

Power2**METHANE**

1st WEBINAR | 5th June 2020

Power2Methane: outcomes and future perspectives

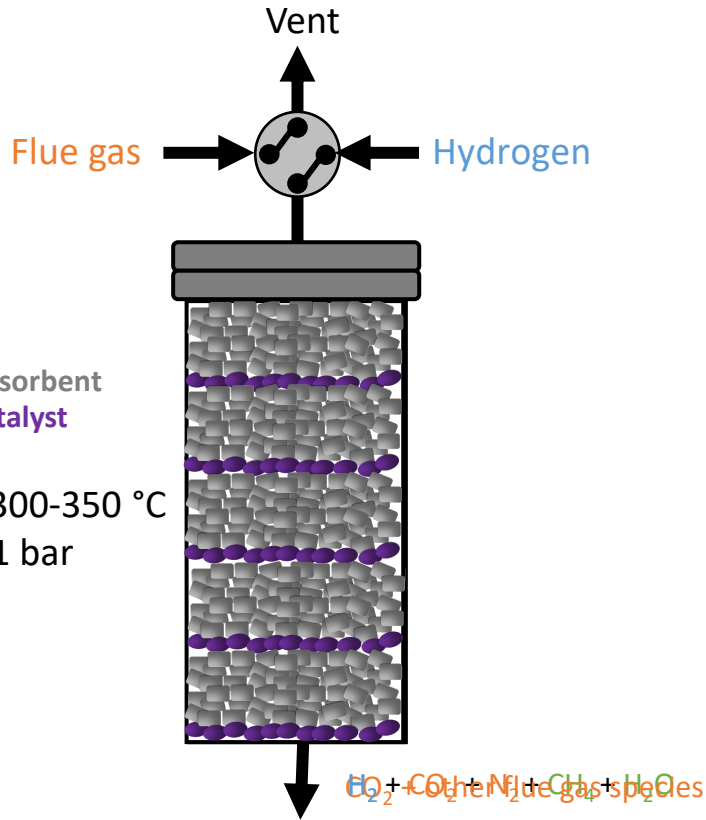
Carlos Miguel



Outline

- 1** The sorptive reactor concept
- 2** Power2Methane project outcomes
- 3** Future perspective

APPROACH: TURN WASTE (CO₂) TO VALUE (CH₄)



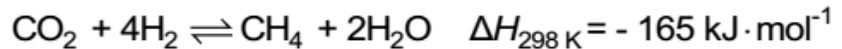
ADSORPTIVE REACTOR

CO₂ CAPTURE

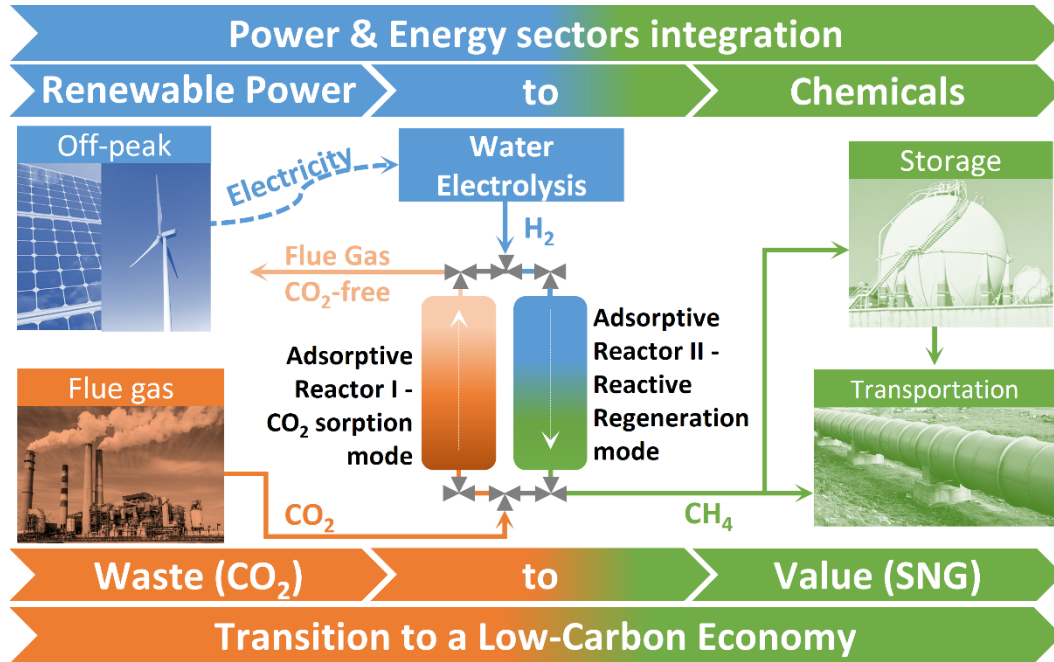
Diluted CO₂ from flue gas is separated from other species and its concentration inside the reactor is increased

CO₂ CONVERSION

H₂ is fed to the reactor and CO₂ is purged from the adsorbent while becoming available to react in the catalyst layers to produce methane (and water) – reactive regeneration



POWER-TO-GAS



OBJECTIVES

- 1** Storage of renewable energy surpluses
- 2** Minimization of CO₂ emissions
- 3** Natural gas replacement by renewable-based synthetic natural gas

INNOVATION

	LURGI	TREMP (Haldor Topsoe)	VESTAS (Foster Wheeler/Clar iant)	COMFLUX (PSI)	ETOGAS/ ZSW	Agnion	EBI	EBI	FEUP/LEPABE
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

MAIN ADVANTAGES

- Lower number of operation units (the sorptive reactor simultaneously captures and converts CO₂).
- Since the reactor operates at high temperature, warm flue gas can be used minimizing energy requirements.
- Heat integration between reaction (exothermic) and CO₂ desorption (endothermic)

