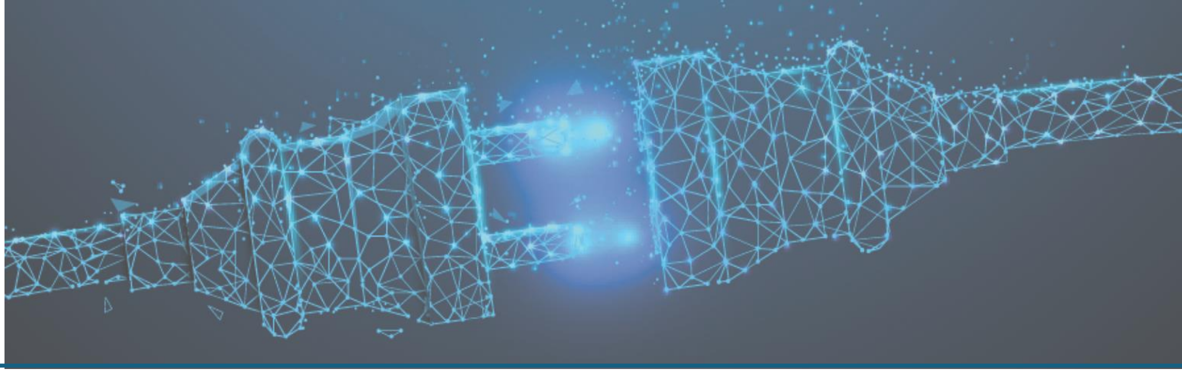
Winter School
Membrane Reactors in Chemical Industry
Organized by AMBHER Project and MACBETH project
January 29th-30th, 2024 – TU/e Eindhoven



Electrification of structured catalysts

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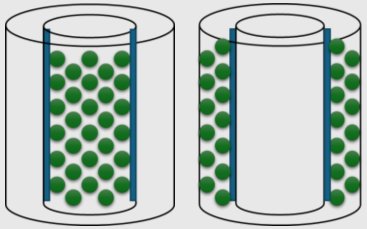
Pro ceed LAB
Processes & Catalysis for Energy & Environment depollution

MEMBRANE REACTORS

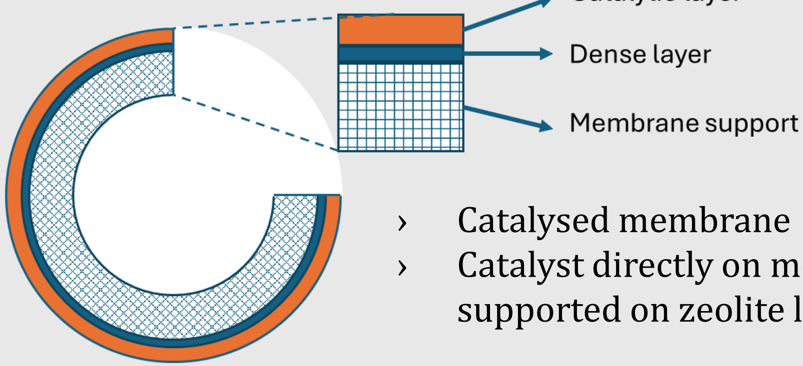
A process intensification technology, combining the <u>membrane separation</u> process with <u>chemical reactions</u> in a single unit.

Packed Bed Membrane Reactor



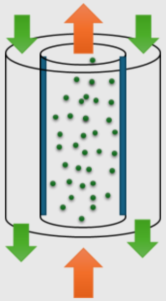
- Pellets or powder catalyst
- Inert membrane

Catalytic Membrane Reactor



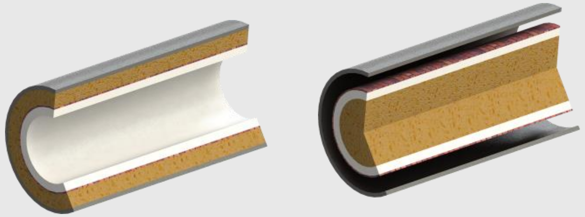
- Catalysed membrane
- Catalyst directly on membrane matrix or supported on zeolite layer

Fluidized Bed Membrane Reactor



- Powder catalyst
- Inert membrane

Structured Catalyst Membrane Reactor



- Foam or wire catalysts
- Inert membrane
- Optimal mass and heat transfer management

MEMBRANE AND CATALYSTS

Easy to couple?

Threshold temperatures

Operating temperature range

Reactor temperature profile

Composition profile

Pressure

Driving force

Catalyst-Membrane interactions

Catalyst selectivity vs membrane deactivation

Catalyst vs Membrane regeneration conditions

Pressure

MEMBRANE AND CATALYSTS

Easy to couple?

High operating pressure enhance permeation driving force but

- **Could decrease conversion (MSR, PDH,ESR…)**
- **Could favor side reaction (coke formation)**

Optimization of the catalytic system to achieve high selectivity and reduce deactivation rate

Operating temperature

MEMBRANE AND CATALYSTS

Easy to couple?

Catalyst Threshold temperature

The use of a catalytic formulation able to
reduce activation temperature

Exothermic reactions

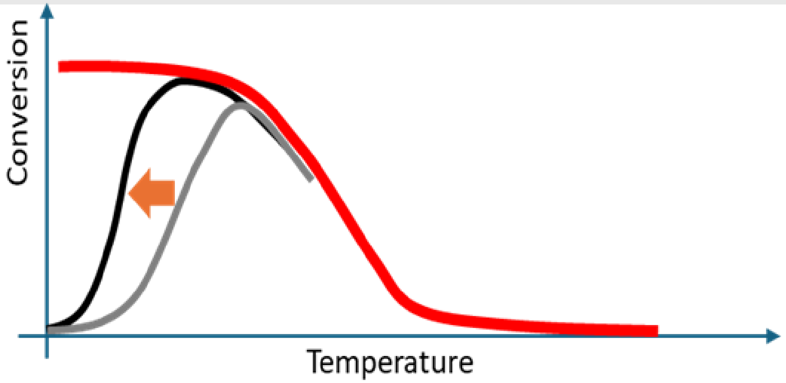
Thermodynamically favoured at low temperatures

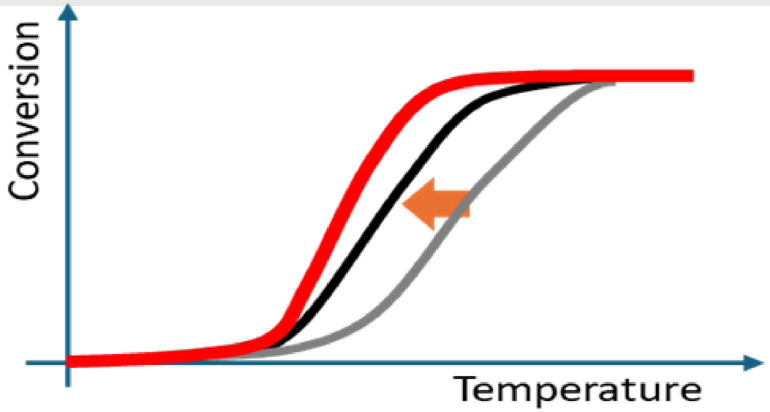
↳ **Slow reactions kinetics at low temperatures**

Endothermic reactions

Favoured at high temperatures

↳ **Higher heat fluxes supply**





MEMBRANE AND CATALYSTS

Some catalytic membrane assisted processes Studied at PROCEED

- **Methane Steam reforming**
- **Ethanol steam and Oxidative reforming**
- **Propane Dehydrogenation**
- **CO Water-gas shift**

H_2 removal overcomes thermodynamic limitations

Pure hydrogen recovery

H_2 permselective
Pd based membranes

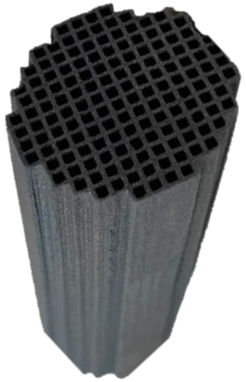
How we can try to optimize the coupling?

