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Adsorption Materials and Processes for Carbon Capture from Gas-Fired Power Plants – AMPGas

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AMPGas Project

Partners:

The University of Edinburgh (Coordinator)

University of St. Andrews

Heriot-Watt University

Industrial Partner:

Howden Group Ltd

Other industrial contributions:

Chemviron Carbon; Purolite; Thomas Swan and UOP

AMPGas Project

Aims:

- Apply a range of experimental techniques to determine equilibrium and kinetic properties of nanoporous materials, which are being developed for CO_2 capture from dilute streams;
- Predict the performance of an integrated adsorption process based on rapid thermal swing;
- Demonstrate the proposed process using a bench scale rotary wheel adsorber.

Materials:

Thanks to the expertise of the partners different materials can be tested:

Zeolites (St. Andrews University)

Amine-containing MOFs (St. Andrews University)

Amine-based Silicas (Heriot-Watt University & St. Andrews University)

Amine-containing Carbon and Carbon Nanotubes (University of Edinburgh)

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Adsorbents: the challenges

Tailoring novel adsorbents for CO_2 separation from dilute streams:

Physisorption (optimised zeolites)

- Structures
- Cation types
- Cation distribution
- Hydrophilicity

Chemisorption (amine-based adsorbents)

- Supporting material
- Pore size/volume
- Amine groups
- Synthesis process
- Chemical and thermal stability
- Behaviour in presence of water

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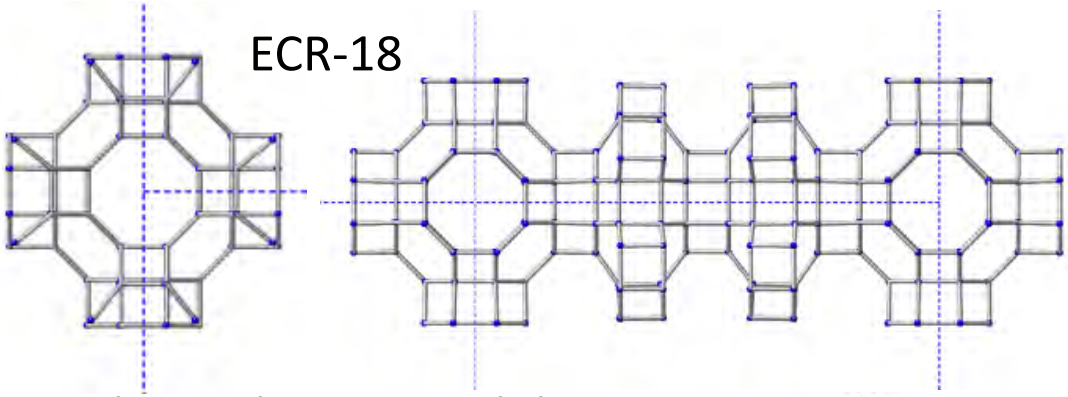
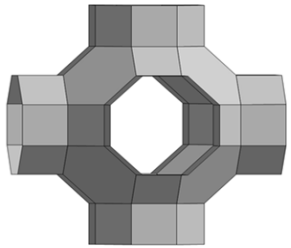
Cation Gating Zeolites: Flexible, highly selective adsorbents

Zeolites containing double 8 membered rings, such as:

ECR-18

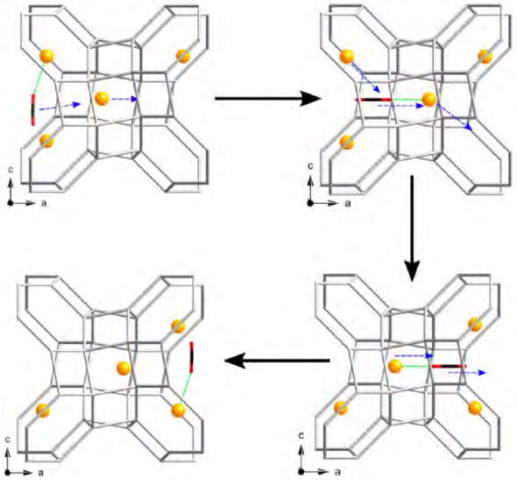


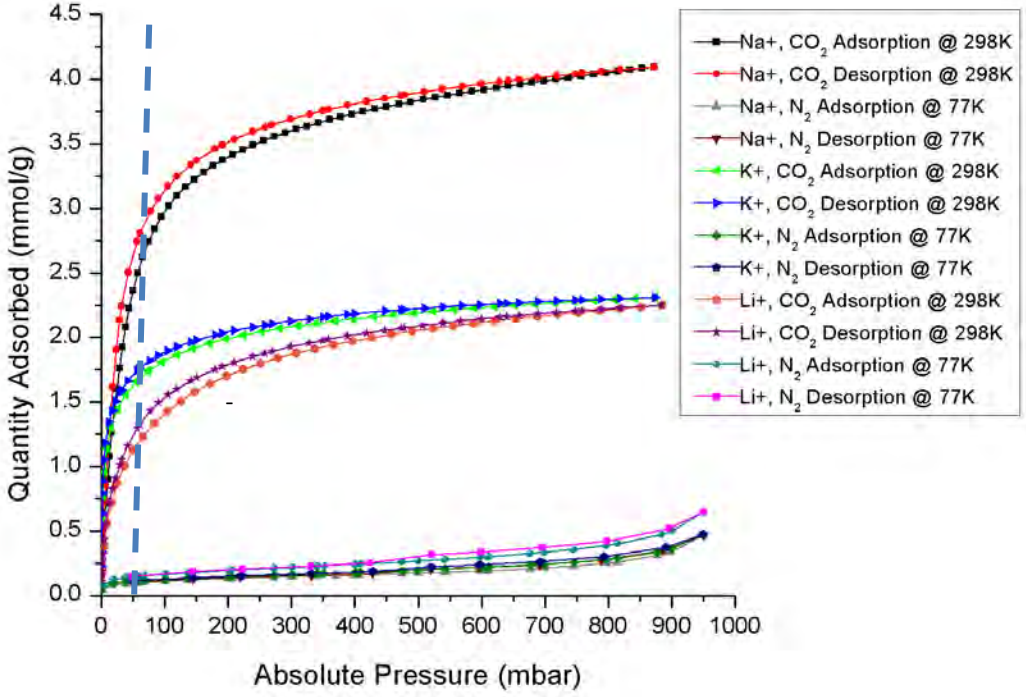


Hydrogen form
(*Im3m*)

Dehydrated cationic form
($I\bar{4}3m$)

Have been shown to exhibit excellent CO_2/N_2 selectivity due to a cation gating mechanism:





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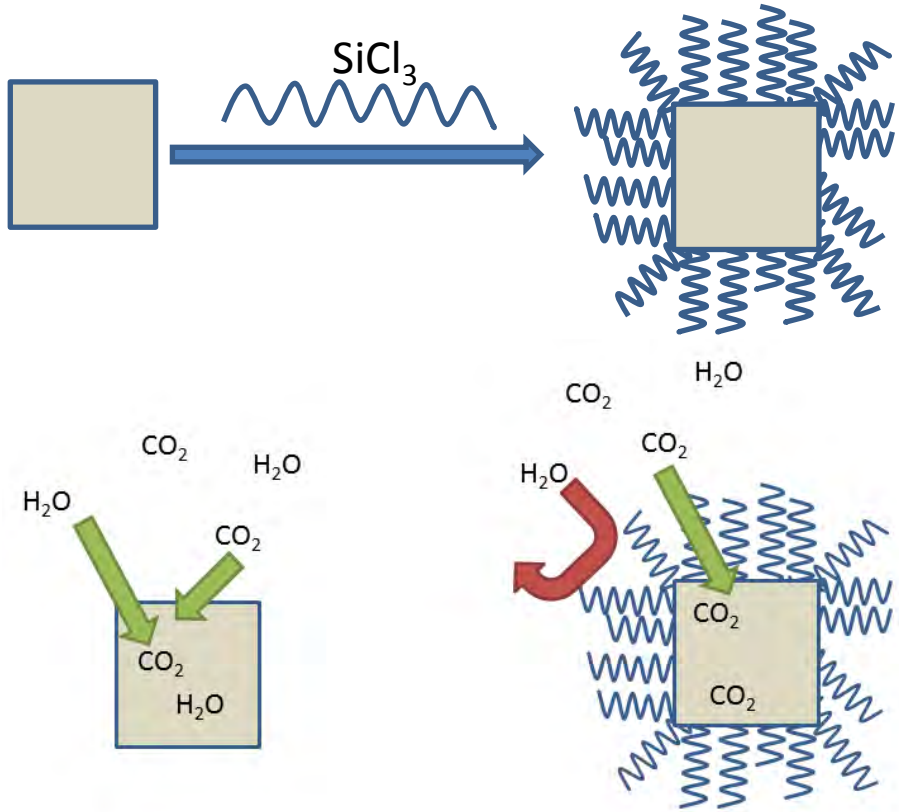
Reducing hydrophilicity of Cation Gating zeolites

Improving performance of zeolitic materials by implementing an hydrophobic shell with long alkyl chain functionalised silanes