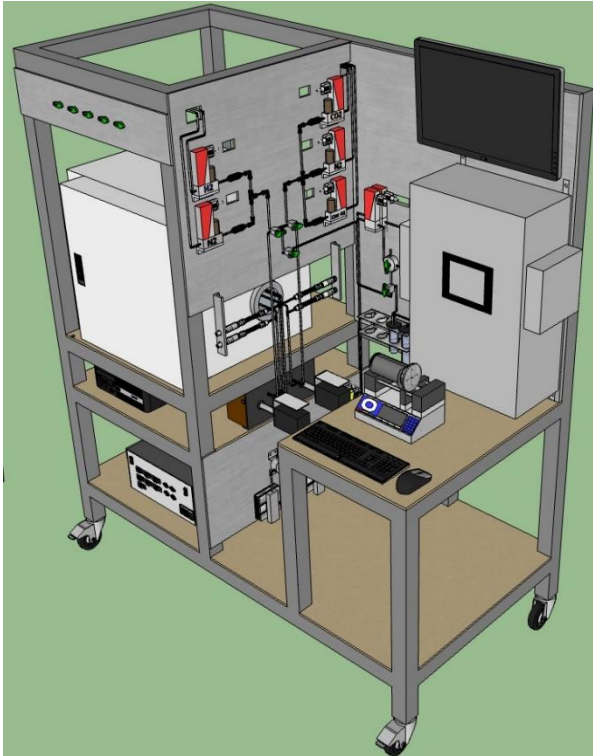
MAIN DRAWBACKS

- Higher complexity
- Low TRL

PROJECT MILESTONES

	Status
Launch of project website	Achieved
Organization of 2 seminars	50% achieved
Prototype ready for testing	Achieved
Catalyst selection	Achieved
Sorbent selection	80% achieved
Validation of mathematical model for the sorptive reactor	60% achieved
Selection of best reactor configuration	Ongoing
Techno-economic assessment	Ongoing

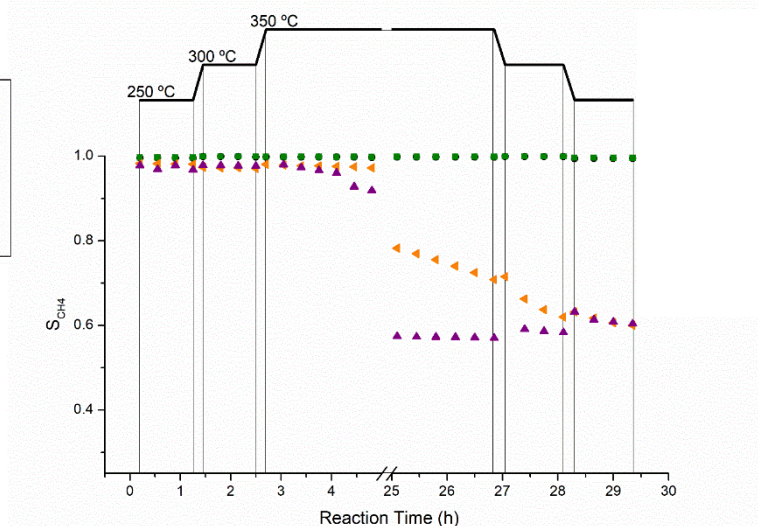
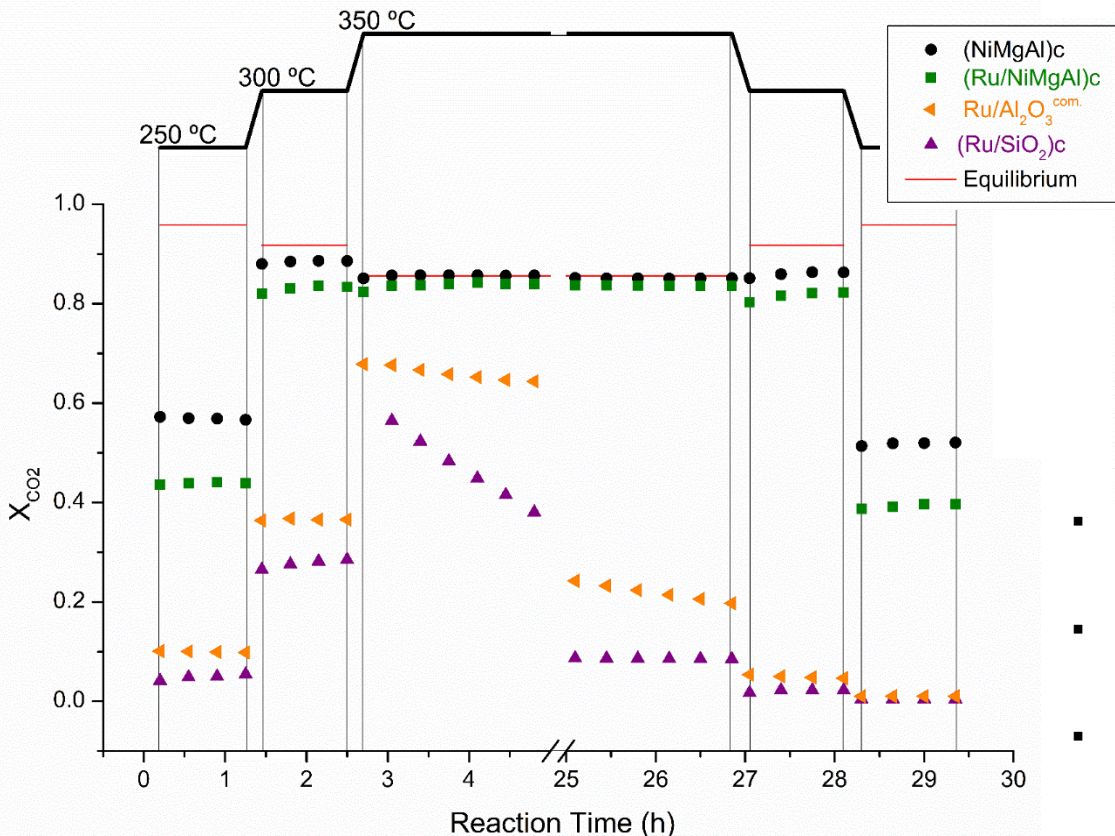
BENCH-SCALE PROTOTYPE DESIGN & ASSEMBLING



