PCC Science & Technology Seminar

ABBA : Amine Based and Beyond Amines

CSIRO Energy Centre, Newcastle

Tuesday 26 March 2013

9.00-09.15	Registration and refreshments	
9:15-09:30	Introduction and Safety moment	Noel Simento & Paul Feron
9.30-10.00	Membrane process development and modelling	Prof Eric Favre (ENSIC, France)
10.00-10.30	Post-Combustion capture with Ultra-porous Materials	Dr Matthew Hill, (CSIRO, Australia)
10:30-11:00	Hydrogen separations using membranes	Dr Michael Dolan (CSIRO, Australia)
11.00-11.15	Coffee/tea	
11.15-11.45	The NET Power Cycle and the combustor and turbine development	Dr Hideo Nomoto (Toshiba, Japan)
11.45-12.15	Solid sorbents for PCC and mine-gas remediation	Dr Su Shi (CSIRO, Australia)
12.15-13.15	Lunch and Lab visit	
13.15-13.45	CO_2 Capture Research in the Netherlands	Mr Maurice Hanegraaf (TNO, Netherlands)
13:45-14:15	Calcium-oxide looping	Dr Borja Arias (INCAR/CSIC, Spain)
14:15-14:45	Progress in development of liquid absorbent PCC technologies at CSIRO	Dr Graeme Puxty (CSIRO, Australia)
14:45-15:15	CSIRO PCC pilot plant research in Australia	Mr Aaron Cottrell (CSIRO, Australia)
15.15-15.30	Presentation of PCC course material to ANLEC R&D Coffee/tea – Seminar close	

an ANLEC R&D Science Leadership activity

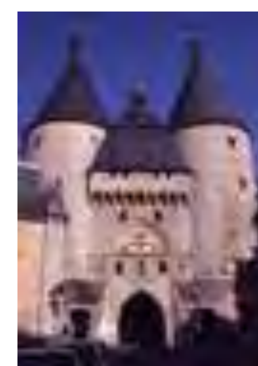
Membranes and post-combustion carbon dioxide capture

Eric FAVRE

Laboratoire Réactions & Génie des Procédés (UPR CNRS 3349)

Université de Lorraine Nancy FRANCE

Nancy… somewhere in France



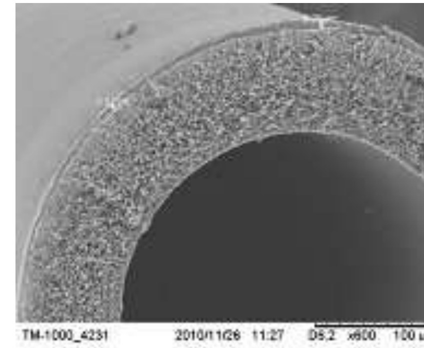
Nancy, Lorraine, France

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)

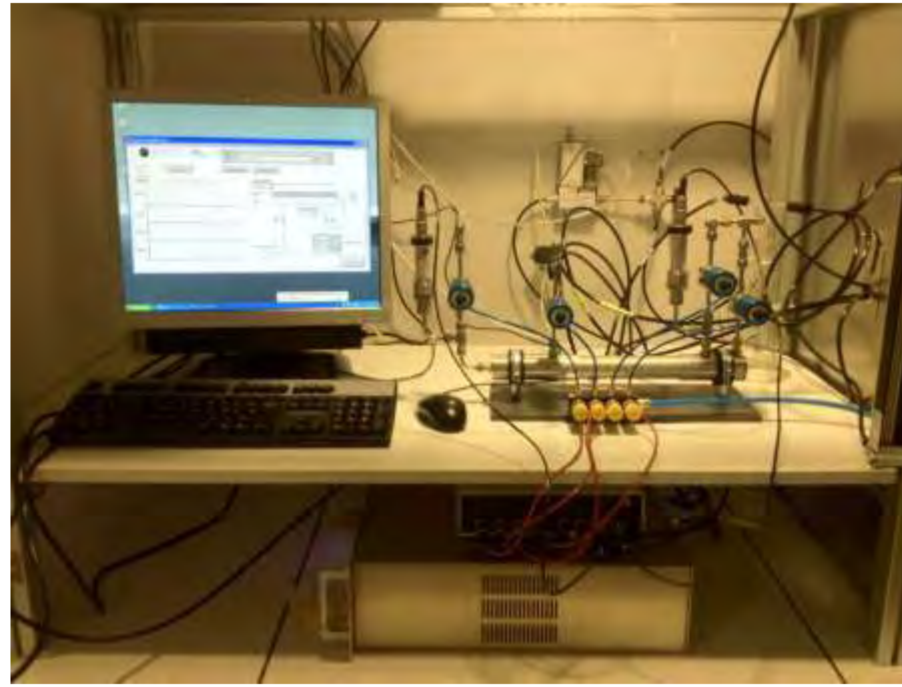
Process modelling (M3Pro software)

Hybrid processes:

Oxygen enriched air combustion / membrane capture (Cocase ICEEL)

Membrane concentration / cryogenic condensation (with EDF)

Prospective & breakthrough approaches

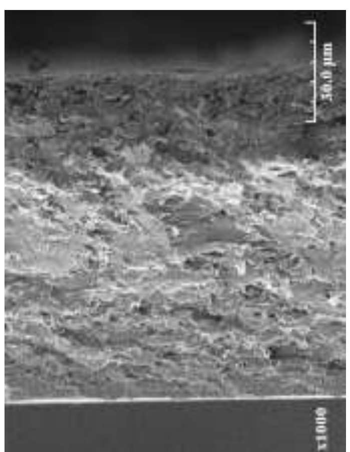


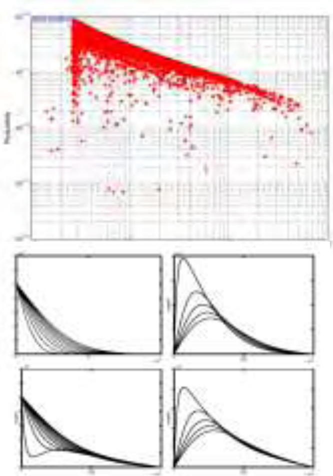
Liquid membranes (TIPS Russia)

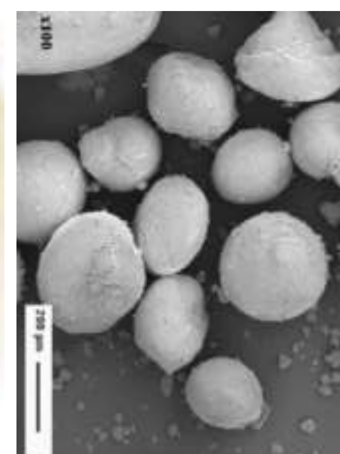
Impregnated particles (MESR)

Electrical swing adsorption (ACI Procap)

Cyclic membrane gas separations (ICEEL)

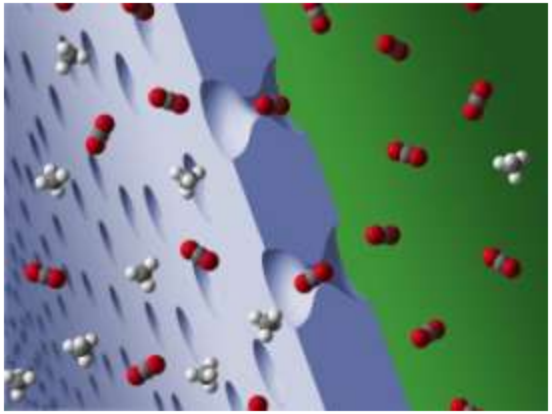




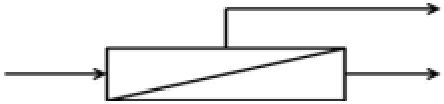


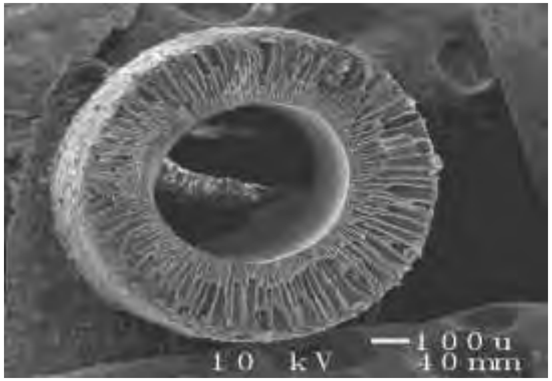
Outline

i) *Introduction*

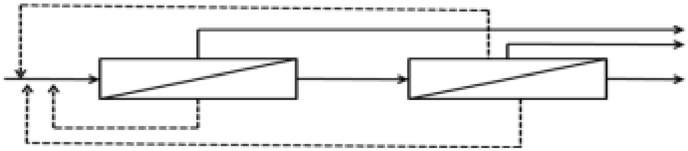


ii) *Single stage parametric sensitivity*





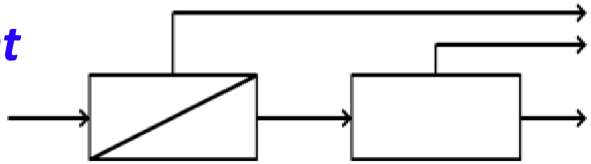
iii) *Multistage approaches*



iv) *Hybrid process:*

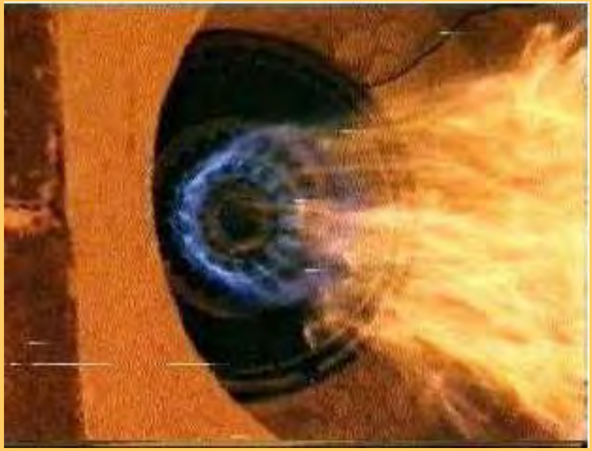
Coal power plant

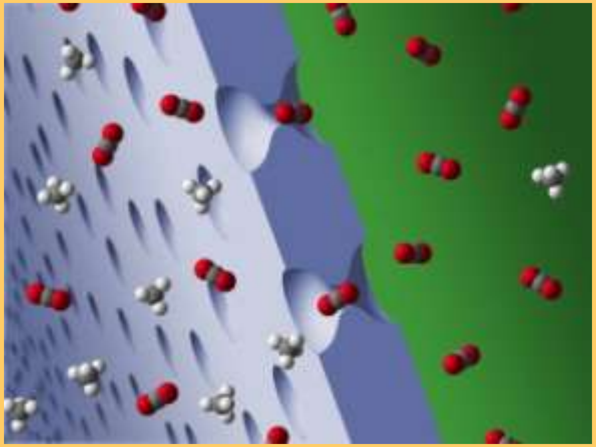
Gas turbine



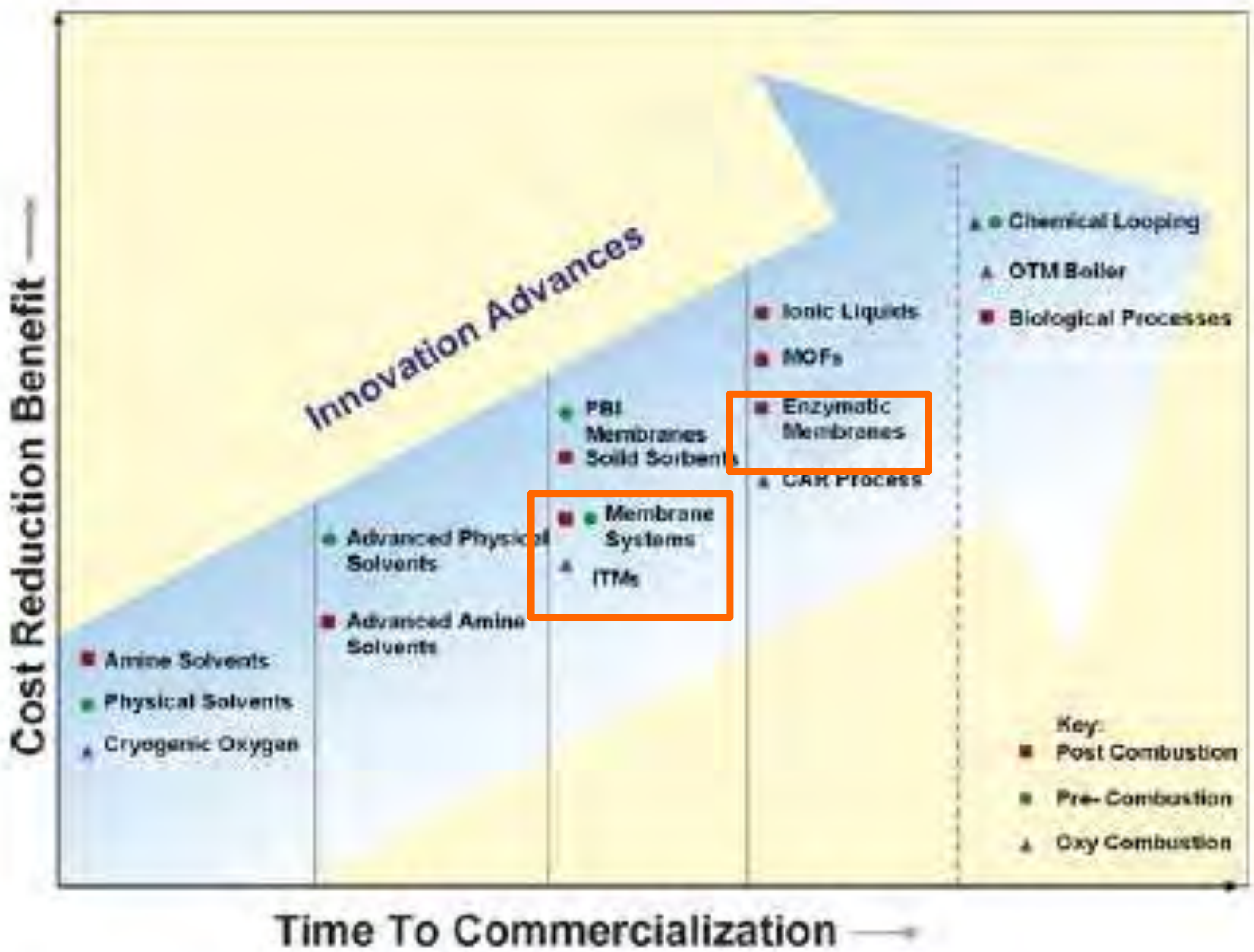
v) *Conclusion*

Introduction





Membranes: a potential 2nd generation carbon capture process

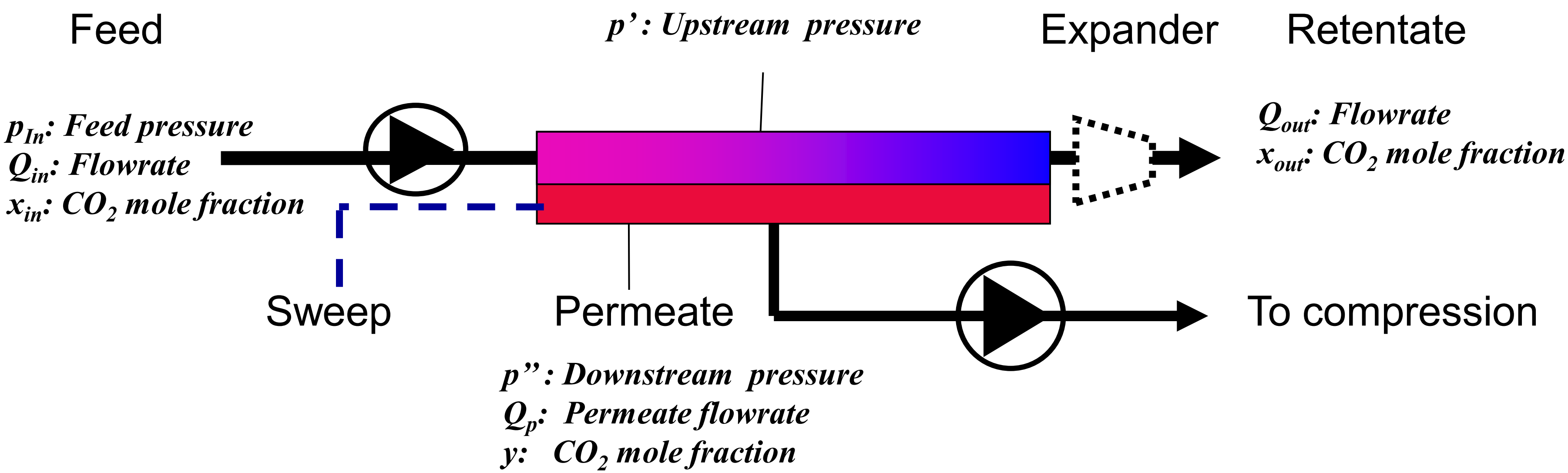


Source: Figueirao J. et al. DOE (2007) Int. J. Greenhouse Gas Control

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



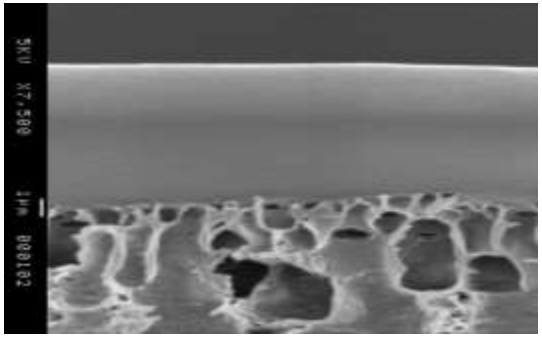
Permeability of A $\equiv P_A = D_A S_A$

where D_A = diffusion coefficient

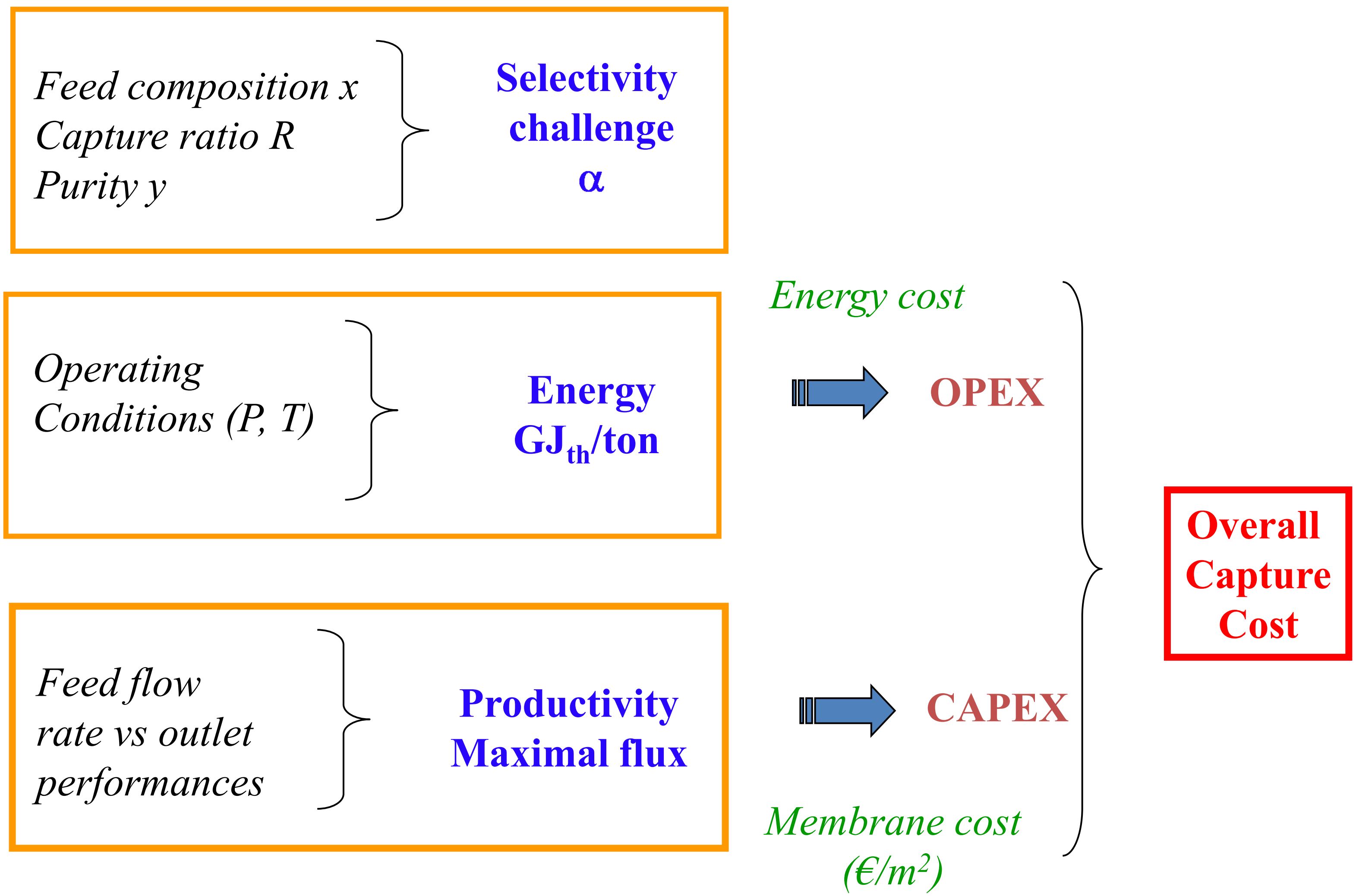
S_A = solubility coefficient

Selectivity

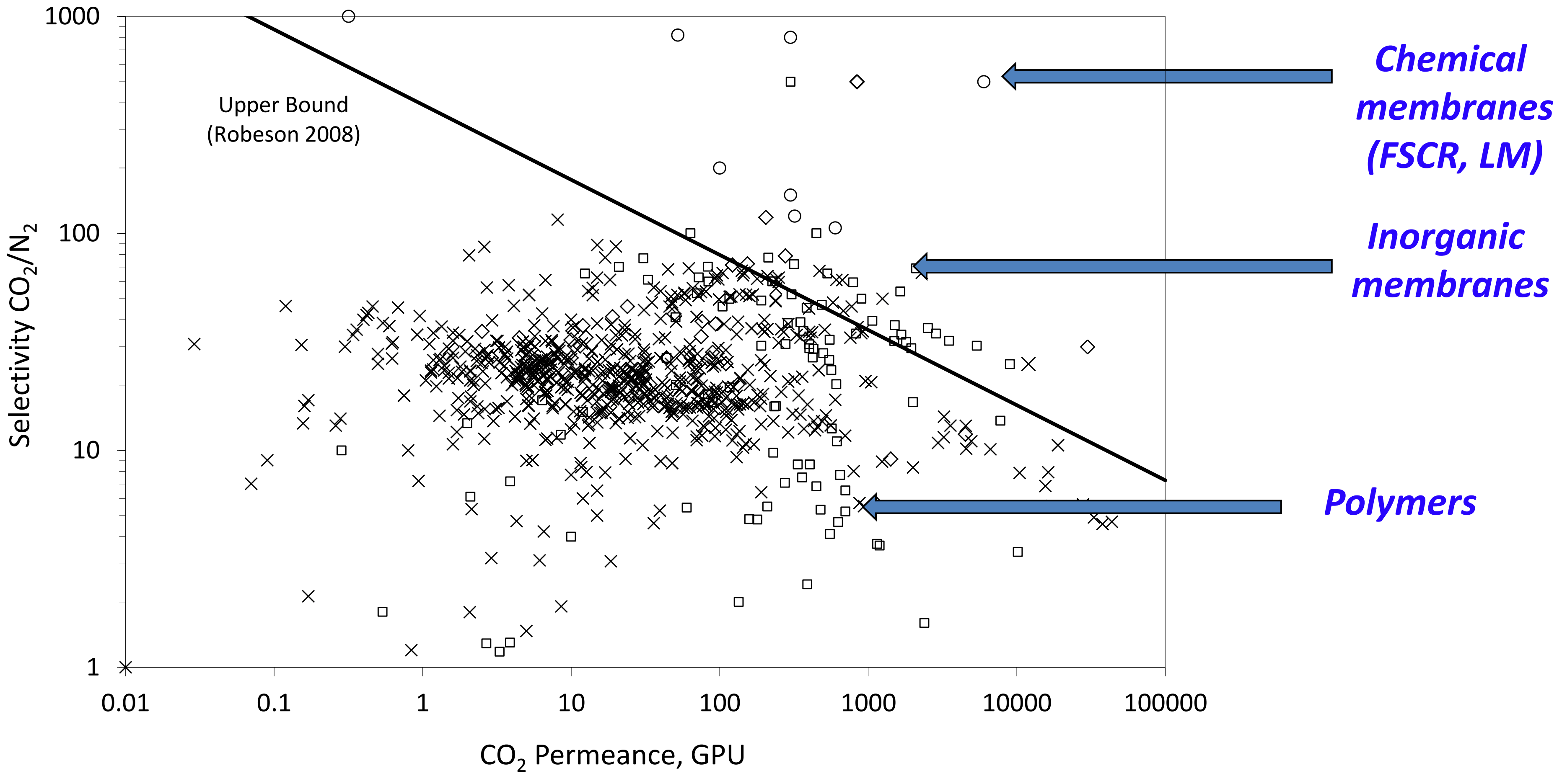
$$\alpha_{A/B} = \left(\frac{P_A}{P_B}\right) = \left(\frac{S_A}{S_B}\right)\left(\frac{D_A}{D_B}\right)$$



Membrane separation & CCS: a simplified overview



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**

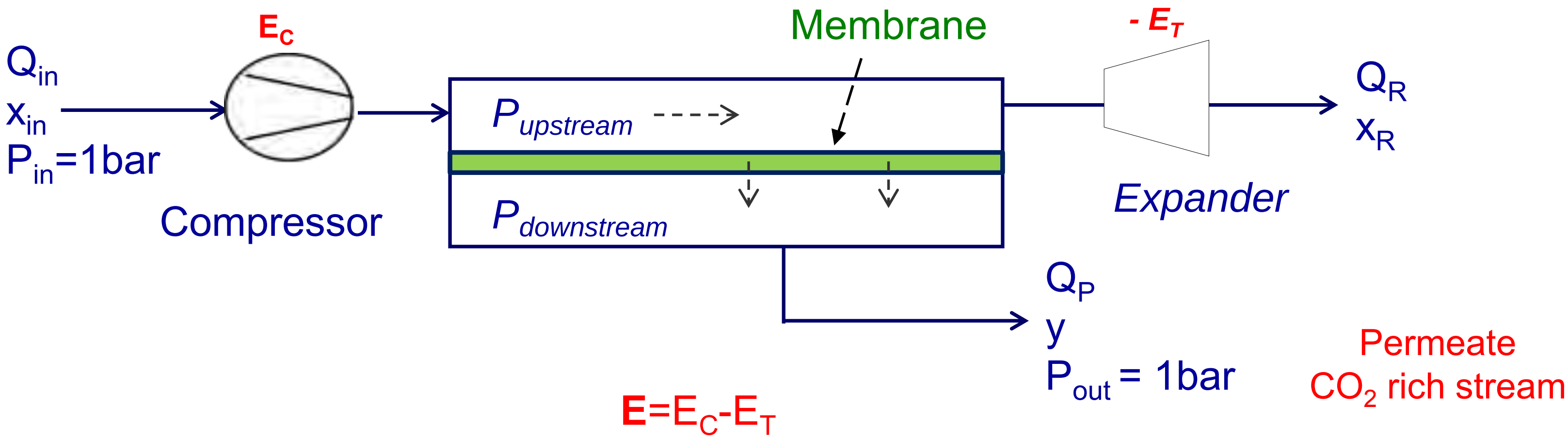
Materials performances for post-combustion carbon capture

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	

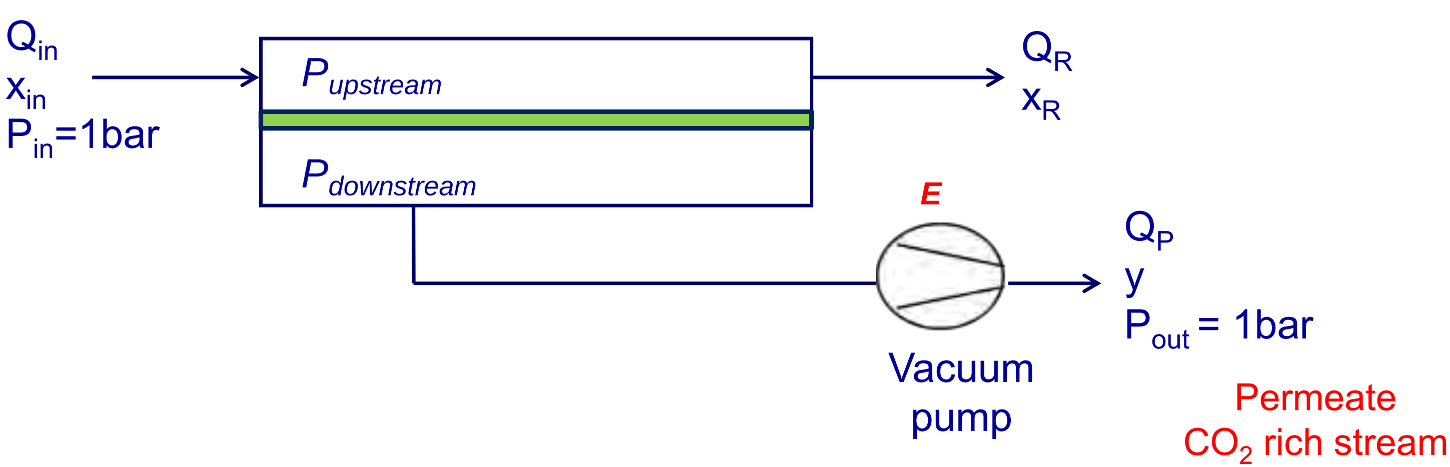
← *Baseline case for simulations* (Polaris™, 50, 1000 GPU)

Single stage simulations: Process alternatives

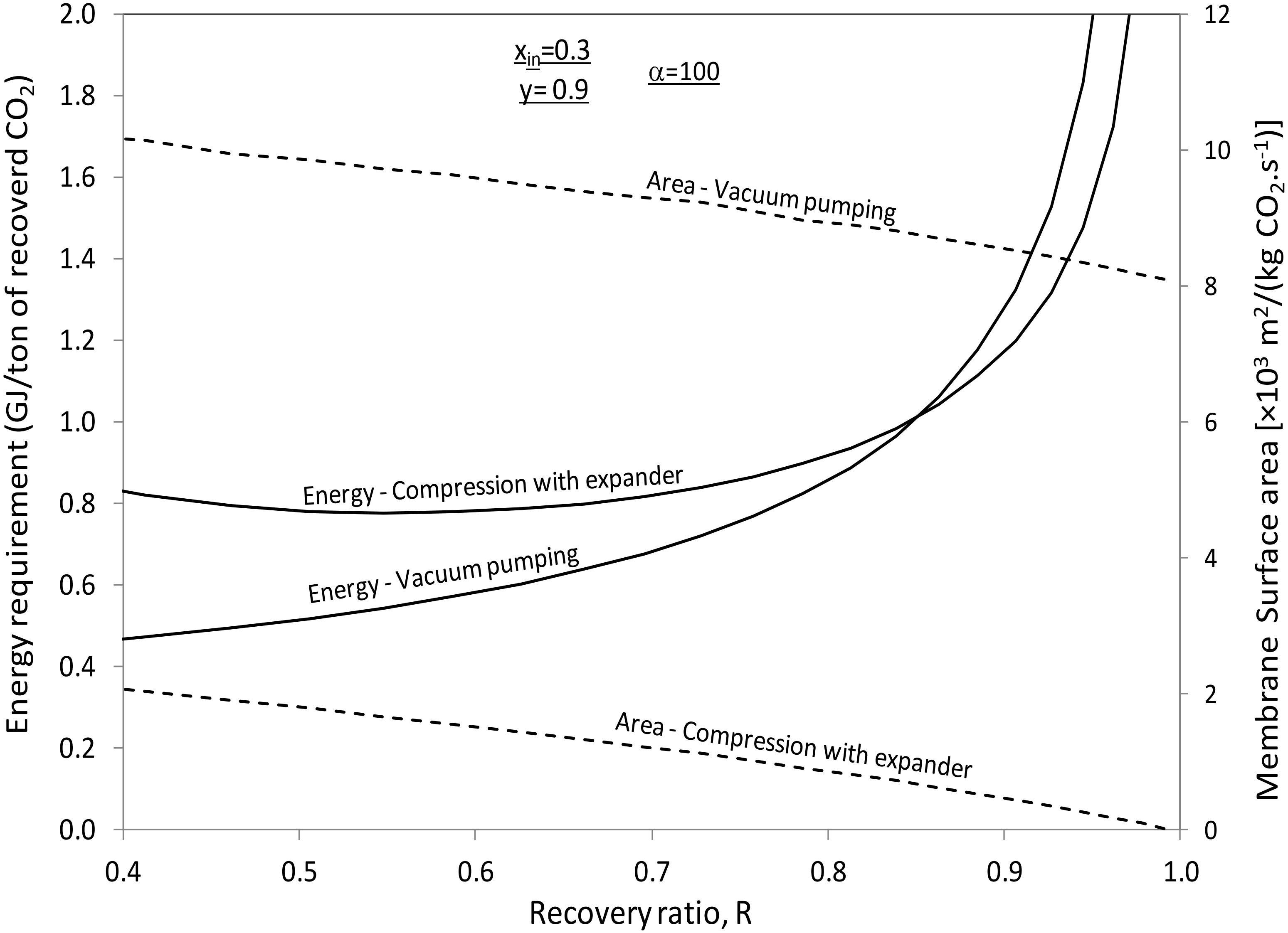
Feed compression with ERS on the retentate



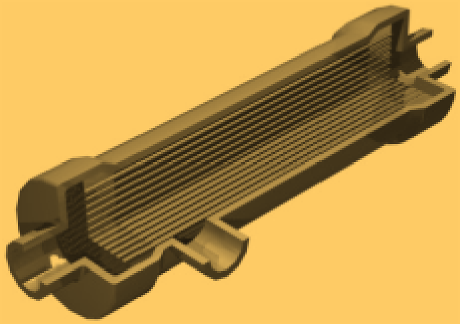
Permeate vacuum pumping



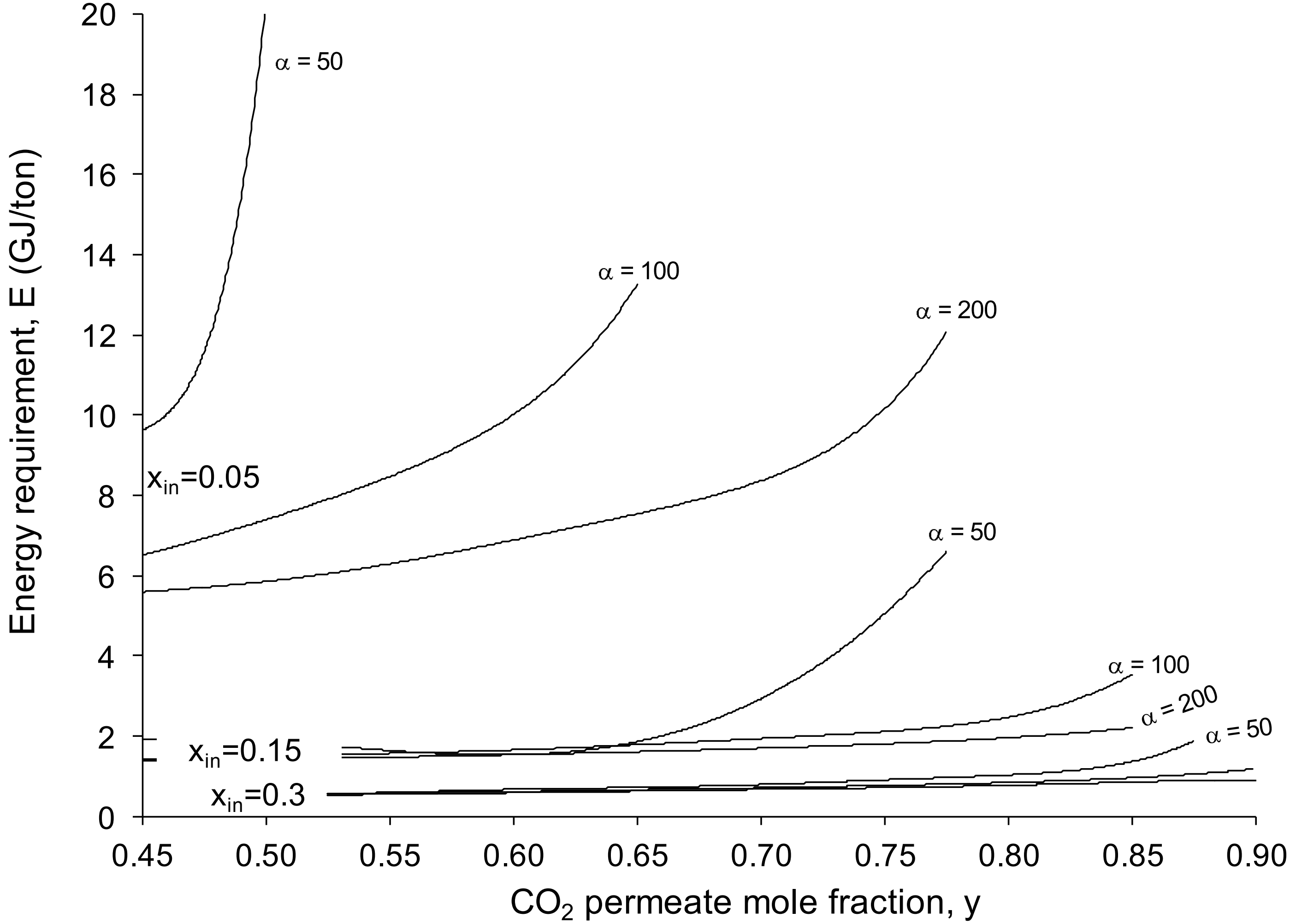
The feed compression / vacuum pumping dilemma



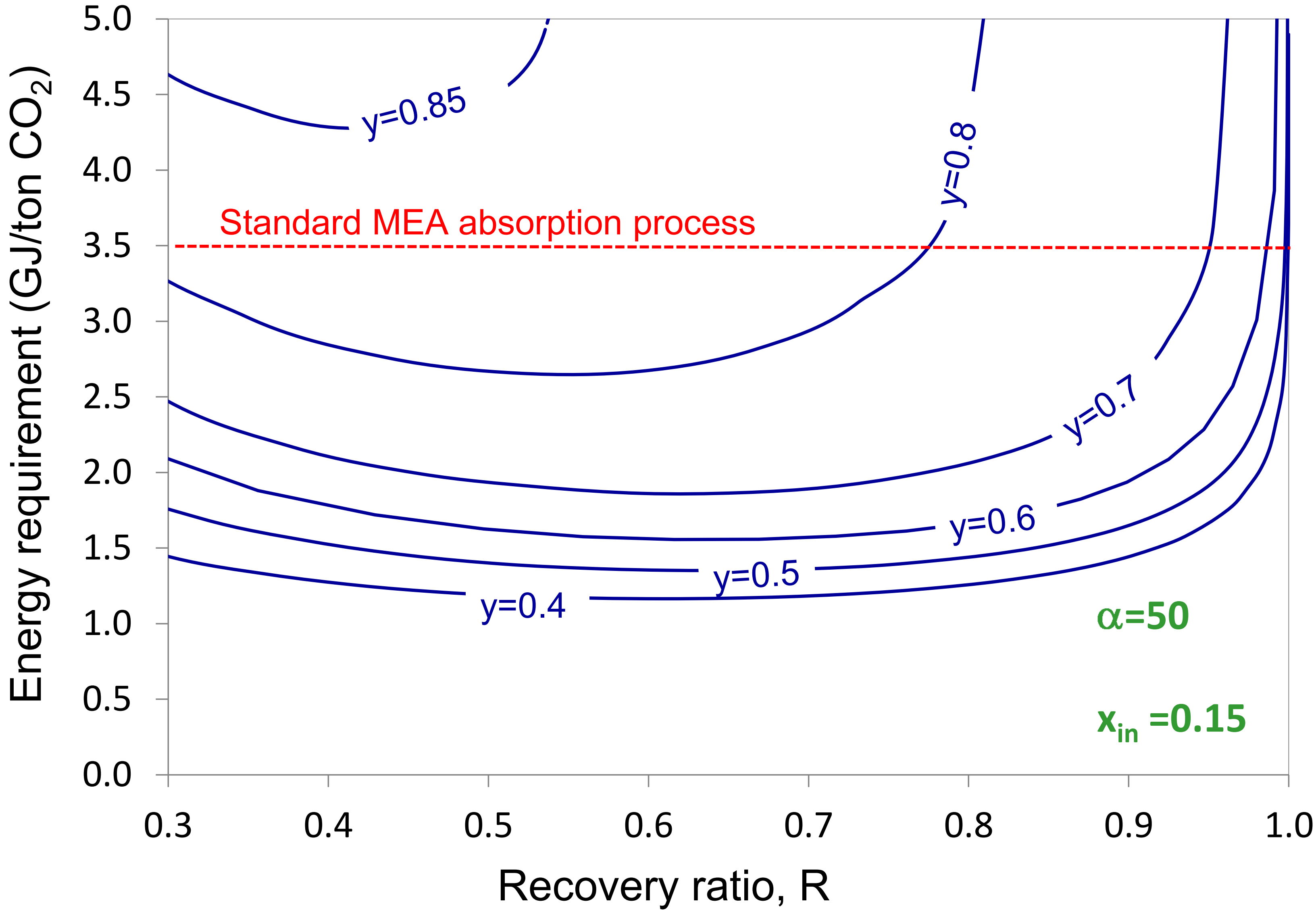
Parametric study of a single stage gas permeation module



Strong parametric sensitivity on feed composition

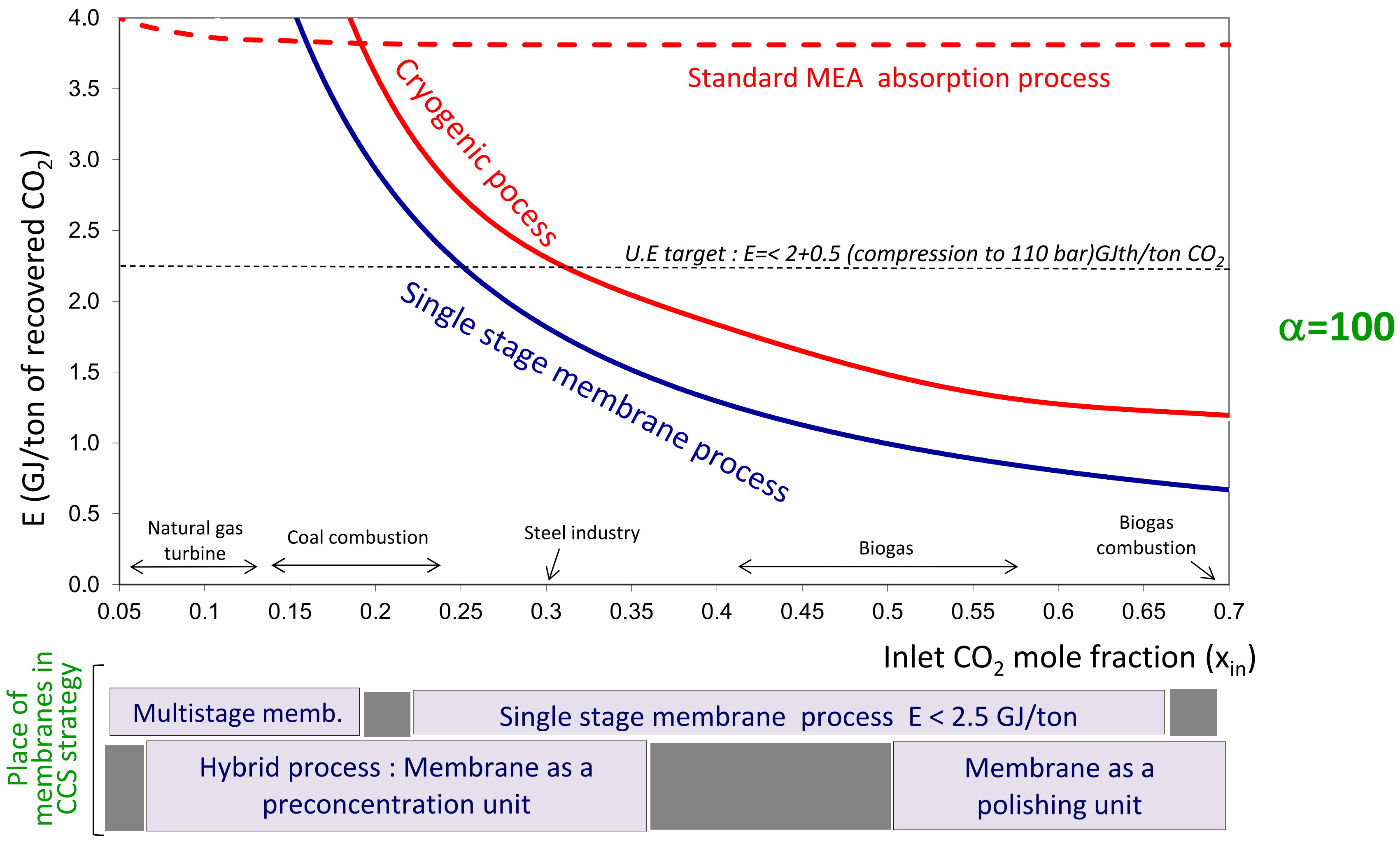


Tackling the capture ratio / purity challenge



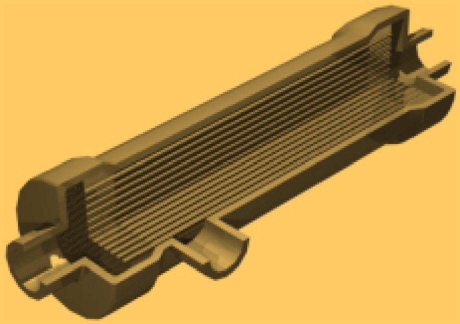
B. Belaissaoui , D. Willson , E. Favre, Chemical Engineering Journal, 211-212 (2012) 122-132

A tentative process selection map

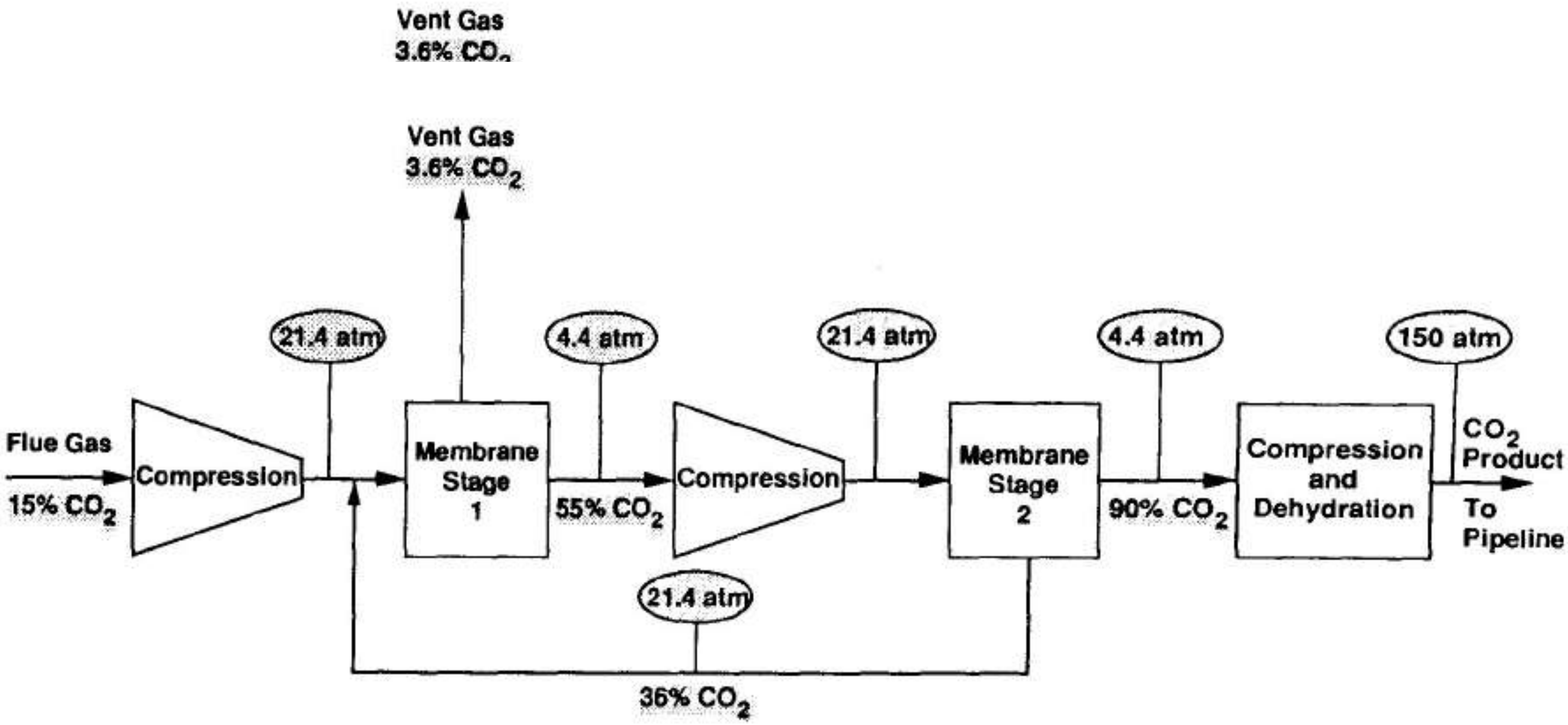


B. Belaissaoui , D. Willson , E. Favre, Chemical Engineering Journal, 211-212 (2012) 122-132

Multistage gas permeation modules for carbon capture



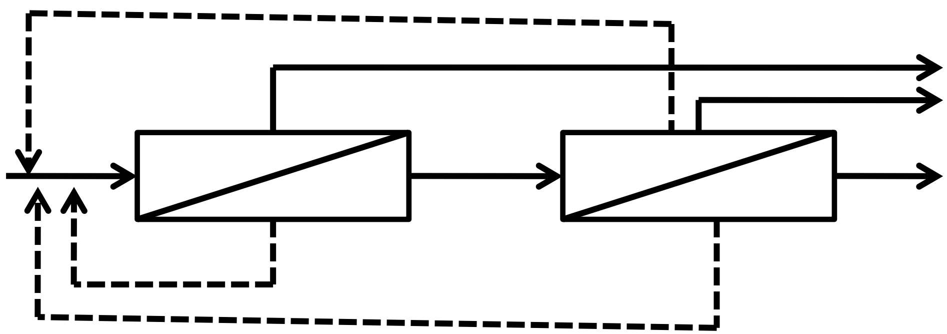
First two stages membrane gas separation process



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

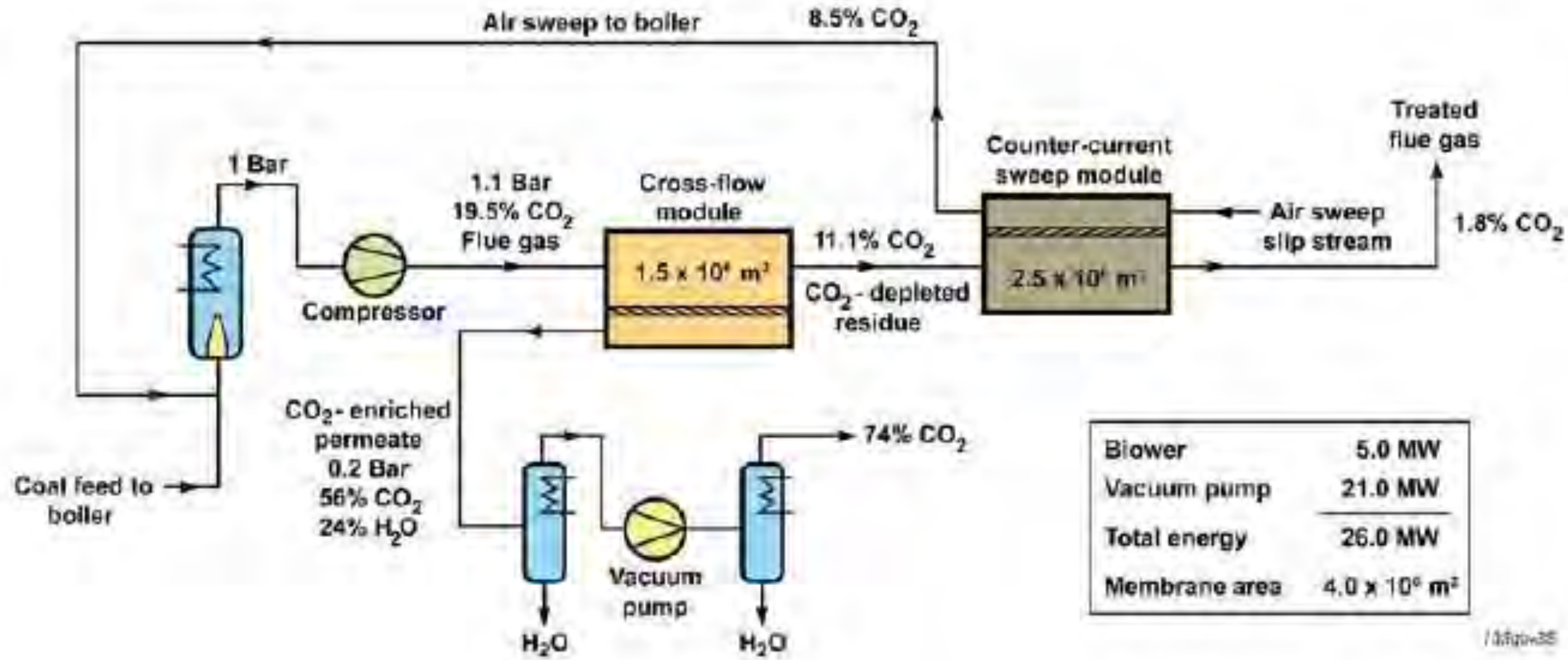
Herzog et al., Environ. Prog. (1991) 10, 64-74.