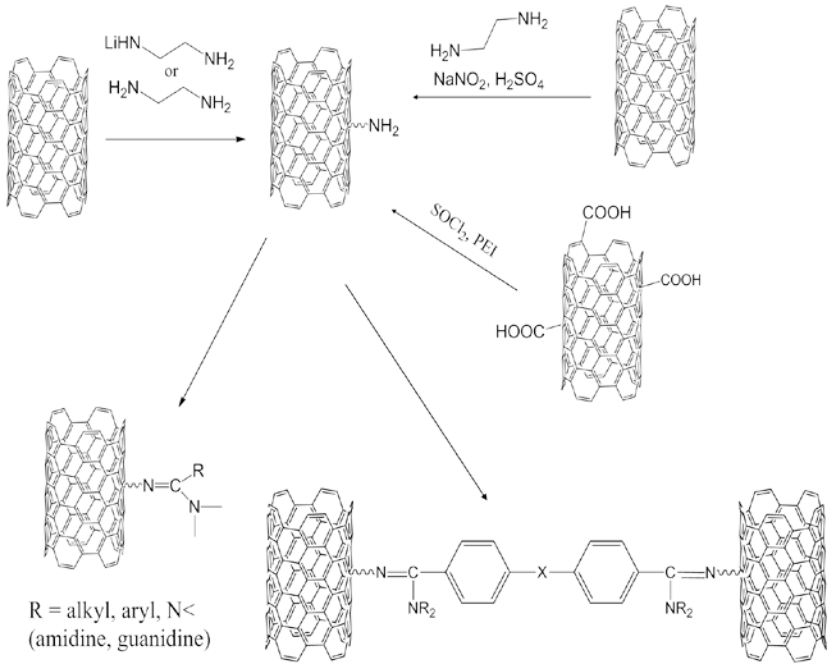
Hydrophilic zeolite, deactivated by water

Hydrophobic zeolite, retains high CO_2 capacity

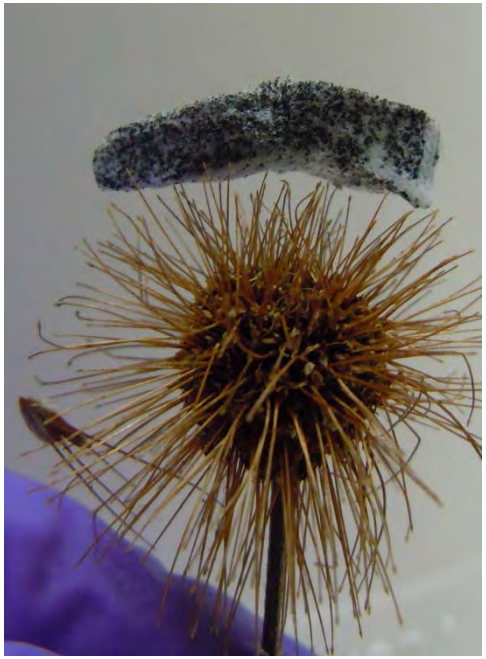
Details on the experimental results on the hydrophobic materials can be found in the poster of Dr. Eleni Shiko

Functionalization of Carbon Materials

Functionalization of carbon nanotubes with basic amine moieties



MWCNT/agarose aerogel produced by lyophilisation



- Carbon nanotubes can be functionalized for selective carbon capture
- Functionalized CNTs can be utilised to create 3D structures with high specific surface area
- Can be heated ohmically for cyclic regeneration of the adsorbent

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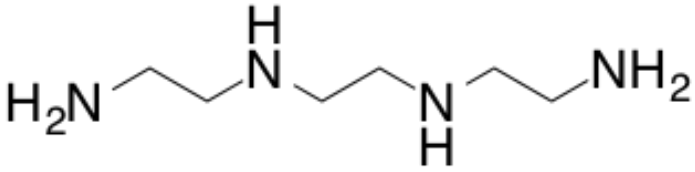
Material Preparation

Three main types of material prepared:

1. CNTs grafted with a basic amino functionalities
2. Activated carbon grafted with amino functionalities
3. A physical impregnation of amino groups to the surface of two different types of porous carbon

Linear Triethylenetetramine (TETA):



Amine	Grafted carbon nanotubes (CNT-CO-NHR)	Amine grafted porous carbon	Amine impregnated porous carbon (various loadings)
EDA	√	√	√
DETA	√	-	√
TETA	√	√	√
PEI (MW600)	√	√	√
PEI (MW10000)	√	√	√
PEI (MW750000)	√	-	-

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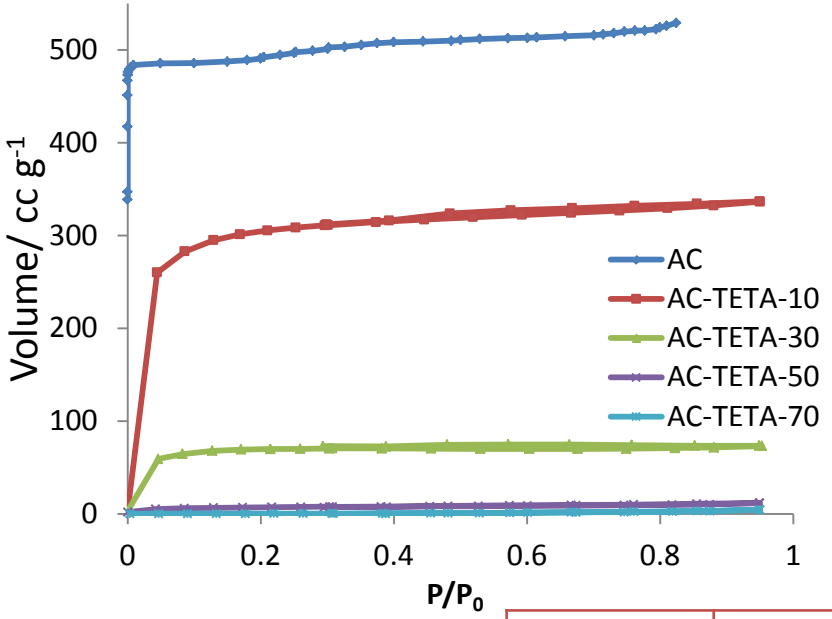
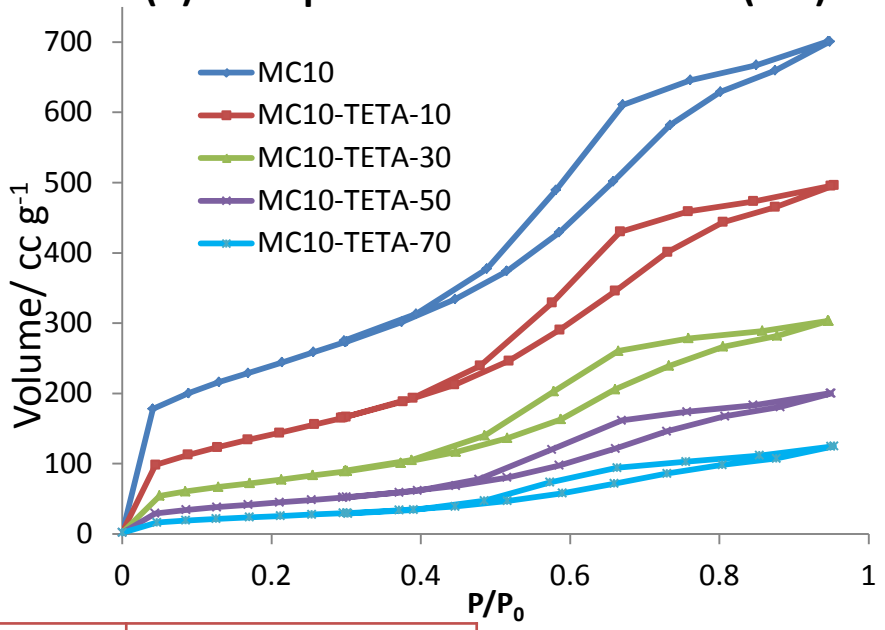
Physical impregnation of amine onto porous carbons

N_2 isotherms at 77 K at various weight loadings of TETA:

(A) Microporous activated carbon (AC)



(B) Mesoporous activated carbon (MC)



	Surface Area [m^2 /g]		Pore Volume [cc/g]	
	AC	MC	AC	MC
Raw	1280	849	0.74	1.09
TETA-10	972	525	0.52	0.77
TETA-30	220	281	0.11	0.47
TETA-50	23.9	166	0.02	0.31
TETA-70	1.10	95.6	0.01	0.19