MEMBRANE AND CATALYSTS

- **To use HIGH CONDUCTIVE STRUCTURED CATALYSTS in order to:**

✓ Improve the heat management
✓ Improve mass transfer mechanisms in solid-gas phase
✓ Reducing the T gradient along radial and axial directions

The use of high thermal conductivity catalytic carriers able to increase the efficiency of the heat transfer may help us to optimize the coupling realizing:



- **Improved Heat transport in Radial and axial direction along the catalyst**
- **Lower reactor wall T**
- **Flattened T profile along z axis**

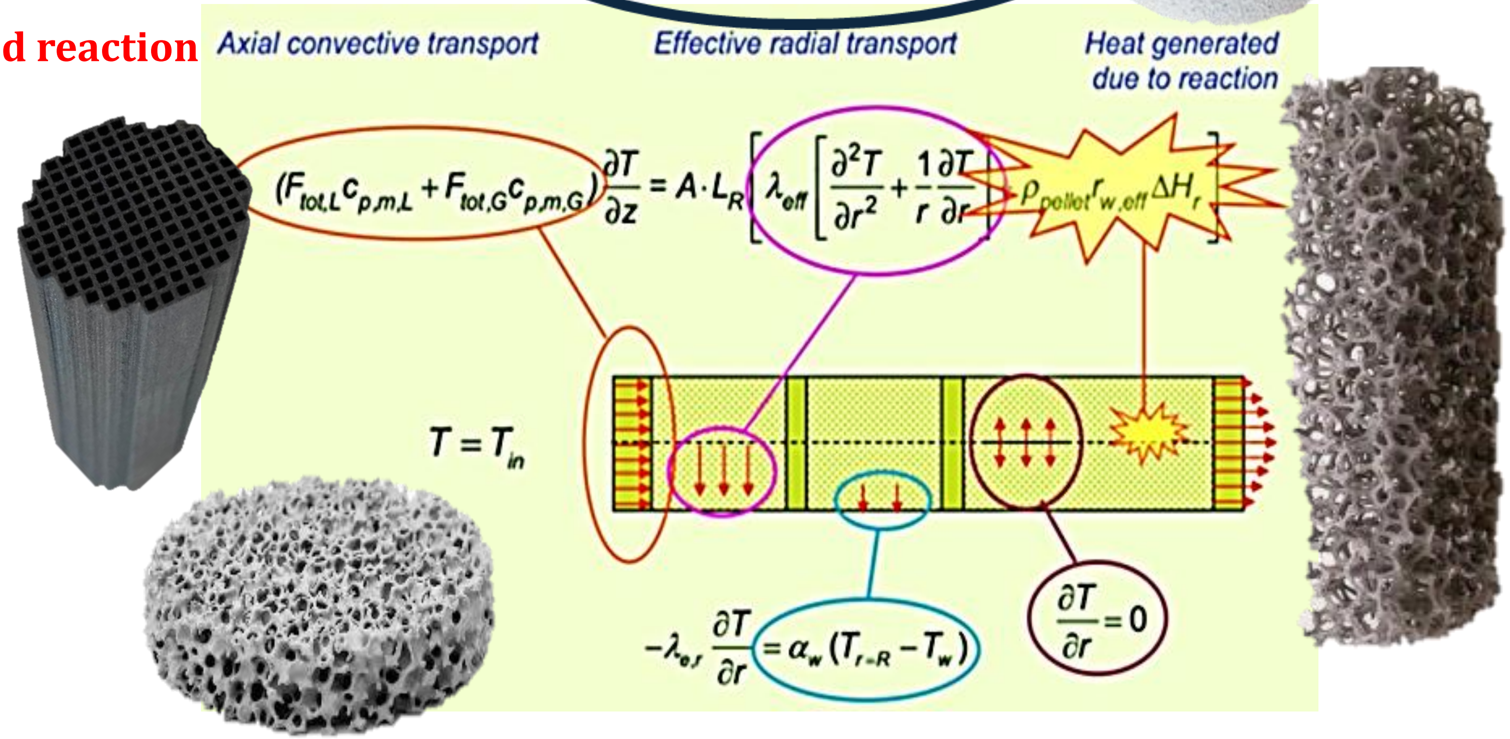
MEMBRANE AND CATALYSTS

Why using Structured catalysts ?

- **Better mass and heat transfer in the catalytic zone**
- **More homogeneous thermal profile**
- **Higher surface to volume ratio**
- **Better catalyst utilization in mass transfer limited reaction**
- **Compactness of the configuration**

Material	Thermal conductivity at 25 °C [W m^{-1} K^{-1}]
Al	237
SiC	350
Steel	50
Alumina	30

Structured Catalytsts
Monoliths or Open cells Foams
Very important parameter:
THERMAL CONDUCTIVITY



$$(F_{tot,L}c_{p,m,L}+F_{tot,G}c_{p,m,G})\frac{\partial T}{\partial z} = A\cdot L_R\left[\lambda_{eff}\left[\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right]+\rho_{pellet}r_{w,eff}\Delta H_r\right]$$

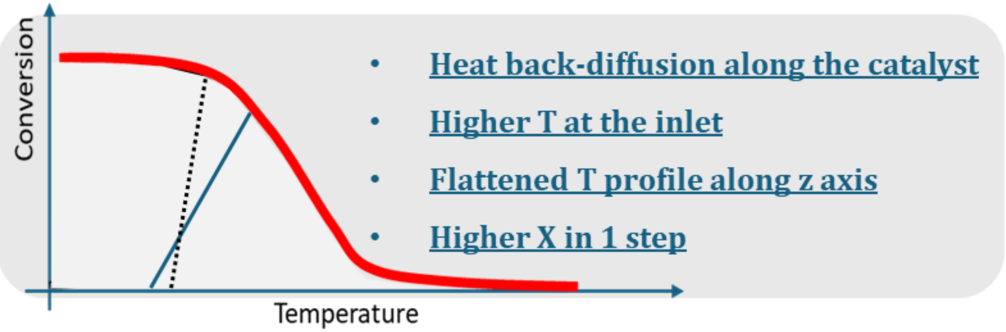
$$T = T_{in}$$

$$-\lambda_{er}\frac{\partial T}{\partial r} = \alpha_w(T_{r=R}-T_w)$$

$$\frac{\partial T}{\partial r} = 0$$

✓ **Choosing the right morphology, structured carriers (foams, cross-flow structures, novel 3D printing products) can be designed for optimal axial and radial convection and the combination with catalyst coating solves both issues of heat management and catalyst inventory.**

