LSRE-LCM Shaking the Present Shaping the Future

# Cyclic Adsorption/Reaction Processes in CO2 Capture and Utilisation

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Webinar POWER2METHANE

June 5, 2020

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# Outline

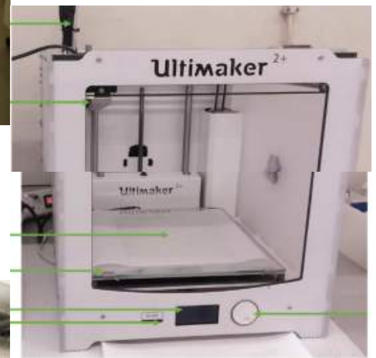
- The old days
    - Searching “high-temperature” adsorbents for $CO_2$ capture in steam methane reforming for $H_2$ production
    - $CO_2$ capture pilot plant in Shangai – cooperation with ECUST(China) & UFSC(Brazil)
- PSA for $CO_2$ capture from coal or biomass gasification and produce $H_2$/CO mixture for MeOH synthesis or Fischer Tropsch
- Cryogenic adsorption $CO_2$/$CH_4$ separation (PTSA)
- Electric Swing Adsorption (ESA) for $CO_2$ capture: shaping and 3D printing of composite monoliths
- Power-to-Gas project: SERP process with $CO_2$ capture and methanation to produce SNG

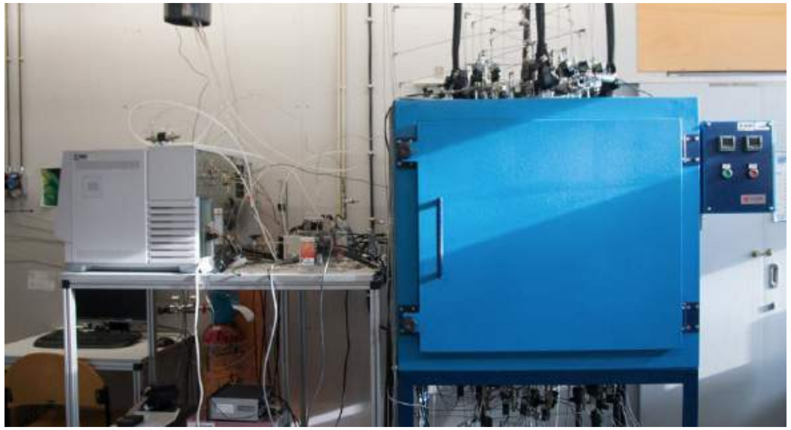
# Cyclic Adsorption/Reaction Processes

Cyclic Adsorptive Processes
Multifunctional Reactors/Process Intensification





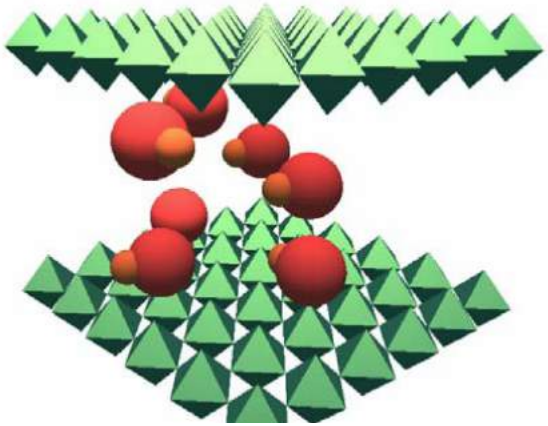




# The old days

Methane steam reforming for H2 production (112,000 Nm3/h)
25-40 bar; 1100 K

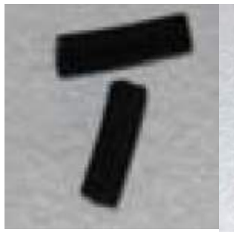
| | | |
|---|---|---|
| $CH_4 + H_2O \leftrightarrow CO + 3H_2$ | $\Delta H = 205.8$ kJ/mol | SMR |
| $CO + H_2O \leftrightarrow CO_2 + H_2$ | $\Delta H = -41.2$ kJ/mol | Water gas shift |
| $CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$ | $\Delta H = 164.6$ kJ/mol | Global SMR |

**CO2 capture with high temperature adsorbents for Sorption Enhanced Reaction Processes (SERP)**



$$M^{2+}_{1-x}M^{3+}_{x}(OH^{-})_2(A^{n-})_{x/n}\cdot mH_2O$$

$$0.2 \le x \le 0.33$$

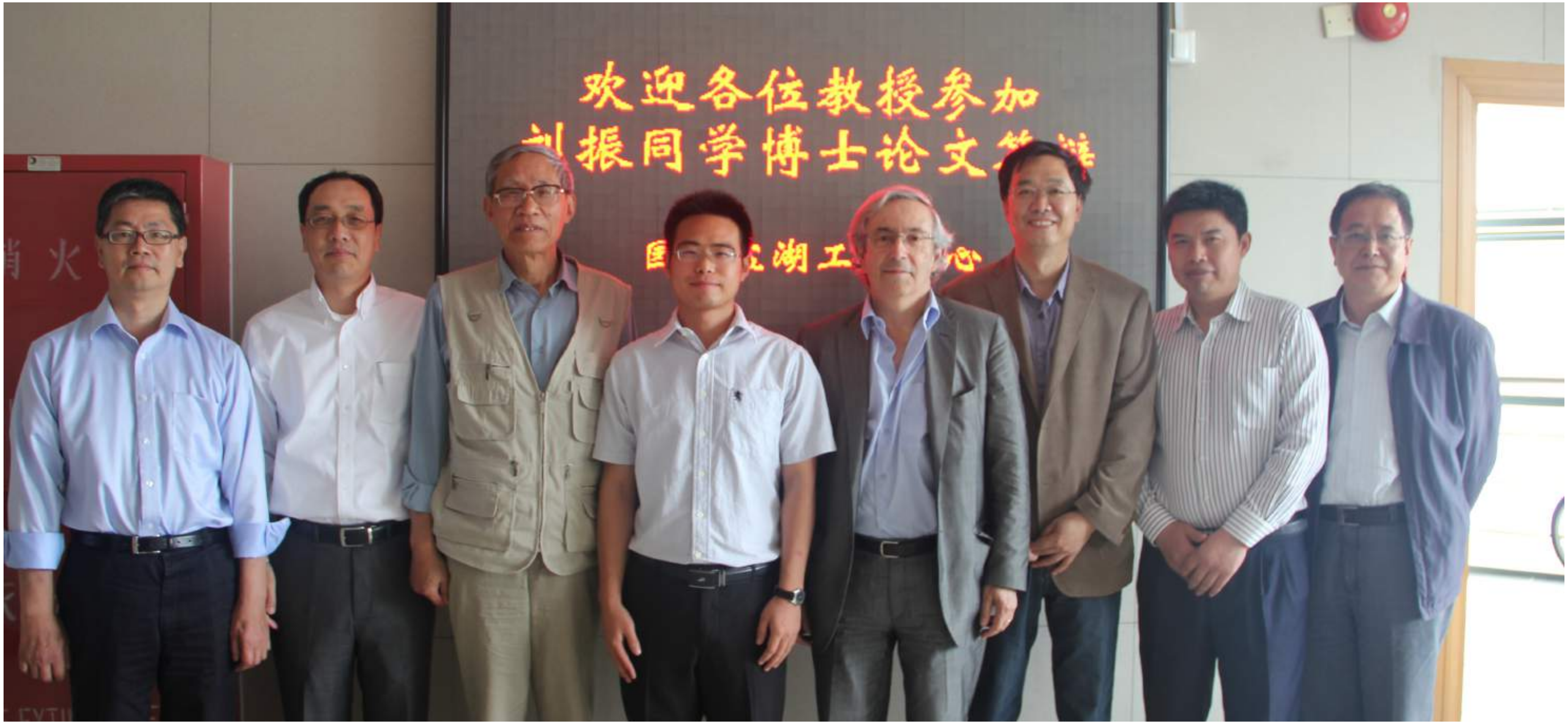


SERP

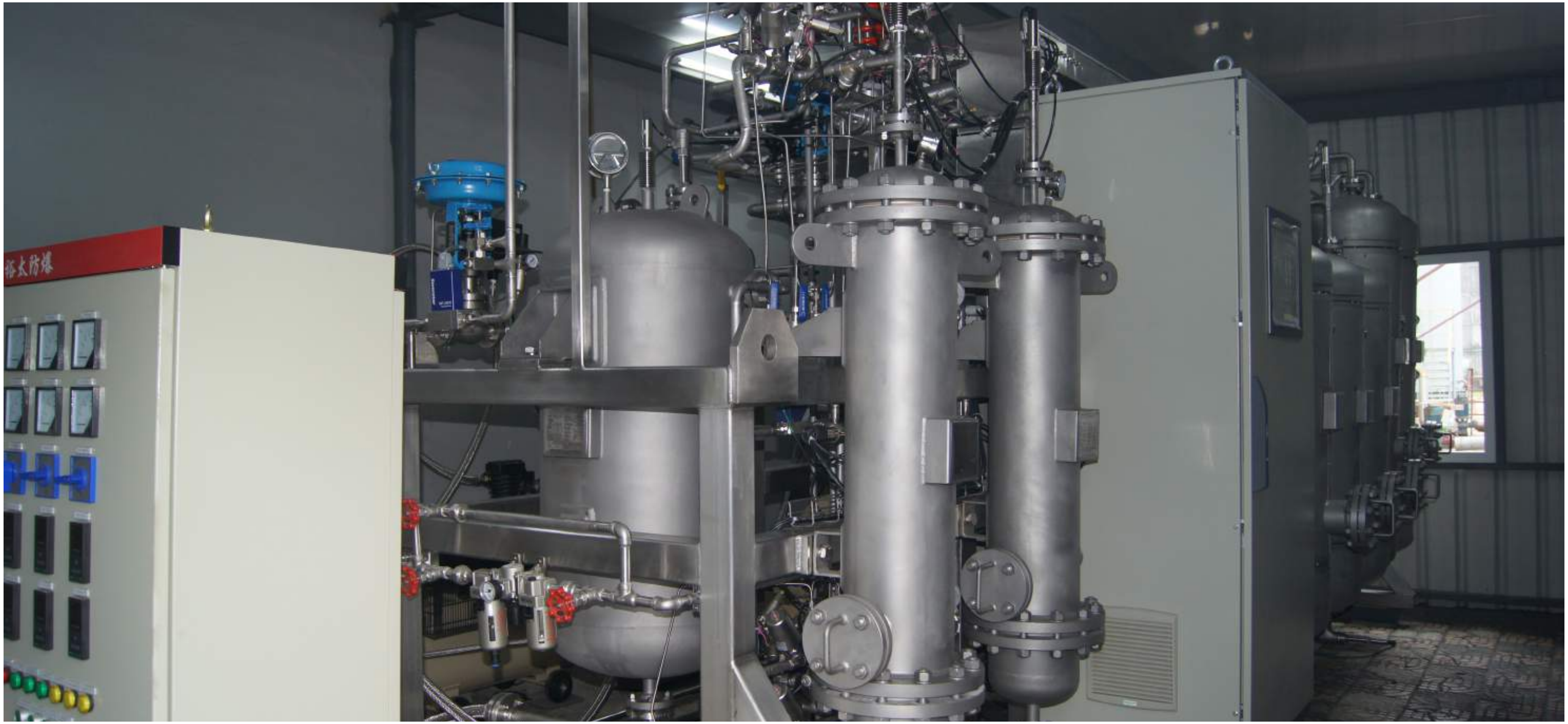
# Materials & Sorption Enhanced Reaction Processes (SERP)

- Zou Yong , Vera Mata and A.E.Rodrigues, “Adsorption of carbon dioxide on basic alumina at high temperatures”, *J. Chem and Engineering Data* **45** (6) 1093-1095(2000)
- Zou Yong, Vera Mata and A.E.Rodrigues, “Adsorption of carbon dioxide onto hydrotalcite-like compounds (HTlcs) at high temperatures”, *Ind Eng Chem Res* **40**, 204-209 (2001)
- Zou Yong, Vera Mata and A.E.Rodrigues, “Adsorption of carbon dioxide on chemically modified high surface area carbon-based adsorbents at high temperatures”, *Adsorption* **7**(1) 41-50 (2001).
- Zou Yong and A.E. Rodrigues,”Adsorbent materials for carbon dioxide”, *Adsorption Science and Technology*, **19** (3) 255-266 (2001)
- Zou Yong, Vera Mata and A.E. Rodrigues, “Adsorption of carbon dioxide at high temperature: a review”, *Sep. Pur. Tech*, **26** (2/3) 195-205 (2002)
- G.H. Xiu, P.Li and A.E.Rodrigues, “Sorption enhanced reaction process with reactive regeneration” *Chem Eng Sci* **57**, 3893-3908 (2002)
- G.H.Xiu, J.L.Soares, P.Li and A.E.Rodrigues, “Simulation of a five-step one-bed sorption-enhanced reaction process”, *AIChEJ* **48** (12) 2817-2832 (2002)
- Guo hua Xiu, Ping Li and A.E. Rodrigues, “New generalized strategy for improving sorption-enhanced reaction process”, *Chem Eng Sci* **58,** 3425-3437 (2003)
- Guo hua Xiu, Ping Li and A.E. Rodrigues, “Adsorption-enhanced steam-methane reforming with intraparticle limitations ”, *Chem Eng J* **95**(1-3), 83-93 (2003)
- G.Xiu, P. Li and A.E.Rodrigues, “Subsection controlling strategy for improving sorption-enhanced reaction processes”, *Chem Eng Res Dev*, **82**(A2) 192-202 (2004)
- Yi-Ning Wang and A.E. Rodrigues, “Hydrogen Production from Steam Methane Reforming coupled with in-situ CO2 capture: conceptual parametric study”, *Fuel* , **84**, 1778-1789 (2005)

