Porous systems for high performance CO_2 capture: *The MATESA selective CO_2 capture materials*

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CENTRE FOR NANOSTRUCTURED INTERFACES AND SURFACES

MATESA Dissemination Day, Jun. 16th , 2016, OSLO, NORWAY

Outline: the materials of MATESA project

- The adsorbers of MATESA
  - Characterization of the materials
  - MATESA selective CO_2 capture materials adsorbents
  - Scale up of MATESA CO_2 capture materials adsorbents
- The conductive media – bio carbon
- Final remarks

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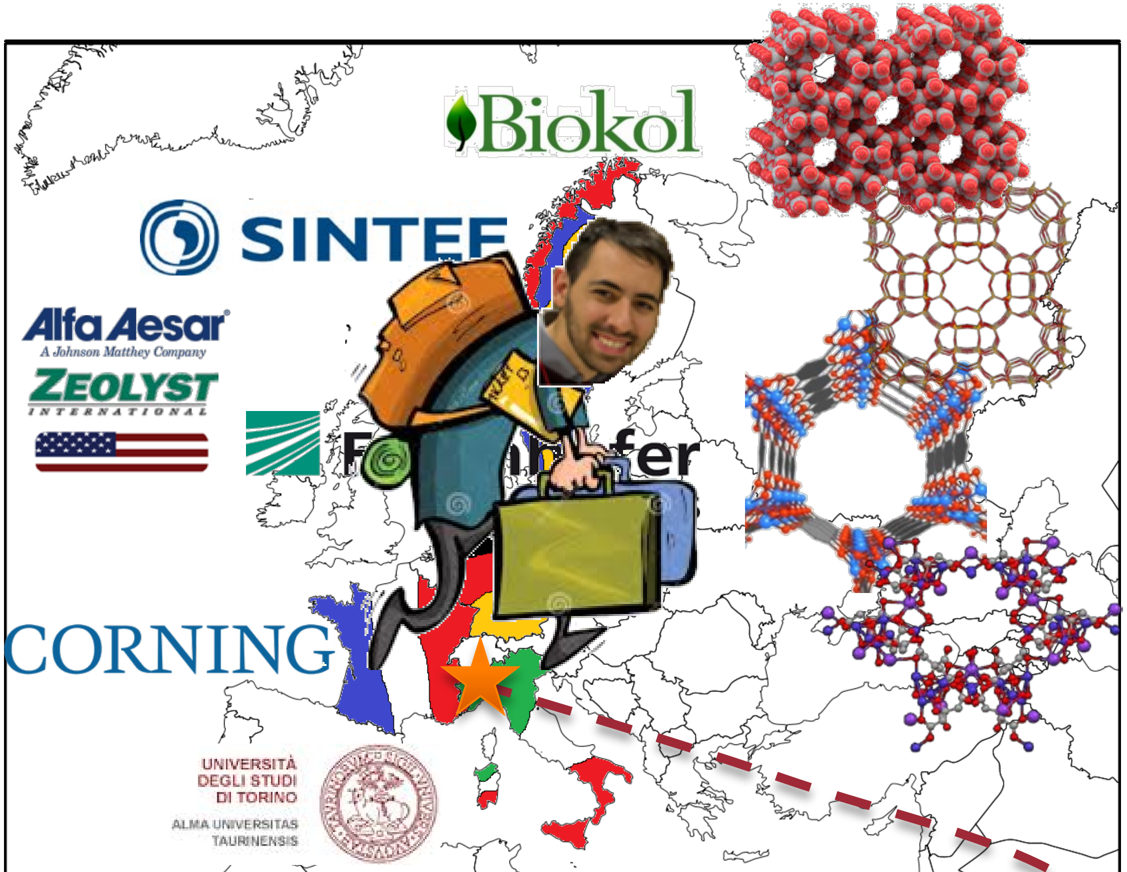
The adsorbers of MATESA

TARGET: Performing CO_2 adsorbers for Electric Swing Adsorption (ESA)



REFERENCE ADSORBENTS

(Selective CO_2 capture adsorbent)

13-X zeolite

NH_4-ZSM5 zeolite

Commercial materials

ADVANCED ADSORBENTS

(Selective CO_2 capture adsorbent)

CPO-27-Ni MOF

UTSA-16 MOF

Laboratory materials

BIO CARBONS

REAL PROCESS ADSORBERS

Active phase

+

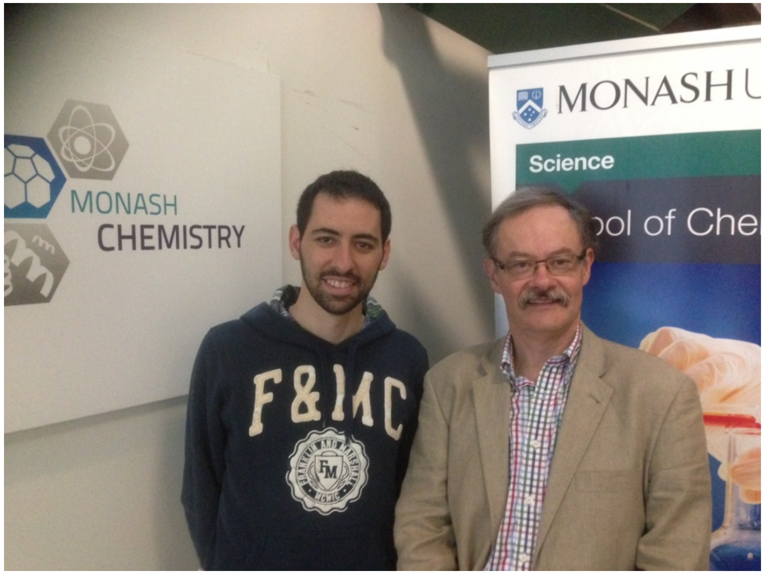
Conductive phase

Static characterization of physical-chemical properties

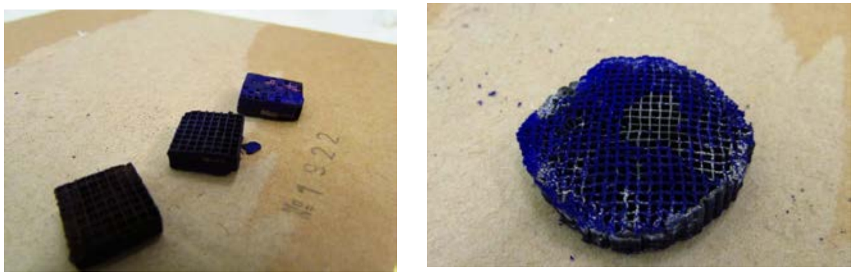
Dynamic characterization of physical-chemical properties