Water gas shift reaction: catalysts comparison

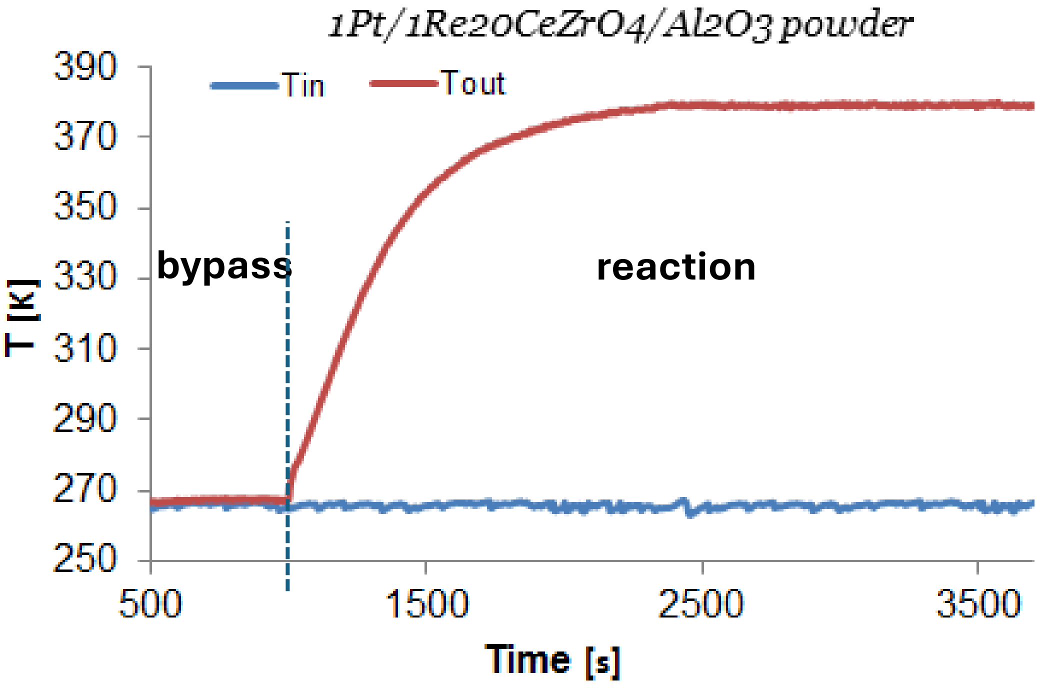


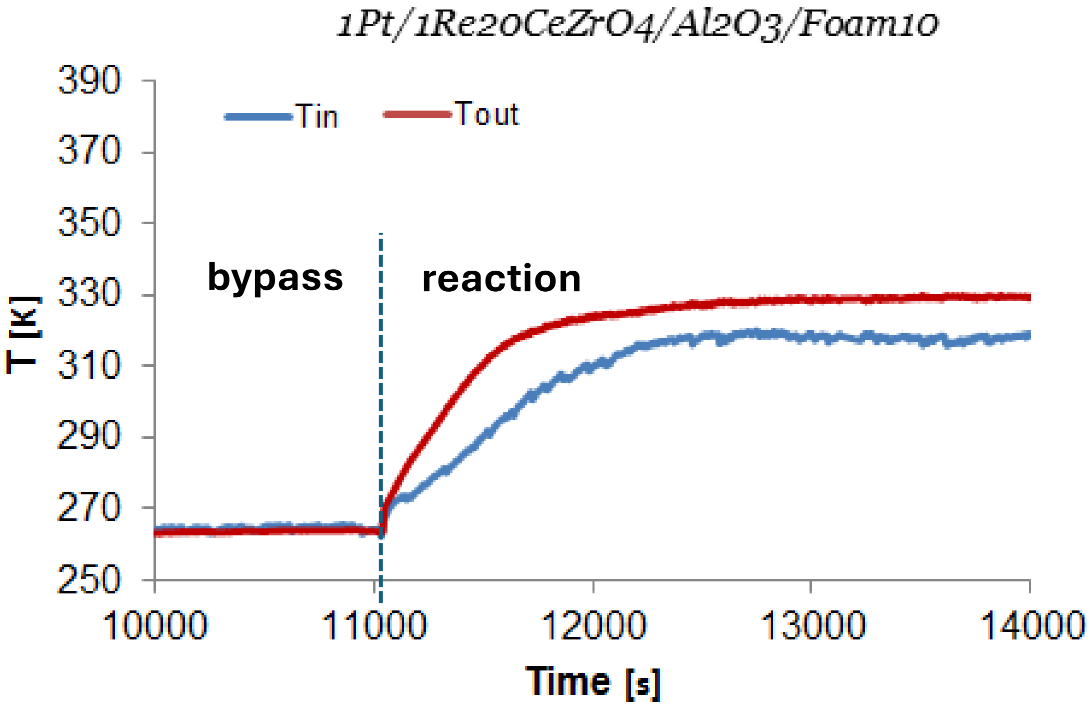
- Heat back-diffusion along the catalyst
- Higher T at the inlet
- Flattened T profile along z axis
- Higher X in 1 step

$CO + H_2O \rightleftharpoons CO_2 + H_2$ ΔH° = – 41 kJ/mol

Powder vs Al Foam

1Pt/1Re20CeZrO4/Al2O3.



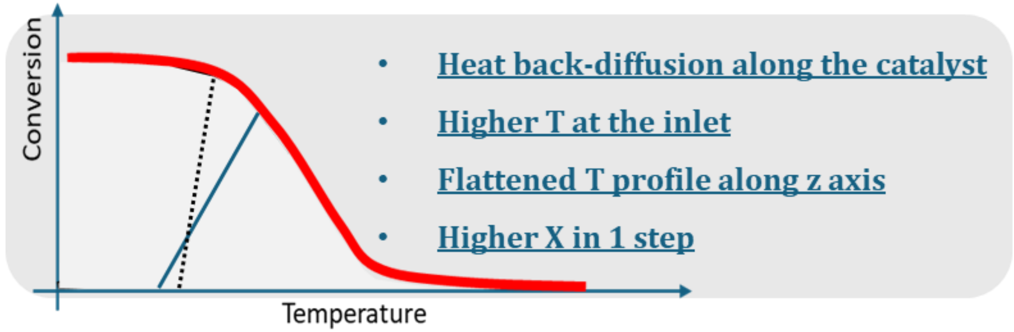


Operative conditions:

T: 533 K (Constant heat flux from the oven); P: 1 atm; CO inlet: 21 vol%; H_2O inlet: 79 vol%, WHSV : 16 $g_{CO}/g_{1Pt1Re/CeZrO4}h^{-1}$

Water gas shift reaction: catalysts comparison

$CO + H_2O \rightleftharpoons CO_2 + H_2$ ΔH° = – 41 kJ/mol



- Heat back-diffusion along the catalyst
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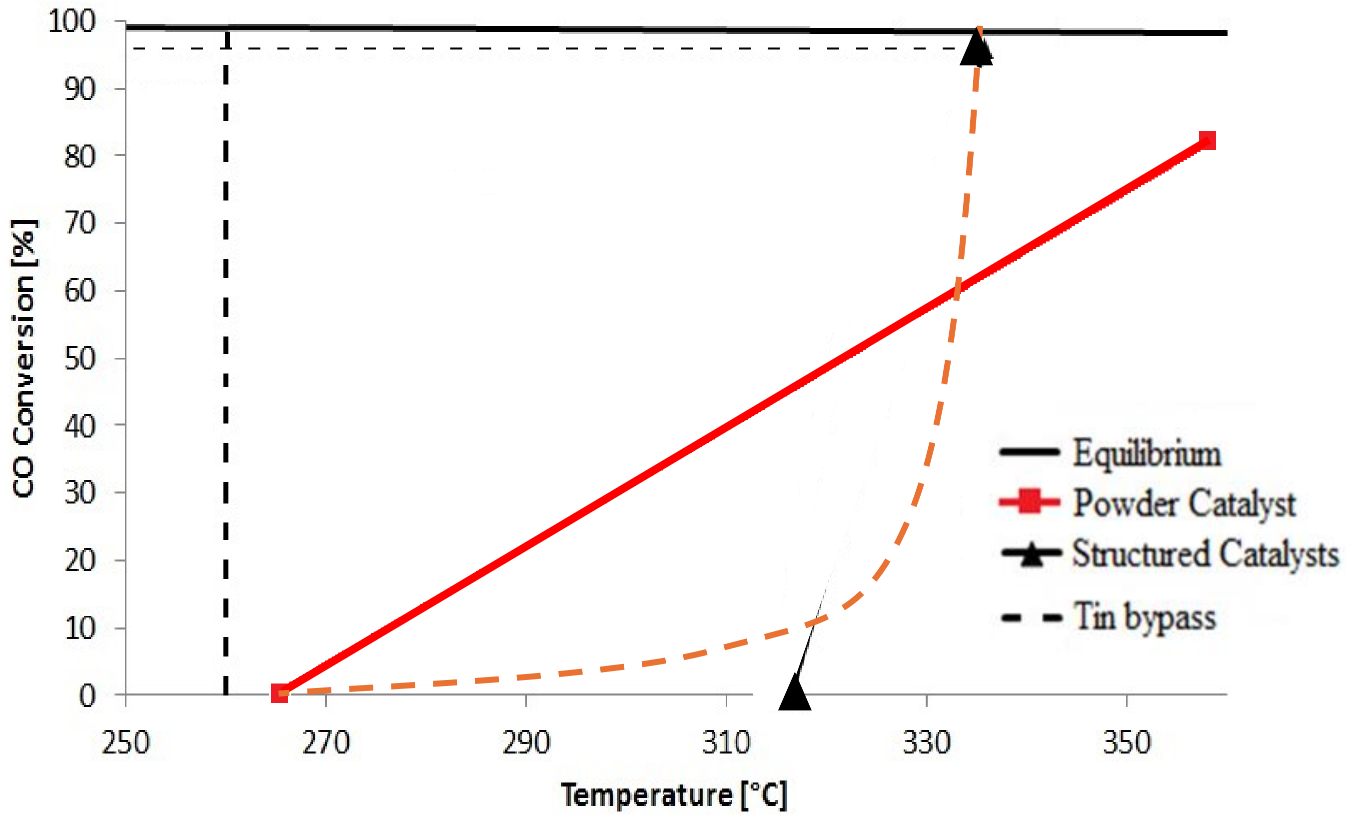
WGS structured catalysts



