al., Environ. Prog. (1991) 10, 64-74.

Multistaged membrane gas separation processes: overview



Module type	***Operating conditions***	***Author***
Two stage with recycle	Compression (21.4 Bar)	Herzog et al. (1991)
Two stage with expander	Compression (54 Bar)	Van der Sluis et al.(1992)
Two stage with recycle	Compression (1.5 Bar) and vacuum (80 mBar)	Ho et al. (2008)
Multistage with or without recycle	Compression (10 bar), vacuum (0.03 Bar)	Zhao et al. (2009)
Two stage with recycle	Compression (3 Bar) and vacuum (0.2 Bar)	Merkel et al. (2009)
Two stage with or without sweep	Compression (2-5 Bar) or vacuum (25-125 mBar)	Hussain et al. (2010)

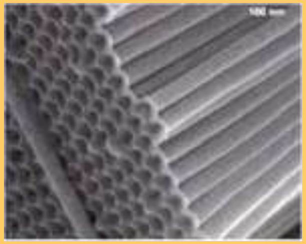
MTR DOE two stages membrane gas separation process

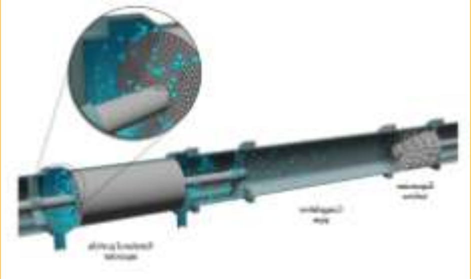


MTR novel 2 stage membrane flowsheet for post-combustion CCS application

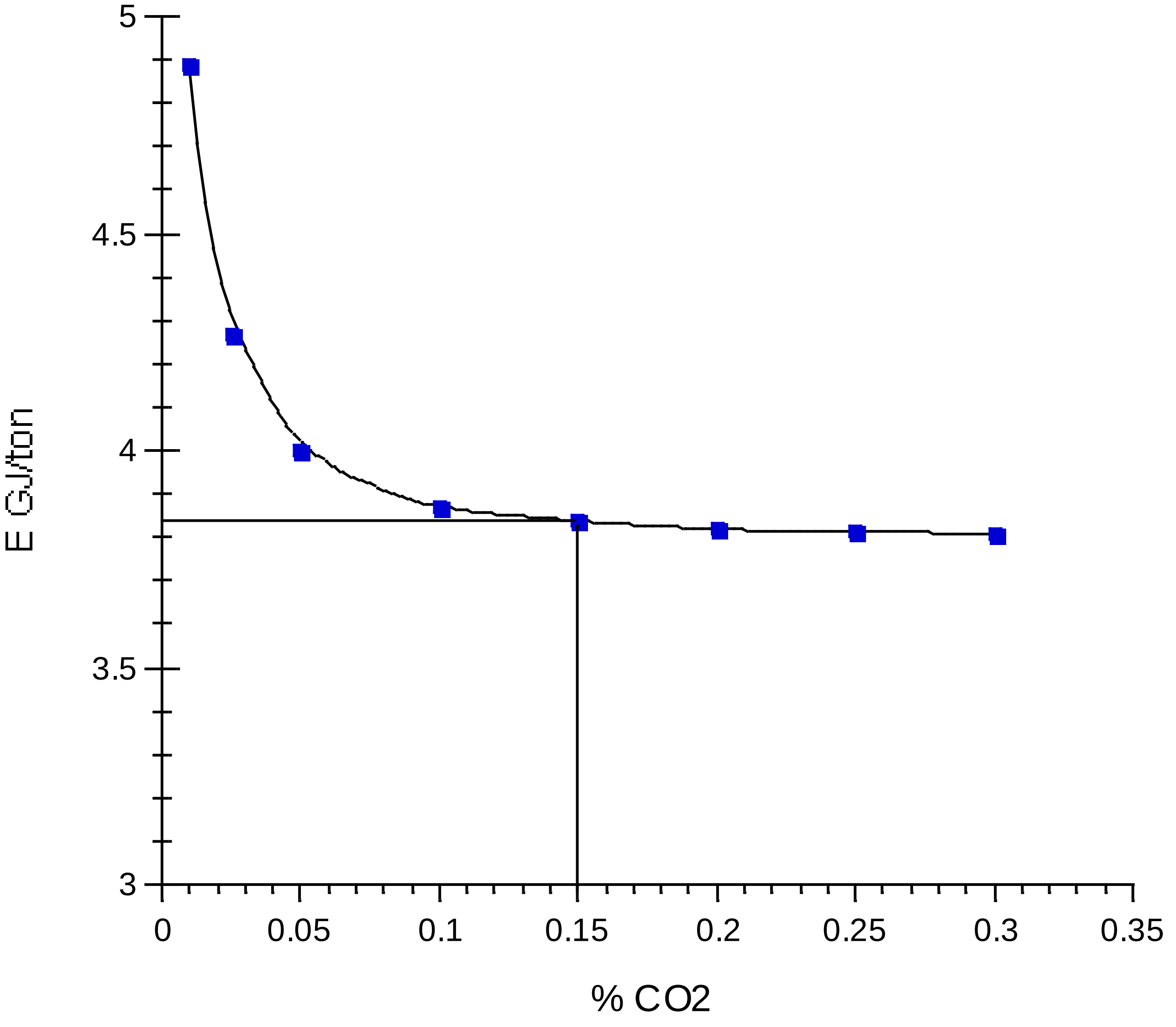
Merkel et al., J. Membrane Science (2010) 359, 126-139.