TETA-X: X= Percentage weight loading of amine

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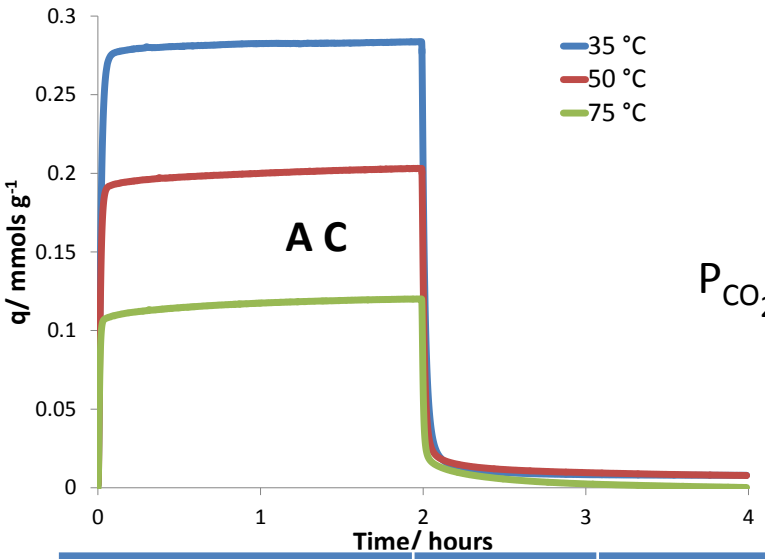
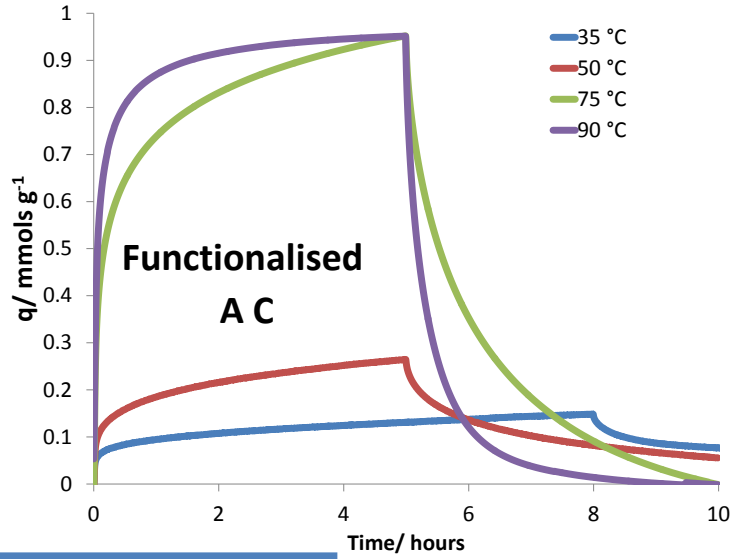
Thermal gravimetric analysis (TGA)



P_{CO_2} = 0.1 bar



	T, °C	ΔH_{ADS}, kJ mol^{-1}	ΔH_{DES}, kJ mol^{-1}
AC	35	-28.0	26.2
	50	-27.8	26.3
	75	-28.5	28.6
AC-TETA-50	35	-97.4	98.0
	50	-88.9	88.7
	75	-90.9	90.7
	90	-90.5	91.1
MC-TETA-30	75	-87.8	85.7
MC-TETA-50	75	-91.2	91.3
MC-PEI600-100	75	-92.5	92.4

27 kJ mol^{-1}

90 kJ mol^{-1}

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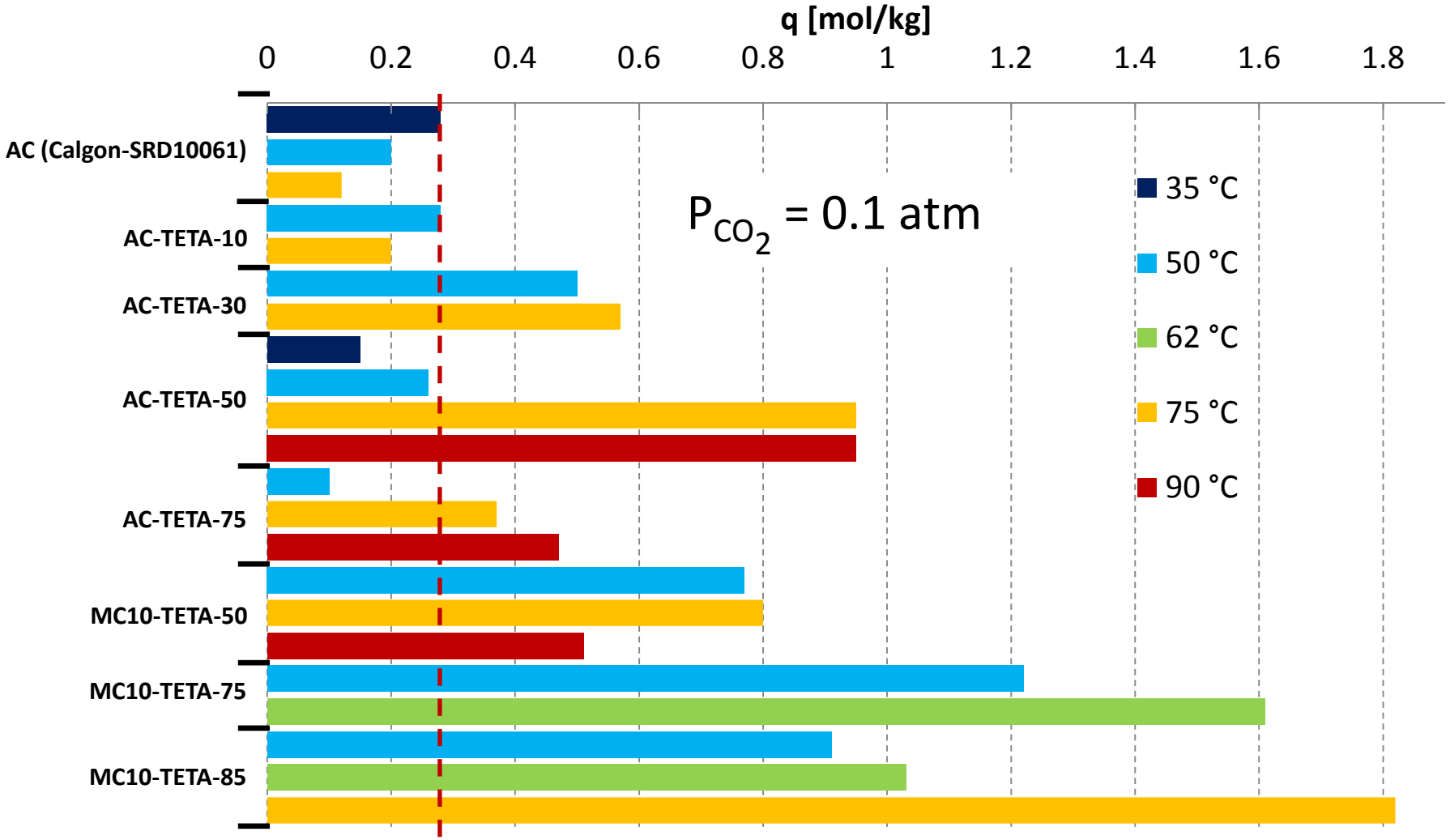
Ranking of CO_2 capacity for selected carbon materials (UoE)



AC-microporous activated carbon;
MC- mesoporous activated carbon;
Benchmark: Commercial AC (Calgon)