Foam catalyst

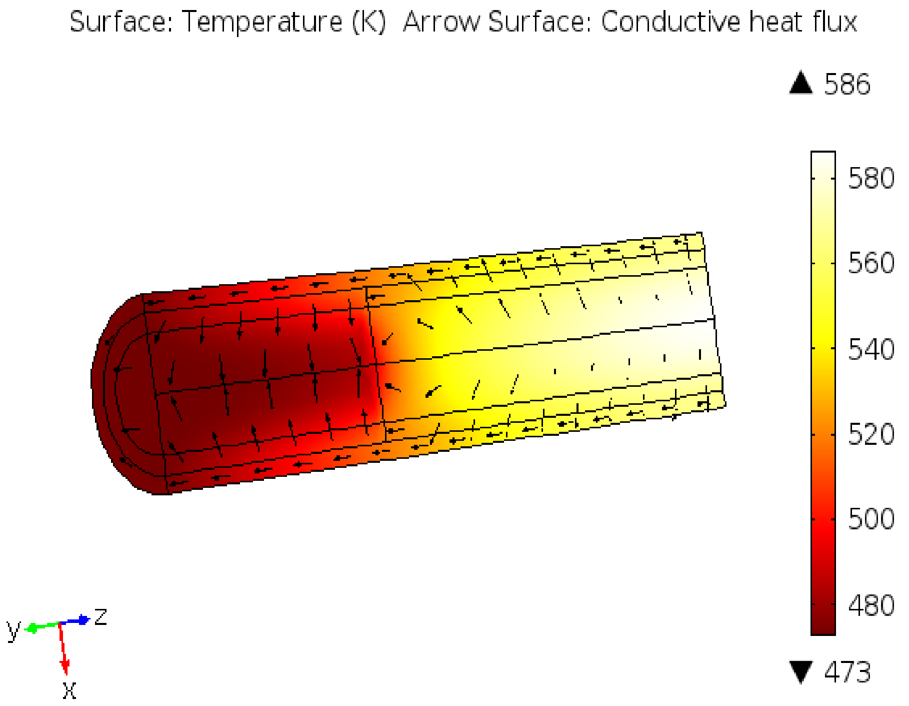
T_{in} higher than powder
T_{out} lower than powder

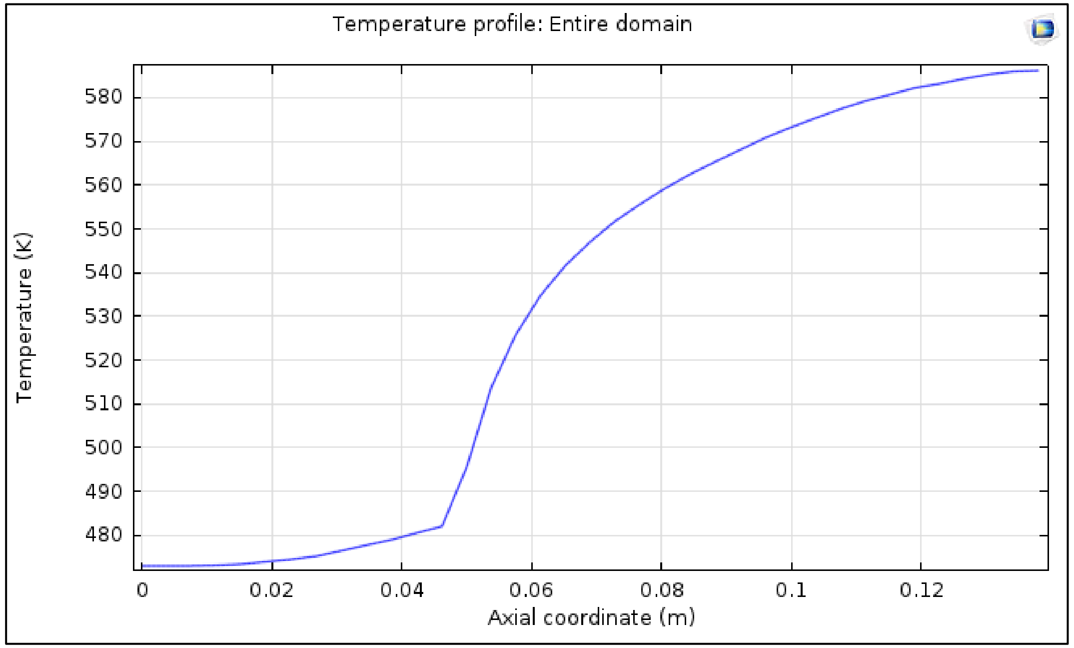
Quasi-Isothermal conditions
Higher CO conversion

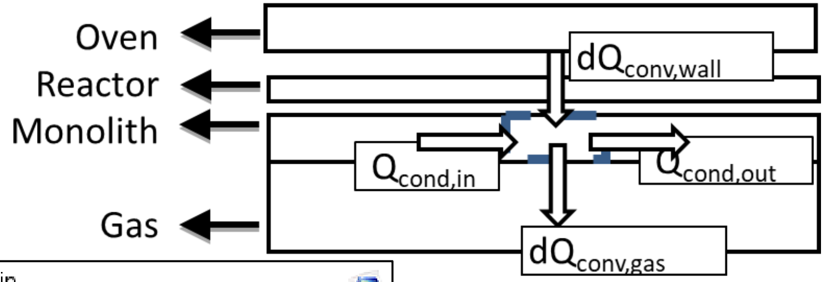
Water gas shift reaction: powder catalyst simulation

$CO + H_2O \rightleftharpoons CO_2 + H_2$ $\Delta H° = – 41$ kJ/mol

POWDER Catalyst in WGS reaction







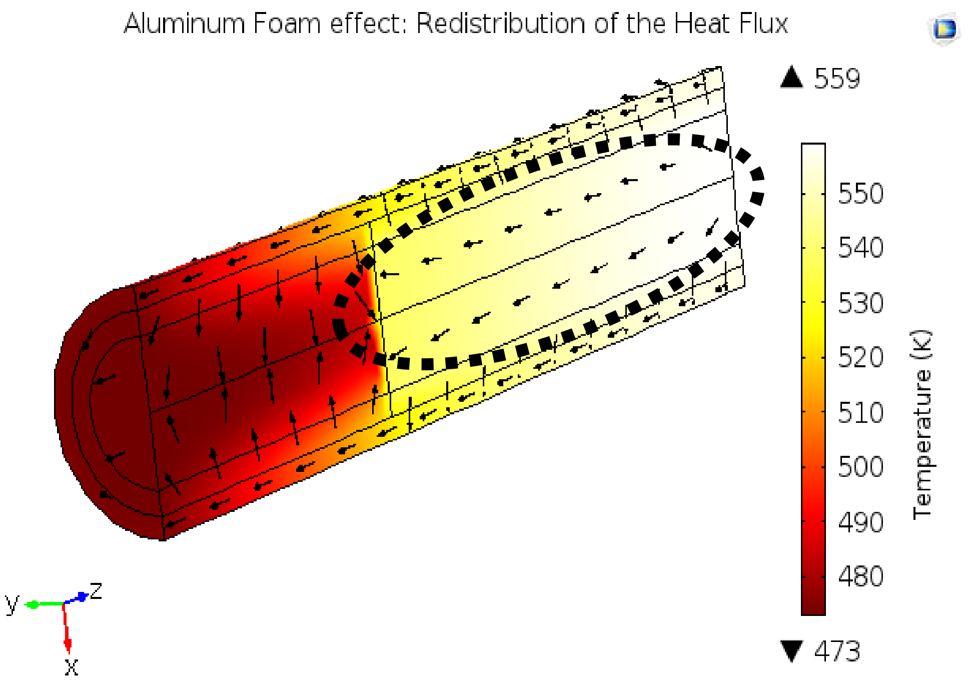
Adiabatic reactor

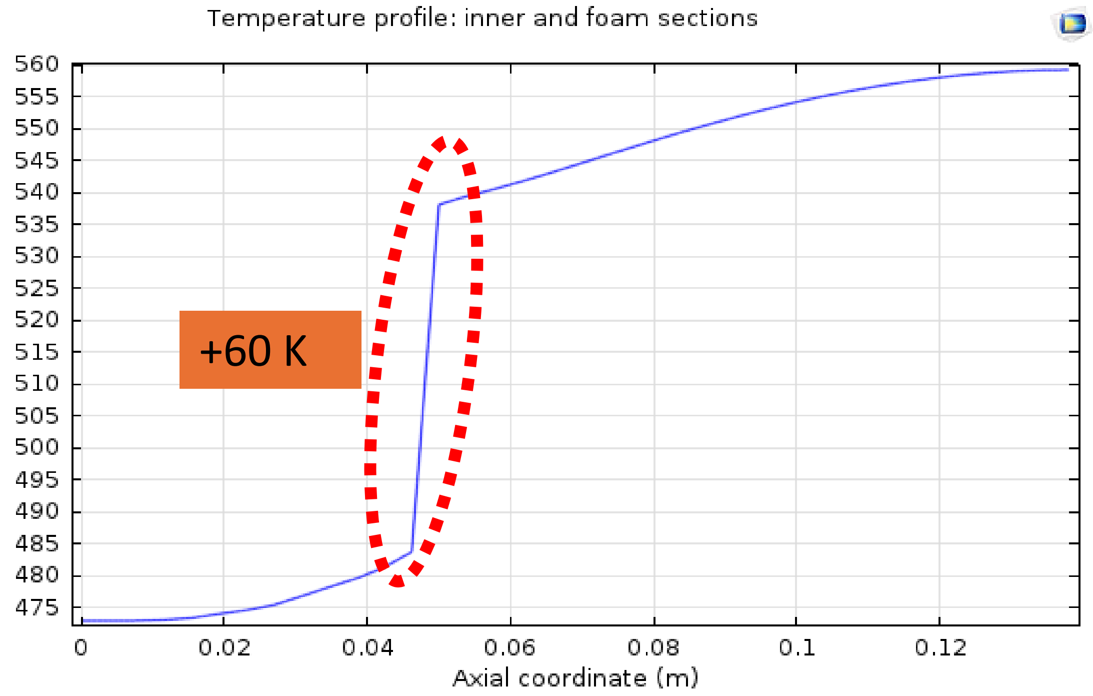
Conductive flux mainly due to the stainless steel reactor