Hybrid processes with membrane modules for carbon capture

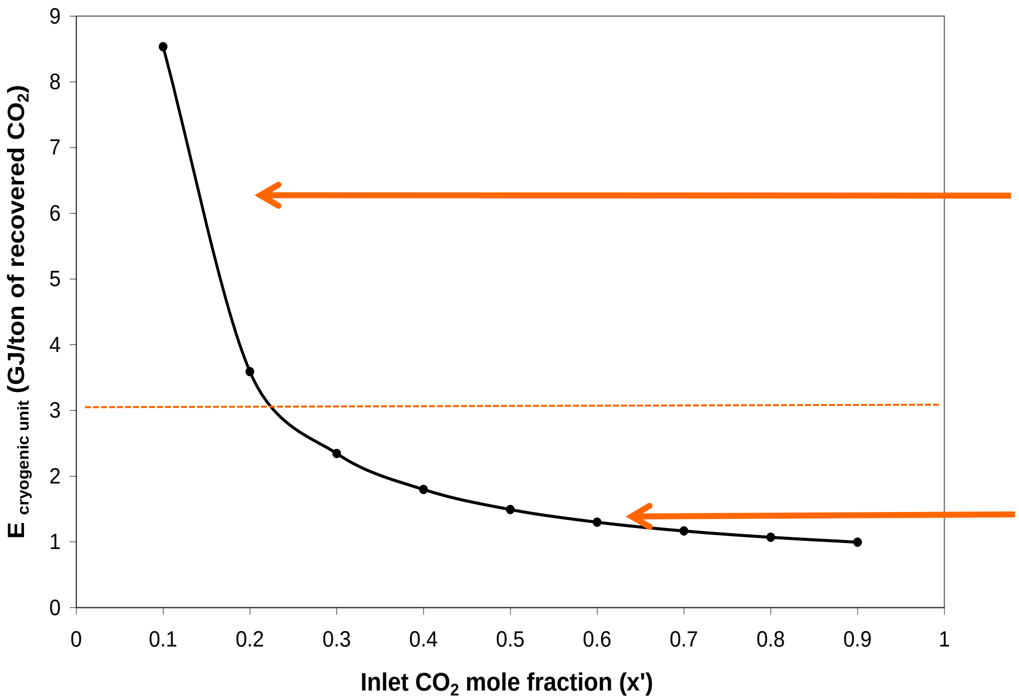




A membrane / absorption hybrid process is (probably) not relevant

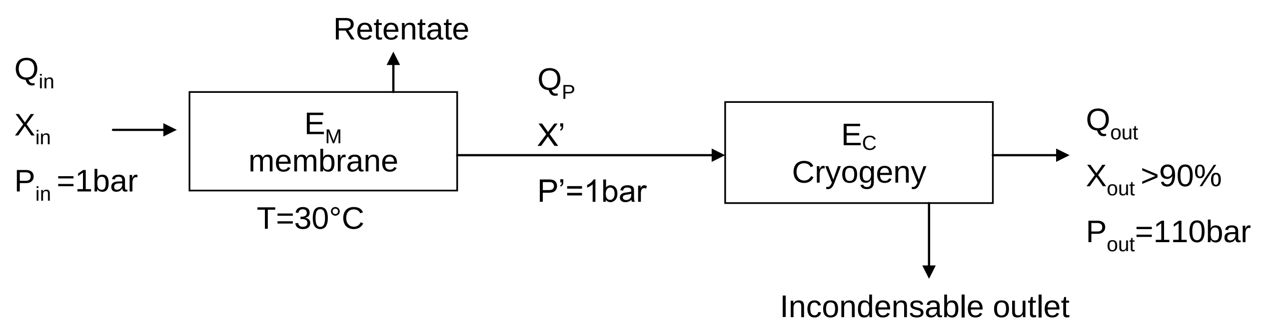


Hybrid process: Membrane preconcentration + cryogeny



Cryogenic CO_2 capture is not efficient for low CO_2 content

Cryogenic CO_2 capture can be very efficient for high CO_2 content

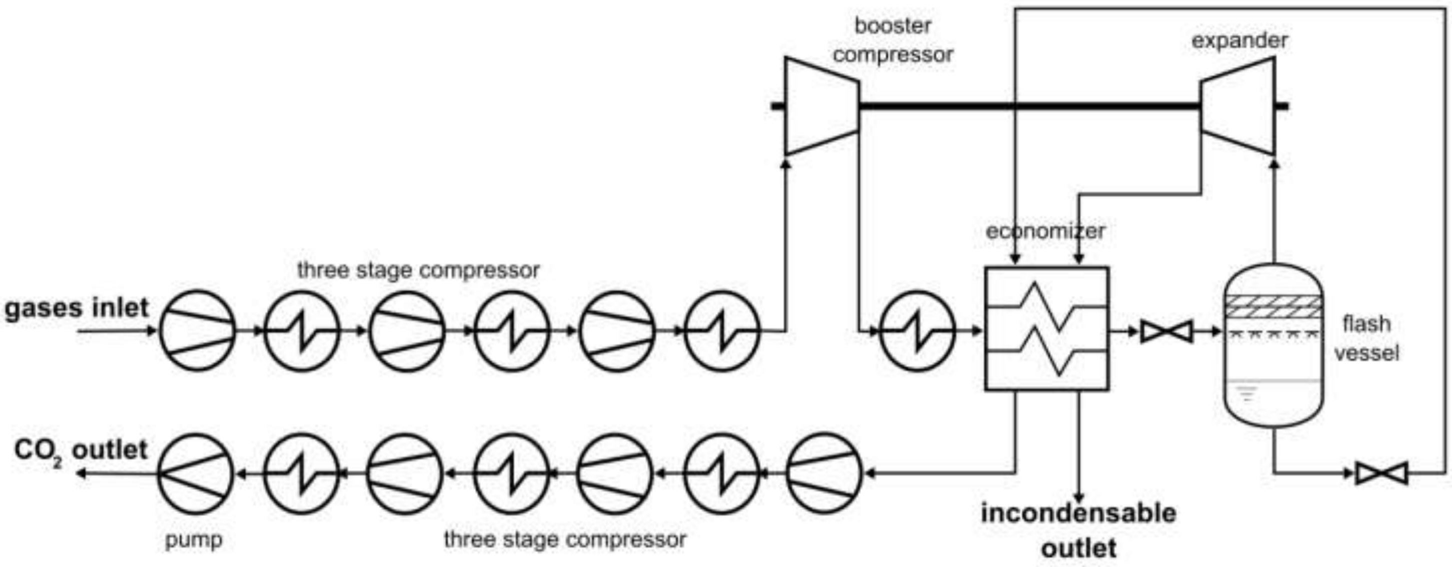


Cryogenic separation: simulation

Three-stage compression with intercoolers (*Aspen software*)