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)

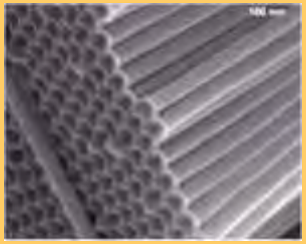
MTR DOE two stages membrane gas separation process

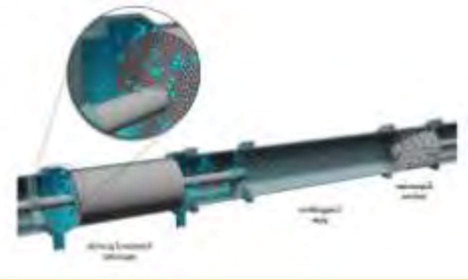


MTR novel 2 stage membrane flowsheet for post-combustion CCS application

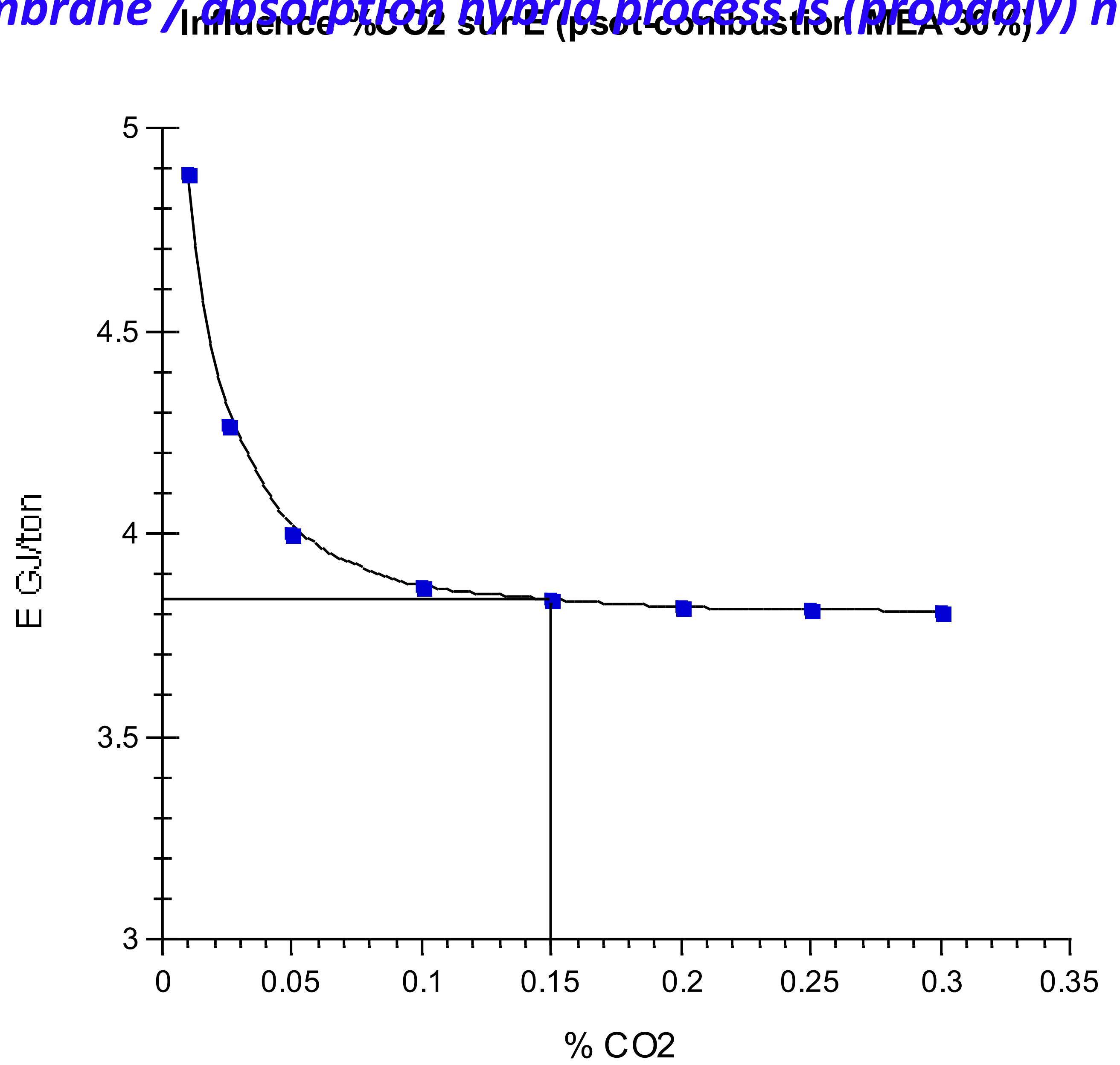
Merkel et al., J. Membrane Science (2010) 359, 126-139.

Hybrid processes with membrane modules for carbon capture

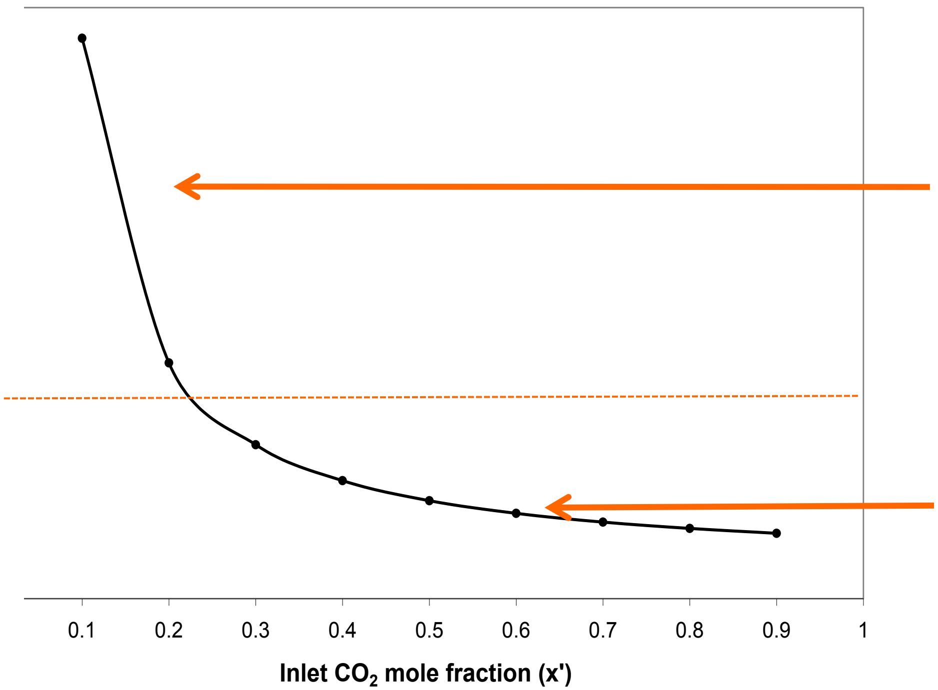




A membrane / absorption hybrid process is (probably) not relevant

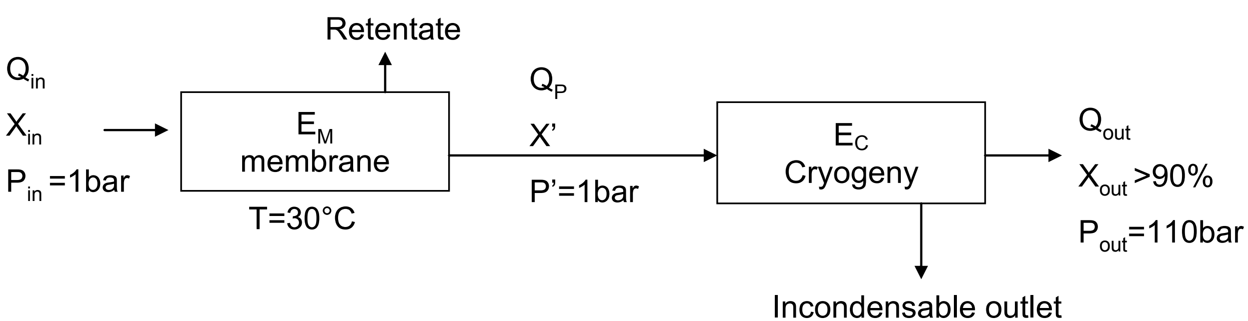


Hybrid process: Membrane preconcentration + cryogeny



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

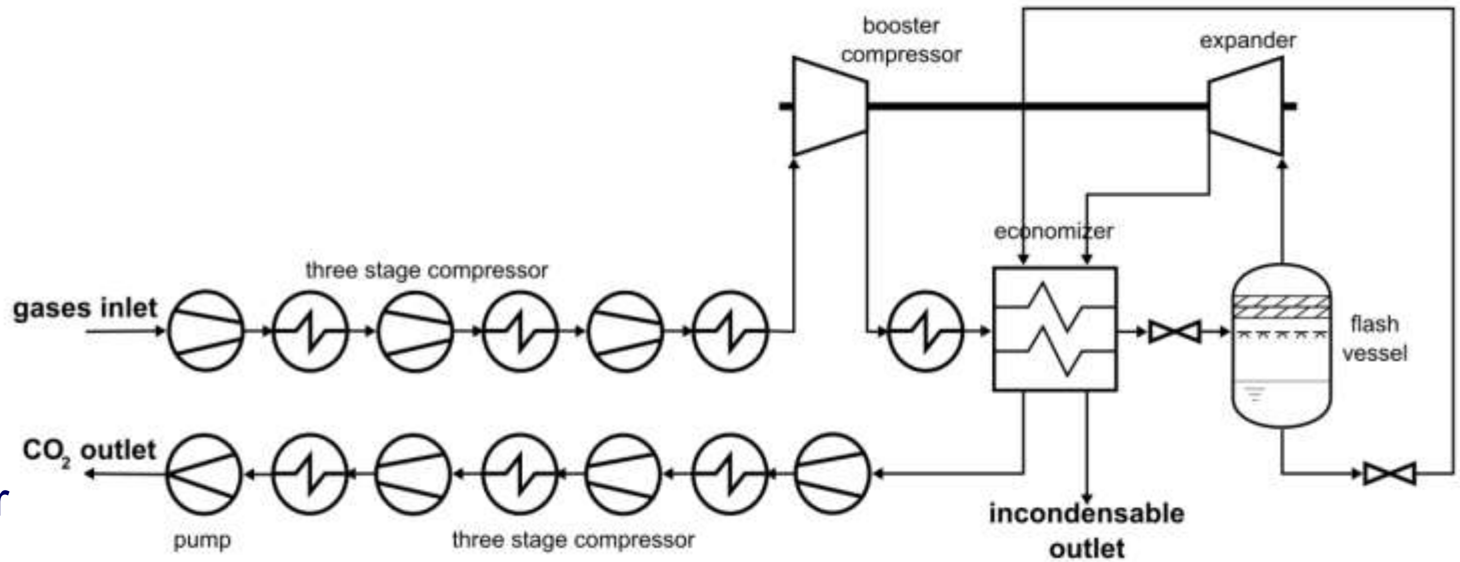


Cryogenic separation: simulation

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

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

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

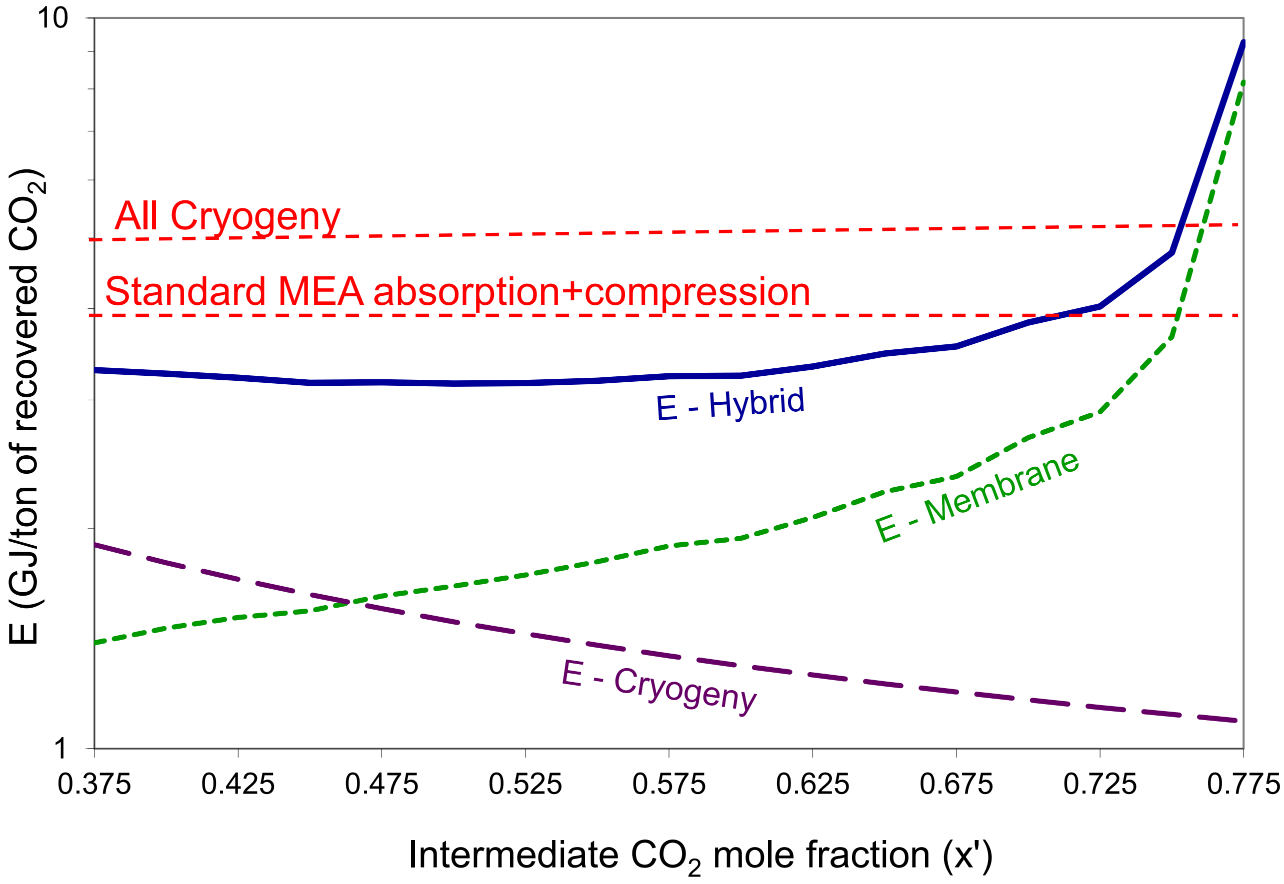


CO_2 capture ratio	>0.95
CO_2 purity (x_{out})	>0.98

Pump Isentropic efficiency :	0.8

Compressor isentropic efficiency :	0.85

Hybrid process: performances



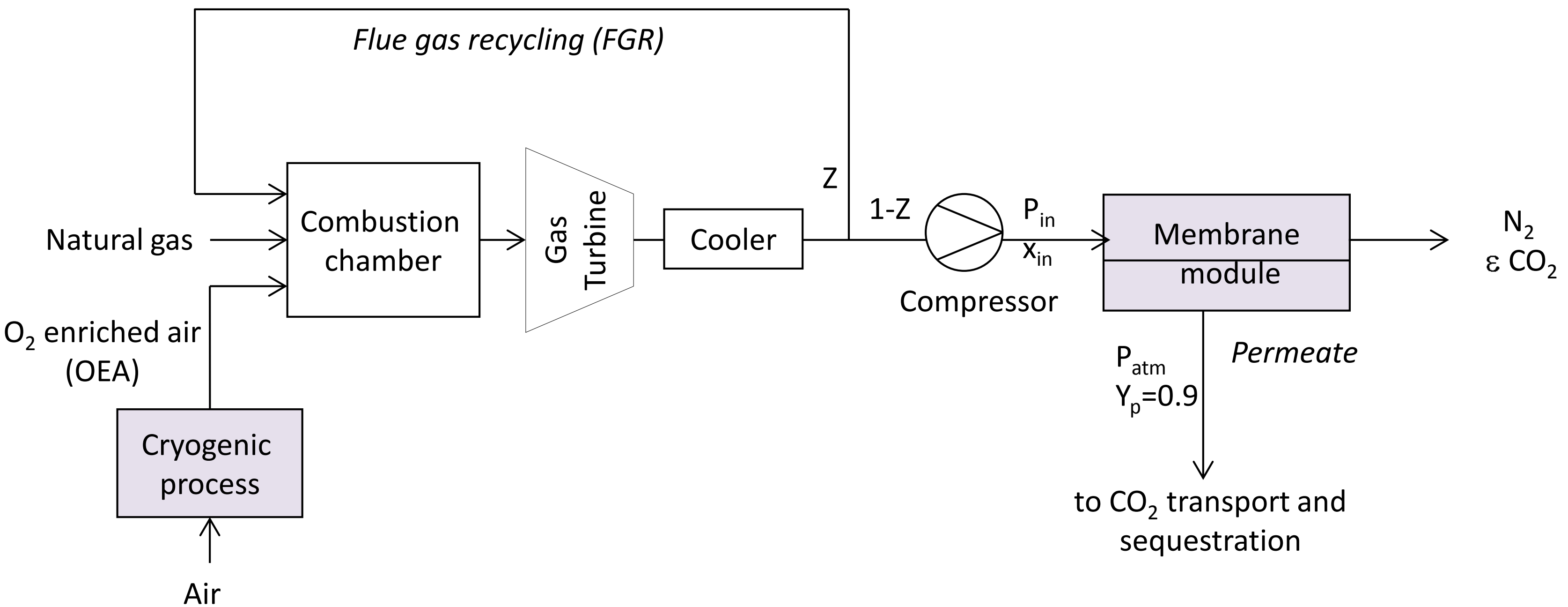
20% energy decrease

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

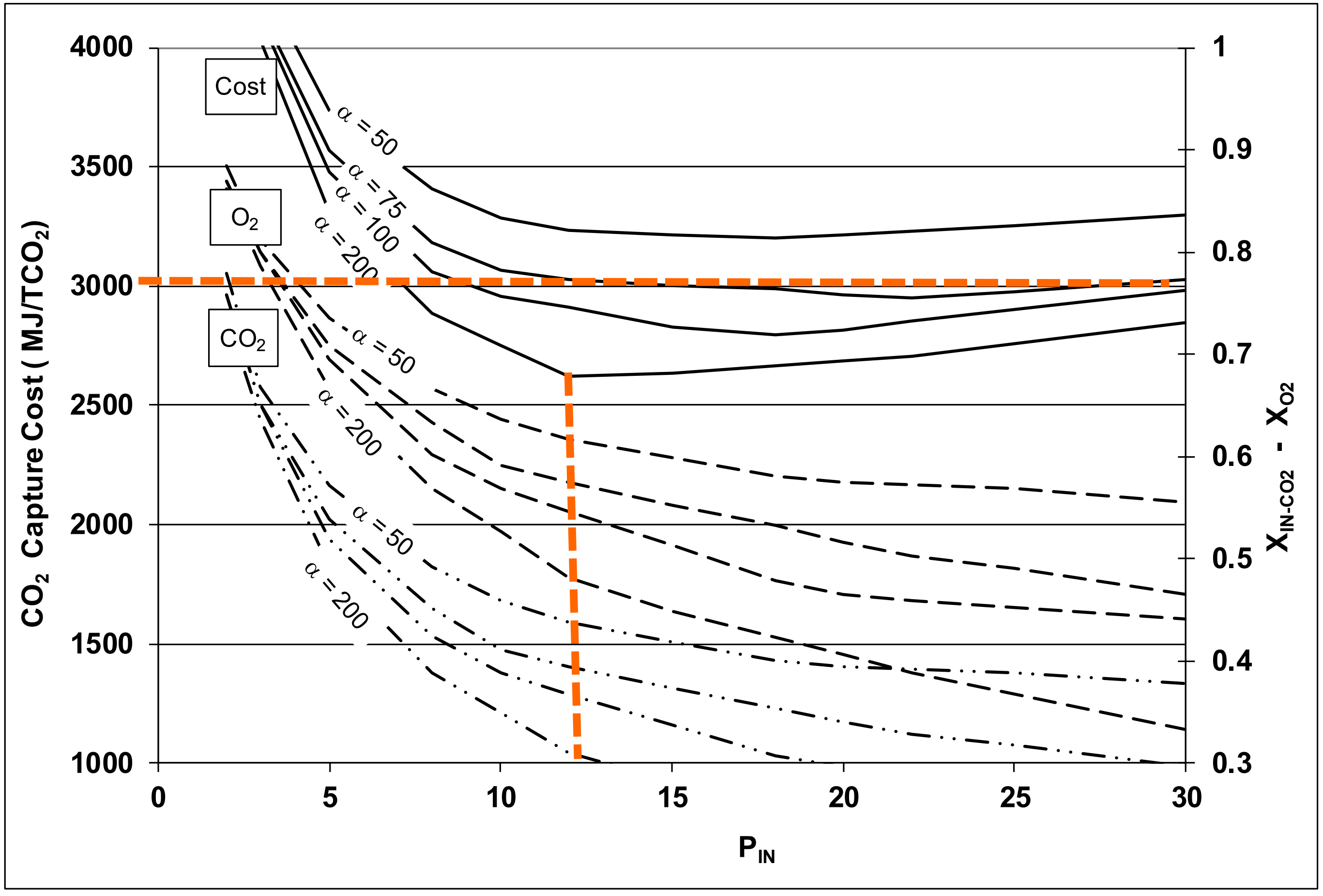
B. Belaissaoui , Y. Le Moullec, D. Willson , E. Favre, Journal of Membrane Science, 415-416 (2012) 424-434

Hybrid process: Membrane / OEA / FGR on Gas turbine

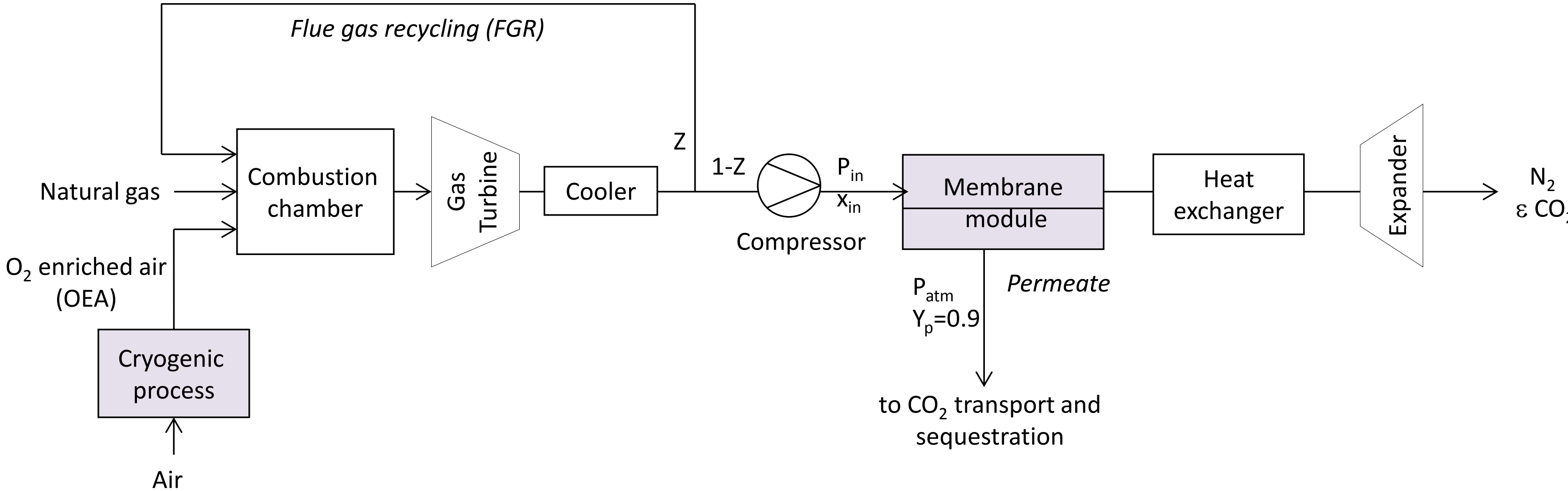
There is a substantial benefit from increasing the inlet CO_2 content: flue gas recirculation and/or combustion in oxygen enhanced air (OEA)



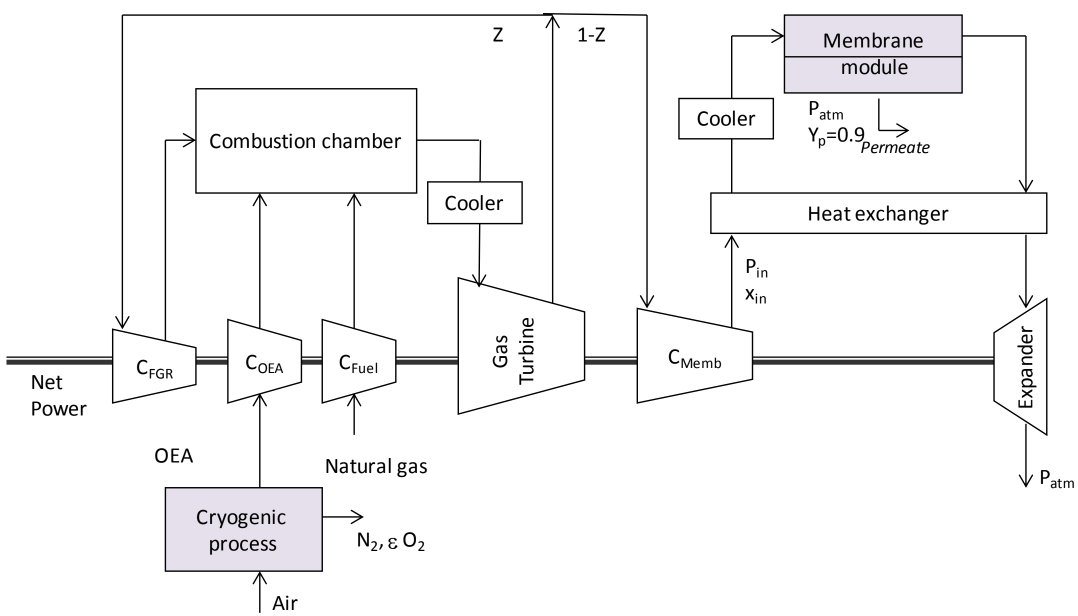
Improved energy efficiency Selectivity helps



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

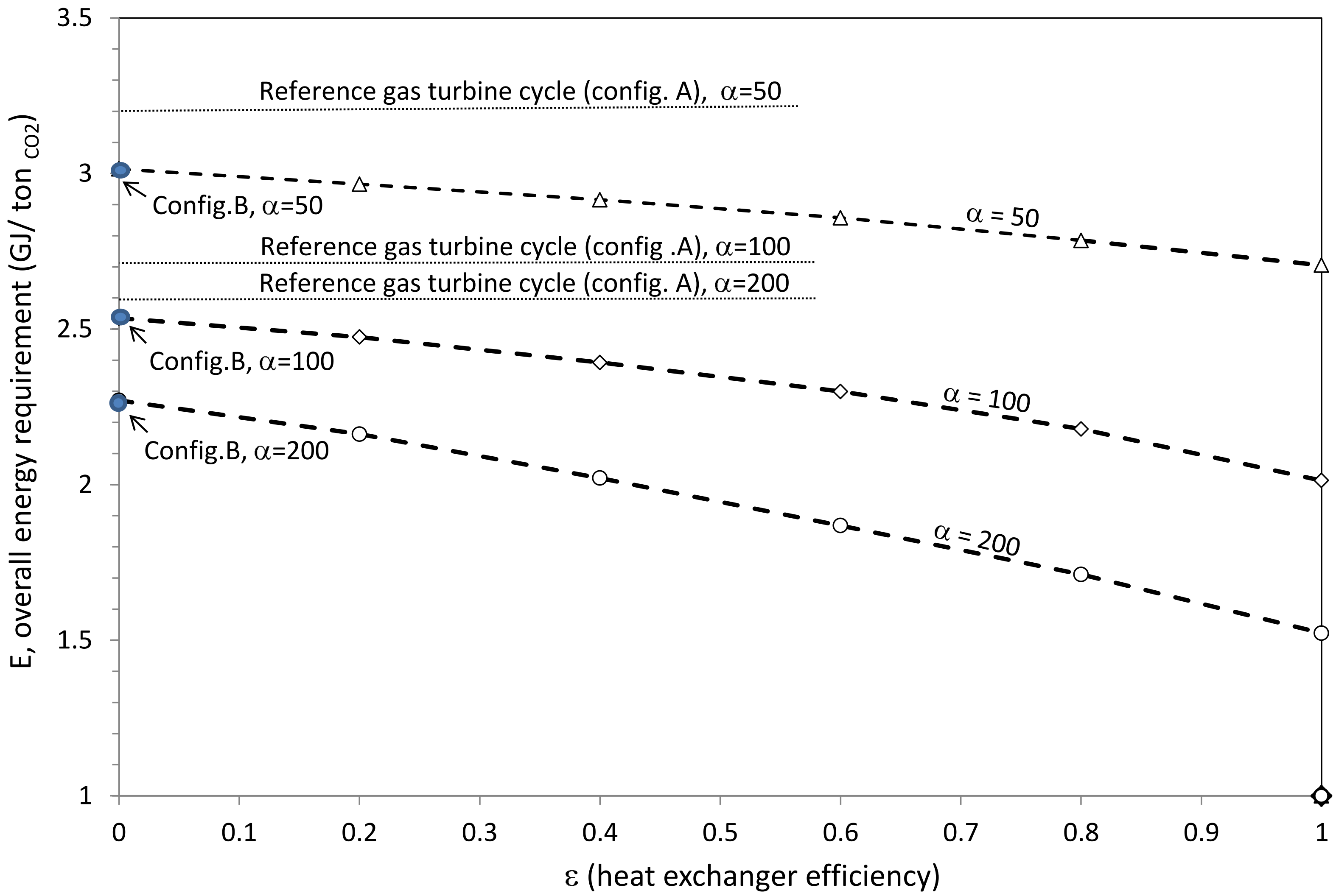


Flue gas recycling (FGR)
Natural gas
Combustion chamber
Gas Turbine
Cooler
Z
1-Z
Compressor
P_{in}
x_{in}
Membrane module
Heat exchanger
Expander
N_2
ε CO_2
O_2 enriched air (OEA)
Cryogenic process
Air
P_{atm}
Y_p=0.9
Permeate
to CO_2 transport and sequestration



Z
1-Z
Membrane module
Combustion chamber
Cooler
Cooler
P_{atm}
Y_p=0.9
Permeate
Heat exchanger
P_{in}
x_{in}
C_{FGR}
C_{OEA}
C_{Fuel}
Gas Turbine
C_{Memb}
Expander
Net Power
OEA
Natural gas
Cryogenic process
N_2, ε O_2
Air
P_{atm}

Integrated approach: Performances



Conclusion

Membranes processes and post combustion CCS: utopy or opportunity?

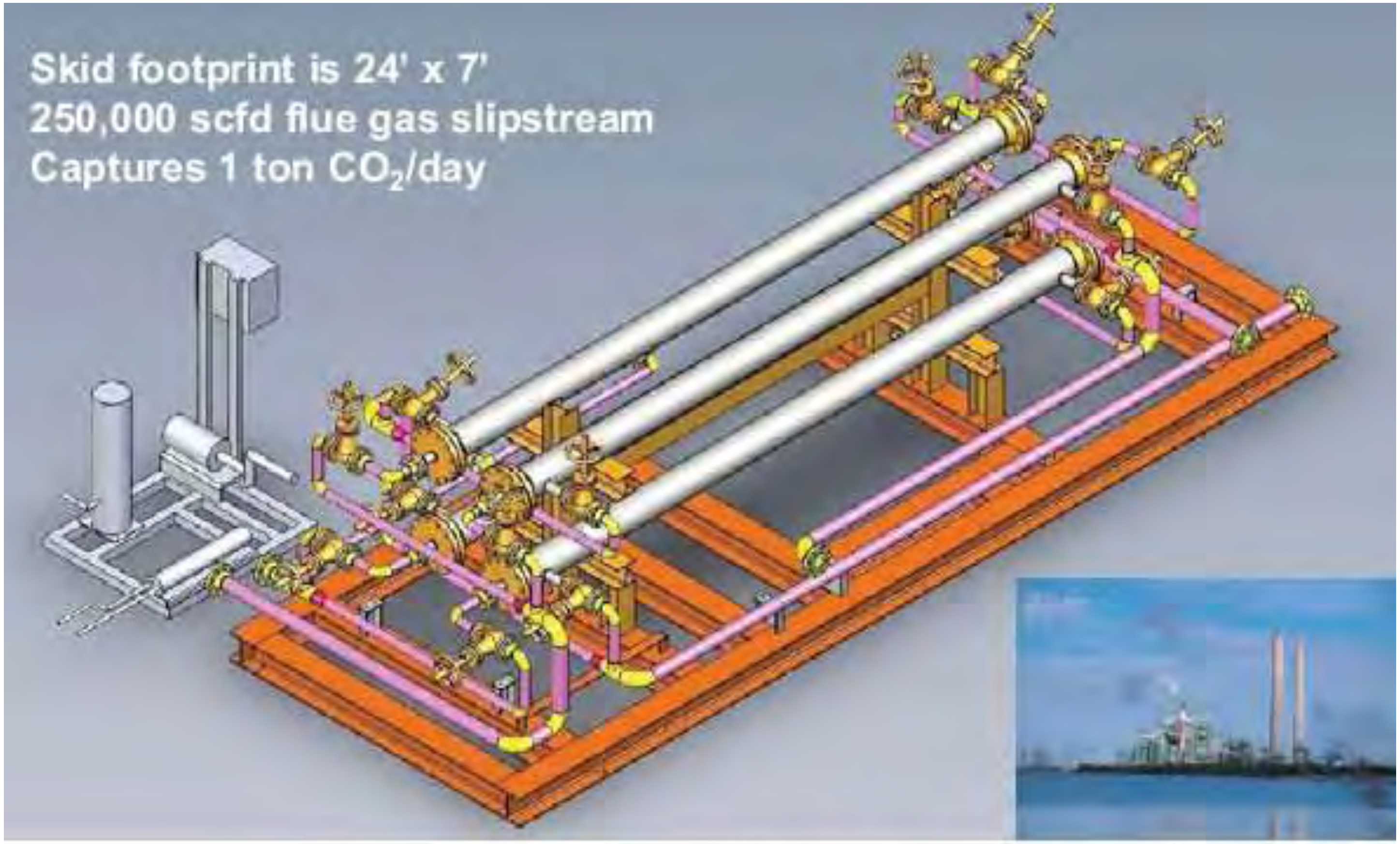
- *Membranes processes offer a large variety of potential applications in a CCS framework (separation, concentration, polishing)*

- *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*

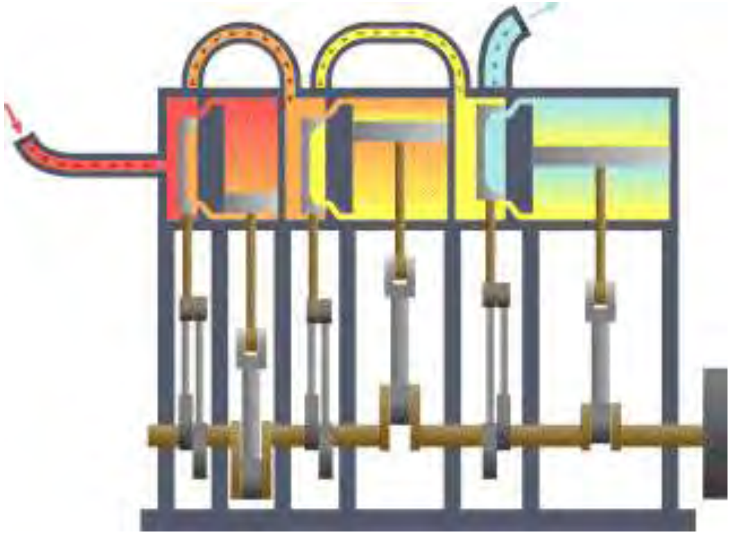


The APS Cholla power plant
1 ton/day field test pilot unit

Fresh module

After 45 days of
operation at Cholla

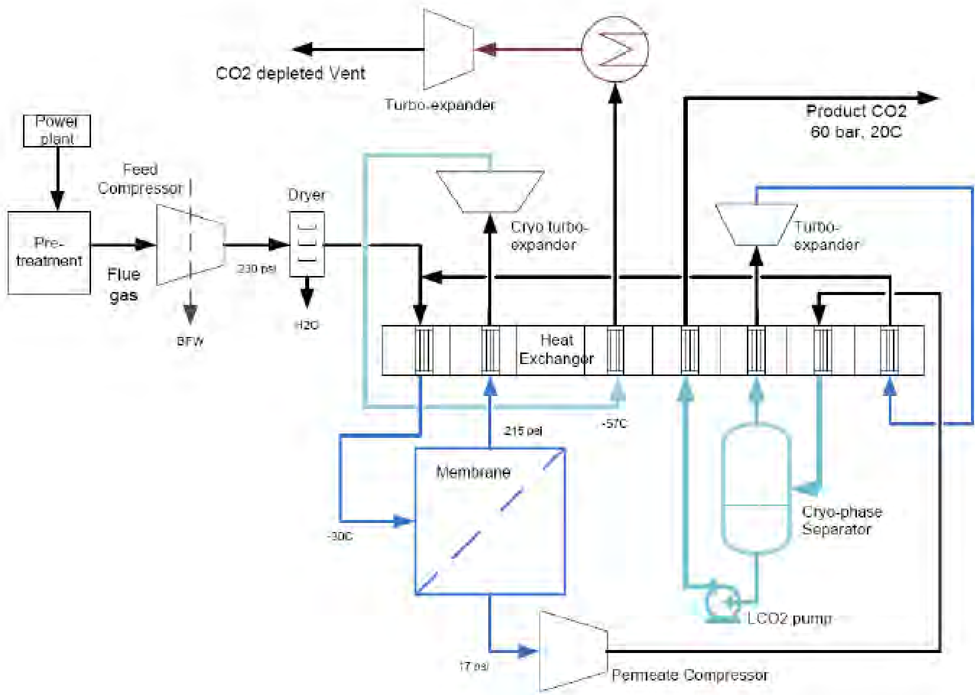
Thank you for your attention!

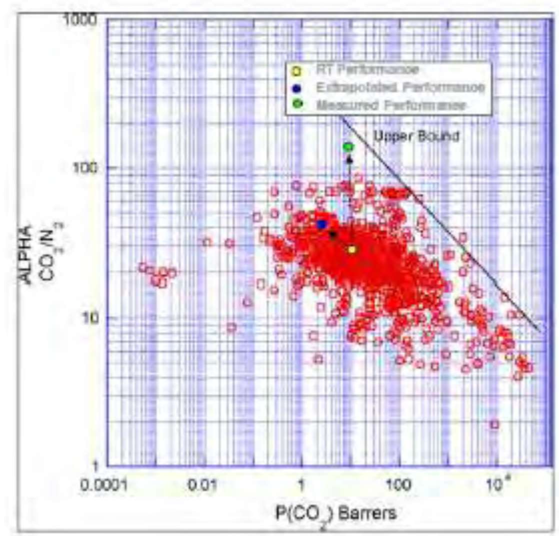


Eric.Favre@univ-lorraine.fr

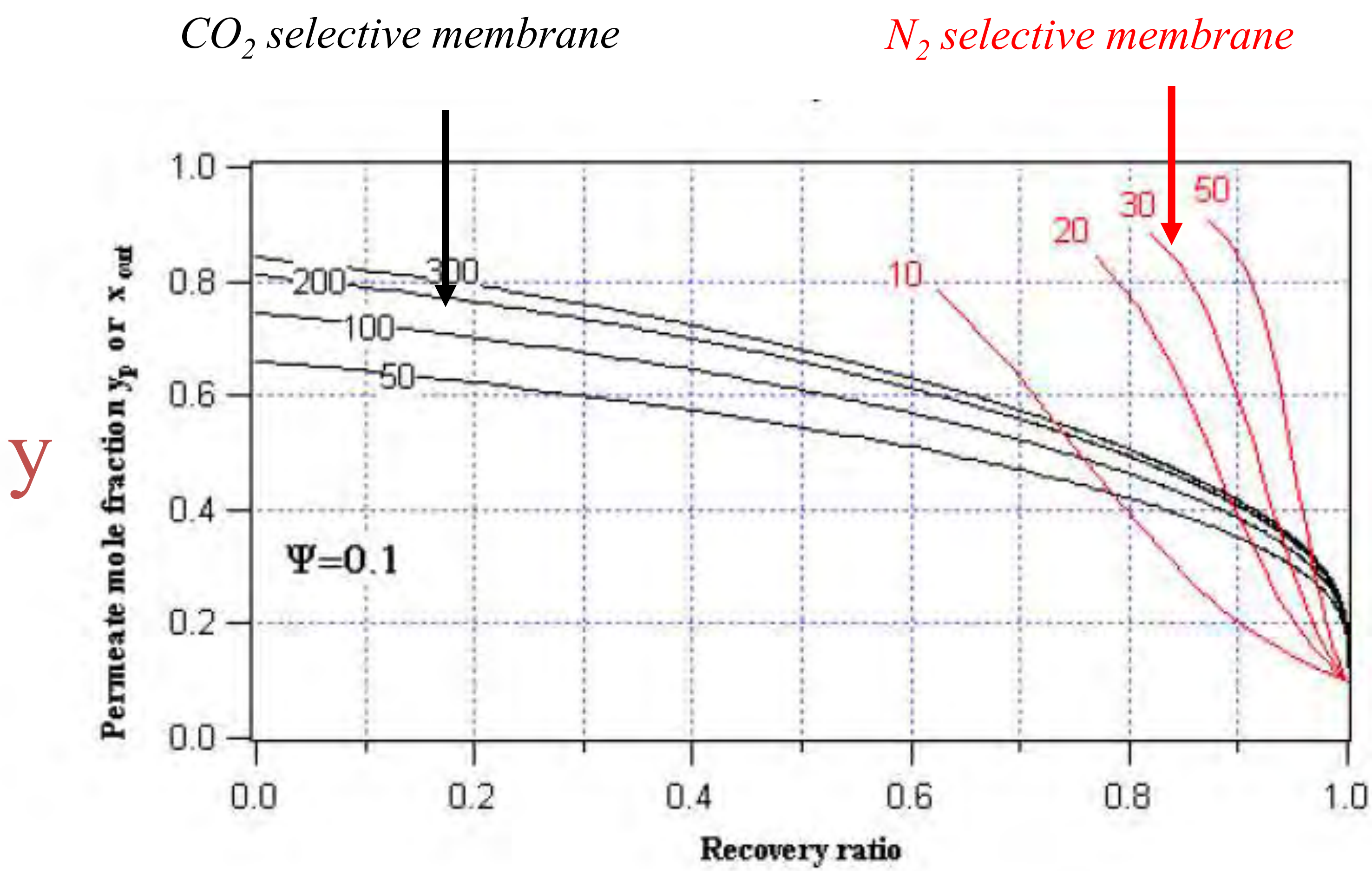
Air Liquide DOE project

Project DE-FE004278



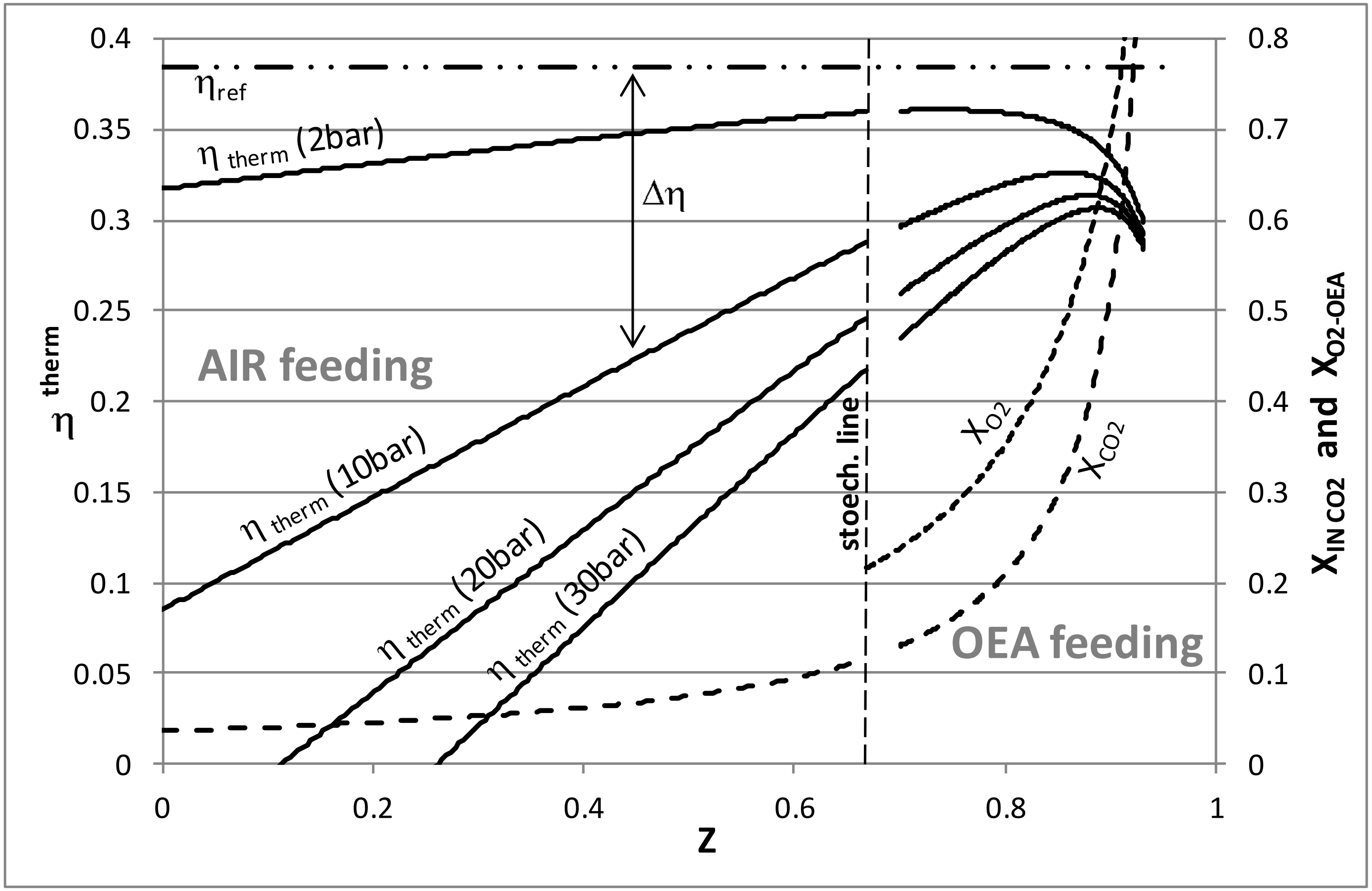


Unconventional approach : Reverse selective membranes



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

Hybrid process: Impact on energy efficiency



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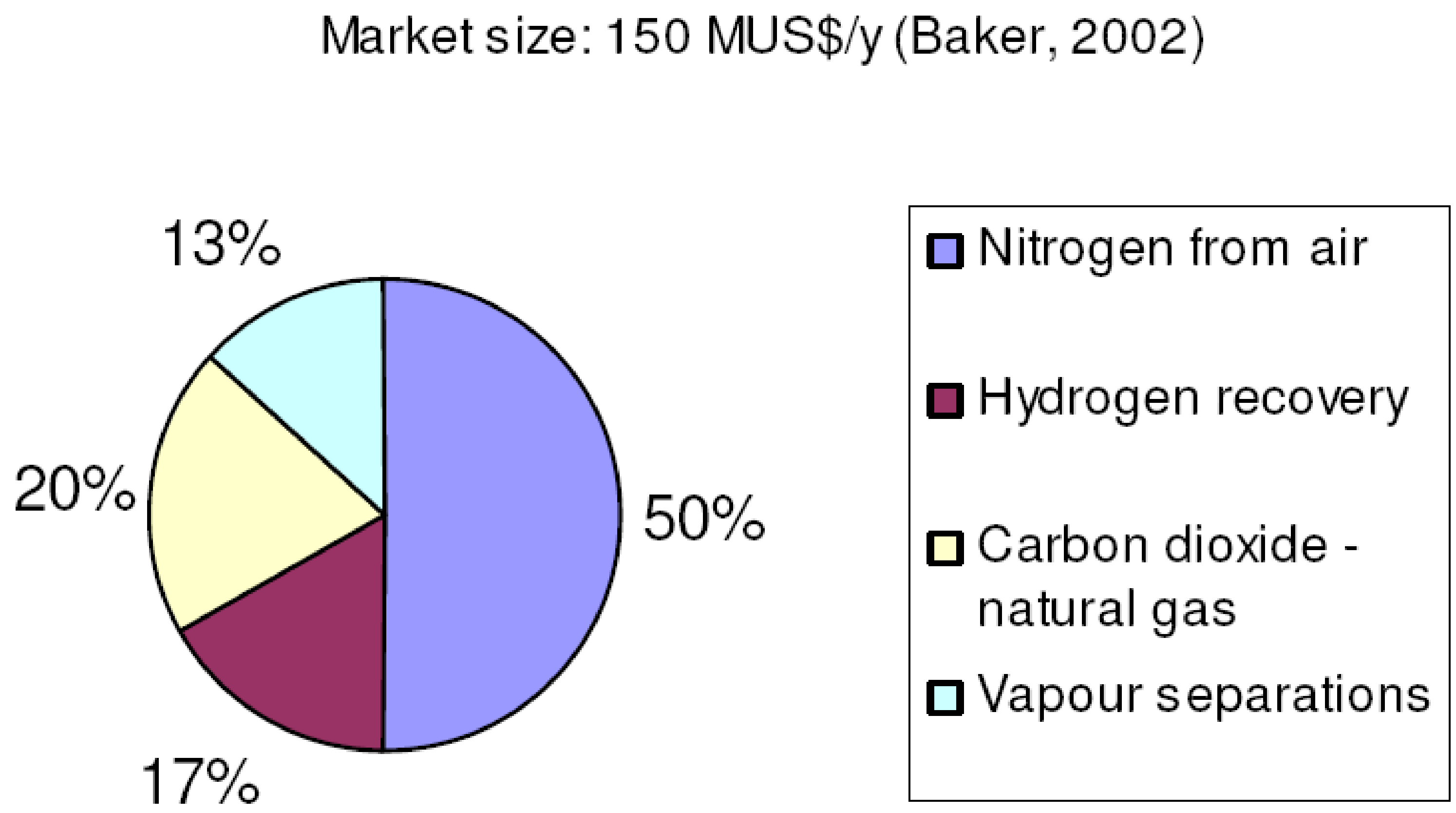
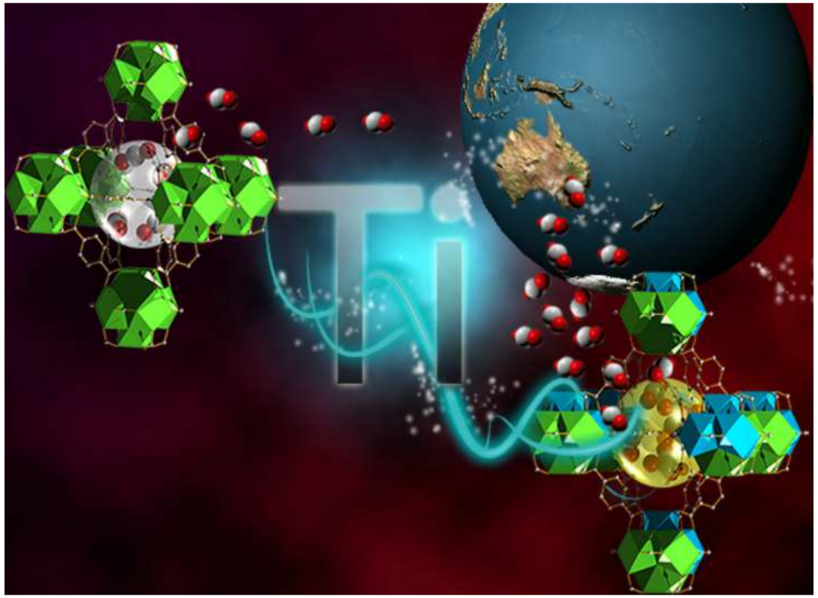
Membrane Gas Separation: Applications & Market

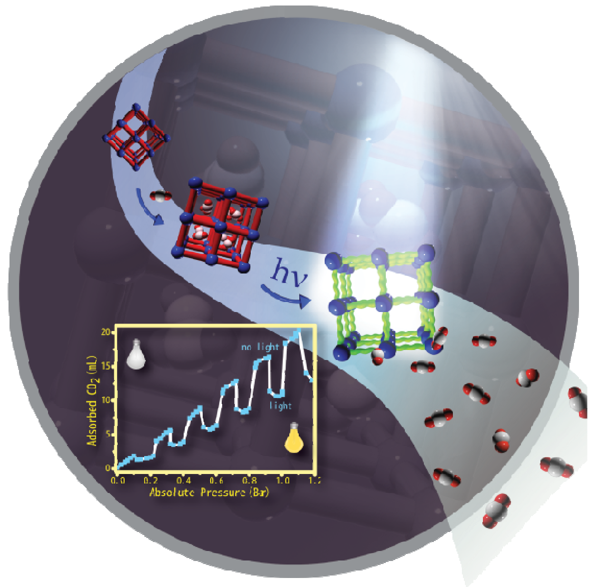


Ashkelon desalination plant

- 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.