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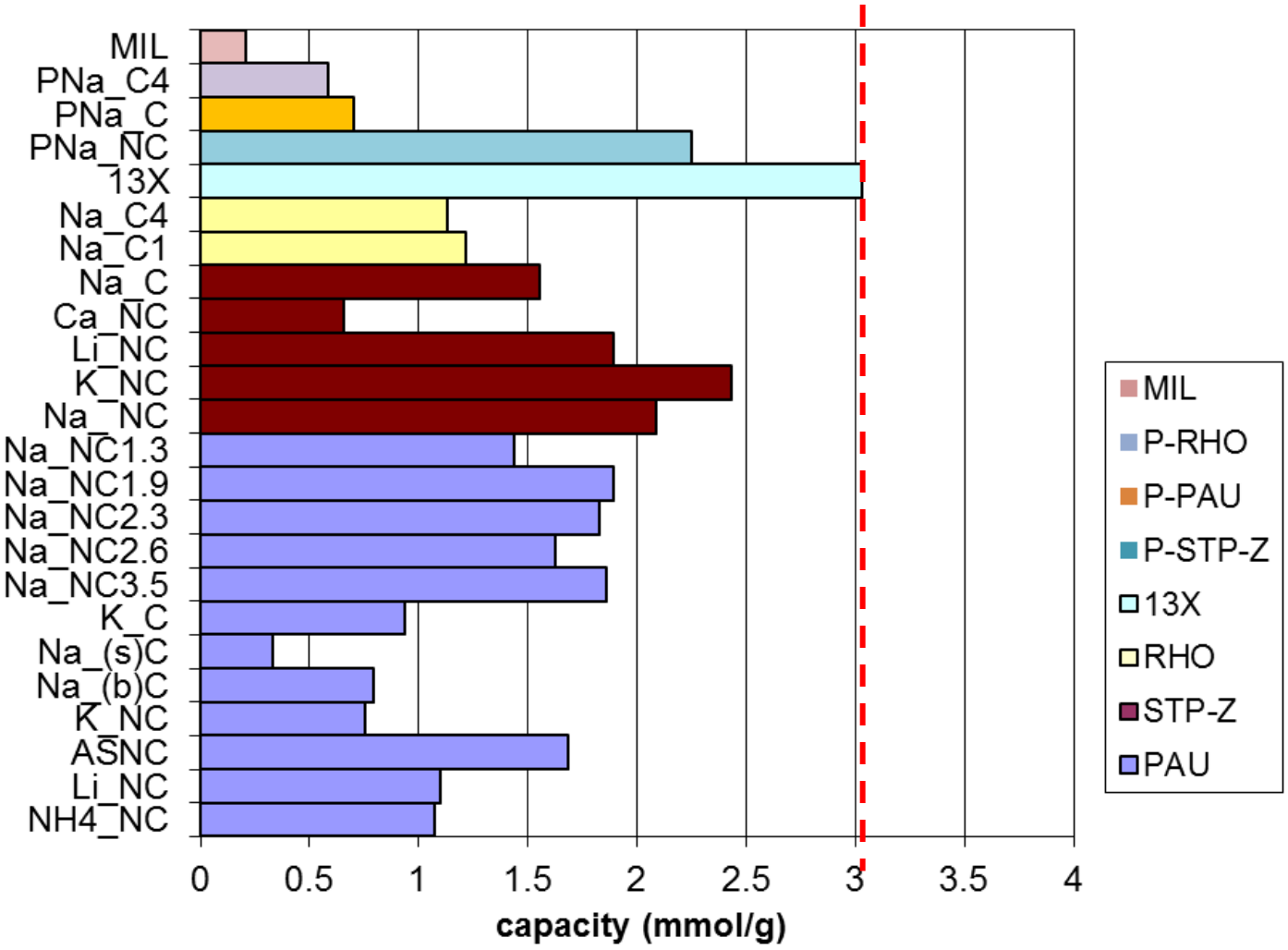
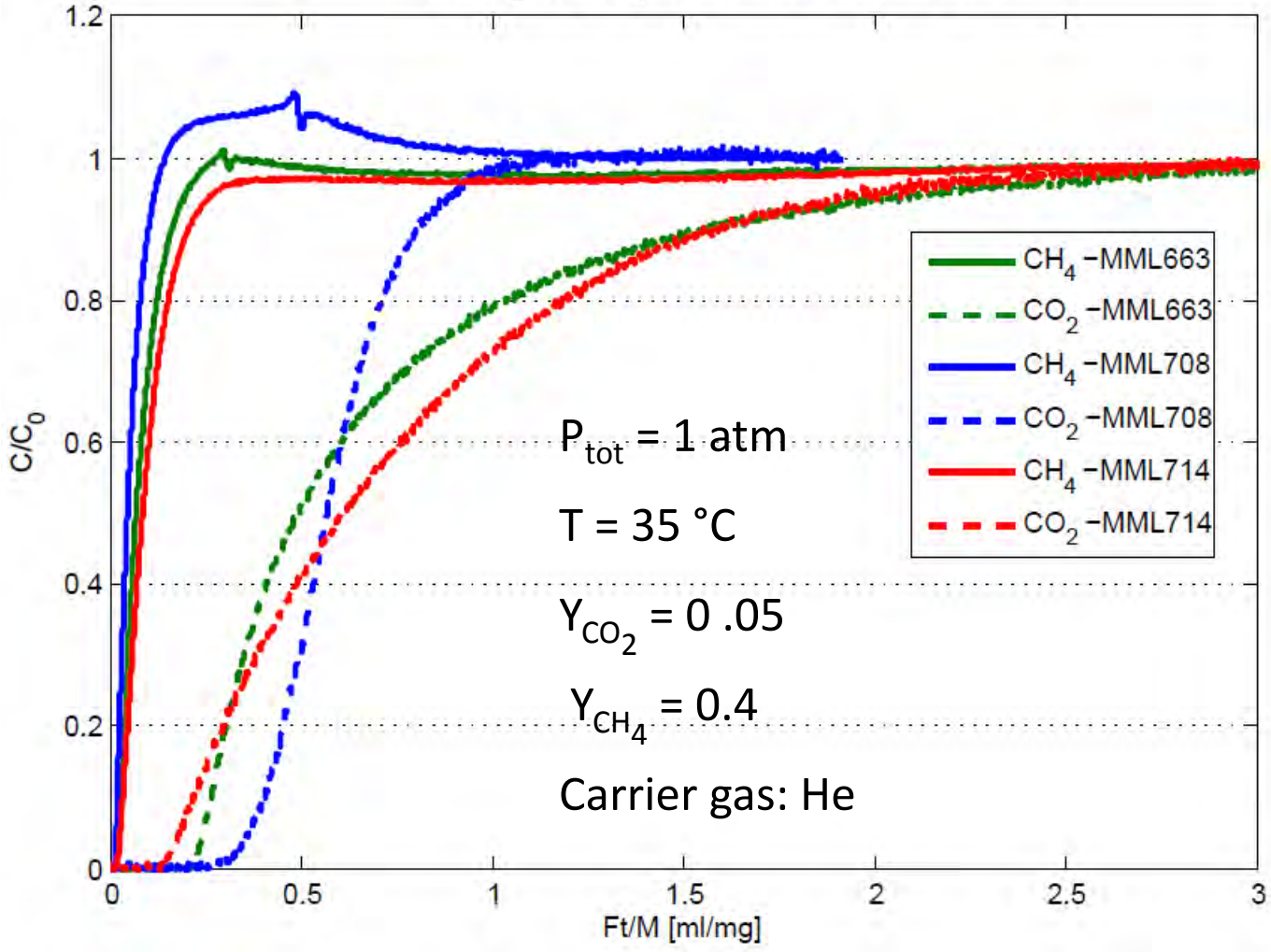
Ranking of CO_2 capacity for Zeolites (UoStA)