P'_{out}= 1 bar
x'_{CO2}

x_{out} >98%
P_{out}=110bar

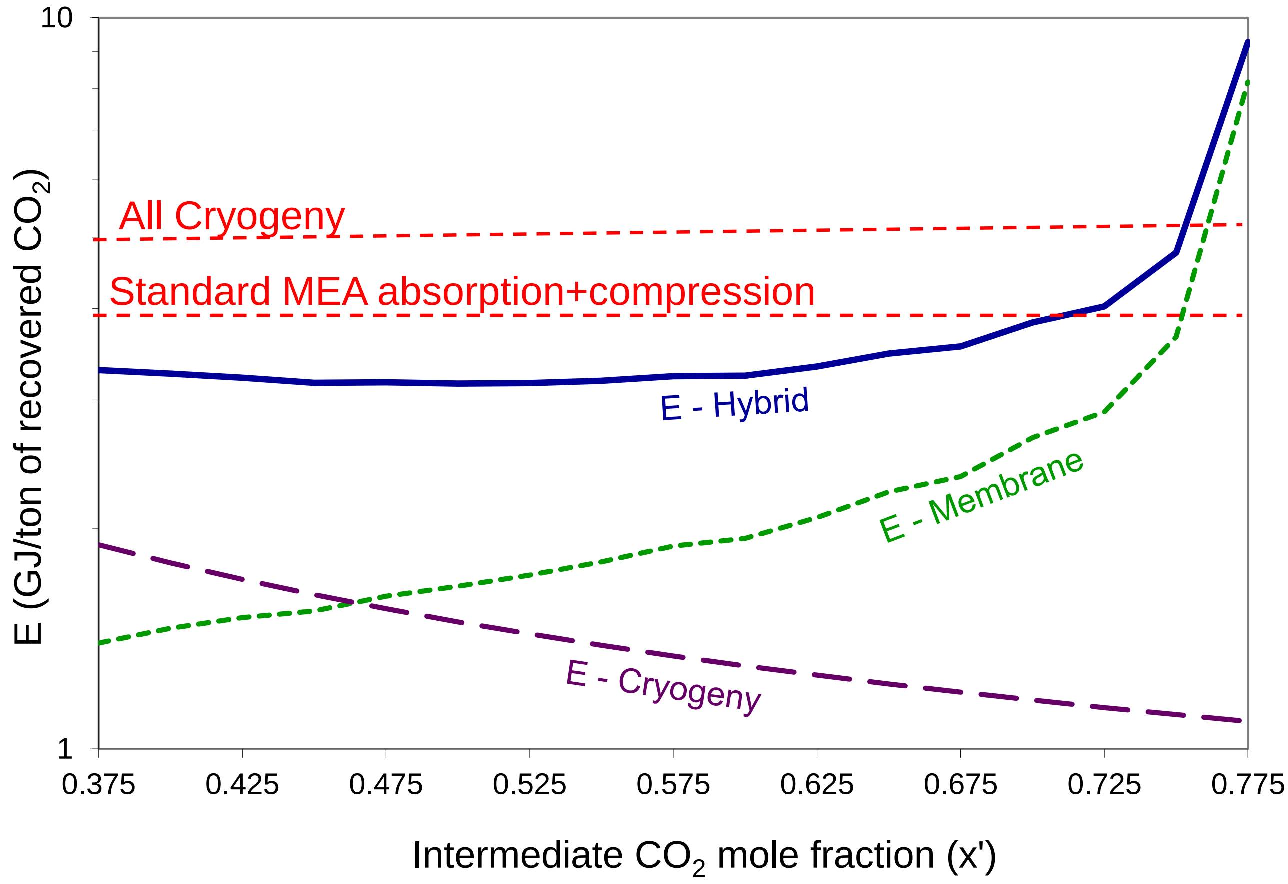


CO_2 capture ratio	>0.95
CO_2 purity (x_{out})	>0.98

Pump Isentropic efficiency :	0.8

Compressor isentropic efficiency :	0.85

Hybrid process: performances



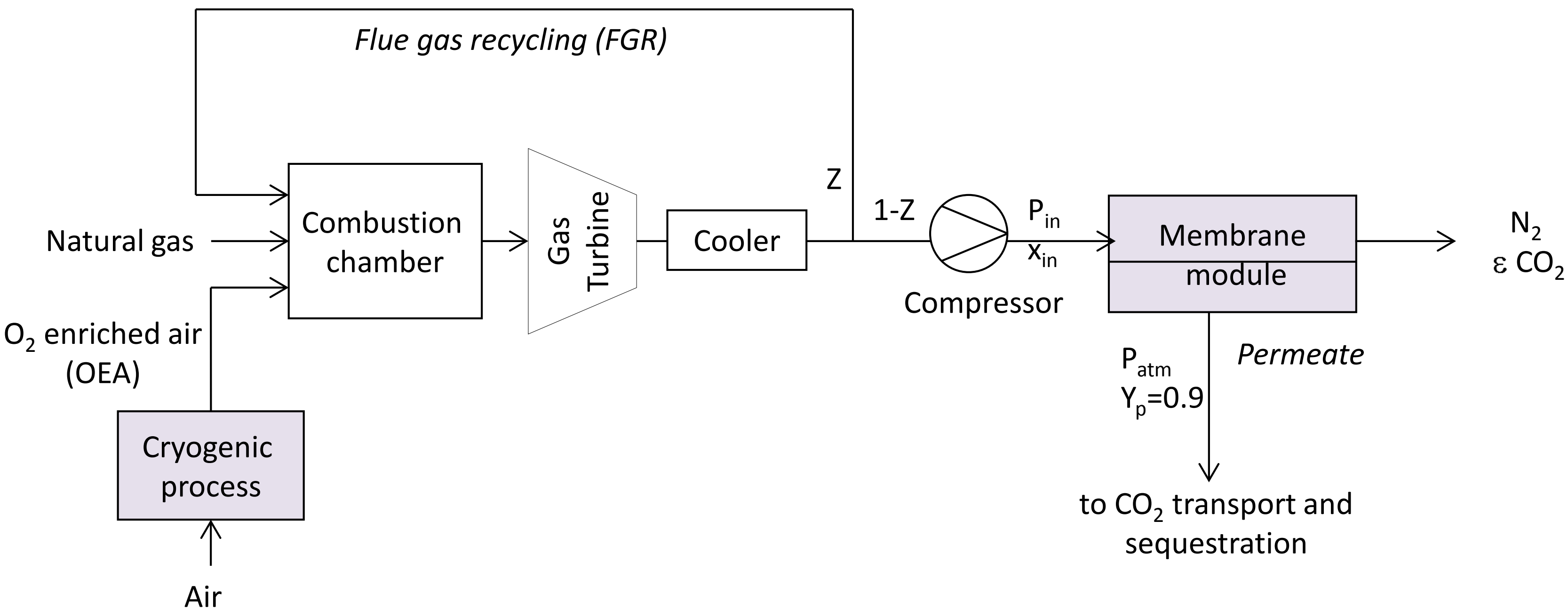
20% energy decrease

The hybrid process significantly decreases the energy requirement compared to the standalone cryogenic separation and MEA absorption.