The adsorbers of MATESA

Under the supervision of Prof. Alan Chaffee



MONASH University



TARGET

Synthesis and grafting of UTSA-16 over different types of carbonaceous supports

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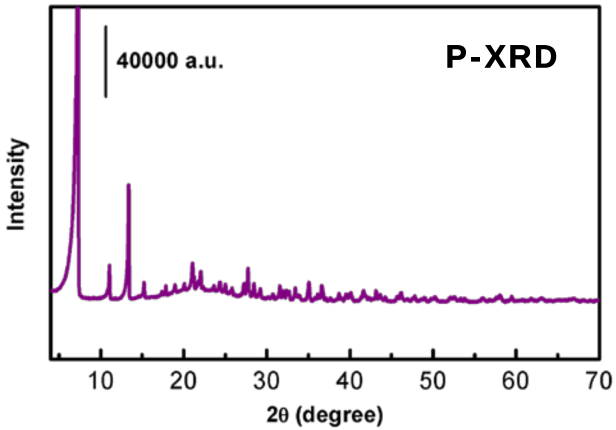
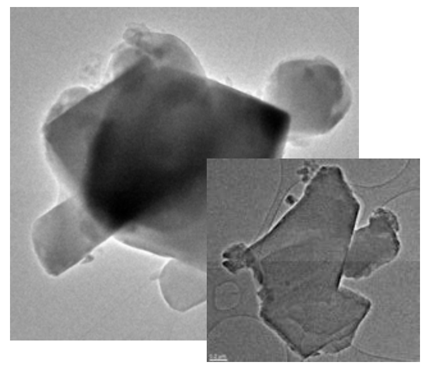
Characterization of the material





TEM + EDX

SURFACE AREA

5000 m^2 g^{-1}

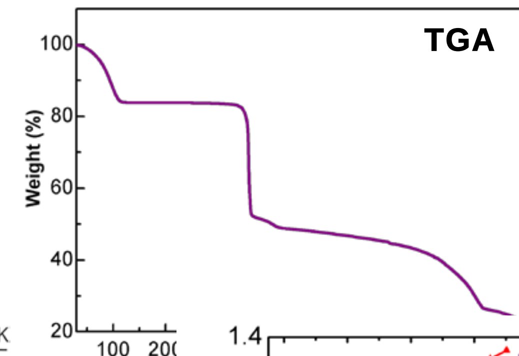
2000

800

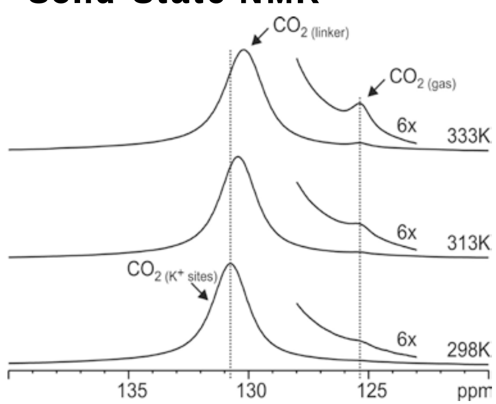
100

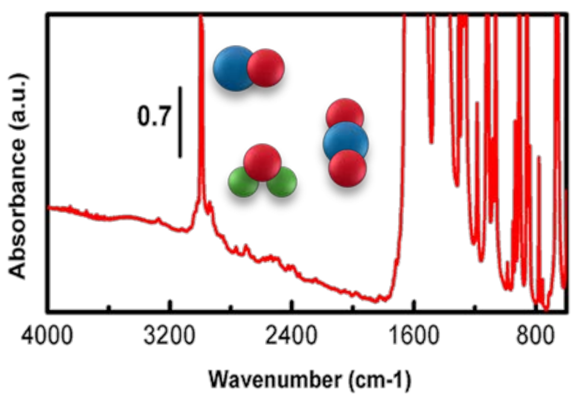
20

N_2 @77 K adsorption

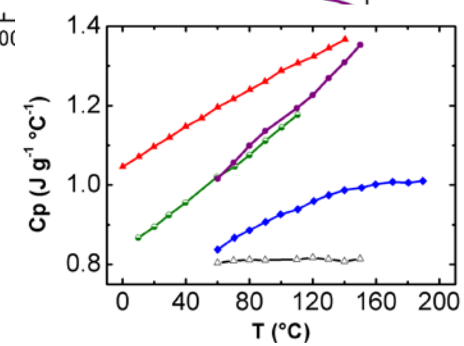


Solid-State NMR





IR SPECTROSCOPY+ PROBE MOLECULES

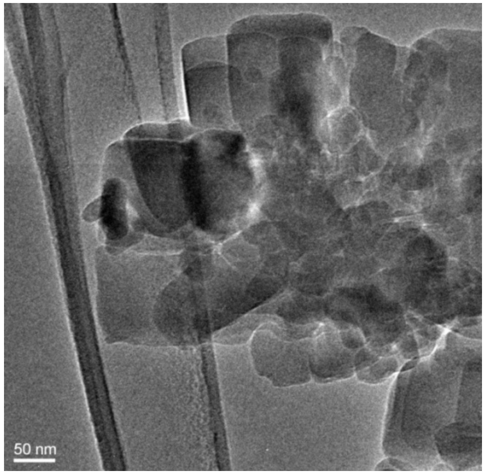


Heat Capacity

Characterization of the material

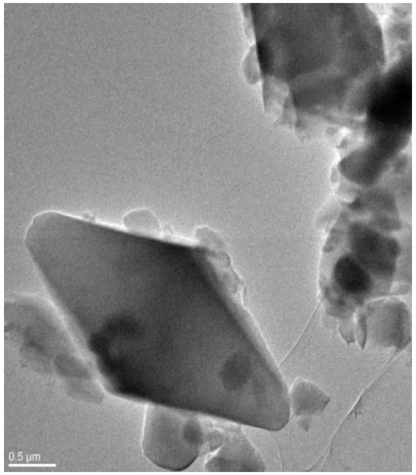
Transmission Electron Microscopy + EDX analysis: Morphology and composition