$T = 35\ °C;\ P_{CO_2} = 0.1\ atm$



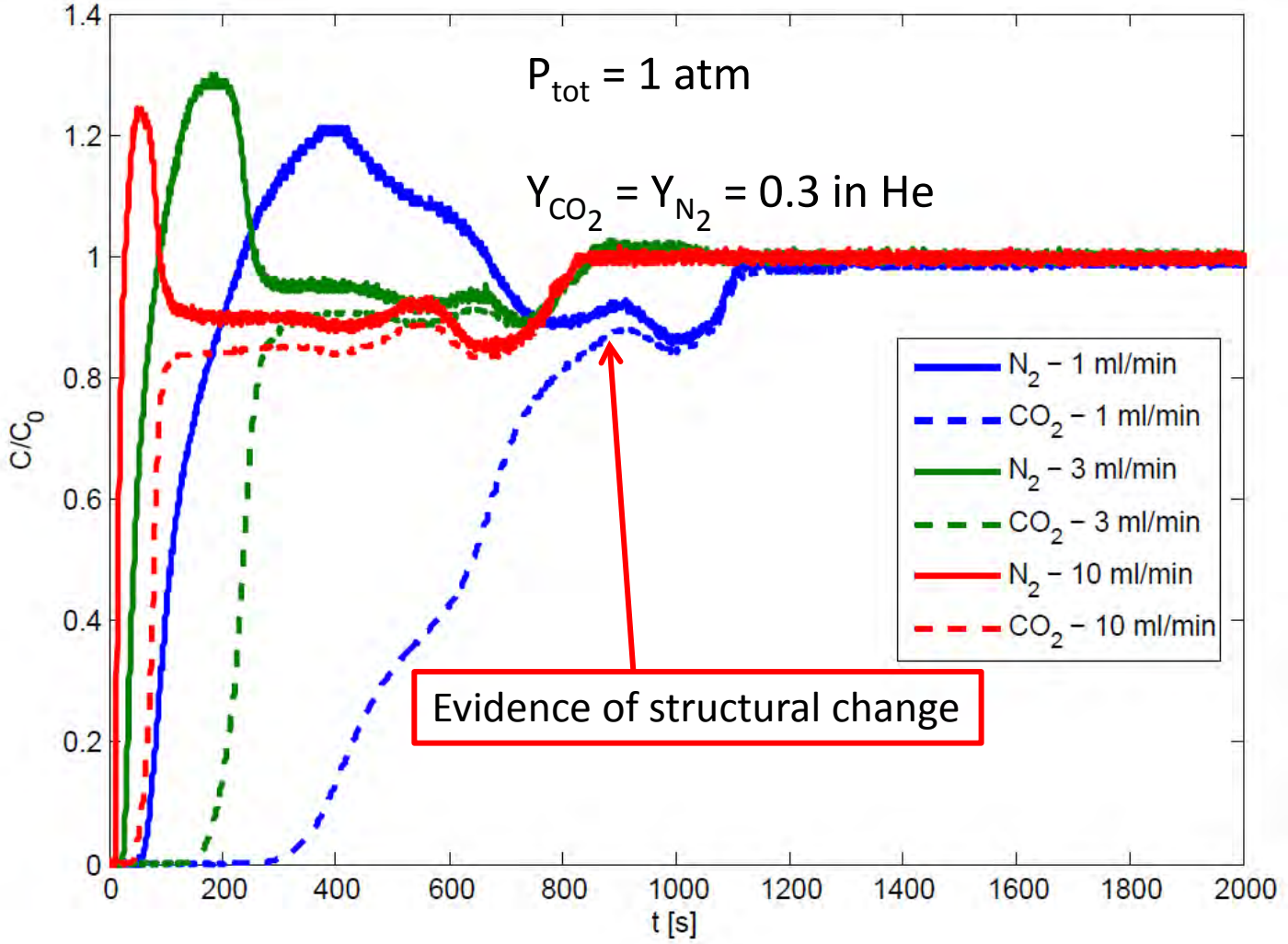
Breakthrough experiment on Li - Rho

CO_2/CH_4 selectivity

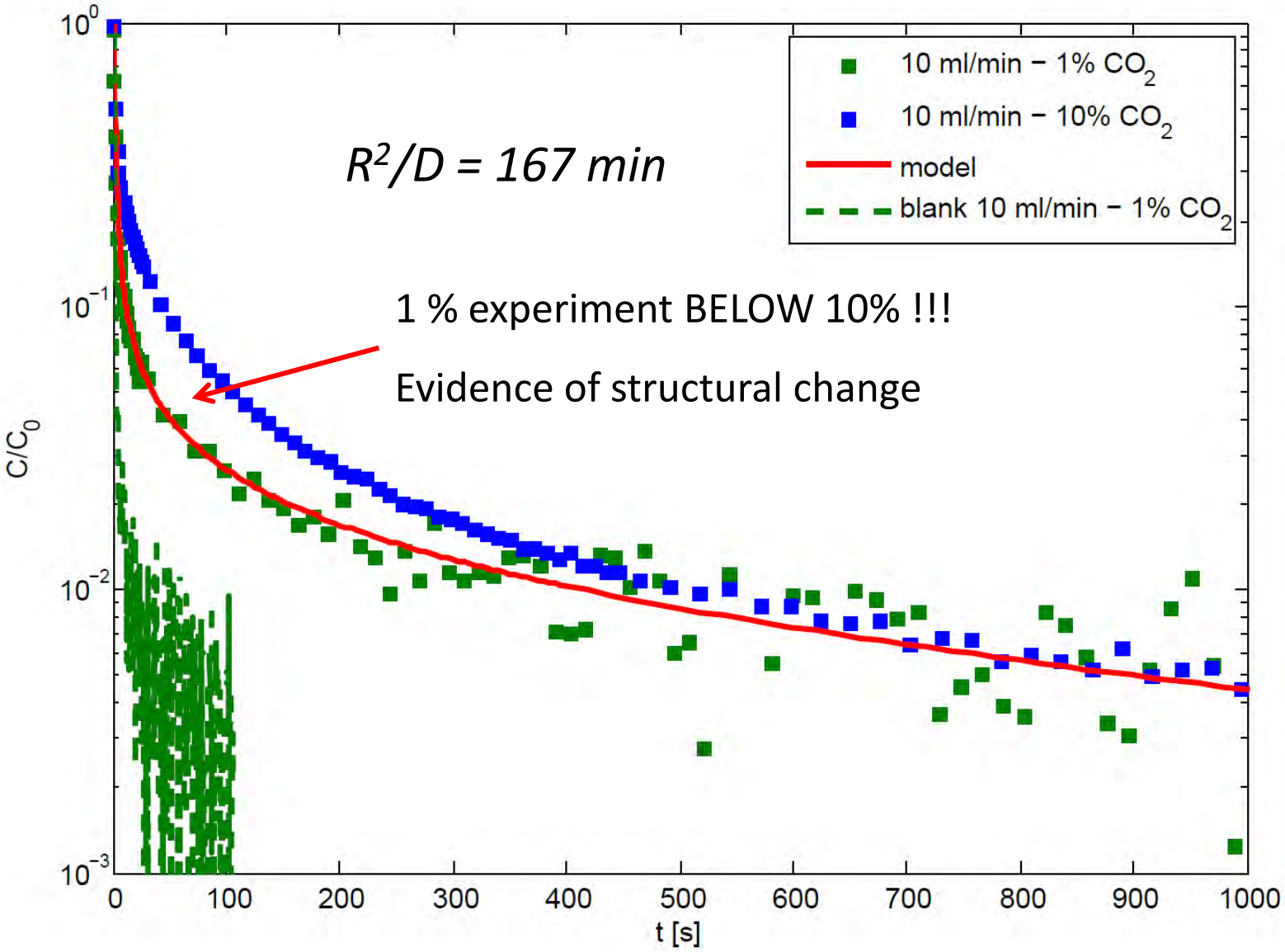


Breakthrough experiments on Paulingite

CO_2/N_2 selectivity



ZLC kinetic experiments on Na-Rho – 1% CO_2

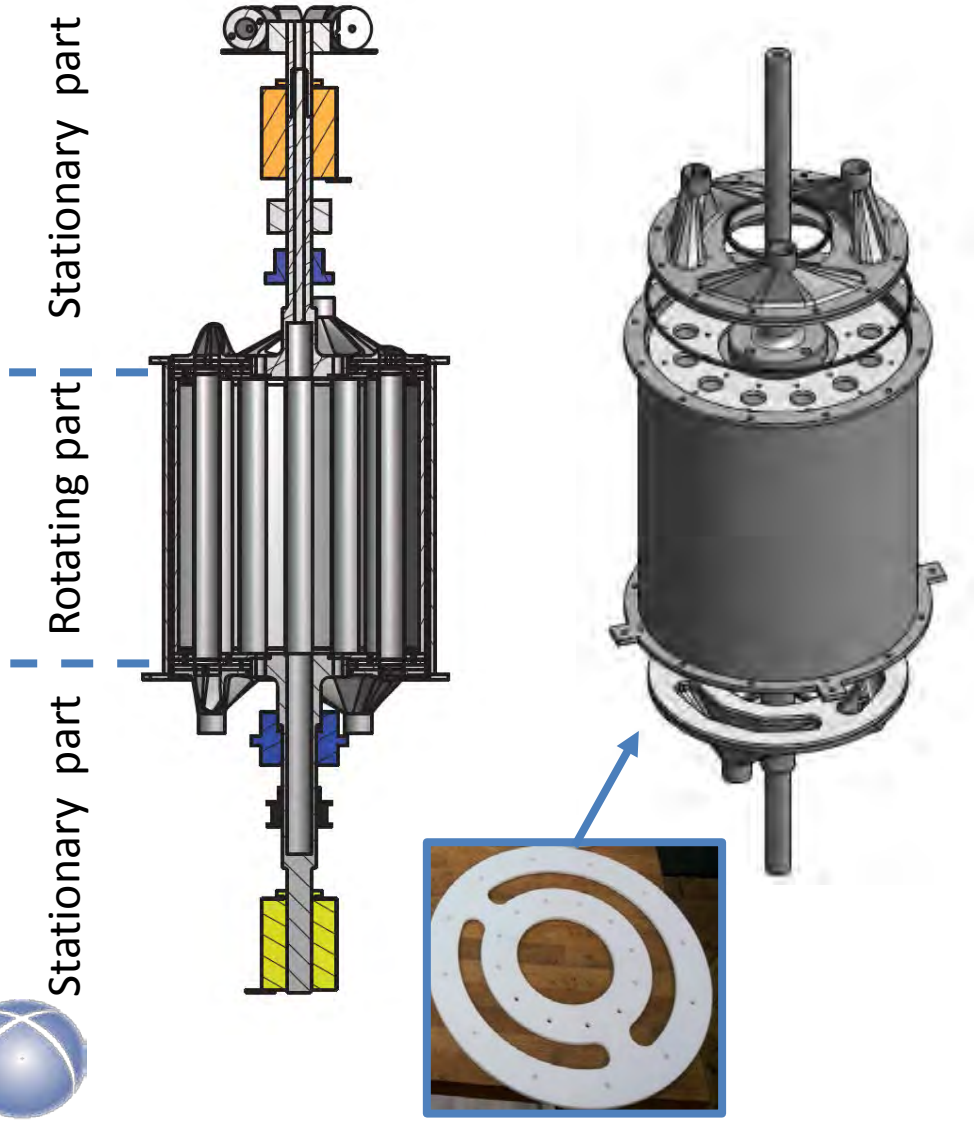


Rotary Wheel Adsorber for carbon capture – Advantages

Due to very low concentration of CO_2 thermal swing adsorption is required for rapid regeneration of the adsorbent.
A properly designed rotary wheel adsorber:

- Can treat large volumes of gas
- Lower capital cost (no multiple columns, piping , valves, etc…)
- Efficient heat integration
- Low pressure drop
- Can perform rapid temperature swings
- Thermal cycles of few minutes: 10 times faster than traditional TSA in fixed bed
- Significant reduction of the size of the capture plant

Bench scale Rotary Wheel Adsorber for carbon capture



- 12-columns rotary system
- Each column is detachable and can be independently tested
- Up to 24 thermocouples (2 per column)
- Large amount of data to be sent in real time
- Max. rotational speed 1 rpm
- Regeneration using electrical heating elements
- One of the first LiFi communication on moving elements
- Real time computer for data acquisition and control of the system