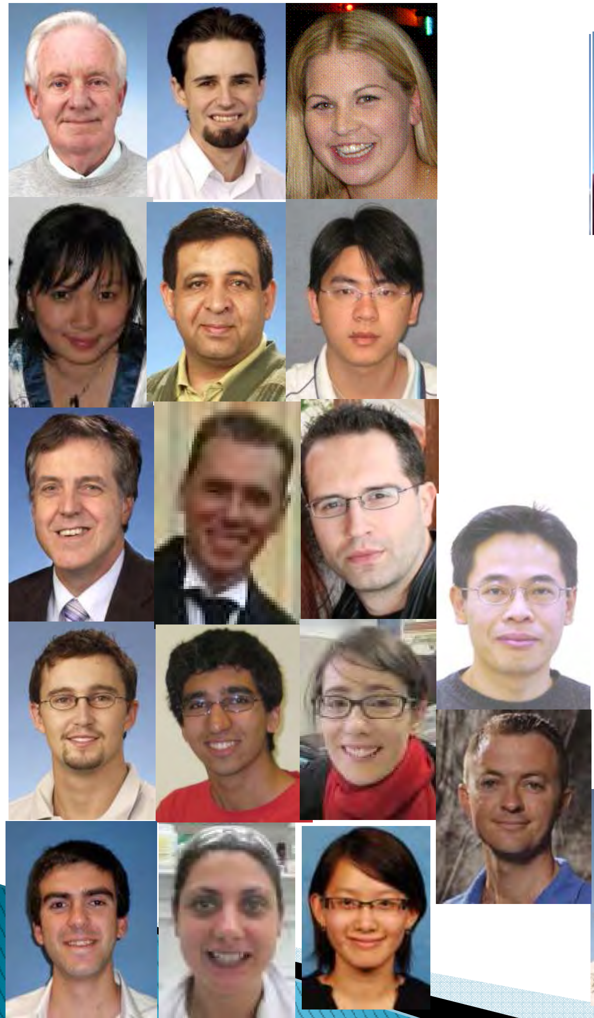
CO_2 Storage and Separation in Metal Organic Frameworks

Matthew Hill

CSIRO /MATERIALS SCIENCE AND ENGINEERING

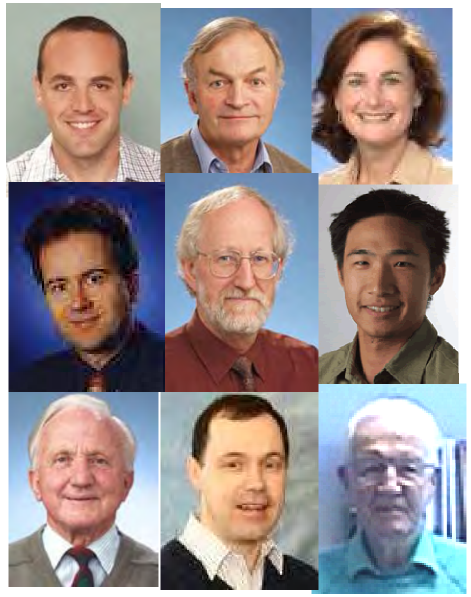
Materials for Energy, Water and Environment group

Nanoporous Materials

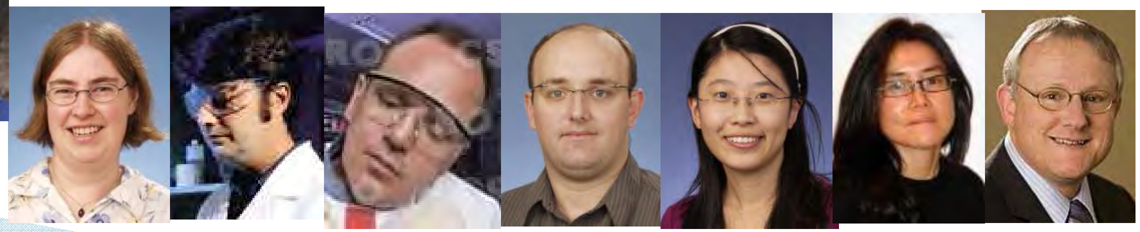


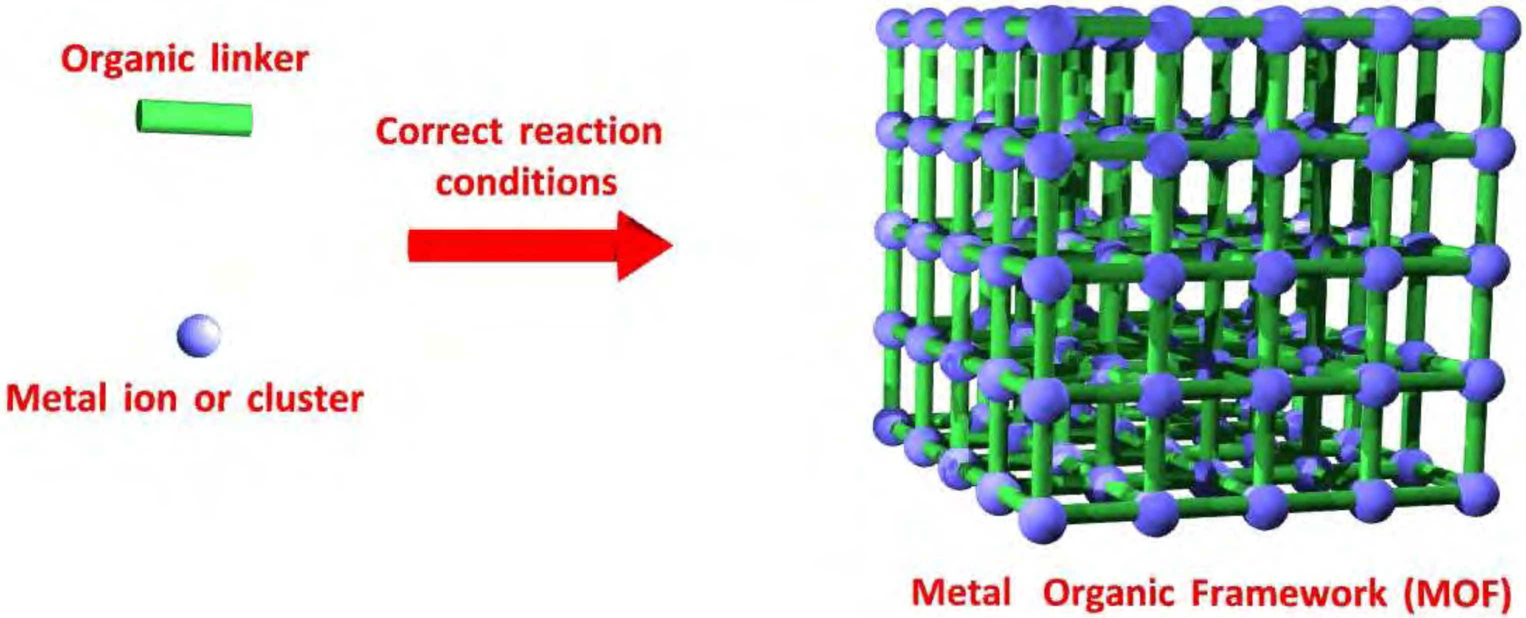
Environmental Catalysis and Membranes

Active Nanostructures



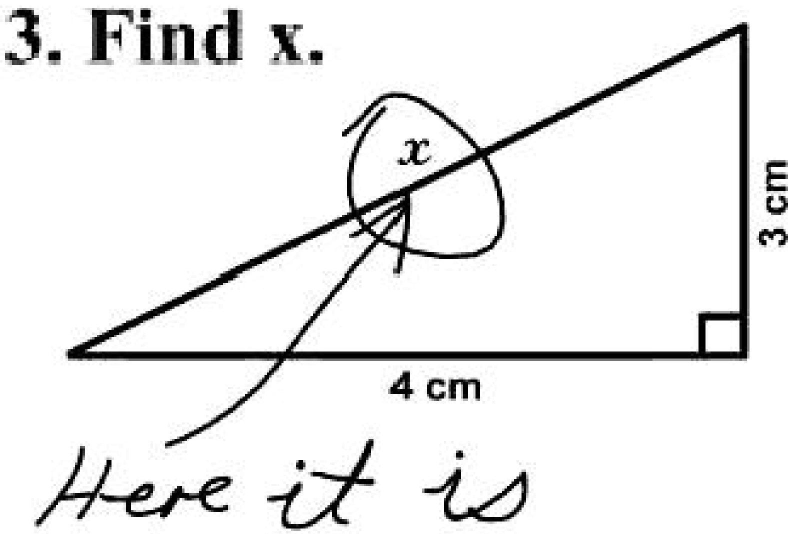
Soft Matter Chemistry and Physics



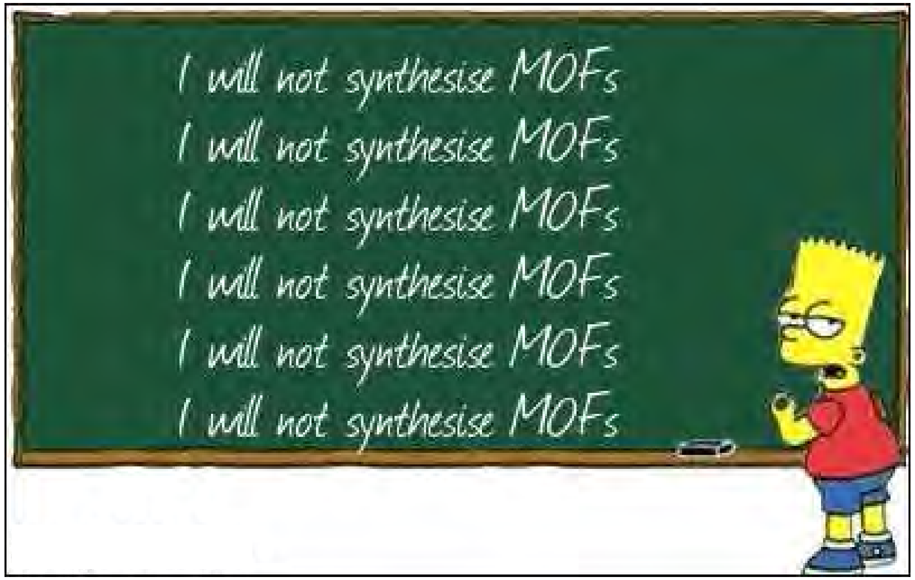

Organic linker
Correct reaction conditions
Metal ion or cluster
Metal Organic Framework (MOF)

MOF synthesis is hard!!!

Geometry
(coordination chemistry)

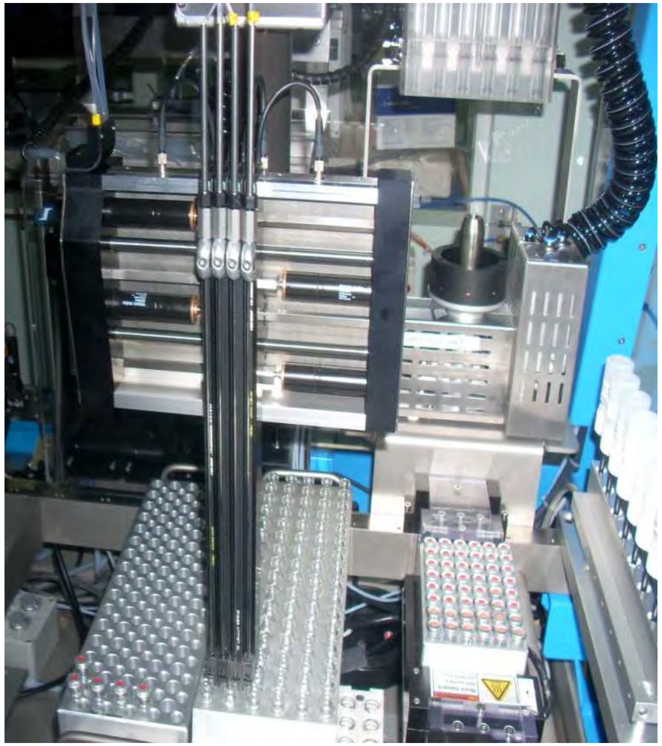


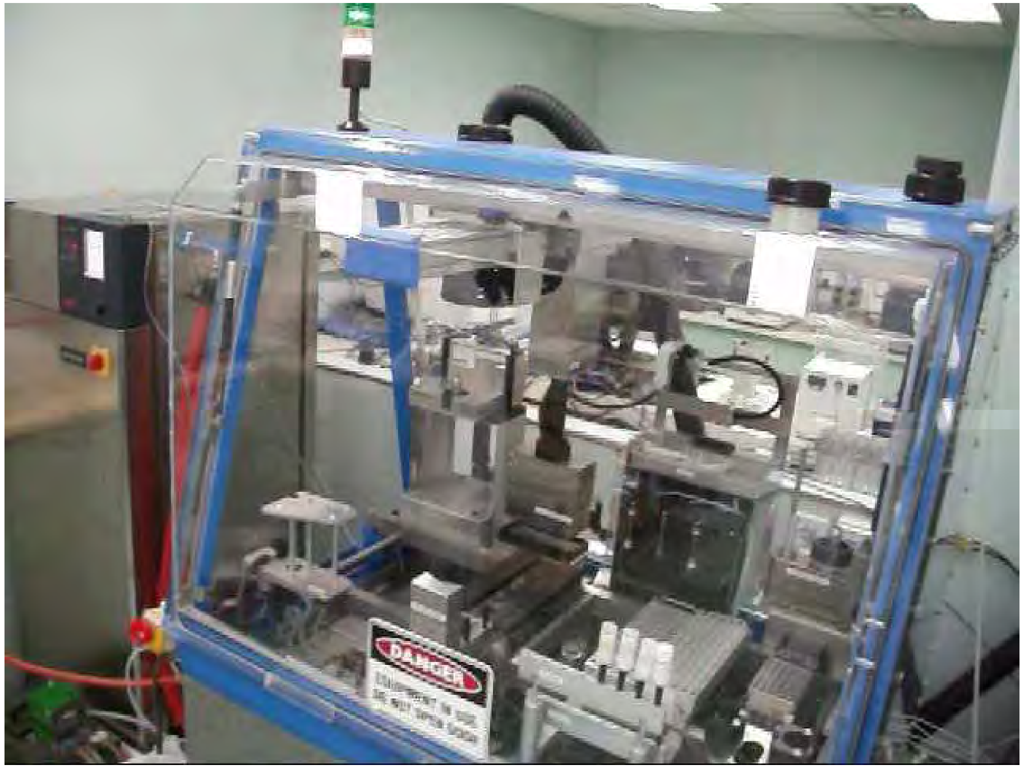
Repetition
(polymer chemistry)



MOFs (aka Coordination polymers) require coordination chemistry + polymer chemistry simultaneously.

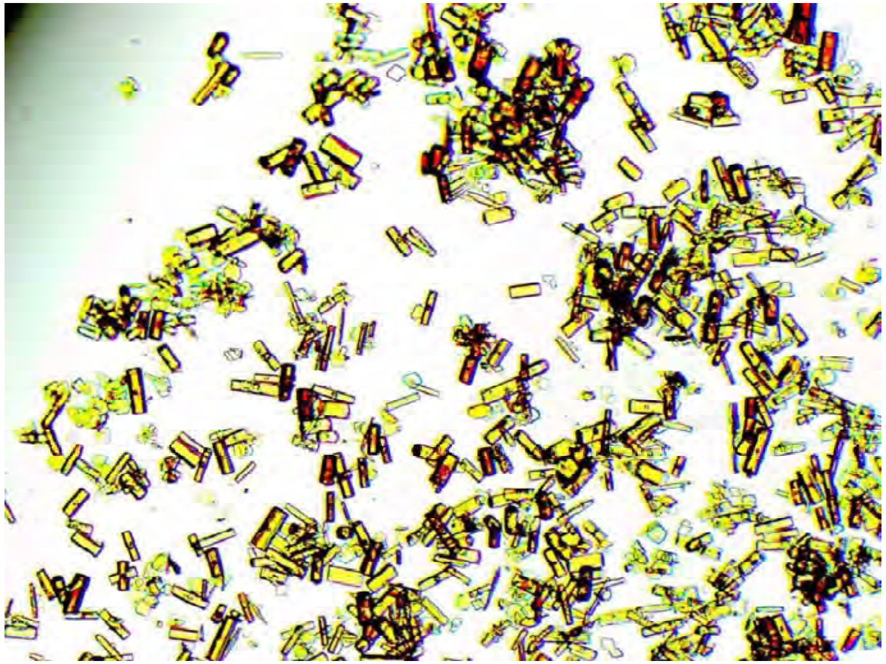
High Throughput Synthesis of MOFs

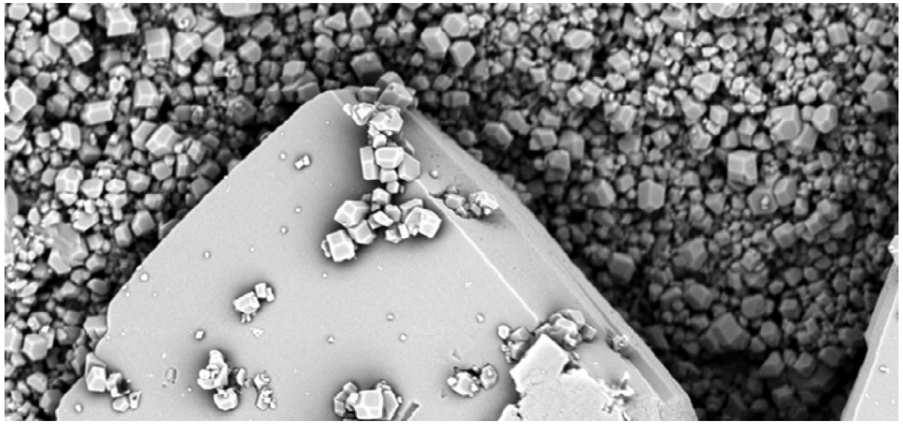




Danielle Kennedy

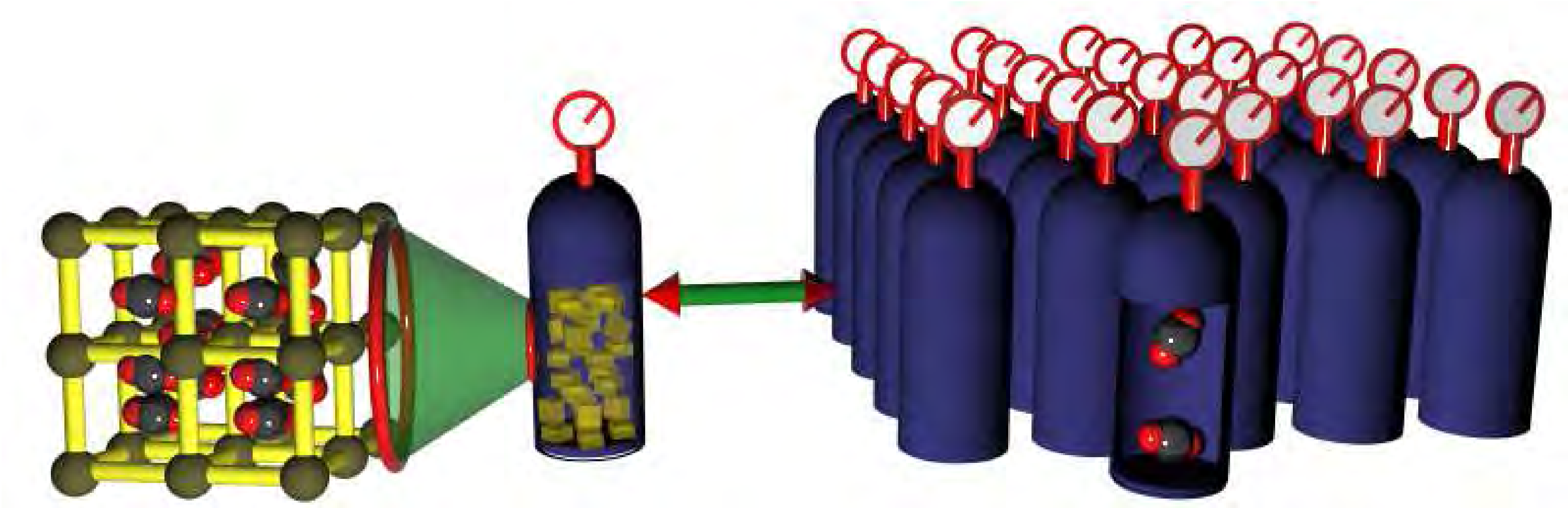
What MOFs look like



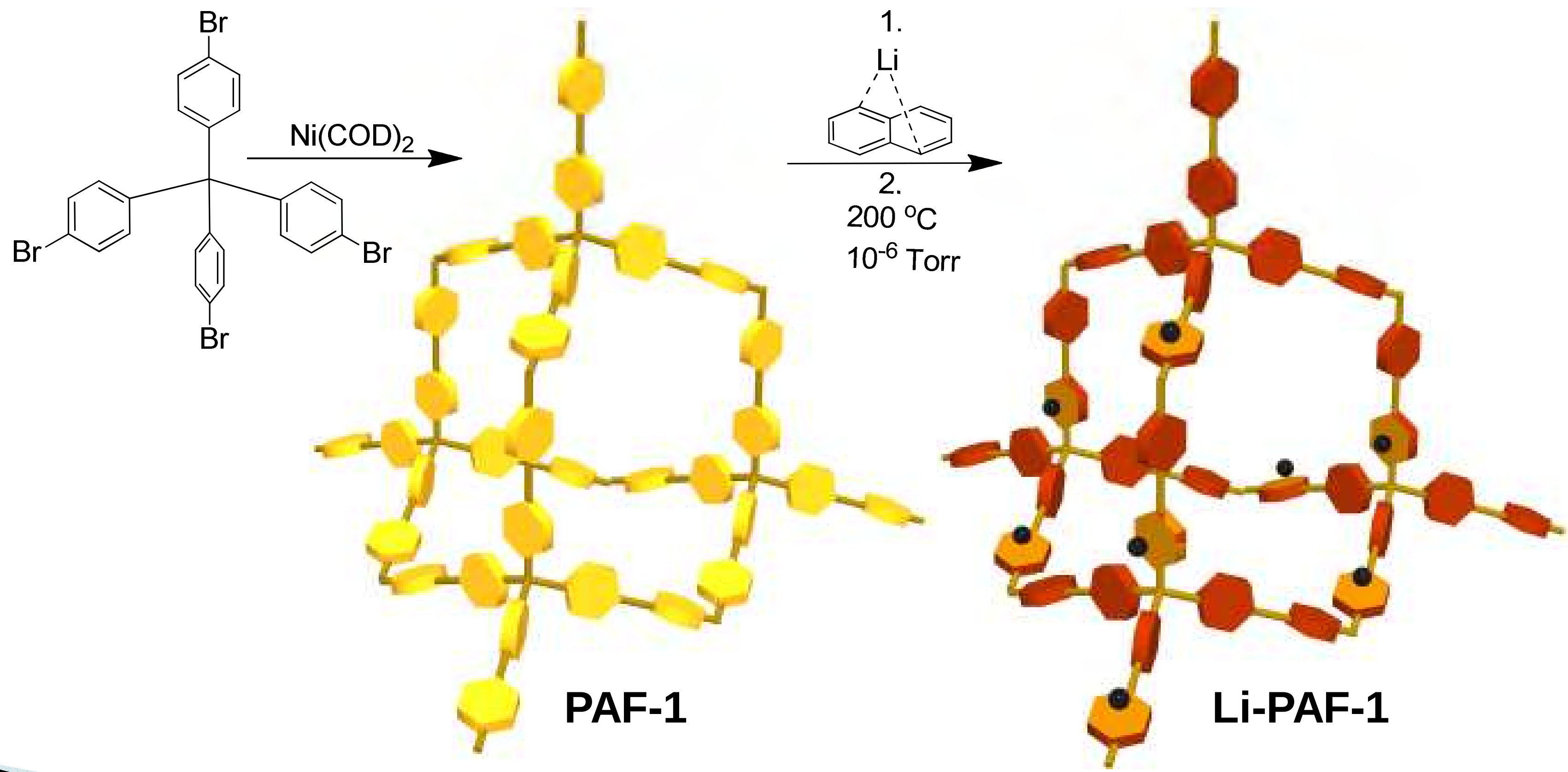


- Similar to salt or sugar crystals.
- Crystalline particles between ~20 nm and 2 mm.

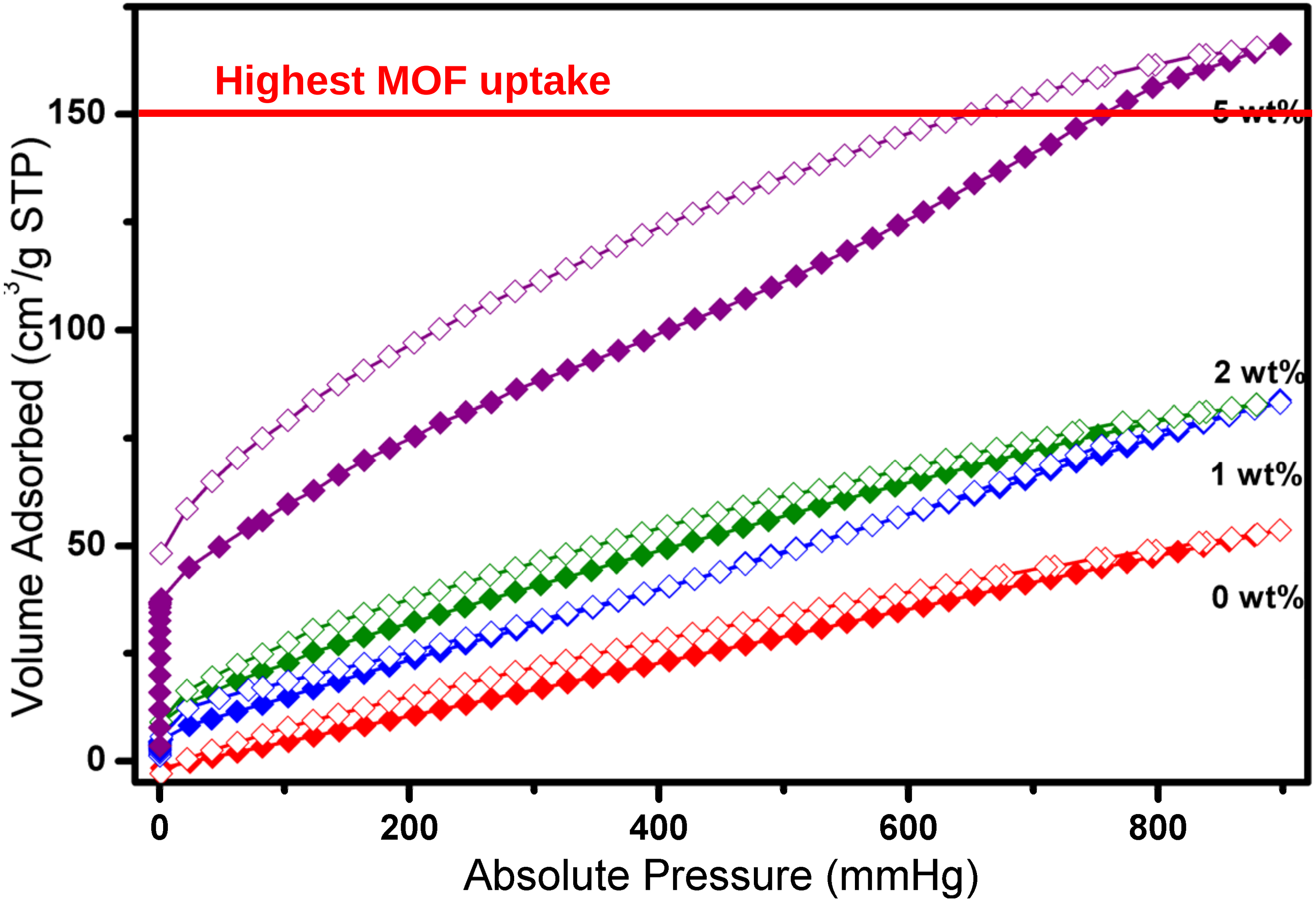
Gas Storage in MOFs



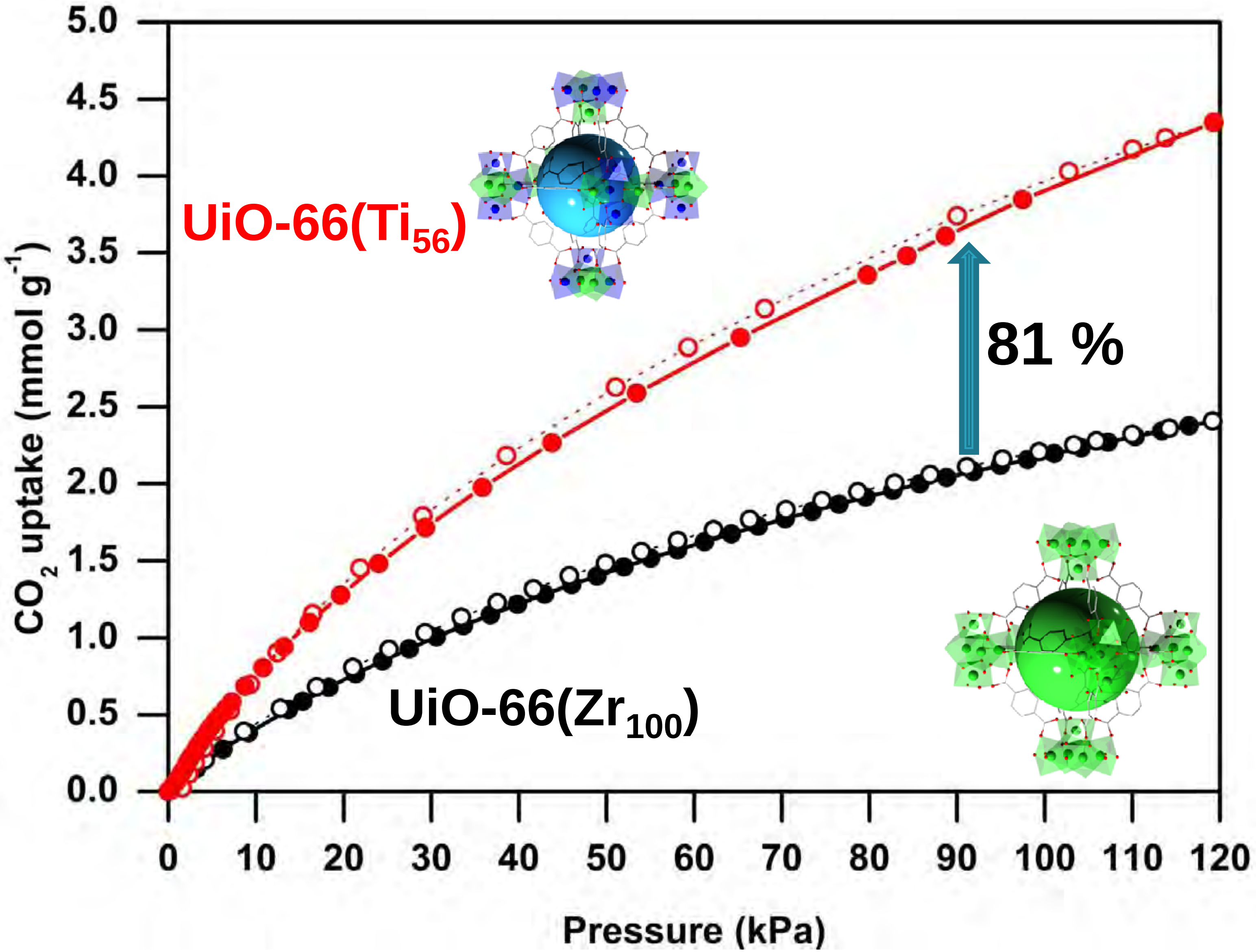
Lithiative reduction of PAFs



CO_2 uptake 273K



K. Konstas, J. W. Taylor, A. W. Thornton, W. X. Lim, B. J. Cox, J. M. Hill, T. J. Bastow, A.J. Hill, D. F. Kennedy, C. M. Doherty, C. D. Wood, M.R. Hill, *Angew. Chem. Int. Ed.*, **2012**, 51(27), 6639.

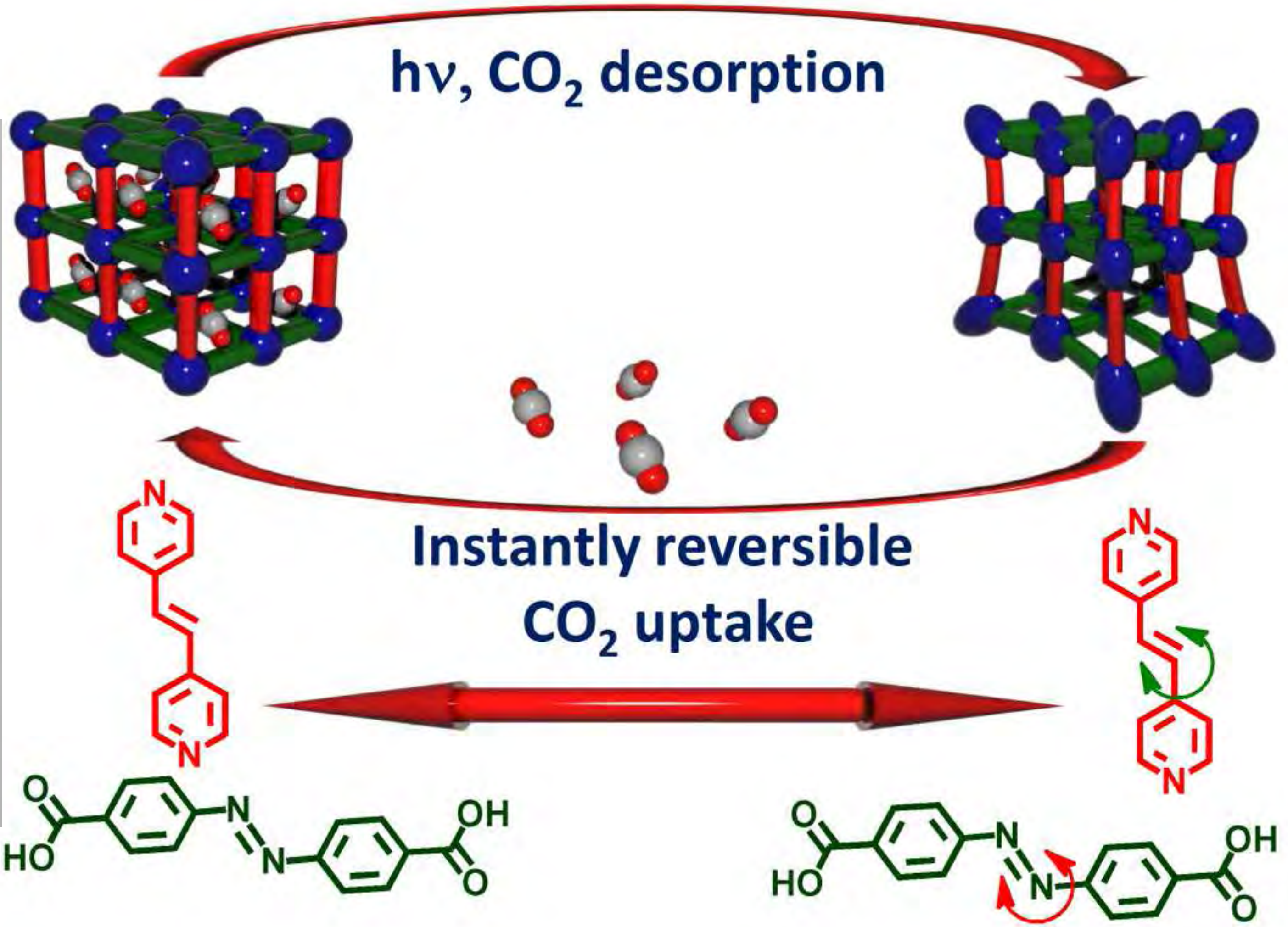


Lau, C. H.; Babarao, R.; Hill, M. R., *Chem. Commun.* **2013**, **DOI:** 10.1039/C3CC40470F, accepted with cover art.

Current CO_2 capture technology

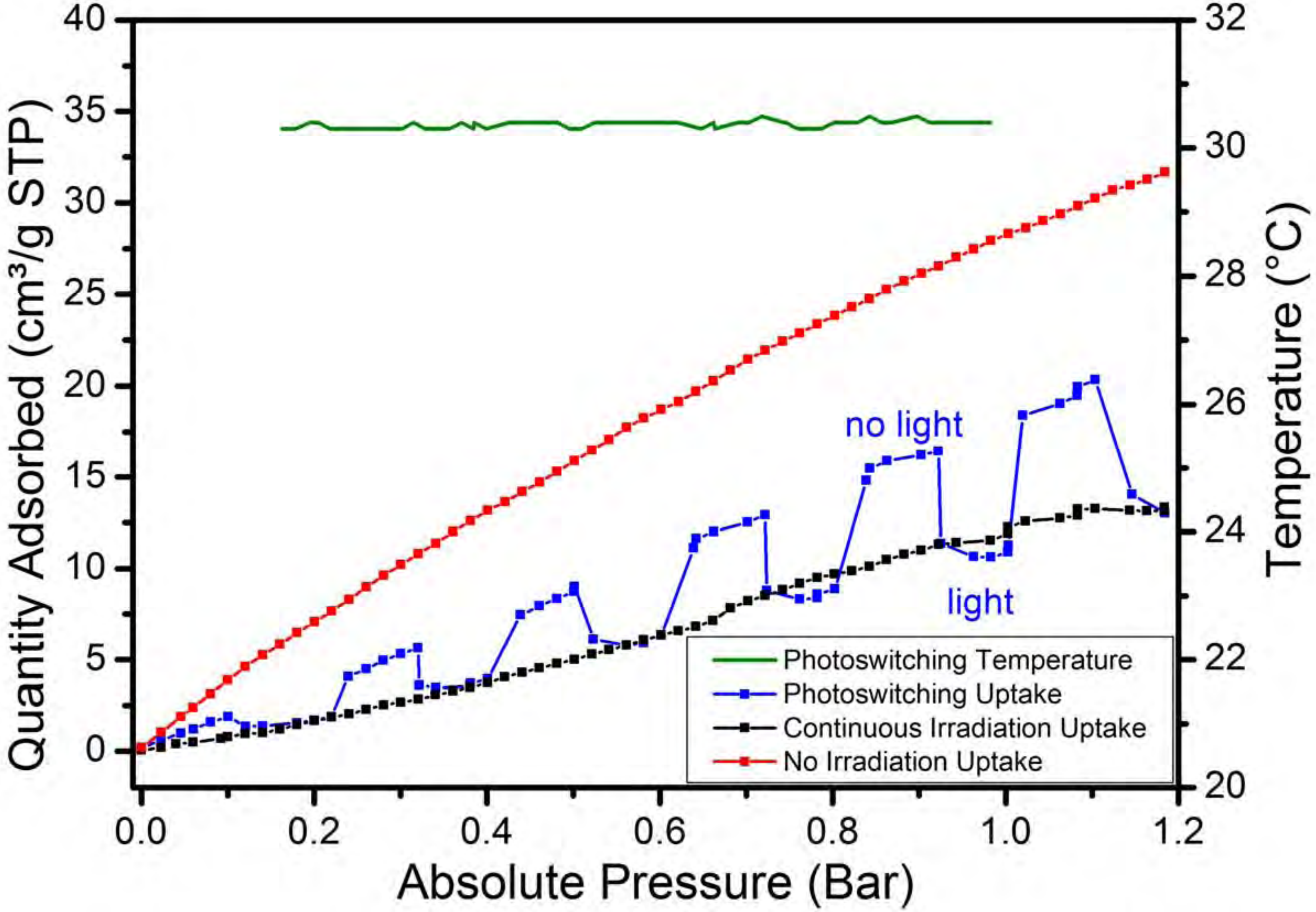
- CO_2 is captured in a 5M solution of monoethanolamine (MEA) or variants.
- This solution is heated to around to remove the CO_2, which is separated, the MEA is then re-used.
- This desorption process can use up significant fraction of the power plant's production capacity.

CO_2 release from dynamic pores

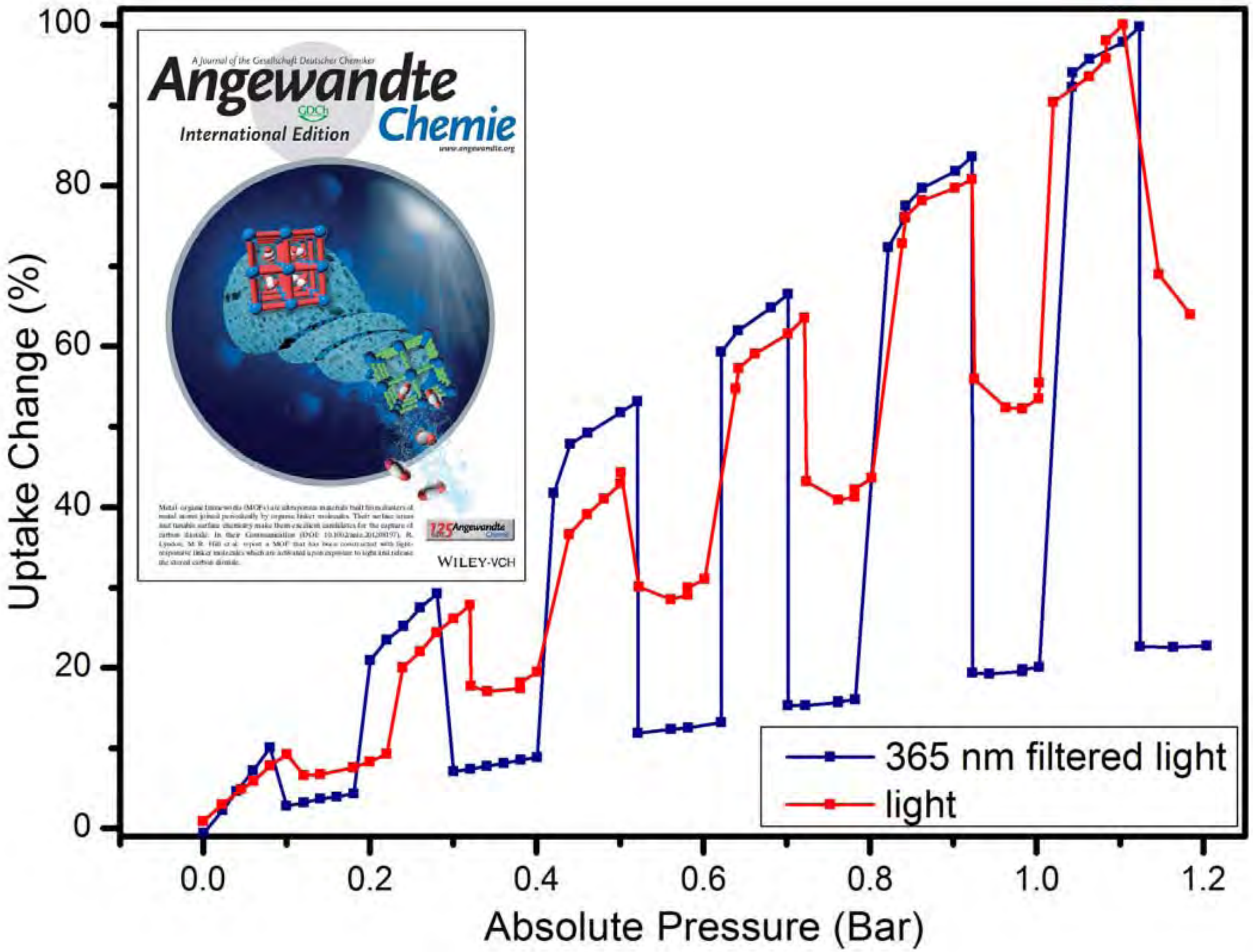


Richelle Lyndon

Light can be used to release CO_2

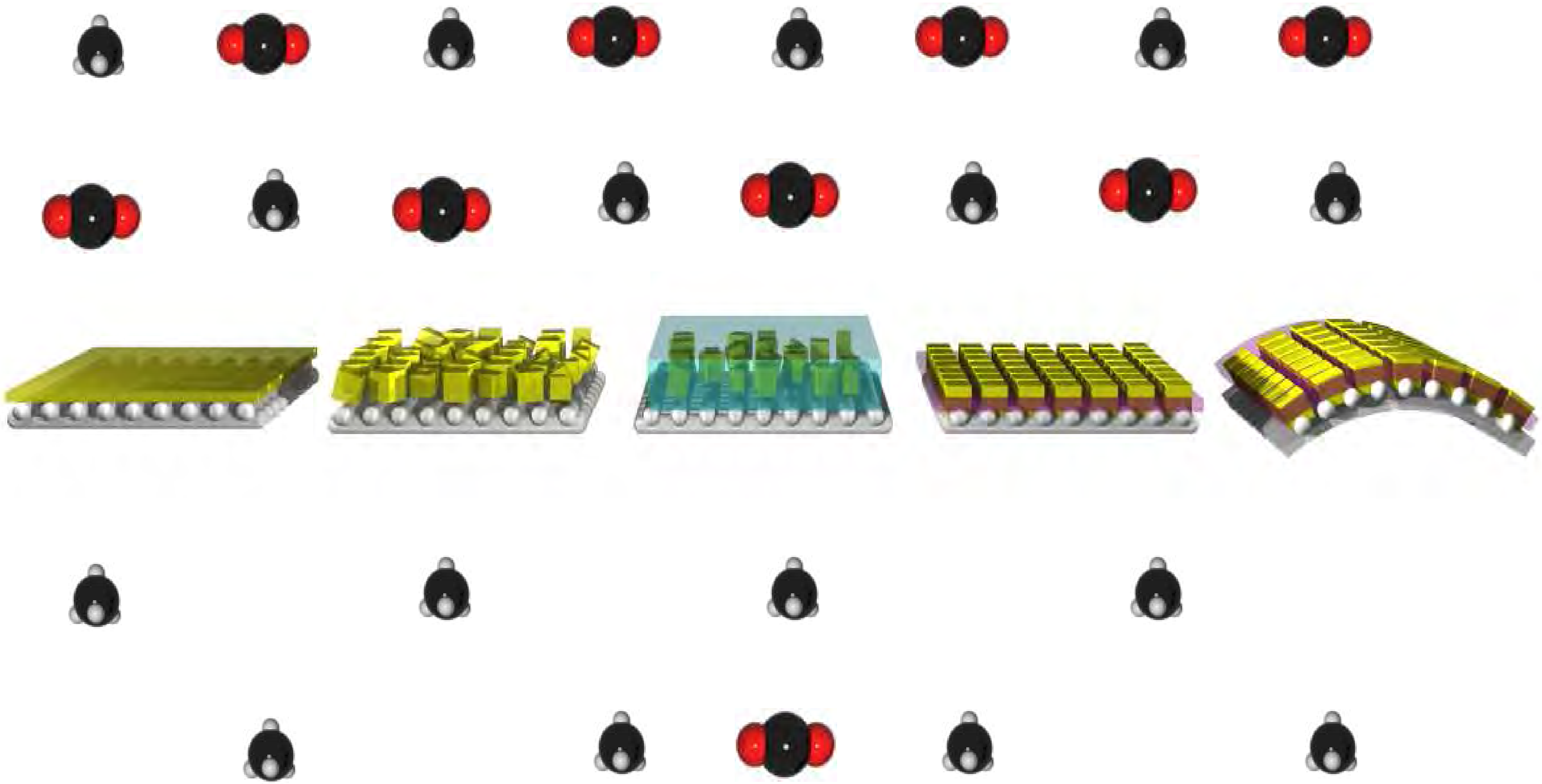


Works at optimal wavelength, or concentrated broadband UV



R. Lyndon, K. Konstas, B. P. Ladewig, P .Southon, C.J. Kepert, M.R. Hill, *Angew. Chem. Int. Ed*., **2013**, *52* (13), 3695-3698, Lyndon, R.; Konstas, K.; Ladewig, B. P.; Hill, M. R. GAS SEPARATION PROCESSES TW8699/AU/PROV, 26-7-2012.

Gas Separations

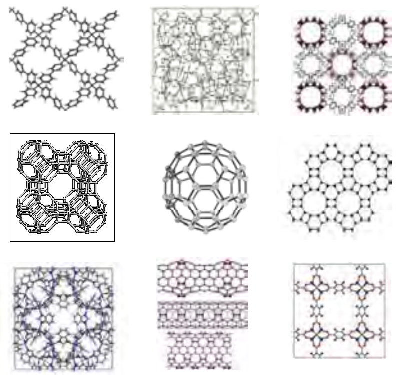


Aaron Thornton, Con Dimitrakakis, Sam Lau, Richard Noble

Virtual Hub for Screening Materials

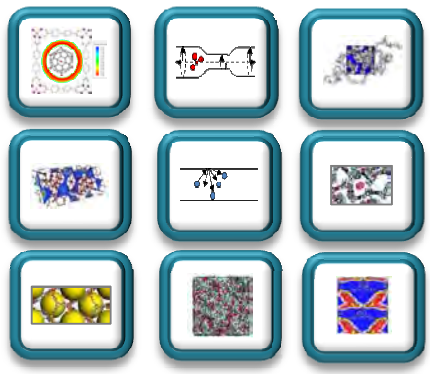
1. Candidate Materials

(> 1 Billion Structures)



2. Screening Tools

(Structure-Property Predictions)



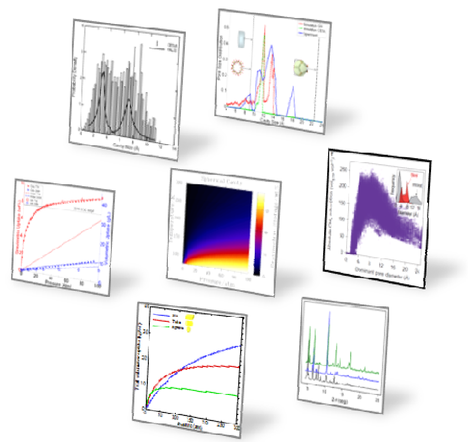
1.Adsorb IT
2.Void IT
3.Surface IT
4.Convert IT

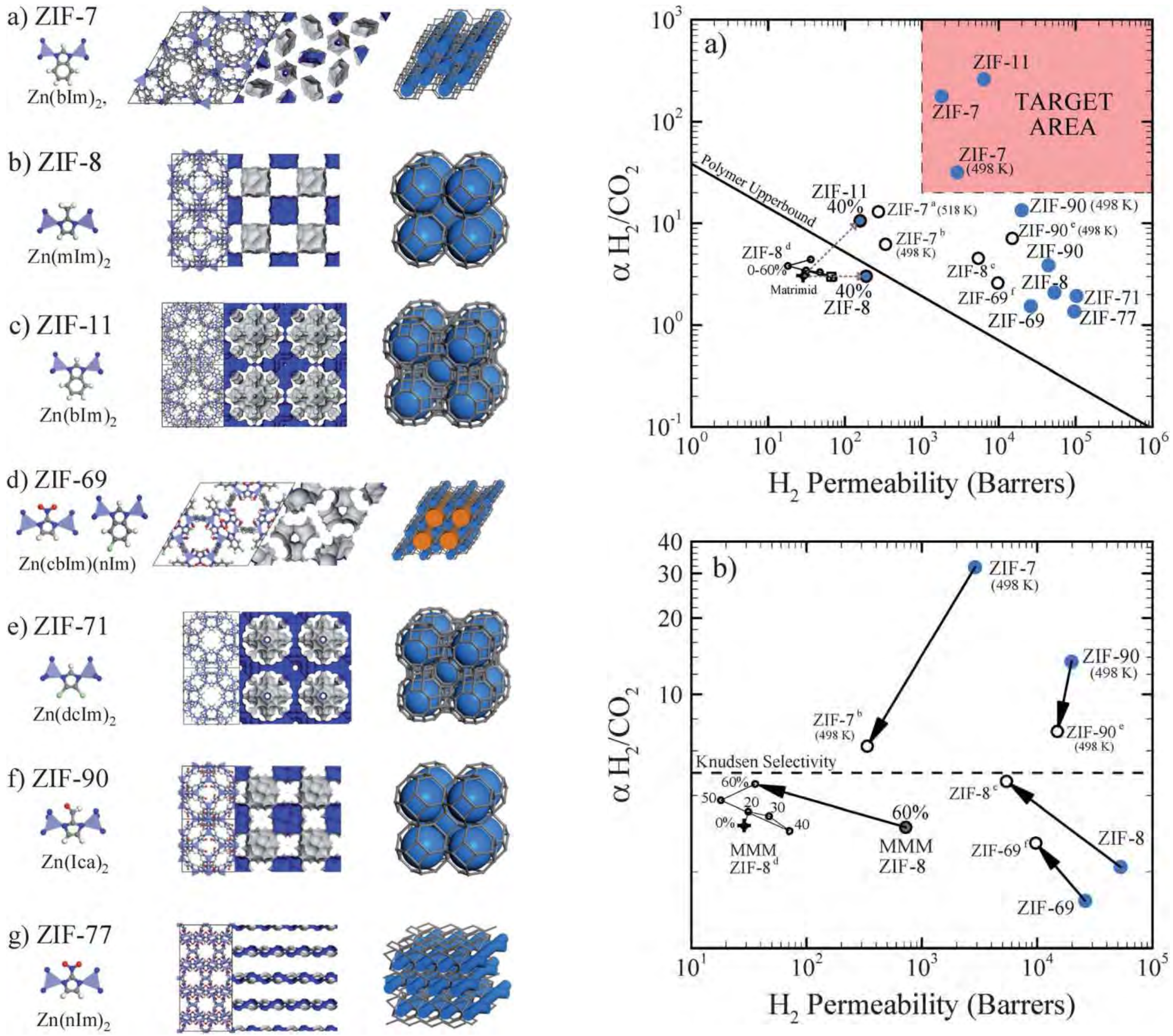
5.Pore Size IT
6.X-ray IT
7.Permeate IT
8.Simulate IT

High Performance Computing

3. Promising Materials

(Meeting Industrial Feasibility Criteria)



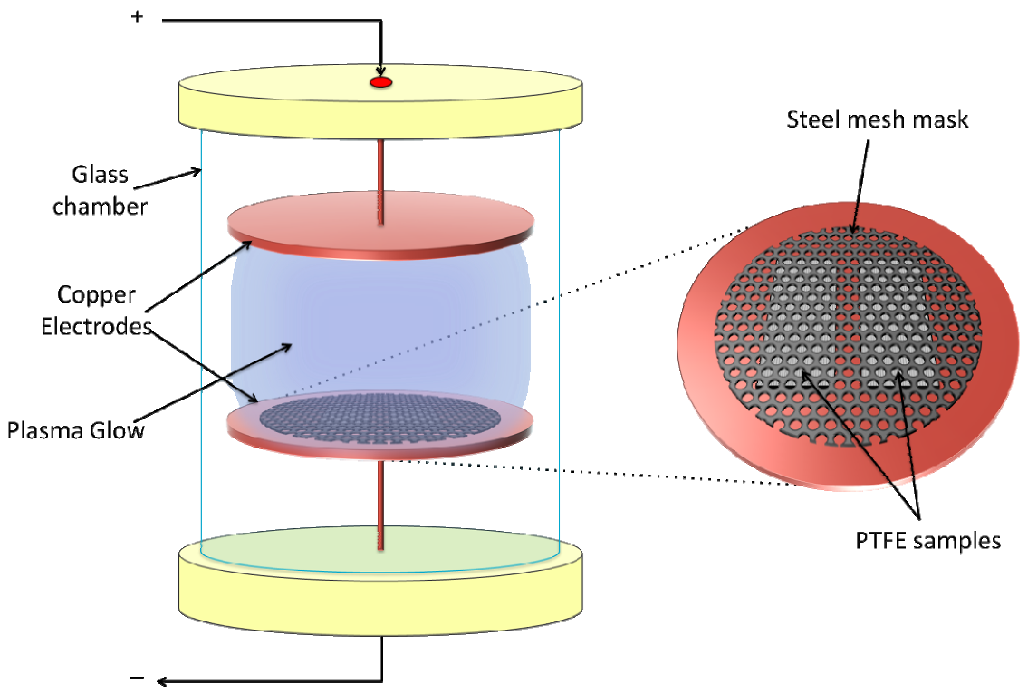


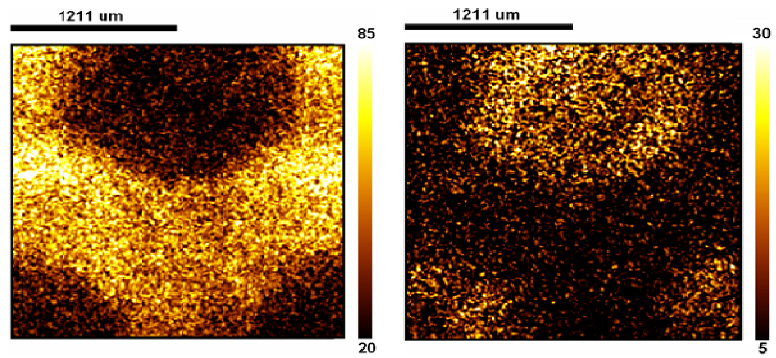
A. W. Thornton, D. Dubbeldam, M. S. Liu, B. P. Ladewig, A. Hill, M. R. Hill, *Energ. Environ. Sci.* **2012**, *5*, 7637 - 7646.

Stopping aging in glassy polymers

- Glassy polymers are attractive as gas separation membranes due to their high fractional free volume (FFV), which means there is high porosity through which gas can permeate quickly.
- Poly (1-(trimethylsilyl)-1-propyne) (PTMSP) has the highest FFV of any glassy polymer.
- However, most glassy polymers, and especially PTMSP, slowly pack into a more dense, lower FFV state, losing the fast gas permeation.
- 10 years ago this was the most active area of membrane research, but it was concluded that the aging could only be stopped by drastically lowering the permeability.