ZSM-5



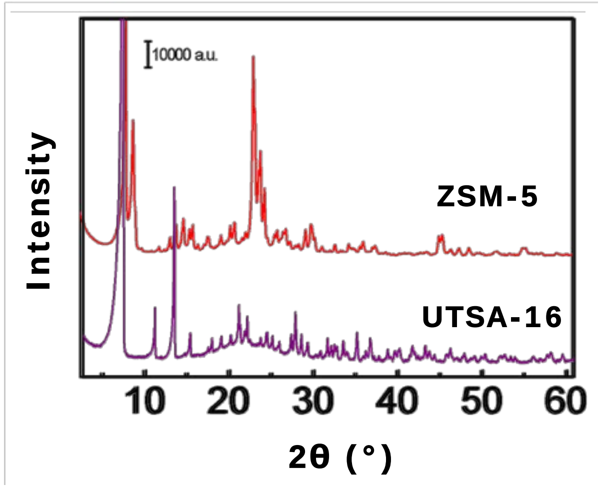
Reference Adsorber

UTSA-16 MOF



Advanced Adsorber

P-XRD



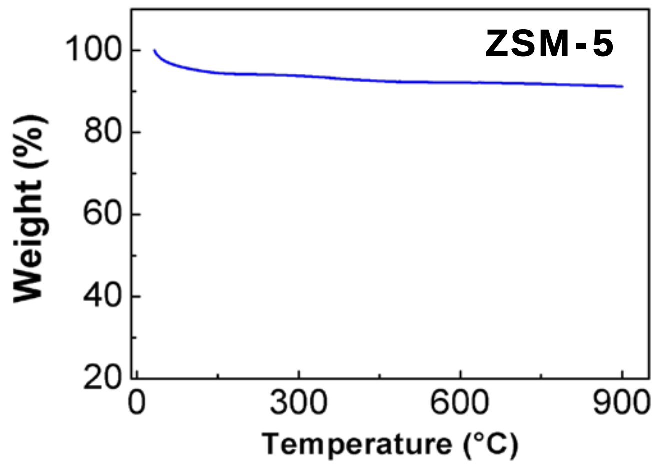
Parallel study on CPO-27-Ni

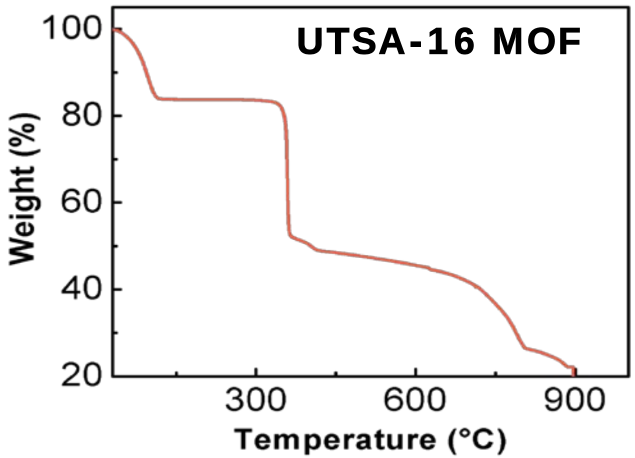
Surface Area and Total Volume of Pores

	UTSA-16	CPO-27-Ni	ZSM-5	13-X
Surface Area ($m^2\ g^{-1}$)	814	1246	467	791
Total Volume of Pores ($cm^3\ g^{-1}$)	0.3	0.5	0.2	0.3

Characterization of the material

Thermogravimetric analysis





Thermal stability of advanced adsorbers till 350 °C

Specific heat capacity

	Temperature (°C)	Heat Capacity (J °C^{-1} g^{-1})
UTSA-16	60	1.0
CPO-27-Ni	60	1.2
ZSM-5	60	0.8