# PhD thesis of Zhen Liu (ECUST)



# CO2 capture pilot plant VPSA) designed by Zhen Liu



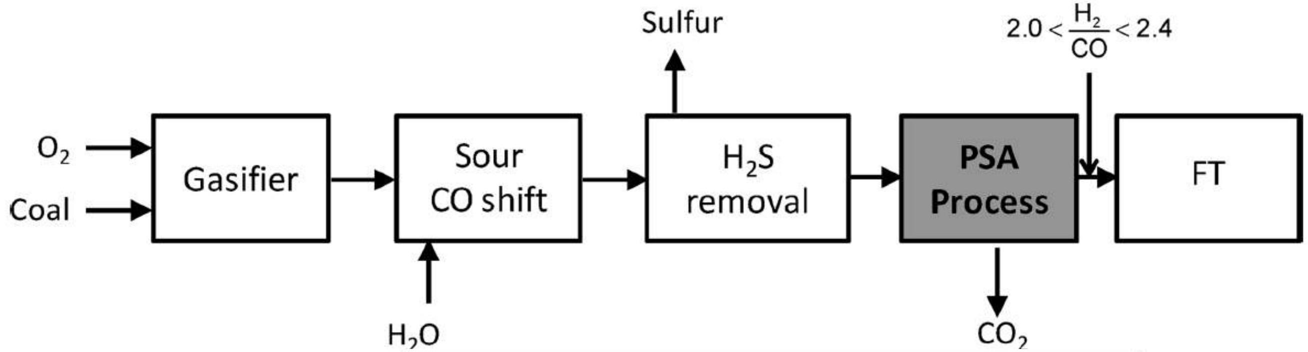
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 2-bed 6-step | Silica gel | 15.0 | 99.6 | 99.6 | 1.81 | 1.94 | Li et al. 2016 |
| 2-bed 4-step | 13X | 15.0 | 94.8±1 | 89.7±5.6 | 1.98±0.099 | 1.22–2.10±0.132 | Krishnamurthy et at. 2014 |
| 3-bed 5-step 4-bed 7-step | 5A-5A | 15.0 | 96.05 | 91.05 | 0.33 | 0.646 | Liu et al. 2011 |
| 3-bed 5-step/ 2-bed 6-step | 13XAPG - 13XAPG | 15.0 | 96.54 | 93.35 | 0.53 | 0.710 | Wang et al. 2012 |
| 3-bed 8-step/ 2-bed 6-step | 13XAPG - 13XAPG | 16.0 | 95.6 | 90.2 | 0.74 | 2.44 | Wang et al. 2013 |
| 2-bed 6-step/ 2-bed 5-step | 13X-MgMOF74 | 15.0 | 97.57 | 90.2 | 3.09 | 0.700 | Nikolaidis et al. 2017 |
| 1-bed 4-step/ 1-bed 4-step | CMS-CMS | 15.0 | 90 | 89.9 | - | 0.990 | Haghpanah et al. 2014 |

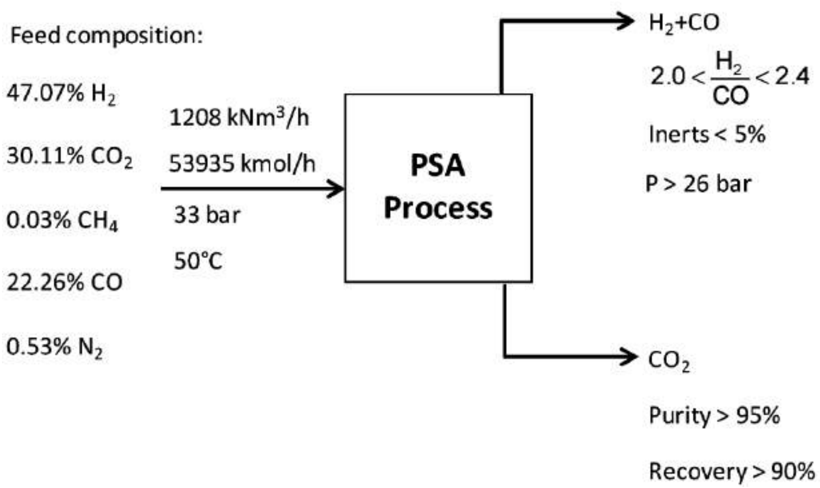
# Cooperation with ECUST and UFSC on $CO_2$ capture

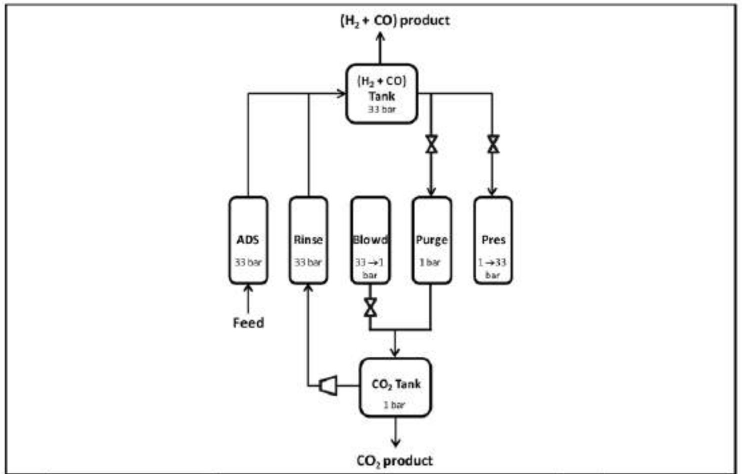
- Liu, Z., C. Grande, Li Ping, Yu Jianguo, A-E.Rodrigues, "Multi-bed Vacuum Pressure Swing Adsorption for $CO_2$ capture from flue gas", Sep Pur Tech, 81(3) 307-317 (2011)
- Z. Liu, Lu Wang, X. Kong, Ping Li, Jianguo Yu and A.E. Rodrigues, On site $CO_2$ capture from flue gas by adsorption process in coal-fired power plant", *Ind Eng Chem Res* **51**, *7355-7363* (2012)
- Lu Wang, Z. Liu, X. Kong, Ping Li, Jianguo Yu and A.E. Rodrigues, Experimental and modeling investigation on post-combustion $CO_2$ capture in zeolite 13 APG by hybrid VTSA process", *Chem Eng J* **197**, 151-161 (2012)
- Lu Wang; Ying Yang; W. Shen; X. Kong; Ping Li; Yu Jianguo; A. E. Rodrigues, " $CO_2$ capture from flue gas in an existing coal-fired power plant by pilot-scale two successive VPSA units", *Ind Eng Chem Res* **52** (23) 7947-7955 (2013)
- Lu Wang, Ying Yang, W. Shen, X. Kong, Ping Li, Jianguo, Yu and A.E. Rodrigues,"Experimental Evaluation of Adsorption Technology for $CO_2$ Capture from Flue Gas in an Existing Coal-fired Power Plant", *Chem Eng Sci* **101**, 615-619 (2013)
- J.L. Soares, R. Moreira, H.J. José, C. Grande and A.E. Rodrigues, "Hydrotalcite materials for carbon dioxide adsorption at high temperature: characterization and diffusivity measurements", *Separation Science and Technology* **39** (9), 1989-2010 (2004)
- J.L.Soares, G. Casarin, H.J. José, R.Moreira and A.E. Rodrigues "Experimental and theoretical analysis for the $CO_2$ adsorption on hydrotalcite", *Adsorption* 11:237-241 (2005)
- R. Moreira, J. Soares, G. Casarin and A. E. Rodrigues, "Adsorption of $CO_2$ on Hydrotalcite-like Compounds in a Fixed Bed", *Sep Sci Tech* , **41** (2), 341-357 (2006)

# PSA for CO2 capture from coal or biomass gasification and to produce H2/CO mixture for MeOH synthesis or Fischer Tropsch

## Coal to FT process

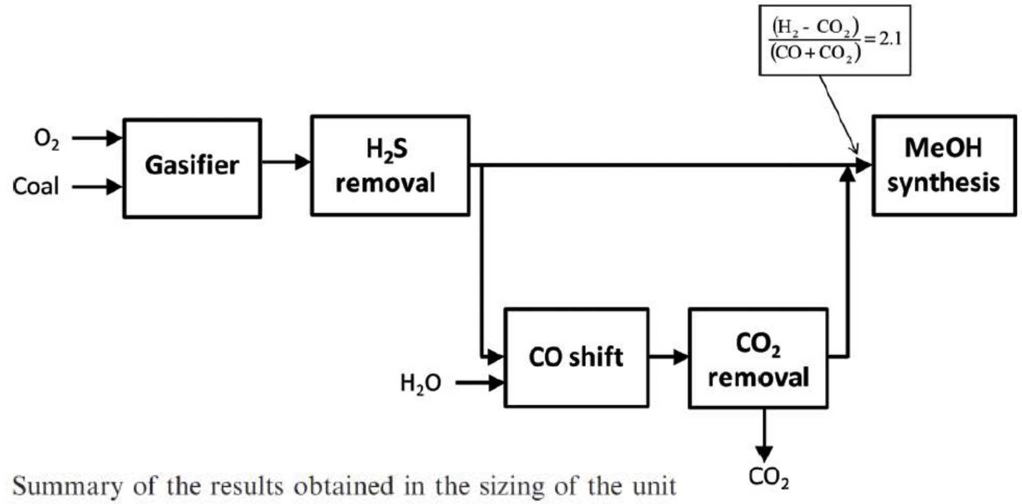


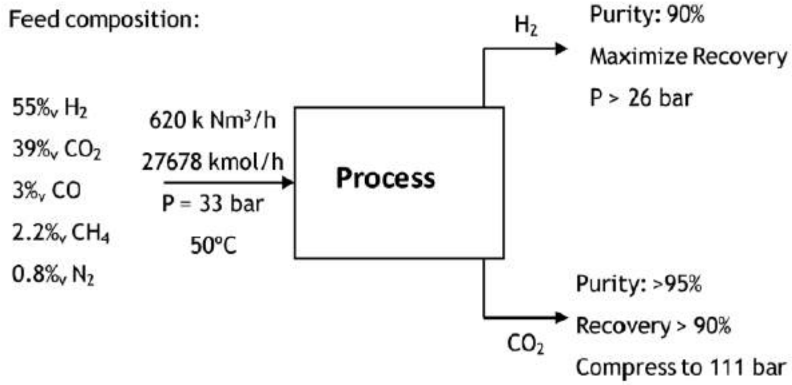




| | | | | | | |
|---|---|---|---|---|---|---|
| C1 | Adsorption | | Rinse | Blowdown | Pg | Pressurization |
| C2 | Pg | Pressurization | Adsorption | Rinse | Blowdown | |
| C3 | Blowdown | | Pg Pressurization | Adsorption | Rinse | |
| C4 | Rinse | | Blowdown | Pg Pressurization | Adsorption | |

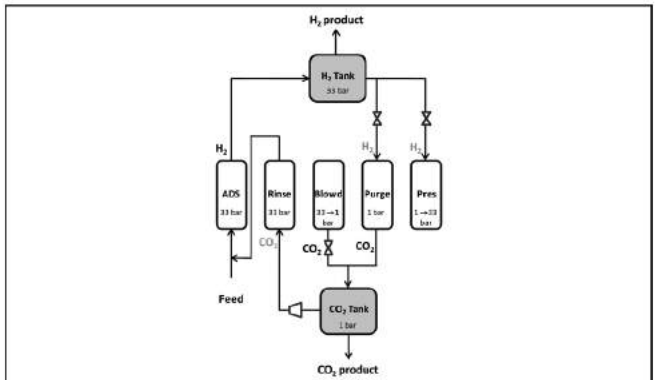
# Coal to MeOH




Summary of the results obtained in the sizing of the unit

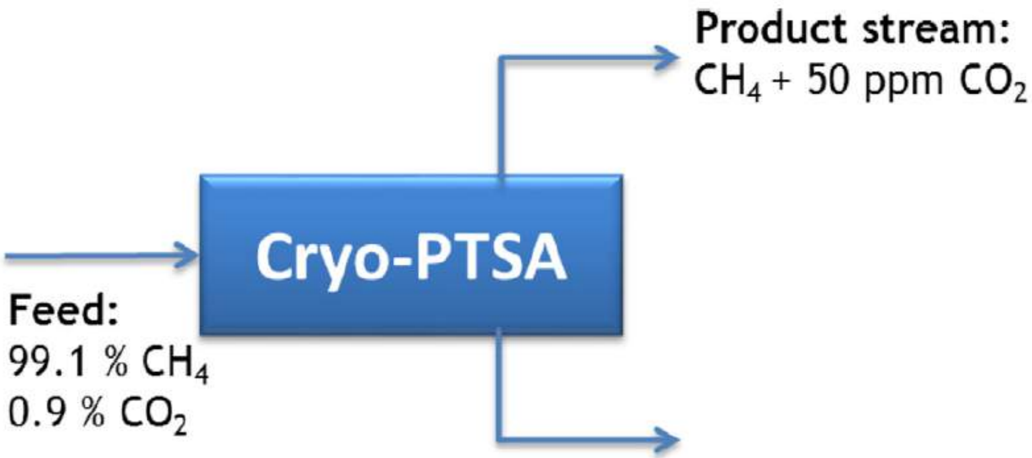
| Adsorbent | Activated carbon Norit R2030 |
|---|---|
| Adsorbent apparent density (kg/m3) | 874 |
| Bed porosity | 0.38 |
| Adsorbent working capacity (mol/kg) | 4.17 |
| Duration of the adsorption step | 640 s |
| Number of units required | 8 |
| Column diameter (m) | 5 |
| Column length (m) | 9 |
| Superficial feed velocity (m/s) | 0.04 |




| | | | | | |
|---|---|---|---|---|---|
| Adsorption | | Rinse | Blowdown | Pg | Pressurization |
| Pg | Pressurization | Adsorption | Rinse | | Blowdown |
| Blowdown | | Pg Pressurization | Adsorption | | Rinse |
| Rinse | | Blowdown | Pg Pressurization | | Adsorption |

Pg – purge

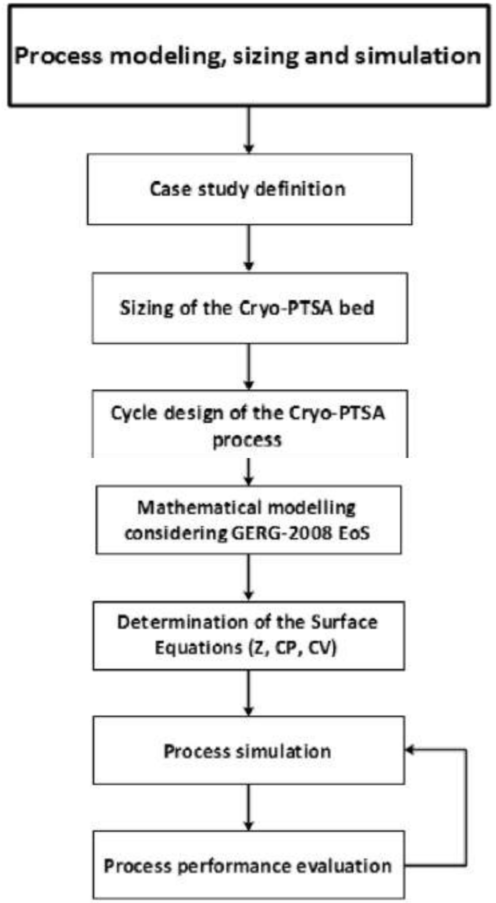
# Cryogenic adsorption for CO2/CH4 separation (PTSA)