Features:

- Portability
- Automated operation and data acquisition in Labview
- Two sorptive reactors (500 cm³ each)
- High-temperature switching valves for cyclic operation
- $T_{\max}=350\text{ °C} / P_{\max}=7\text{ bar}$
- Online measurement of CO₂, H₂, CH₄, CO, H₂O and O₂

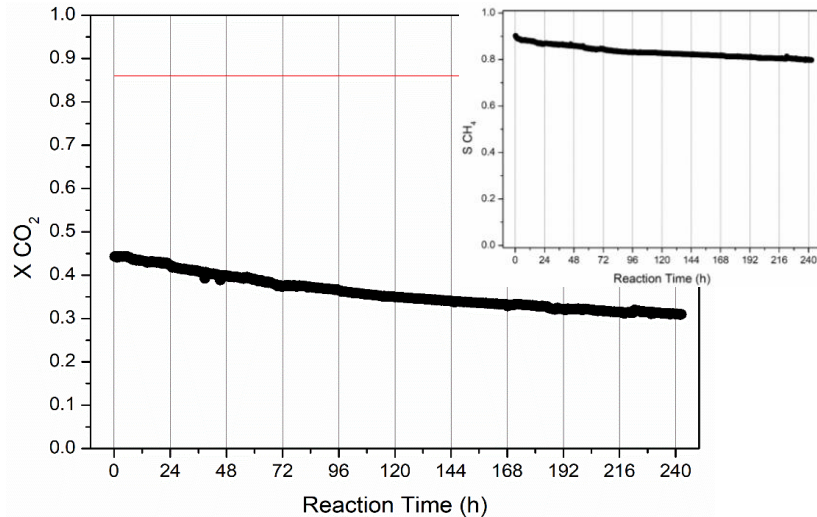
CATALYST DEVELOPMENT AND SCREENING



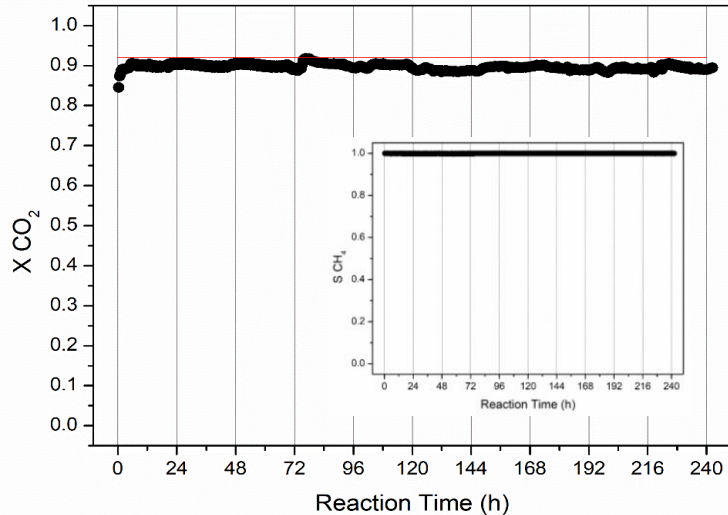
- **Hydrotalcite derived catalysts** were the most promising showing high activity and selectivity;
- **Ru/Al₂O₃^{com.}** and **Ru/SiO₂** showed loss of activity and selectivity during the screening experiments
- **NiMgAl** estimated price is lower than Ru/NiMgAl (962.55 \$/kg vs. 1203.83 \$/kg, respectively).

CATALYST DEVELOPMENT AND SCREENING

- T=350 °C
- WHSV=24,000 mL_{N,CO₂} · g⁻¹ · h⁻¹



- T=300 °C
- WHSV = 2,400 mL_{N,CO₂} · g⁻¹ · h⁻¹



- **NiMgAl** long-term stability (10 days) significantly depends on the operating conditions: high temperature and high WHSV favours CO formation leading to catalyst deactivation and lower selectivity.
- Long-term stability and near full methane selectivity found at 300 °C and low WHSV conditions.

CATALYST DEVELOPMENT AND SCREENING

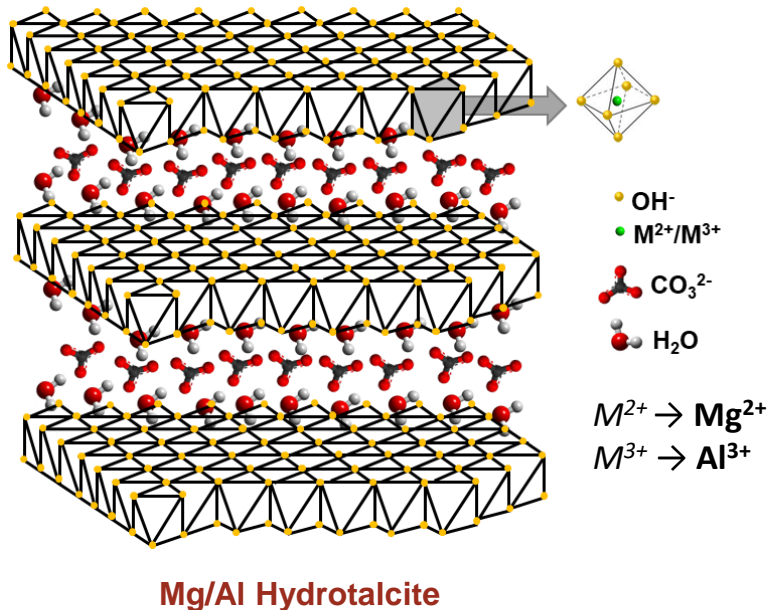
Catalyst	WHSV (mL _{n,CO2} g ⁻¹ h ⁻¹)	T (°C)	Y _{CH4}
NiMgAl	2 400	250	0.57
	2 400	300	0.88
	2 400	350	0.85
	24 000	350	0.40
METH 134	2 383	250	0.07
	2 383	350	0.63
	14 545	350	0.33

J. Martins et al., *Catalysts* **2019**, 9, 1008.

C.V. Miguel et al., *J. CO2 Util.* **2018**, 25, 128–136.