Cp of water: 4.18 J °C^{-1} g^{-1}

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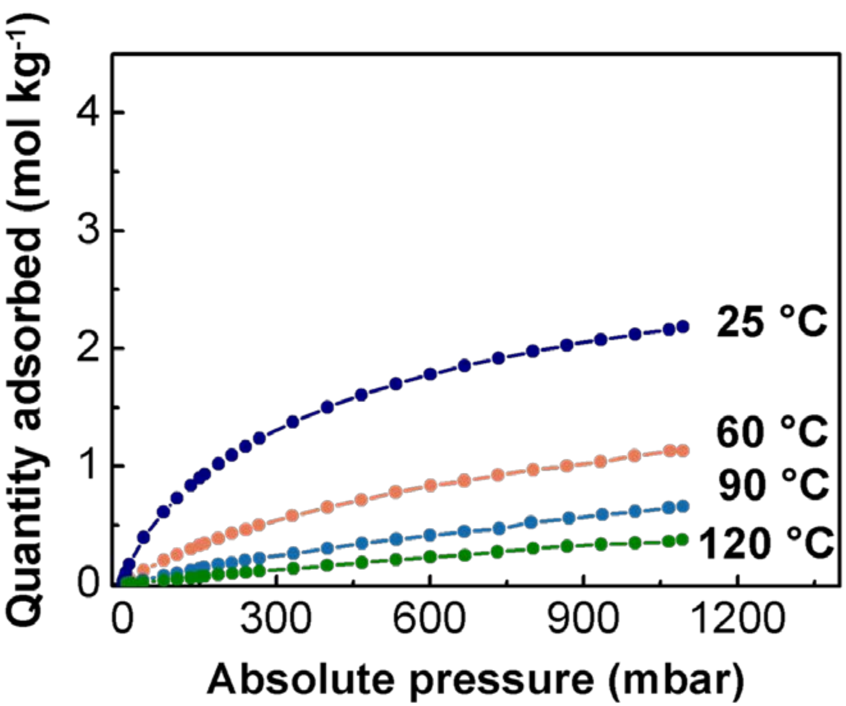
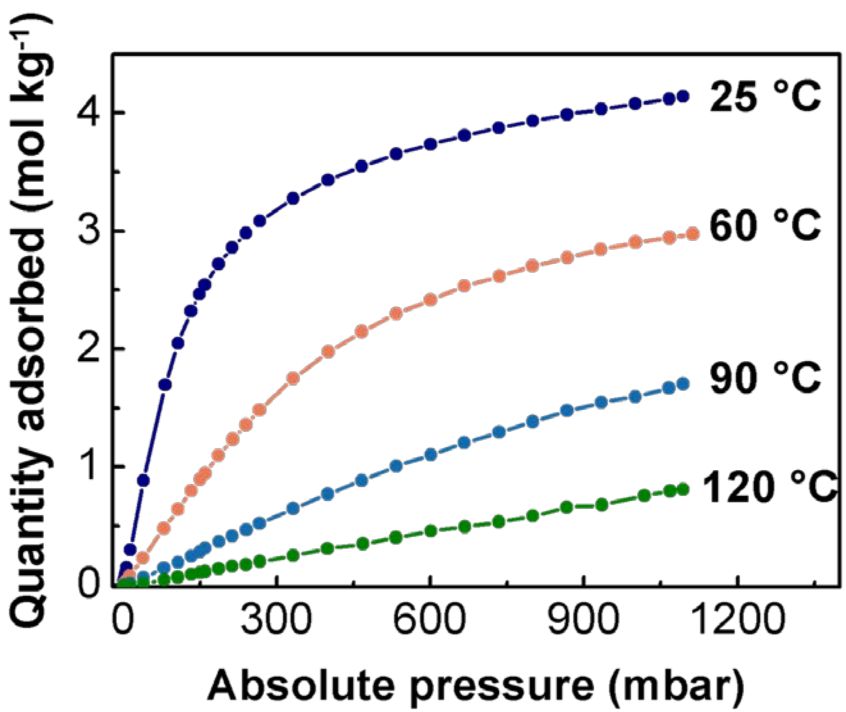
Adsorption of CO_2

STATIC adsorption isotherms of CO_2

ZSM-5



UTSA-16

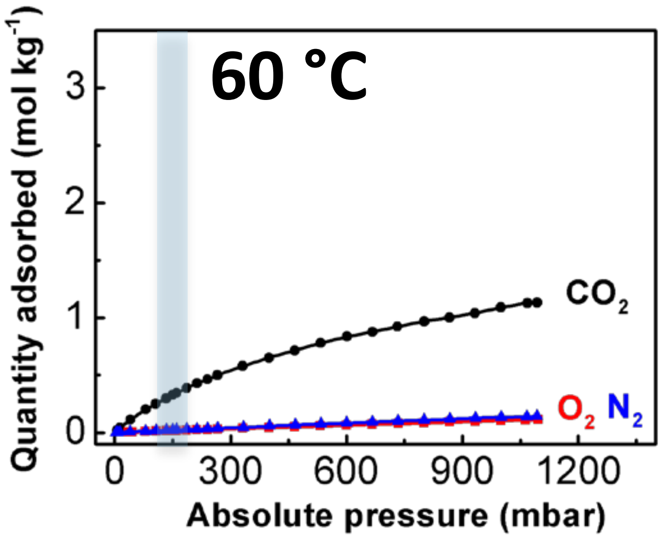


The adsorption of CO_2 has been studied at relevant temperature and pressures

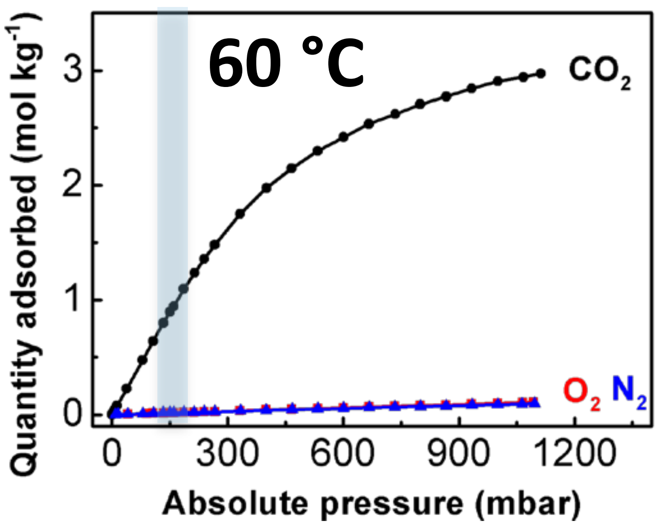
Adsorption of CO_2, N_2 and O_2

STATIC **adsorption isotherms of CO_2 ,N_2 and O_2**

ZSM-5



UTSA-16



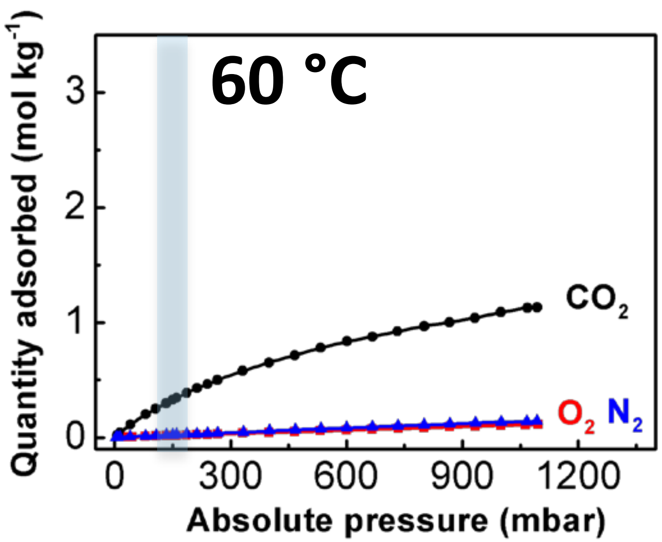
Adsorption at CO_2 partial pressure of 0.15 bar

	CO_2 uptake (mol kg^{-1})	N_2 uptake (mol kg^{-1})	O_2 uptake (mol kg^{-1})
ZSM-5	0.33	0.08	0.02
UTSA-16	0.92	0.08	0.003