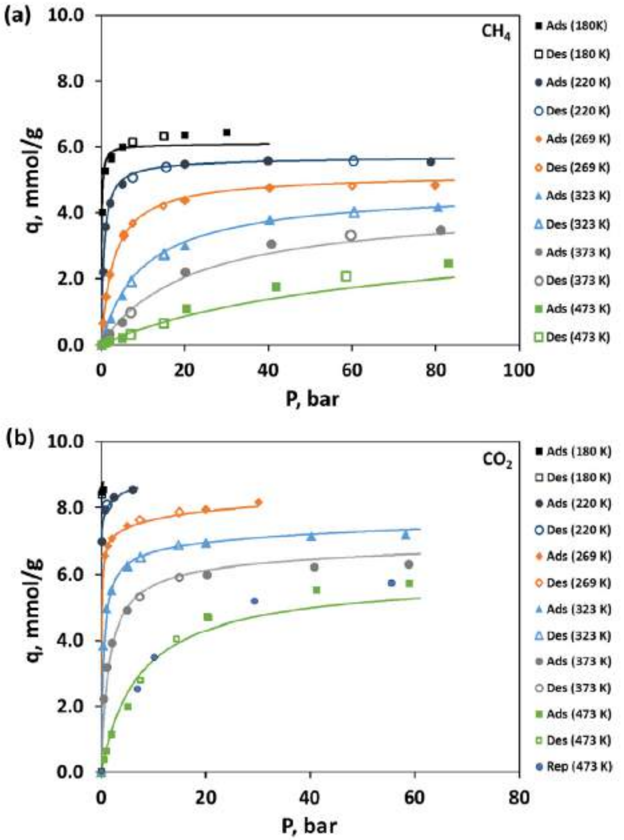

P = 40 bar
T = 190 K
$F_{in}$ = 8280 kmol/h

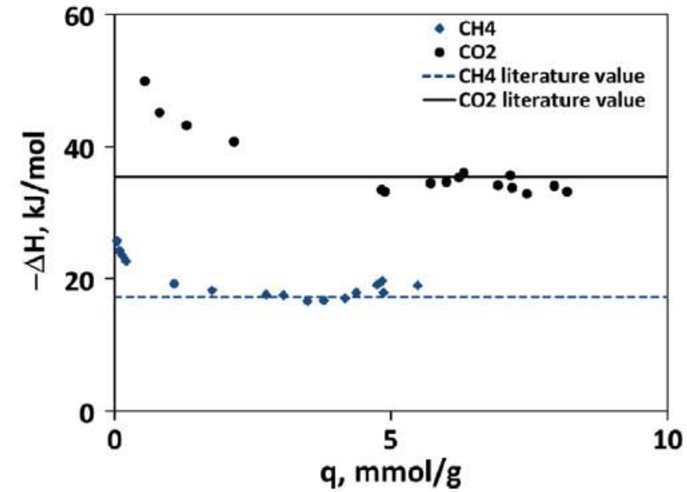
**Purge - Product stream:**

P = 5 bar
T = 473 K
Molar flow rate to be optimized



# Binderless 13X zeolite – adsorption equilibrium isotherms

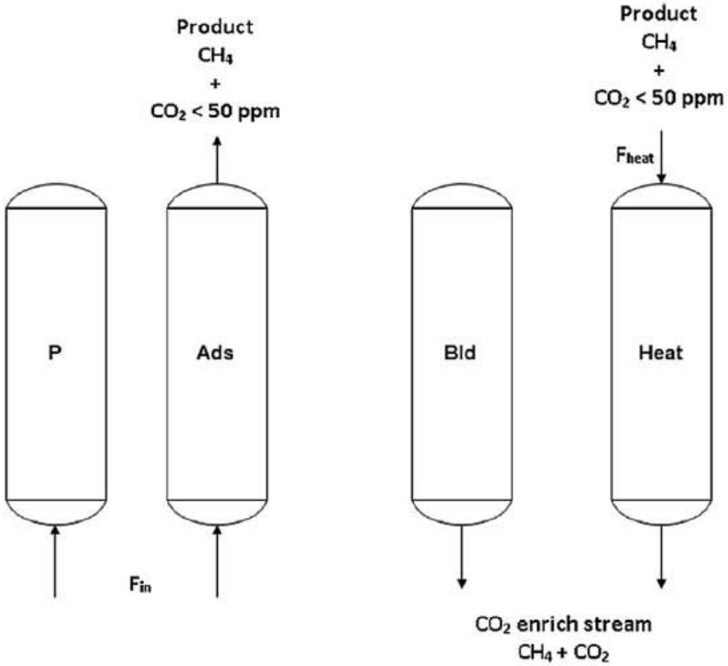


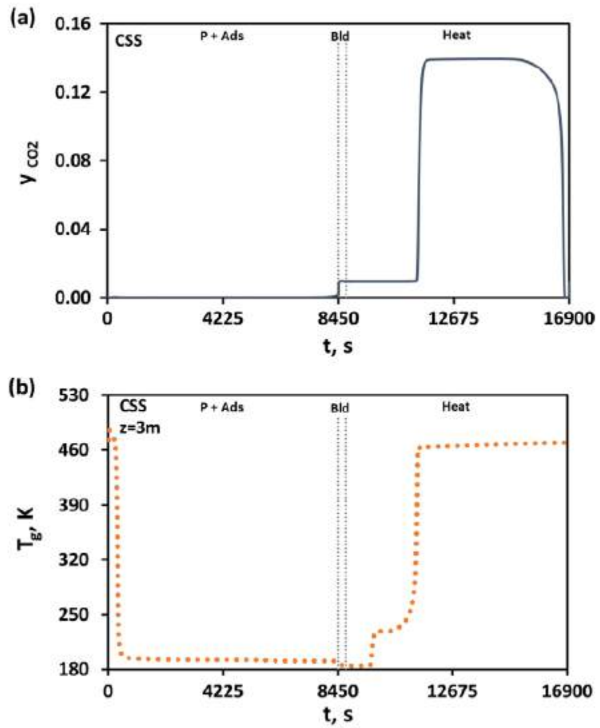

The mathematical model described previously involves a system of partial differential and algebraic equations (PDAEs), which can be solved using modelling software. The modelling software chosen was gPROMS® ModelBuilder (PSE) [82], which is a reliable simulation tool. gPROMS® provides a general interface that can incorporate other external property and thermodynamic tools. In this way, REFPROP was integrated in the gPROMS® simulation tool by the use of REFPROP CAPE-OPEN (Computer Aided Process Engineering) physical properties socket [83].

# PTSA cycle and process performance

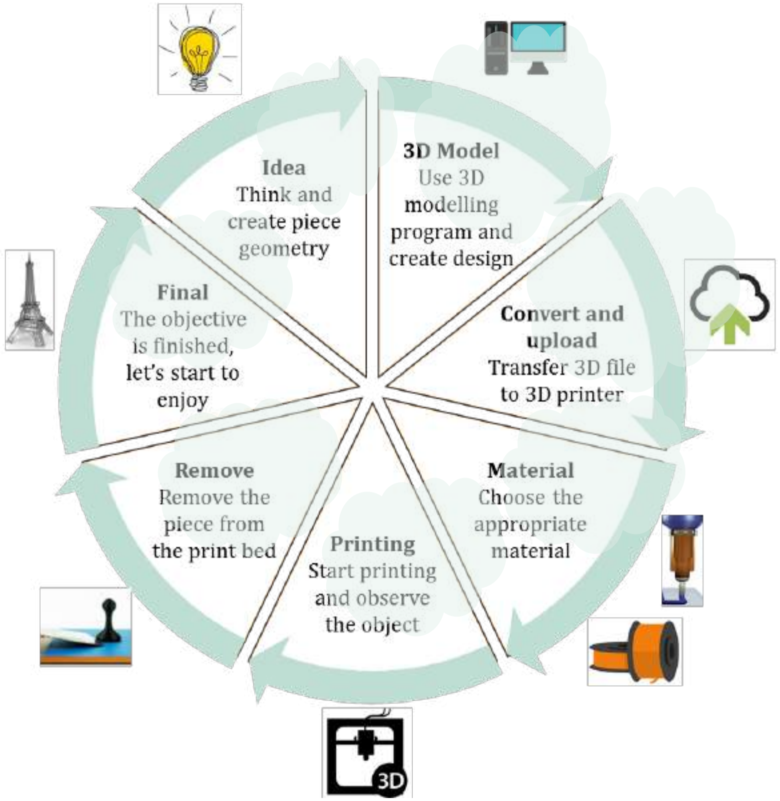
Recovery of $CH_4$ = 90.7%
Product stream with 41.8 ppm in $CH_4$
$CH_4$ productivity 100.1 mol/Kg ads/h
Power consumption 2.2 MW (compared with 22.3 MW in cryogenic distillation)




| | | |
|---|---|---|
| P + Ads | Bld | Heat |
| Bld | Heat | P + Ads |

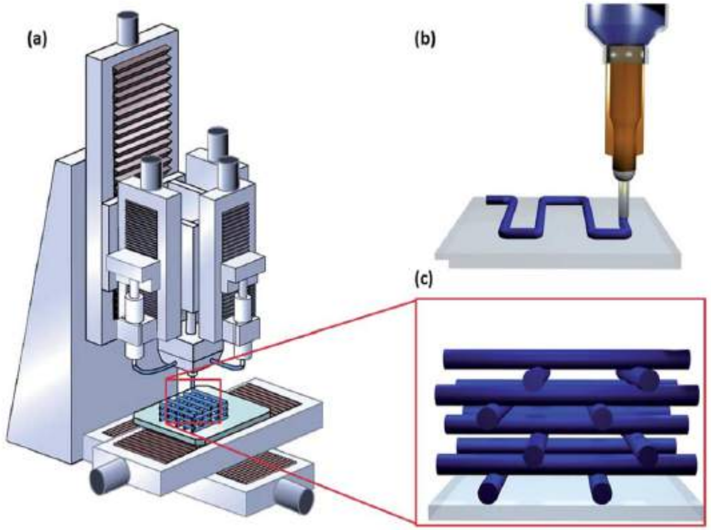


# ADDITIVE MANUFACTURING - 3D




## Direct Ink Writing method

Print structures with solid free-form fabrication from an ink with high viscosity;
Printing occurs with a pressure delivery of an ink through one or multiple capillaries or syringes




Farahani, R. D., Chizari, K., and Therriault, D. Three-dimensional printing of freeform helical microstructures: a review. Nanoscale 2014, 6, 10470-10485.

# 3D-PRINTING IN GAS SEPARATION

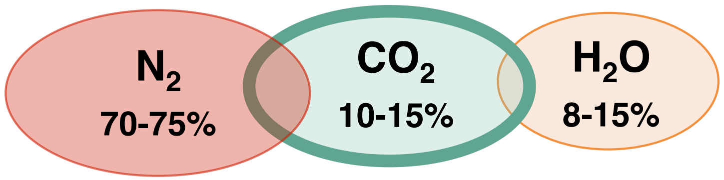
Recently, additive manufacturing gained worldwide attention in the development of adsorbents for **gas separation processes** applications

**Advantages:**

- controlled properties: shape and size, wall thickness, density

Can be used as alternative or a complement to the extrusion process

**Flue gases from Post-Combustion process**




**Cyclic Adsorption Processes**

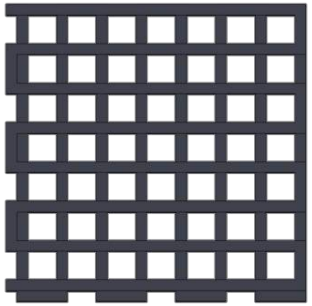
**ELECTRIC SWING ADSORPTION**

heat generated by electric current (Joule effect) in the adsorbent

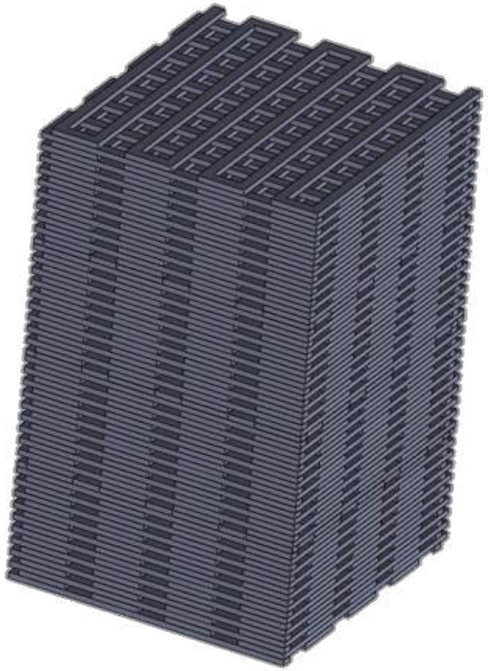
# 3D-PRINTING: MONOLITH DESIGN

## Monolith design - Why?

- High mechanical stability
- High resistance toward abrasion/attrition
- Higher surface area to volume ratio
- Homogeneous power distribution
- Lower pressure drop