Control of ZIF growth at membrane surfaces



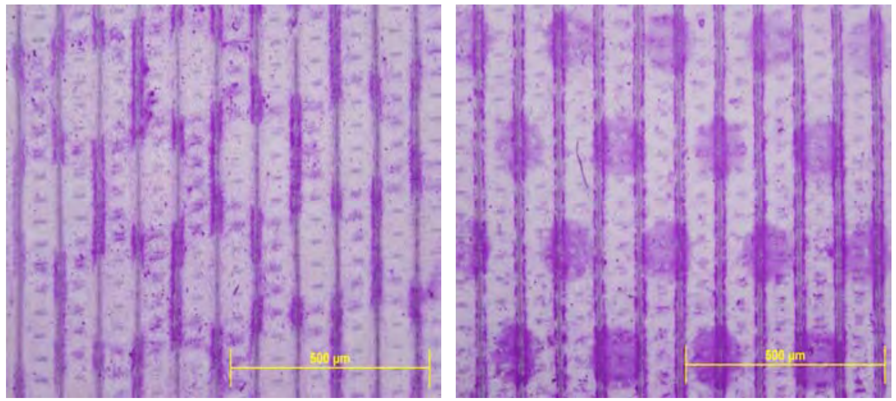


F 1s

C 1s

allylamine

diglyme



Inhibit growth

Promote growth

C. Dimitrakakis, B.W. Muir, C Easton, B.P. Ladewig, M.R. Hill, Adv Mater, **2013**, in press.

Scale up synthesis of MOFs

- Key capability challenge for any new MOF technology

- CSIRO are world leaders in scale up synthesis focussing on low energy, high speed, high sustainability processes for a range of materials.

- We have proof-of-concept that these methods work in the production of MOFs at scale.

Key CSIRO MOF capabilities

- Virtual screening for new and existing structures with potential for adsorption or separations.
- High throughput synthesis and characterisation to speed new materials discovery.
- Ability to develop large scale synthesis routes.
- Track record of working with industry partners in the MOF field.
- Platform technology IP, with 8 patents and 3 invention notes.

Thank you

Matthew Hill
Phone: 03 9545 2841
Email: matthew.hill@csiro.au
http://www.csiro.au/matthewhill

Hydrogen separation using membranes

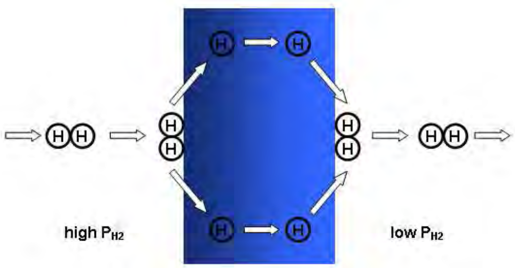
Michael Dolan | Research Team Leader
26 March 2013

ENERGY TECHNOLOGY
www.csiro.au

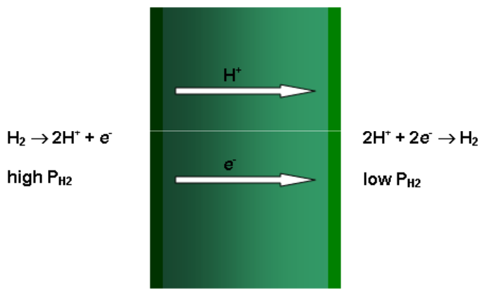
Scope

- High-temperature H_2-selective membranes
- The role of membranes in pre-CC
- Catalytic membrane reactors
- CMR performance characteristics
- CMR optimisation

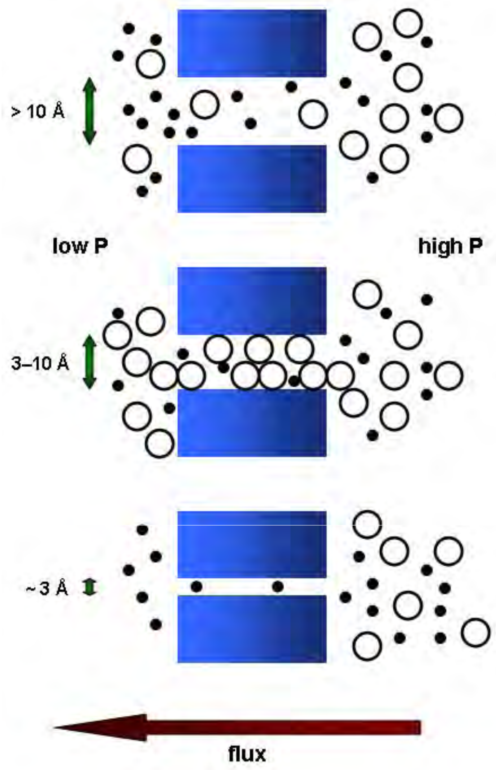
High-temperature H_2-selective membranes



Alloy (Pd, Pd-coated V)
300-600C
Pure H2 product

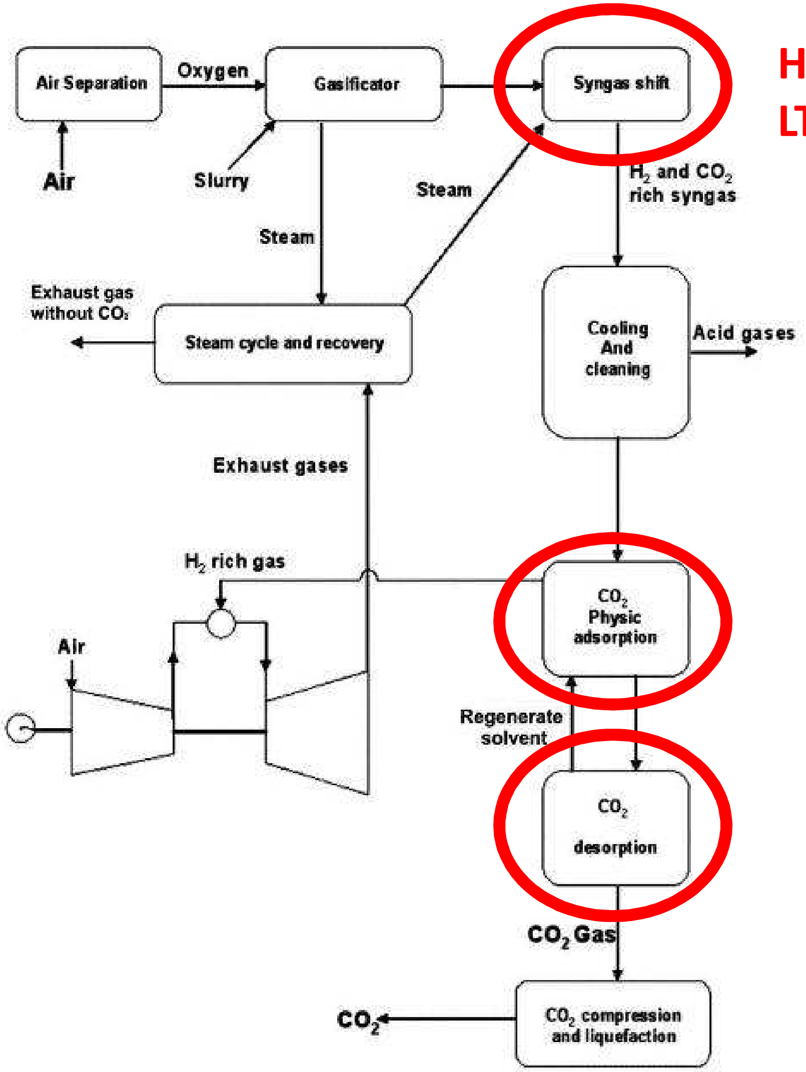


Dense ceramic
600C
Pure H2 product



Microporous (eg, SiO2)
< 300C
< 100% H2 (depending on pore size)

Pre-combustion CO_2 capture (conventional)

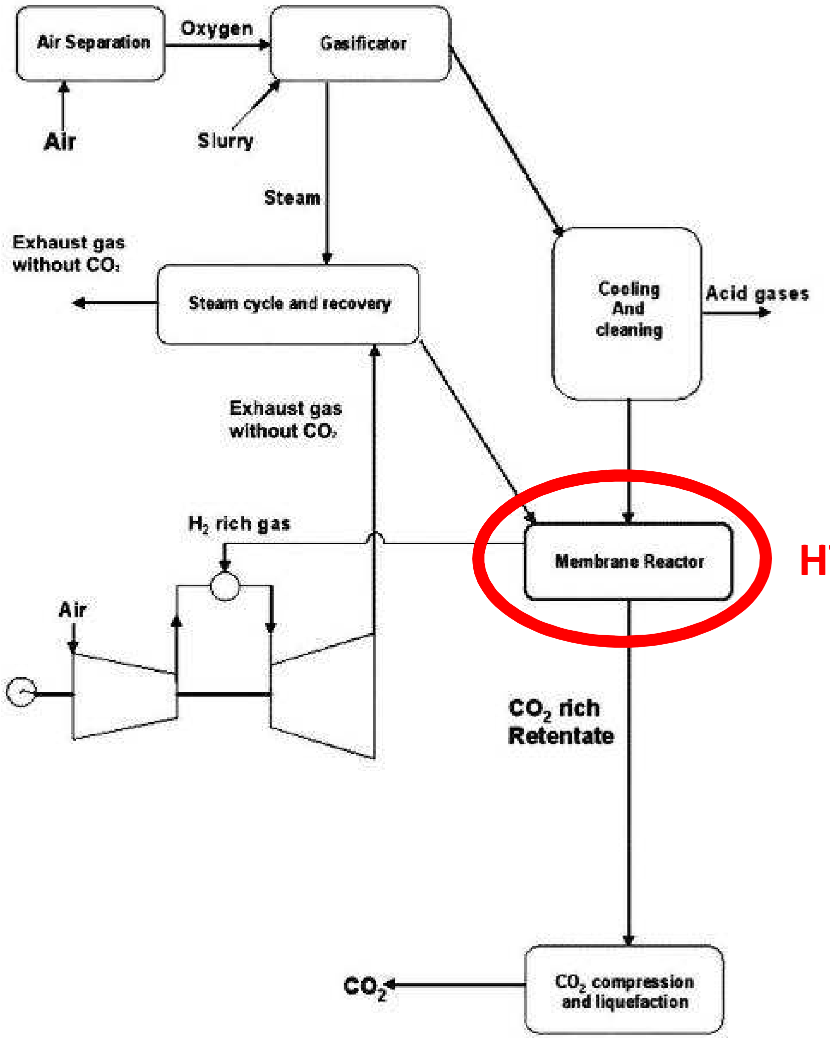


HT: 450C

LT: 200C

Amelio et al, Integrated gasification gas combined cycle plant with membrane reactors: Technological and economical analysis. Energy Conversion and Management 2007;48(10):2680-2693.

Pre-combustion CO_2 capture (membrane reactor)

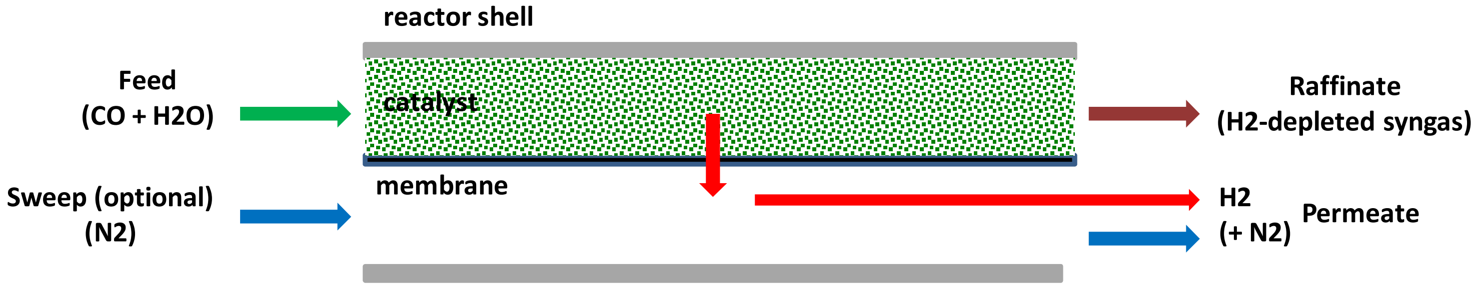


Pre-CMR desulfurisation

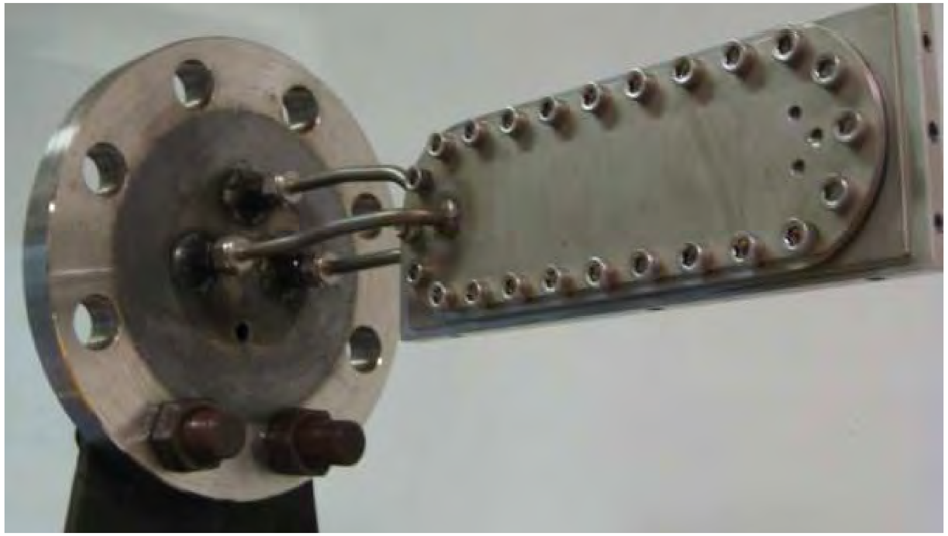
HT: 450C

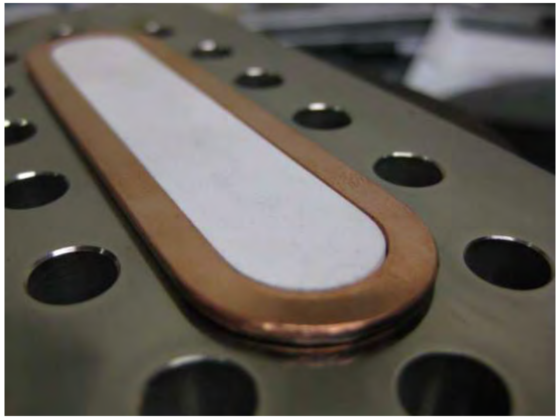
Amelio et al, Integrated gasification gas combined cycle plant with membrane reactors: Technological and economical analysis. Energy Conversion and Management 2007;48(10):2680-2693.

The catalytic membrane reactor



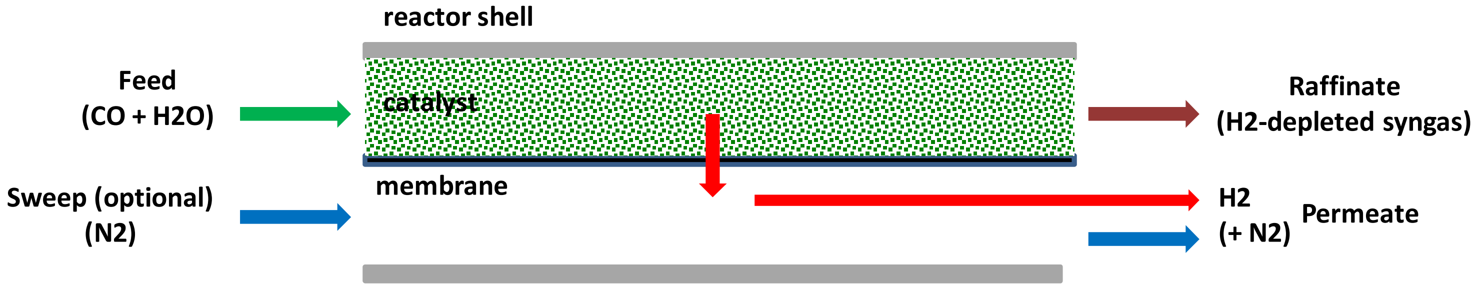
$$CO + H_2O \leftrightarrow CO_2 + H_2$$



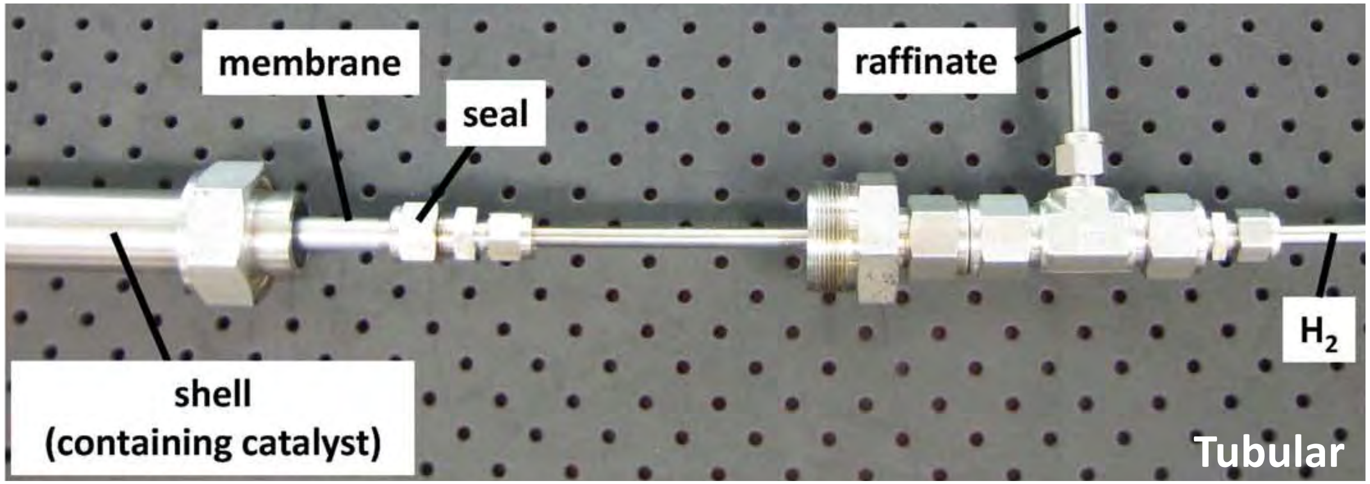


Planar

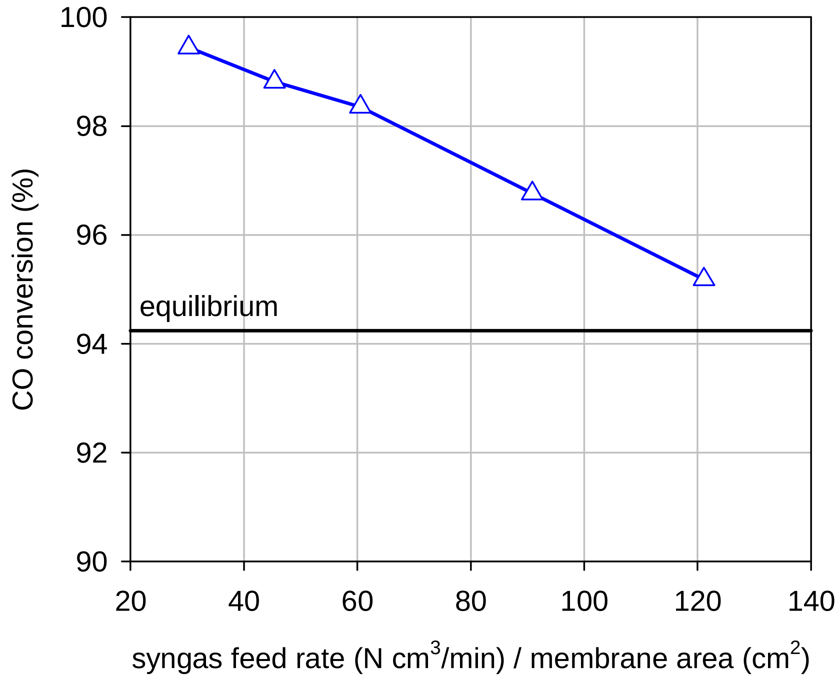
The catalytic membrane reactor



$$CO + H_2O \leftrightarrow CO_2 + H_2$$



CMR performance characteristics



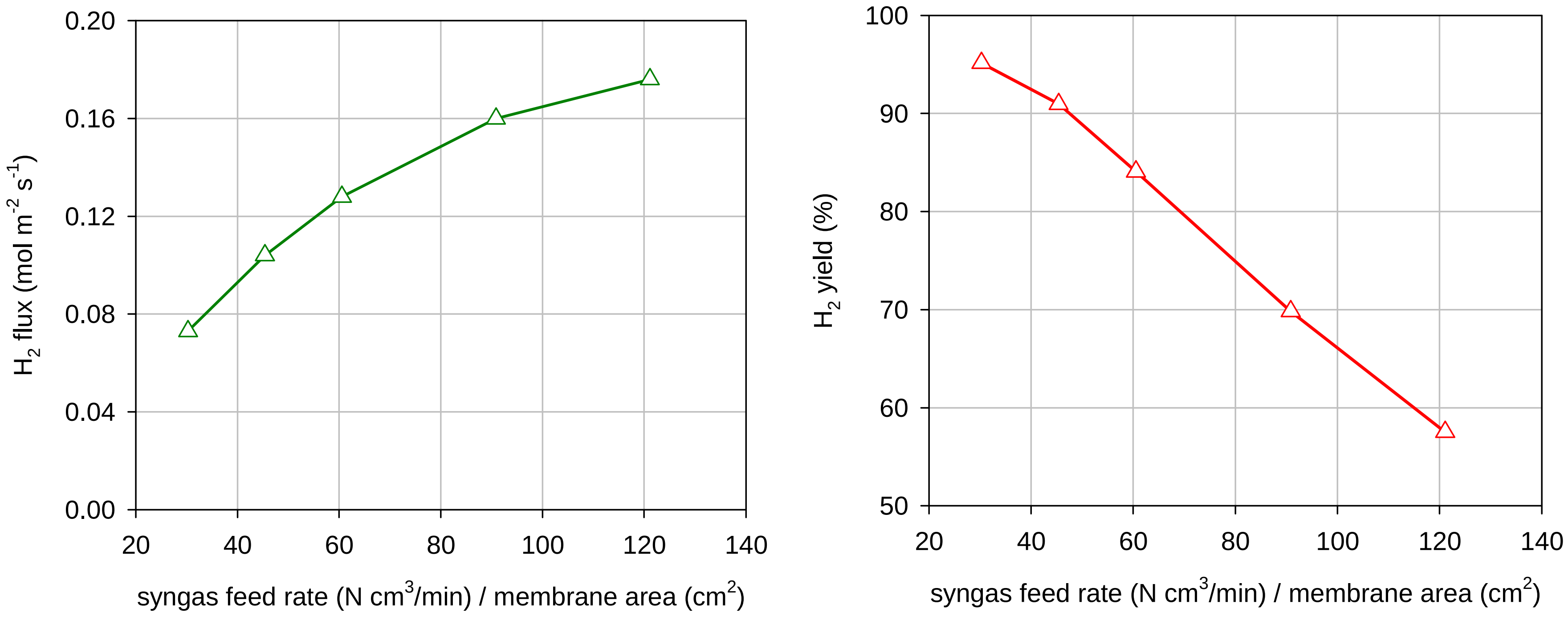
Removing H2 from reactor promotes forward WGS reaction

Creates artificially-high equilibrium

Eliminates requirement for low-temperature WGS reactor

400C, 20 bar, 3:1 H_2O:C

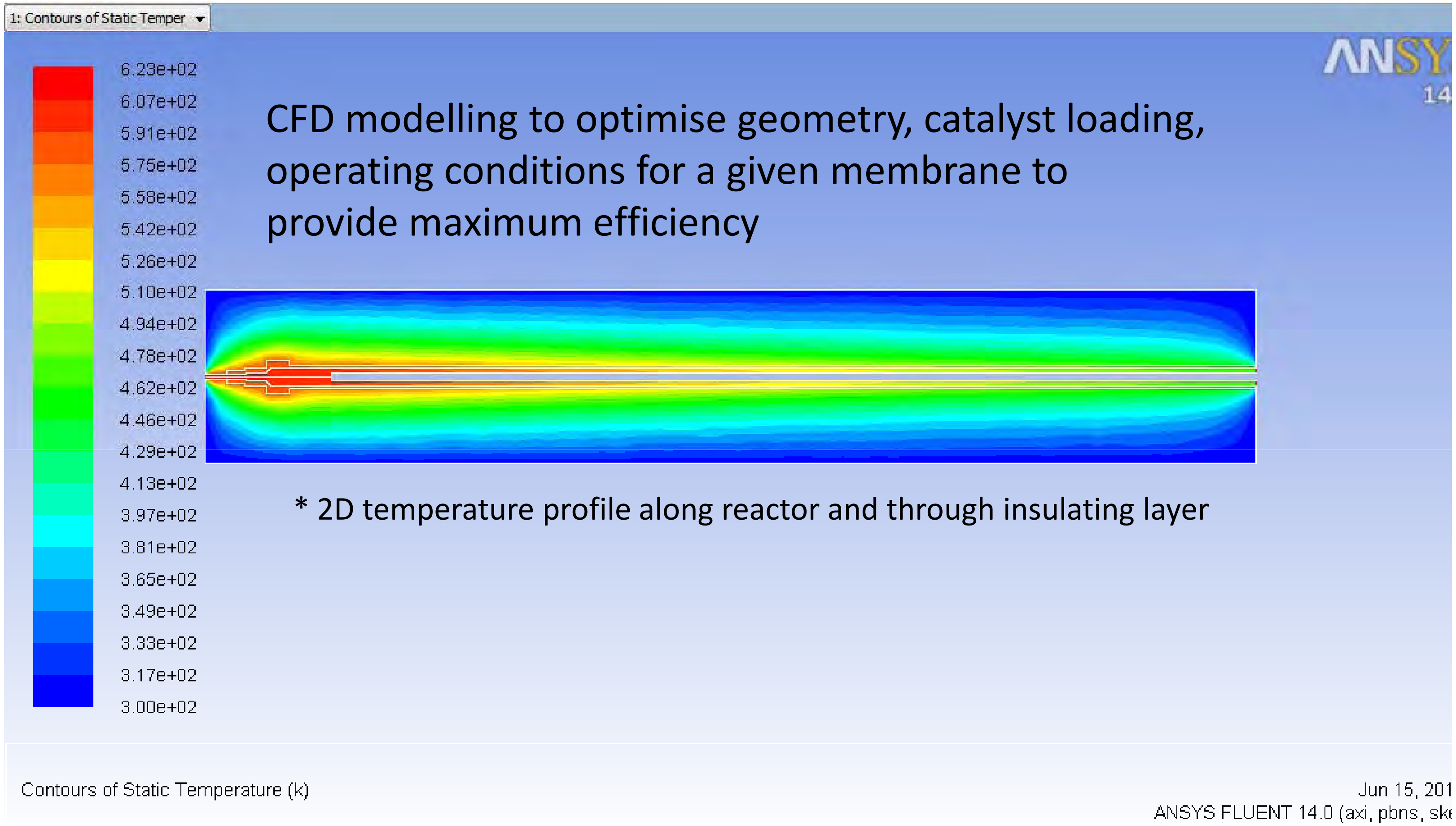
CMR performance characteristics



400C, 20 bar, 3:1 H_2O:C

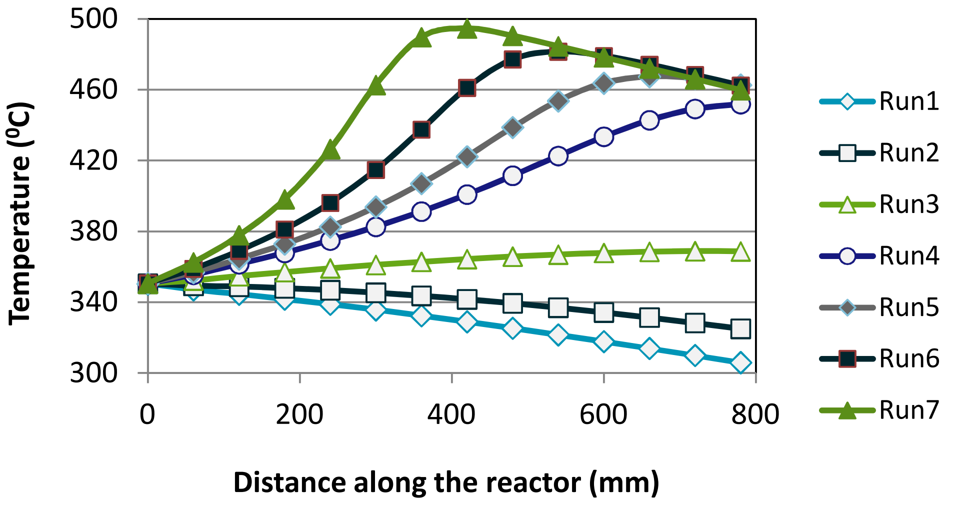
Modelling heat flow and reaction rate

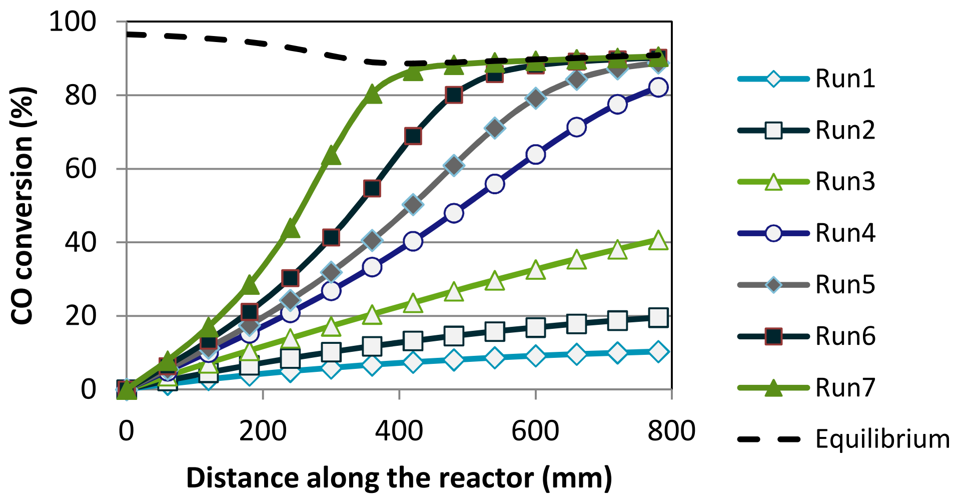
CFD modelling to optimise geometry, catalyst loading, operating conditions for a given membrane to provide maximum efficiency



* 2D temperature profile along reactor and through insulating layer

Modelling heat flow and reaction rate





Temperature varies along reactor length due to i) exothermic WGS reaction and ii) radiative and conductive heat losses

Membranes operate in fairly narrow temperature ranges (350-450C for V-based alloy membranes)

Catalyst loading and feed flow rates must be tailored to minimise temperature gradient along reactor length

Summary

- Membranes: alloy membranes are infinitely selective to H_2
  - Can be used as a stand-alone H_2/CO_2 separator to produce pure H_2, or in a water-gas-shift membrane reactor
- Materials issues: the membrane is the key component
  - Must provide high H_2 flux, low cost, H_2S tolerance, tolerance to thermal cycling
- Catalytic Membrane Reactor: offers process intensification by combining several shift and separation stages in a single reactor
  - CO_2 captured pre-combustion at high pressure; chemical energy in syngas shifted from CO to H_2 for use in turbine, fuel cell, chemical synthesis, etc.

Acknowledgements

- ANLEC R&D (2012 -)
- Centre for Low Emission Technology (2004-2009)
- CSIRO Advanced Coal Technology and Advanced Materials Platform
- San Hla, Daniel Liang, Michael Kellam, Leigh Morpeth, Richard Donelson

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TOSHIBA

Leading Innovation >>>

NETPOWER

The NET Power Cycle and the Combustor and Turbine Development

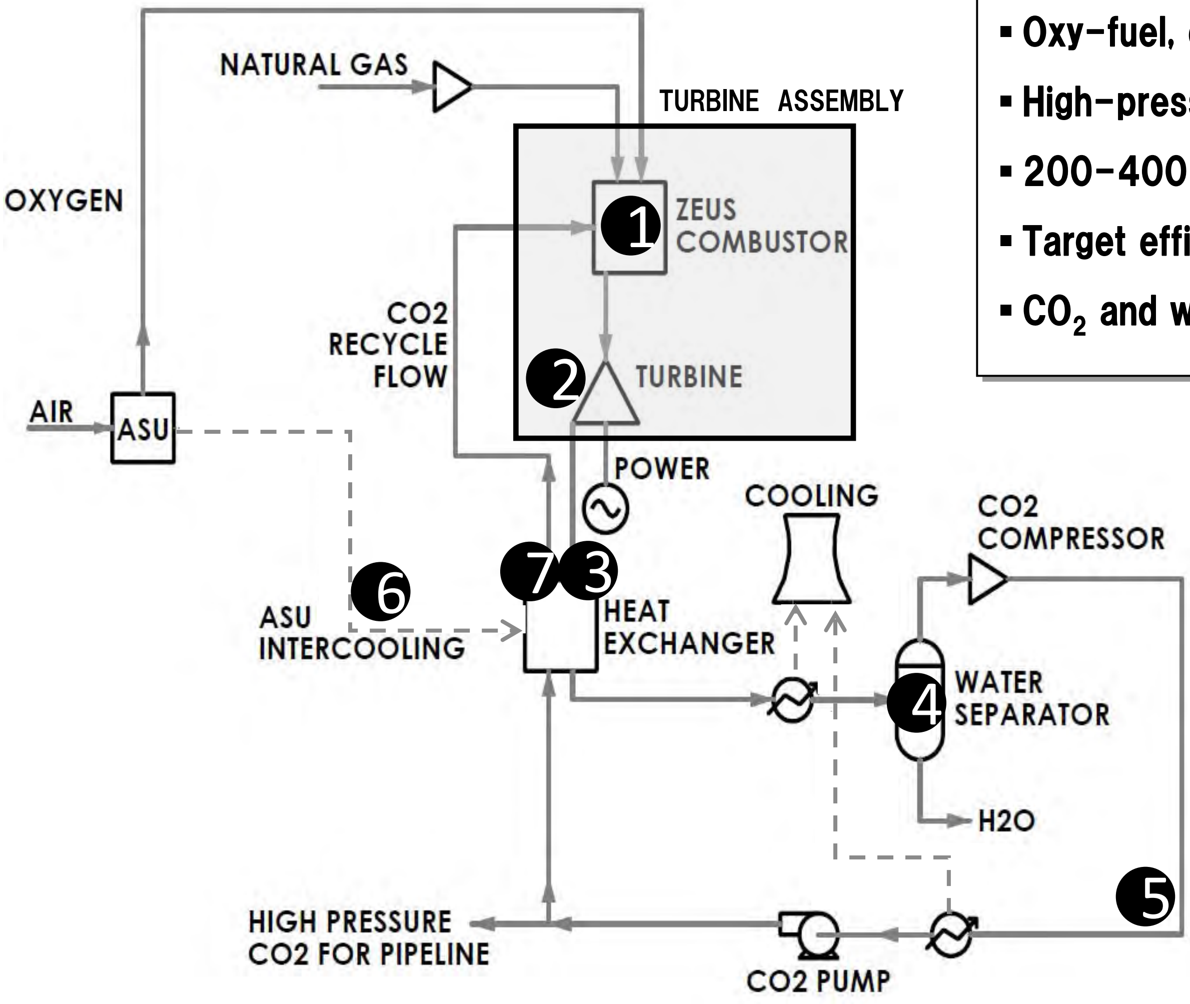
March 2013

Toshiba Corporation

Power Systems Company

Contents

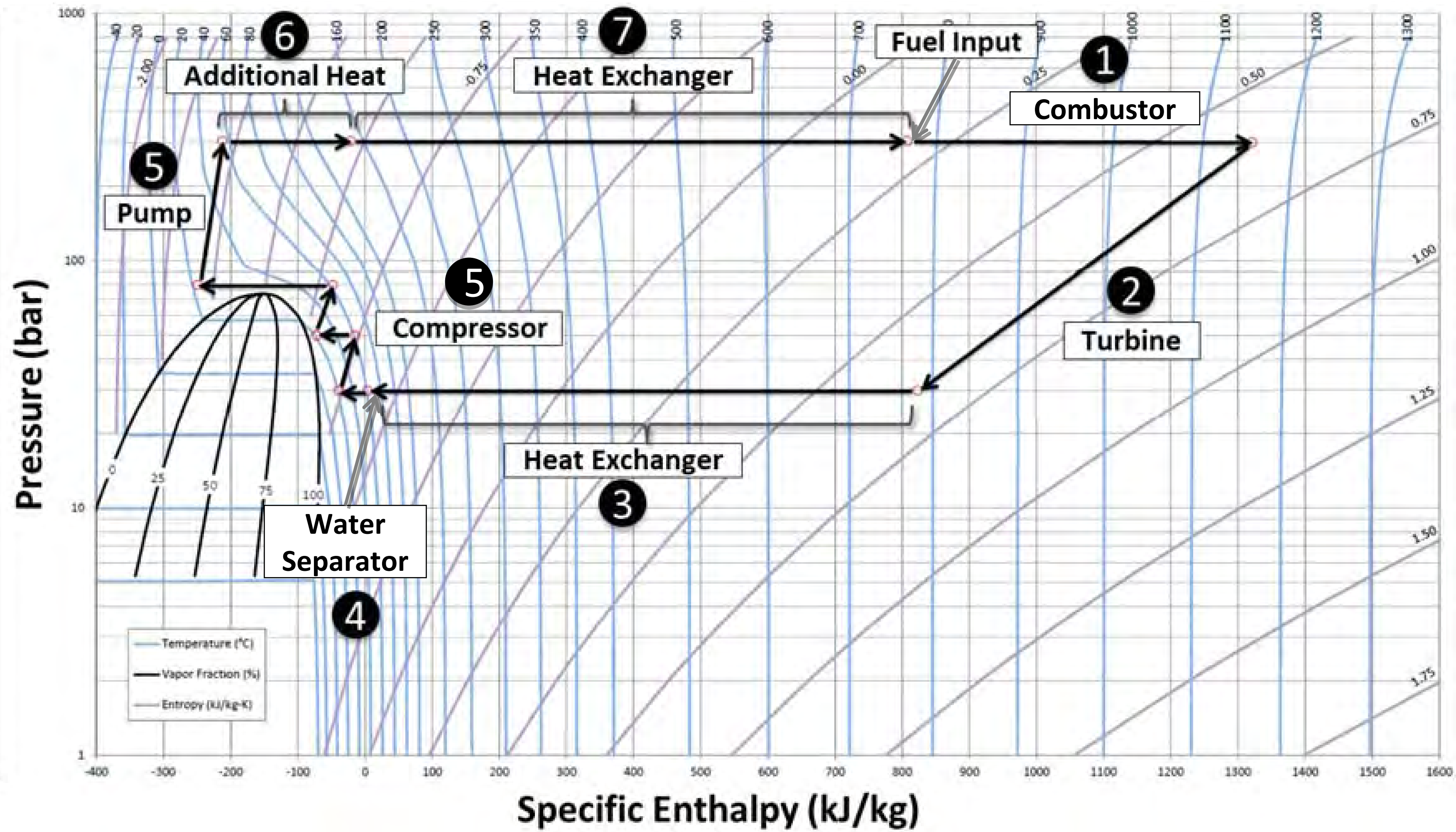
Natural Gas Cycle: The Platform



- Oxy-fuel, closed-loop, CO_2 working fluid
- High-pressure-low-pressure ratio
- 200-400 bar; 6-12 pressure ratio
- Target efficiency 59% (LHV with 100% CC)
- CO_2 and water are the only by-products

1. Fuel Combustion
2. CO_2 Turbine
3. Heat Rejection
4. Water Separation
5. Compression and Pumping
6. Additional Heat Input
7. Heat Recuperation

Pressure and Enthalpy Diagram



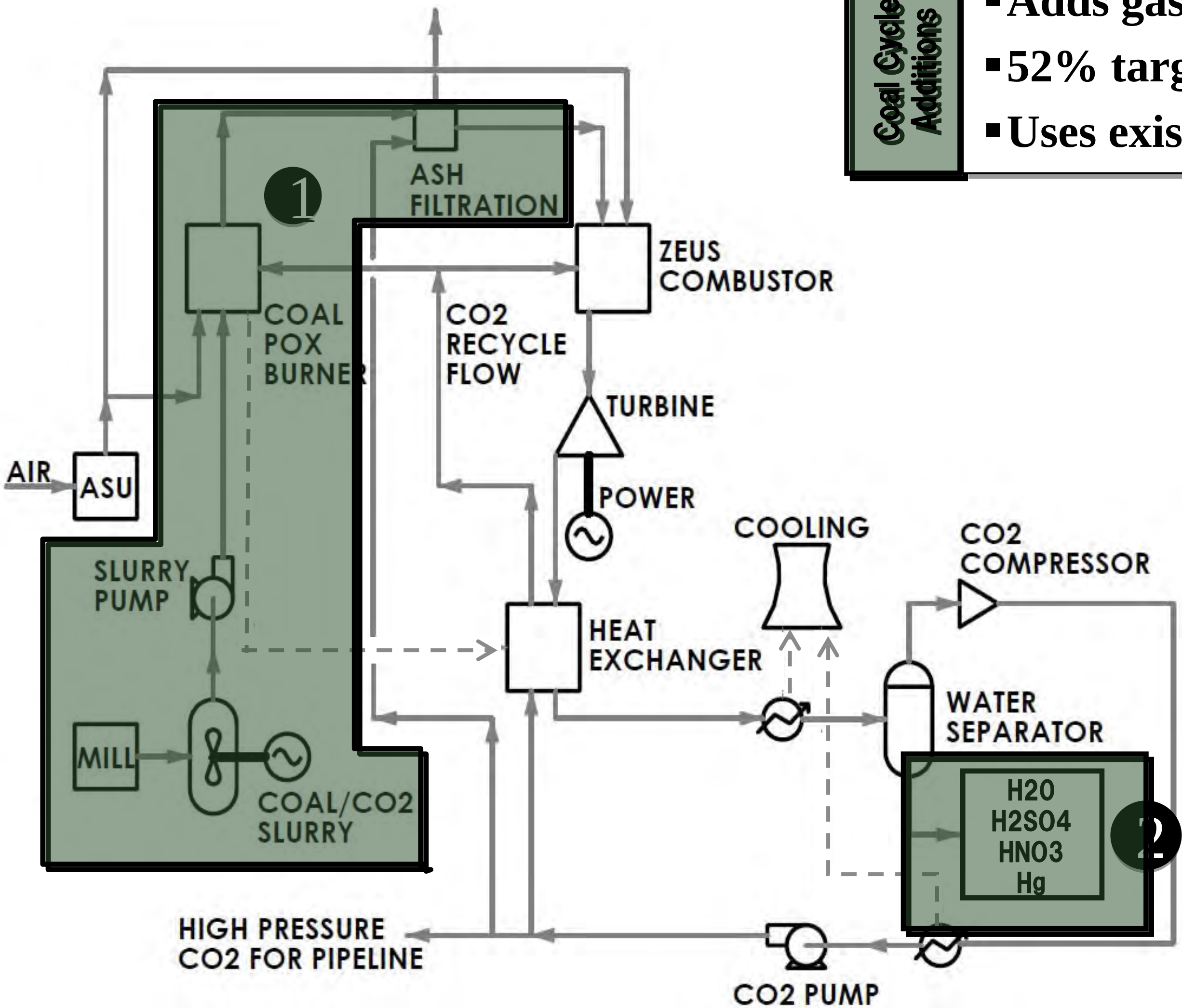
NET Power Platform Target Efficiency

Natural Gas Platform Target Efficiencies (100% CO_2 Capture at 300 bar)		
Energy Components	HHV	LHV
Gross Turbine Output	75%	83%
CO_2 Compressor Power	-11%	-12%
Plant Parasitic Power (primarily ASU)	-11%	-12%
Net Efficiency	53%	59%

Coal Application

Coal Cycle Additions

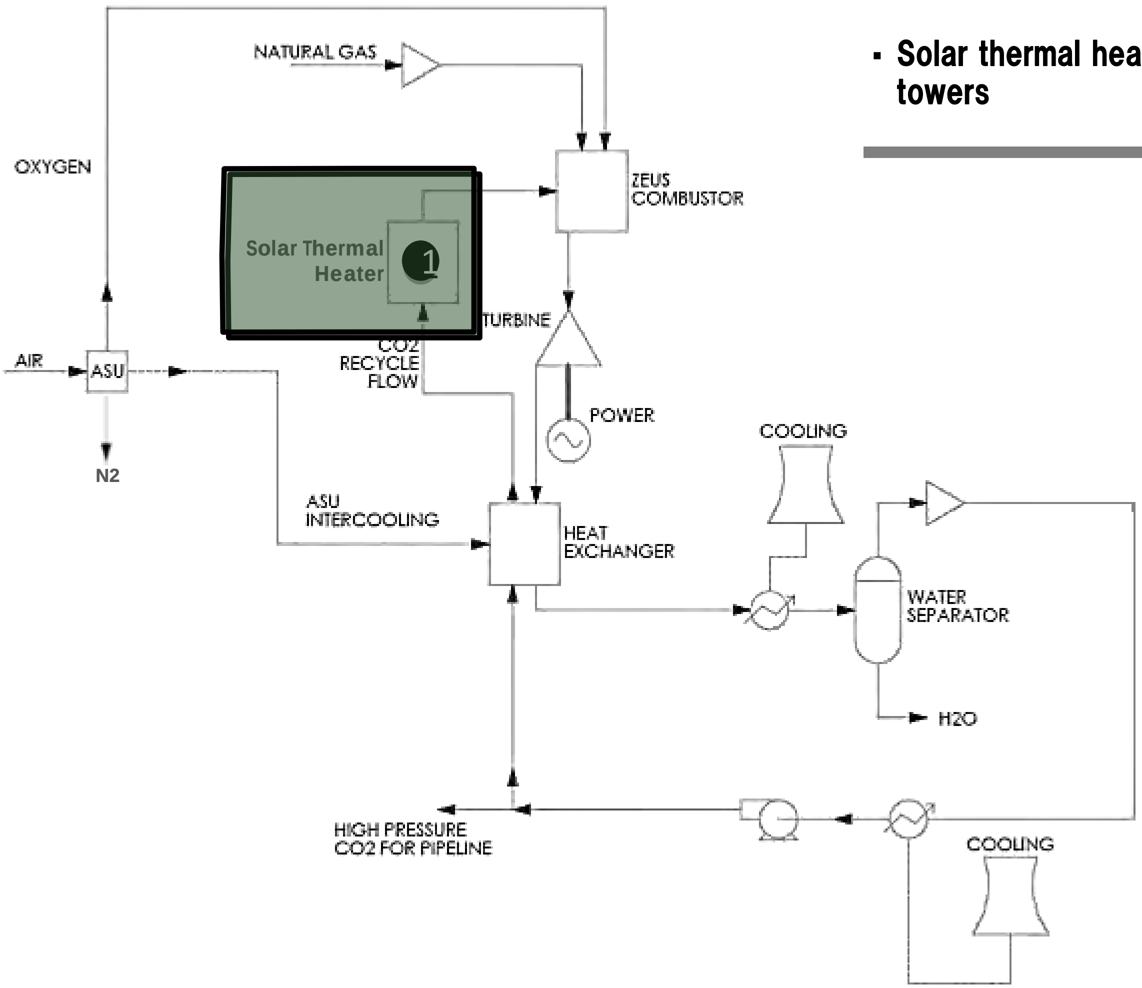
- **Adds gasification & cleanup**
- **52% target eff. (LHV with 100% CC)**
- **Uses existing gasification technology**



1 **Coal Gasification**

2 **Impurity Cleanup**

Direct Solar Integration

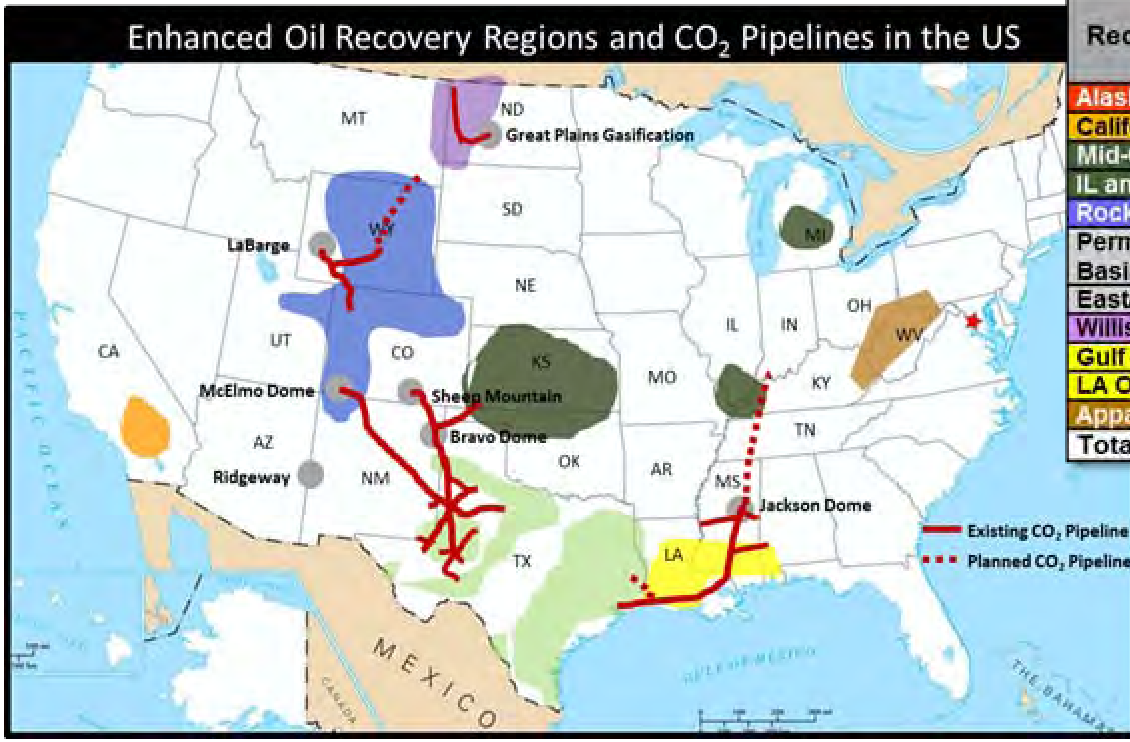


- **Year-long efficiency at 74% in US Southwest**
- **Solar thermal heat most likely in the form of solar power towers**

❶ Solar-thermal heat source

EOR Market: A Large Financial and CO_2 Storage Opportunity

85 billion barrels technically recoverable in the US; industry is tethered to current pipeline and geologic CO_2 infrastructure



Technically Recoverable Oil in US (Billion BBls)	
Alaska	12.4
California	6.3
Mid-Cont.	10.6
IL and MI	1.2
Rocky Mts.	3.6
Permian Basin	15.9
East/Cent. TX	17.6
Williston	2.5
Gulf Coast	7.0
LA Offshore	5.8
Appalachia	1.6
Total	84.8

Source: DOE NETL

470-1,000 billion barrels of oil technically recoverable globally

GLOBAL CO_2 EOR POTENTIAL	
Region	**Billion Bbls**
Middle East	230
Russia	78
United States	85
S. America	32
Asia Pacific	18
Europe	16
Africa	15

Assuming a plant size of 550 MW, this need would support the CO_2 production from 1382 NET Power gas plants (691 coal).

Four Way Agreement and Commercial Relationships

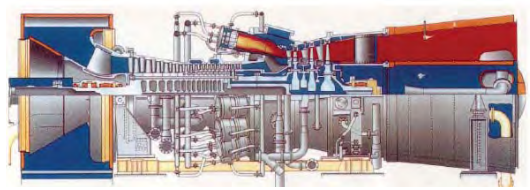
NET Power*	Inventor and developer of the technology. Responsible for overall project development, systems engineering and commercial development
Toshiba* / **Goodwin Steel***	Developing the turbine and combustor
CB&I (Shaw*)	Provided substantial investment in this project and performing EPC services.
Exelon	Assisting with the siting, permitting, and commissioning of the natural gas demo facility; providing operations and maintenance support.

*Note; UK grant was awarded for the development.

Necessary Technology for NET-Power Turbine

Gas Turbine Technology

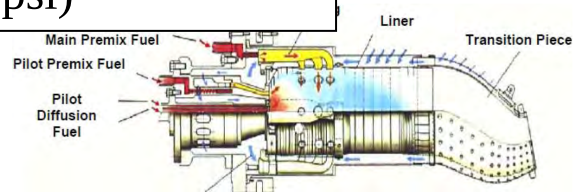
1100-1500C (2012-2730F)



Working fluid; CO_2
Pressure;2MPa⇒30MPa
(290psi→4350psi)

Temperature; E-Class
Pressure; USC & A-USC

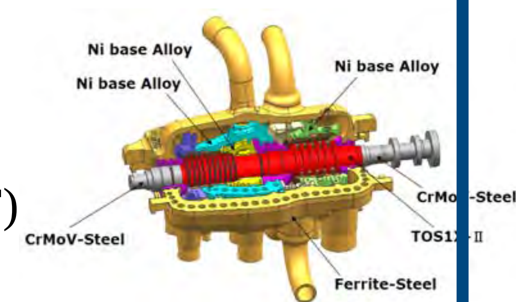
Combustor Technology
1100-1500C



Working fluid; CO_2
Pressure;2MPa⇒30MPa

Turbine & Combustor for Net Power
Temp. 1150C (2110F)
Press. 30MPa (4350psi)

Steam Turbine Technology
USC& A-USC
Pressure; 24-31MPa (3500-4500psi)
Temperature; 600-750C (1112-1382F)

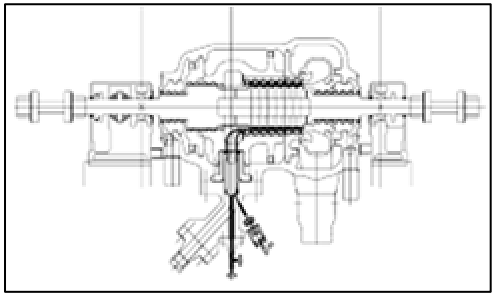


Temperature ⇒1150C (2110F)

Toshiba is the only company that manufactured commercial turbine of 31Mpa main steam pressure.
Toshiba has been keen on A-USC development.

Turbine for 25MWe Demo Plant

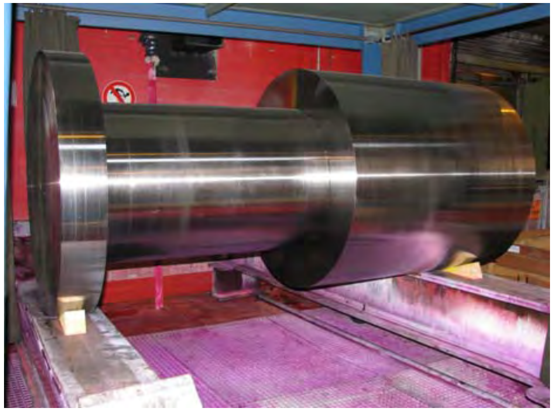
A) Intended to be a scale model of commercial turbine (250MWe) as much as possible
B) Rotational speed is 6000rpm and connected to compressor and reduction gear
C) Double shell configuration
D) Rotors are welded together
E) Single can type combustor for 25MWe turbine



Materials
Rotor; Ni base forging and CrMoV forging are welded together
Casings; Ni base casting for high temperature part
CrMoV casting for lower temperature part
Blades; Ni base casting

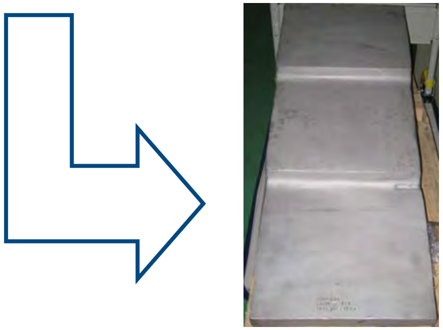
All the necessary materials have been already developed.
Purchase orders for long-lead materials will be placed soon.