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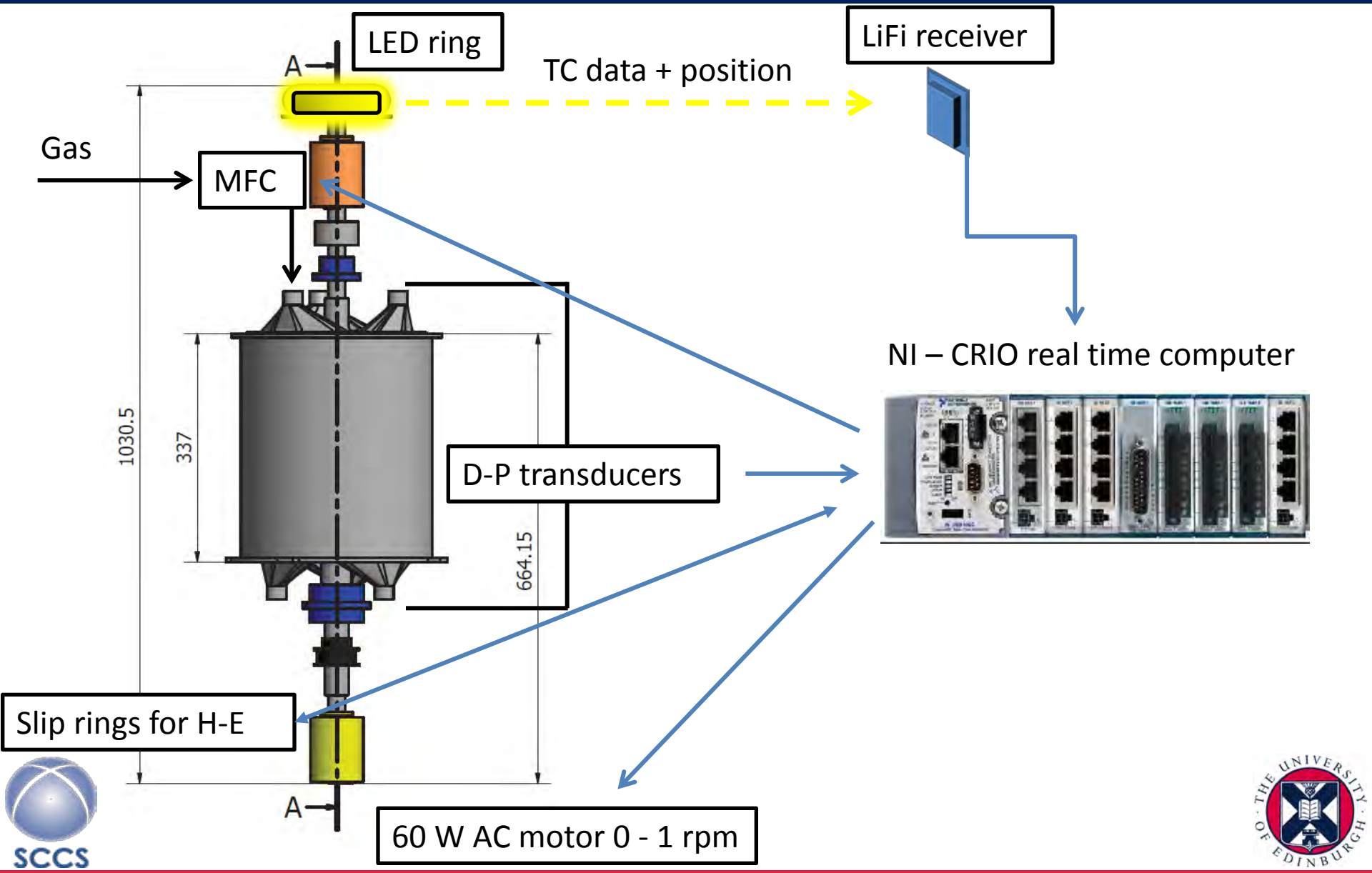
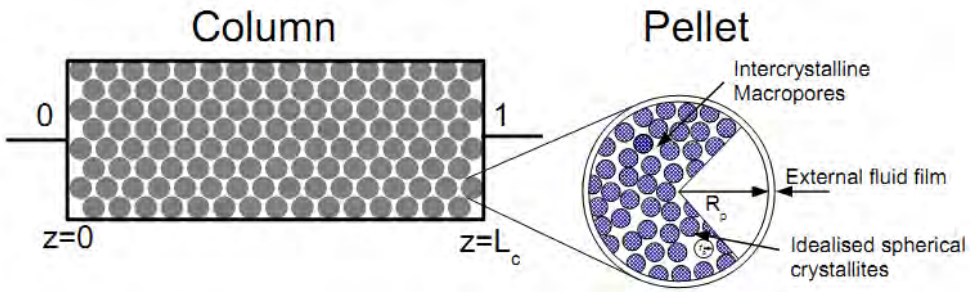
RWA concept - system control



Real rotary system

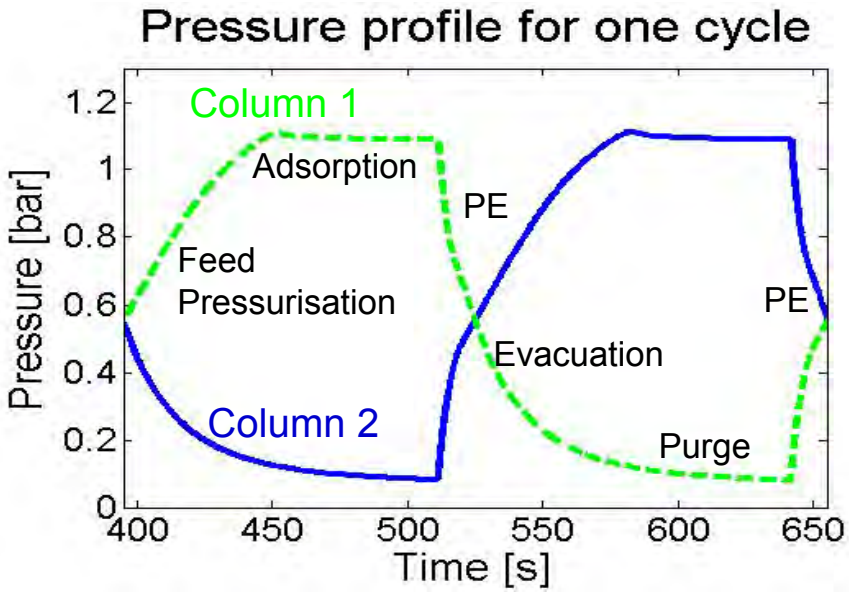
Adsorption model hierarchy



- Complete model
  - Isothermal
    - Pressure drop
    - No Pressure drop
      - No Film resistance
        - No Macropore
          - Micropore Equilibrium
          - Micropore LDF
          - Micropore Diffusion
          - MS-Surface diffusion
        - Macropore LDF
        - Macropore Diffusion
        - Dusty Gas Model
      - Film resistance
  - Non-Isothermal: 1T
  - Non-Isothermal: 2T
  - Non-Isothermal: 3T

Now including also Ideal Adsorption Solution Theory methods for multicomponent adsorption

General adsorption cycle simulator



Adsorption systems

- Multiple adsorption columns
- Connected by splitters, mixers, valves and tanks
- Series of cycle steps: pressurisation, feed, purge, …

Extend column simulation to general adsorption cycles

- Modular system with different units: adsorption columns, valves, splitters, tanks, ...
- Arbitrary number and connection of the units
- Simulate different cycle configurations by time events, e.g. switching of valves

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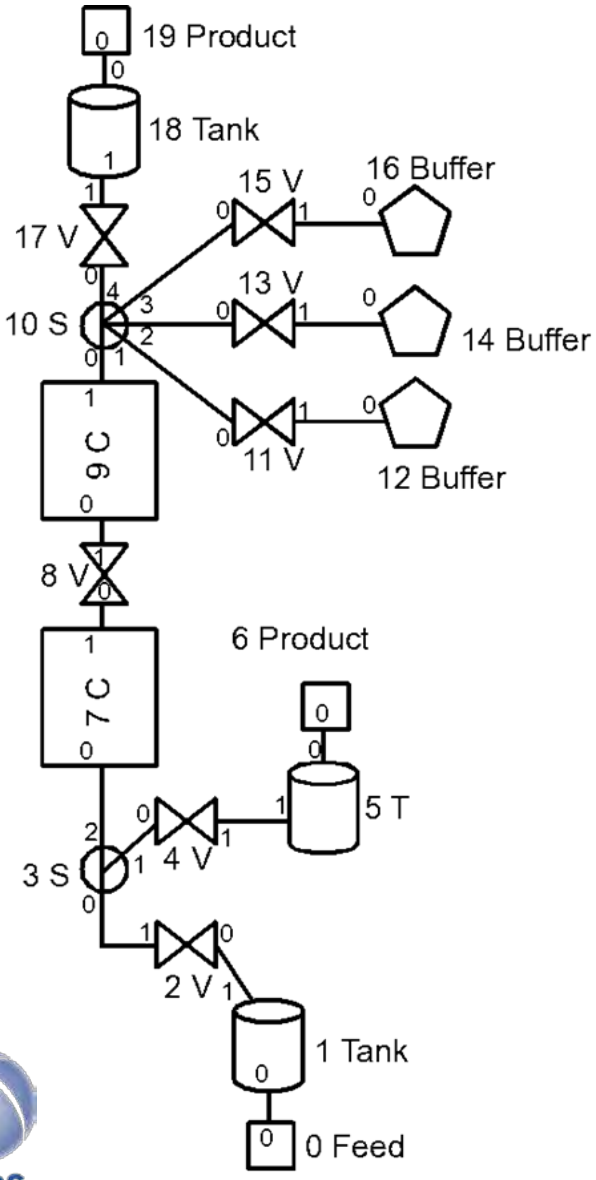
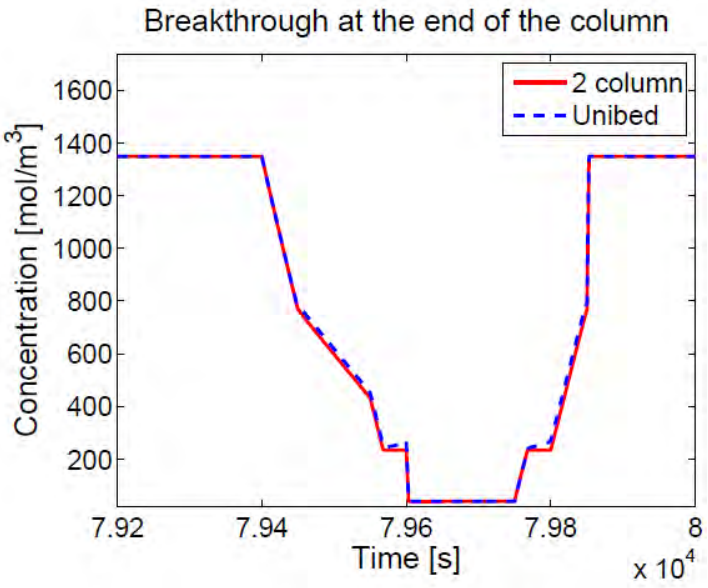
Buffer unit for unibed approach