- **NiMgAl** outperforms **METH 134** commercial catalyst, particularly at lower temperatures and lower WHSV (i.e. where was found long-term stability and methane selectivity)

SORBENT DEVELOPMENT AND SCREENING



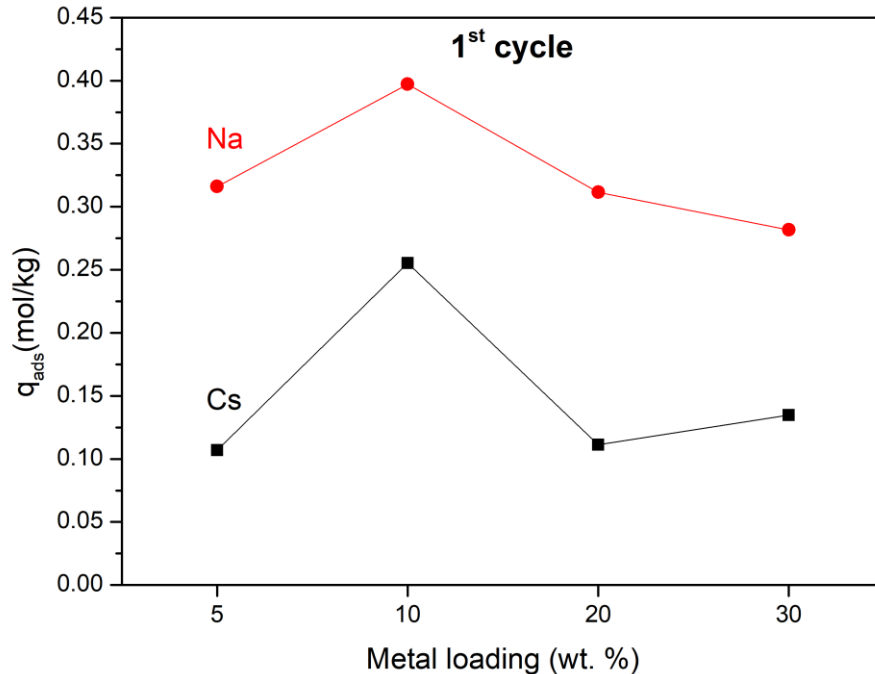
Impregnation



Sample name	Promoter (wt. %)
HTC - 2	-
HTC - 2 - 20K ¹	K (20 %)
HTC - 2 - 20K ²	K (20 %)
HTC - 2 - 5Na	Na (5 %)
HTC - 2 - 10Na	Na (10 %)
HTC - 2 - 20Na	Na (20 %)
HTC - 2 - 30Na	Na (30 %)
HTC - 2 - 5Cs	Cs (5 %)
HTC - 2 - 10Cs	Cs (10 %)
HTC - 2 - 20Cs	Cs (20 %)
HTC - 2 - 30Cs	Cs (30 %)

¹Potassium carbonate as potassium precursor.
²Potassium acetate as potassium precursor.

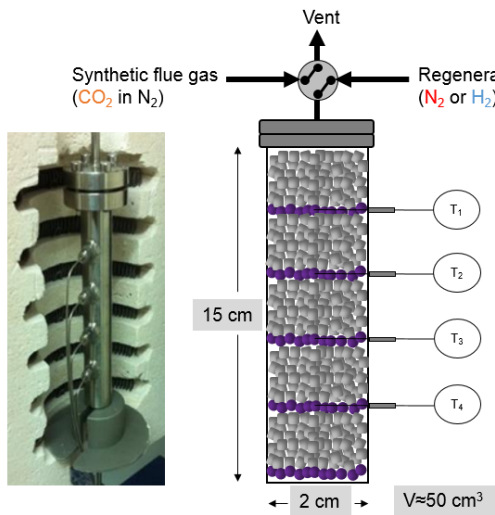
SORBENT DEVELOPMENT AND SCREENING



- 5 cycles of adsorption (30 min) + desorption (30 min)
- T=300 °C
- pCO₂= 0.15 bar
- Desorption under vacuum (P <0.001 bar)

- All samples reach their working capacity after 3 cycles
- Doping with Cs and Na improves sorption capacity, **particularly Na**
- The sample doped with 5% Na has the same working capacity of sample with 10% Na
- **MG30K (from Sasol) outperforms all tested samples so far**

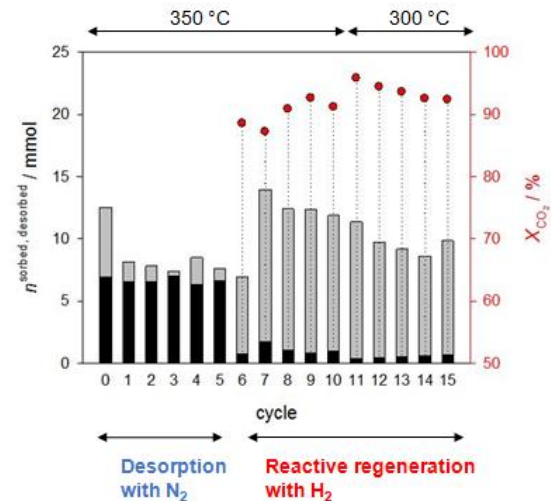
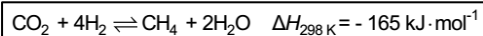
MODELLING WORK – SORPTIVE REACTOR FOR CO₂ CAPTURE AND CONVERSION TO CH₄



Layered bed with compatible materials

- Sorbent:
K-promoted hydrotalcite (Pural MG30-K from Sasol)
- Catalyst:
Nickel-based catalyst (from Clariant)

$$\frac{W_{\text{sorb}}}{W_{\text{cat}}} = 3.15$$



C.V. Miguel et al., Chem. Eng. J. 322 (2017) p. 590-602.