Water gas shift reaction: structured catalyst simulation

$CO + H_2O \rightleftharpoons CO_2 + H_2$ $\Delta H° = -41$ kJ/mol

Foam Catalyst in WGS reaction


Aluminum Foam effect: Redistribution of the Heat Flux


Temperature profile: inner and foam sections

Heat redistribution due to the high conductive Aluminum carrier

MEMBRANE AND CATALYSTS

How we can try to <u>further</u> optimize the coupling?

- <u>**ELECTRIFICATION OF STRUCTURED CATALYSTS**</u> **in order to:**
  - ✓ Generate Heat directly on the catalyst volume/surface
  - ✓ Selective heating of the catalytic zone
  - ✓ Precise control of the temperature profile
  - ✓ Avoid hot spots and thermal stress of the membrane
  - ✓ Increase the selectivity of the system (higher stability?)

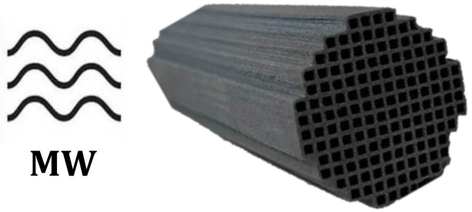
ELECTRIFICATION METHODS

THE STRUCTURED ELECTRIFIED CATALYSTS CAN COMBINE THE CATALYTIC ACTIVITY WITH THE HEATING FUNCTIONALITY

MICROWAVE HEATING (Direct Heating)

The alternating electric field of the microwaves generates heat by moving **dipolar molecules** or by getting absorbed in the so-called “dielectric lossy” **solid nonmagnetic materials**.

Example:



Silicon carbide (SiC)

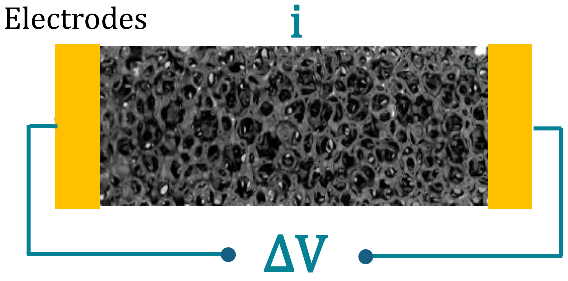
Excellent microwave-heating capability

OHMIC OR JOULE HEATING (Indirect Heating)

The electric current circulating in a conductive material causes power loss in the form of heat generation.

Conductive structured support

Example:

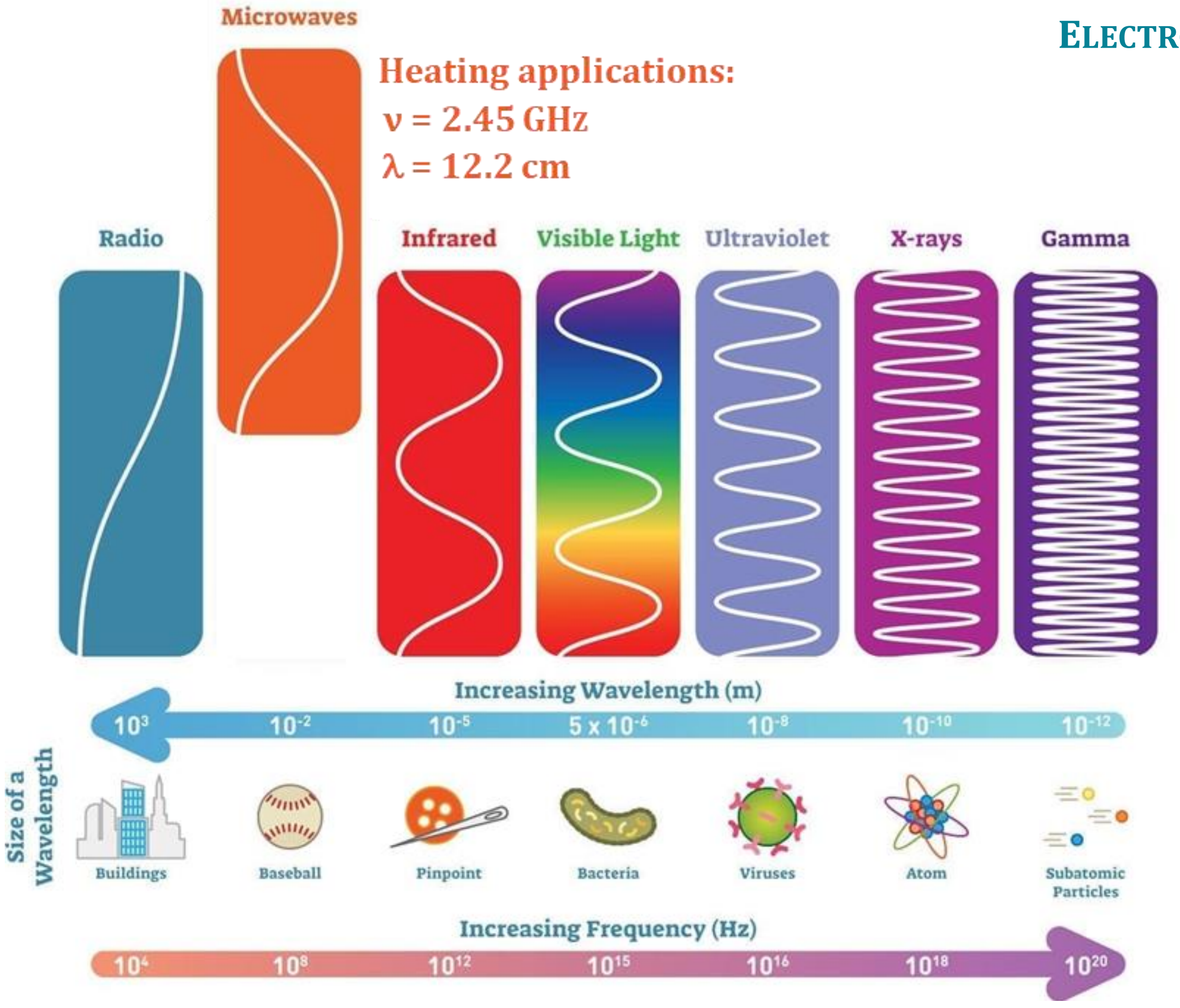


Silicon-doped silicon carbide (SiSiC)

High conductive material

MICROWAVE HEATING

MICROWAVE HEATING TECHNOLOGY

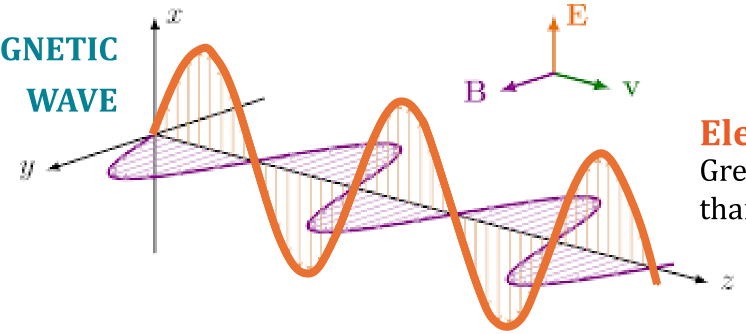


Heating applications:

$\nu = 2.45$ GHz

$\lambda = 12.2$ cm

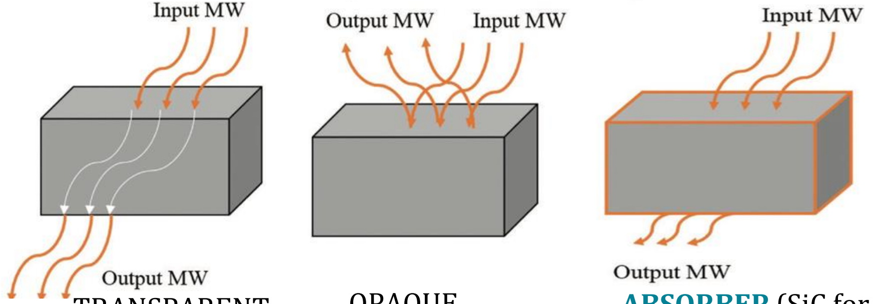
ELECTROMAGNETIC WAVE



Electric field

Greater effect on the matter than the magnetic field

DIFFERENT BEHAVIOUR OF THE MATERIALS TO THE MW$_S$ RADIATION:

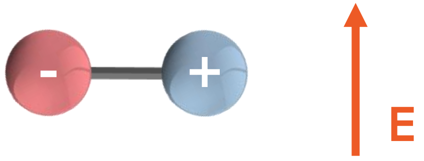


TRANSPARENT

OPAQUE

ABSORBER (SiC for example)

It converts MWs energy to heat through **polarization phenomena:**

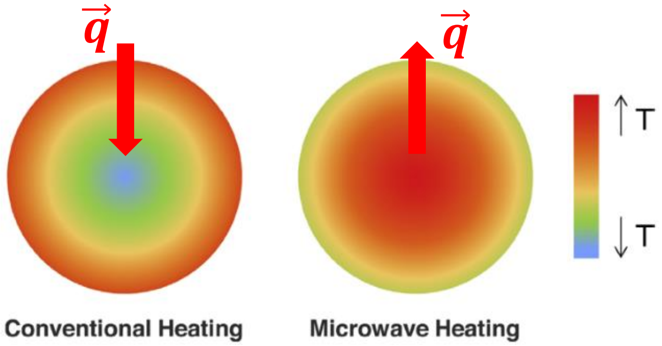


ALTERNATING E

MOLECULAR FRICTION

HEATING

MICROWAVE ASSISTED CHEMICAL PROCESSES



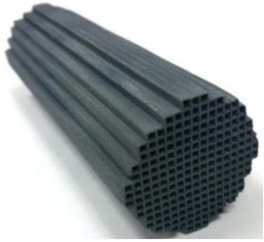
Main features

- **Reverse of the heat flux** from the inside to the outside of the catalytic bed
- Selective heating of the catalyst based only on the **dielectric properties of the material**

Applications

- Biomass valorization [1,2]
- Methane steam reforming [3]
- CO_2 desorption from zeolites [4]
- Propane dehydrogenation [5]

SiC monolith as support for catalysts



- **Excellent MW-heating capacity**
- **High thermal conductivity**

[1] Ricciardi et al, Reactive Extraction Enhanced by Synergic Microwave Heating: Furfural Yield Boost in Biphasic Systems. ChemSusChem **2020**, 13, 3589–3593.
[2] Motasemi et al, Multicomponent conjugate heat and mass transfer in biomass materials during microwave pyrolysis for biofuel production. Fuel **2018**, 211, 649–660.
[3] Meloni et al, Ultracompact methane steam reforming reactor based on microwaves susceptible structured catalysts for distributed hydrogen production. Int. J. Hydrogen Energy **2020**, 46, 13729–13747.
[4] Meloni et al, Intensification of TSA processes using a microwave-assisted regeneration step. Chem. Eng. Process. Process Intensif. **2020**, 160, 108291.
[5] Ramirez et al, Microwave-activated structured reactors to maximize propylene selectivity in the oxidative dehydrogenation of propane. Chem. Eng. J. **2020**, 393, 124746.

MICROWAVE ASSISTED CHEMICAL PROCESSES

CASE STUDIES

1. METHANE DRY REFORMING
2. METHANE STEAM REFORMING
3. DEHYDROGENATION OF PROPANE

MICROWAVE ASSISTED CHEMICAL PROCESSES

CASE STUDIES

1 **METHANE DRY REFORMING**

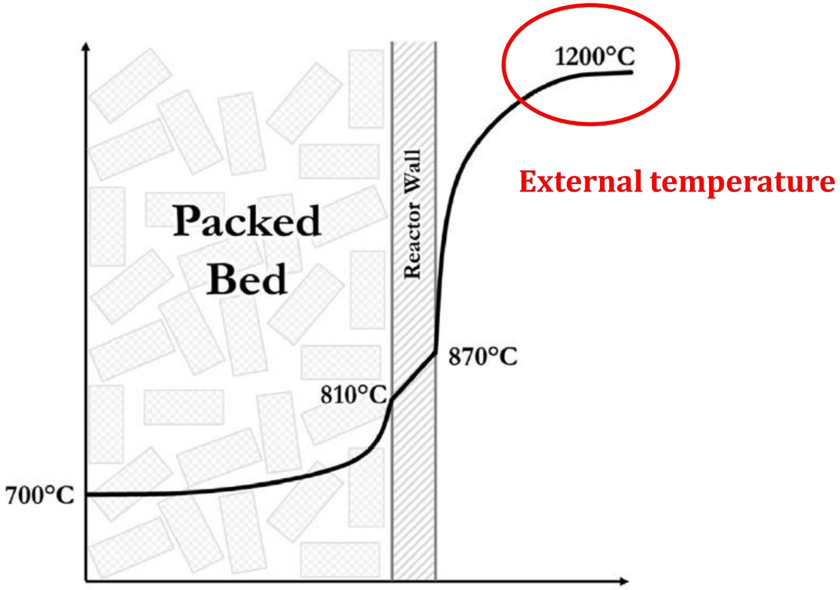
2 METHANE STEAM REFORMING

3 DEHYDROGENATION OF PROPANE

1 DRY REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H^0_{298} = 247 \text{ kJ/mol}$$

Traditional heating method



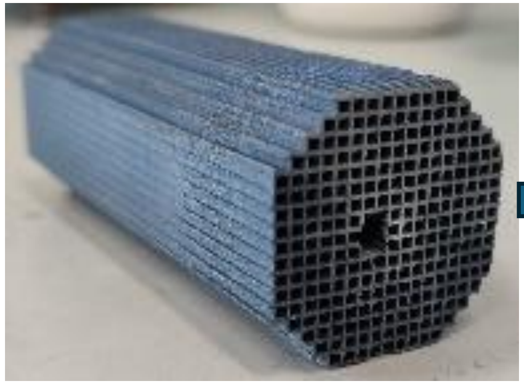
Process intensification →

1. Preparation and characterization of Ni-based structured catalyst by using a SiC carrier;
2. Preliminary microwave heating test
3. Microwave-assisted catalytic activity test