View from the top

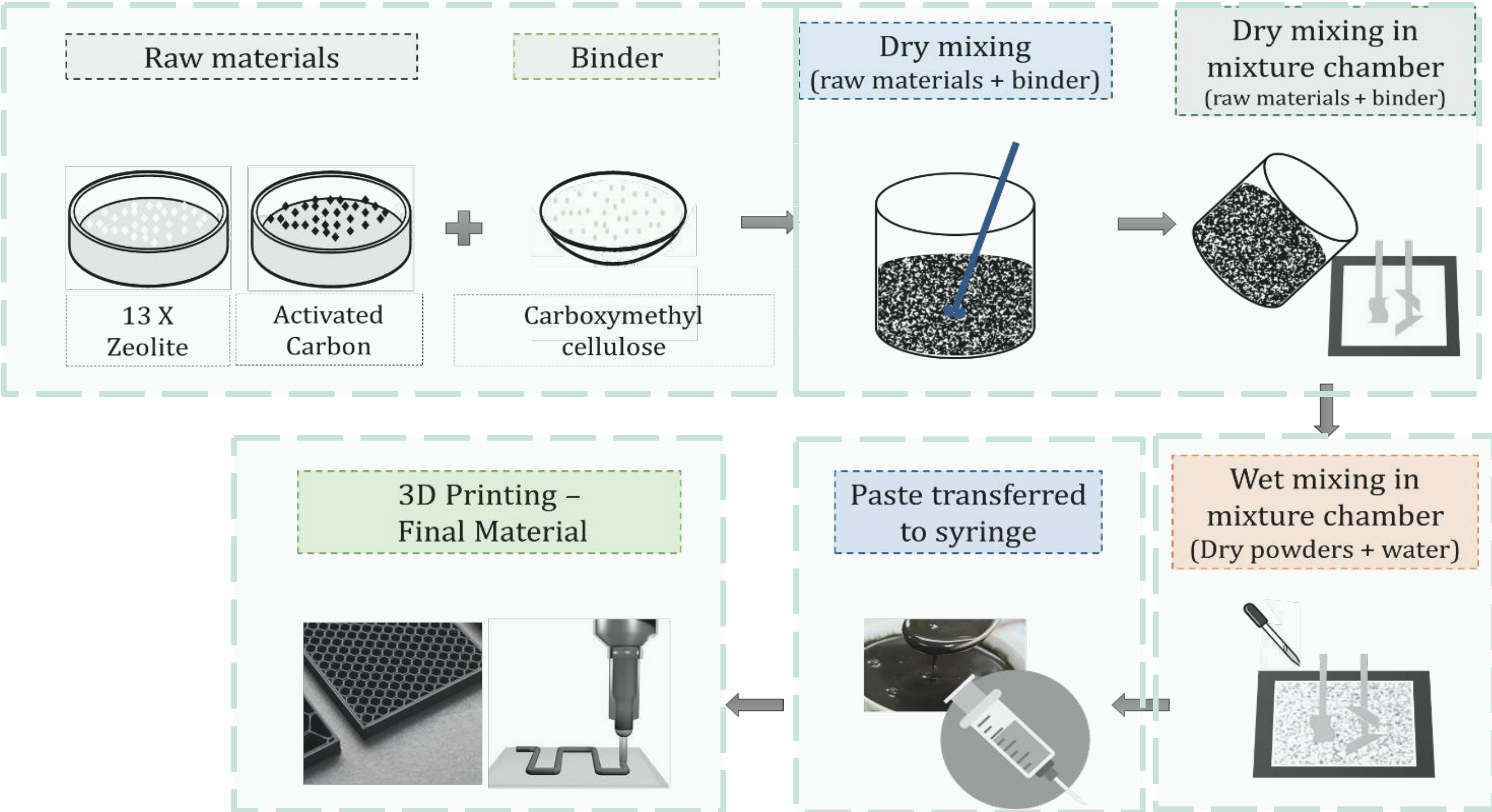


## Monolith properties – Which?

- High $CO_2$ adsorption capacity
- High electric conductivity

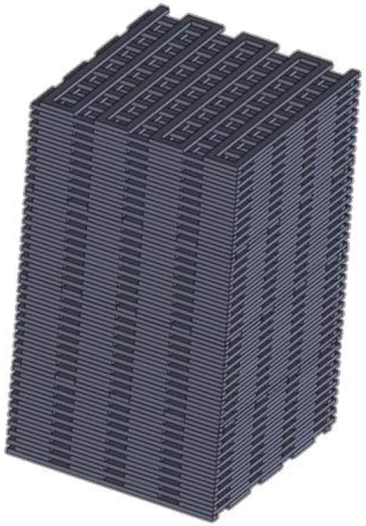
**Design of STL file:**
SolidWorks 2017®
**G-code generation file:**
Ultimaker Cura 3.1.0

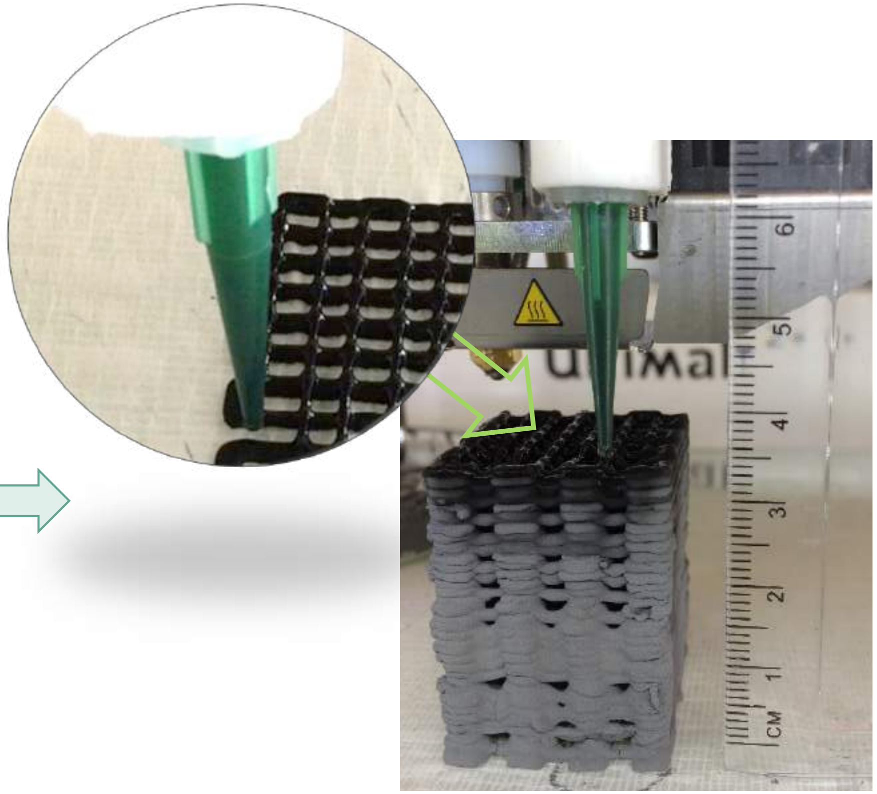
# 3D-Printing: Ink Preparation



# 3D-Printing: Monolith printing

**From Design (.STL) to…**



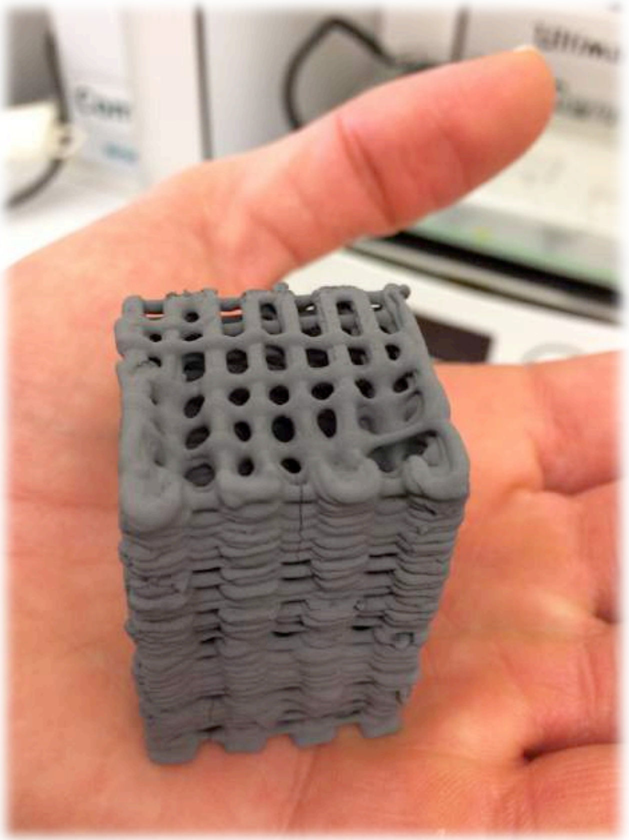



**…construction (3D)!**

# 3D-PRINTED MONOLITH

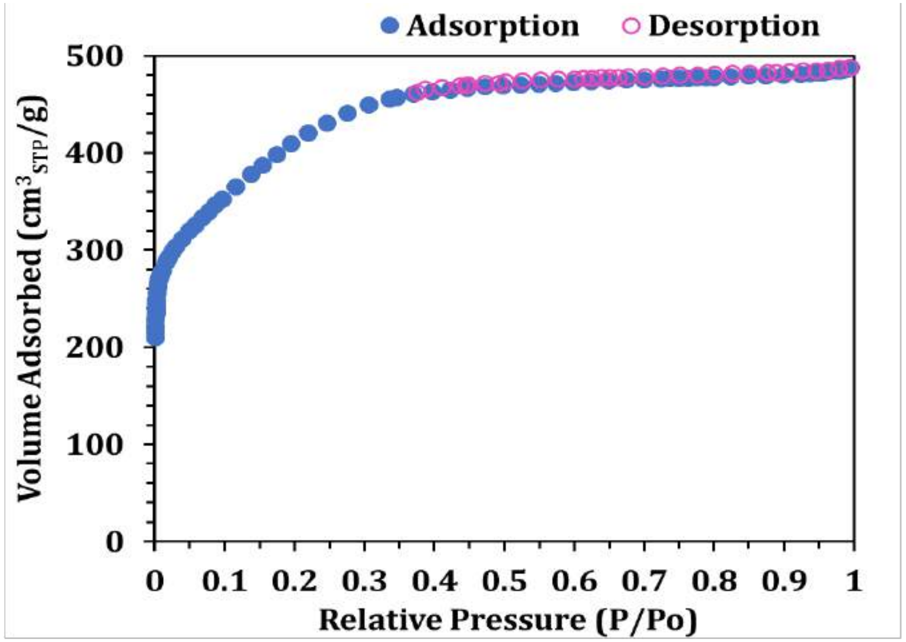
Final monolith material: **30 × 30 × 43 mm**