	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
Targets (2021)	1.0	100	3.0	88

Mass balance

Partial mass balance to species i in the **GAS PHASE** at the **SORBENT LAYER**

$$\frac{\partial C_{i,\text{gas}}}{\partial t} = D_{\text{ax}} \frac{\partial}{\partial z} \left(C_T \frac{\partial y_{i,\text{gas}}}{\partial z} \right) - \frac{\partial (u_{\text{int}} C_{i,\text{gas}})}{\partial z} - \left(\frac{1 - \varepsilon_c}{\varepsilon_c} \right) \frac{a_{\text{v,sorb}} k_{\text{f,sorb}}}{Bi + 1} (C_{i,\text{gas}} - \bar{C}_{i,\text{sorb}})$$

Partial mass balance to species i in the **GAS PHASE** at the **CATALYST LAYER**

$$\frac{\partial C_{i,\text{gas}}}{\partial t} = D_{\text{ax}} \frac{\partial}{\partial z} \left(C_T \frac{\partial y_{i,\text{gas}}}{\partial z} \right) - \frac{\partial (u_{\text{int}} C_{i,\text{gas}})}{\partial z} - \left(\frac{1 - \varepsilon_c}{\varepsilon_c} \right) a_{\text{v,cat}} k_{\text{r,cat}} (C_{i,\text{gas}} - C_{i,\text{cat}}|_{r_{\text{cat}}=R_{\text{cat}}})$$

Mass transfer of species i from gas phase to the **SORBENT PELLETT**

$$\frac{\partial \bar{C}_{i,\text{sorb}}}{\partial t} = \left(\frac{Bi}{Bi + 1} \right) \frac{15 D_{\text{p,sorb}}}{R_{\text{sorb}}^2} (C_{i,\text{gas}} - \bar{C}_{i,\text{sorb}}) - \frac{\rho_{\text{sorb}}}{\varepsilon_{\text{p,sorb}}} k_{\text{CO}_2} (q_{i,\text{eq}} - \bar{q}_i)$$

LDF Model

Mass balance of species i in the **CATALYST SPHERE** (Pore diffusion + Reaction)

$$\frac{\partial C_{i,\text{cat}}}{\partial t} = D_{\text{p,cat}} \left(\frac{\partial^2 C_{i,\text{cat}}}{\partial r_{\text{cat}}^2} + \frac{2}{R_{\text{cat}}} \frac{\partial C_{i,\text{cat}}}{\partial r_{\text{cat}}} \right) + \frac{\rho_{\text{cat}}}{\varepsilon_{\text{p,cat}}} v_i R$$

Energy balance

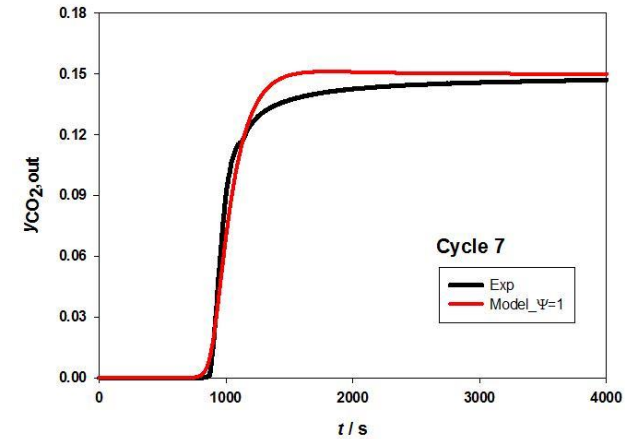
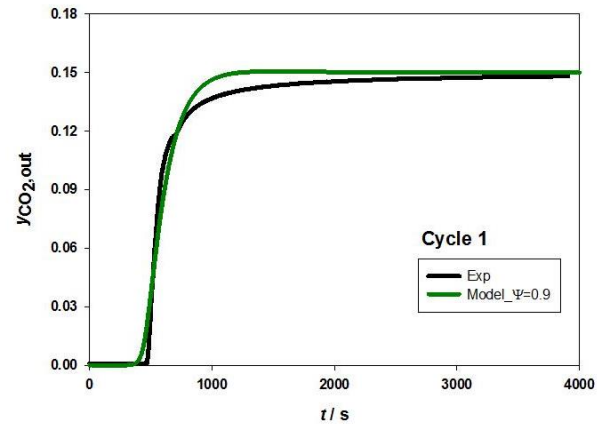
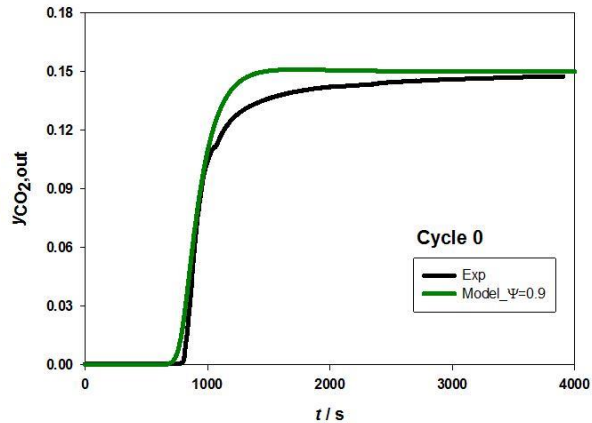
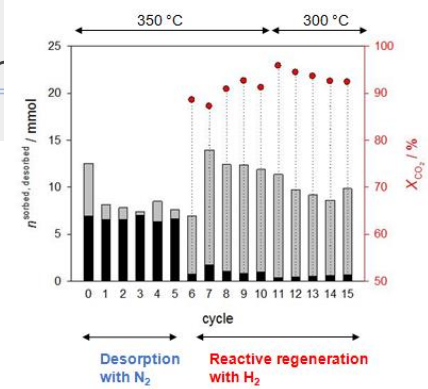
GAS PHASE at the **SORBENT LAYER** $(\varepsilon_c C_T \hat{C}_{\text{vg}} + (1 - \varepsilon_c) \rho_{\text{sorb}} C_{\text{p,sorb}}) \frac{\partial T}{\partial t} = \varepsilon_c RT \frac{\partial C_T}{\partial z} + (1 - \varepsilon_c) \varepsilon_{\text{sorb}} RT \frac{\partial \bar{C}_{\text{sorb}}}{\partial t} + \frac{\partial}{\partial z} \left(\lambda_{\text{ax}} \frac{\partial T}{\partial z} \right) - u C_T \hat{C}_{\text{pg}} \frac{\partial T}{\partial z} - \frac{2h_w}{r_c} (T - T_w) + \rho_{\text{sorb}} \frac{\partial \bar{q}_{\text{CO}_2}}{\partial t} (\beta(-\Delta H) + (1 - \beta)E)$