R&D results of Ni base Forging and Ni base Casting
- Make the best use of R&D results for A-USC -



First trial forging for TOS1X was completed (above photograph)
Second trial forging for rotational test will be manufactured soon.

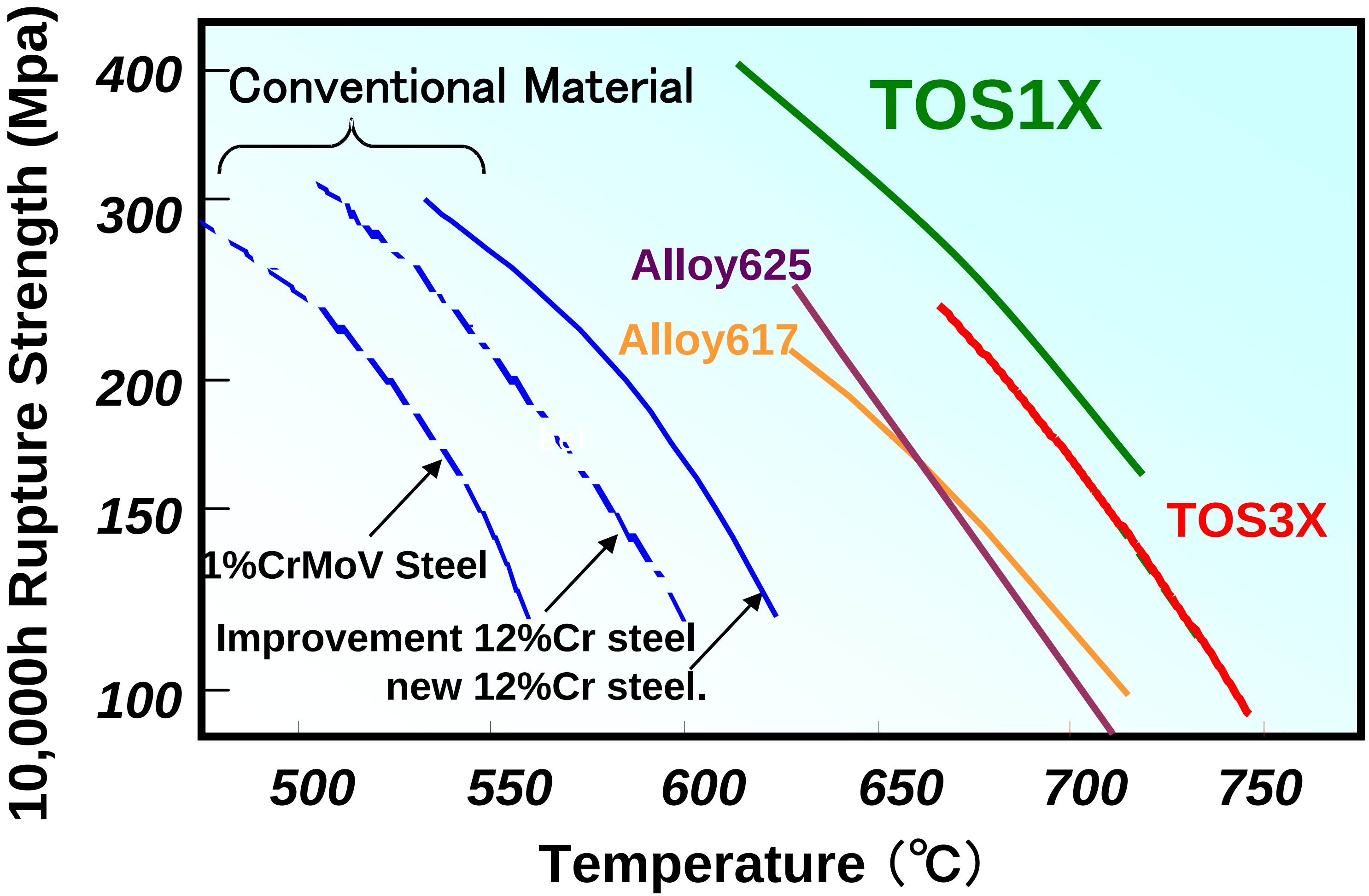
Alloy625
Trial Inner casing for A-USC



TOS3X Test Piece

Two candidates, Alloy 625 and TOS3X, are available for S-CO2 Turbine

Comparison of Creep Rupture Strength



Necessary materials are already applicable

Cooling Design

High Temperature

- Needs cooling both for nozzles and moving blades
- However, very complicated cooling technology is not necessary because the temperature is not extremely high compared with cutting-edge gas turbines.

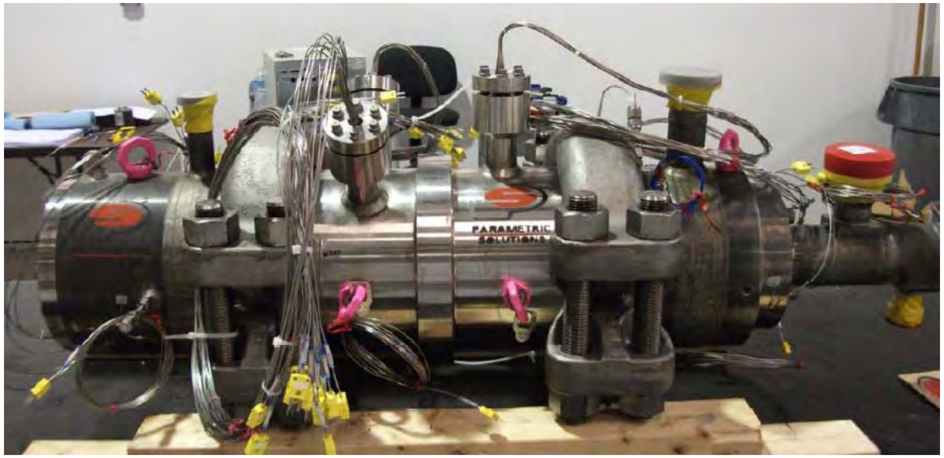
Both mean temperature and local temperature satisfy design criteria thanks to two contributor

- Convection cooling by cold CO2
- Thermal barrier coating

Temp. Contour

Concept of Combustor Design

No NOx Emission	→	No need of complex pre-mix technology Simple Diffusion Flame can be used
High Pressure	→	Thick Wall Casing against high Pressure
Rather moderate temperature compared with gas turbines	→	Experienced Cooling Scheme

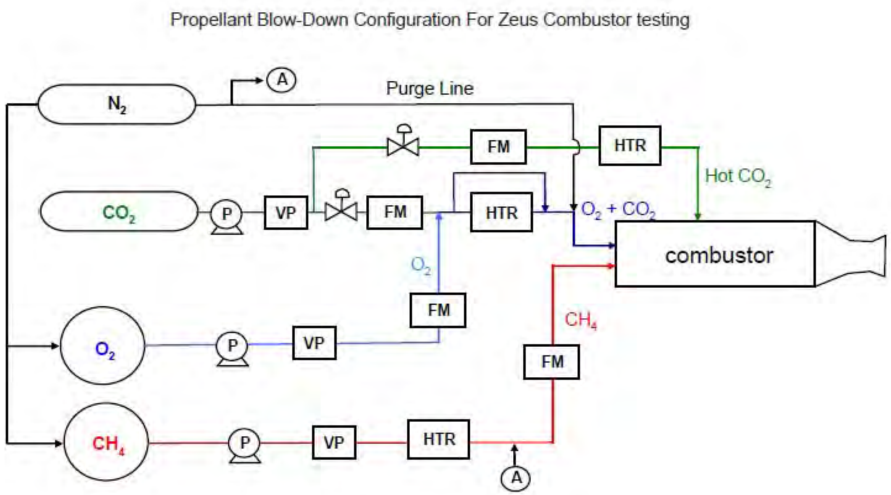


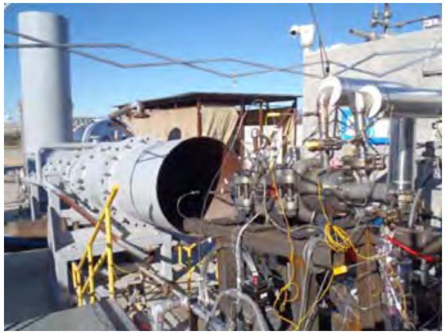
5MWt Rig Test Combustor

Rather simple combustion and cooling are expected , yet verification under high pressure using a rig test combustor is necessary.

Present Status of Combustor Development

- ✓ First Ignition was successfully done at the middle of January using test facility in U.S.A.
- ✓ Phase 1 Test up to 5Mpa has been completed.
- ✓ All the test data was carefully checked and evaluated.
- ✓ Stable flame was confirmed enabling us to proceed to higher pressure test (Phase 2).
- ✓ Modification of facility is being done for Phase 2 test.
- ✓ Design of the combustor for 25MW Demo plant will be synchronized with Turbine Development.





Rig Test Combustor at the Test Stand

END

Carbon-Based Adsorbents for CO_2 & VAM Capture

PCC Science & Technology Seminar
26 March 2013 | Newcastle

Shi Su

ENERGY FLAGSHIP/EARTH SCIENCE AND RESOURCE TECHNOLOGY
www.csiro.au

Carbon-Based Adsorbent Research Program

- Fundamental study on high-performance carbon-based adsorbent development
  - Carbon fibre (CF) composite
  - Carbon nanotube (CNT) composite
  - CF\CNT composite
  - Biomass (macadamia nut shell) carbon composite
- Various applications of carbon-based adsorbents
  - Post-combustion CO_2capture (PCC)
  - Ventilation air methane (VAM) capture
  - Flue gas cleaning
  - Industrial purification processes
- Process & equipment development
  - Lab scale and large scale test units for CO_2 and VAM capture
  - Site trials and demonstration of prototype units
  - Data & experience for scaling up

Why carbon-based adsorbents

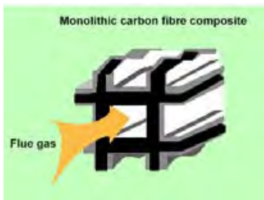
- Chemically stable against steam, SO_x and NO_x
  - ✓Avoid flue gas pre-treatment prior to CO_2 capture (this is important as no FGD and SCR $DeNO_x$ for coal fired power plants in Australia)
  - ✓More suitable for PCC applications compared to moisture sensitive zeolites and other SO_x/NO_x intolerable adsorbents e.g. supported amine
- No degradation issue → secondary environmental impact
- Lower heat capacity of solid adsorbent than liquid absorbent of conventional solvent technologies thus requiring lower energy for thermal regeneration
- Physical adsorption
  - ✓Low heat of CO_2 desorption
  - ✓Potential to reduce the cost of LECT by using the waste heat of flue gas for adsorbent regeneration
- Low cost of adsorbent materials

Commercial in Confidence

3 | CSIRO carbon-based adsorbents for PCC & VAM

Novel CO_2 Capture Technology

- CO_2 adsorption using honeycomb carbon fibre composite monoliths
  - ✓ Enable CO_2 capture in a dry process
  - ✓ Suit high dust environment with low pressure drop
  - ✓ Low energy consumption (lower heat capacity of solid than liquid in conventional solvent technologies thus requiring lower energy for regeneration; flue gas waste heat for desorption)
  - ✓ Stable with SOx and NOx, no degradation issue



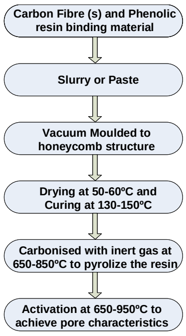
4 | CSIRO carbon-based adsorbents for PCC & VAM

Lab Scale Study

Fabrication and Testing of Lab Size Honeycomb Carbon Fibre Composite Monoliths

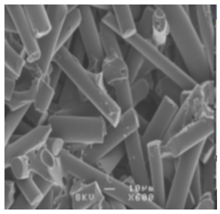
Molding equipment

3 processing furnaces



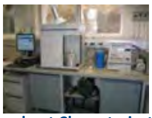
Length: 80mm, Dia: 30mm, Number of Channels: 17,

Fabricated (HMCFC)



Microscopic morphology

Adsorbent Testing Equipments



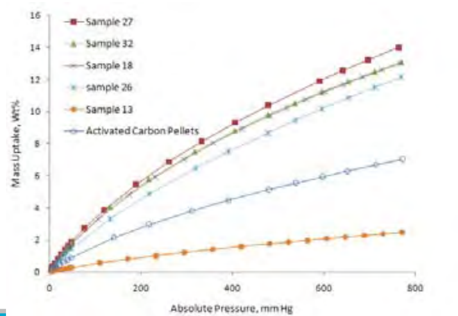
Adsorbent Characterisation

Breakthrough Test Rig with Lab Scale Adsorption Chamber

Lab Scale Study (continued)

Characteristics of monoliths from different carbon fibres

Carbon Fibre Monolith Types as Sample Numbers	Burn-off, %	BET - N_2 Surface area, m^2/g	DA- Method		CO_2 Mass Uptake, %	
			Pore width, nm	Pore volume, cm^3/g	0ºC	25ºC
27	37	1305	1.8	0.6828	20.87	13.8
18	28.8	855.3	1.61	0.4685	19.36	13
32	24.6	1017.2	2.14	0.6078	19.46	13.2
26	68.4	1873.9	1.93	1.588	19.18	12.2
13	21.7	347.74	1.81	0.1905	4.2	2.5



Adsorption isotherms at 25ºC

Large Scale Capture-Regeneration Studies

Fabrication of large scale adsorbents

Large scale moulding unit for composite fabrication

Large size adsorbents (Ø 123 mm), 267 small gas channels, 13 big channels for heating/cooling

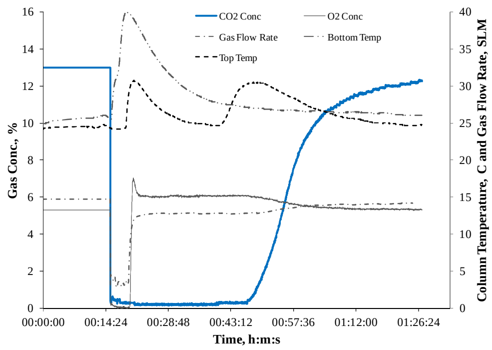
Test Unit Coupled with regeneration

Large scale CO_2 capture –regeneration unit and process schematic

- Two 2 meter long columns stacked with adsorbents
- Designed for higher gas throughputs up to 200SLM
- Repetitive capture & discharge capability
- Thermal and vacuum swing regeneration

Summary of Large Scale Study Results

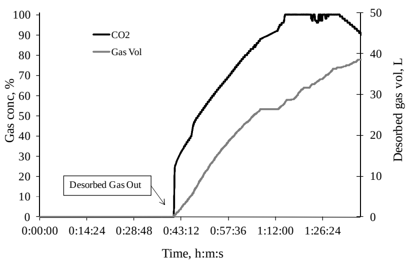
Adsorption Breakthrough Profile Showing CO_2 capture at Real Time



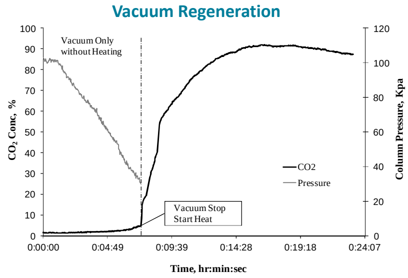
- CO_2 capture carried out at ambient temperature and pressure
- Simulated flue gas consisting of 13% CO_2, 5.5% O_2 and balance N_2
- CO_2 capture efficiency > 97% from adsorption breakthrough

Thermal and Vacuum Regeneration

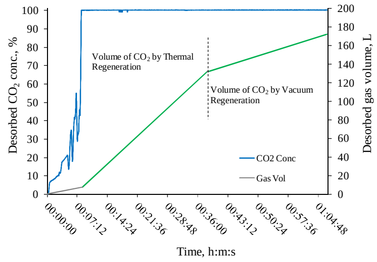
Individual Thermal Regeneration



Vacuum Regeneration



Combined Thermal and Vacuum Regeneration



- Residual CO_2 inside column after thermal regeneration
- Vacuum regeneration alone ineffective
- Heating is essential to desorb CO_2
- Combined thermal and vacuum regeneration with pure product purge most effective
- Very high purity of Recovered CO_2
- CO_2 recovery > 95%

Site Trials of Prototype CO_2 Capture Unit at Vales Point Power Station

- Objective: to conduct site trial of CO_2 Capture technology at Vales Point Power station to evaluate the performance of novel HMCFC solid sorbent using real flue gas
- Unit currently being commissioned and to be tested

Development of New-Generation Carbon Composite Adsorbents

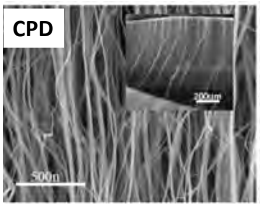
- **Objective**
  - ➢ Enhance CO_2 adsorption capacities (smaller footprint, lower capital and operating costs)
  - ➢ Lower the cost of sorbents

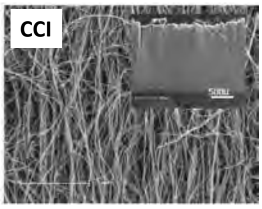
- **New-generation carbon composite adsorbents**
  - Carbon nanotube (CNT) modified carbon composite monoliths
  - Macadamia nut shell biomass carbon

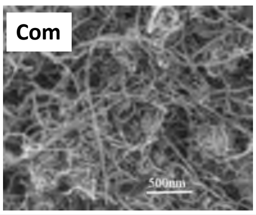
Preparation of CNT Composites

Source of CNTs

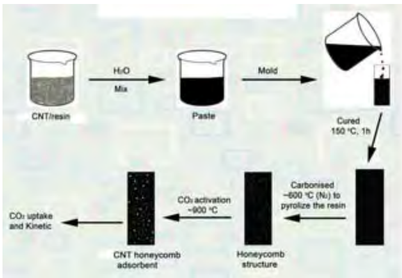
Three types of multi-wall CNTs were used for adsorbent fabrication.







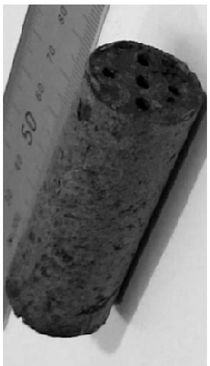
Preparation process of CNT composites



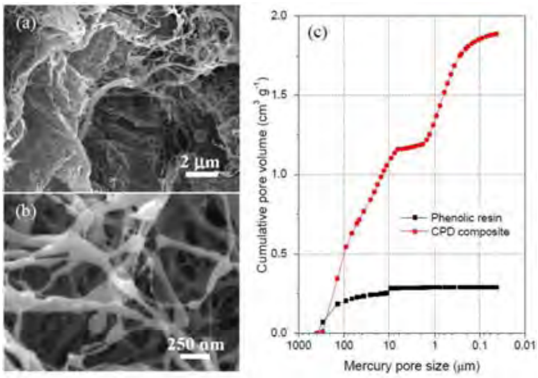
Specifications of as-produced/as-received CNTs

CNT samples	Diameter, D (nm)	Length, L (μm)	Alignment	Purity (%)	Aspect ratio, L/D
CPD	10	300	highly aligned	99.8	30,000
CCI	80	1500	aligned, some branching	97	18,750
Com	10-20	5-15	very tangled	95	400-1,500

Morphology of CNT composites



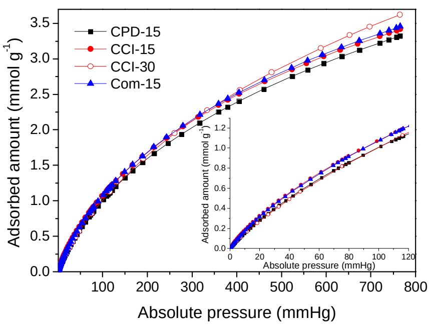
Prepared CNT carbon composite monolith



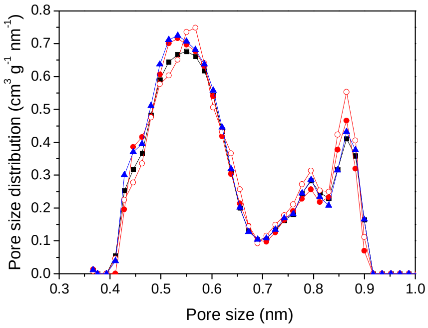
Morphology and macropore size distributions

CO_2 Adsorption Capacities of CNT Composites

CO_2 uptake at 25 °C



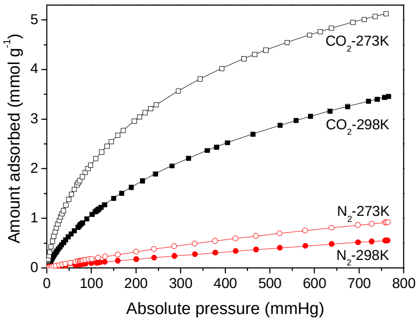
Narrow micropore size distributions



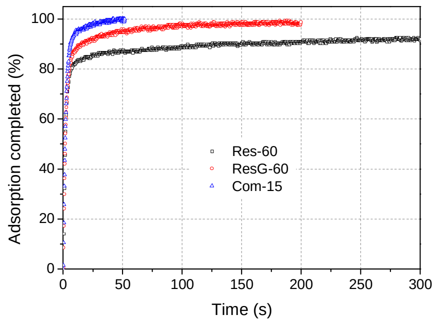
- 159 mg CO_2 g^{-1} at 25 °C and 1 atm
- 52 mg CO_2 g^{-1} at 25 °C and 114 mmHg

Adsorption Selectivity & Kinetics

CO_2 & N_2 uptake adsorption Isotherms at 0 and 25 °C



Rates of CO_2 adsorption at 25 °C and 25 mmHg



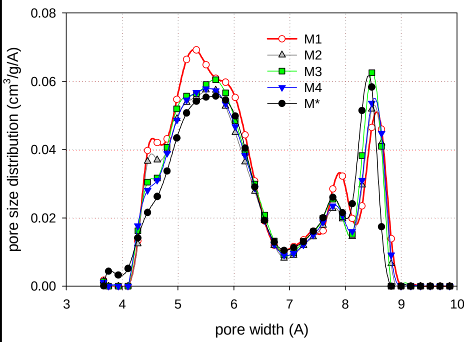
- CO_2/N_2 selectivity: 32.6 at 273 K and 19.8 at 298 K
- Fast adsorption kinetics observed in the CNT composites

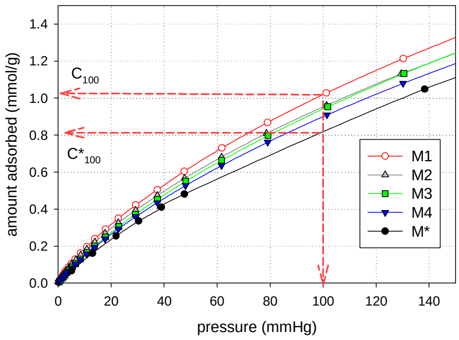
Macadamias around the World

- ❑ Only grow in tropical climates.
- ❑ Cultivated mainly in Australia, the USA and South Africa. The industries are expanding around the world
- ❑ In Australia, according to the Australian Macadamia Society:
  - ➢ ~ 40 % of the world's production in 2009
  - ➢ 35-40,000 tonnes nut in shell (NIS) yearly
  - ➢ ~ 65 % are shell.

http://www.macadamias.org.uk/

Micropore Size Distribution (MPSD)

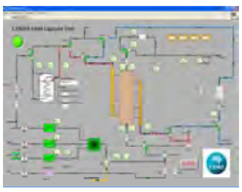




- M1 has the highest C_{100}, which is related to the MPSD in the range of 4-6 Å.
- Carbonized MNSs as a composite precursor are better than activated ones.
- Adding carbon fibre does not enhance the sorbent performance.

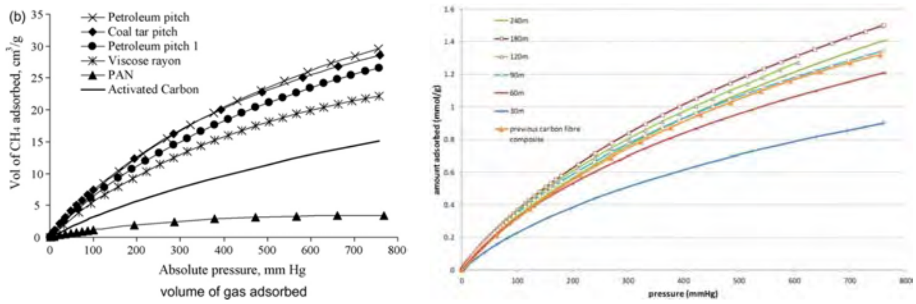
VAM capture technology

- Adsorbents
- Prototype test unit coupled with swings



VAM capture technology (Continued)

- **Adsorption isotherms**
  - Petroleum pitch-based composite adsorbents: **more than twice** the adsorption capacity compared to conventional activated carbon



CH_4 adsorption isotherms at 25°C - different carbon fibre monoliths

Closing Remarks

- Porous carbon composite monoliths show great promise in CO_2 and VAM capture
- Development of high-performance adsorbents is highly important in the applications:
  - High CO_2 (or CH_4) loading capacity
  - High CO_2 (or CH_4)/N_2 selectivity
  - Fast adsorption kinetics
  - Suitable interaction for easy regeneration
  - Good mechanical, thermal and chemical stability

Acknowledgements

- Funding support from NSW Coal Innovation
- Funding support from ANLEC R&D
- Funding support from ACARP
- Funding support from CSIRO
- Site support from Delta Electricity
- Contributions from colleagues

Thank you

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CSIRO PCC Science & Techonology Seminar
26 March, CSIRO Energy Centre, Newcastle

“Ca-looping for post-combustion CO_2 capture"

Borja Arias Rozada

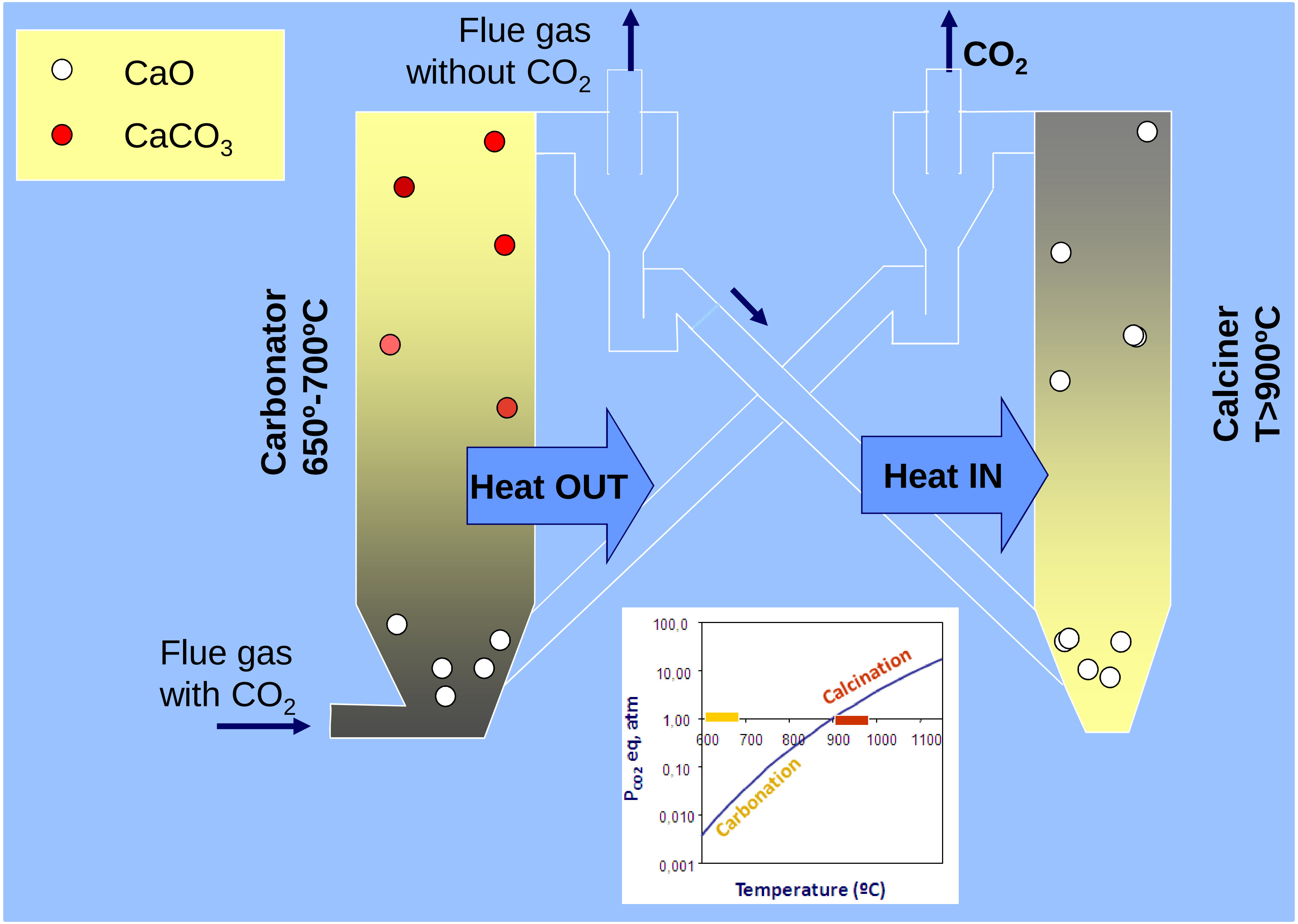
borja@incar.csic.es

CO_2 Capture Group
Spanish Research Council (INCAR-CSIC)

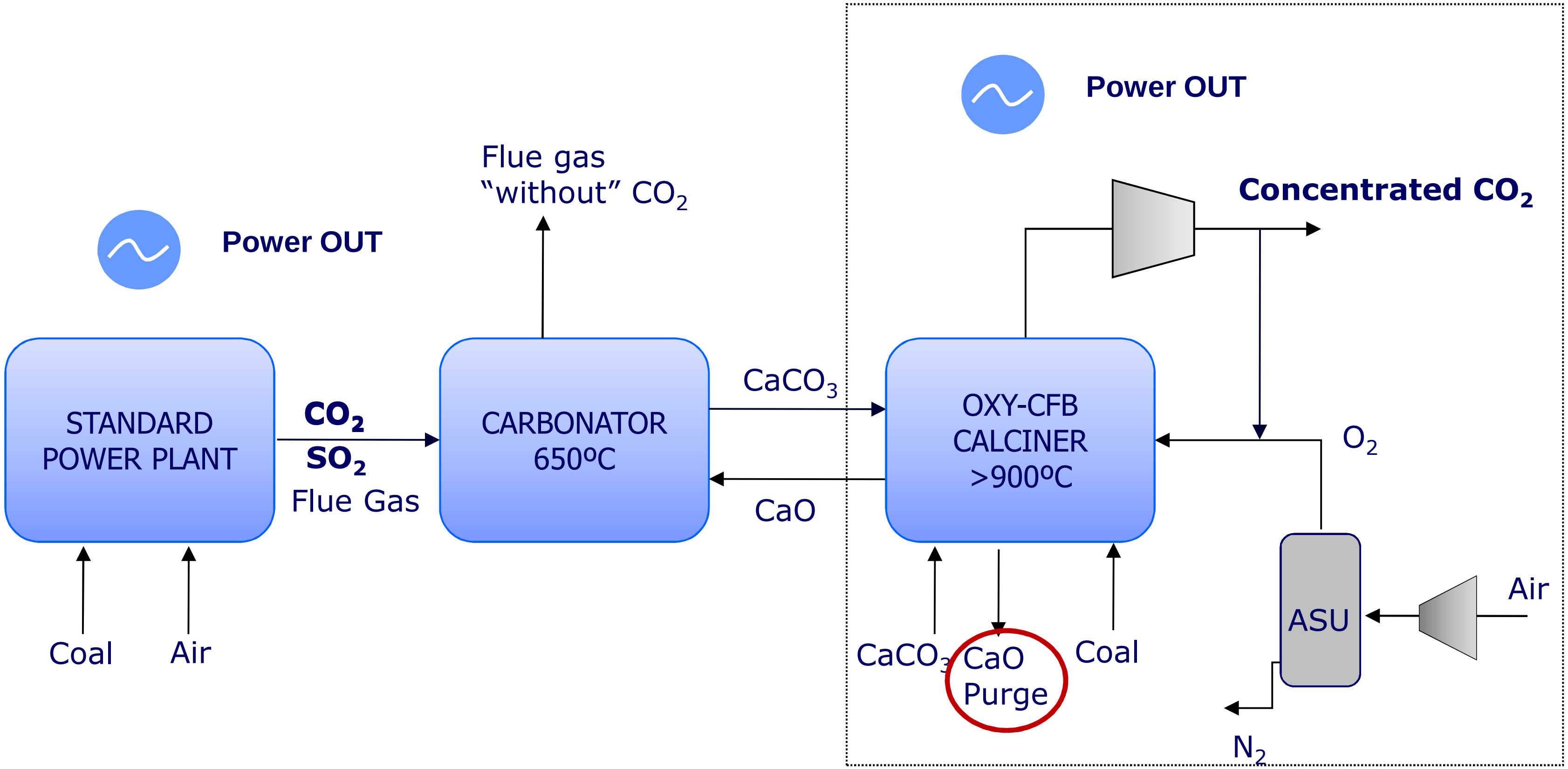
OUTLINE

- Postcombustion Calcium Looping concept
- Pilot plant results from the “CaOling” project
  - Testing lab scale facilities (<30 kW_{th})
  - Testing results from a 1.7 MW_{th} pilot
- Conclusions

Ca-looping: The main process concept



Main process concept: Post-combustion CO_2 capture

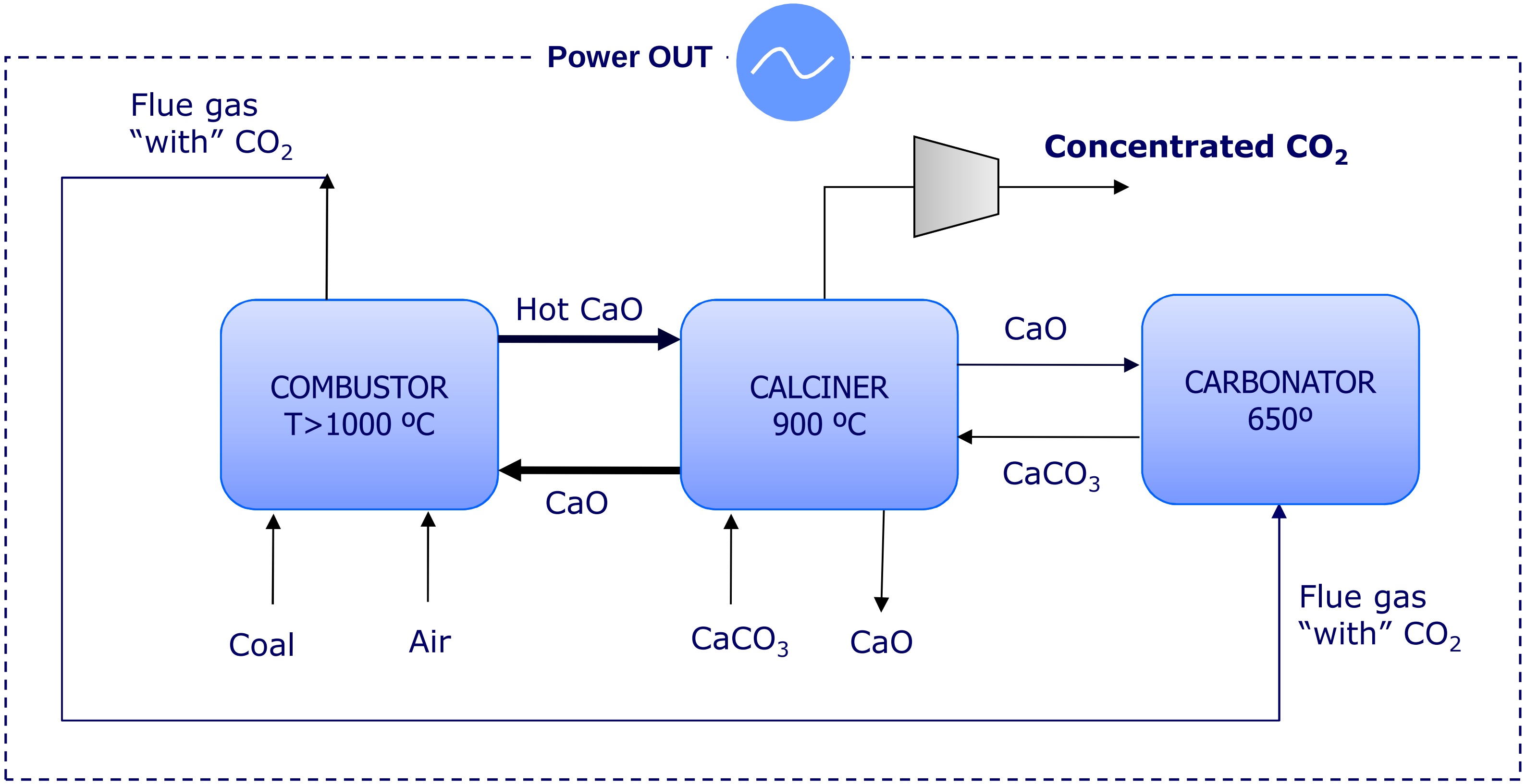


Some features of postcombustion Ca-looping :

- Low energy penalty (6-7 net points)/low cost per ton CO_2 captured
- Purge of CaO: synergies with cement industry and others (i.e. desulfurization of FG)
- Low cost sorbent precursor (low toxicity of materials involved)
- Pre-treatment of flue gas no needed (SO_2 co-capture)
- Benefits and limitations of large scale CFBCs (including oxy-CFB)

Shimizu et al , 1999, *Trans. IChemE 77A, 62–68*

Advanced CaL concept: power plant with inherent CO_2 capture



Some advantages of a Ca-L power plant calcining with "hot CaO":

- **No air separation unit required, no energy penalties other than compression and aux.**
- **Key CFBC equipment already available, but high combustion temperatures asks for coal quality**
- **High solid circulation required and new scaling up issues for FB calciner.**

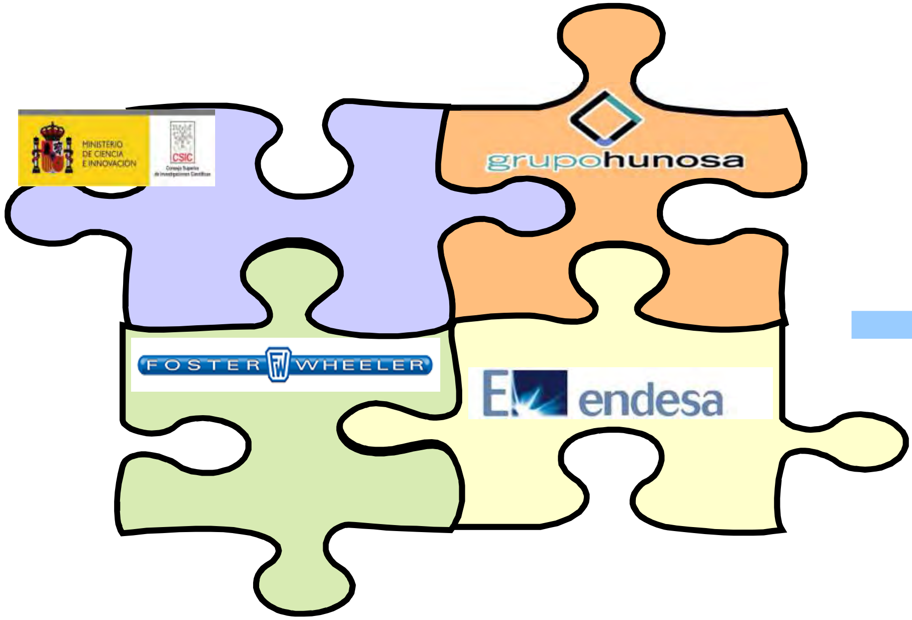
Martínez et al , 20011*Int. J. of Greenhouse Gas Control* 5, (3498-504

OUTLINE

- Postcombustion Calcium Looping concepts
- **Pilot plant results from the “CaOling” project**
  - **Testing lab scale facilities (<30 kW_{th})**
  - **Testing a 1.7 MW_{th} pilot**
- Conclusion

Consortium agreement: CaOling project

23 FEB 2007



23 APR 2009 **29 JUL 2008**

CaOling

uOttawa
lut.fi
ifk
Imperial College London

DEC 2009

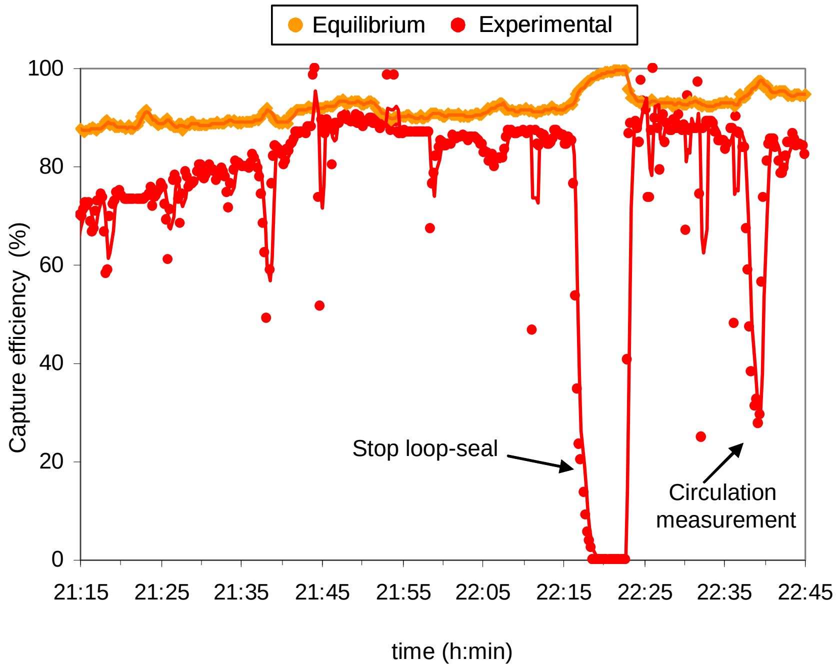
“Development of postcombustion CO_2 capture with CaO in large testing facility”

European Union 7th Framework Programme-FP7

Validation of Ca-looping for post-combustion CO_2 capture at small facilities

Small pilot plant at INCAR-CSIC (30 kWt)

CO_2 capture efficiency in CFB carbonator



Main features:

- Two CFB reactors (Height~6.5 m, diameter=100 mm)
- Electrically heated
- Continuous monitoring temperature, pressure drops, gas composition etc)
- Occasional measurement of solid circulation rates
- More than 450 hours of operation

N. Rodríguez, et al . AIChE Journal, 57, 1356-1366,2010

Results: Characterization of the carbonator reactor

CARBONATOR REACTOR MODELLING

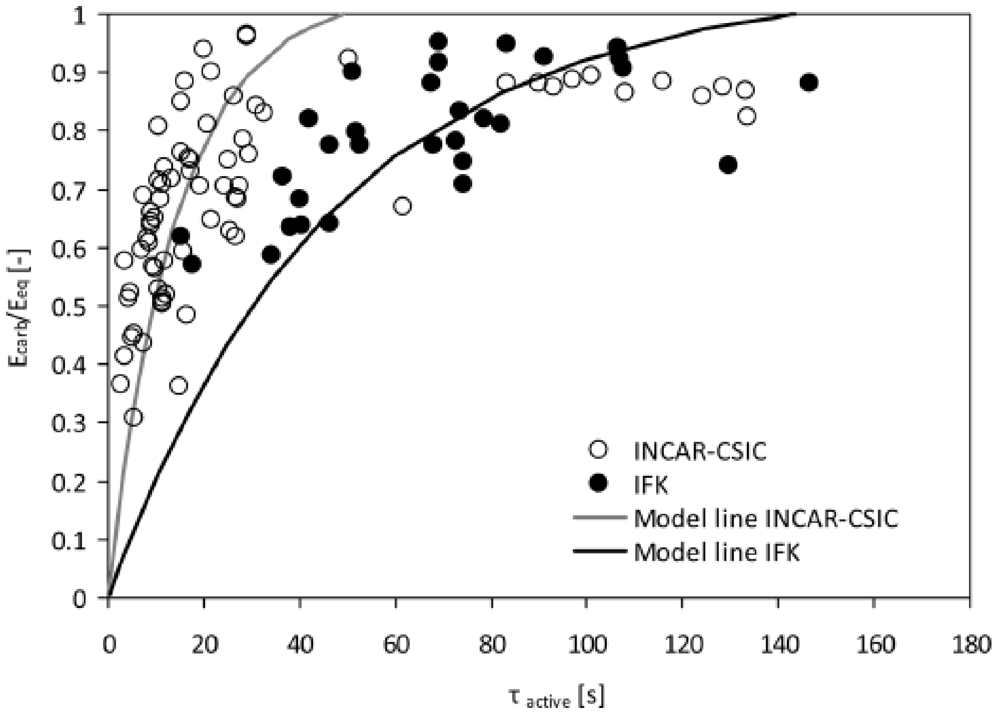
CO_2 reacting with CaO in the bed = CO_2 removed from the gas phase

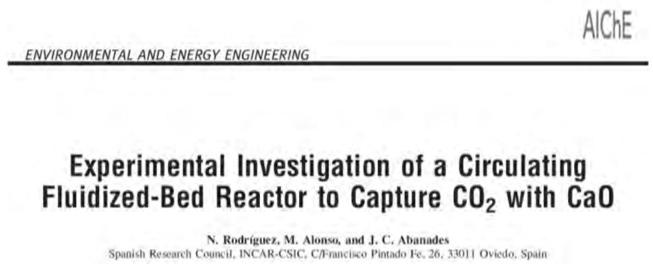
Initial assumptions carbonator reactor:

- Instantaneous and perfect mixing of the solids
- Plug flow for the gas phase

$$E_{carb} = \tau_{active} \varphi k_s \left(\overline{f_{CO2} - f_e} \right) \qquad \tau_{active} = \frac{N_{CaO}}{F_{CO2}} f_a X_{ave}$$

EXPERIMENTAL RESULTS FROM THE SMALL FACILITIES AT INCAR-CSIC AND IFK (10's kW)



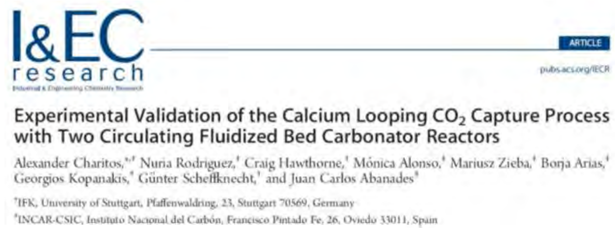

AIChE

ENVIRONMENTAL AND ENERGY ENGINEERING

Experimental Investigation of a Circulating Fluidized-Bed Reactor to Capture CO_2 with CaO

N. Rodríguez, M. Alonso, and J. C. Abanades

Spanish Research Council, INCAR-CSIC, C/Francisco Pintado Fe, 26, 33011 Oviedo, Spain


I&EC research

ARTICLE

pubs.acs.org/IECR

Experimental Validation of the Calcium Looping CO_2 Capture Process with Two Circulating Fluidized Bed Carbonator Reactors

Alexander Charitos,[*,†] Nuria Rodriguez,[‡] Craig Hawthorne,[†] Mónica Alonso,[‡] Mariusz Zieba,[†] Borja Arias,[‡] Georgios Kopanakis,[†] Günter Scheffknecht,[†] and Juan Carlos Abanades[‡]

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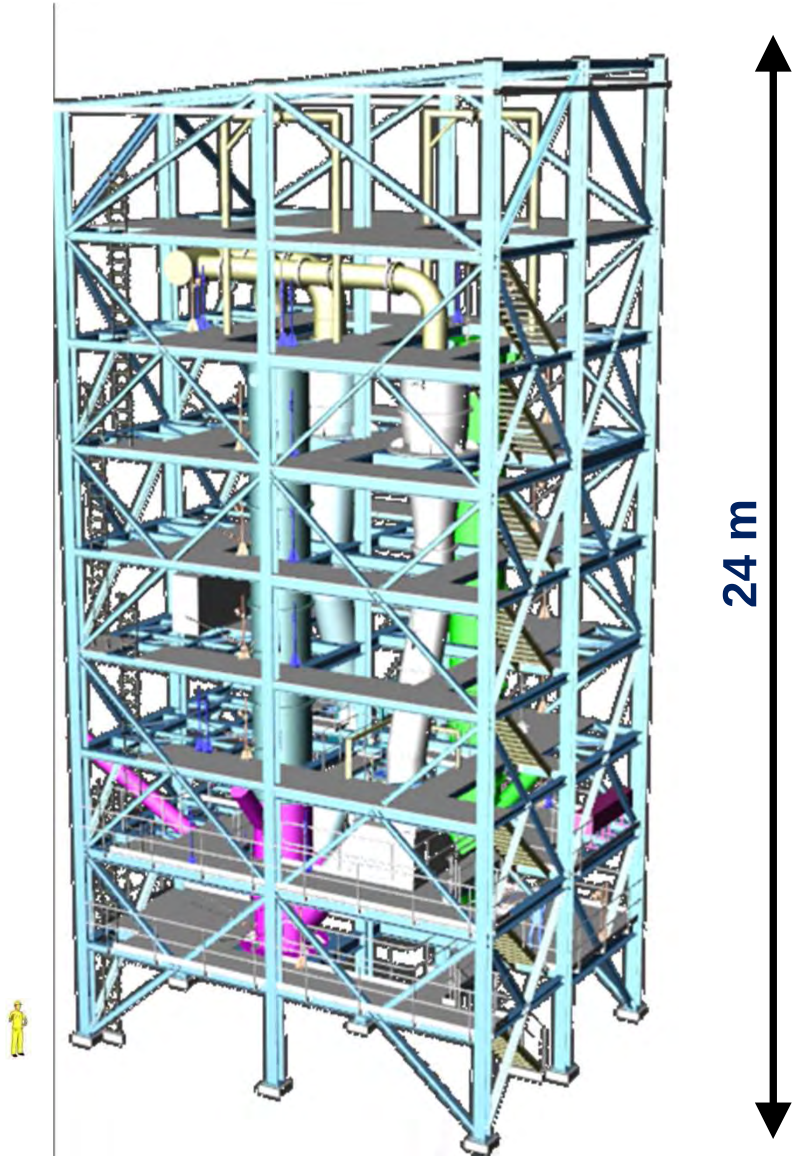
Scaling up: La Pereda CO_2 Ca-L pilot plant

CSIC lab-plant

2008: 30 kWt

x 60



2011: 1,7 MWt

La Pereda CO_2 pilot plant: Current status

Status of the pilot plant

-Building finished in September 2011

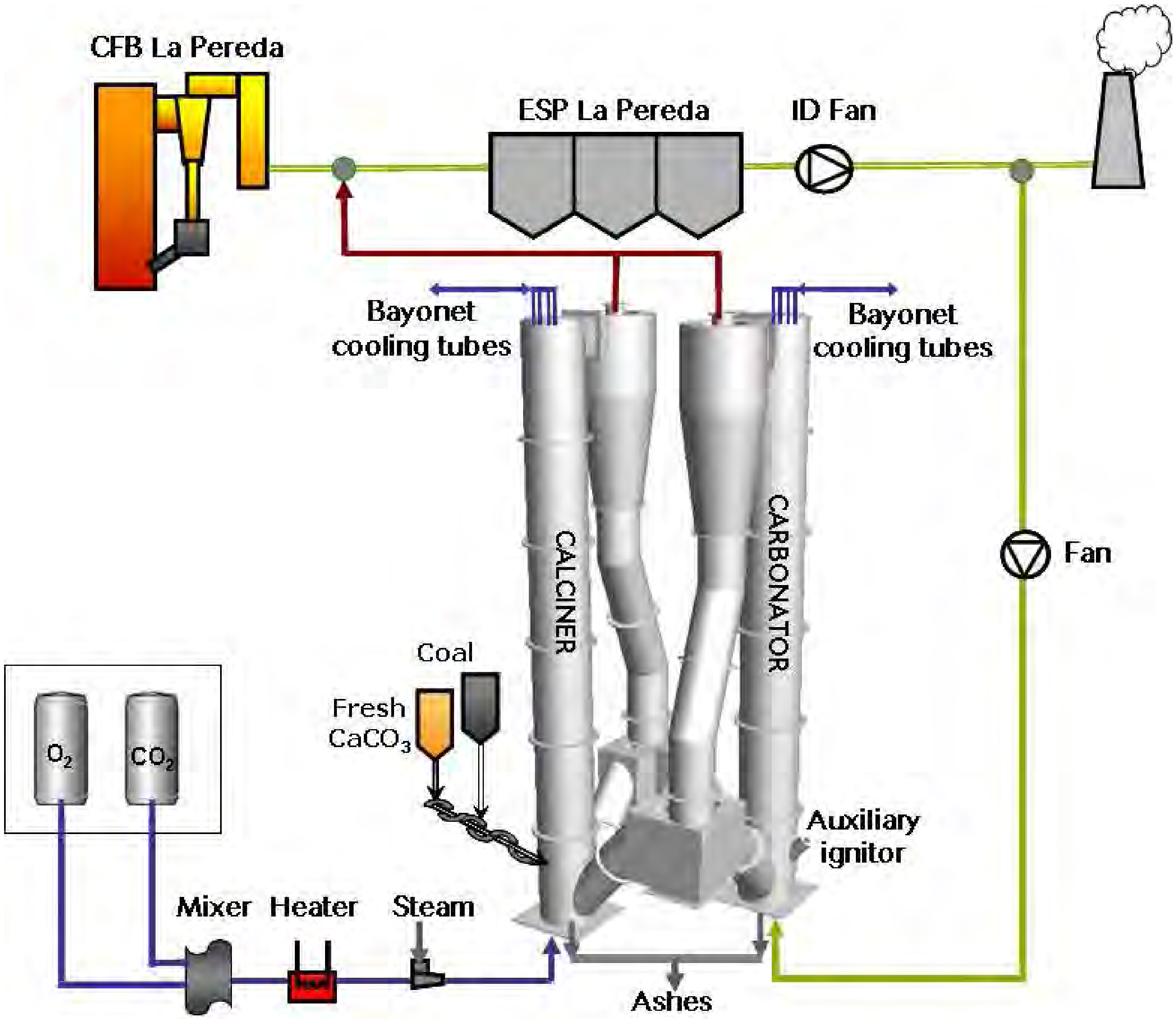
-Start of cold commissioning: October 2011

- Start of hot commissioning: January 2012

- Operational hours with coal combustion (dual fluidized bed mode): ~ 1500 h

- Operational hours in CO_2 capture mode : ~ 310 h (approximately 120 h with the calciner working under oxy-fuel conditions)