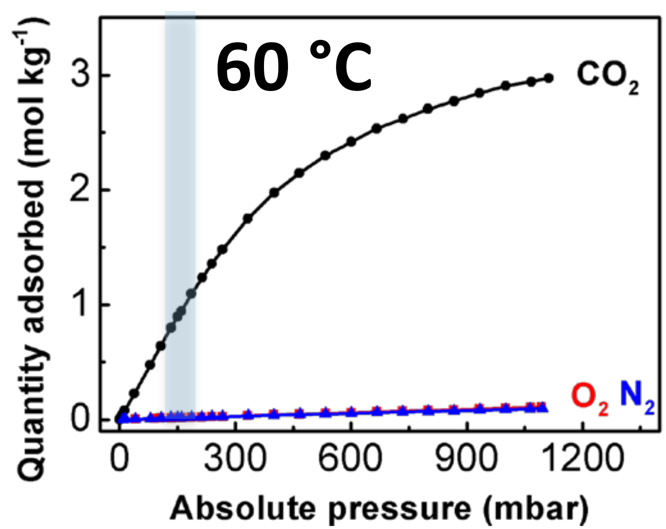
Adsorption of CO_2, N_2 and O_2

Strength of CO_2 ,N_2 and O_2 adsorption isotherms → **Q_{st} Isosteric heat of adsorption**

ZSM-5



UTSA-16

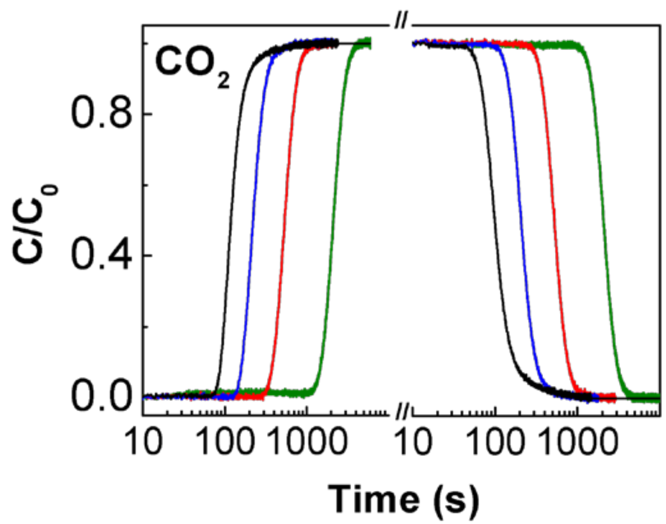


	Q_{st} CO_2 ($kJ\ mol^{-1}$)	Q_{st} N_2 uptake ($kJ\ mol^{1}$)	Q_{st} O_2 uptake ($kJ\ mol^{-1}$)
ZSM-5	35	15	18
UTSA-16	37	13	14

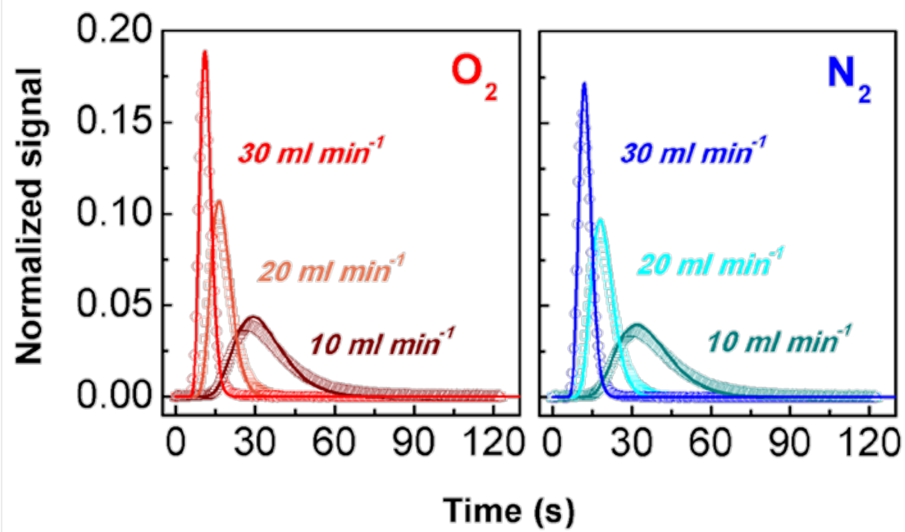
Adsorption of CO_2, N_2 and O_2

DYNAMIC adsorption of CO_2 ,N_2 and O_2 on UTSA-16 MOF

Breakthrough experiment



Pulsed chromatography



Henry Constant K_H for CO_2 ,N_2 and O_2

	T (°C)	CO_2 K_H	N_2 K_H	O_2 K_H
UTSA-16	60	112.6	3.3	3.0

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Scale up of CO_2 capture adsorbents

5.5 liter batch reactor

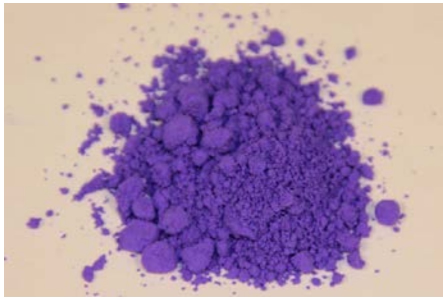
Properties:

- Volume: 1.5 gallon (~5.5 liters)
- Pressure up to 200 bar
- Temperature to 500 °C
- Internal stirring

Literally a heavy work

Scale up of CO_2 capture adsorbents

UTSA-16 scaled-up successfully (>100g/batch)



Scale up of CO_2 capture adsorbents

CPO-27-Ni was also scaled-up to > 100g/batch

Synthesis was based on water (as seen in LCA results)

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The conductive media – bio carbon