GAS PHASE at the **CATALYST LAYER** $(\varepsilon_c C_T \hat{C}_{\text{vg}} + (1 - \varepsilon_c) \rho_{\text{cat}} C_{\text{p,cat}}) \frac{\partial T}{\partial t} = \varepsilon_c RT \frac{\partial C_T}{\partial z} + (1 - \varepsilon_c) \varepsilon_{\text{cat}} RT \frac{\partial \bar{C}_{\text{cat}}}{\partial t} + \frac{\partial}{\partial z} \left(\lambda_{\text{ax}} \frac{\partial T}{\partial z} \right) - u C_T \hat{C}_{\text{pg}} \frac{\partial T}{\partial z} - \frac{2h_w}{r_c} (T - T_w) + \rho_{\text{cat}} R(-\Delta H)$

Momentum balance equations

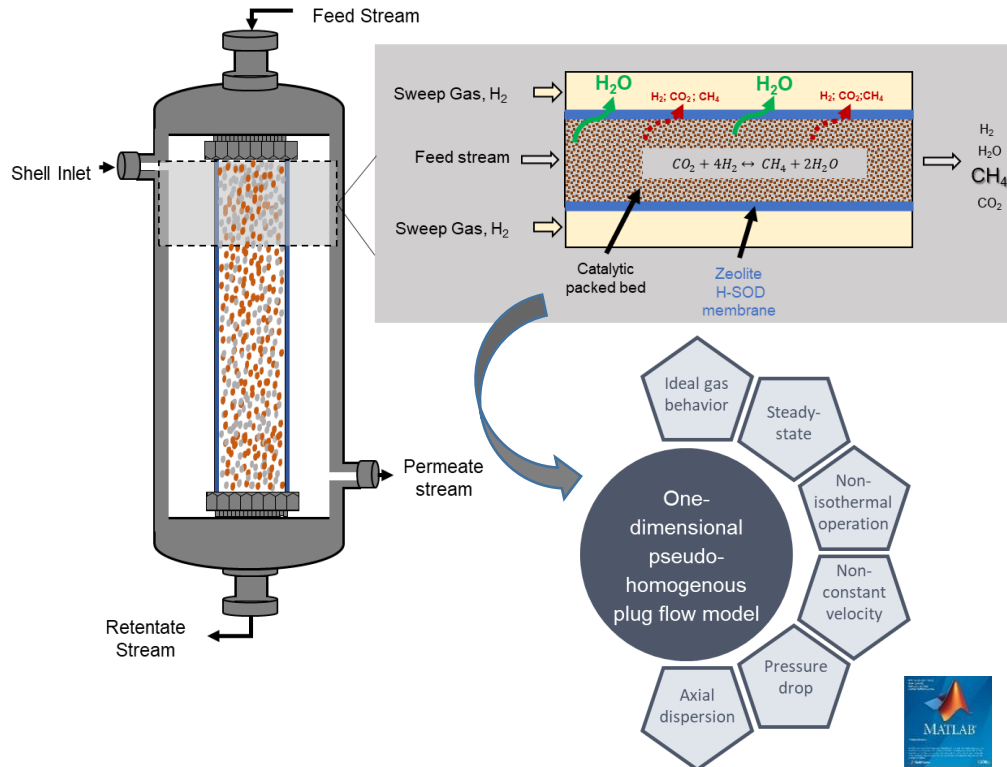
$$\frac{dP}{dz} = -150 \frac{\mu_g (1 - \varepsilon_c)^2}{4 R_{\text{p}}^2 \varepsilon_c^3} u + 1.75 \frac{(1 - \varepsilon_c) \rho_g}{2 R_{\text{p}}^2 \varepsilon_c^3} u^2$$

MODELLING WORK – SORPTIVE REACTOR FOR CO₂ CAPTURE AND CONVERSION TO CH₄



- The model implemented in gPROMS can describe the cyclic reactor behavior during the CO₂ capture stage
- Implementation of the reactive regeneration stage is ongoing

MODELLING & SIMULATION OF A STEAM-SELECTIVE MEMBRANE REACTOR FOR BIOGAS UPGRADING



Simulation conditions

Retentate zone

- Feed composition ca. (vol. %):
 - Base: 20:80 (CO₂:H₂);
 - Biogas 1.11: 16:56:18 (CO₂:H₂:CH₄);
 - Biogas 2.96: 13:50:37 (CO₂:H₂:CH₄);
- Temperature range: 250-300 °C;
- Pressure range: 1 – 5 bar;
- Contact time ($W_{cat}/F_{CO_2,in}$): 0.5-10 g·h·mol⁻¹