La Pereda CO_2 pilot plant: Power plant integration



RESULTS

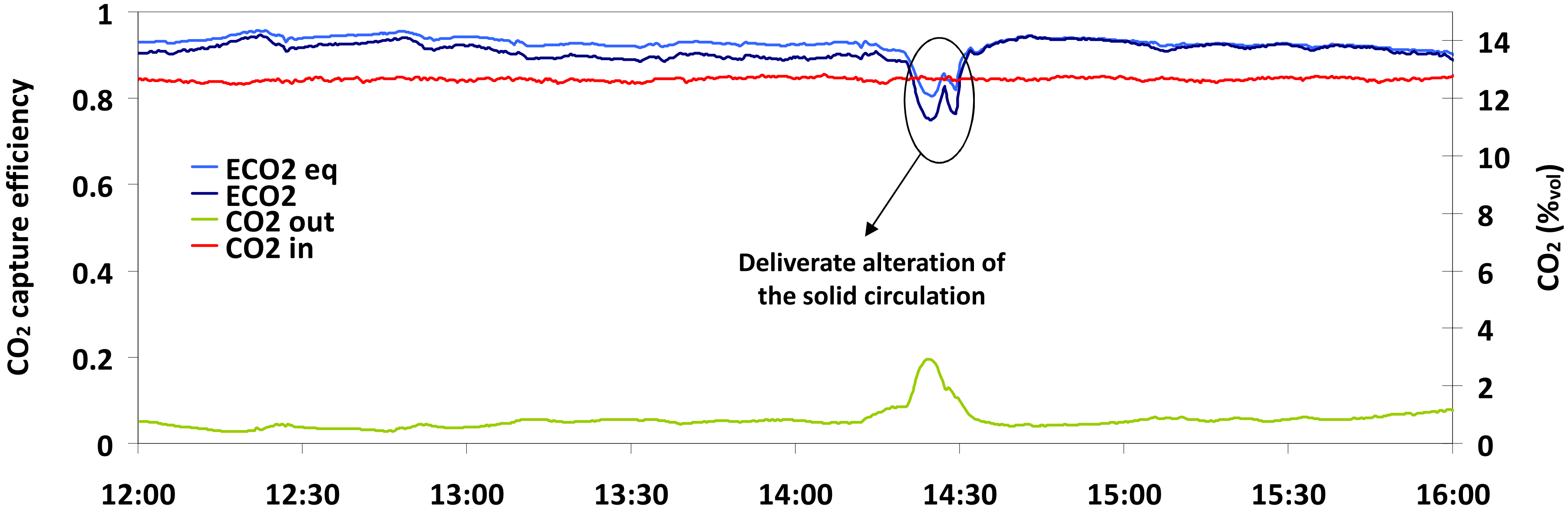
Range of conditions during the CO_2 capture test:

Carbonator temperature (ºC)	600-715
Carbonator superficial gas velocity (m/s)	2.0-5.0
Inlet CO_2 volume fraction to the carbonator	0.12-0.14
Inlet SO_2 concentration to the carbonator (mg/m^3)	100-250
Inventory of solids in the carbonator (kg m^{-2})	100-1000
Maximum CO_2 carrying capacity of the solids	0.10-0.70
Calciner temperature (ºC)	820-950 ºC
Inlet O2 volume fraction to the calciner	0.21-0.35
Inlet CO2 volume fraction to the calciner	0-0.75
CO_2 capture efficiency	0.4-0.95
SO_2 capture efficiency	0.95-1.00

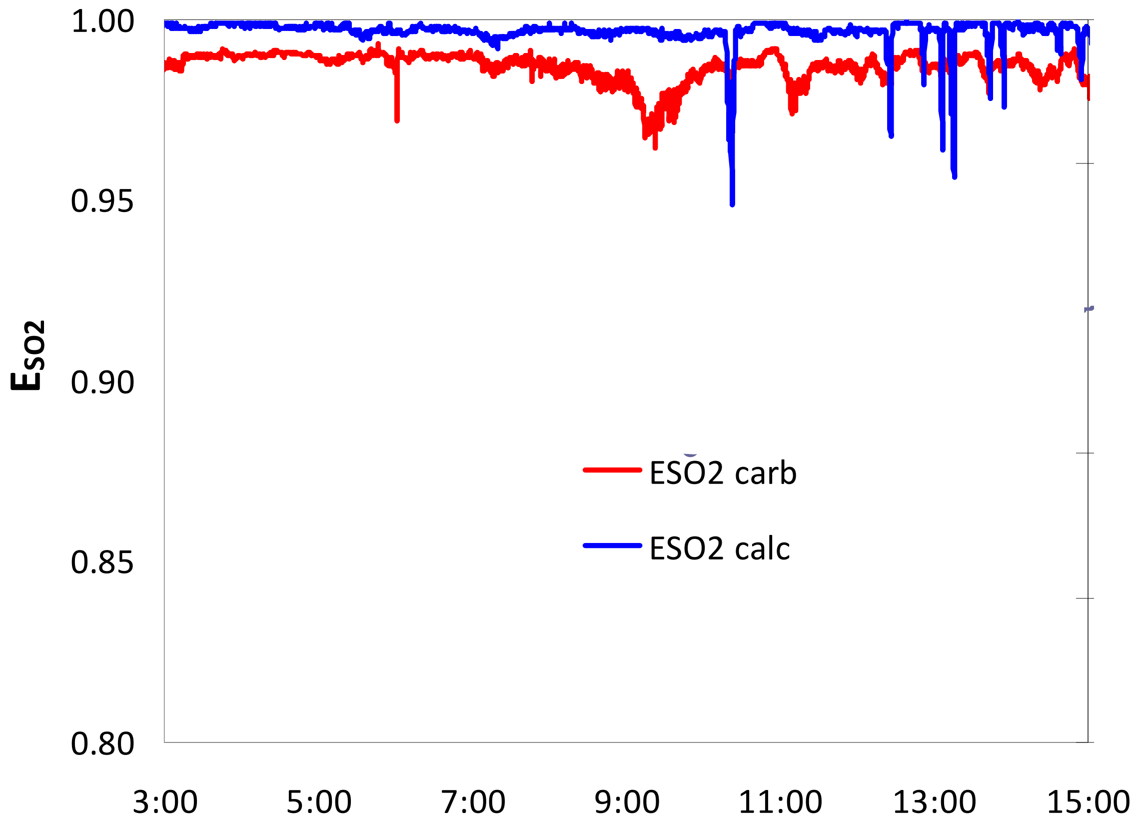
Results from the 1.7 MWth CaL pilot plant of la Pereda

Typical examples of steady state tests

- Inventory of solids in carbonator = 300-400 kg/m2
- Average carbonator temperature= 660 ºC
- Xave = 0.3-0.1

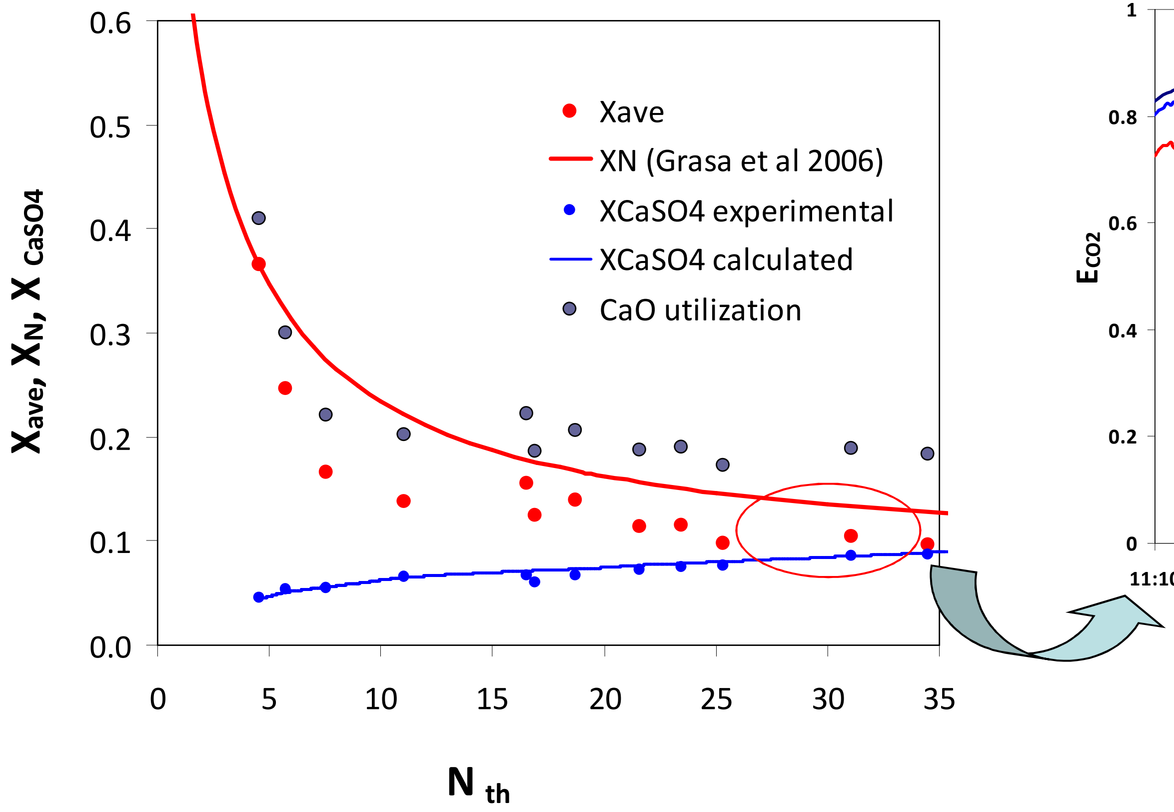


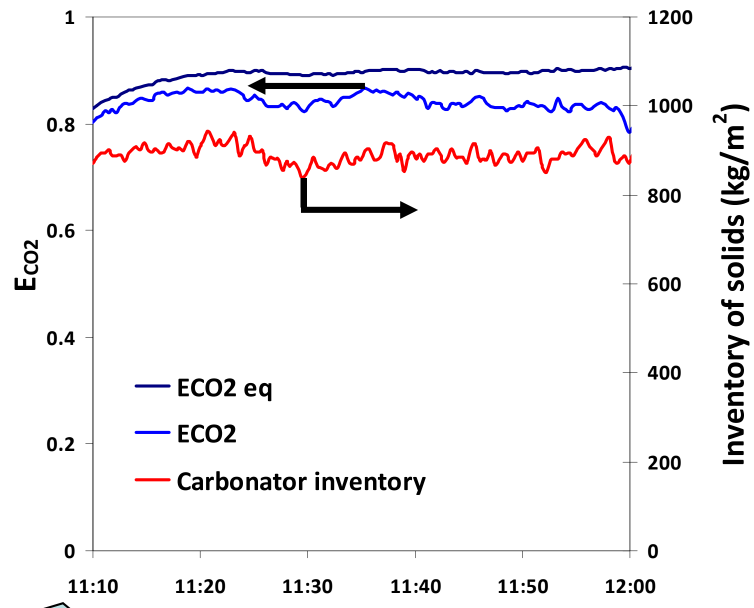
SO_2 capture in the Ca-looping facility



Results from the 1.7 MWth CaL pilot plant of la Pereda

Evolution of sorbent utilization with "lifetime" of particles in the system





Number of times that the inventory of CaO is carbonated up to the maximum CO2 carrying capacity

$$N_{th} = \int_0^t \frac{F_{CO2}\, E_{carb(t)}}{N_{Ca}\, X_{ave}}\, dt$$

MAIN CONCLUSION

- **A flexible experimental facility is in operation in La Pereda Power Plant aiming to validate the technology in the 1MW's size**
- **CO_2 capture efficiencies over 90% achievable in a CFB carbonator reactor operating with "standard" CaO solids, bed inventories, gas velocities, solid circulation rates and reaction conditions in the carbonator and calciner reactors (oxyfuel coal combustion)**
- **SO_2 capture in the CFB carbonator is over 95%**
- **The concept of post-combustion Ca-looping in continuous mode of operation has been successfully proven with two interconnected CFBCs at the MWth scale**

CSIRO PCC Science & Techonology Seminar
26 March, CSIRO Energy Centre, Newcastle

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

“Ca-looping for post-combustion CO_2 capture"

Borja Arias Rozada

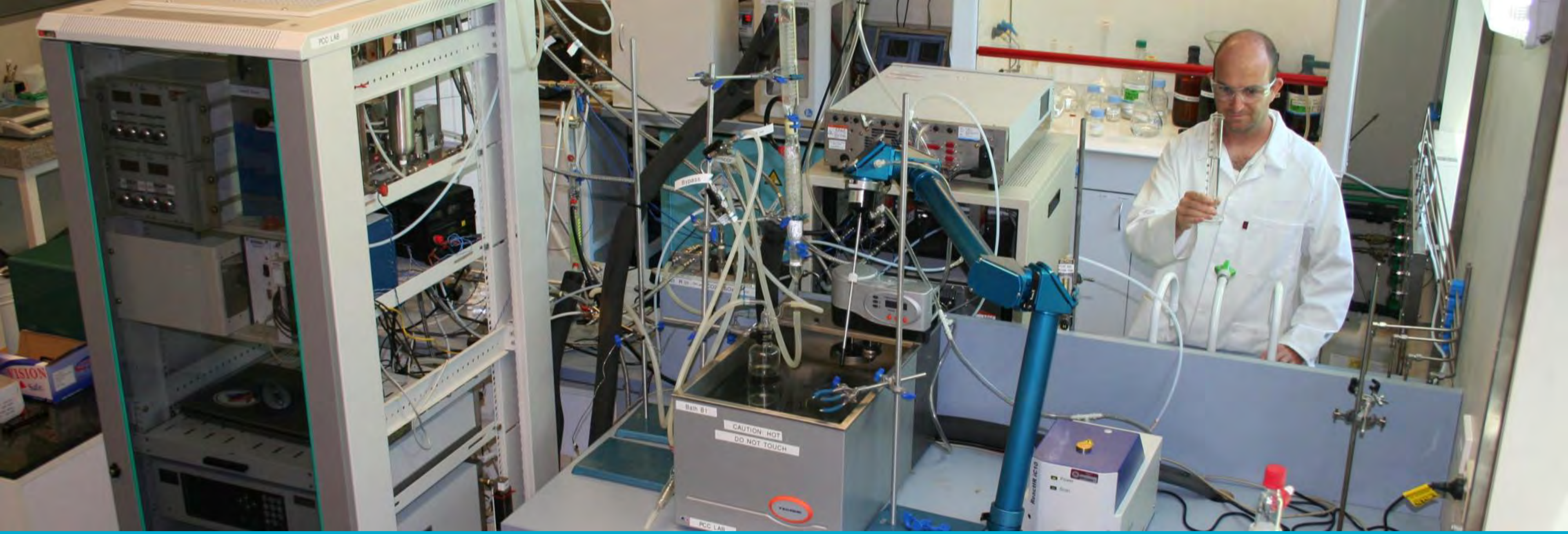
borja@incar.csic.es

Thanks for your attention

SEVENTH FRAMEWORK PROGRAMME

www.caoling.eu

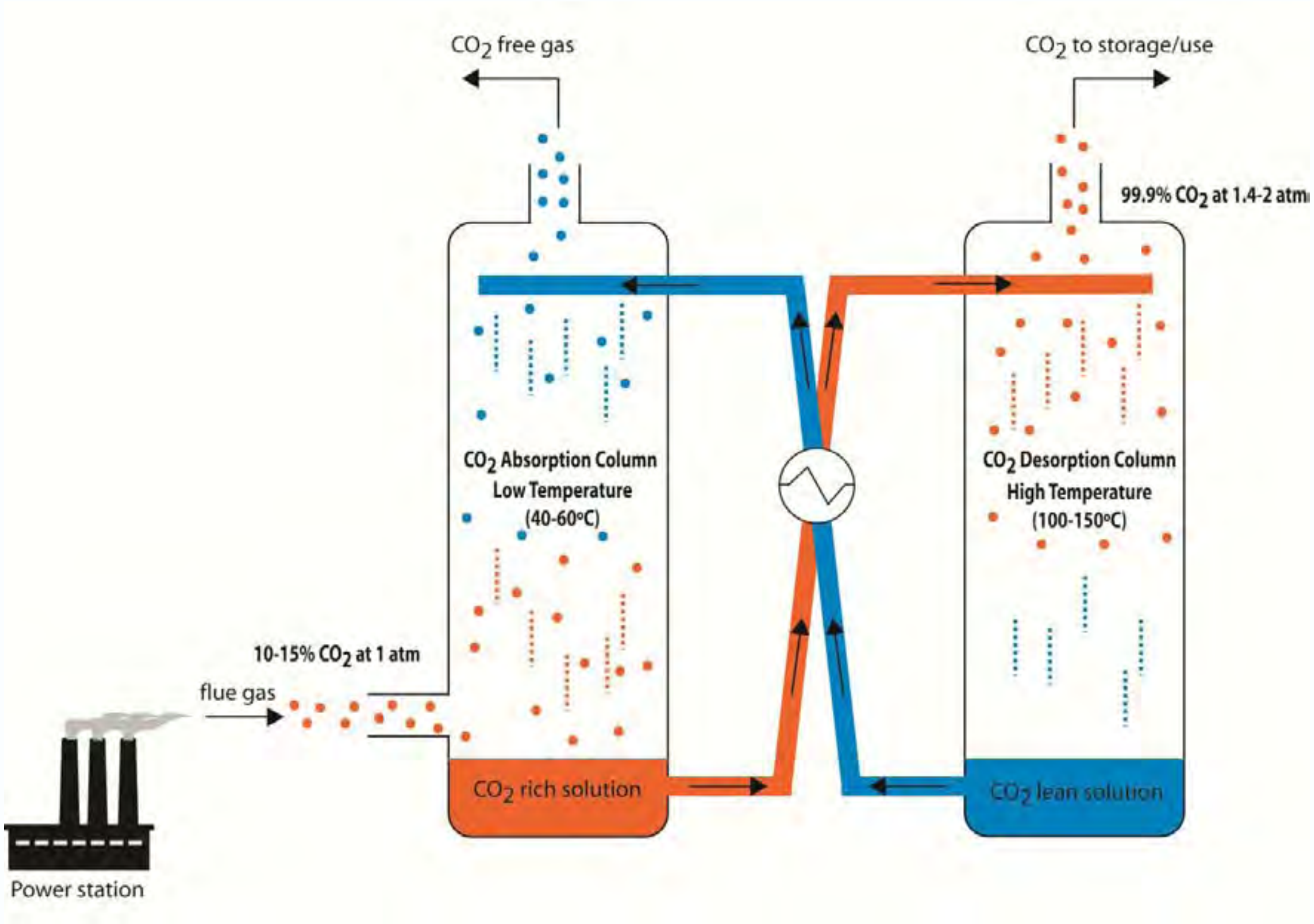
The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under GA 241302-CaOling Project and from Asturian PCTI.



Progress in development of liquid absorbent PCC technologies at CSIRO

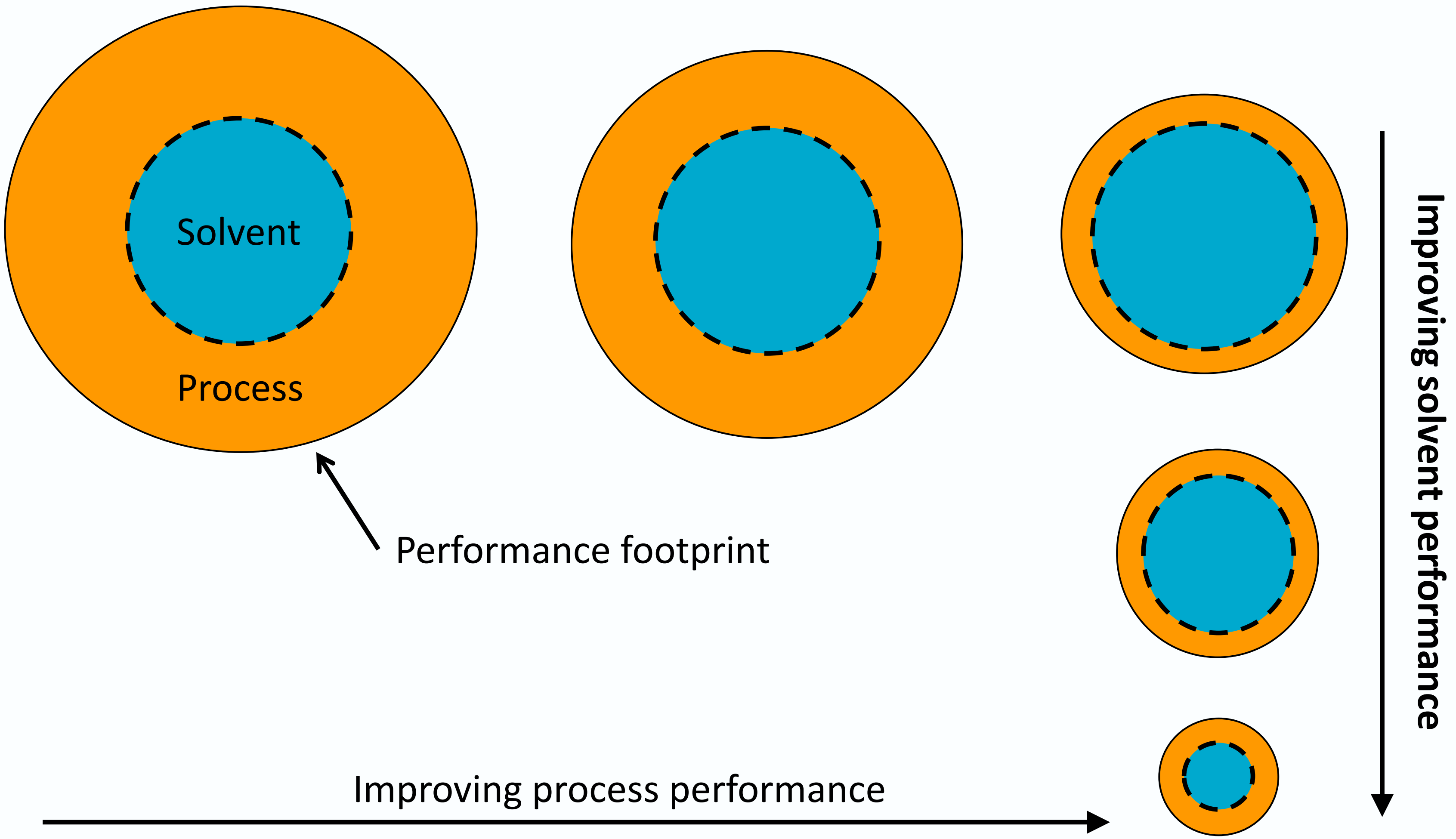
Graeme Puxty | Research Scientist
26th March, 2013

Post combustion CO_2 capture



Why do we care about the solvent?

The solvent defines the performance limits that can be achieved



The science challenges for solvent development

The flue gas environment is a challenging one for a solvent:

- CO_2 needs to be separated from a mixture of N_2, O_2, SO_x, NO_x and particulates
- As part of the process the solvent is continually heated and cooled (40-120°C)
- The solvent is in contact with steel

In the face of these challenges our goal is to develop solvents that deliver better performance in the following ways:

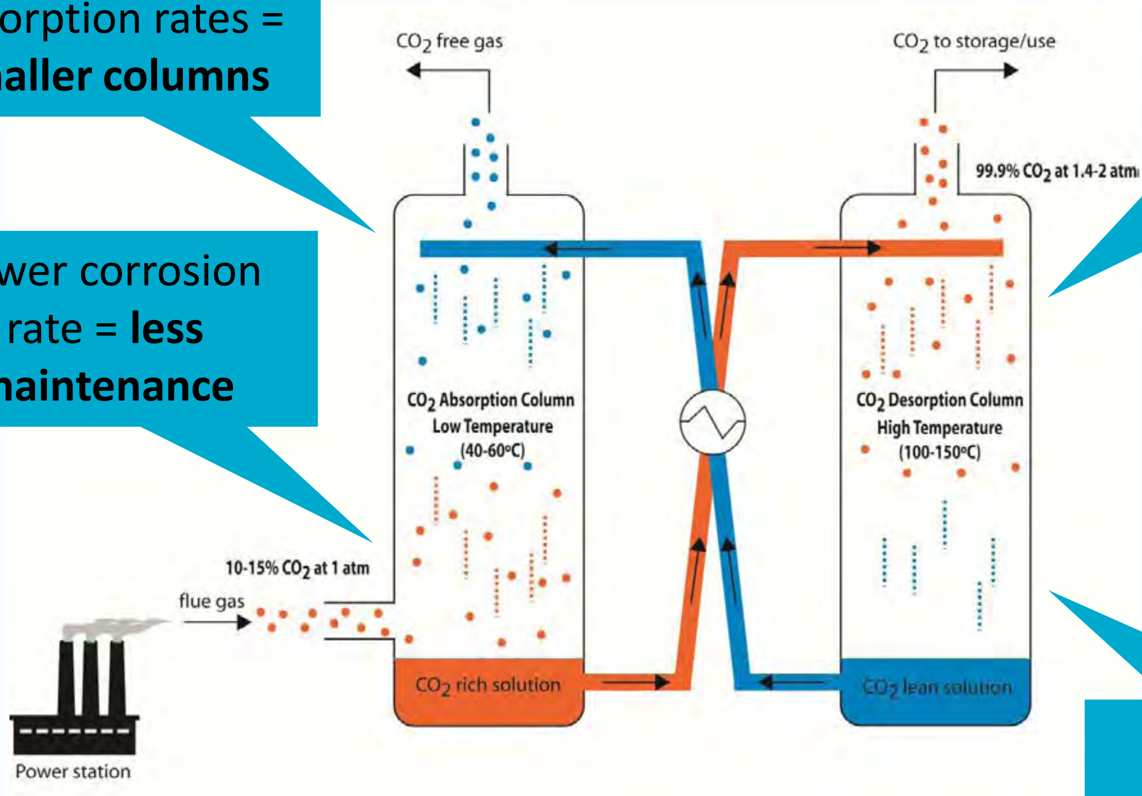
The goals for improved solvent performance

Faster CO_2 absorption rates = **smaller columns**

Lower corrosion rate = **less maintenance**

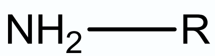
Lower rates of thermal and oxidative degradation = **longer solvent life**

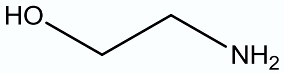
Larger CO_2 cyclic capacity = **lower energy requirement**



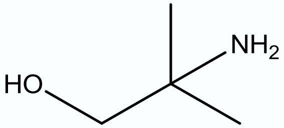
Types of solvents

Primary Amines



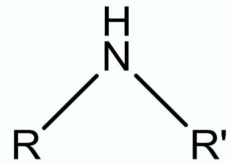


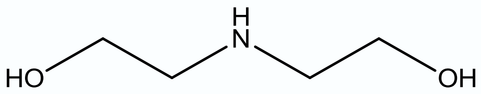
MonoEthanolAmine (MEA)



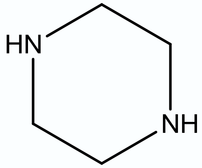
2-Amino-2-Methyl-1-Propanol (AMP)

Secondary Amines



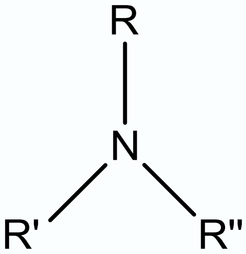


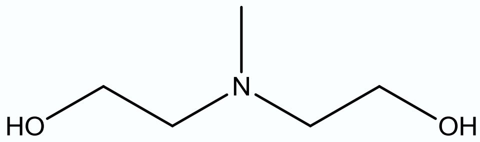
DiEthanolAmine (DEA)



PiperaZine (PZ)

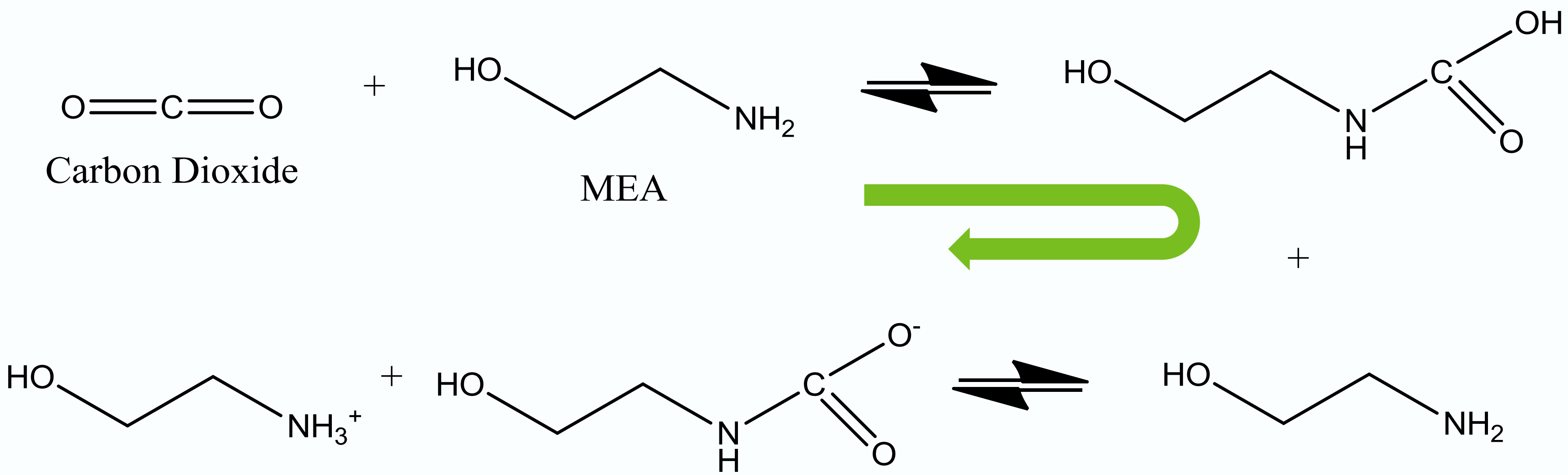
Tertiary Amines





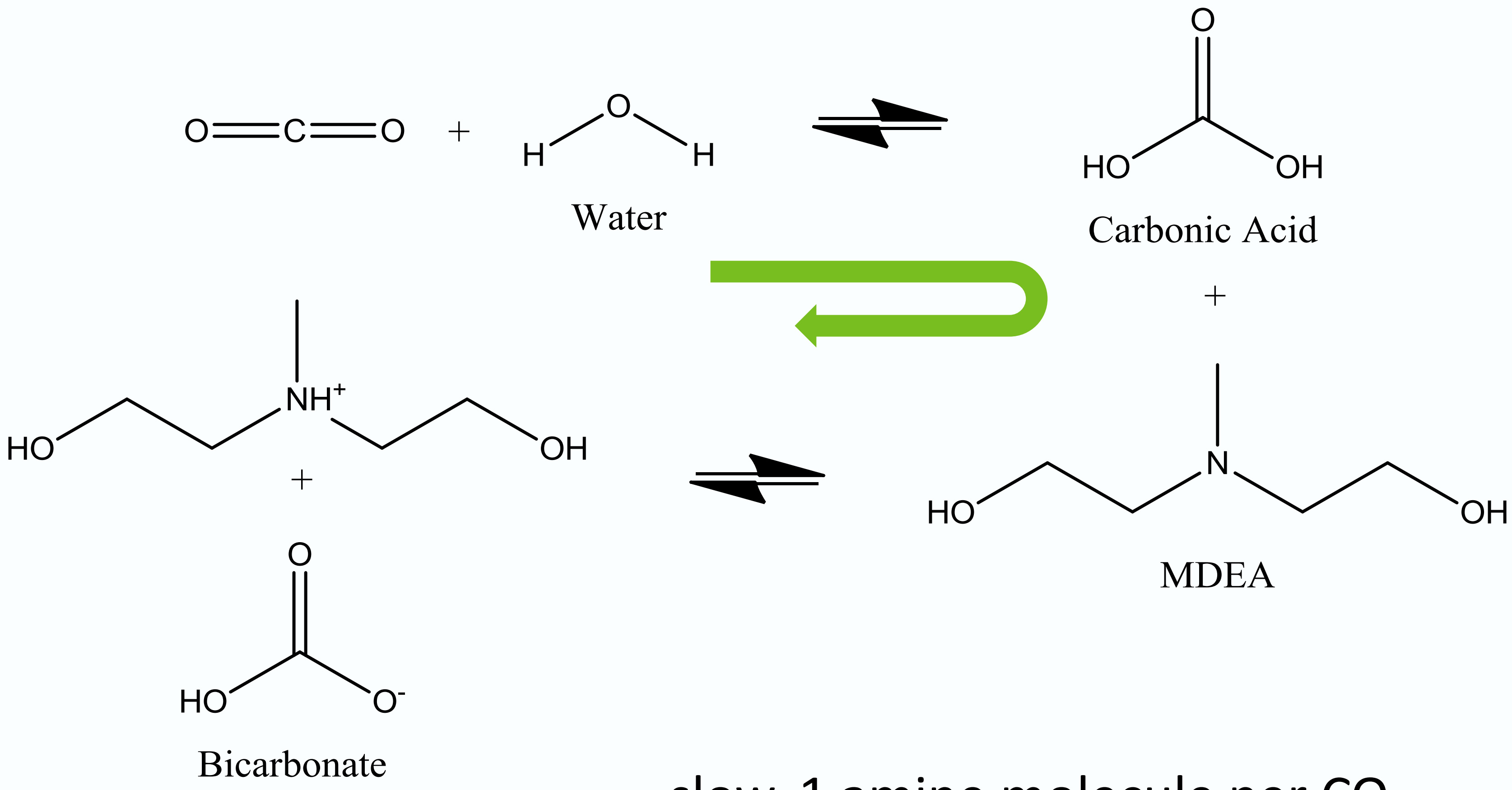
MethylDiEthanolAmine (MDEA)

Solvent chemistry – primary and secondary amines



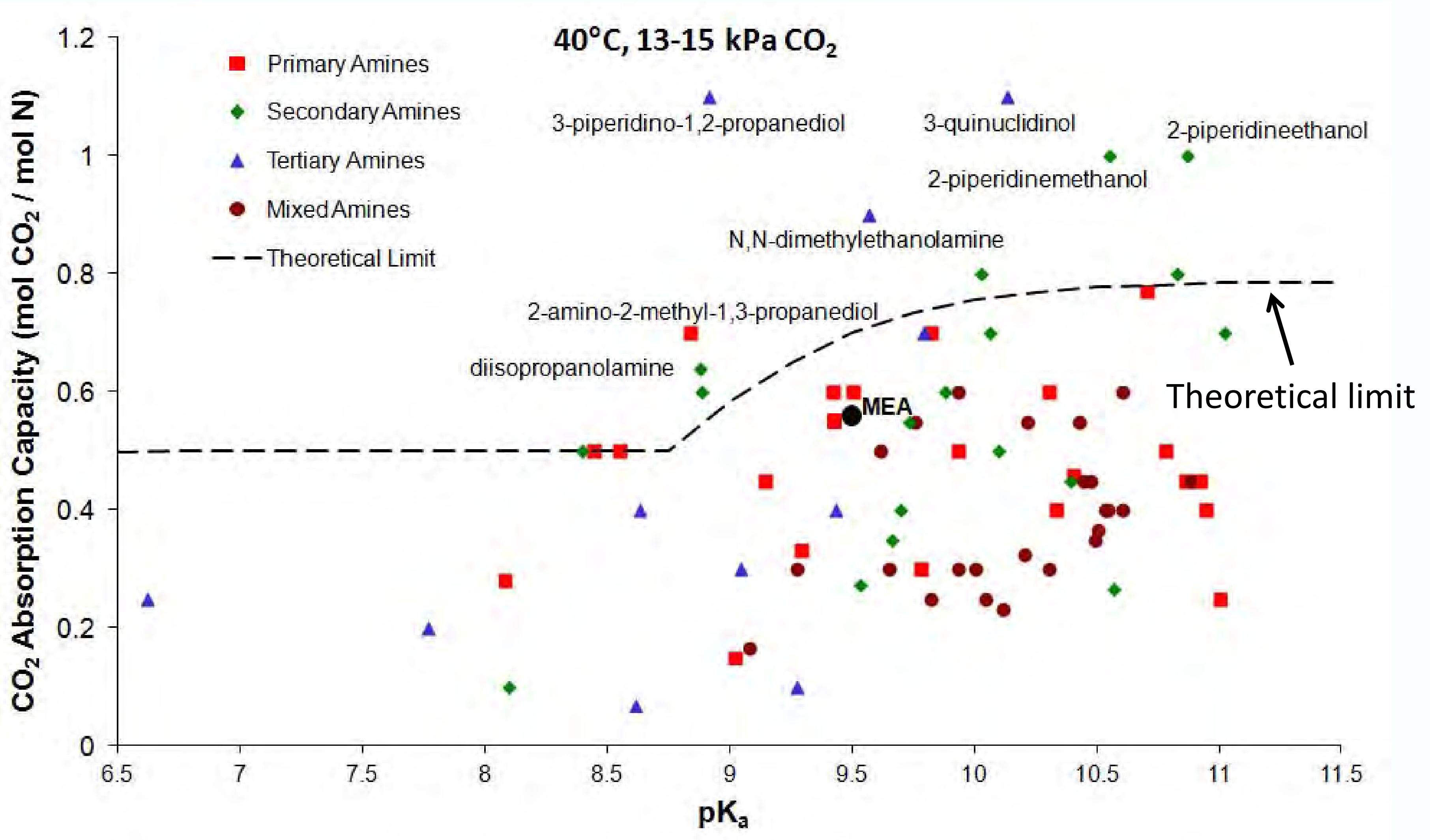
fast, 2 amine molecules per CO_2

Solvent chemistry – tertiary and hindered amines

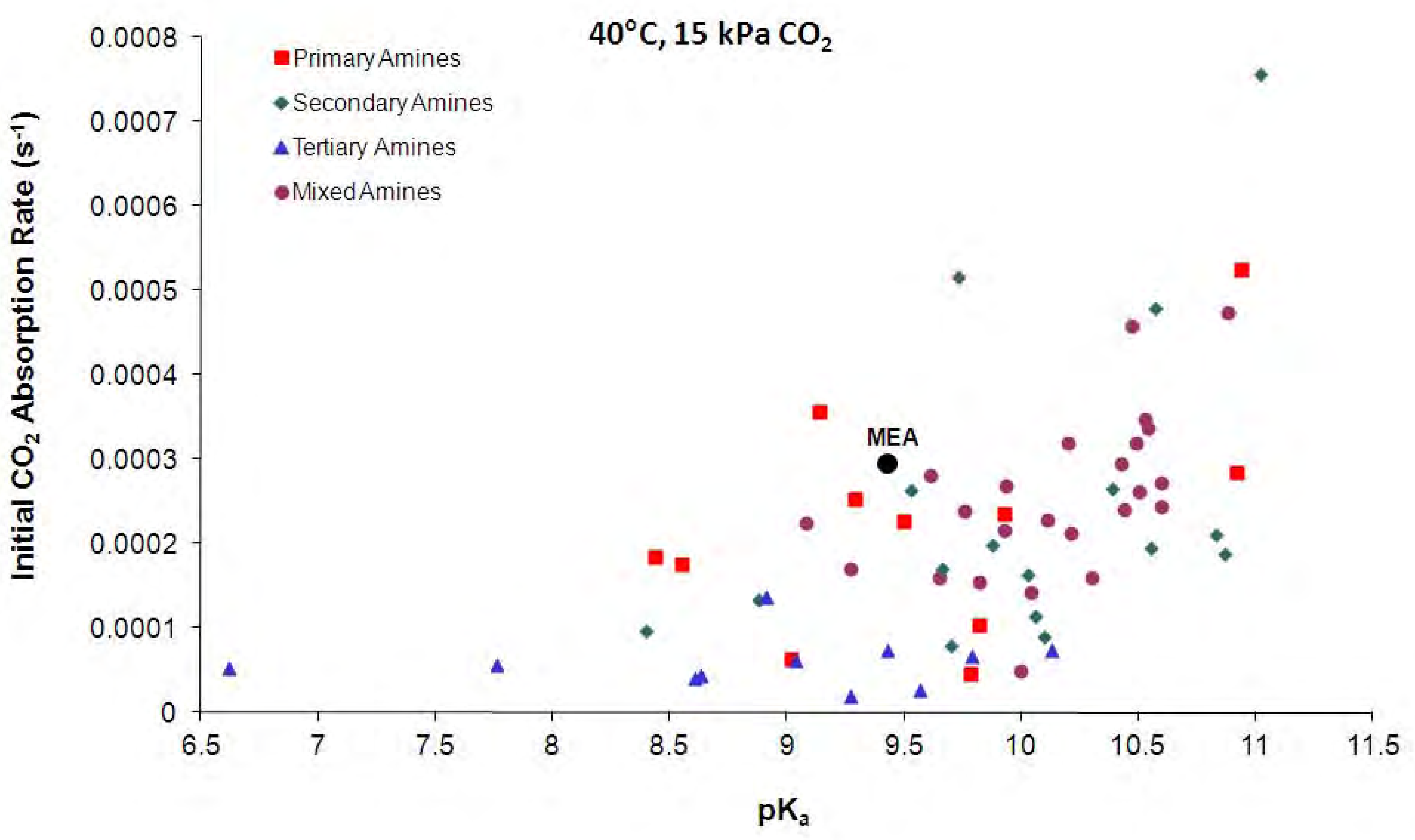


slow, 1 amine molecule per CO_2

Solvent screening – measuring CO_2 absorption capacity



Solvent screening – measuring initial CO_2 absorption rate



Screening study - outcome

Over 100 amines screened for CO_2 absorption capacity and initial absorption rate at a single set of conditions (40°C, 13-15 kPa CO_2)

A combination of model predictions and experimental results allowed identification of **7 amines that performed better than expected**

Results have been **patented and published**:

M. I. Attalla, G. D. Puxty, A. W. Allport, M. Bown, Q. Yang and R. C. Rowland, Carbon dioxide capturing process, involves contacting carbon dioxide containing gas stream with aqueous alkanolamine solution, where alkanolamine solution is selected from group consisting of Tricine and salts. WO2009121135-A1 (2009).

G. Puxty, R. Rowland, A. Allport, M. Attalla, Q. Yang, M. Bown, R. Burns and M. Maeder, Carbon dioxide post combustion capture: a novel screening study of the carbon dioxide absorption performance of 76 amines. *Environmental Science & Technology*, 43 (2009) 6427-6433.

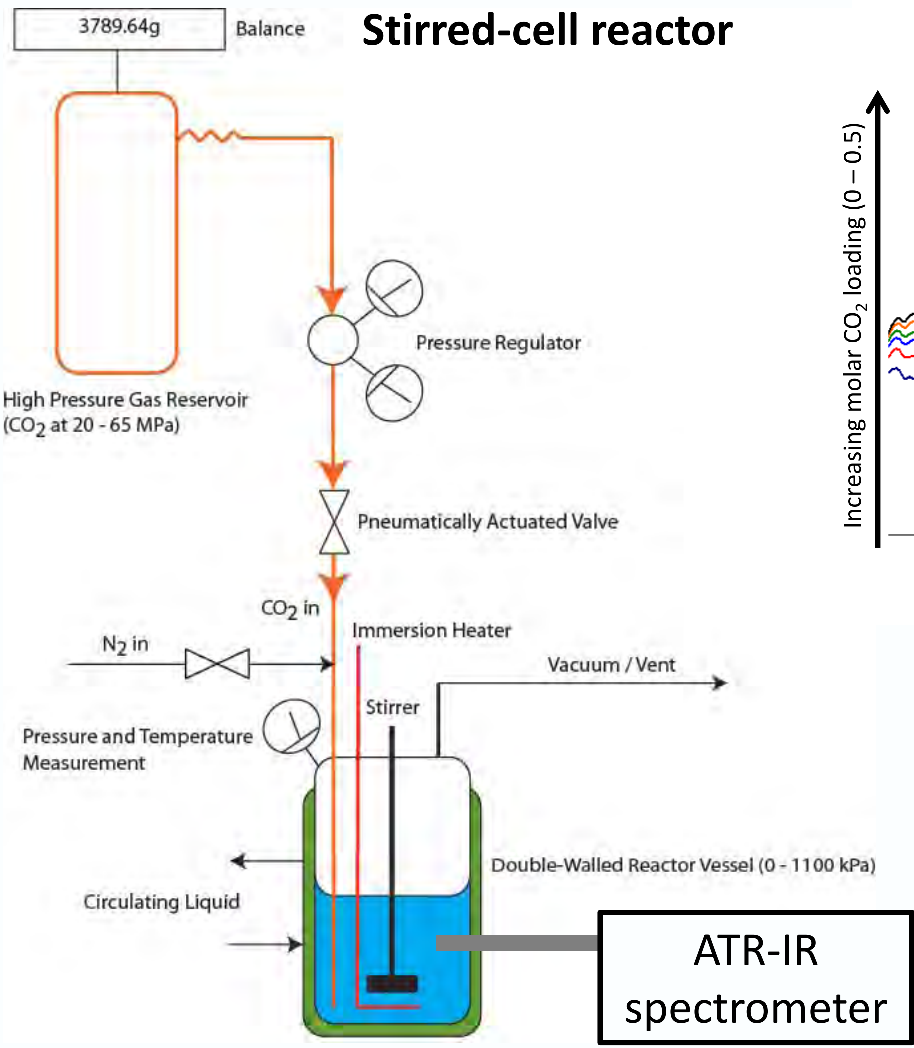
Detailed characterisation

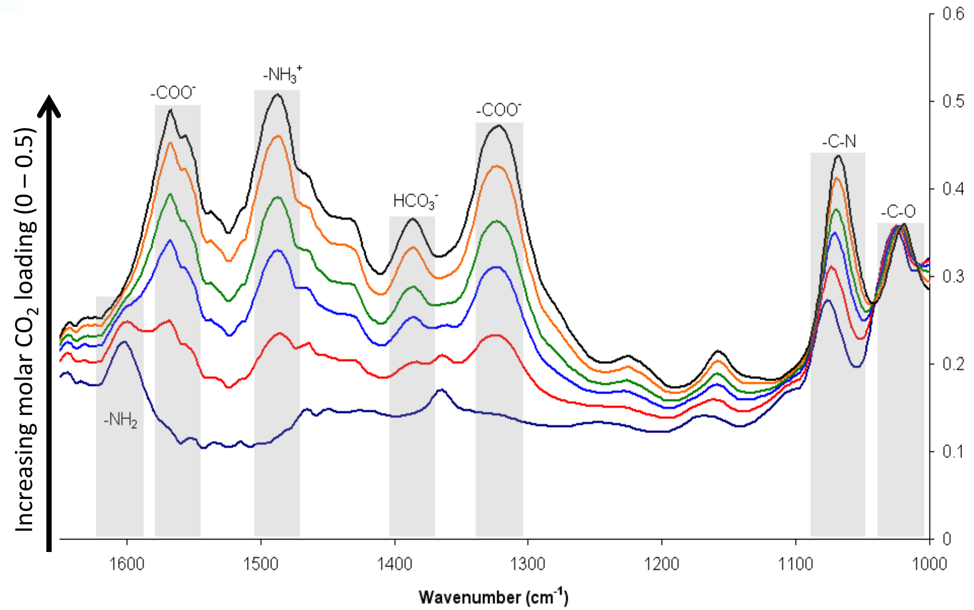
To understand the factors responsible for the performance of particular absorbents requires understanding of:

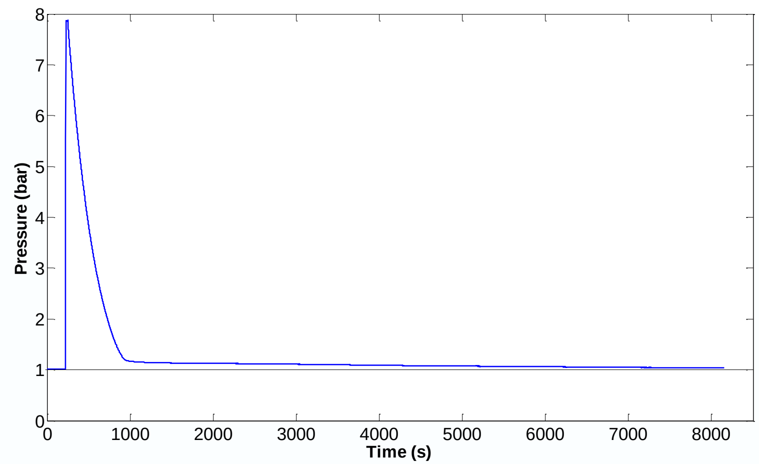
- CO_2 absorption capacity as a function of temperature and pressure
- CO_2 mass transfer as a function of temperature, pressure and loading
- Chemical reaction kinetics and thermodynamics
- Physical properties

Detailed measurements of capacity

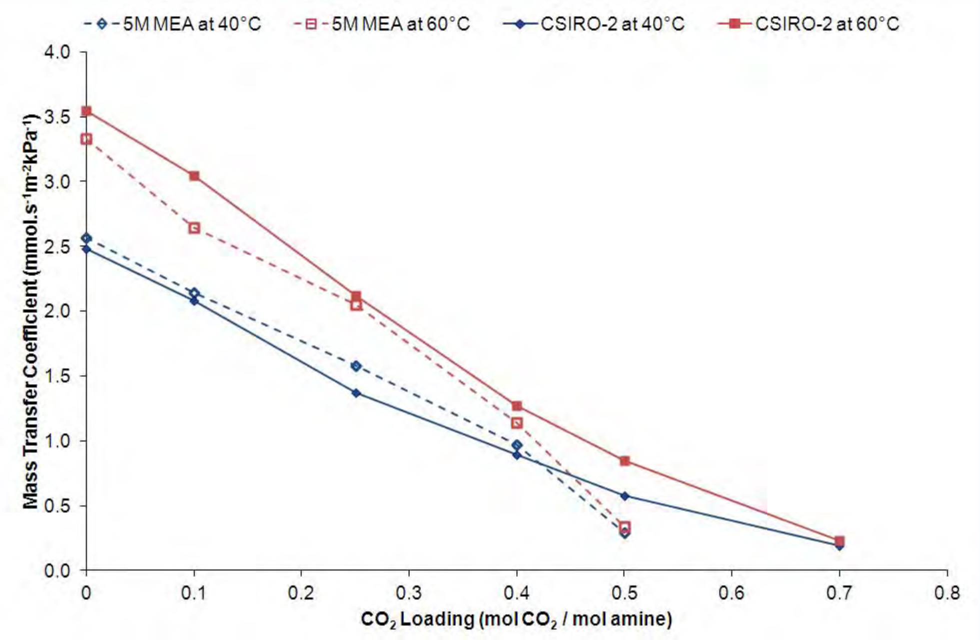
Stirred-cell reactor





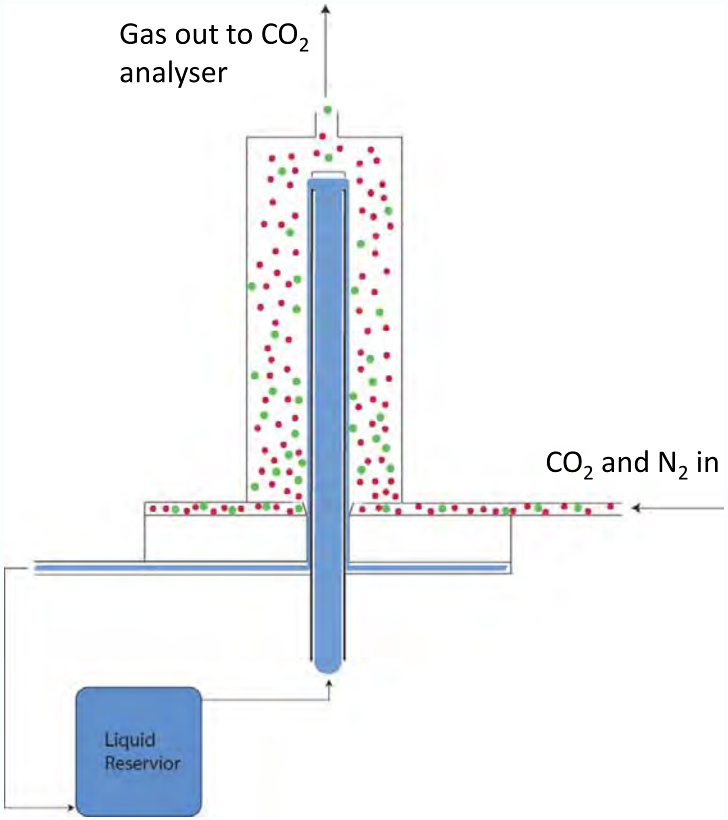


Detailed measurements of mass transfer



$$N_{CO2} = K_G(P_{CO2} - P^*_{CO2})$$

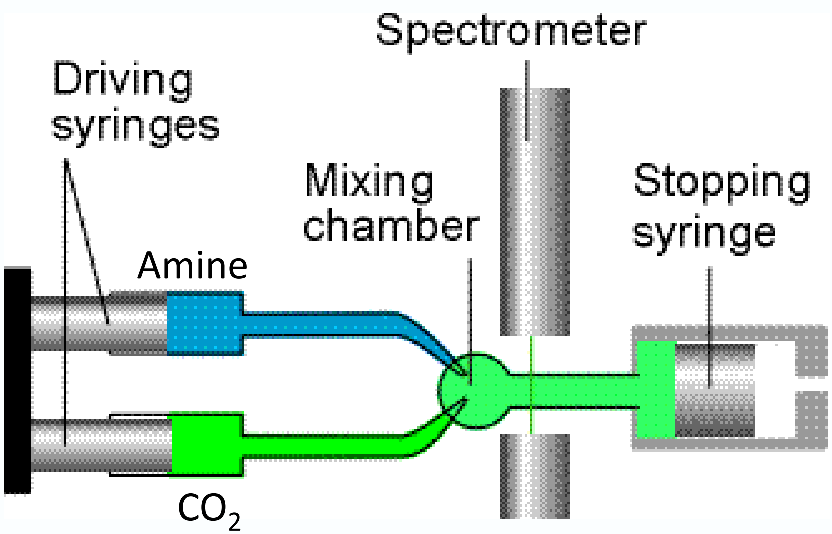
Wetted-wall reactor

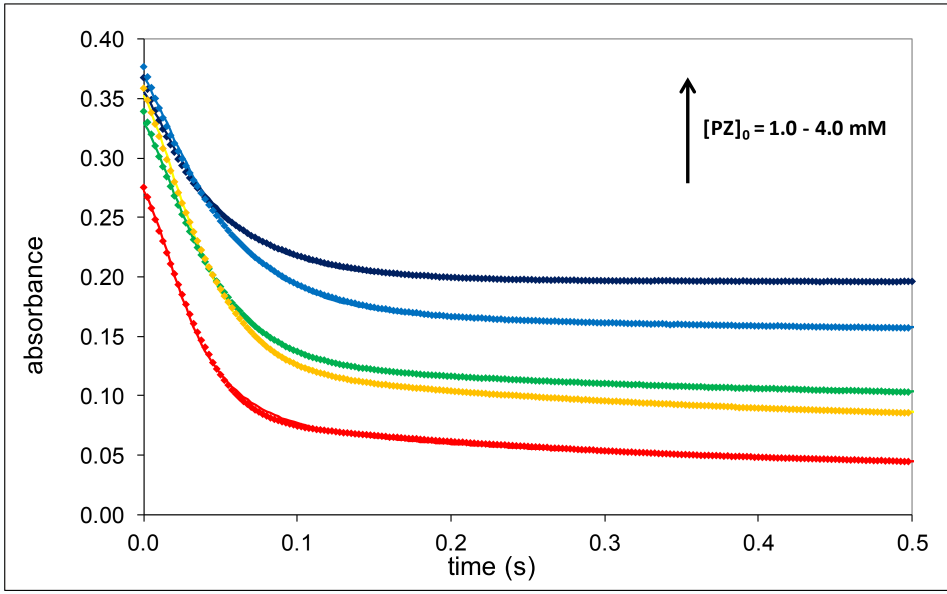


Chemical reaction kinetics and thermodynamics

Stopped-flow and UV-visible spectroscopy used to determine CO_2-amine reaction kinetics