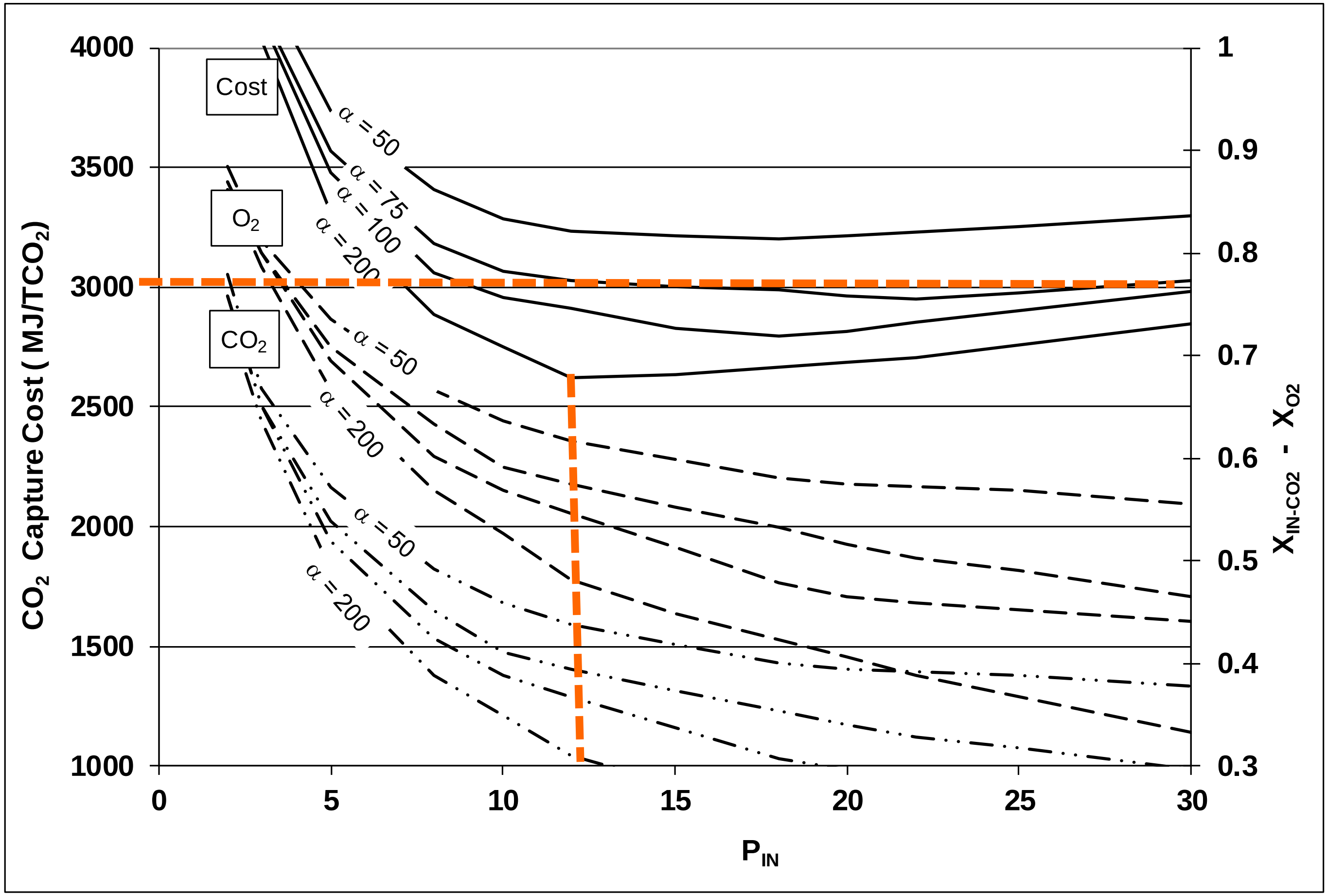
B. Belaissaoui , Y. Le Moullec, D. Willson , E. Favre, Journal of Membrane Science, 415-416 (2012) 424-434

Hybrid process: Membrane / OEA / FGR on Gas turbine

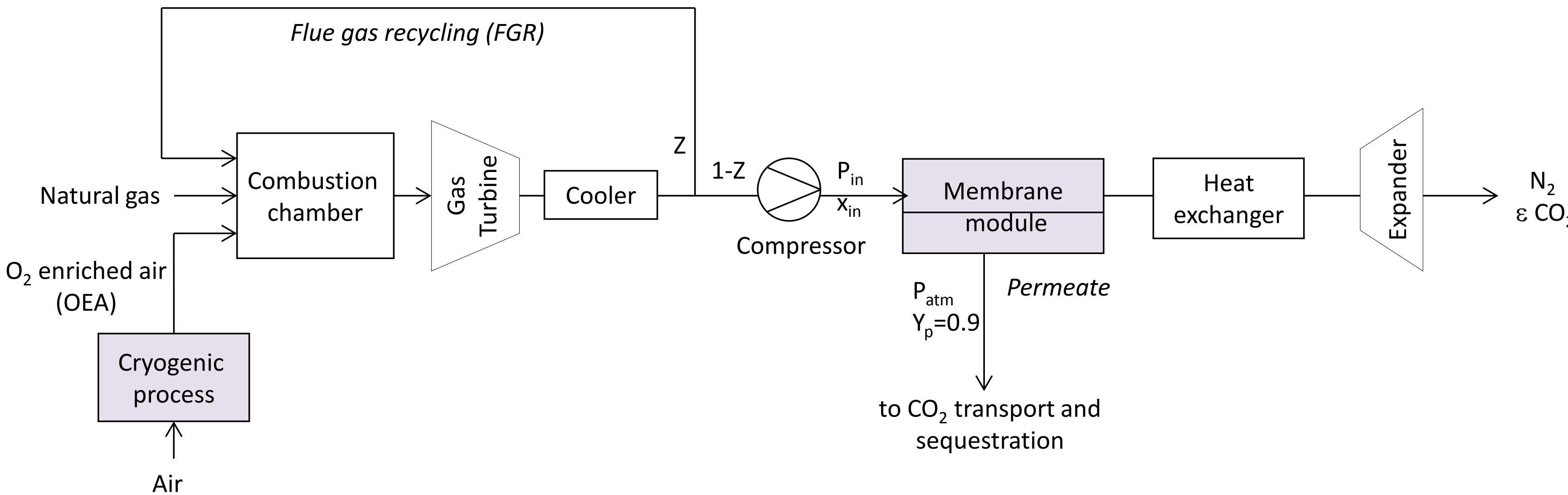
There is a substantial benefit from increasing the inlet CO_2 content: flue gas recirculation and/or combustion in oxygen enhanced air (OEA)