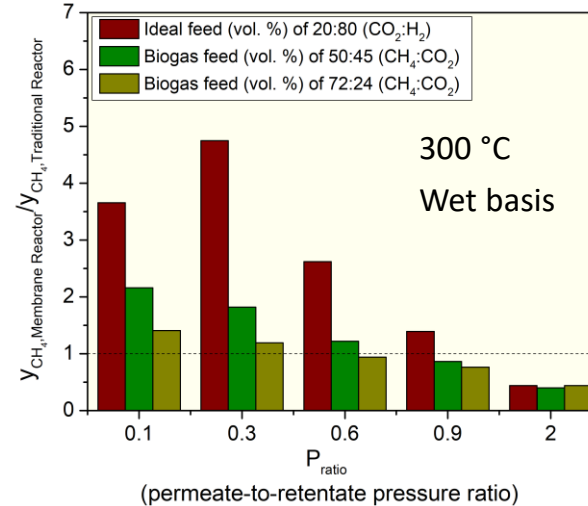
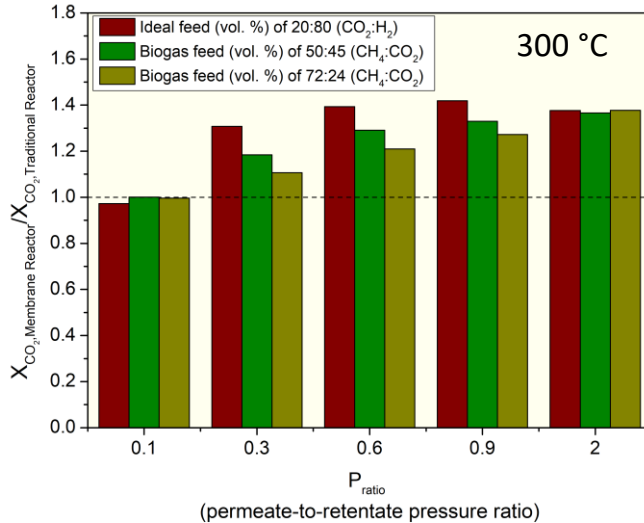
Permeate zone

- Sweep gas used: N₂ or H₂
- Permeation to reaction side pressure ratio, P_{ratio} : 0.1–2
- Sweep gas to feed molar flow rate ratio, F_{ratio} : 1-20

MODELLING & SIMULATION OF A STEAM-SELECTIVE MEMBRANE REACTOR FOR BIOGAS UPGRADING

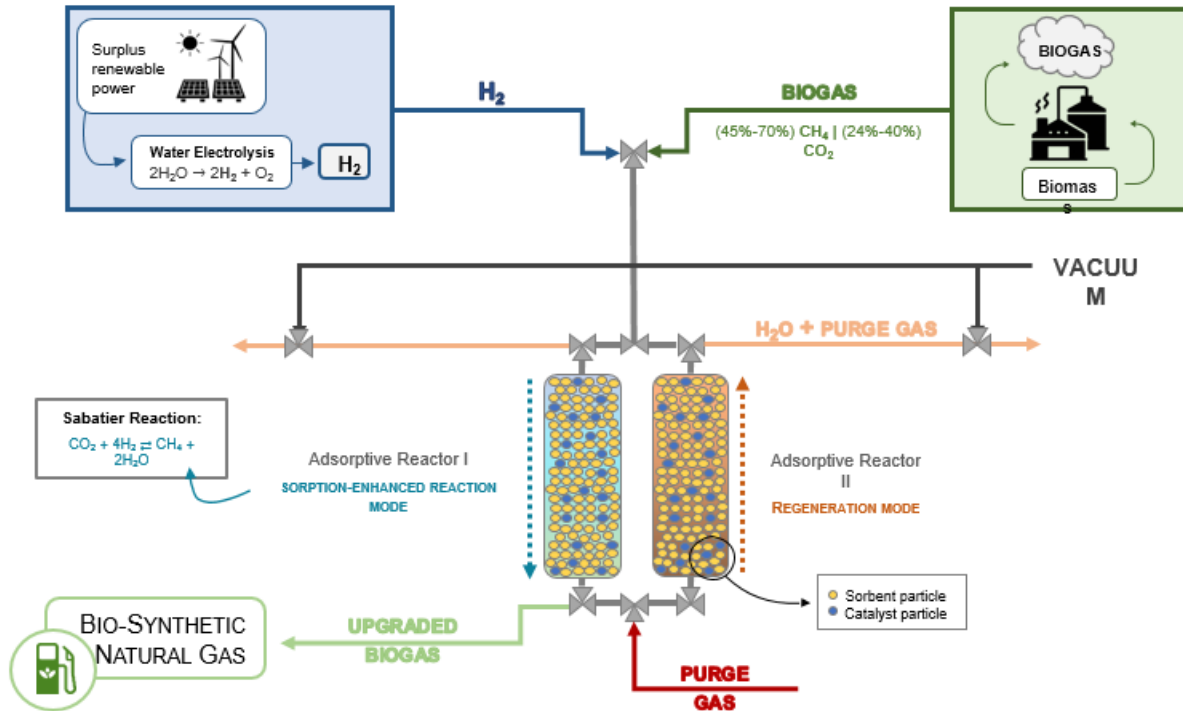
Retentate side	Permeate side ^a
Partial mass balance for species <i>i</i>	
$\frac{d}{dz} \left(D_{ax} C^R \frac{dy_i^R}{dz} \right) - \frac{L}{\varepsilon_b} \frac{d(u_0^R C_i^R)}{dz} + \frac{\rho_b L^2}{\varepsilon_b} \nu_i R_1 - \frac{2\pi r^R L^2}{\varepsilon_b A^R} J_i = 0 \quad (2)$	$\frac{d(u_0^P C_i^P)}{dz} - \frac{2\pi r^R}{A^P} J_i = 0 \quad (3)$
Total mass balance	
$\frac{d(u_0^R C^R)}{dz} - \rho_b L \sum_i \nu_i R_1 + \frac{2\pi r^R}{A^R} \sum_i J_i = 0 \quad (4)$	$\frac{d(u_0^P C^P)}{dz} - \frac{2\pi r^R}{A^P} \sum_i J_i = 0 \quad (5)$
Momentum balance	
$\frac{dP^R}{dz} + L \left\{ 150 \frac{(1-\varepsilon_b)^2 \mu_i^R}{\varepsilon_b^3 d_p^2} u_0^R + 1.75 \frac{(1-\varepsilon_b) \rho_i^R}{\varepsilon_b^3 d_p} u_0^{R^2} \right\} = 0 \quad (6)$	Not applicable
Energy balance	
$\frac{d^2 T^R}{dz^2} - \frac{u_0^R \rho_i^R C_{p,i}^R L}{\lambda_{ax}} \frac{d(T^R)}{dz} + \frac{\rho_b r^R L^2}{\lambda_{ax}} (-\Delta H^R R_1) - \frac{2\pi r^R L^2}{\lambda_{ax} A^R} (T^R - T^P) \left[U^R + \sum_i (J_i C_{p,i}) \right] = 0 \quad (7)$	$C_{p,i}^P \frac{d(T^P)}{dz} - \frac{2\pi L}{A^P u_0^P \rho_i^P} \left[r^R (T^R - T^P) \left(U^R + \sum_i (J_i C_{p,i}) \right) - r^P U^P (T^P - T^I) \right] = 0 \quad (8)$