- All columns cycle through the same steps
- Steps with interaction between two columns
  - Output of one column is input of the other column
  - Add a buffer unit for each interaction pair
- Data in buffer unit is half a cycle out of date
- Same result at Cyclic Steady State
- Order of magnitude faster



Preliminary simulations

Adapting Cysim cycle simulator for the simulation of a base case study:

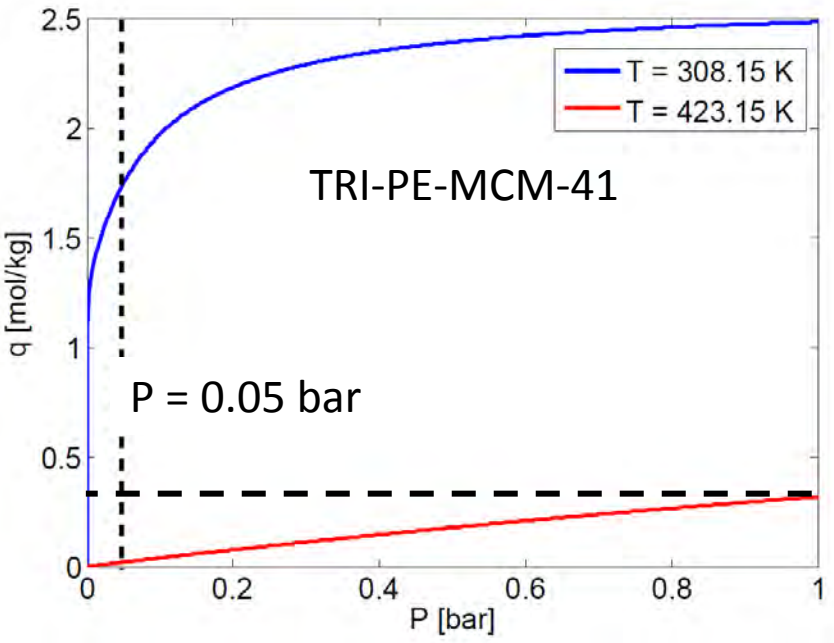
Adsorbent : TRI-PE-MCM-41(Y. Belmabkhout, et al., 2010)