**70% zeolite 13X and 30% AC**

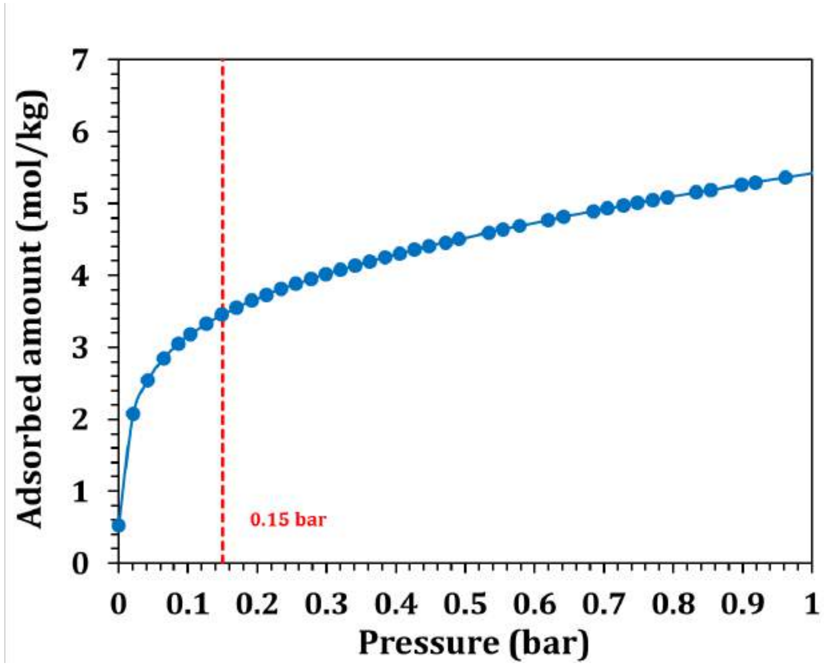



# TEXTURAL CHARACTERIZATION

**$N_2$ adsorption at 77 K**



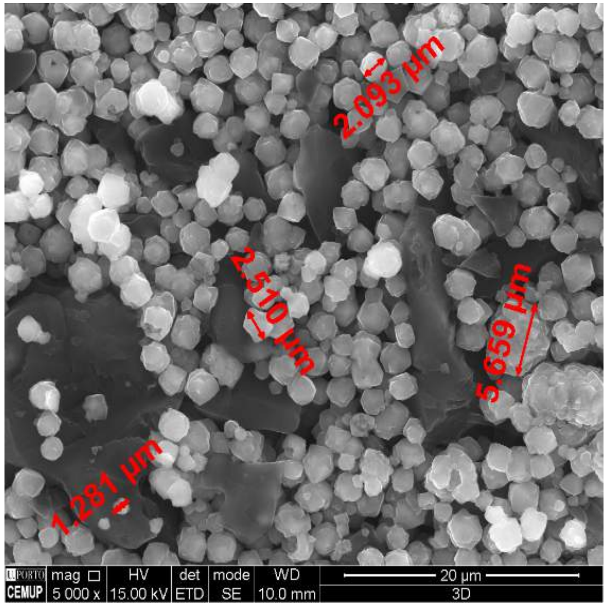

**$CO_2$ adsorption at 273 K**

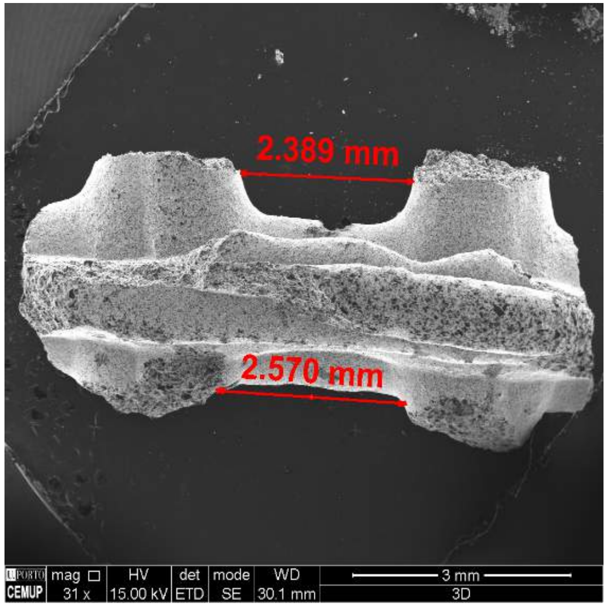


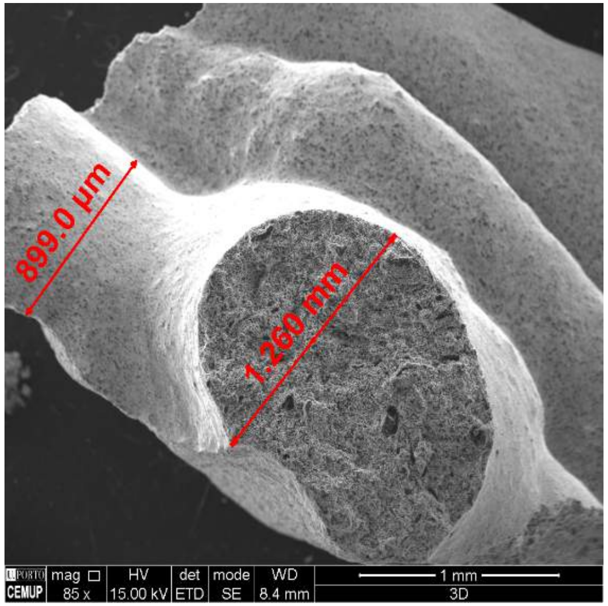

Langmuir surface area: **2028** $m^2/g$

# TEXTURAL CHARACTERIZATION

**SEM**



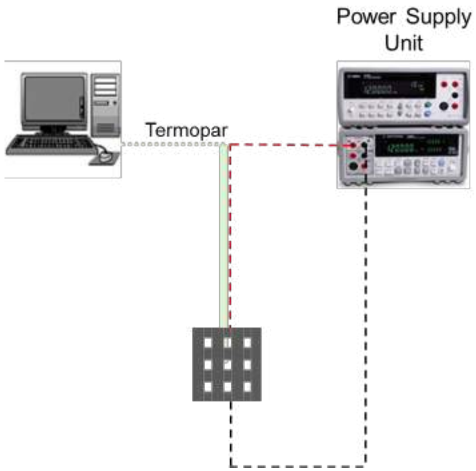



# Heating tests and Mechanical strength

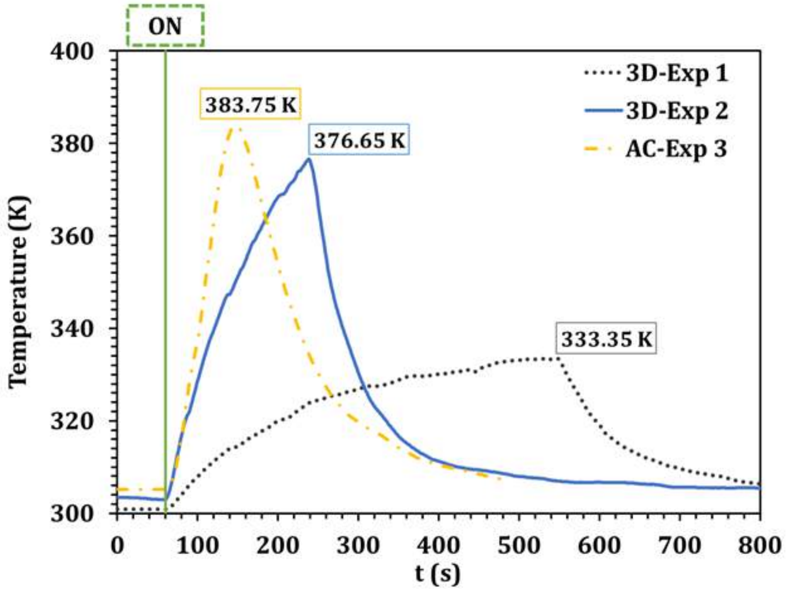
## Heating tests with electric current

- Piece of 10×10×4 mm




| Exp | Material | Constant voltage applied (V) | Current measured (A) | Delivered power (W) [a] |
|---|---|---|---|---|
| 1 | 70% 13X + 30% AC | 16 | 0.05 – 0.06 | 1 |
| 2 | 70% 13X + 30% AC | 25 | 0.05 – 0.13 | 3.25 |
| 3 | 100% AC | 10 | 4.00 – 4.14 | 41.4 |

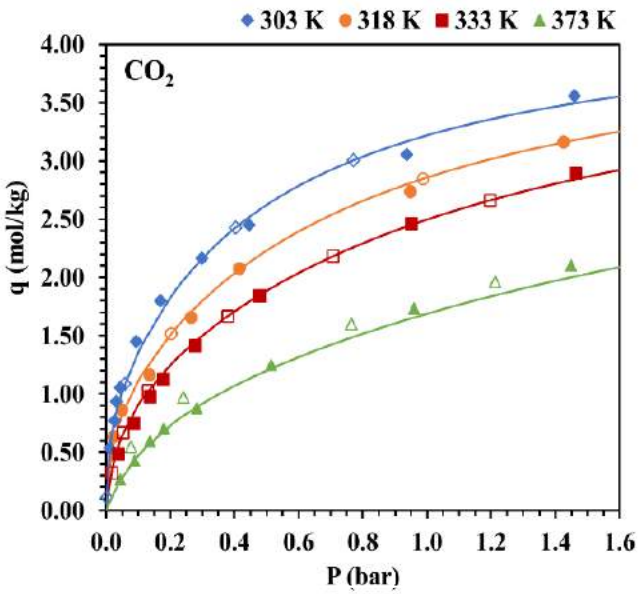
[a] Considering the maximum value of watts consumed during the experiment

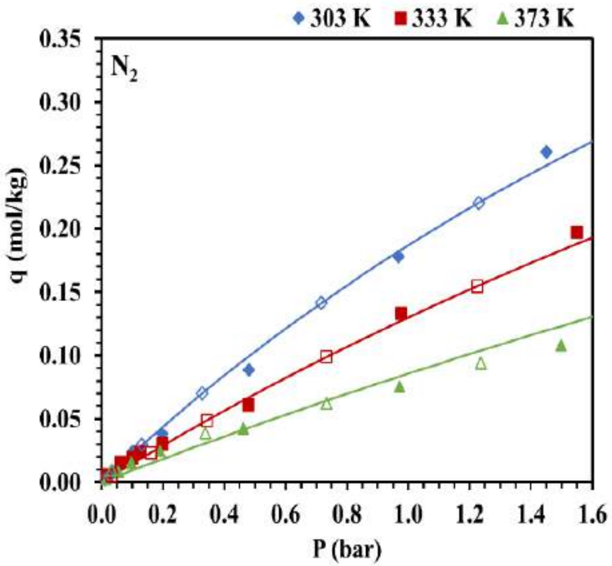



## Mechanical strength

- Piece of 10×10×4 mm: **5 MPa**

# Adsorption equilibrium isotherms



## POWER2METHANE PROJECT

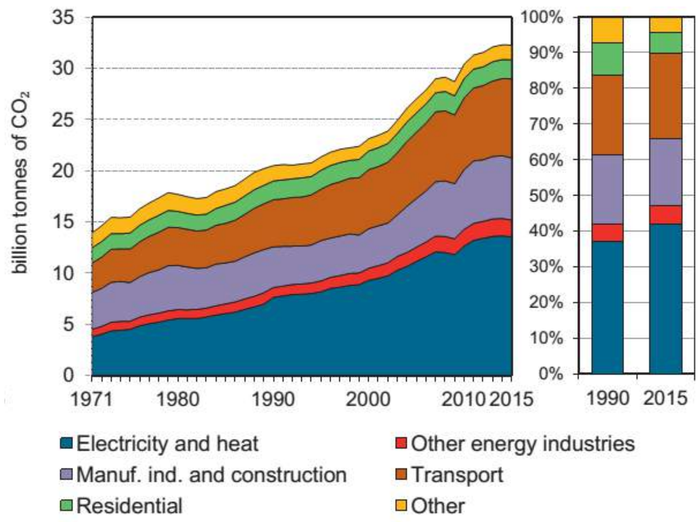
**POWER2METHANE (NATIONAL PROJECT)**

Duration: 2018-2020 | Granted funding: 239 k€

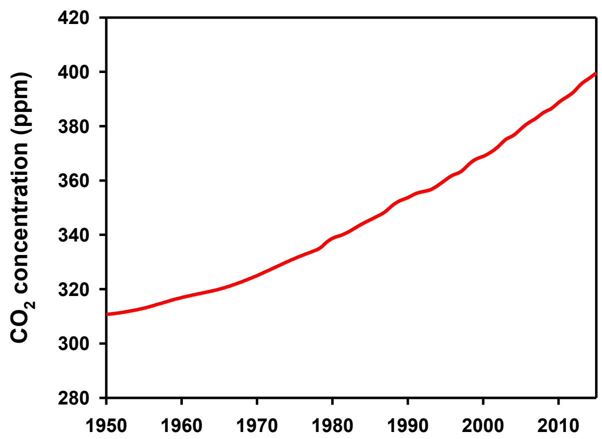
LM Madeira PI | AER | C. Miguel | M. Soria Junior posdocl res | Catarina Faria | Joana Martins

**PROBLEM**

## $CO_2$ EMISSIONS [1]




## $CO_2$ CONCENTRATION [2]




## CLIMATE CHANGE [3]

Increased area affected by **drought**

Increased frequency of **heavy precipitation** events

Increased frequency of **heat waves** events

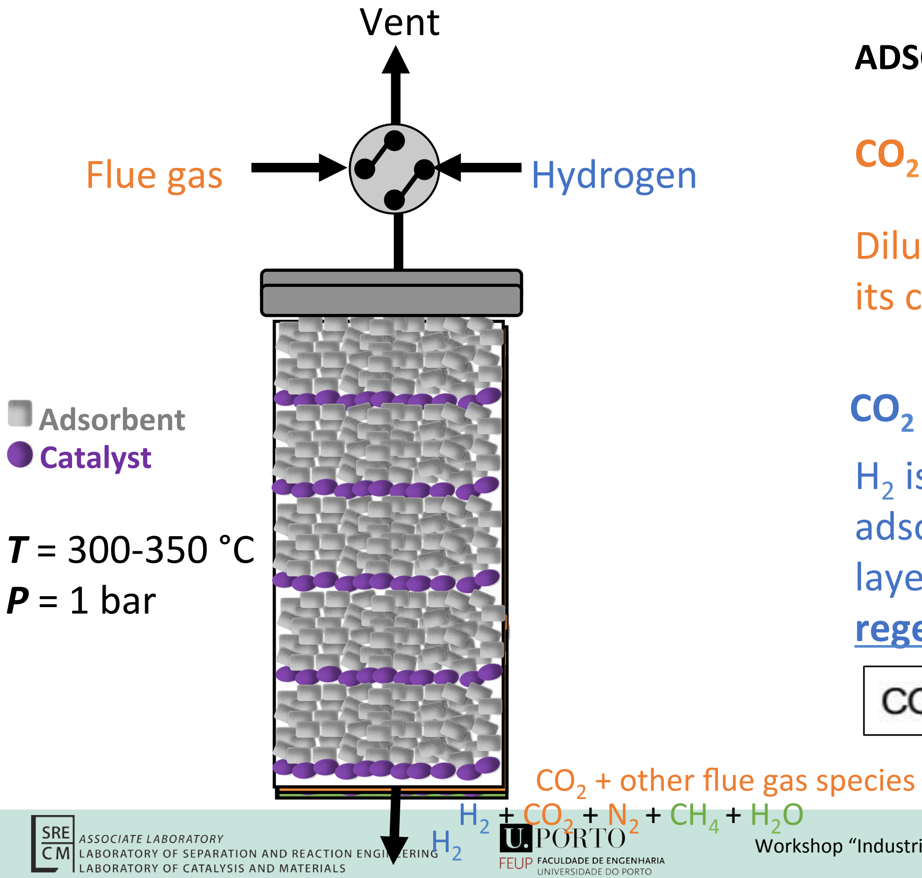
Average **artic temperatures** increased twice the global average rate in the past 100 years

**[1]** – International Energy Agency (**2017**), "$CO_2$ emissions from fuel combustion 2017 : highlights.

**[2]** – European Environment Agency (**2018**): https://www.eea.europa.eu

**[3]** – R.K. Pachauri (**2012**), The latest essential scientific findings that feed the assessment of the Intergovernmental Panel on Climate Change, $CO_2$ Forum, Lyon 2012.