MODELLING & SIMULATION OF A STEAM-SELECTIVE MEMBRANE REACTOR FOR BIOGAS UPGRADING

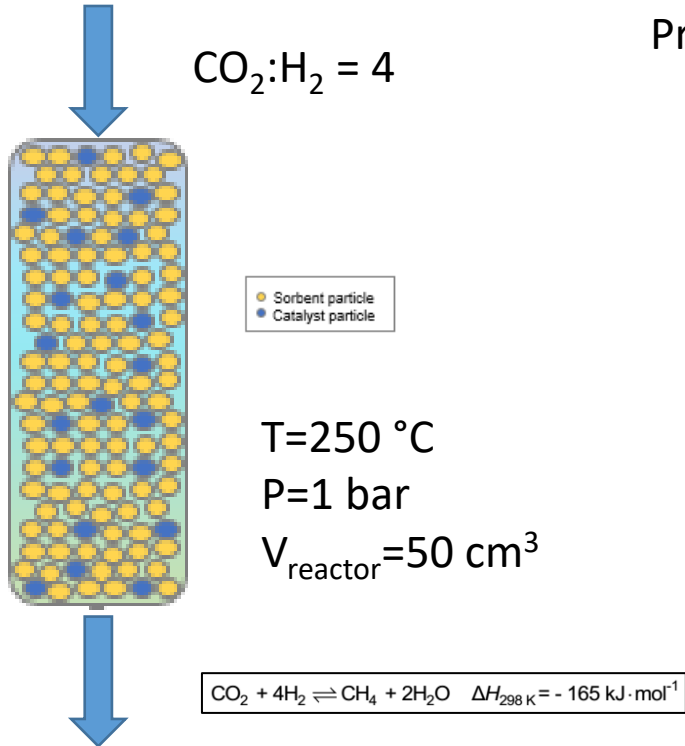


- H-SOD MR can enhance the TR CO₂ conversion in ~10-43 % depending on the feed and P_{ratio}
- H-SOD MR can enhance the TR CH₄ purity in ~19-475 % (wet basis)
- Conversion enhancement depends on the sweep gas used (N₂ or H₂) due to H-SOD

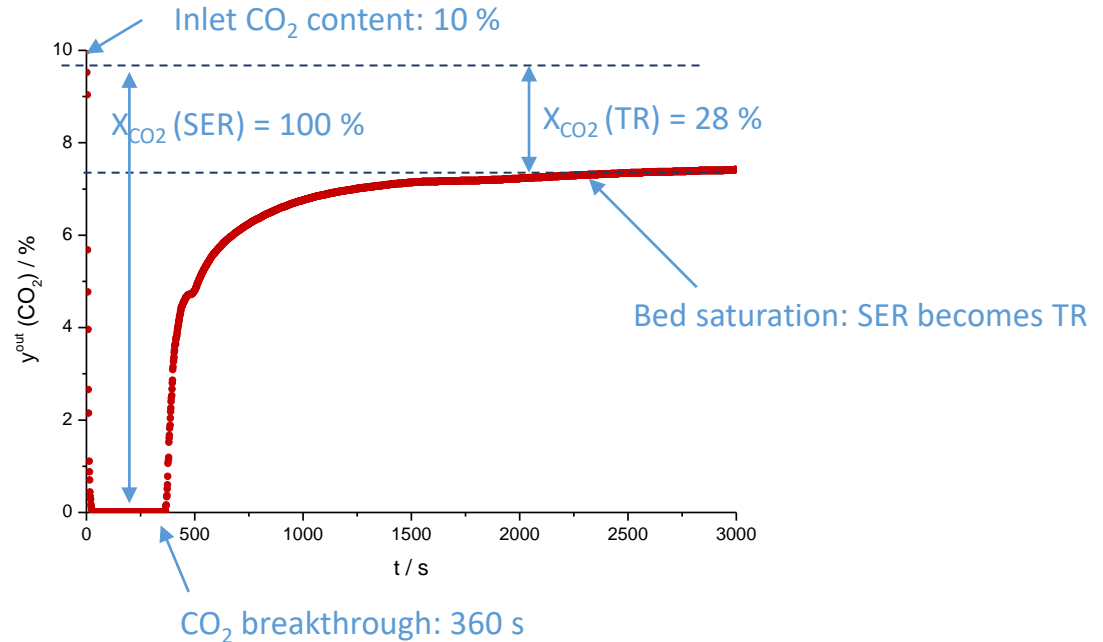
SORPTION-ENHANCED REACTOR (BY STEAM SEPARATION) FOR BIOGAS UPGRADING



SORPTION-ENHANCED REACTOR (BY STEAM SEPARATION) FOR BIOGAS UPGRADING



Preliminary results:



FUTURE PERSPECTIVES

POWER2METHANE

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



2017



2018

2019



2020

2021



2022

OPTIMIZATION

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

DEMONSTRATION

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

PROOF-OF-CONCEPT

Adsorptive reactor for CO₂ capture and conversion using a synthetic flue gas stream successfully tested at lab-scale - **TRL 3**

PROTOTYPE

Prototype for testing the concept in cyclic mode (i.e. 2 reactors in parallel)

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. ²²

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Novel Materials and Reactor Concepts for
CO₂ Conversion into Methane, Methanol
and DME

Guest Editors
Dr. Carlos V. Miguel, Prof. Luís Madeira, Prof. Dr. Alírio E. Rodrigues

Deadline
31 December 2020

Special Issue

mdpi.com/si/37966 Invitation to submit

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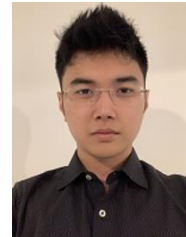
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