1 DRY REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

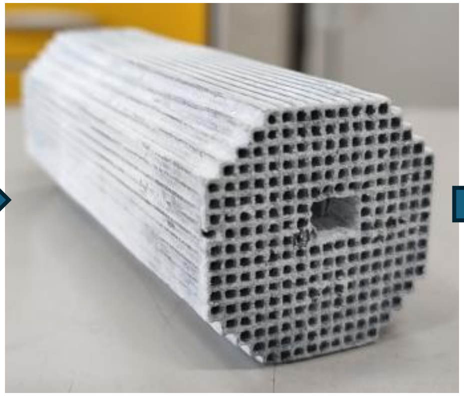
Catalyst preparation

MW SUSCEPTOR AND STRUCTURED SUPPORT



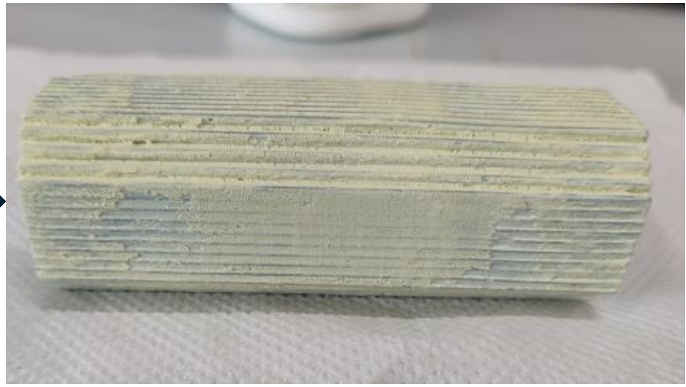
SiC honeycomb monolith

Dip-coating



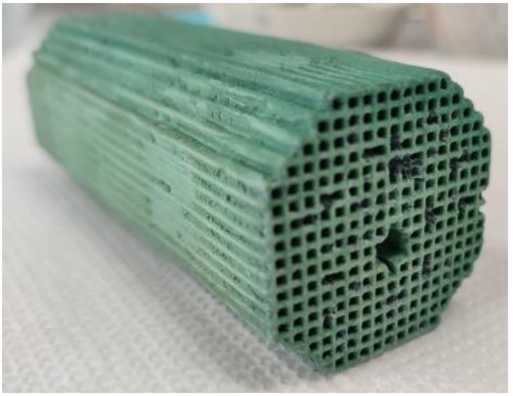
30 wt% of γ-Al_2O_3

Wet impregnation - Ceria



10 wt% of CeO_2

Wet impregnation - Ni

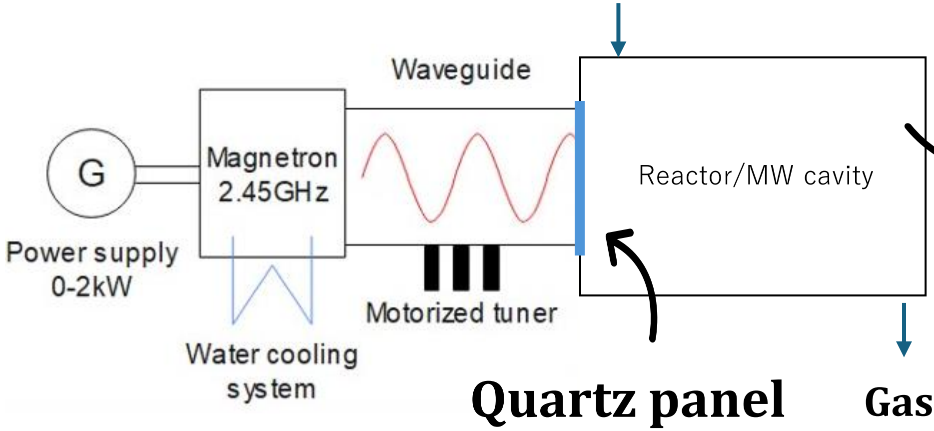


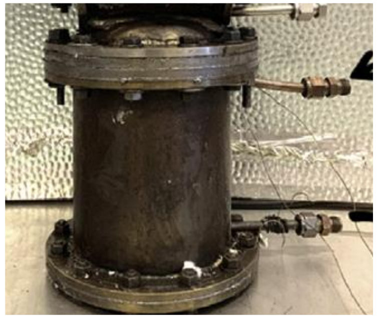
10 wt% of NiO

1 DRY REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

MW apparatus and reactor
EASY TO COUPLE?

Gas inlet





Quartz panel

It lets MWs through,
avoiding gas backflow

Gas outlet

The reactor acts as a wave's guide,

and it must be carefully designed

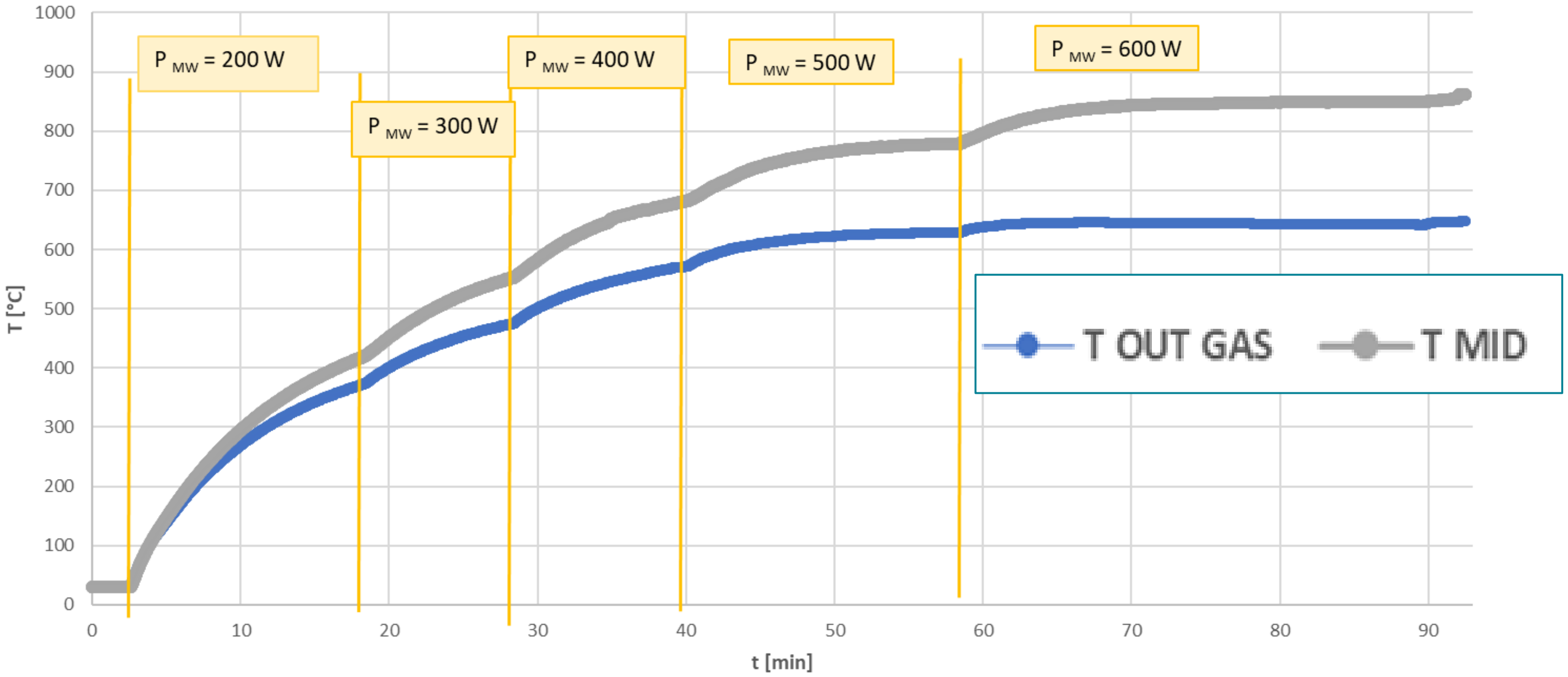
Crossover wavelength for a tubular geometry:

$$\boxed{\lambda_c = 4\,d}$$

MW wavelength
For 2,45 GHz
λ=12cm

1 DRY REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

Preliminary heating test



Feeding	Argon
Flowrate (NL/min)	2
MW Power (W)	200-600
Pressure (atm)	1

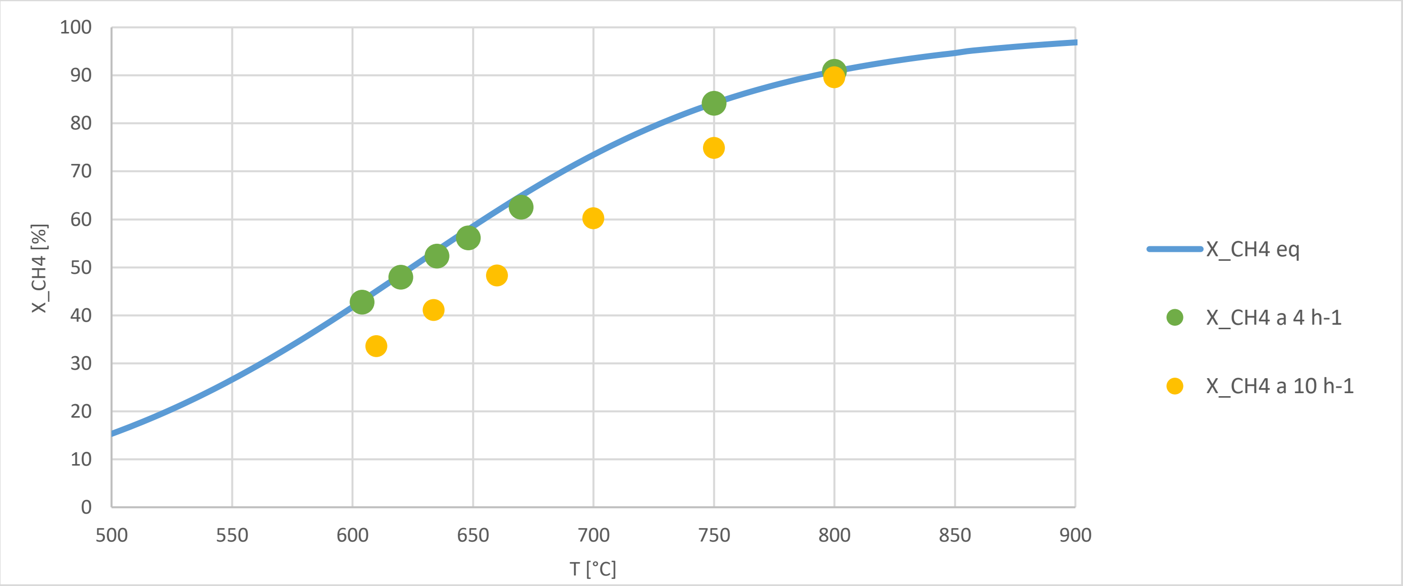
2 thermocouples in the middle and outlet section of the monolith to use the silicon carbide itself to shield them from the electromagnetic field

The reaction temperature is reached by using a power of 600 W.