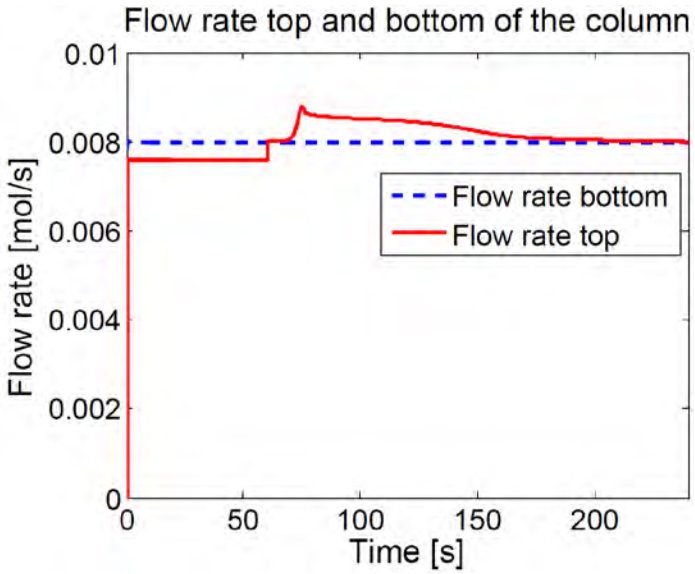
Feed: 5% CO_2 in N_2

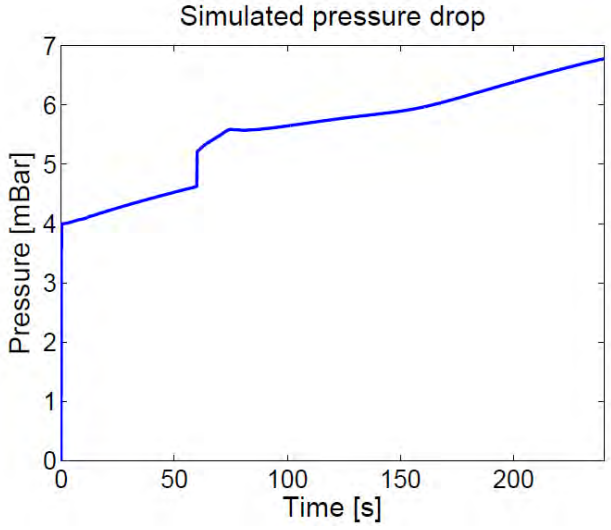
Adsorption time: 1 min 35 °C

Heating time: 3 min

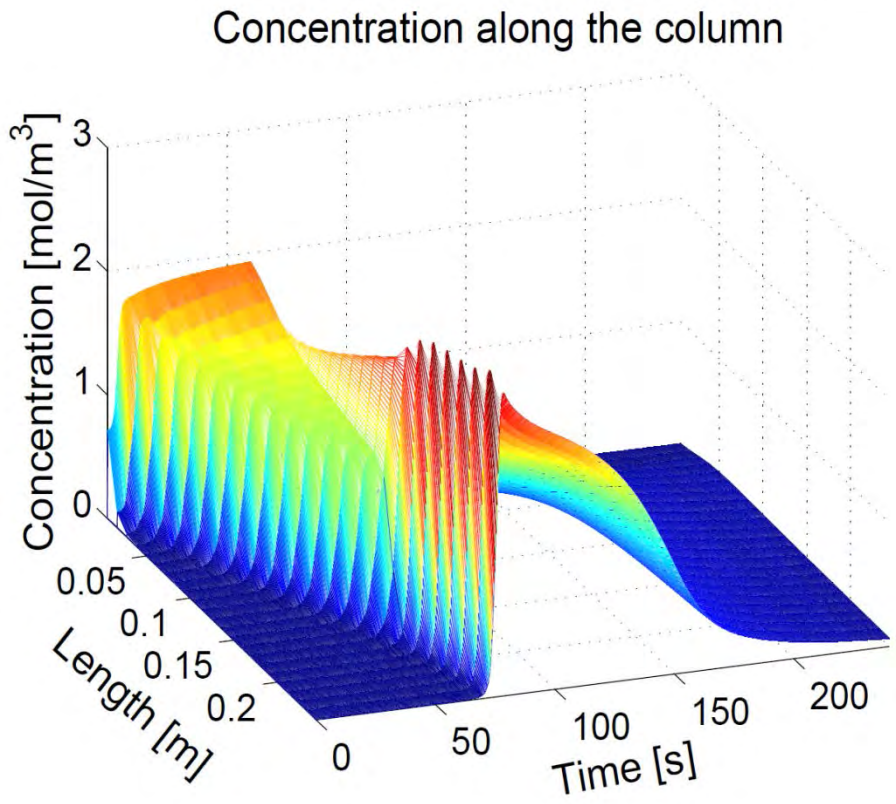
F = 200 cc/min

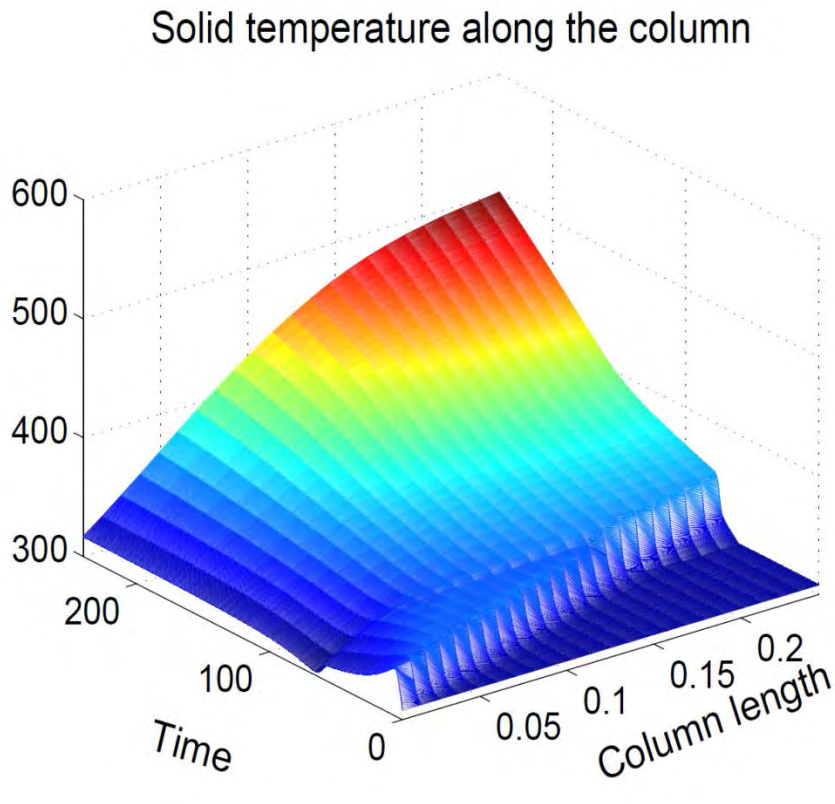




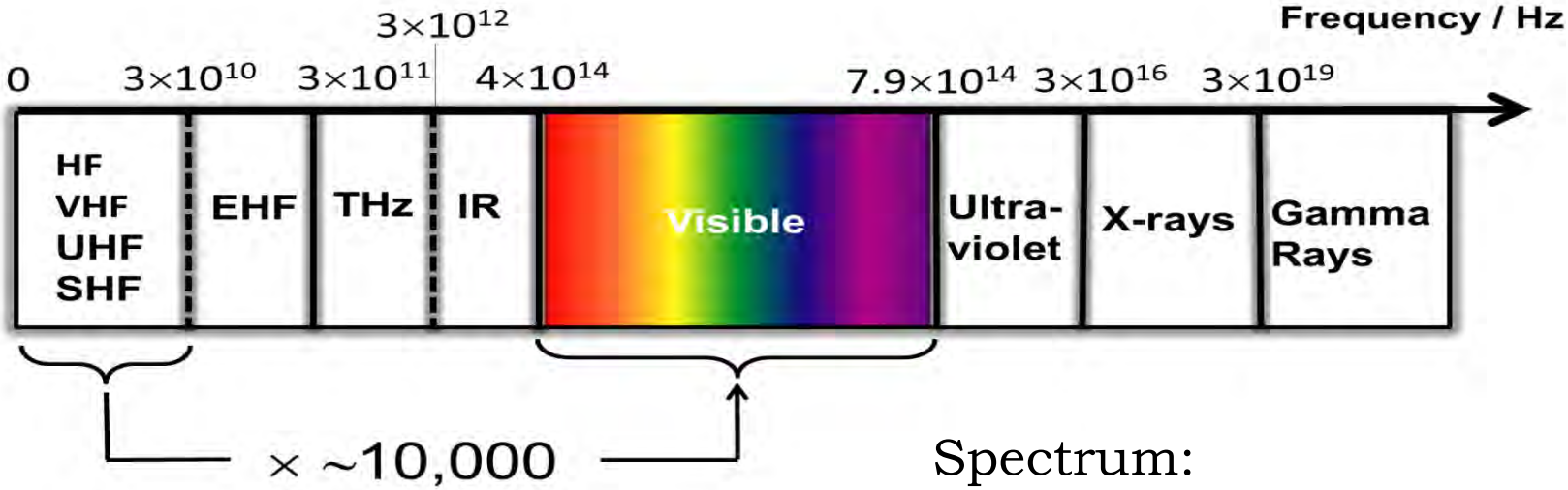


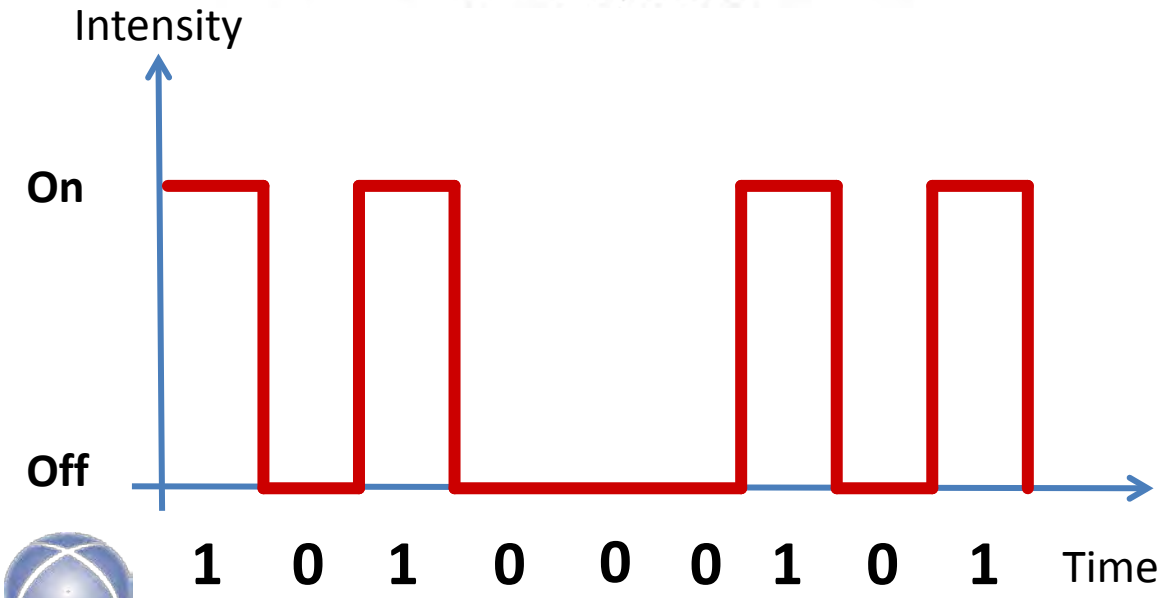
Preliminary simulations





LiFi – how does it work?





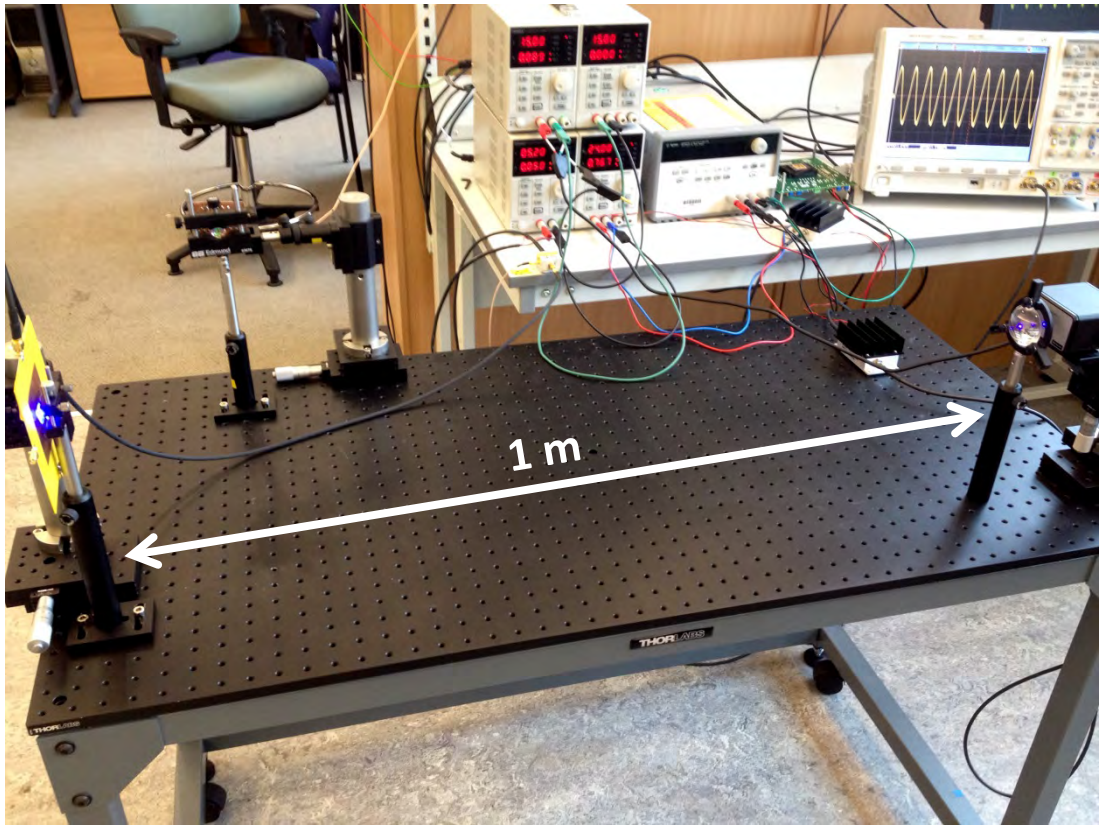
Spectrum:

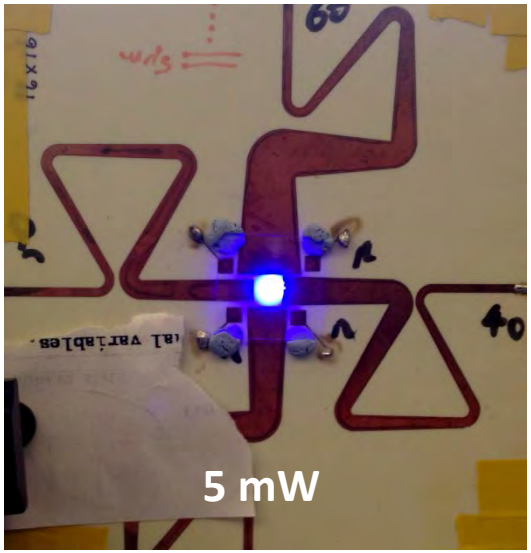
- Unregulated (free)
- Huge
- Safe

Existing Infrastructure

Inexpensive devices

Recent ‘hero’ demonstrations





3.5 Gbps from **single color** LED at **5 mW**

1.1 Gbps at **10 m** at **5 mW**

Conclusions

- Several materials have been developed and tested using different techniques (ZLC, TGA, Breakthrough)
- Some of the amine-based carbons show a clear chemisorption process
- Some of the zeolitic frameworks show evidence of structural modification associated to the presence of CO_2
- A novel bench scale rotary wheel adsorber has bee designed and is being built at the UoE
- CySim is being modified to predict the performance of the bench scale prototype
- A novel LiFi communication system (one of the first on moving elements) is being developed for the data acquisition in the RWA

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