# APPROACH: TURN WASTE ($CO_2$) TO VALUE ($CH_4$)




***T*** = 300-350 °C
***P*** = 1 bar

**ADSORPTIVE REACTOR**

## $CO_2$ CAPTURE

Diluted $CO_2$ from flue gas is separated from other species and its concentration inside the reactor is increased

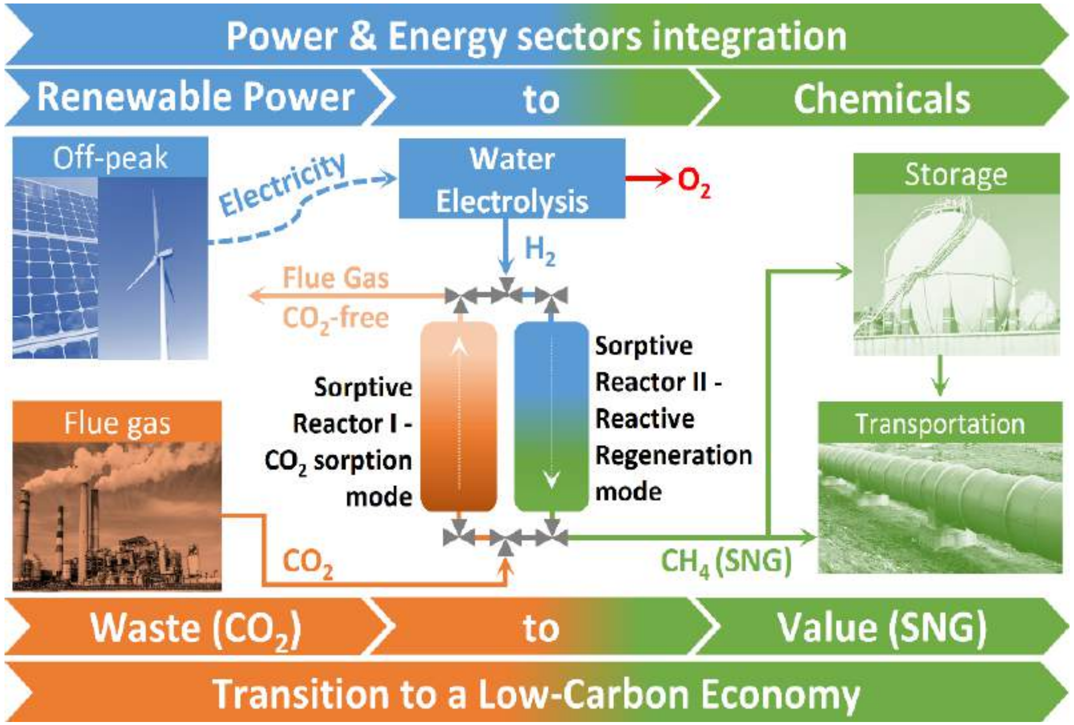
## $CO_2$ CONVERSION

$H_2$ is fed to the reactor and $CO_2$ is purged from the adsorbent while becoming available to react in the catalyst layers to produce methane (and water) **– reactive regeneration**

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H_{298\,K} = -165\ kJ \cdot mol^{-1}$$

# CCU Technology for Power-to-Gas Applications

**CCU TECHNOLOGY FOR POWER-TO-GAS APPLICATONS**




**OBJECTIVES**

1. Storage of renewable energy surpluses
2. Minimization of $CO_2$ emissions
3. Natural gas replacement by renewable-based synthetic natural gas

## R&D ROADMAP

**2017**

### PROOF-OF-CONCEPT

Adsorptive reactor for $CO_2$ capture and conversion using a synthetic flue gas stream successfully tested at lab-scale - **TRL 3**

**2018**

### POWER2METHANE

Funding from FCT was granted to further develop the technology and POWER2METHANE starts in mid-2018

**2019**

### PROTOTYPE

Prototype for testing the concept in cyclic mode (i.e. 2 reactors in parallel) in early 2019 with commercial materials

**2020**

### OPTIMIZATION

Adsorbents and catalysts screened for improved performance and reactor model ready for process optimization - **TRL 4**

**2021**

### TECHNO-ECONOMIC ANALYSIS

Reactor model embedded in ASPEN software for process simulation in identified end-users and estimation of technical indicators as well as CAPEX and OPEX.

**2022**

### DEMONSTRATION

Technology demonstration by identified end-users – **TRL5-6**

## COLLABORATIVE WORK

| | PARTICLE SCALE | | REACTOR SCALE |
|---|---|---|---|
| | ADSORBENTS | CATALYSTS | PROCESS |
| COMPANIES | sasol | CLARIANT | sysadvance |
| UNIVERSITIES / LABS | VNIVERSIDAD D SALAMANCA CAMPUS DE EXCELENCIA INTERNACIONAL | LUND UNIVERSITY | TU/e |

**OUTCOMES AND CHALLENGES**

- ✓ Proof-of-concept of the adsorptive reactor for $CO_2$ capture and conversion application
- ✓ Captured $CO_2$ could be almost completely converted to methane (90 %)
- ✓ Good compatibility and cyclic stability of tested adsorbent and catalyst

**PERFORMANCE INDICATORS** @ $T$=350 C, $P_t$=1 bar and $y_{CO2}$=0.15

| | $CO_2$ adsorption capacity (mol/kg$_{ads}$) | $CO_2$ conversion ( %) | $CH_4$ productivity (mol/(kg$_{cat}$ h) | $CH_4$ purity (%) |
|---|---|---|---|---|
| Baseline* (2018) | 0.3 | 90 | 2.4 | 36 |
| Target* (2019-2020) | 1.0 | 100 | 3.0 | 84 |

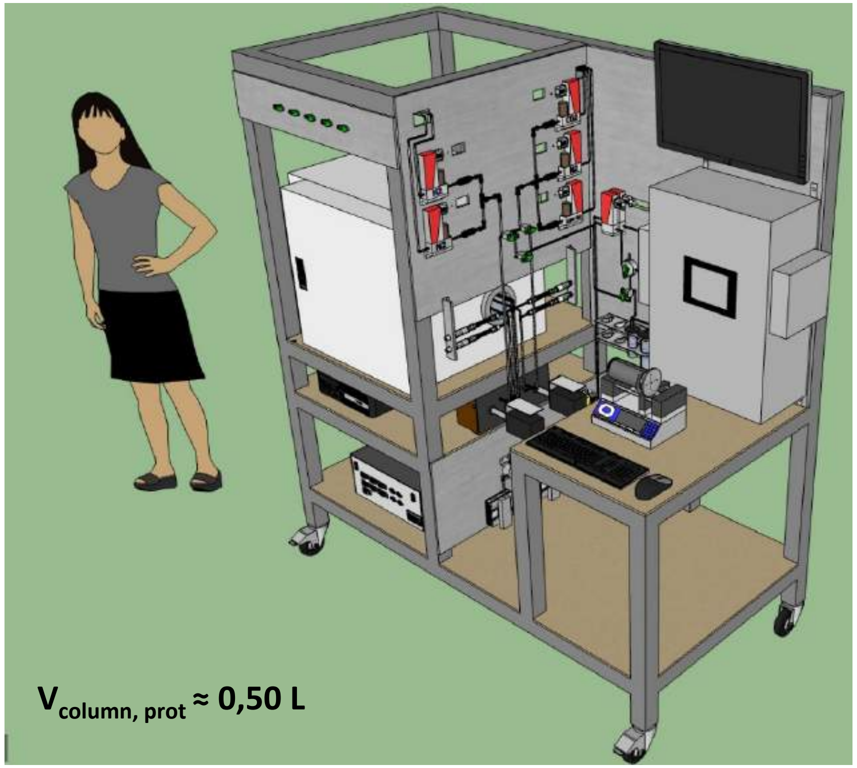
* Carlos V. Miguel, $CO_2$ capture and conversion to chemicals: methane production, PhD thesis, University of Porto, 2018.

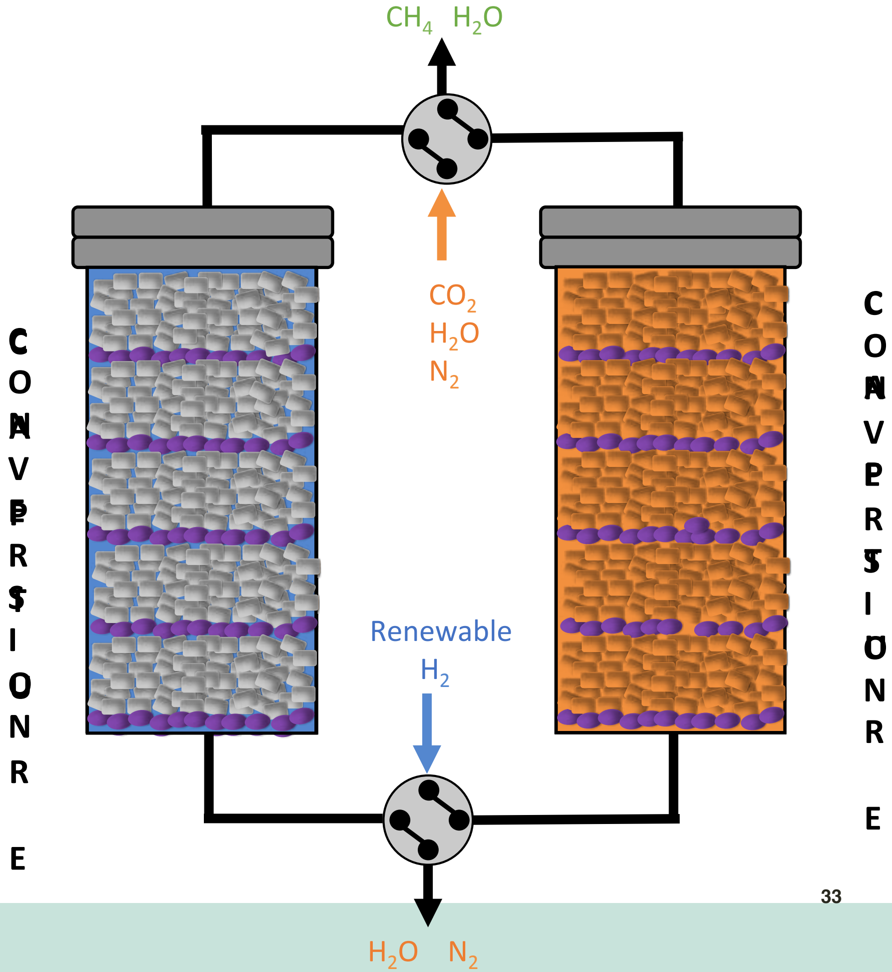
** Within the scope of FCT project POWER2METHANE (www.power2methane.fe.up.pt)

## ONGOING R&D WORK

| | | TASK | GOALS |
|---|---|---|---|
| MATERIALS | ADSORBENTS | Synthesis, characterization and screening of Na-, Cs- and K-promoted hydrotalcites for $CO_2$ adsorption at high temperature. | • Improve $CO_2$ adsorption capacity<br>• Improve adsorption/desorption kinetics |
| | CATALYSTS | Synthesis, characterization and screening of catalysts for $CO_2$ methanation: Ru, Ni, Ru-Ni and Ni catalysts featuring $CO_2$ adsorption capacity (i.e. dual-function materials). | • Improve $CH_4$ productivity<br>• Improve $CH_4$ purity |
| PROCESS | REACTOR | Modeling of the cyclic adsorptive reactor unit in gPROMS | • Optimization of the reactor performance<br>• Estimation of CAPEX and OPEX |

## PROTOTYPE FOR CYCLIC OPERATION




$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

# Innovation

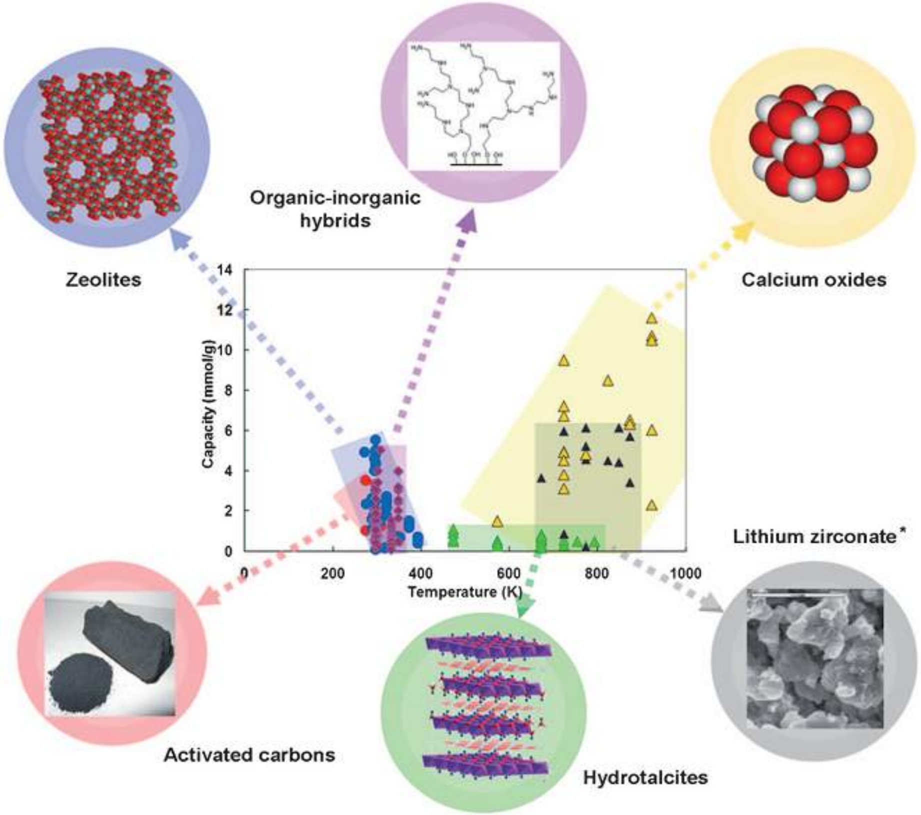
**INNOVATION**

| | LURGI | TREMP (Haldor Topsoe) | VESTAS (Foster Wheeler/ Clariant) | COMFLUX (PSI) | ETOGAS/ ZSW | Agnion | EBI | EBI | FEUP |
|---|---|---|---|---|---|---|---|---|---|
| **Type of reactor** | Series of adiabatic fixed beds with intermittent and recirculation cooling | | | Isothermal bubbling fluidized bed reactor | Polytropic fixed bed with several injection points and cooling zones | Polytropic fixed bed with partial cooling | Polytropic fixed bed with conductive catalyst support | Isothermal bubble column reactor | **Adsorptive Reactor (cyclic process)** |
| **Simplicity** | + | + | + | -- | -- | o | o | -- | **o** |
| **Low nr. of units** | -- | -- | -- | + | + | ++ | + | o | **+** |
| **High temperature of cooling** | + | ++ | + | -- | o | o | -- | -- | **--** |
| **Flexibility** | o | o | o | ++ | + | o | + | ++ | **+** |
| **Sufficient mass transfer** | + | + | + | + | + | + | + | -- | **+** |
| **Good heat transfer** | n.a. | n.a. | n.a. | ++ | o | o | + | ++ | **++** |
| **Low challenges for catalyst** | o | - | o | -- | o | -- | o | + | **o** |
| **TRL** | 9 | 9 | 7-8 | 7,8 | 8 | 5 | 4 | 4 | **3** |

++ very much given; + given; o less given; - not given; -- not given at all; n.a. not applicable

# High temperature $CO_2$ capture by adsorption

## Materials for $CO_2$ adsorption

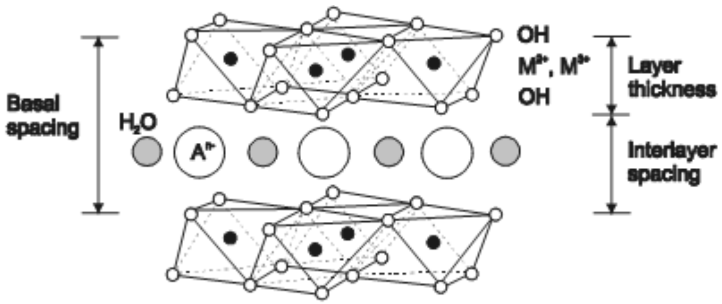



Source: ChemSusChem 2 (2009) 796-854.