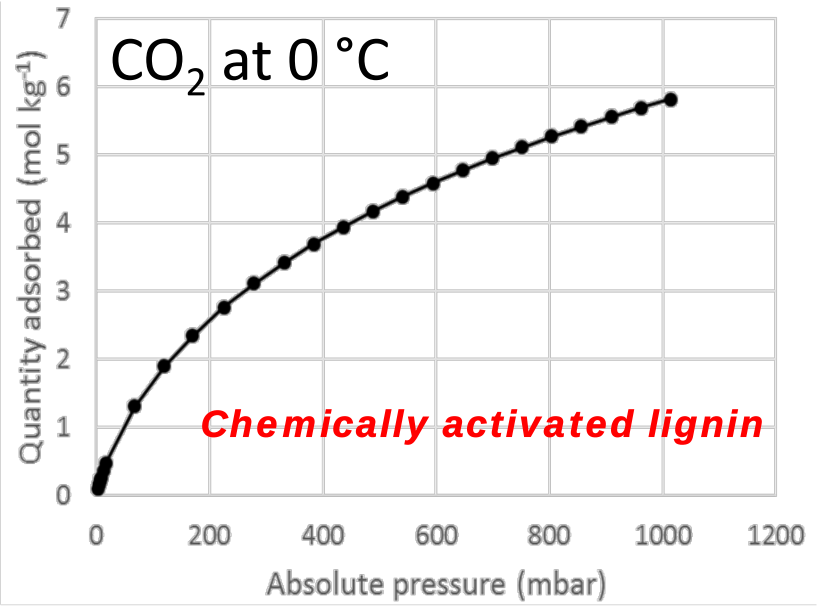
Biokol

TARGET: Performing conductive carbon for Electric Adsorption (ESA)

Bio carbon from lignin (nature's most abundant aromatic polymer)

Carbonized lignin:

- Carbon content: 95.2 wt. %
- Surface area: 155 $m^2\ g^{-1}$



Chemically activated lignin:

- Activation agent: K_2CO_3
- Surface area: 1099 $m^2\ g^{-1}$
- CO_2 uptake at 0 °C and 0.2 bar: 2.6 mol kg^{-1}
- **Electrical conductivity is comparable with carbon black values.**

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Final remarks

ZEOLITE SELECTIVE CO_2 CAPTURE ADSORBENTS

- ZSM-5 zeolite can selectively adsorb CO_2 with respect to N_2 or O_2
- Specific heat capacity of ZSM-5 is < 1 J g^{-1} °C^{-1}.
- ZSM-5 can bear high temperature treatments.

MOF SELECTIVE CO_2 CAPTURE ADSORBENTS

- UTSA-16 and CPO-27-Ni are both very promising materials
- UTSA-16 CO_2 uptake at 0.15 bar and 60 °C is 0.92 mol kg^{-1} (vs. ZSM5: 0.33 mol kg^{-1})
- UTSA-16 is thermally stable till 350 °C.
- UTSA-16 specific heat capacity is 1 J °C^{-1} g^{-1} at 60 °C

MORE DETAILS ARE AVAILABLE IN:

- Masala, A. et al., *Phys. Chem. Chem. Phys*. **2016**, 18, 220 – 227
- Masala, A. et al., *J. Phys. Chem. C*. **2016**, 120, 12068 – 12074

Final remarks

THE BIO CARBON

- Easily prepared from lignin – a residue from the pulp industry.
- Good electrical conductivity comparable to carbon black.
- Fair adsorption CO_2 capacity that can be exploited for selective adsorbers

SCALE UP

- Successful scale-up processes allowed to produce > 100 g of/batch in case of both MOF materials.

Acknowledgments

SINTEF

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nis CENTRE FOR NANOSTRUCTURED INTERFACES AND SURFACES

Biokol

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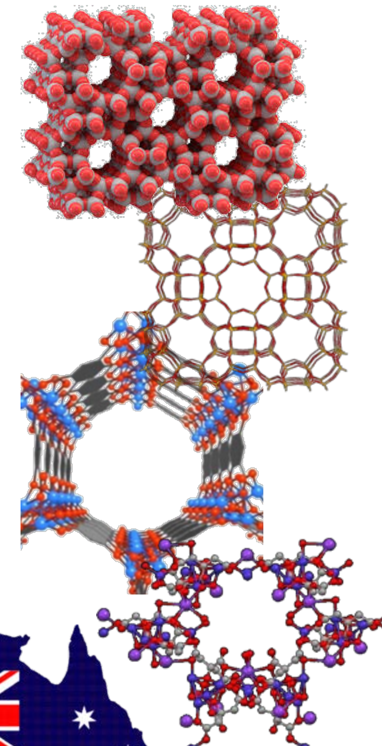
Deliverable 7.3
Proceedings dissemination day

A pdf document will be made and distributed among all the participants and put on the web page.



Edited by: Prof. Silvia Bordiga and Jenny G. Vitillo

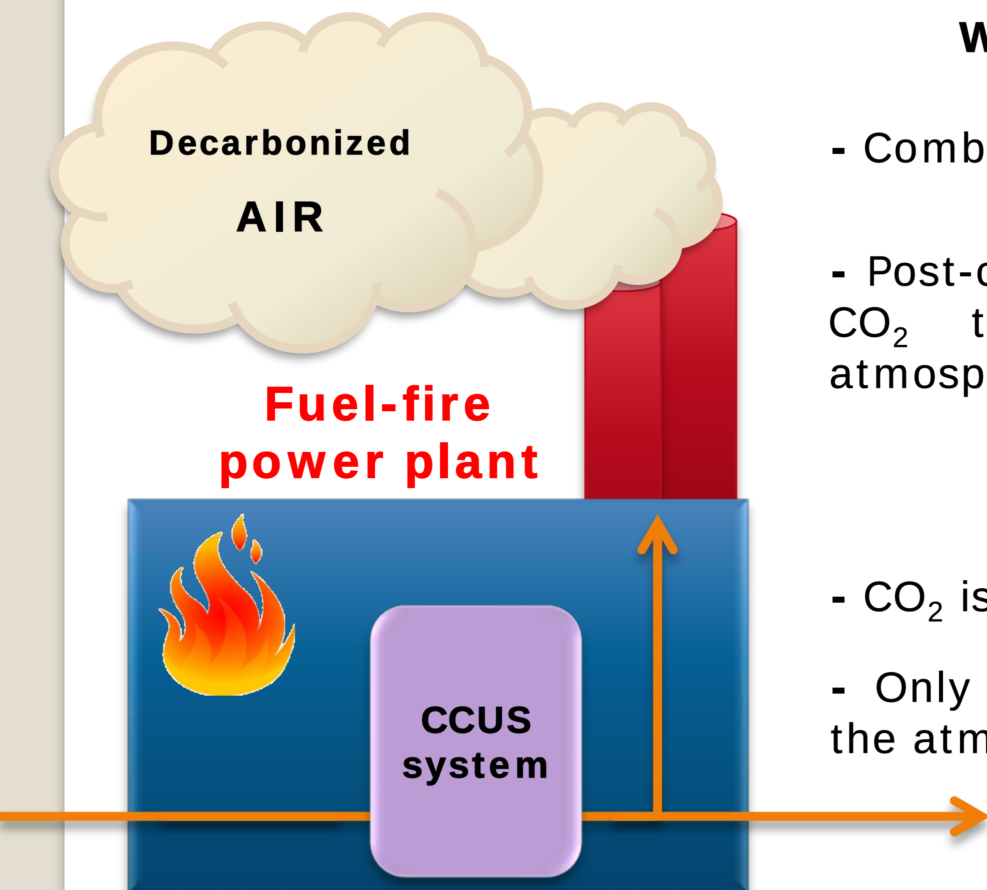
Preface Prof. Silvia Bordiga and Dr. Jenny G. Vitillo