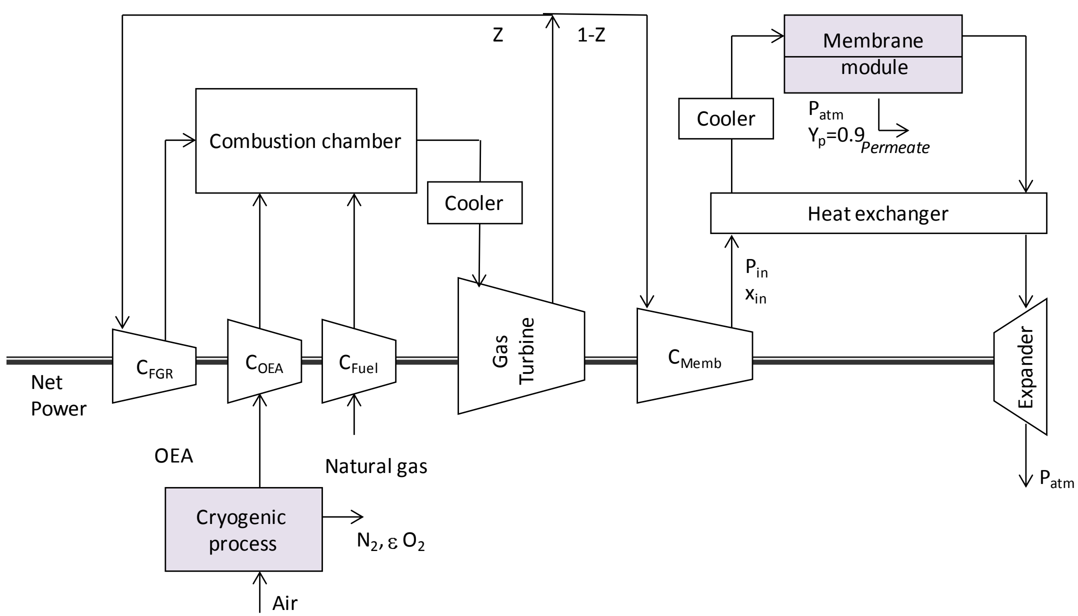
Improved energy efficiency Selectivity helps



B. Belaissaoui, G. Cabot, M.L. Cabot, D. Wilson, E., Favre   Energy (2012) 38, 167-175

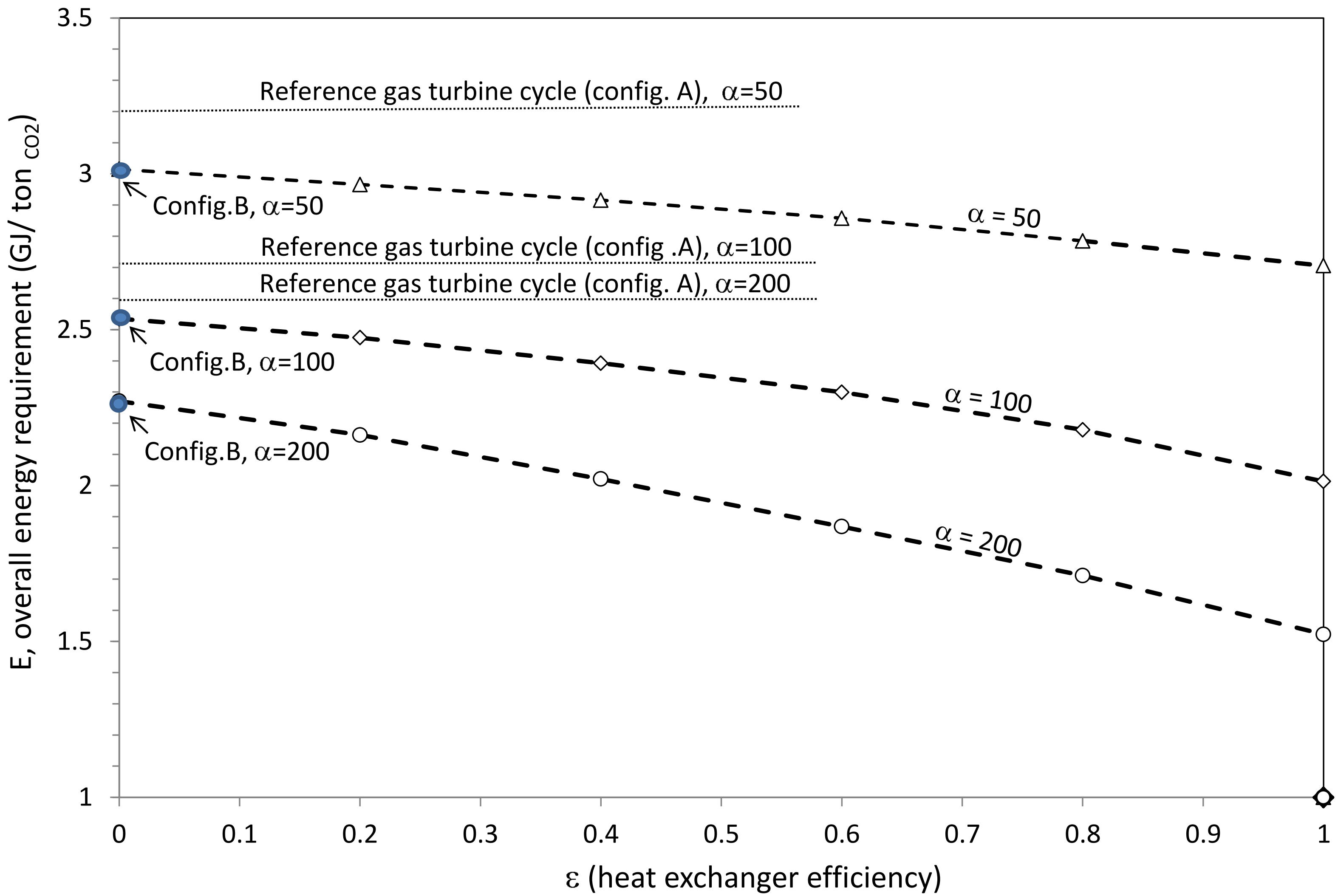


Flue gas recycling (FGR)
Natural gas
Combustion chamber
Gas Turbine
Cooler
Z
1-Z
Compressor
P_in
x_in
Membrane module
Heat exchanger
Expander
N_2
ε CO_2
O_2 enriched air (OEA)
Cryogenic process
Air
P_atm
Y_p=0.9
Permeate
to CO_2 transport and sequestration



Z
1-Z
Membrane module
Combustion chamber
Cooler
P_atm
Y_p=0.9
Permeate
Cooler
Heat exchanger
P_in
x_in
C_FGR
C_OEA
C_Fuel
Gas Turbine
C_Memb
Expander
Net Power
OEA
Natural gas
P_atm
Cryogenic process
N_2, ε O_2
Air

Integrated approach: Performances



Conclusion

Membranes processes and post combustion CCS: utopy or opportunity?