# $CO_2$ capture by adsorption

## Hydrotalcites

Source: Adsorption 14 (2008) 781-789.




$$\left[M^{2+}_{1-x}\ M^{3+}_{x}\left(OH\right)_2\right]\left[A^{n-}\right]_{x/n}\cdot y\ H_2O$$

**$M^{2+}$:** $Mg^{2+}$, $Ni^{2+}$, $Zn^{2+}$ …

**$M^{3+}$:** $Al^{3+}$, $Ga^{3+}$, $Mn^{3+}$ …

**$A^{n-}$:** $CO_3^{2-}$, $Cl^-$, $SO_4^{2-}$ …

## Synthesized hydrotalcites

| Reference | $M^{2+}$ | $M^{3+}$ | | $A^{n-}$ | Promoter | Content (wt.%) |
|---|---|---|---|---|---|---|
| HTC | Mg | Al | - | $CO_3^{2-}$ | - | - |
| HTC-20K | Mg | Al | - | $CO_3^{2-}$ | K | 20 |
| HTC-10Ga | Mg | Al | Ga | $CO_3^{2-}$ | - | - |
| HTC-10Ga-20K | Mg | Al | Ga | $CO_3^{2-}$ | K | 20 |
| HTC-10Ga-20Cs | Mg | Al | Ga | $CO_3^{2-}$ | Cs | 20 |
| HTC-10Ga-20Sr | Mg | Al | Ga | $CO_3^{2-}$ | Sr | 20 |

## Synthesis protocol

1. Hydrotalcites were prepared by the co-precipitation method

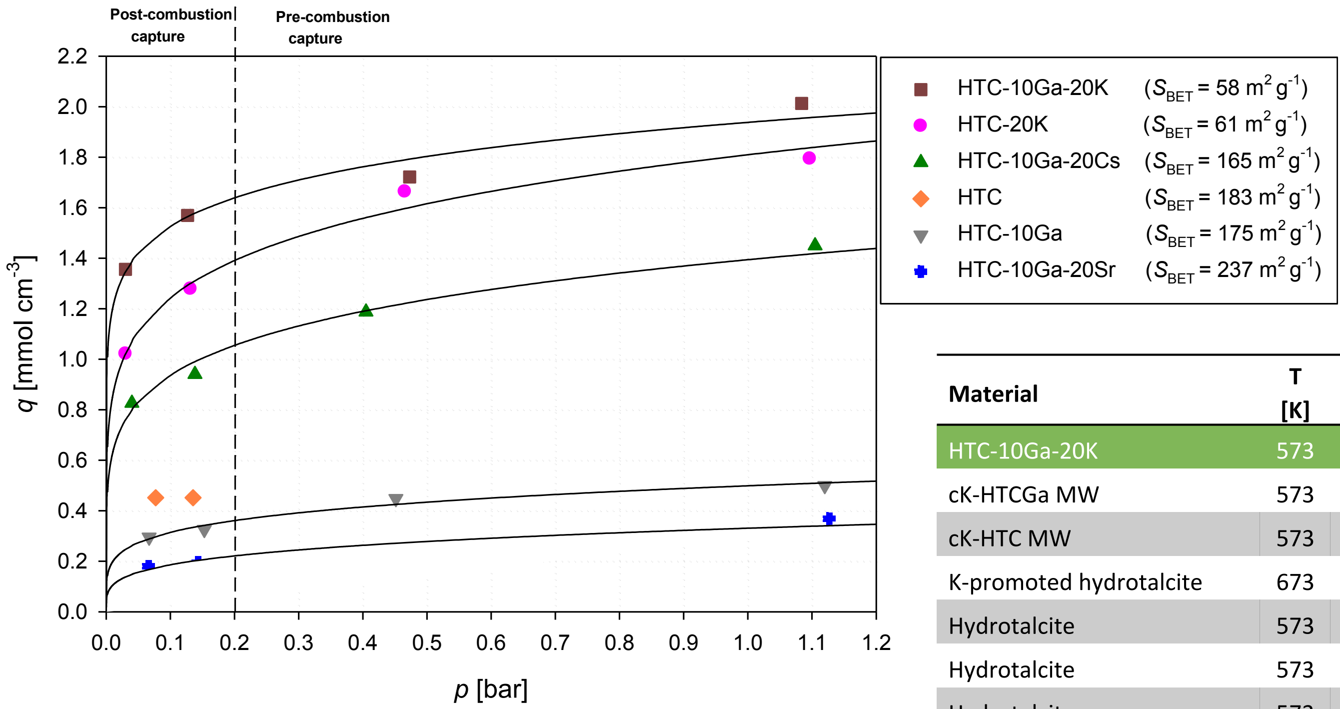
- $M^{2+}/M^{3+}$ = 2:1 (mol. %)
- Al : Ga = 90 : 10 (mol. %)

2. Modification with K, Cs or Sr performed by wet impregnation

3. Calcination at 400 ºC during 2 hours

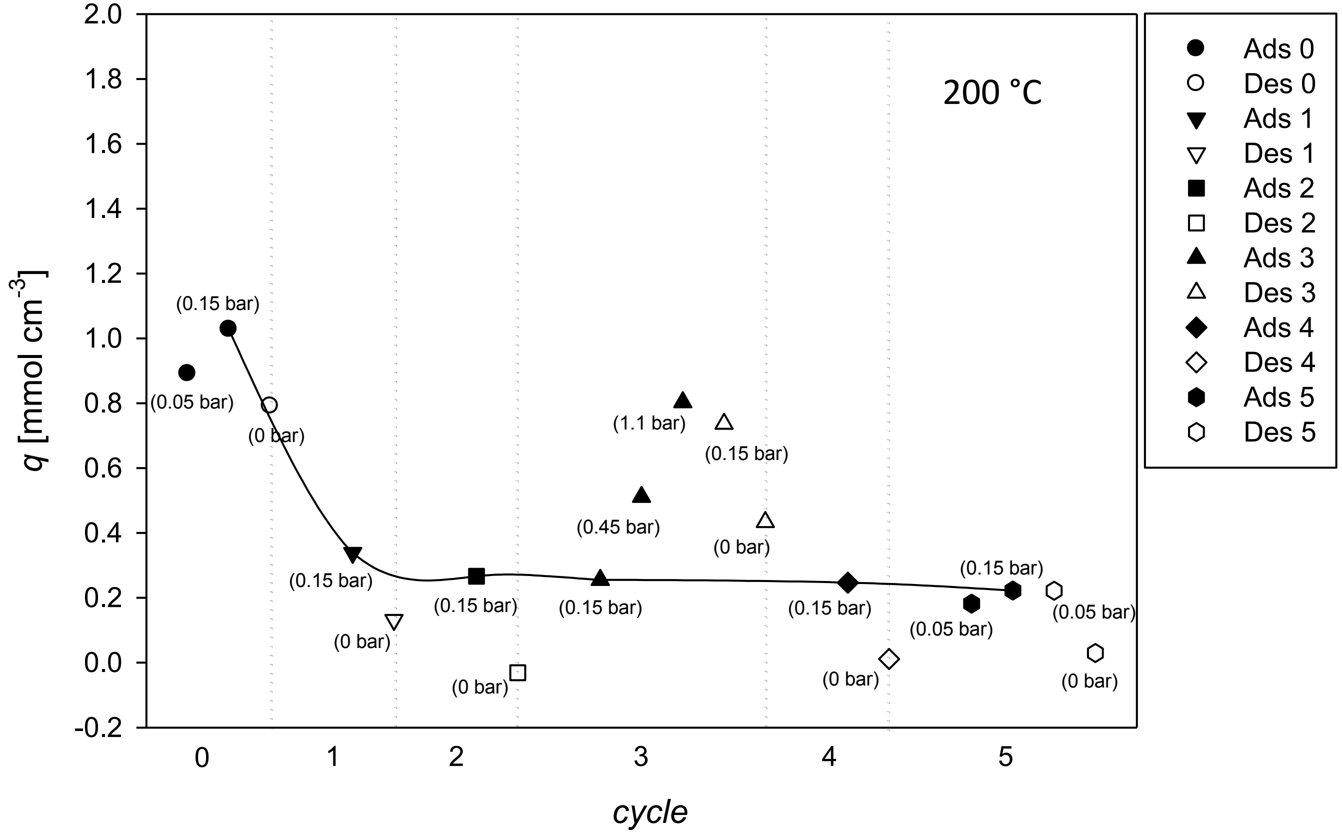
## $CO_2$ sorption equilibrium at 300 ºC

### Sorbent screening




| Material | T [K] | $p_{CO2}$ [bar] | q [mol·kg$^{-1}$] | Ref. |
|---|---|---|---|---|
| HTC-10Ga-20K | 573 | 1.08 | 1.82 | This work |
| cK-HTCGa MW | 573 | 1.05 | 1.70 | Chem. Eng. J., 325 (2017) 25. |
| cK-HTC MW | 573 | 1.05 | 1.35 | Chem. Eng. J., 325 (2017) 25. |
| K-promoted hydrotalcite | 673 | 1 | 0.79 | J. Colloid Interf. Sci., 308 (2007) 30. |
| Hydrotalcite | 573 | 1 | 0.52 | Sep. Purif. Technol. 26 (2002) 195. |
| Hydrotalcite | 573 | 1 | 0.50 | Ind. Eng. Chem. Res. 40 (2001) 204. |
| Hydrotalcite | 573 | 1.1 | 0.25 | Ind. Eng. Chem. Res. 45 (2006) 7504. |