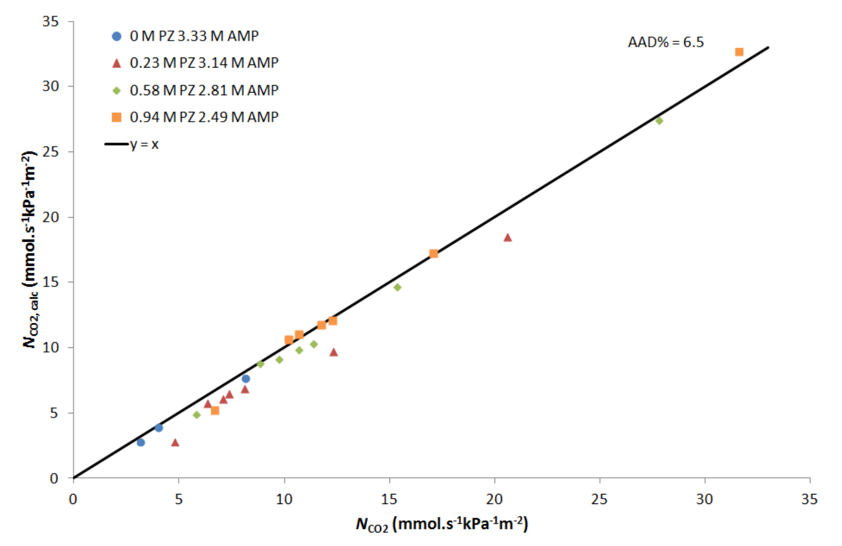
^{1}H-NMR used to determine CO_2-amine reaction equilibria

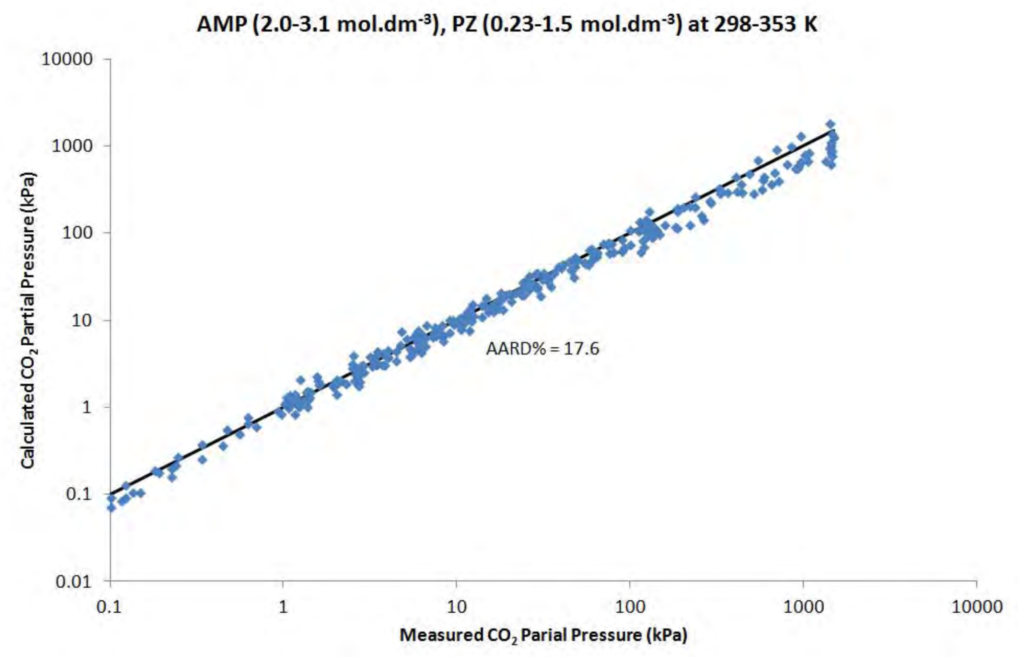




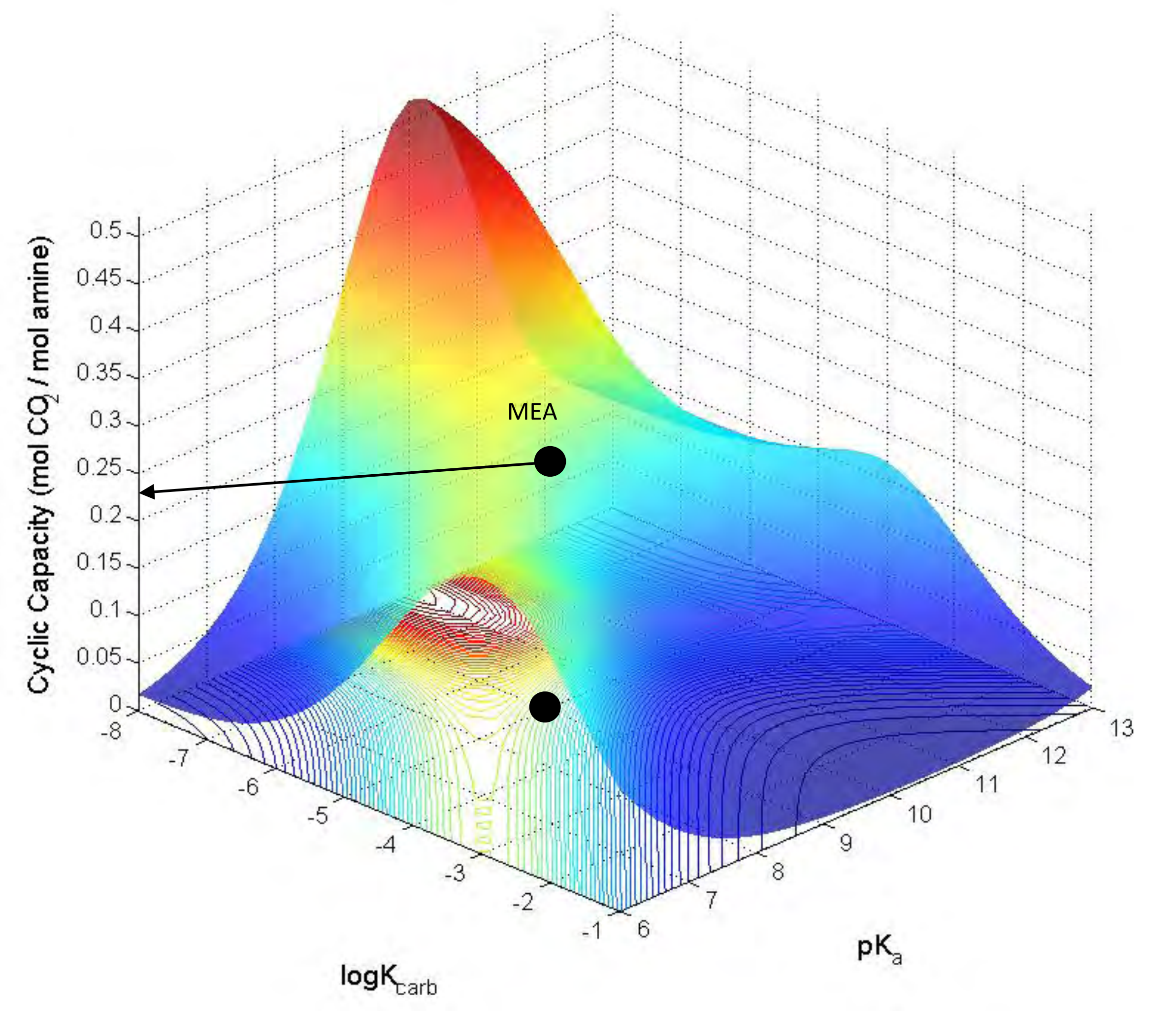
Modelling of chemical behaviour

Once the chemical and physical properties are known we can model absorption behaviour across a range of conditions including as mixtures





Modelling of chemical behaviour



What we learnt - Solvent formulation

No single *known* amine can deliver optimal performance due to a trade-off between absorption capacity and absorption rate

Detailed characterisation allows solvent formulations, or amine mixtures, to be designed that yield better performance than any single amine and tuned to the application

Fast reaction

$$CO_2 + R_1R_2N\text{-}H \longleftrightarrow R_1R_2N\text{-}COO^- + H^+$$

$$H^+ + R_1R_2R_3N \longleftrightarrow R_1R_2R_3N\text{-}H^+$$

Proton sink

ΔH Large pK_a shift on heating

CSIRO solvent formulations

Four new CSIRO solvent formulations:

CSIRO-1 Designed to minimise the solvent regeneration energy requirement while maintaining reasonable absorption rates

CSIRO-2 Designed to maximise absorption rate while maintaining reasonable regeneration energy requirements

CSIRO-3 Designed to have increased absorption rates and better physical properties than CSIRO-1 while maintaining low regeneration energy requirements

CSIRO-4 Under development but will hopefully deliver increased absorption rates with a similar energy demand to CSIRO-3

Estimating solvent performance

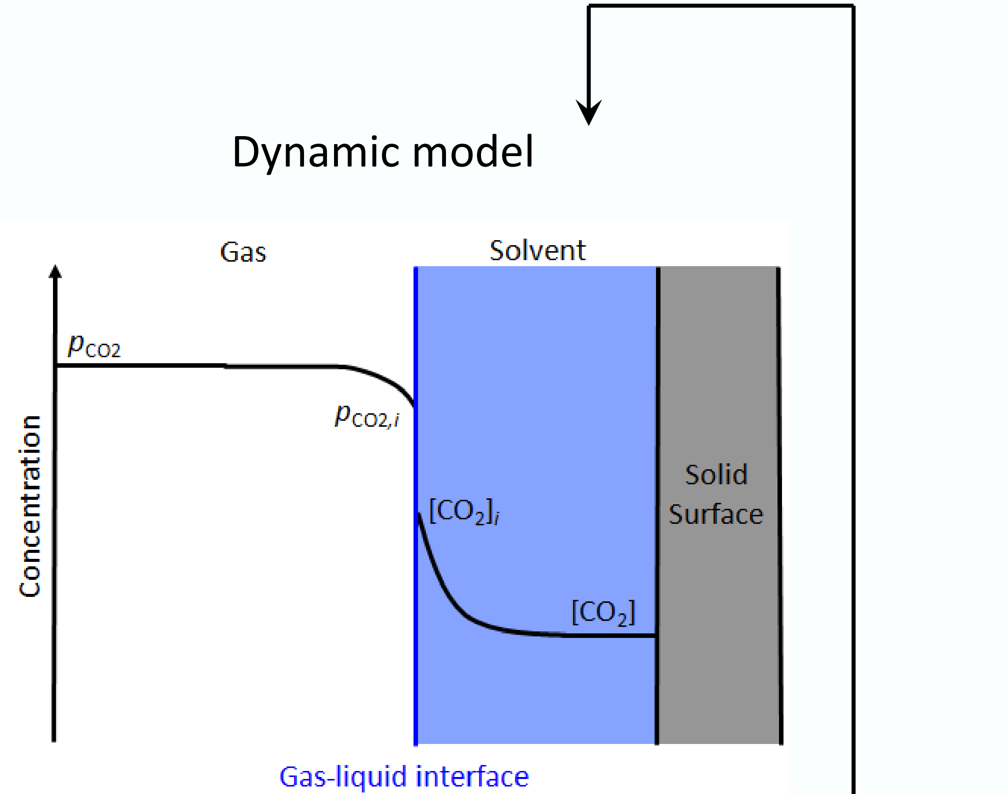
To allow a **fair comparison** solvent performance needs to be evaluated at optimal operating conditions

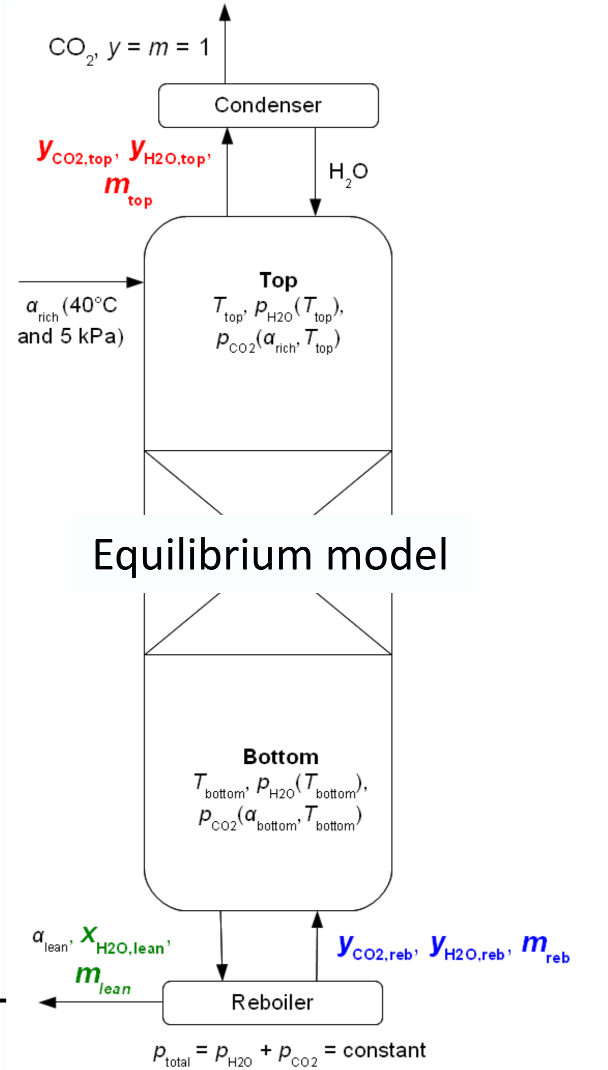
Estimate the **optimal energy requirement** using an equilibrium model:

- Rich loading (α_{rich}) is fixed at 40°C for 5 kPa CO_2
- Optimise stripper bottom temperature and lean loading (α_{lean}) for minimum reboiler energy requirement (assume isobaric)

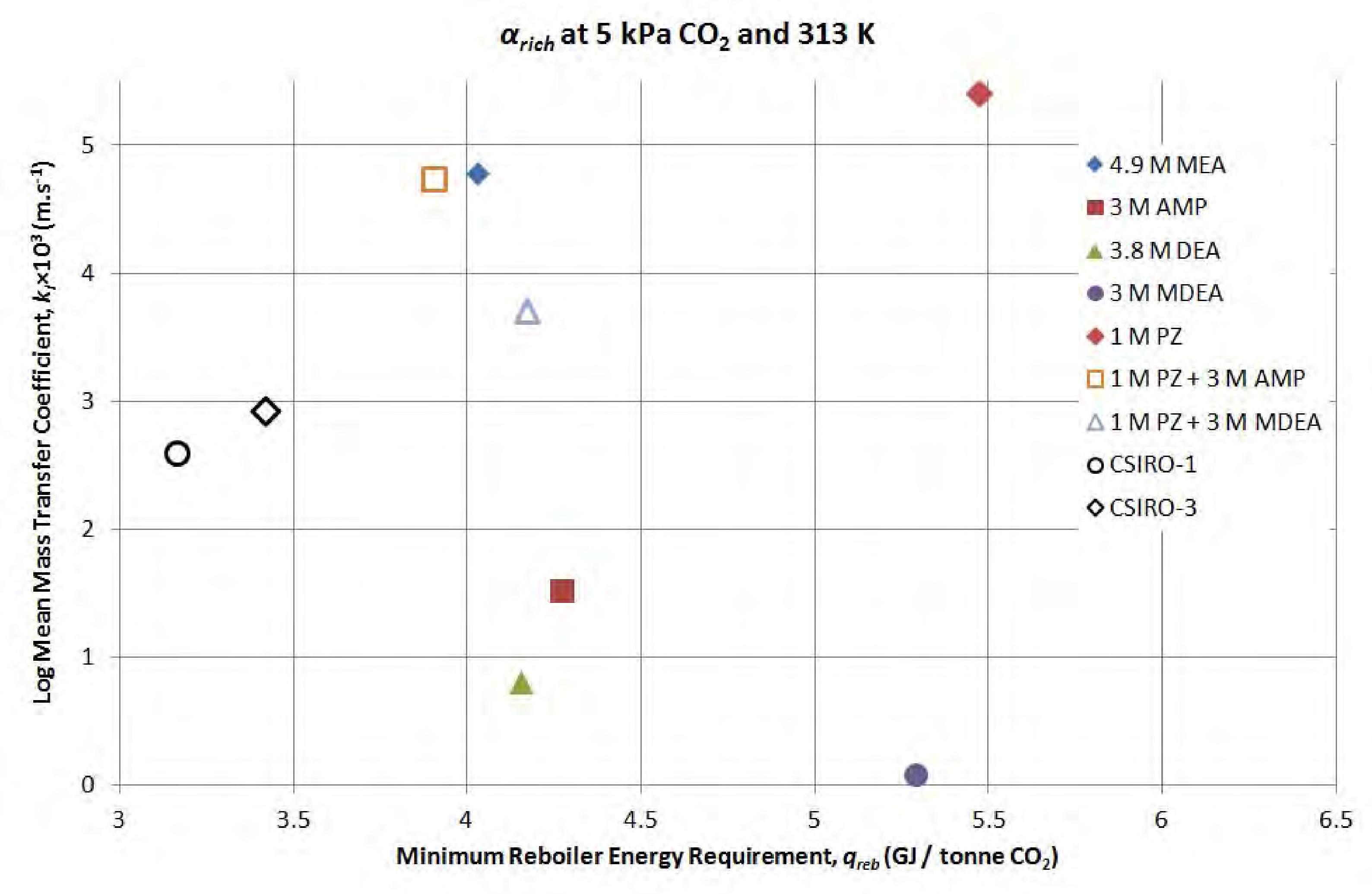
Estimate the **log mean mass transfer coefficient** for the absorber assuming 40°C and using α_{rich} and α_{lean} values from the stripper optimisation

Estimating solvent performance



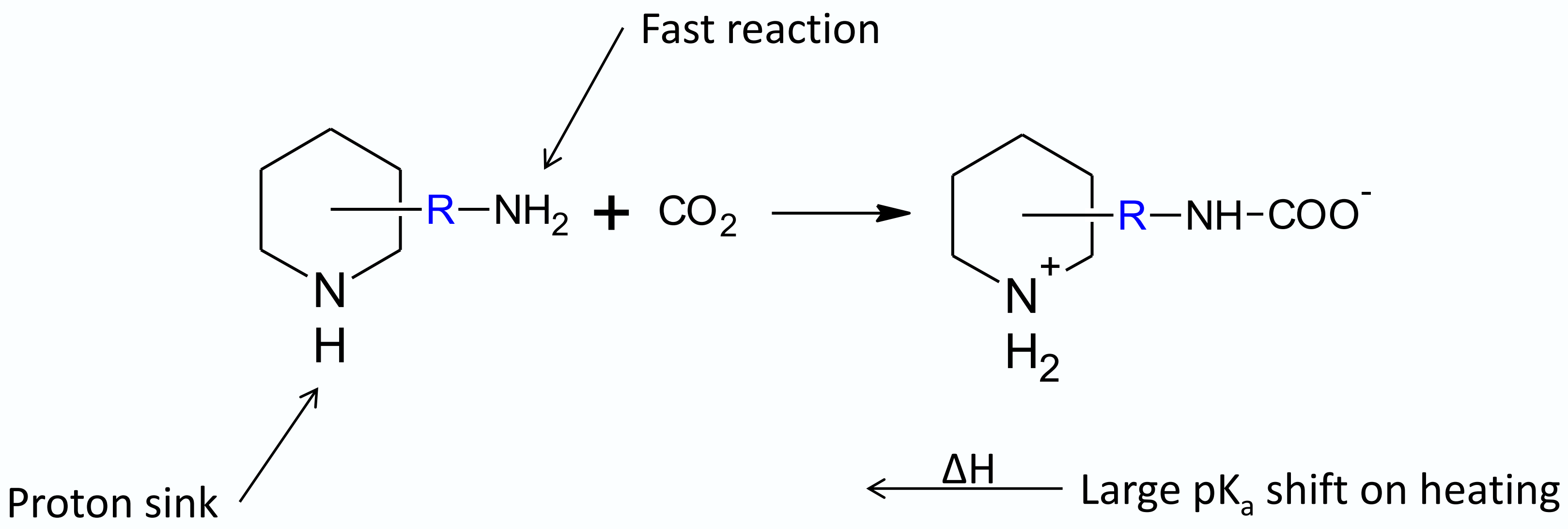


Estimating solvent performance



Molecular design of new amine molecules

The same design philosophy as for solvent formulations but in one molecule



Corrosion – CSIRO-1 < CSIRO-2 = MEA

Corrosion studies were carried out according to ASTM G31-72

- Mild steel tokens were left in contact with solvents for 6-8 weeks at process relevant conditions
- Corrosion extent was determined by mass change

Solvent	Corrosion Rate (mm / yr)
5 M MEA	0.73
CSIRO-1	**0.54**
CSIRO-2	0.71

Less corrosion = less maintenance

Thermal degradation

- Samples were heated in closed stainless steel reactor vessels at 135°C for up to 8 weeks
- At regular intervals samples were collected and analysed for mass loss and degradation product formation
- Preliminary results indicate **CSIRO-1 and CSIRO-2 show greater thermal stability** than MEA

Greater thermal stability = longer solvent life

Summary

The screening study identified a **number of** candidate **amines with better** than expected **performance** forming the basis of a patent

Detailed characterisation and modelling has allows the development of **3 CSIRO solvent formulations** to-date with a 4th in the pipeline

A number of these are moving into pilot plant testing

There is still **scope for greater improvement** through a combination of experiment and modelling and this work is ongoing

The assessment and improvement of CSIRO solvents will lead to commercially valuable solvent options for industry in the near term

This work has been presented in **over 40 journal articles and conference publications**

Looking to the future

The application of our formulation design philosophies to the **design of new single molecules** will allow even better performance

Further enhancements will be achieved by **looking beyond amines** to:

- **Enzymes** such as carbonic anhydrase to enhance absorption rates
- **Ionic liquids** and their favourable physical properties for a clean and low energy process
- Moving towards a **light driven process** rather than a heat driven one that can utilise solar energy

The team behind this work

CSIRO CET

Paul Feron
Gilles Richner
Steven Wei
Will Conway
Robert Bennett
Andrew Allport
Robert Rowland
Moetaz Attalla
Craig Grimmond
Phil Jackson
Kelly Robinson

CSIRO CMSE

Qi Yang
Mark Bown
Susan James
Mat Ballard
Amanda Carnal

The University of Newcastle

Marcel Maeder
Robert Burns
Xiaoguang Wang
Duong Phan
Yaser Beyad
Debra Fernandes
Anh Nguyen

Thank you

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CSIRO PCC pilot plant research in Australia

Aaron Cottrell, PCC pilot plant project manager, CSIRO

PCC Science & Technology seminar, Tuesday 26 March 2013

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Australian Government
Department of Resources, Energy and Tourism

anlecr&d

The University of Texas at Austin

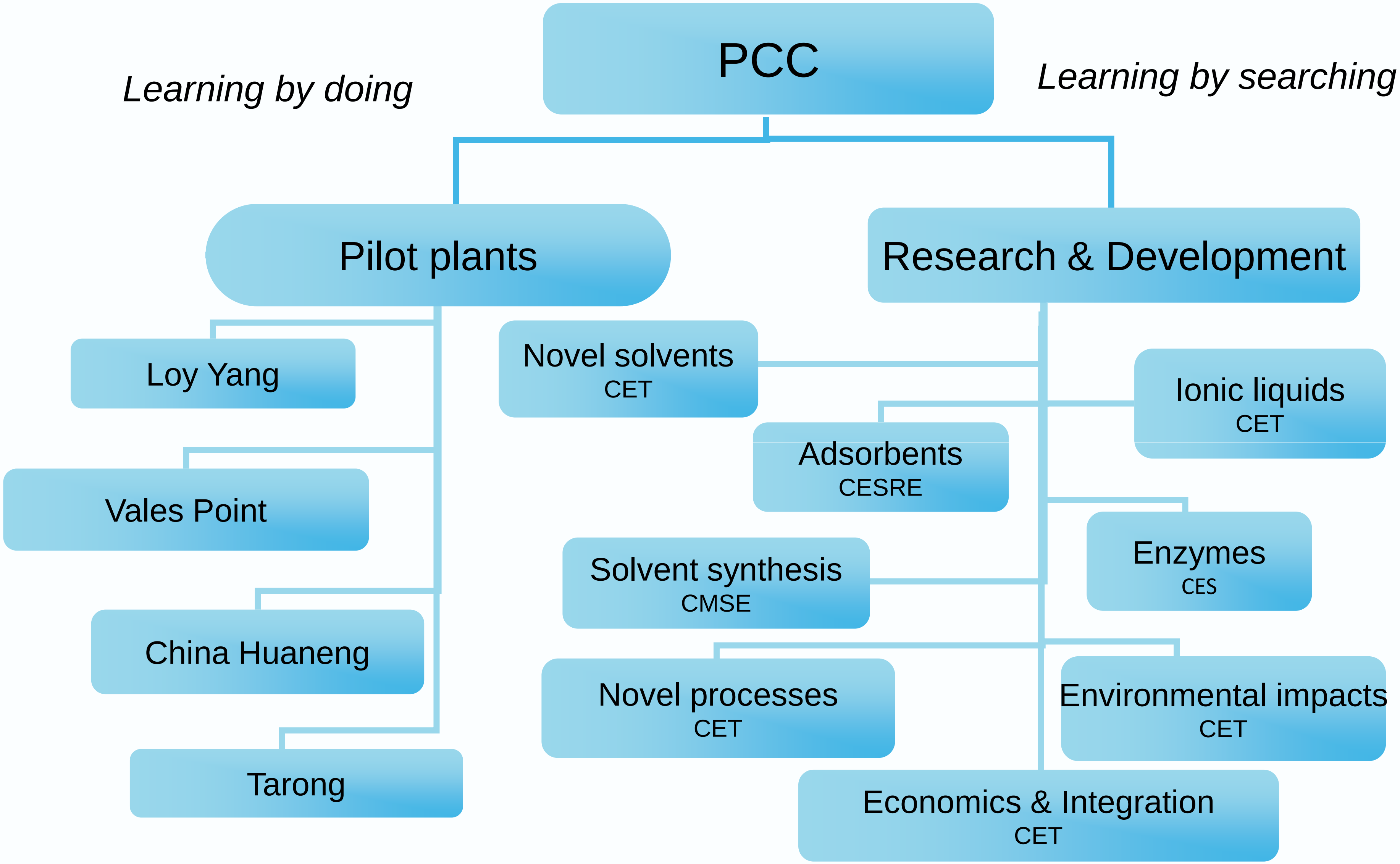
NSW Government Trade & Investment

MONASH University

Overview

- CSIRO CO_2 capture pilot plants
- The Tarong pilot plant
- Baseline operation with MEA
  - Column profiles
  - Minimum energy operating conditions
  - Process modification evaluation
  - HSS formation
- Conclusions and future work

Integrated PCC R&D Program



Pilot plant summary

Plant	Loy Yang	Munmorah → Vales Point	Tarong	Newcastle PDF
Solvent	Amine	Ammonia/ Amine	Amine	Ammonia/ Amine
Flue gas source	Brown coal	Black coal	Black coal	Synthetic
Scale	50 kg/hr	300 kg/hr	100 kg/hr	20 kg/hr
Focus	Solvent benchmarking	Ammonia operation	Process optimisation	Process development
Other activities	Emission study	Pressurised absorption	Concentrated piperazine	Cutting edge processes

- Matrix approach helps cover many aspects of PCC as well as providing quicker delivery of information

CSIRO

CSIRO pilot plant at AGL Loy Yang

- Brown coal flue gas, amine based solvents
- Previous experimental campaigns – Focus on solvent evaluation
  - Baseline with 30wt% MEA
  - Completed 7 campaigns with different solvents
- Current work also focusing on detailed emissions measurements and solvent degradation
- Collaboration with EU consortium in the coCAPco project (combined CO_2 + SO_2 control process)

Artanto et al. 2012, Fuel 101, 264-275

Munmorah/Vales Point pilot plant

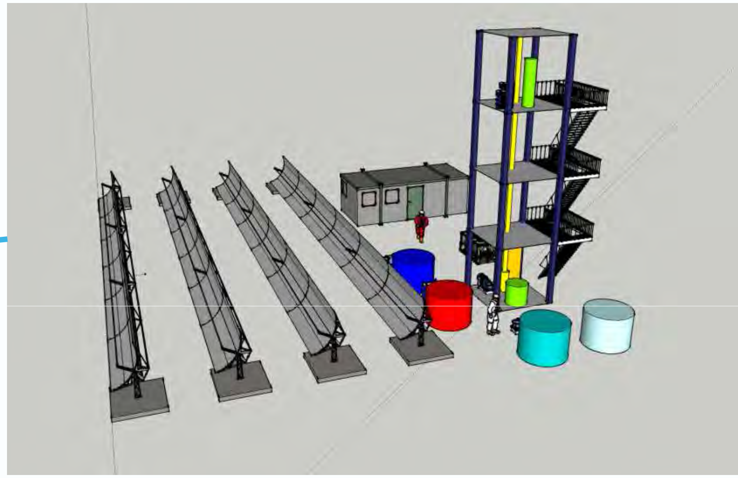
Delta electricity

- Black coal flue gas
- Evaluated ammonia as a CO_2 capture solvent
- Relocated to Vales Point power station. Currently undergoing commissioning
- NH_3 is an interesting solvent for CO_2 capture, however there are challenges:
  - Ammonia loss
  - Low CO_2 absorption rates
  - Solids formation (condenser)
- Supported by Coal Innovation NSW funding

Yu et al. 2012, International Journal of Greenhouse Gas Control 10, 15-25

Vales Point pilot plant – solar

- Design and construction of a pilot scale solar thermal reboiler for thermal regeneration of liquid absorbents.



Tarong CO_2 capture pilot plant

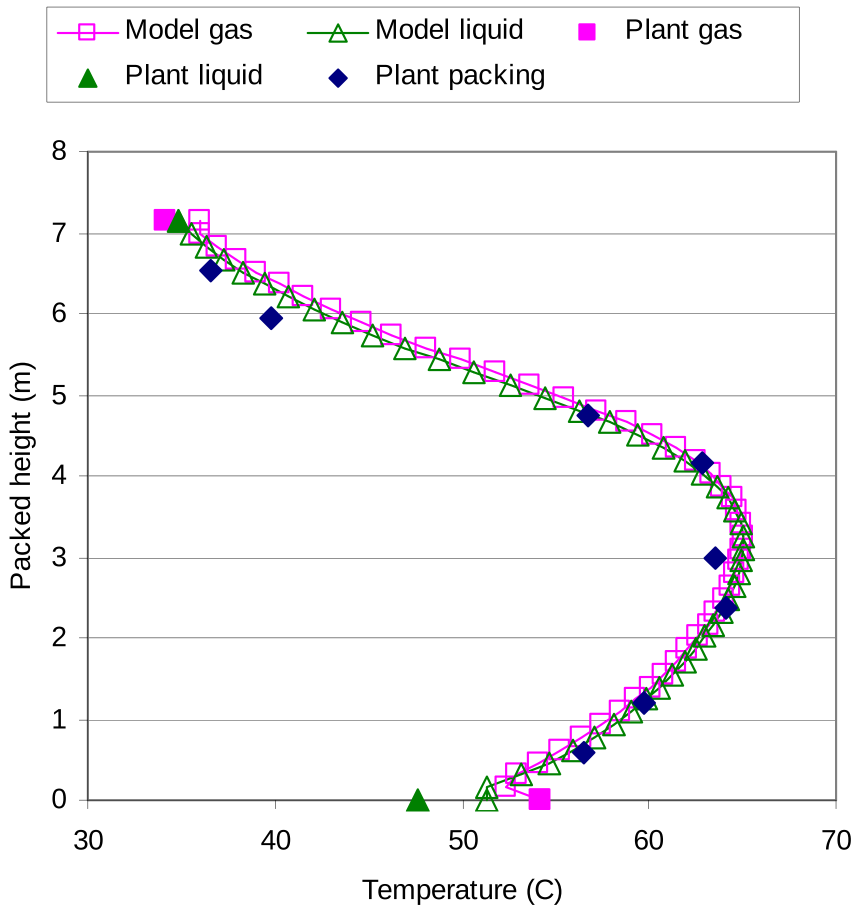
Tarong Power Station
- Sub-critical black coal, built late 1970's
- 4 units, 1400 MW total
- No FGD/DeNox

Operation overview

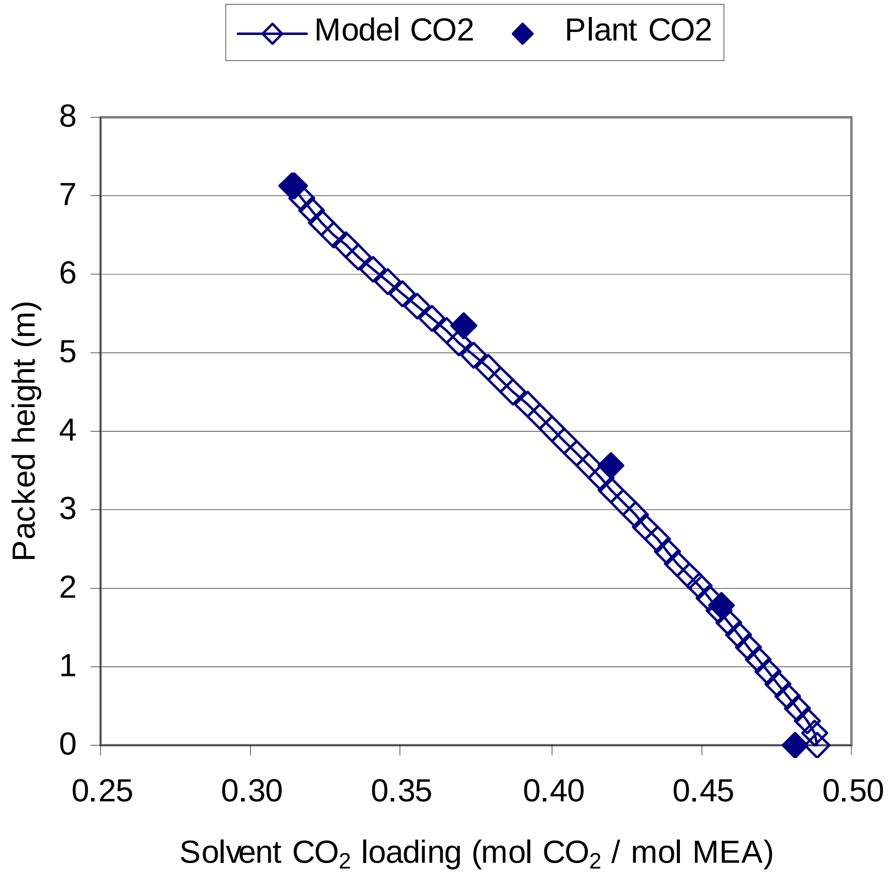
- Construction on site, May – August 2010
- Commissioning, August – November 2010
- Operation with MEA, November 2010 – May 2011
  - Baseline operation (24 hr)
  - Minimum energy operating conditions
  - Process modification evaluation
  - Corrosion coupon analysis
- Initial operation with piperazine, August – October 2011
- APP project completed 2011
- ANLEC R&D project, Evaluation of concentrated piperazine, October 2011 – now

Baseline operation – absorber column profiles

Temperature

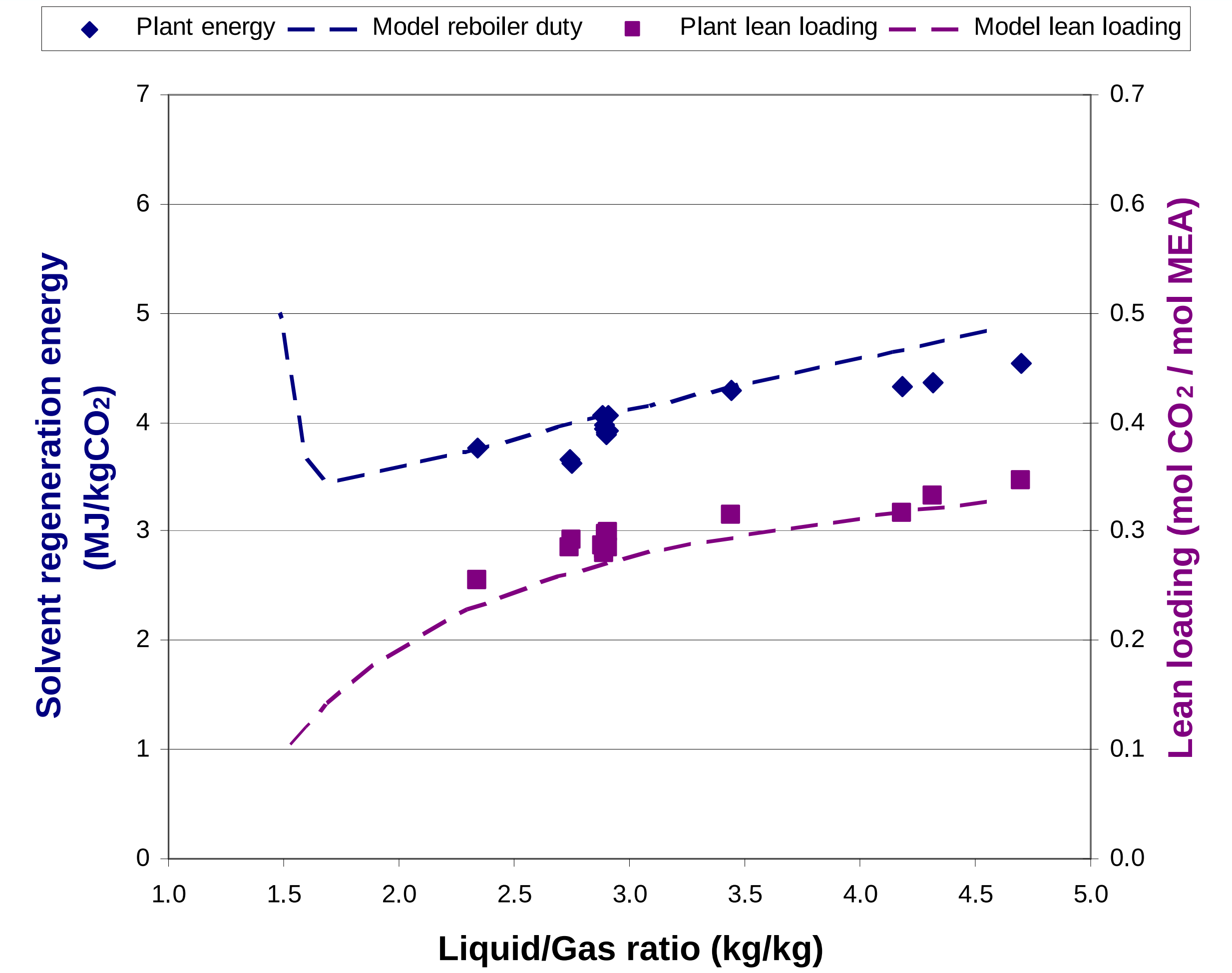


Liquid CO_2 concentration



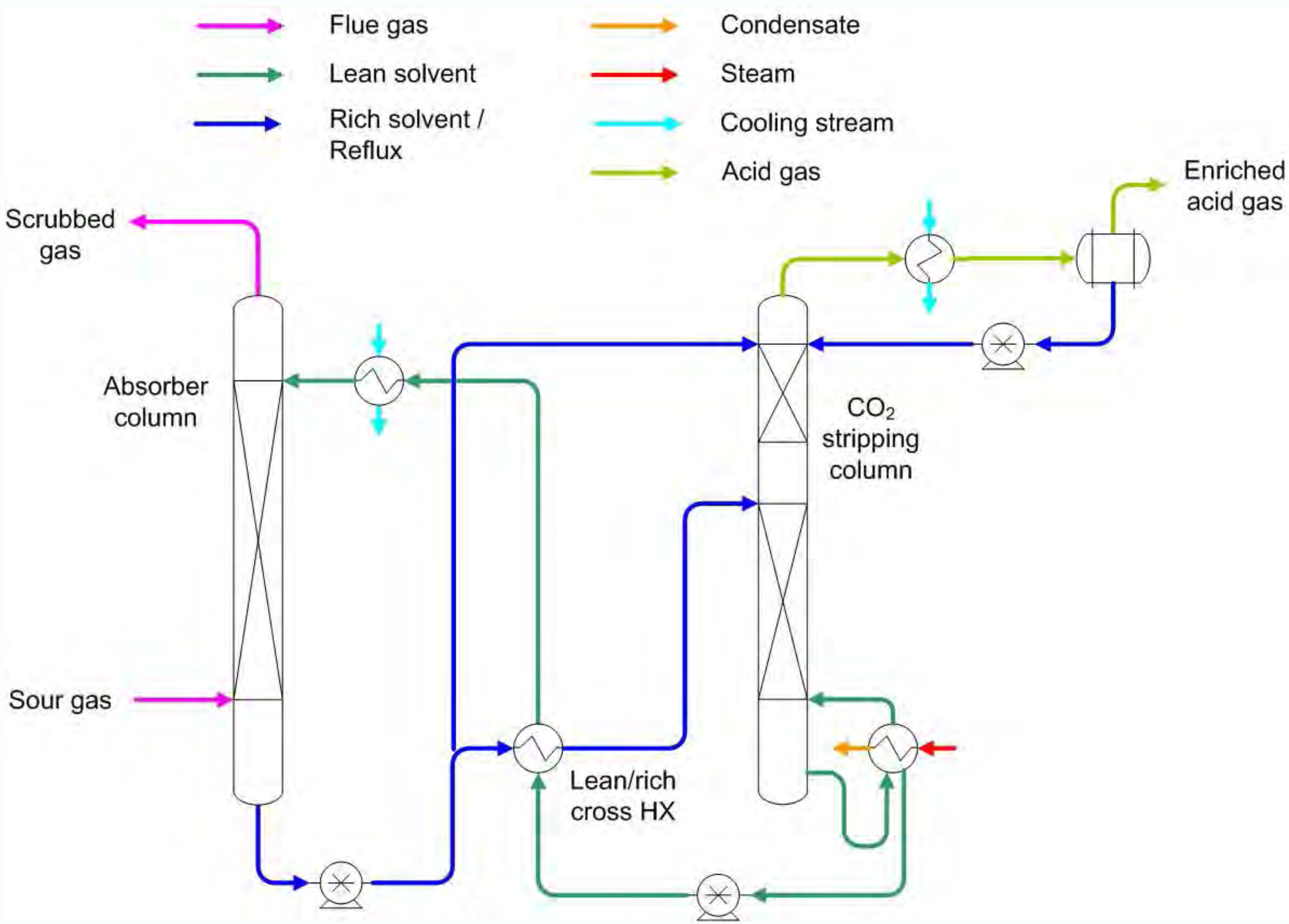
Cousins et al. 2012, Greenhouse Gases: Science and Technology 2, 329-345

Baseline operation – minimum energy operating conditions



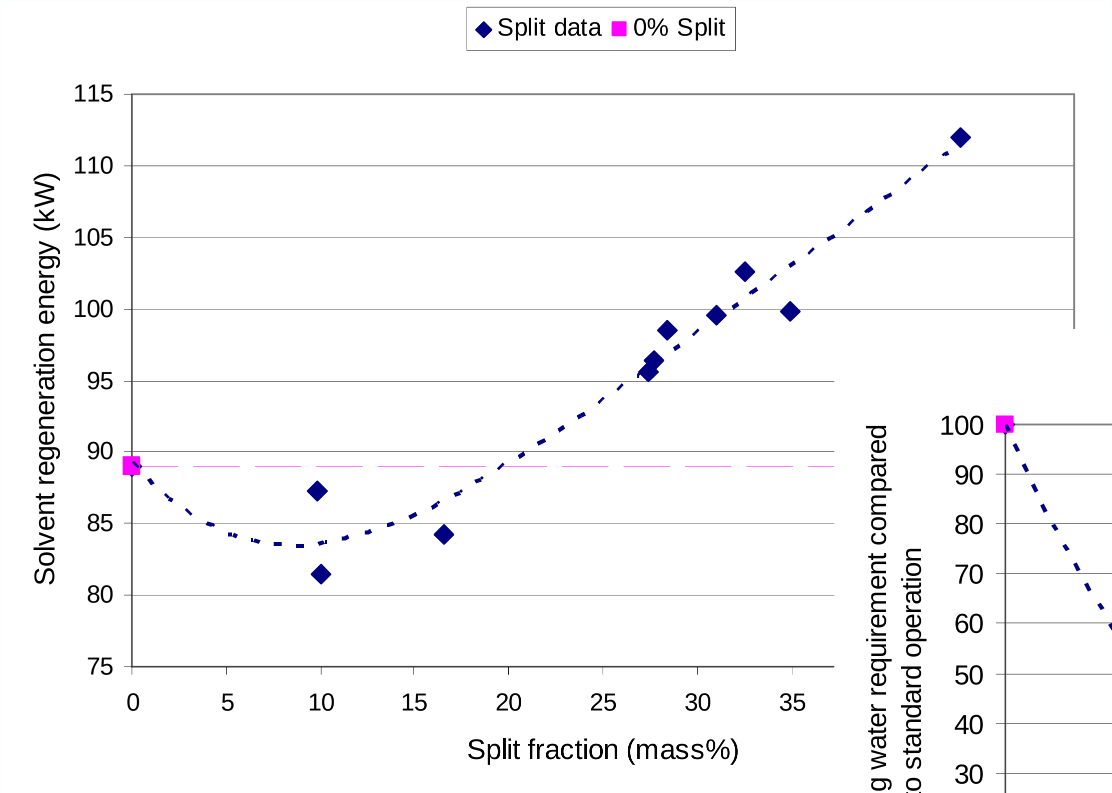
Cousins et al. 2012, Greenhouse Gases: Science and Technology 2, 329-345

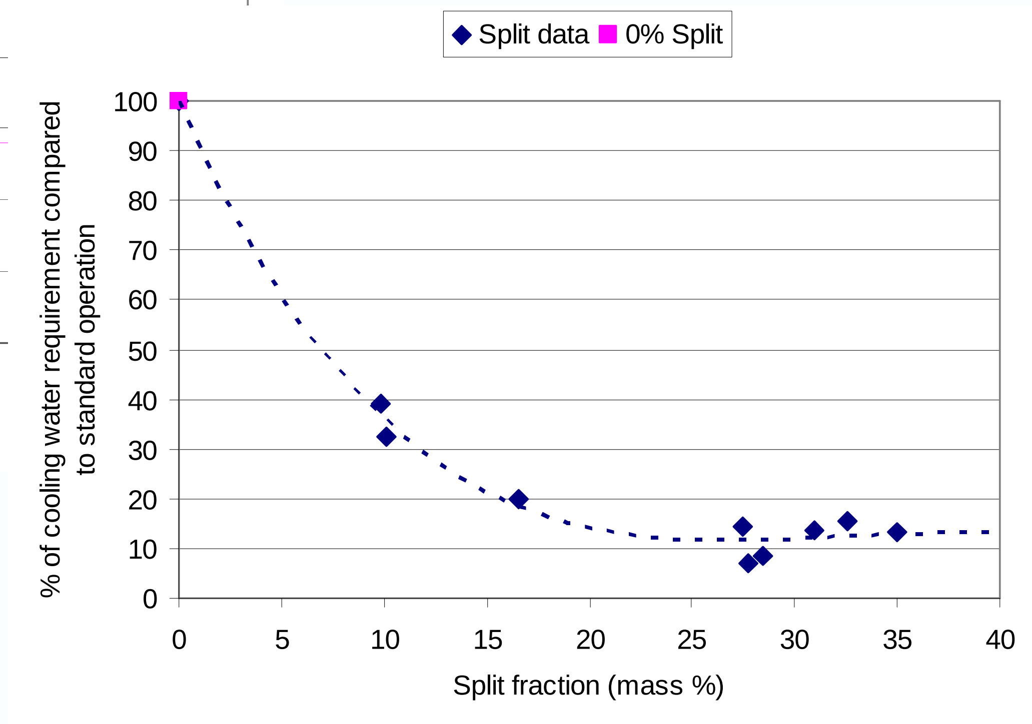
Process modification evaluation – rich split



Based on patent of Eisenberg and Johnson 1979

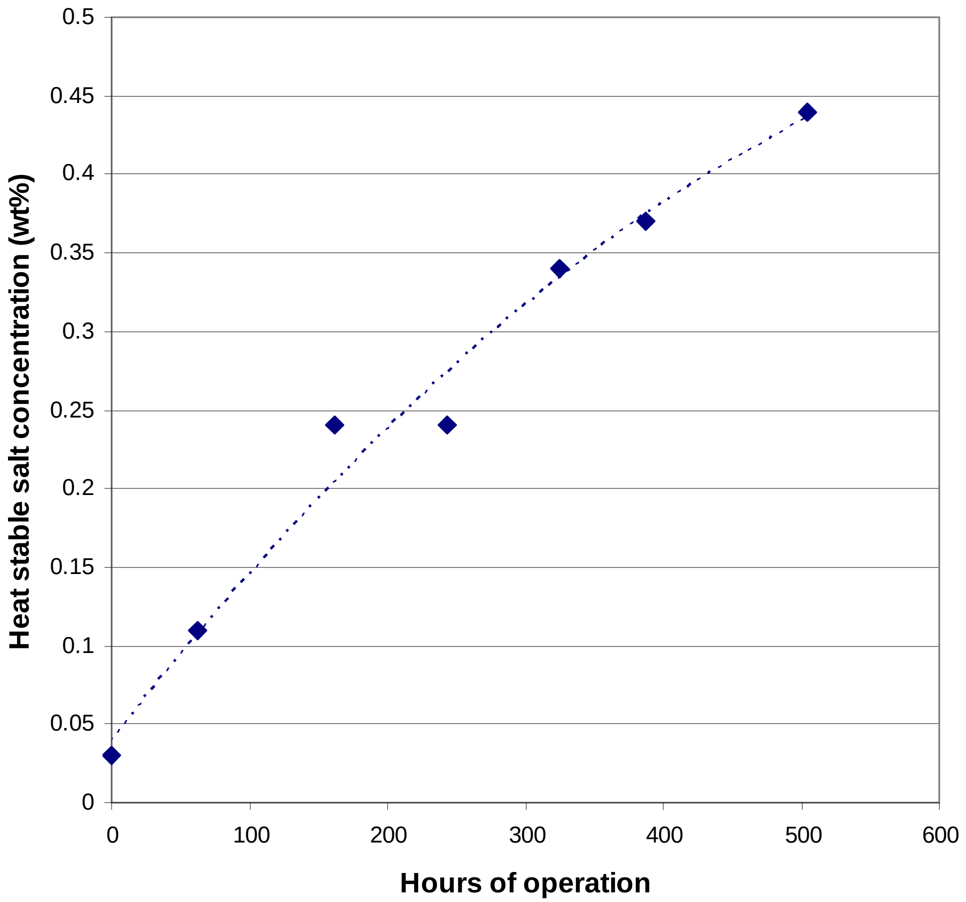
Process modification evaluation – rich split





Cousins et al. 2012, Greenhouse Gases: Science and Technology 2, 329-345

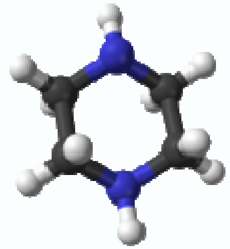
Heat stable salt measurement



- Flue gas after pre-treatment ~
  - 0-5 ppm SO_2
  - 100-220 ppm NO
  - 0-3 ppm NO_2
- HSS content increased ~0.4 wt% after 500 h operation
- Solvent did not exhibit any noticeable decrease in performance

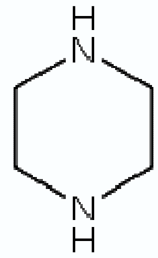
Cottrell 2011, Proceedings 1st Post Combustion Capture conference

Concentrated piperazine



Why piperazine?

- Potentially lower regeneration energy solvent cf. MEA
- More stable (thermal/chemical)
- Low vapour pressure (reduced environmental emissions)



Concerns when operating with piperazine

- Narrow operating window – solubility issues
- Formation of degradation products

In collaboration with the University of Texas, Austin

Conclusions and future work

CSIRO's pilot plants have provided useful information for evaluating CO_2 capture technologies at Australian coal fired power stations.