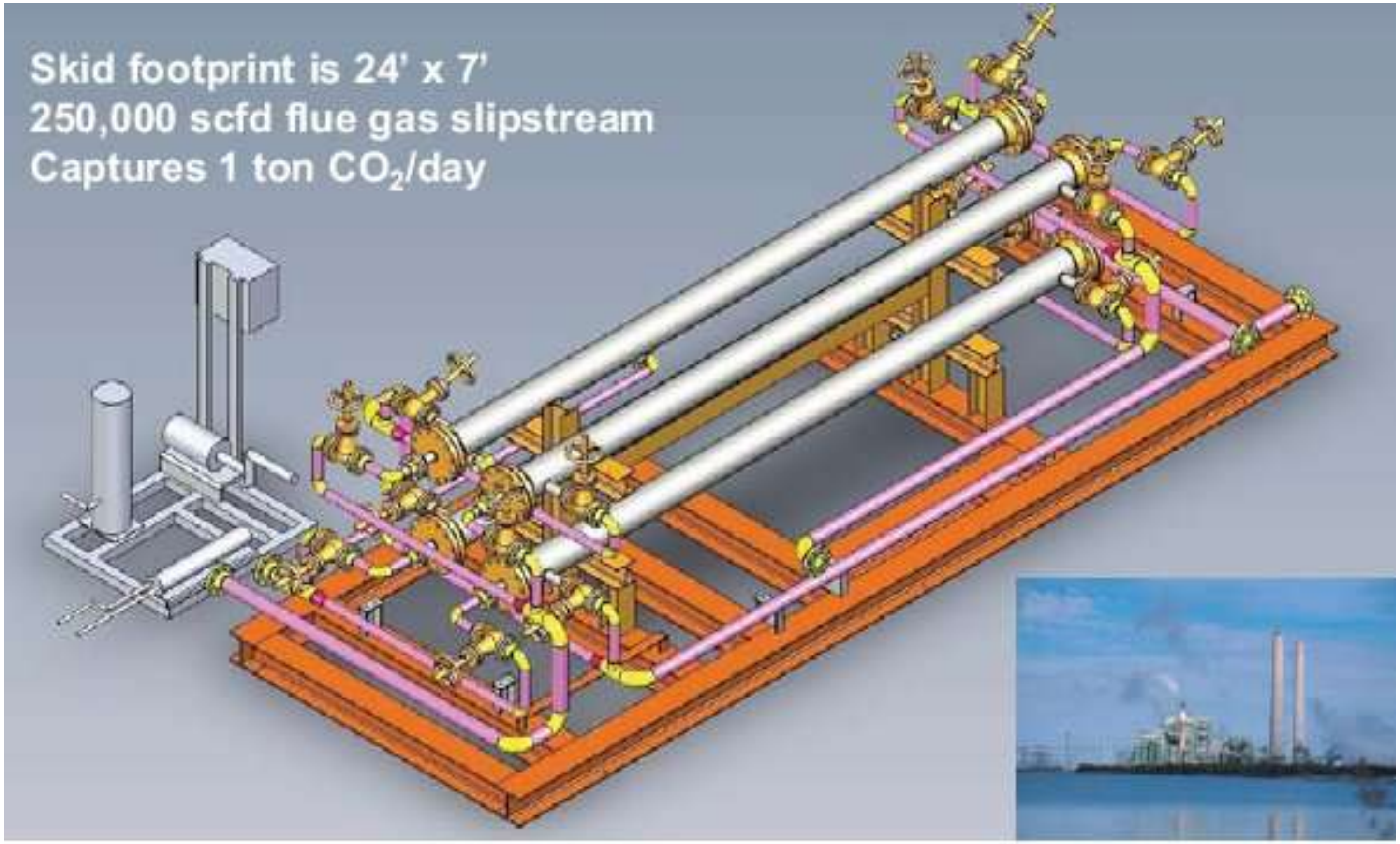
- *Membranes processes offer a large variety of potential applications in a CCS framework (separation, concentration, polishing)*

- *Very large number of publications on materials, few on process, very few on technico-economical studies. The interest of selective vs permeable materials remains controversial*

- *Investigations are mostly limited to model mixtures and at laboratory scale*

- *Crucial need for studies on real flue gases (dust, water, SOx, O_2), ideally at pilot scale*

- *Hybrid and/or integrated processes should be more systematically investigated*

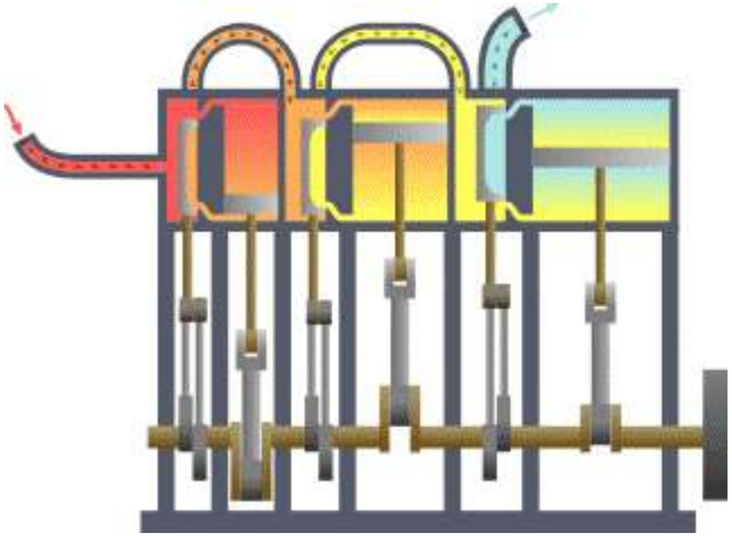


The APS Cholla power plant
1 ton/day field test pilot unit

Fresh module

After 45 days of operation at Cholla

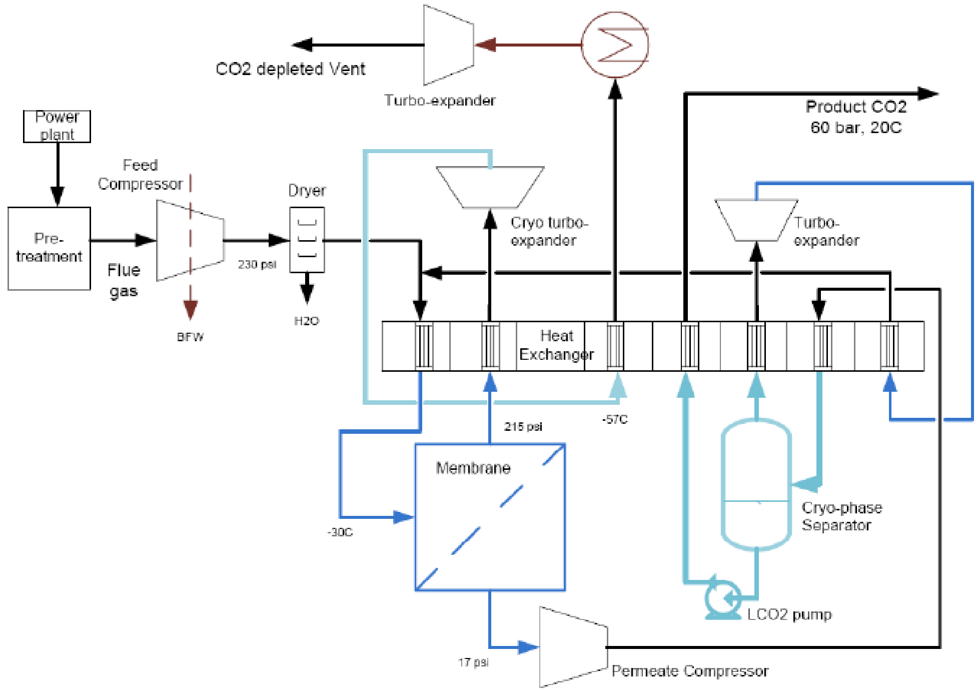
Thank you for your attention!