## Determination of the working capacity



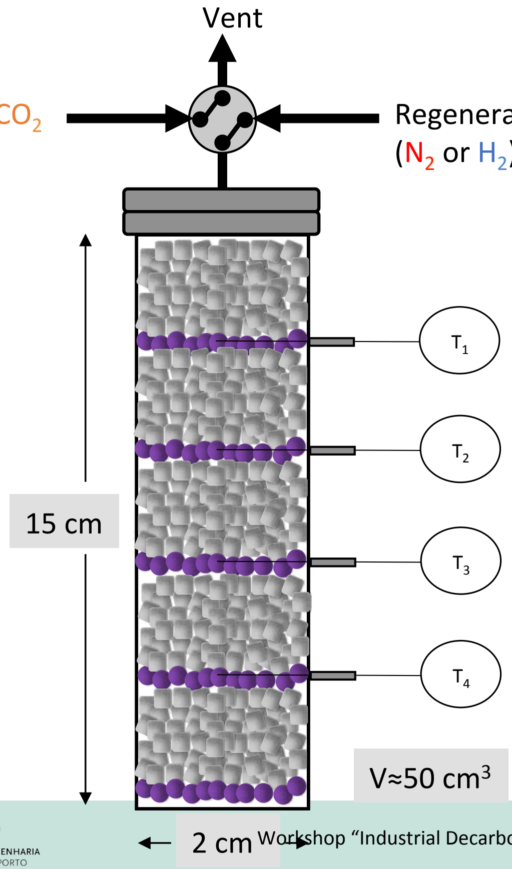

1. Partial substitution with Ga and modification with K substantially increase the sorption capacity

2. The best sorbent (HTC-10Ga-20K) has a higher sorption capacity compared to others reported in the literature

3. The sorption capacity of hydrotalcite increases with temperature

4. The working capacity is reached after 2-3 sorption/desorption cycles

## Sorptive reactor unit description




**Sorbent:**

K-promoted hydrotalcite (from Sasol)
$W_{sorb}$ = 23.9 g

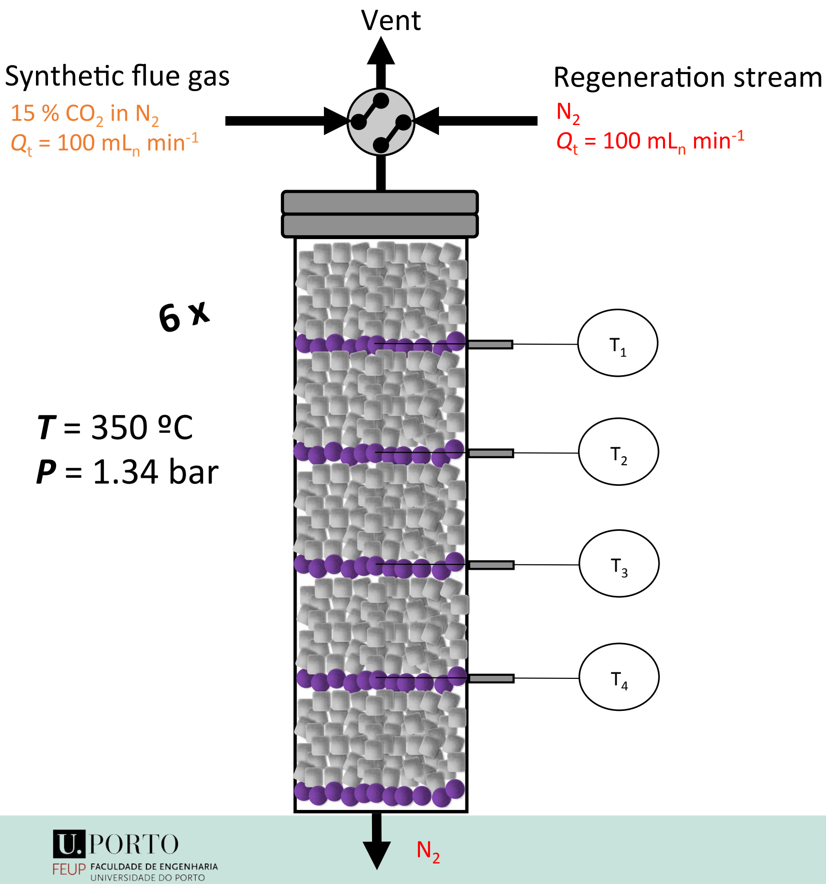
**Catalyst:**

Nickel-based catalyst (from Clariant)
$W_{cat}$ = 7.6 g

$$\frac{W_{sorb}}{W_{cat}} \approx 4$$

# Hybrid process of $CO_2$ capture and conversion

## Sorption-desorption cycles




***T*** = 350 ºC
***P*** = 1.34 bar

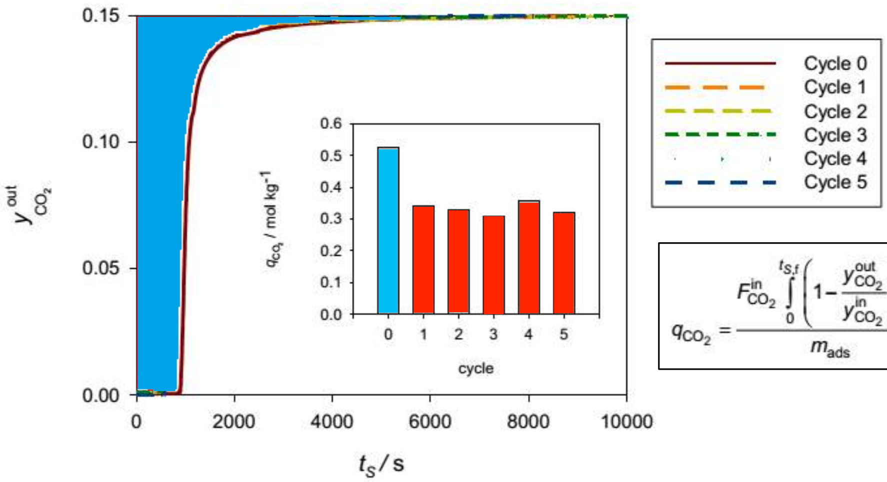
**Stage:**

1. Purge
2. $CO_2$ capture (**full bed saturation**)
3. Regeneration

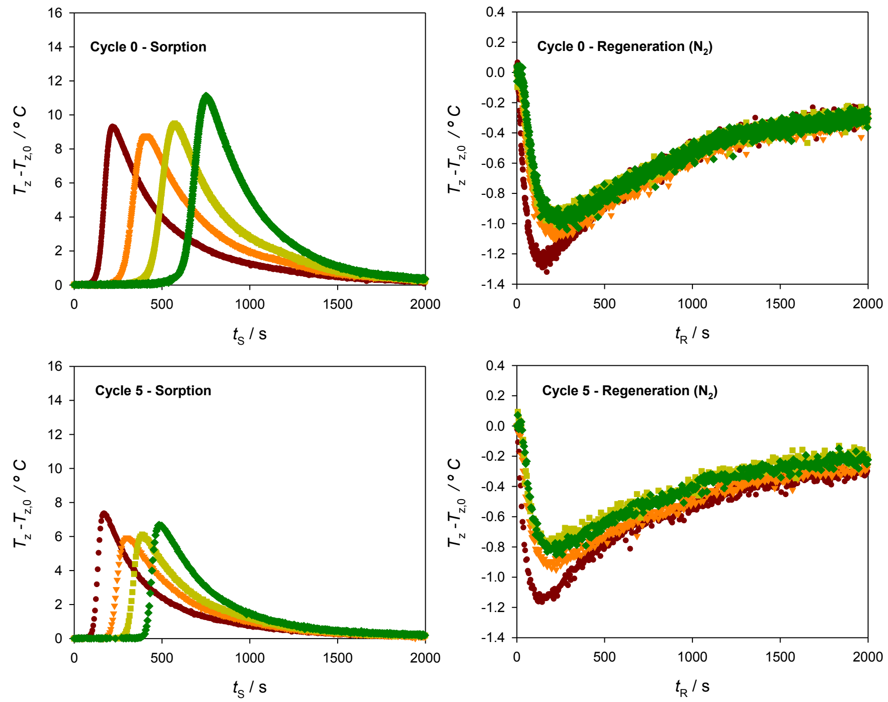
# Hybrid process of $CO_2$ capture and conversion

## Sorption-desorption cycles

### Sorbent working capacity




$$q_{CO_2} = \frac{F^{in}_{CO_2} \int_0^{t_{S,f}} \left(1 - \frac{y^{out}_{CO_2}}{y^{in}_{CO_2}}\right) dt_S}{m_{ads}}$$




**$CO_2$ sorption capacity**

0.52 mol·kg$^{-1}$

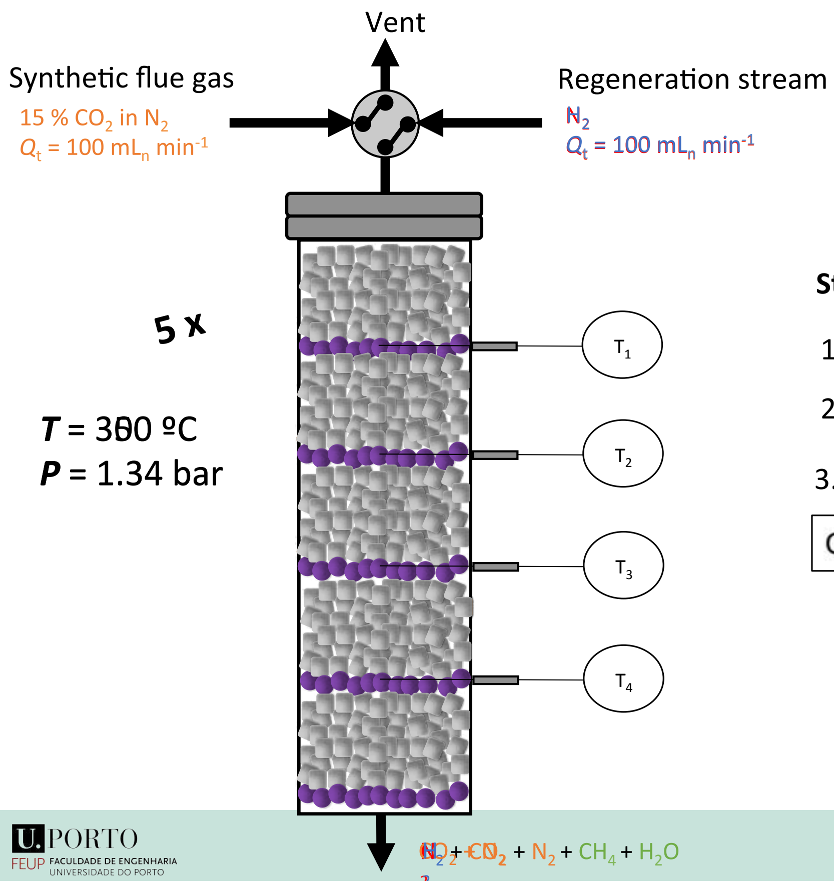
6 cycles

**$CO_2$ working capacity**

0.32 mol·kg$^{-1}$

## Hybrid process of $CO_2$ capture and conversion

# Sorption-reaction cycles




**Stage:**

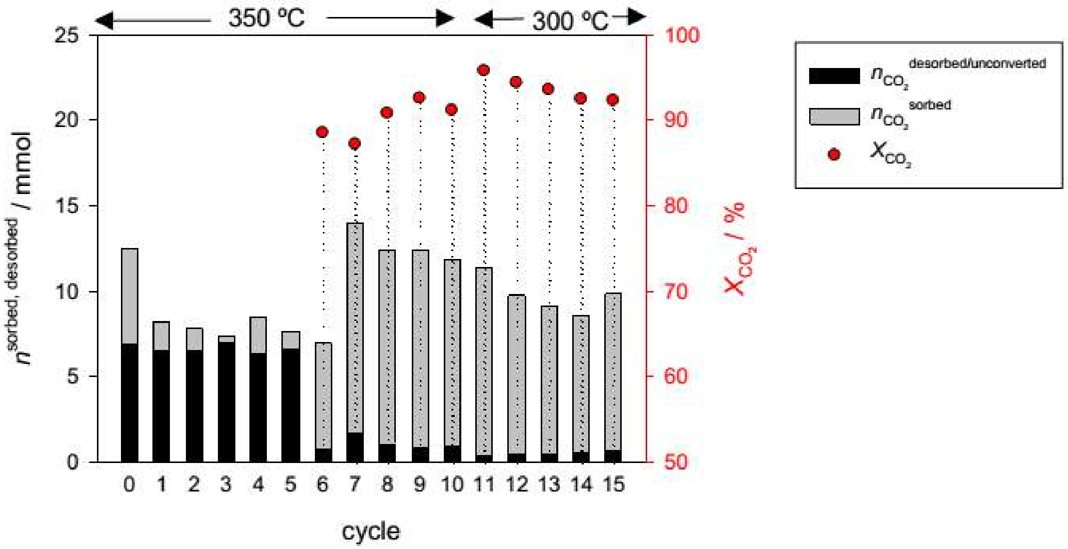
1. Purge
2. $CO_2$ capture (**<u>full bed saturation</u>**)
3. Reactive regeneration

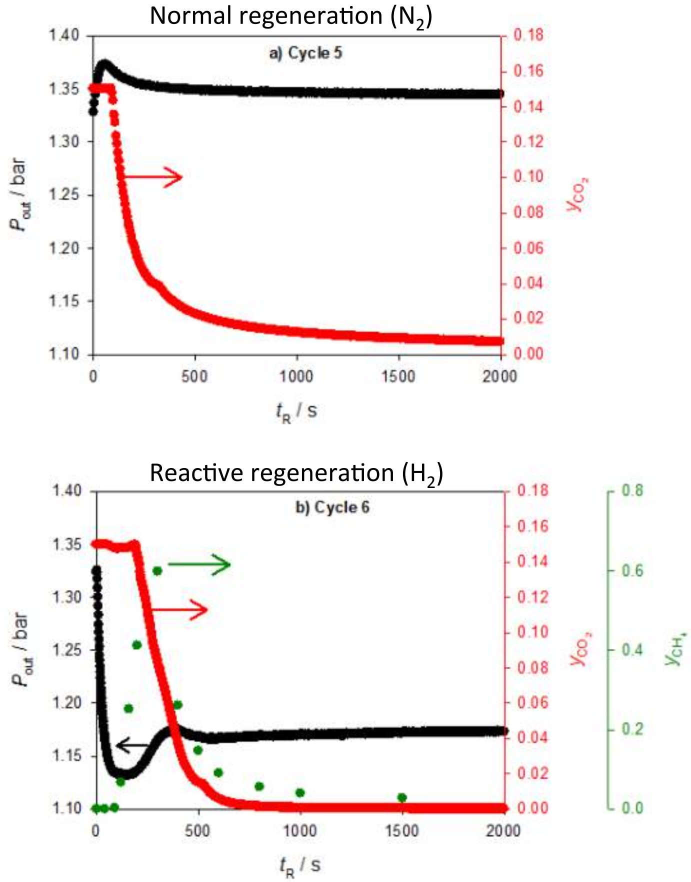
$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H_{298\,K} = -165\ kJ \cdot mol^{-1}$$

# Hybrid process of $CO_2$ capture and conversion

## Sorption-reaction cycles

### Effect of steam



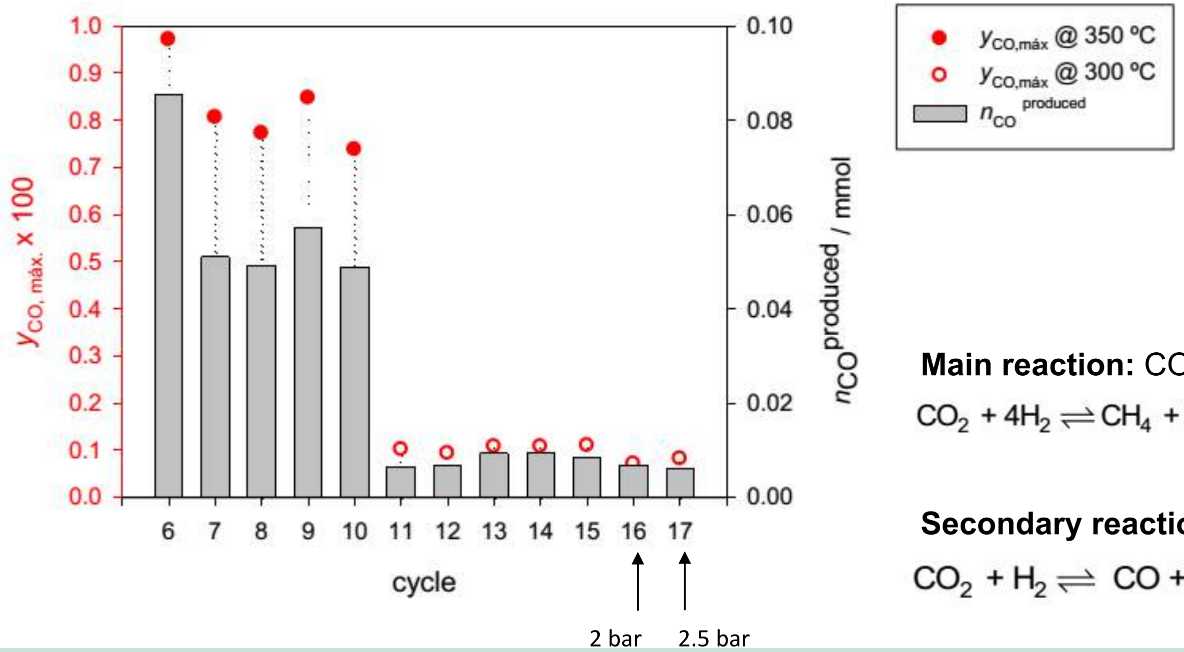

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H_{298\,K} = -165\ kJ\cdot mol^{-1}$$

# Hybrid process of $CO_2$ capture and conversion

## Sorption-reaction cycles

### CO formation

| Cycle | $n_{CH4}/n_{CO}$ |
|---|---|
| 6 | 161 |
| 7 | 249 |
| 8 | 256 |
| 9 | 237 |
| 10 | 262 |
| 11 | 1523 |
| 12 | 1518 |
| 13 | 1076 |
| 14 | 1076 |
| 15 | 1230 |
| 16 | 1466 |
| 17 | 1630 |




**Main reaction:** $CO_2$ methanation

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H_{298\,K} = -165\ kJ \cdot mol^{-1}$$

**Secondary reaction:** Reverse water gas shift

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H_{298\,K} = 41\ kJ \cdot mol^{-1}$$

## Highlights

**1** The concept of integrating $CO_2$ capture and its conversion into $CH_4$ in the same unit is successfully proved

**2** The conversion of captured $CO_2$ was high ($X_{CO2}$ ~ 90 %)

**3** Reactive regeneration improves sorbent capacity and desorption kinetics

**4** CO formation can be minimized by decreasing the temperature and/or increasing the pressure

**5** The commercial materials used were compatible and stable under cyclic operation

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**Book**

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# Porto and FEUP