Future work:

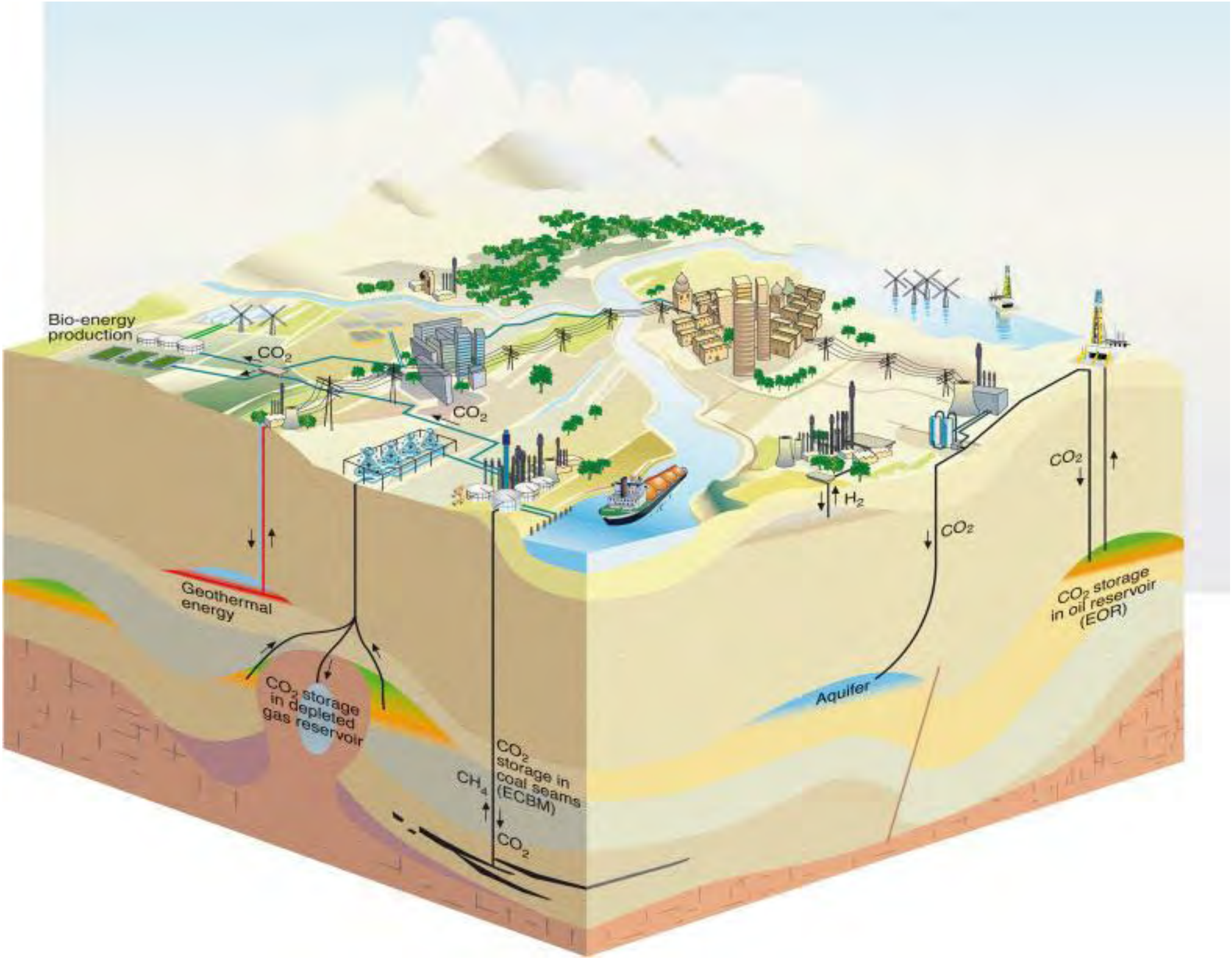
- Loy Yang
  - Combined SO_2 and CO_2 removal as part of the coCAPco project
- Vales Point
  - Pilot plant will be available for additional projects
  - Development of solar thermal reforming
- Tarong
  - Evaluation of concentrated piperazine funded through ANLEC R&D

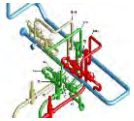
Aaron Cottrell

PCC pilot plant Project Manager
CSIRO Energy Technology
CET, NSW
aaron.cottrell@csiro.au

Thank you

Carbon Capture, Transport, Storage & Utilization





Contents

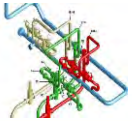
- General introduction TNO
- Status of CCS in Europe & Netherlands
- ROAD project (general)
- CATO; Dutch National R&D Program on CCS
- Air Liquide – Green Hydrogen project

TNO: Netherlands Organization for Applied Scientific Research

- Founded in 1932 by act of parliament (*TNO law*)
- € 640 turn-over (1/3 direct government funding)
- 4.200 staff

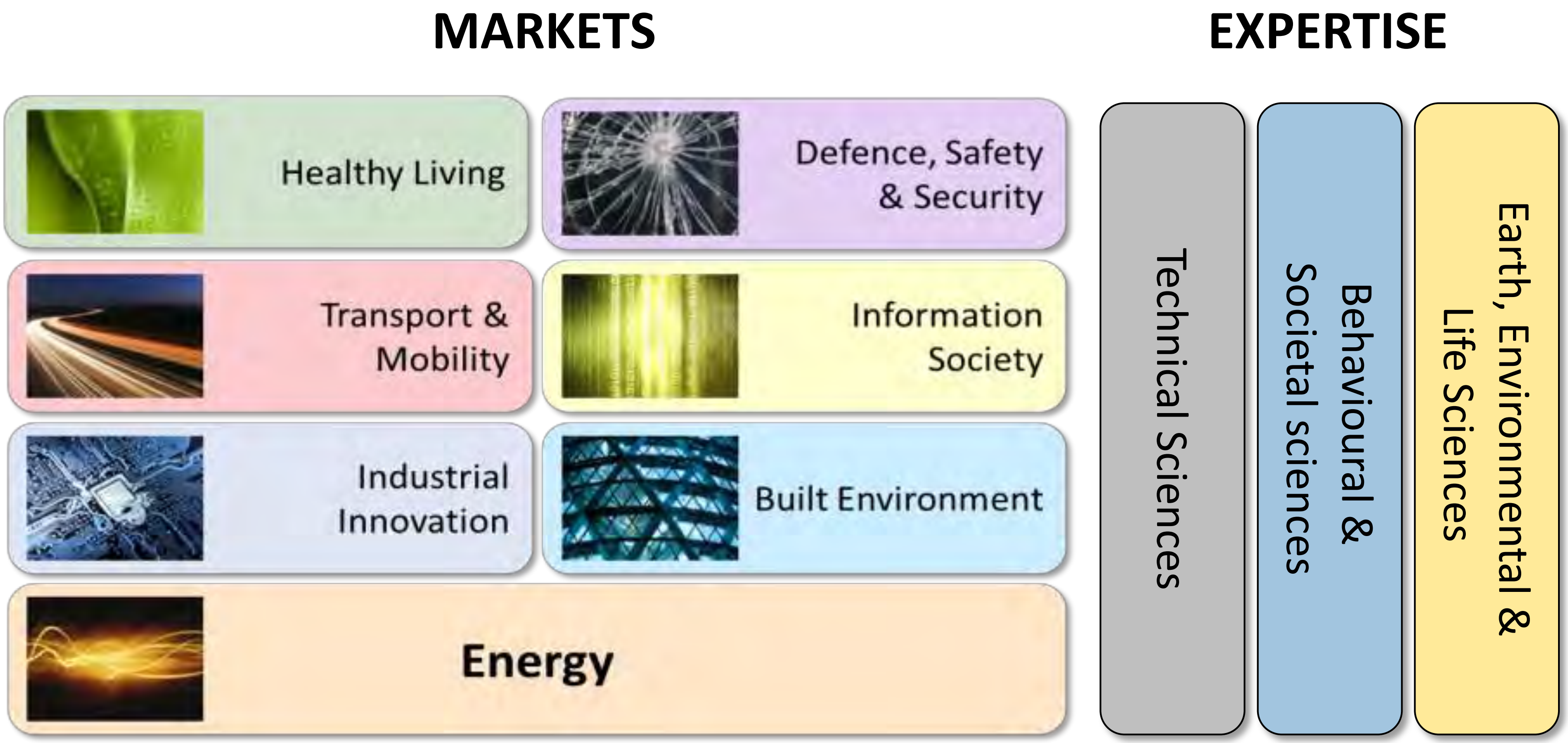
- *Applied* R&D organization
  - technology development
  - contract R&D
  - non-routine consulting
  - special tasks (*Geological Survey of The Netherlands*)

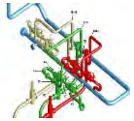
- Independent, transparent, not-for-profit
- Focus on fundamental understanding & knowledge transfer
- *Comparable to IFP, SINTEF, CSIRO, KISR*

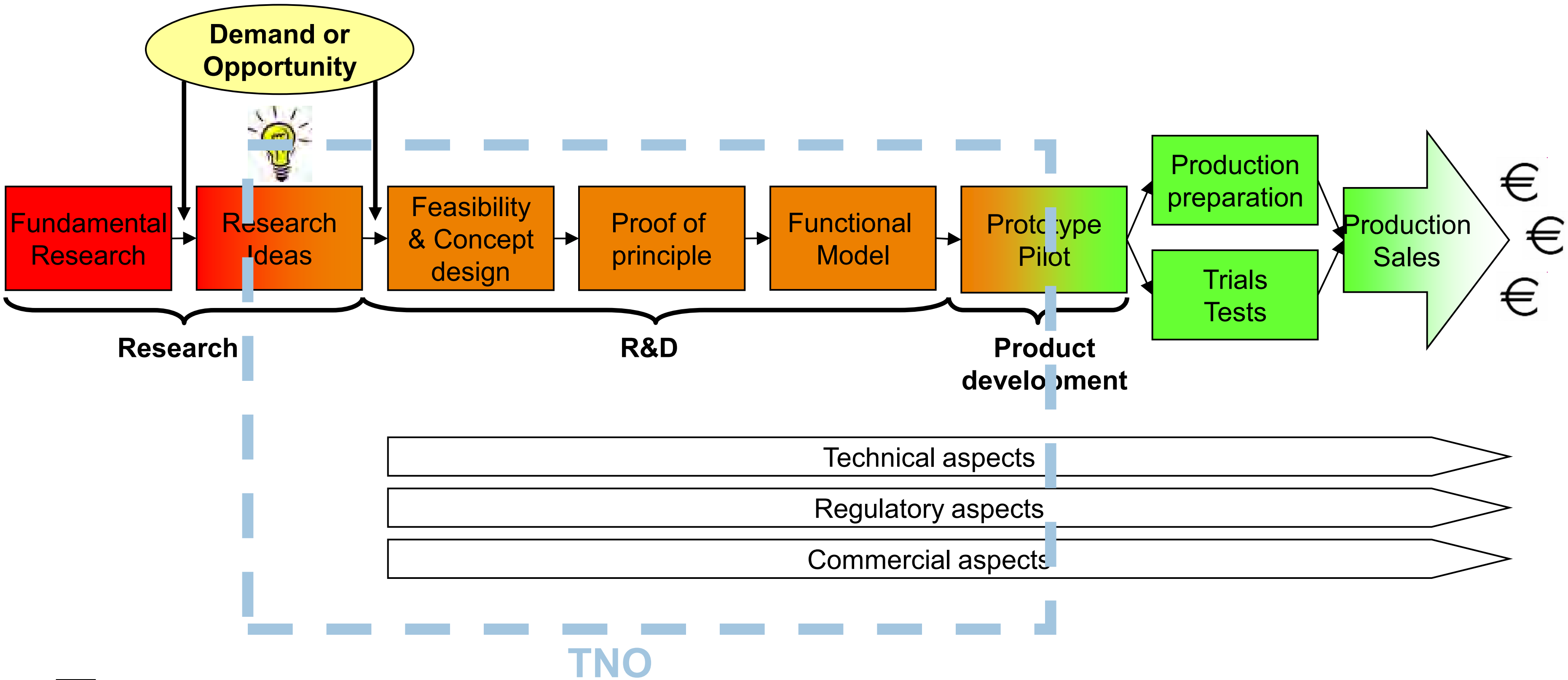
TNO innovation for life

TNO organization

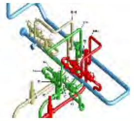




Our position in innovation

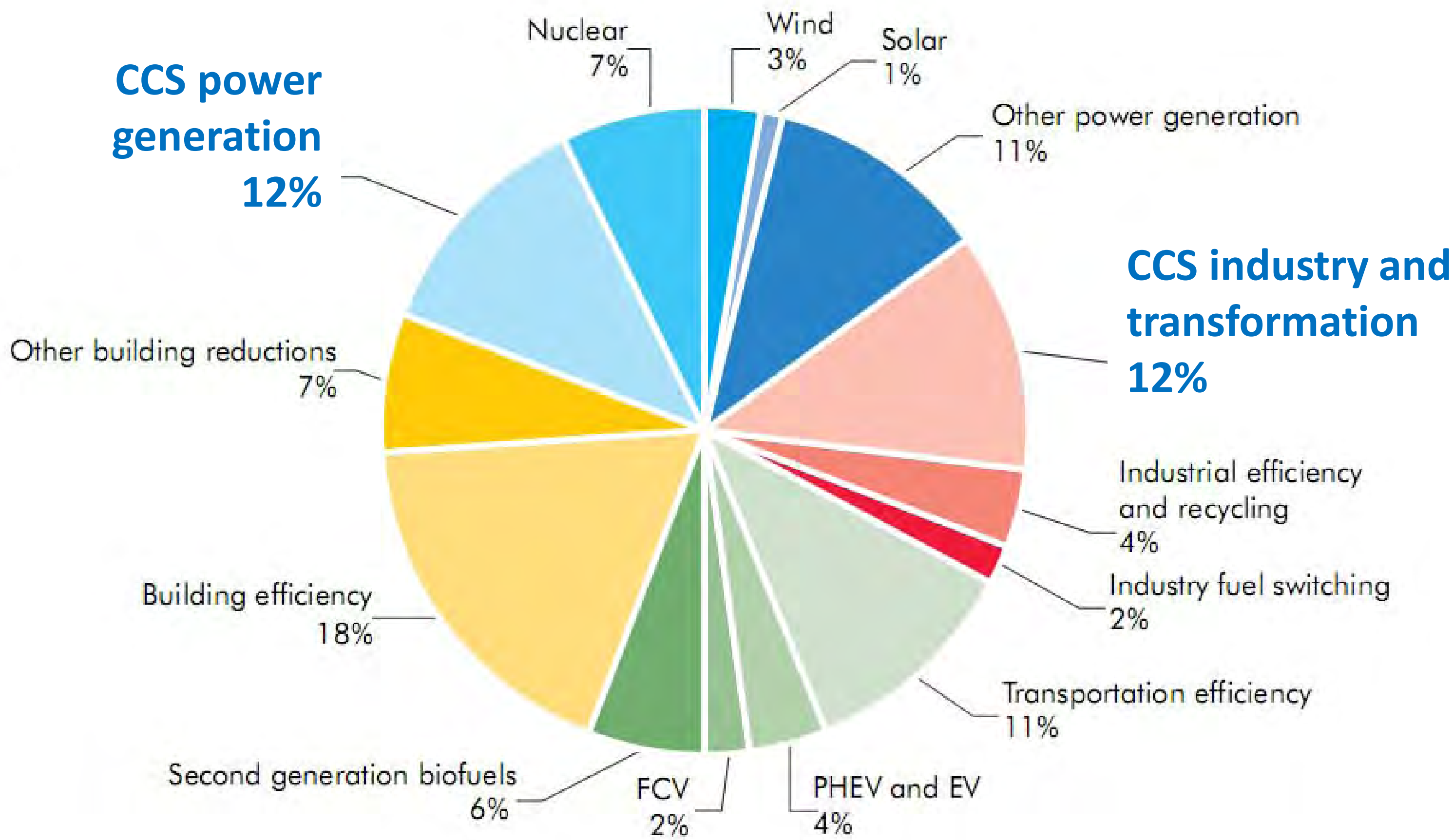


- Universities
- TNO and/or company R&D
- Company and/or manufacturer

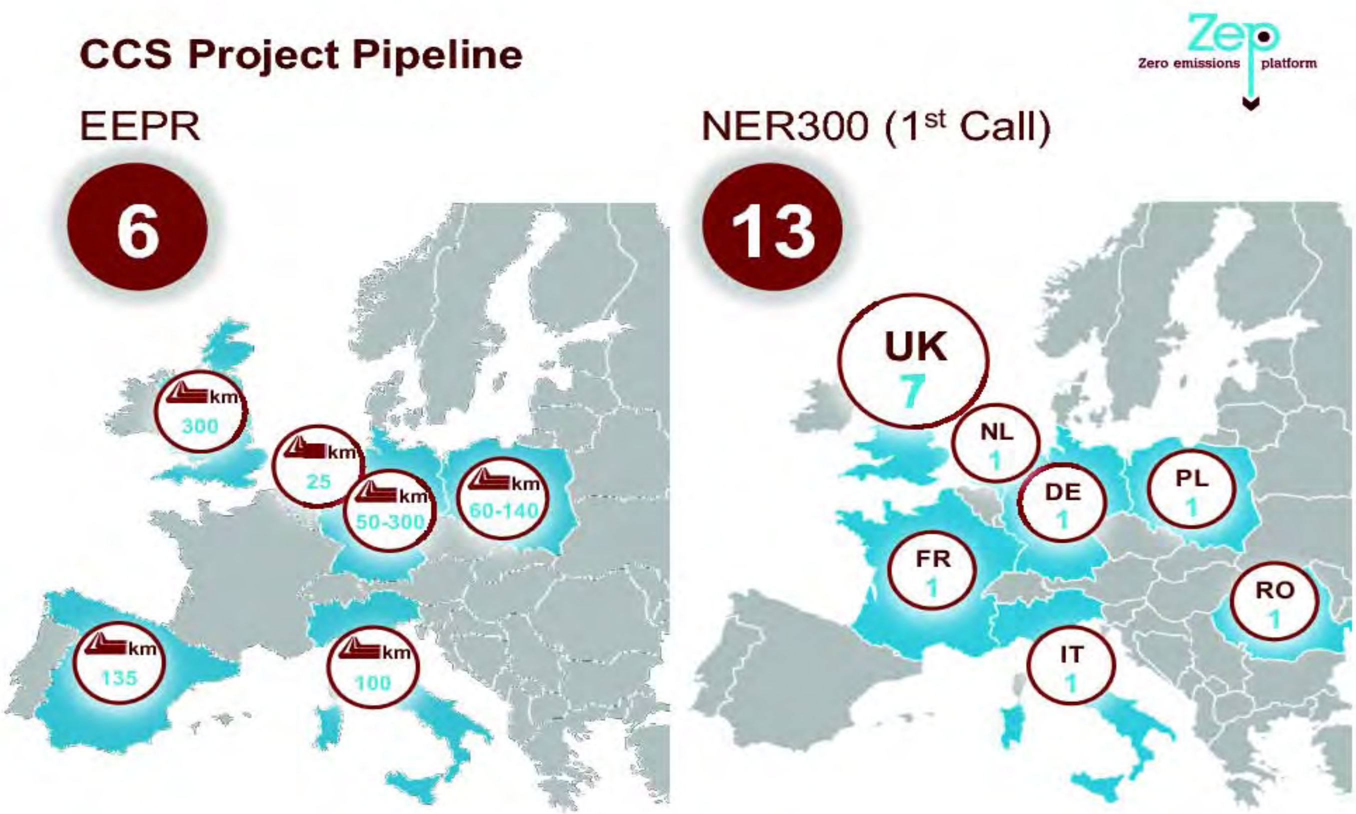


Status of CCS in Europe & Netherlands

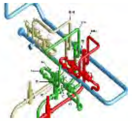
Within Europe CCS provides 24 per cent of the solution in power AND Industrial sector (source IEA).



Overview large scale EU CCS demonstration projects



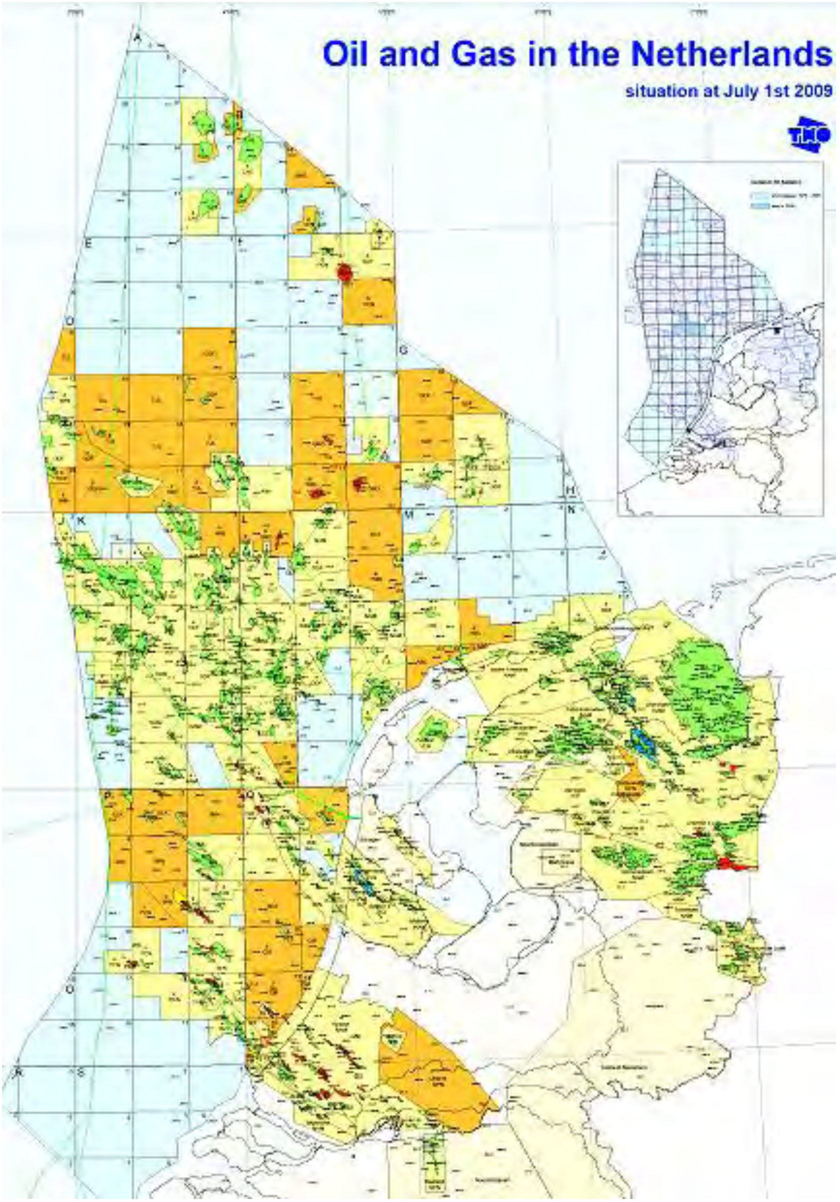
Netherlands; strategically located between CO2 emissions (peaks) and storage locations in North Sea



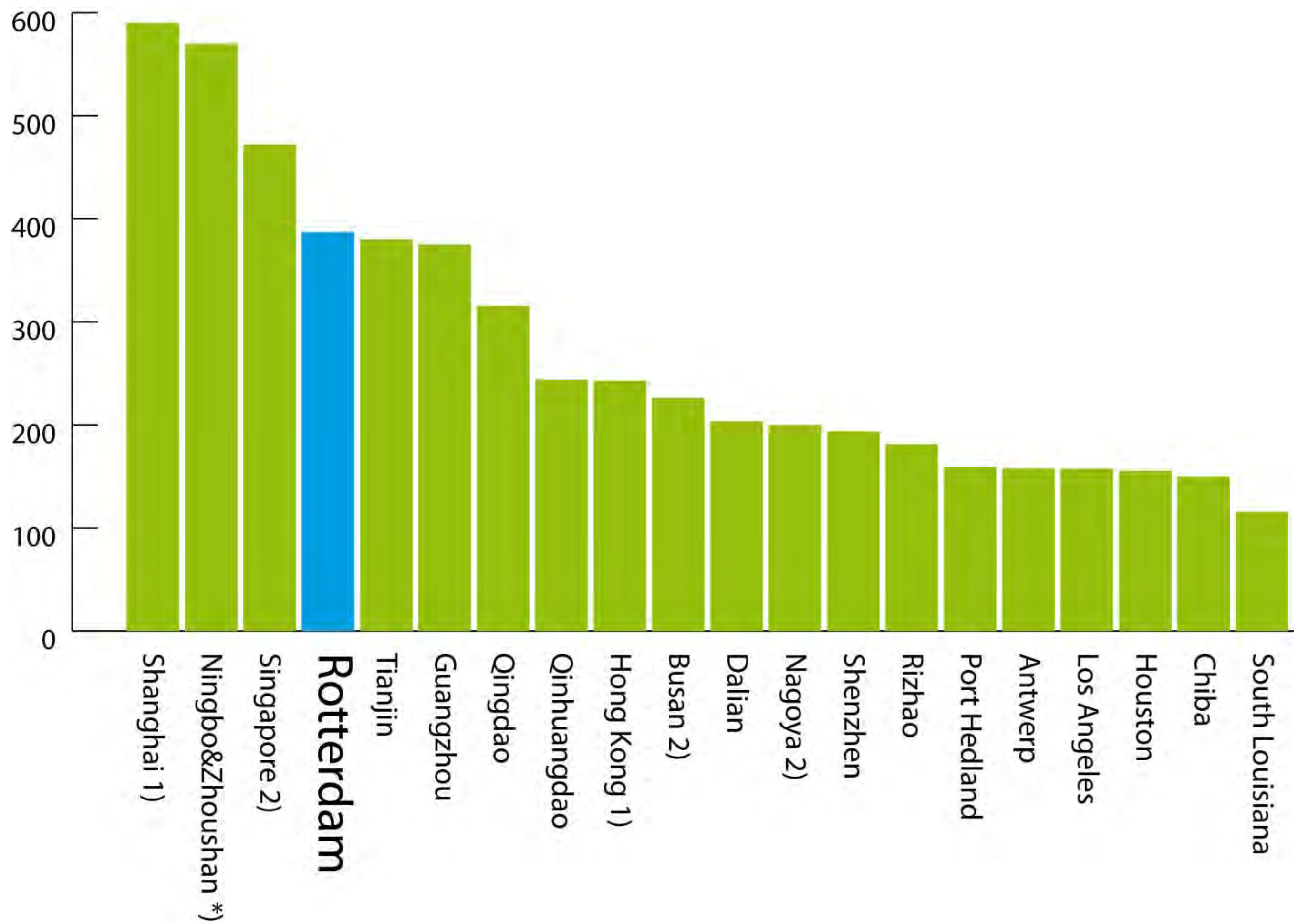
innovation for life

Why CCS and the Netherlands:

- Availability (clustered) large CO_2 point sources
- Large storage capacity; > 3 Gton
- Relatively short transport distances
- Extensive knowledge of oil & gas and CCS
- CATO R&D program since 2004
- Serious business interests and commitment of relevant parties
- Substantial government funding
- 2 large scale demo's



Rotterdam: 4th largest port in the world



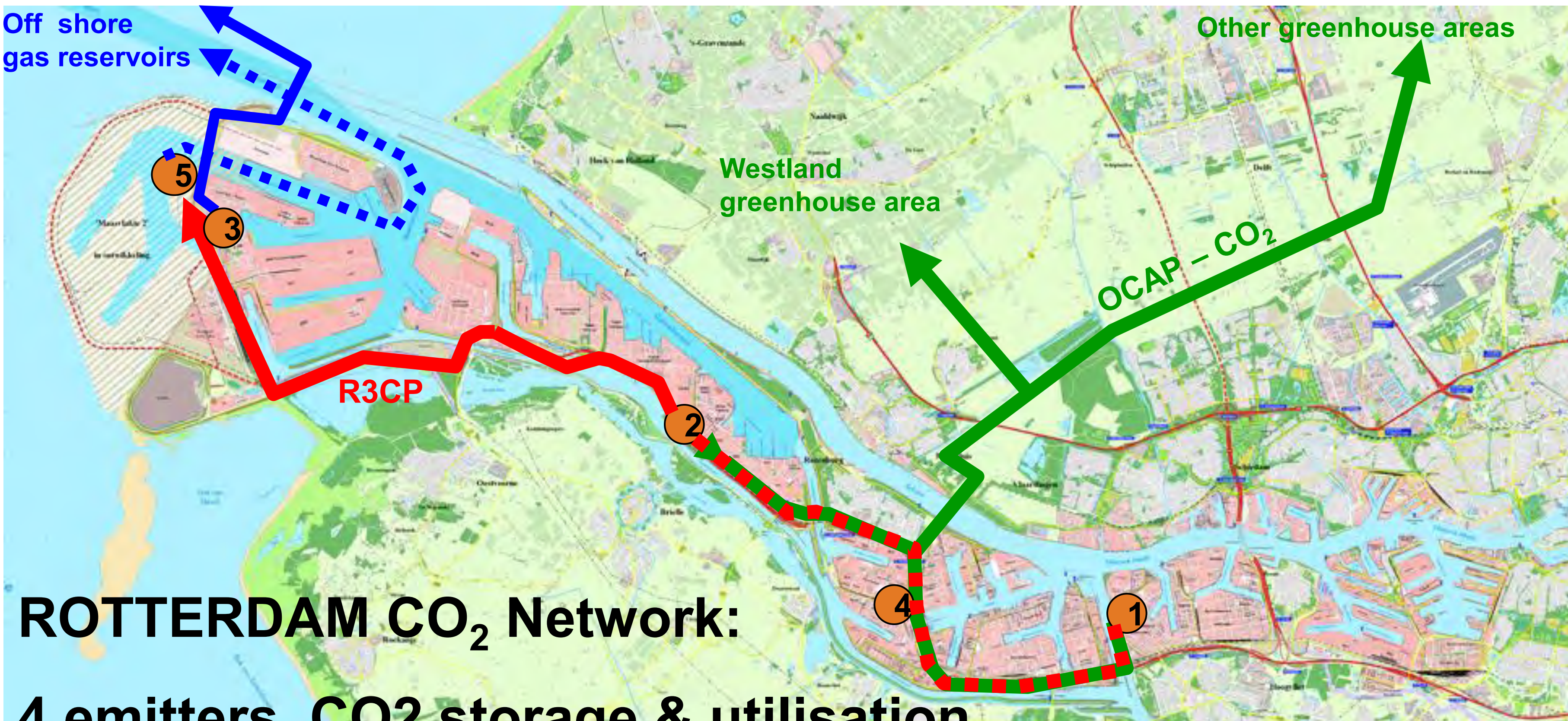
Port of Rotterdam yesterday...


Today…

… and in 2030:

Maasvlakte 2: 1000 hectares new land

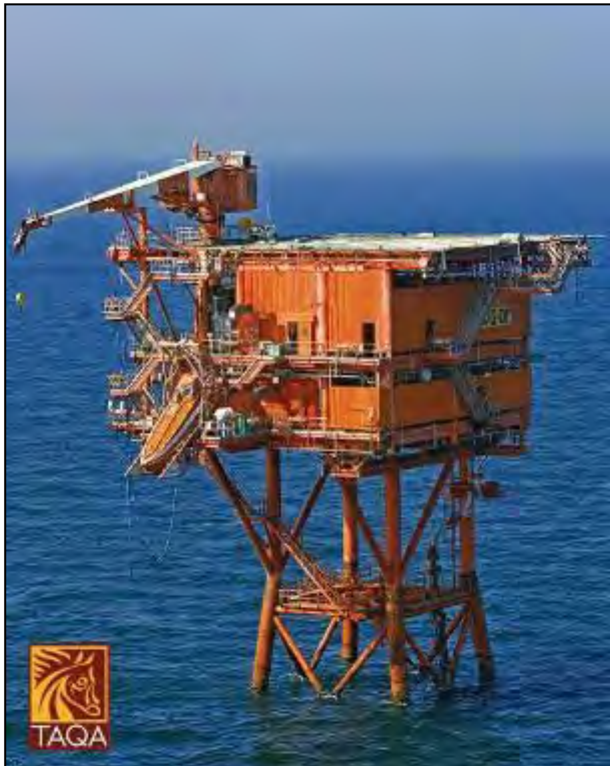
CO_2 sources	CO_2 logistics	CO_2 destinations
1 Shell (since 2005)	OCAP	greenhouses for enhanced crop growing
2 Abengoa (since 2011)	R3CP: common carrier collection pipeline)	
3 ROAD (2016 / 2017)	Offshore pipeline to	Taqa P18 Gasfield
4 Air Liquide (2016 / 2017)		
	5 CO_2 Terminal	EOR North Sea



ROTTERDAM CO_2 Network:

4 emitters, CO2 storage & utilisation

ROAD CCS DEMO (250 MW PC); FEED study P18 storage location executed by TNO



General Overview

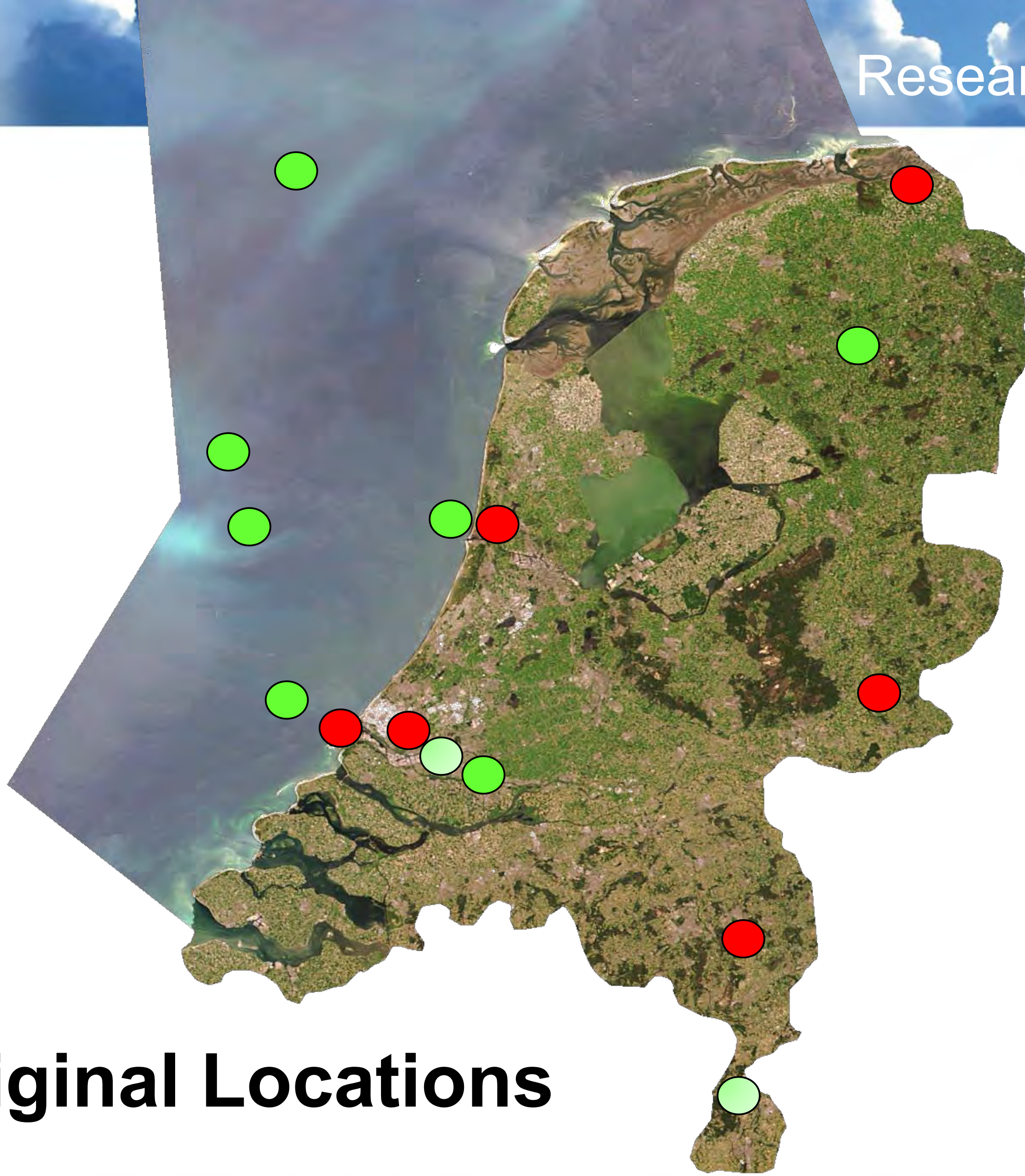
CATO in a glance

- Applied and scientific research
- Complete CCS Chain
- Demand driven & flexible program
- 86 M€ (50% government)
- 200 researchers & 45 PHD students
- Coordination: TNO
- 2004-2013
- Partners from industry, SME, university, NGO

CATO-2 Parties

e.on
RWE
Shell
NUON
TATA
Electrabel GDF SUEZ
DSM Agro
essent
TAQA
gasunie
ebn
wintershall BASF Group
KEMA
ECN
TU Delft
PANterra Geo Consultants BV
IMARES Wageningen UR
Schlumberger
DAP
Grontmij
energy valley
Rotterdam Climate Initiative
ECOFYS
if
Natuur en Milieu
vrije Universiteit amsterdam
TNO
PROCEDE
university of groningen
UNIVERSITEIT TWENTE.
Universiteit Utrecht
uce
SAXION Hogescholen
Universiteit Leiden

	SP	Sub-Programs
	0	Coordination, dissemination, cooperation
	1	Capture
	2	Transport and chain integration
	3	Storage & monitoring
	4	Regulation and safety
	5	Public perception



Original Locations

SP-1: Capture	
Post Combustion	- Applied: Scale-up of first generation capture technology to demo scale - Fundamental: Develop second generation capture technology
Pre Combustion	
Oxy Fuel	
Evaluation & Benchmarking	
CCS in Northern Netherlands	
Toxicology and Ecotoxicology of Carbon Dioxide and CCS by-products	
CO2 Re-use	

CATO2
SP1 Capture

Overview
And
Highlights

Work packages:

WP 1.1A1 User Requirement Specification WP 1.1A2 DEMO Preliminary Design WP 1.1A3 Solvents WP 1.1A4 Absorber WP 1.1A5 STRIPPER WP 1.1A6 Process development WP 1.1A7 Environmental Aspects WP 1.1A9 CO2 capture at Municipal Solid Waste Combustion (MSWC) plants WP 1.1F1 Phase Change Solvents WP 1.1F3 Thermodynamic Models WP 1.1F5 Adsorptive Systems WP 1.1F6 Hybrid system for gas fired power plants WP 1.1F7 Multiple Phases Absorption Liquids WP 1.1F8 Multiple Phases Pilot	1.1 'post'
WP 1.2A1 CO2-CATCHUP: Plant operation and optimization WP 1.2A2 Water gas shift catalysis WP 1.2A3 CO2-CATCHUP: CO2 absorption section WP 1.2A4 Sorption-Enhanced Water Gas Shift (SEWGS) WP 1.2A5 Industrial CCS at Tata Steel WP 1.2F1 Hydrogen Membrane Technologies WP 1.2F2 Nano-structured sorbents for CO2 capture WP 1.2F3 Novel materials for H2 - CO2 separation WP 1.2F6 High pressure and temperature selective solvents	1.2 'pre'
WP 1.3F2 Chemical Looping Combustion WP 1.3F3 Oxy combustion of solid fuels	1.3 'oxy'
WP 1.4 Techno-economic evaluation & Benchmarking WP 1.5 CCS in Northern Netherlands (RWE) WP 1.6 Toxicology and Ecotoxicology of Carbon Dioxide and CCS by-products WP 1.7 CO2 Re-use	

Post Combustion Capture

CATO Pilot (2008) at E.ON Maasvlakte

Flue gas details:

- 1250 m^3/hr flue gas, 250 kg/hr CO_2 captured
- Flue gas gas from pulverized coal power plant
- 90% of CO_2 captured from flue gas side-stream

Pre-Combustion Capture

Pd/alloy membranes

Sorption Enhanced Water Gas Shift

Buggenum pilot plant

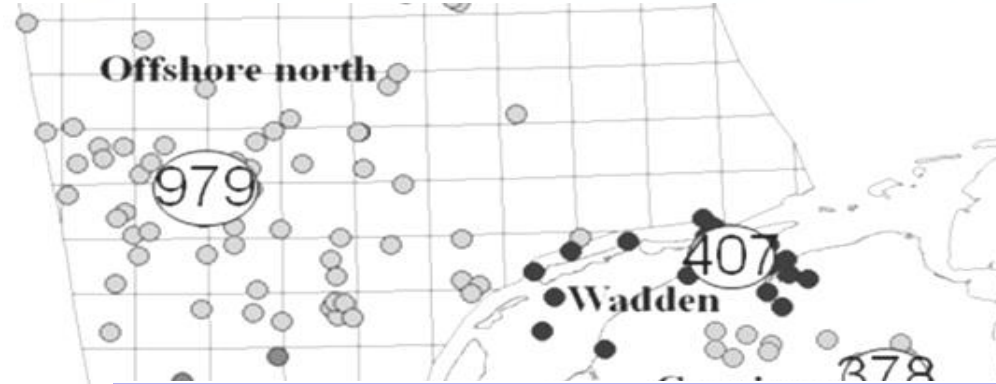
WP1.3 Oxyfuel

- Fundamental research
  - Fixed bed chemical looping combustion (PhD)
  - Oxy combustion of solid fuels

NUON Part of VATTENFALL

TU/e Technische Universiteit Eindhoven University of Technology
Where innovation starts

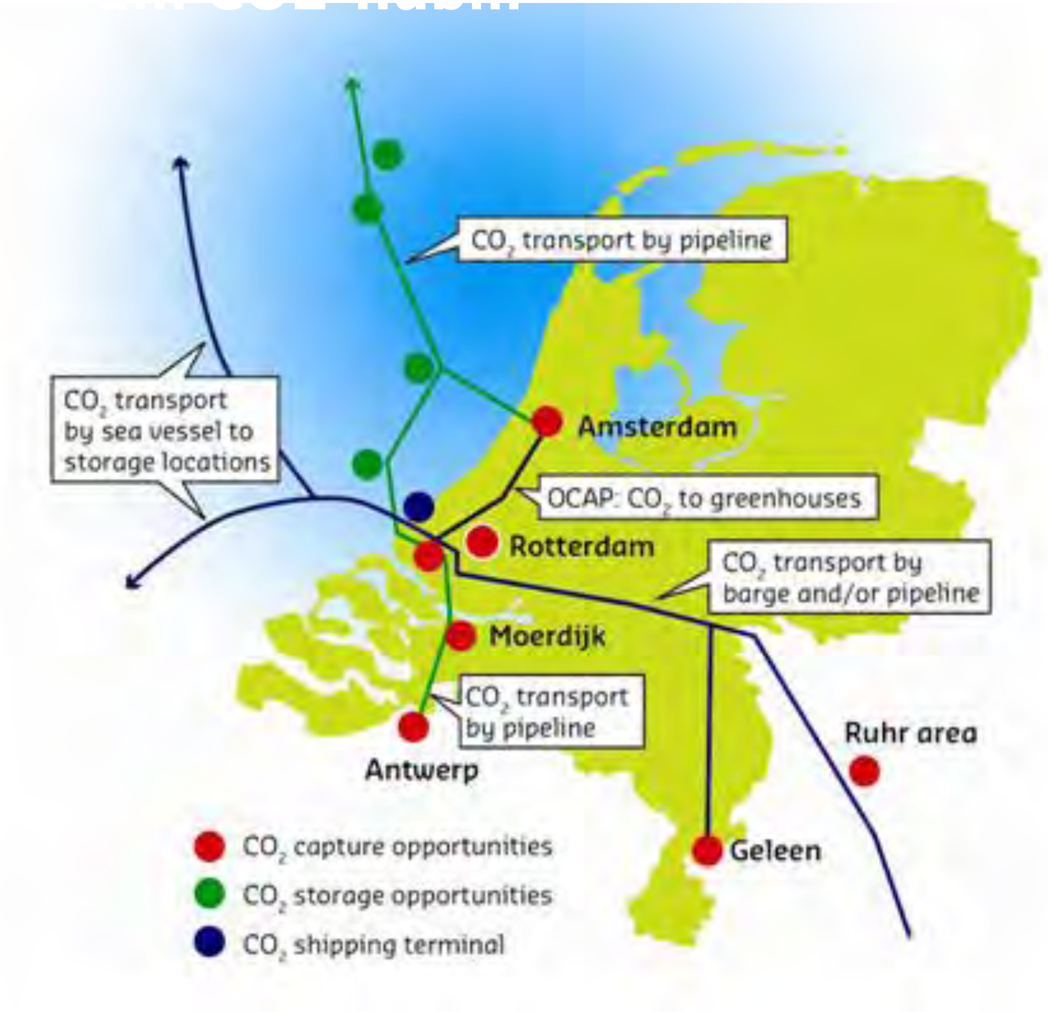
ECN Your energy. Our passion.

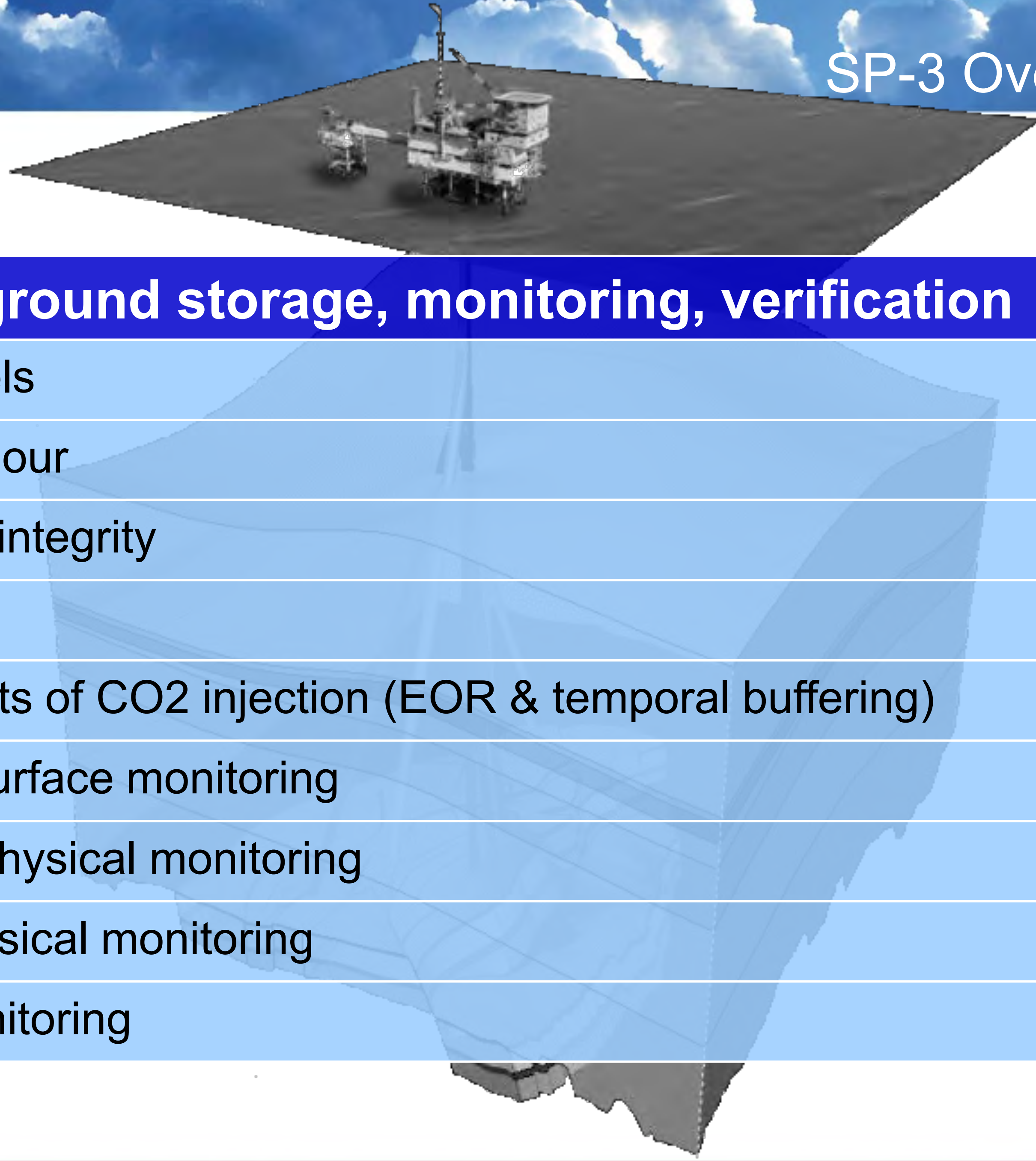


SP-2: CO2 transport and chain integration

- Technical aspects of CO2 transport infrastructure
- Techno-economic chain analysis
- International CCS policy
- Chain integration and CCS implementation plan
- Technical assessment of the ROAD CCS chain in non-steady conditions

CCS Roadmap for the Netherlands

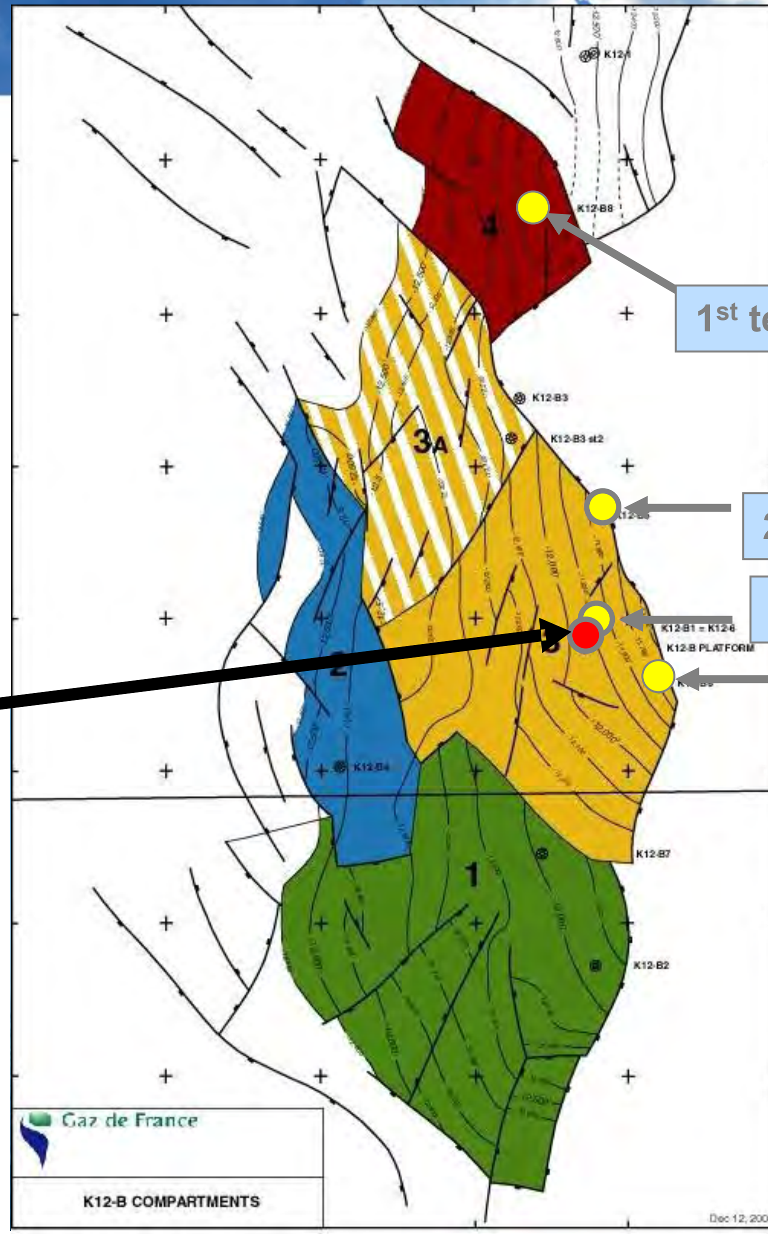




SP-3: Underground storage, monitoring, verification
Geological models
Reservoir behaviour
Cap rock & fault integrity
Well integrity
Additional benefits of CO2 injection (EOR & temporal buffering)
Shallow (sub-) surface monitoring
Permanent geophysical monitoring
Lab exp. geophysical monitoring
Site-specific monitoring

GDF-Suez K-12B

Offshore Enhanced Gas Recovery, CO2 gas treatment

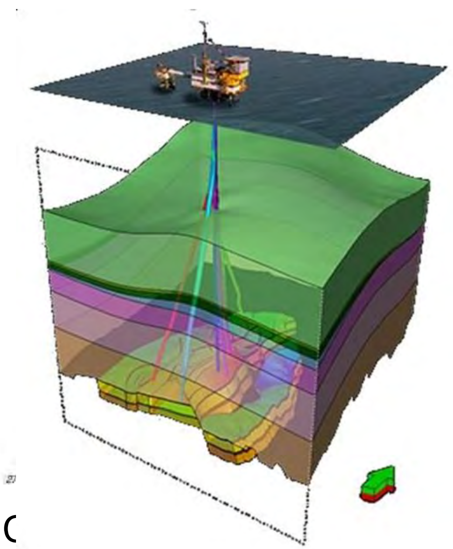


1st test: K12-B8 - Injector

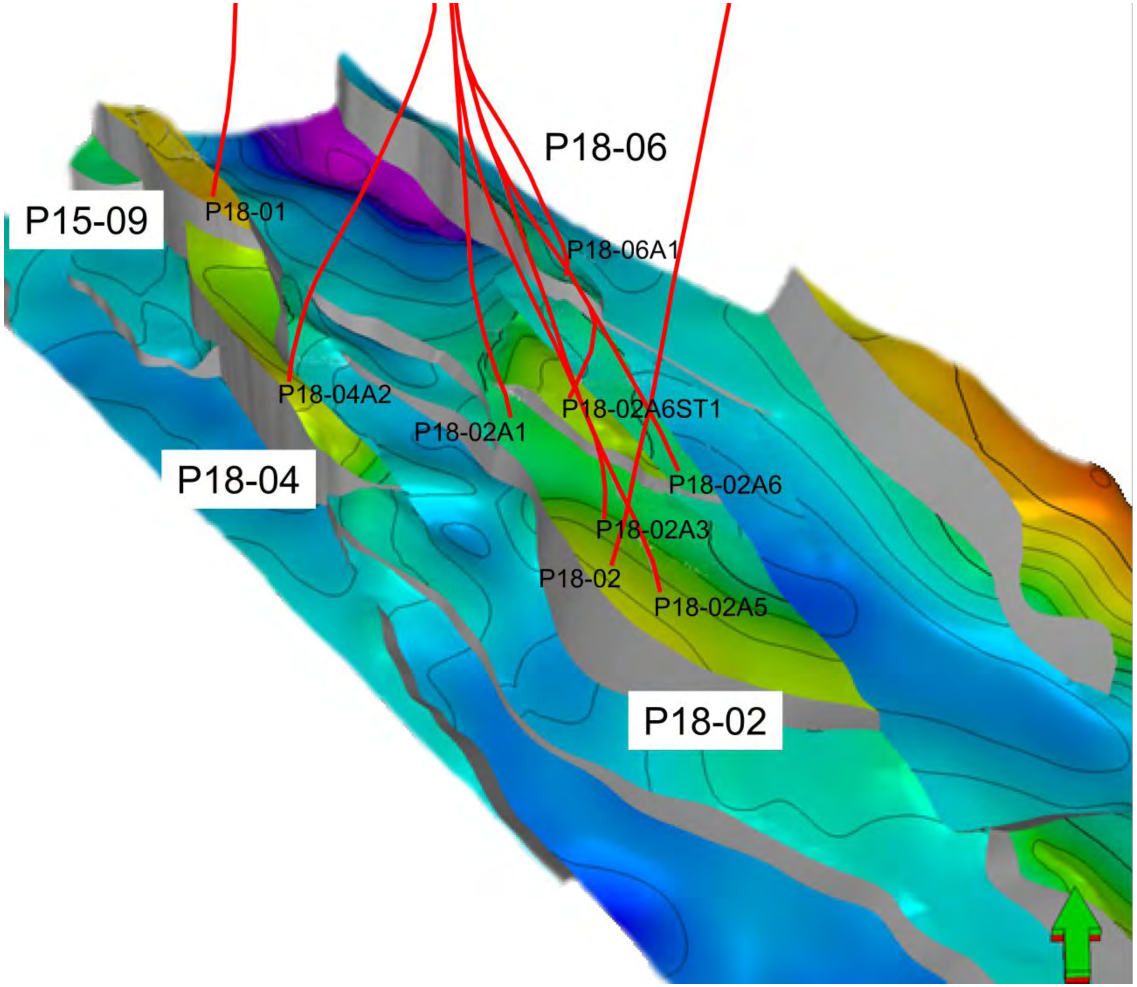
2nd test: K12-B5 - Producer

2nd test: K12-B1 - Producer

2nd test: K12-B6 - Injector



ROAD Storage location; The P18-4 gas field



SP-4: Regulation and safety
Legislative framework & guidance
Permitting & best practice
Environmental performance
Risks CO2 transport
Risks geological storage of CO2

de Volkskrant

Nieuws | Opinie | Cultuur | Opmerkelijk | Video | Service | Webwinkel

Binnenland | Buitenland | Economie | Sport | Kunst | Wetenschap | Internet

Barendrecht gaat in verzet tegen CO2-opslag

ANP op 18 november '09, 17:25, bijgewerkt 19 november '09, 11:46

Barendrecht protesteert tegen CO2-opslag (RTV Rijnmond)

vk.nl/groen BARENDRECHT - De gemeente Barendrecht legt zich er niet bij neer dat in de gemeente een proef komt met de opslag van het broeikasgas CO2.

- Barendrecht krijgt CO2-opslag

DOSSIER

BEKIJK

Nog geen besluit over CO2-opslag

SP-5: Public perception

Local communication near CCS

Framing effects in CCS communication

Trends in public opinion about CCS

Resistance of valid beliefs about CCS against low quality information

Public Website: www.co2-cato.nl

Public Website: www.co2-cato.nl