Table of contents

CO_2 capture: key points

Carbon Capture Utilization and Sequestration technique (CCUS):

A sustainable solution for the reduction of CO_2 emissions.



Without CO_2-capture system

- Combustion of fuel to generate heating

- Post-combustion exhaust contains 15% of CO_2 that will be dispersed in the atmosphere

With CO_2-capture system

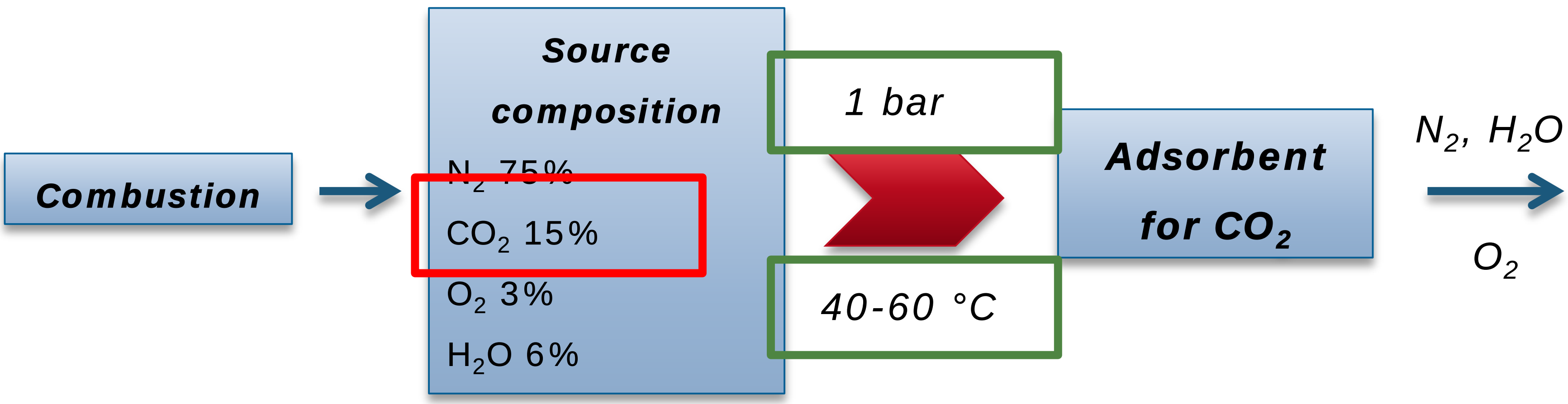
- CO_2 is captured by adsorbers

- Only decarbonized AIR is dispersed in the atmosphere

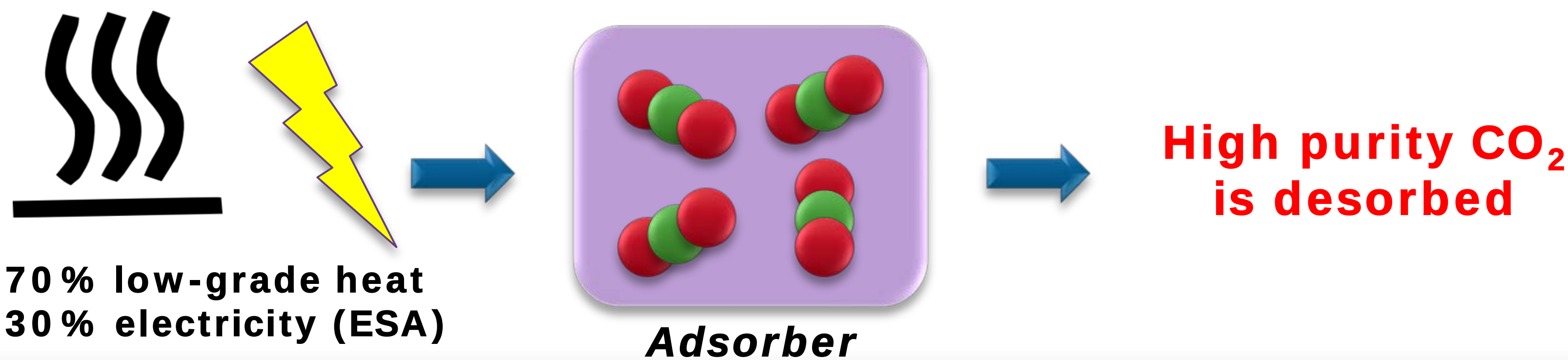
CO_2 is desorbed and stored for utilization / sequestration