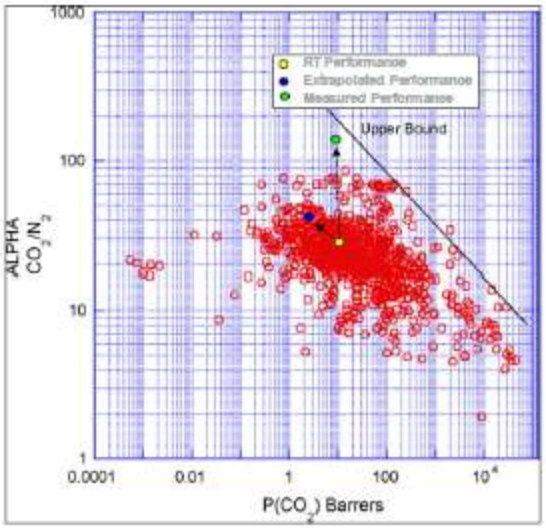


Eric.Favre@univ-lorraine.fr

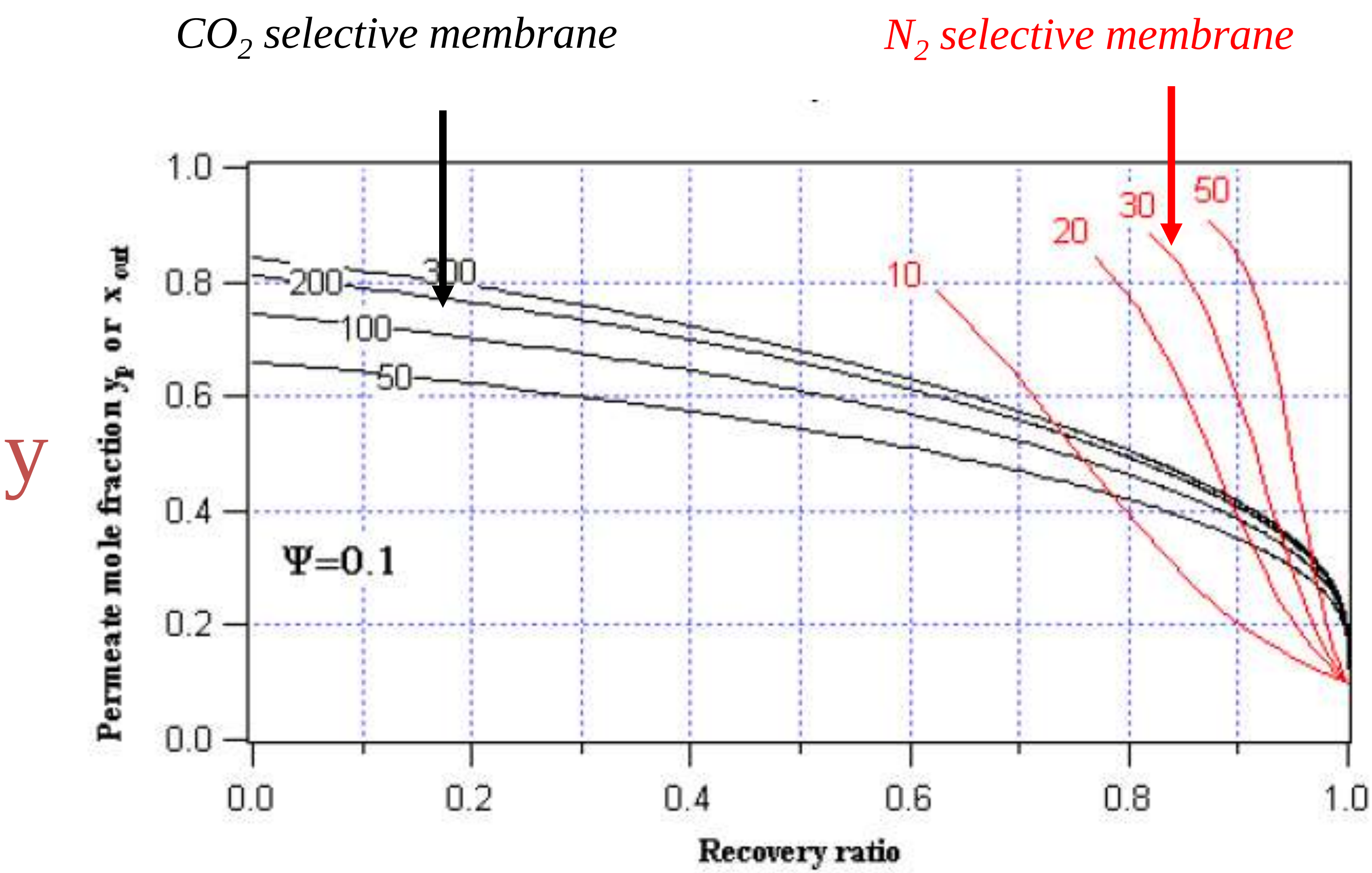
Air Liquide DOE project

Project DE-FE004278



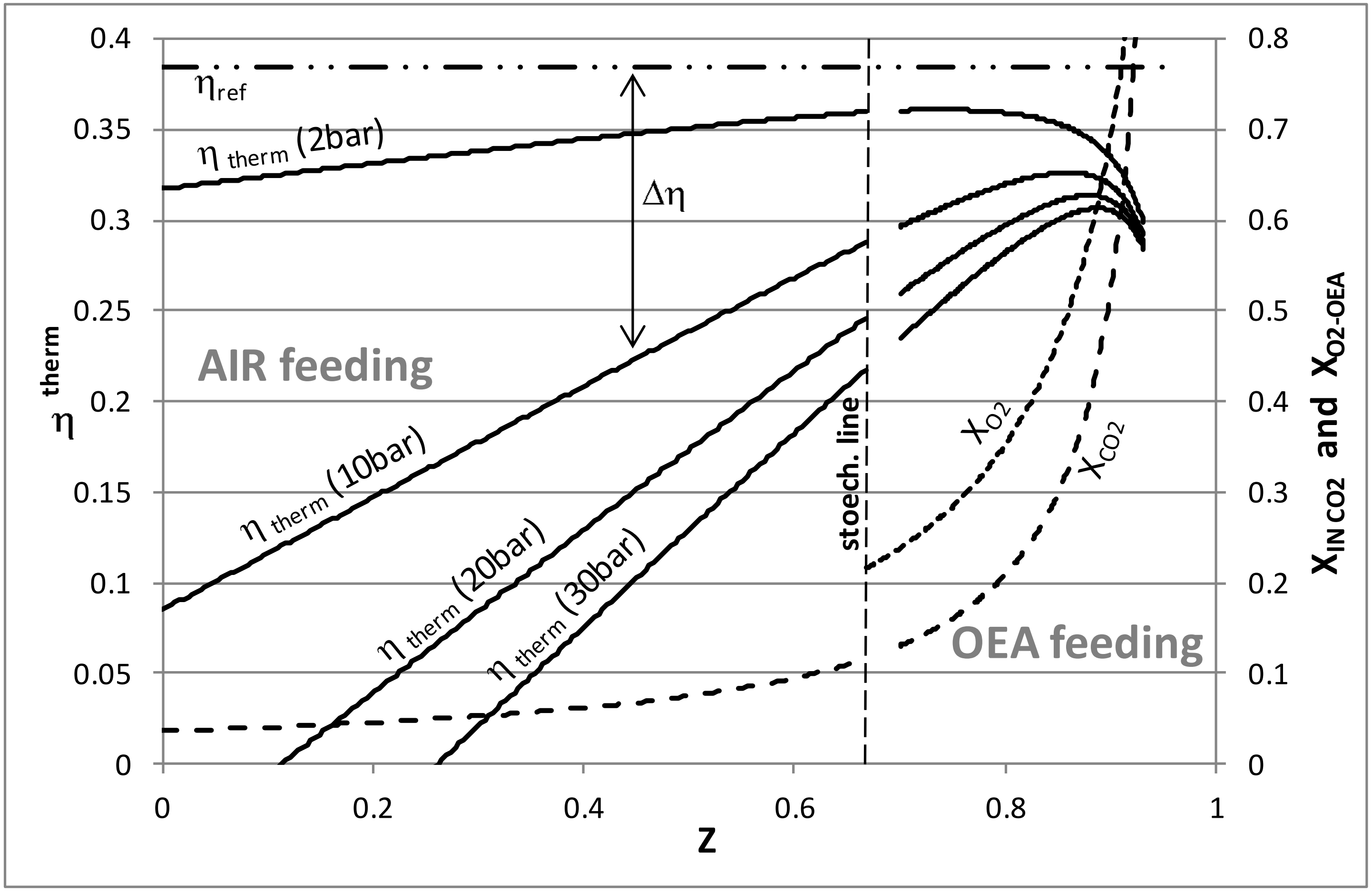


Unconventional approach : Reverse selective membranes



Favre, E., Roizard, D., Koros, W.J. (2009) *Ind. Eng. Chem. Res.*, 48 (7) 3700-3701.

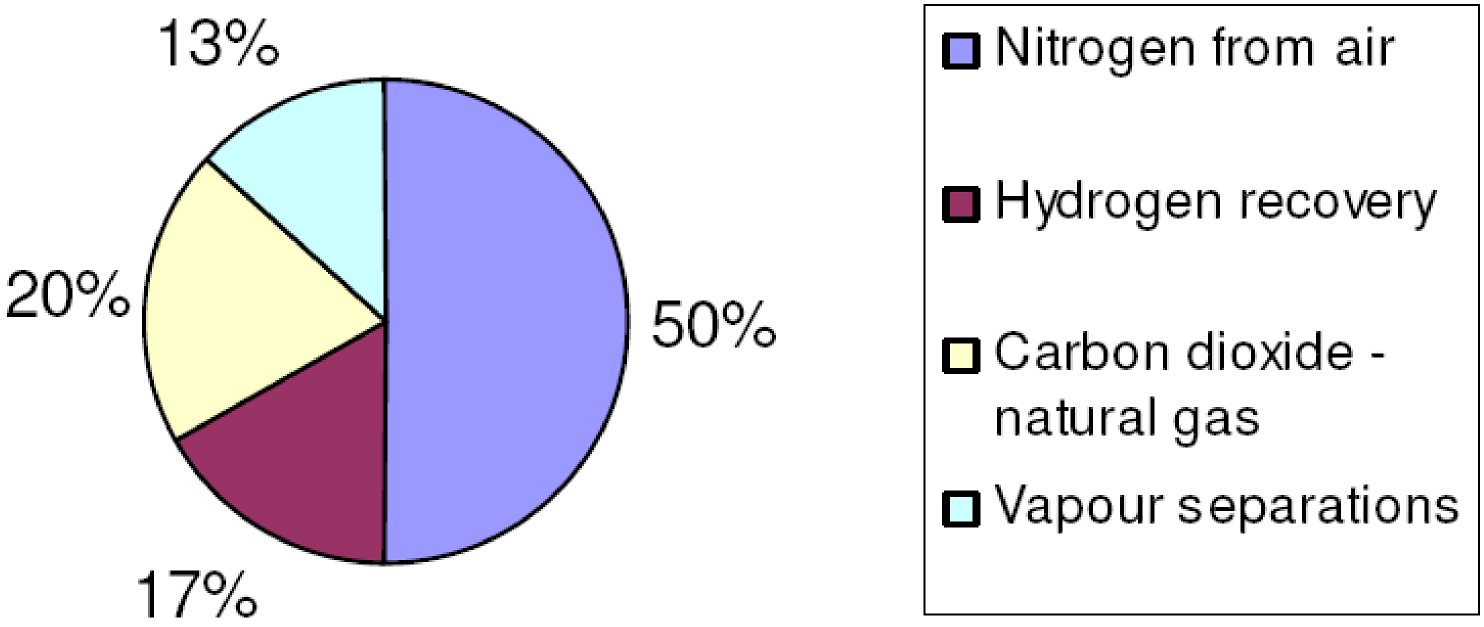
Hybrid process: Impact on energy efficiency



B. Belaissaoui, G. Cabot, M.L. Cabot, D. Wilson, E., Favre Energy (2012) 38, 167-175

Membrane Gas Separation: Applications & Market

Market size: 150 MUS$/y (Baker, 2002)



Ashkelon desalination plant

- 40,000 spiral-wound RO modules
- 1.5 million m^2 membrane area

- Total energy use is 56 MW.
- Plant produces 100 million m^3/yr of water.