The target of MATESA project

TARGET 1. **To capture the largest amount of CO_2 at the following conditions:**



TARGET 2. **To desorb the captured CO_2 by electricity and low-grade heat:**



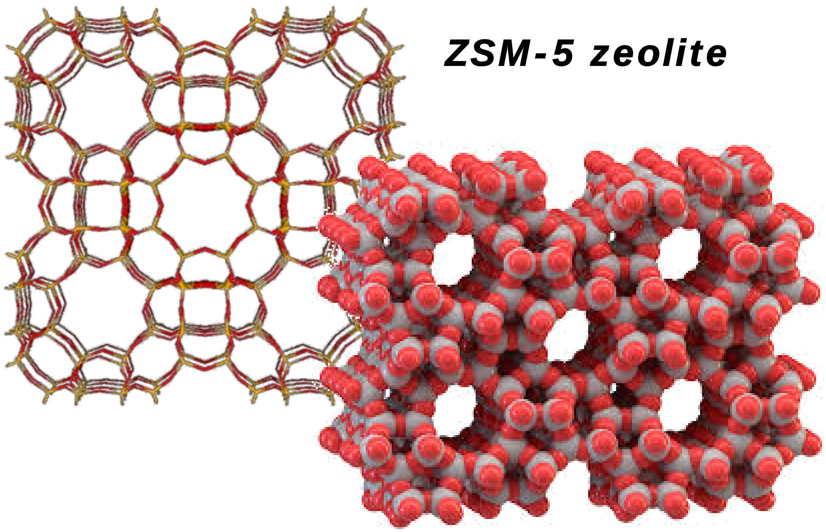
The adsorbers of MATESA

REFERENCE ADSORBER

ZEOLITES

13X zeolite

ZSM-5 zeolite



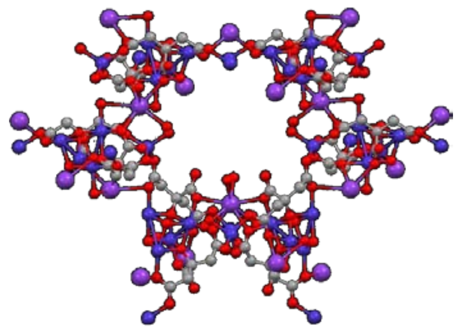
Commercial materials

CORNING

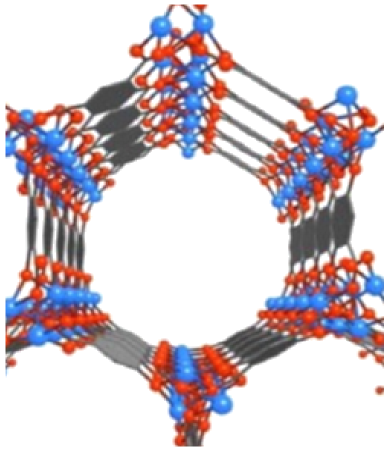
ADVANCED ADSORBER

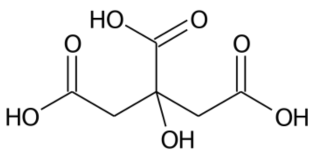
METAL-ORGANIC FRAMEWORKS

UTSA-16



CPO-27-Ni
benchmark





Citrate ligand

Laboratory materials, provided by:

Fraunhofer IKTS

SINTEF

The adsorbers of MATESA

To perform Electric Swing Adsorption, adsorbers must be conductive!

The mixture:

60-70% Active phase

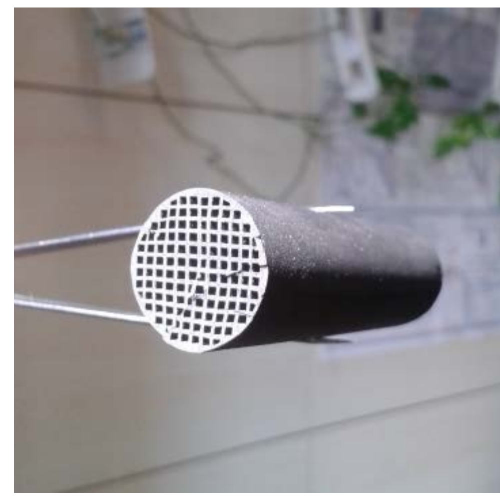
30-40 % Conductive phase

Carbonization process

500-800 °C

FOTO
ZEOLITE

Extrusion process



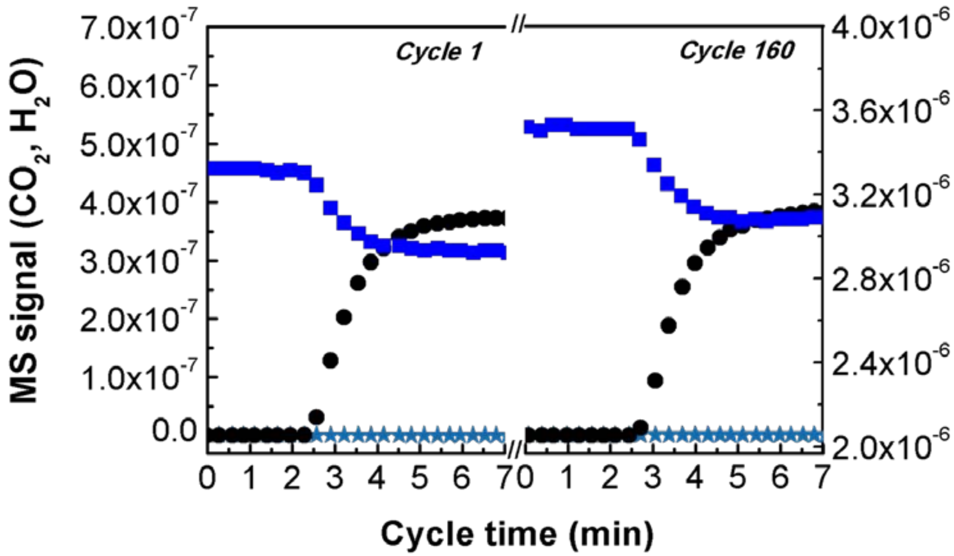
Extruded monolith

Active + Phenolic resin

Adsorption of CO_2 in steam environment

Water vapour constitutes an important fraction (5-20%) of coal and NG-fired plant exhaust.

Dynamic experiment



UTSA-16 is able to uptake CO_2 in presence of water vapour .

UTSA-16 is stable and maintains 70% of the CO_2 working capacity in a steam environment at 40 °C.

Static experiment