1 DRY REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

MW assisted activity tests at two different WHSV

	Carrier	WHSV [h^{-1}]	T [°C]	X_{CH4} [%]	Hydrogen produced [Nm^3/h]	Supplied energy [kW]	Energy consumption [kWh/ Nm^3 H_2]	Theorical limit value [kWh/ Nm^3 H_2]
MW	SiC monolith	4	700	73.5	0.063	0.605	9.52	1.9
		10	700	60.23	0.122	0.526	4.3	



$$X_{CH_4} = \frac{F_{CH_4}^{IN} - F_{CH_4}^{OUT}}{F_{CH_4}^{IN}} \qquad F_i [=] \, mol/min$$

PROMISING RERSULTS

The experimental results approached the thermodynamic equilibrium data at the lower WHSV

MICROWAVE ASSISTED CHEMICAL PROCESSES

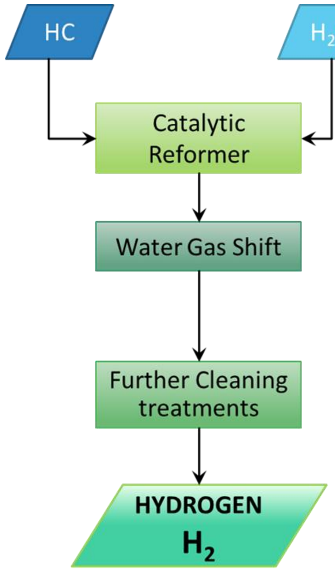
CASE STUDIES

1 METHANE DRY REFORMING

2 **METHANE STEAM REFORMING**

3 DEHYDROGENATION OF PROPANE

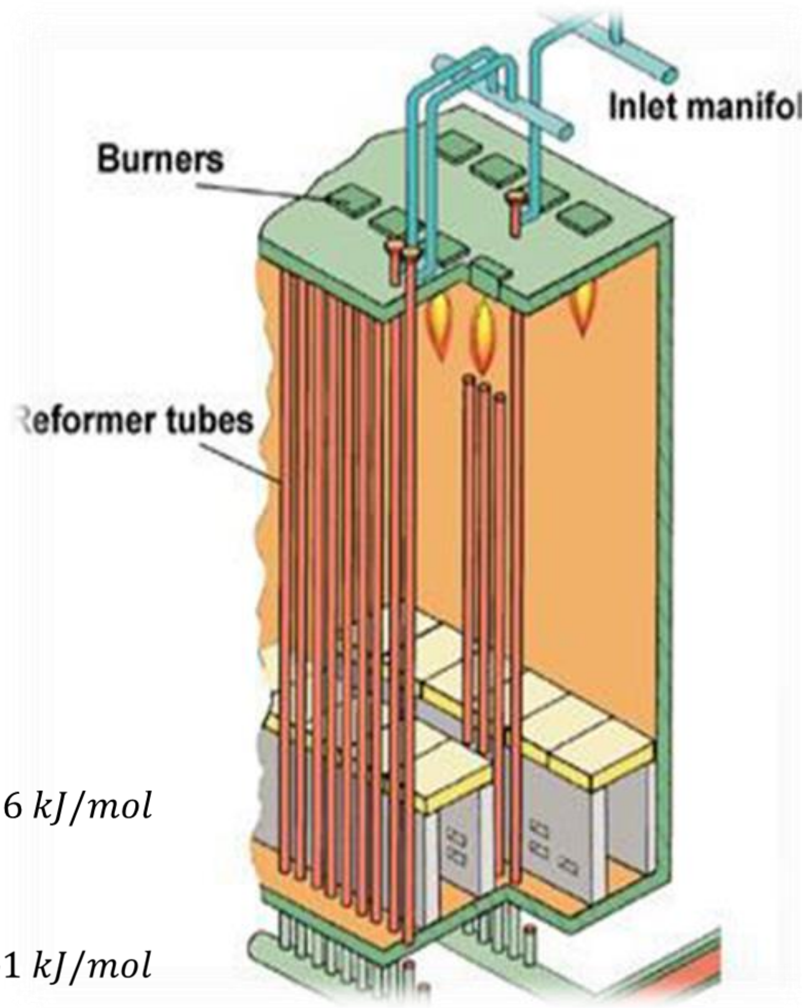
2 STEAM REFORMING:

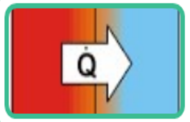


$$C_nH_m + nH_2O \leftrightarrow nCO + \frac{(2n+m)}{2}H_2$$

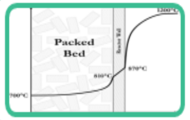
$$CH_4 + H_2O \leftrightarrow \boxed{CO} + 3H_2 \qquad \Delta H_r^{298} = 206\ kJ/mol$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_r^{298} = -41\ kJ/mol$$





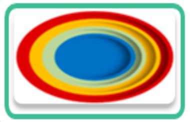
Heat transfer limited reaction



High temperatures

Need of special materials for the tubes

High fixed costs



Radial thermal gradients

Huge plant dimensions

Long transient times

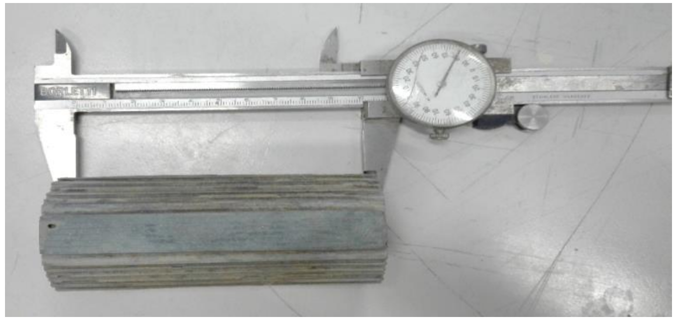
2 STEAM REFORMING: (MW)

$xNiwt\%/10wt\%CeO_2/30wt\%Al_2O_3\_SiC$

SiC 1	
Diameter [cm]	4.1
Length [cm]	10.1
Number of channels	308
Walls thickness [mm]	0.6
Channels length [mm]	1.6
Total volume [cm^3]	133
SiC 2	
Diameter [cm]	6
Length [cm]	9
Number of channels	559
Walls thickness [mm]	0.6
Channels length [mm]	1.6
Total volume [cm^3]	254

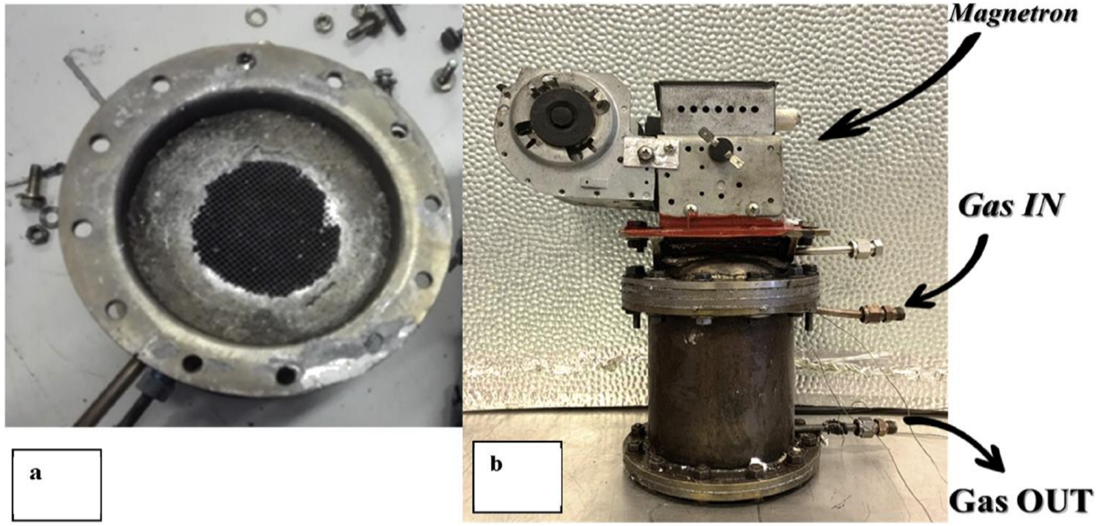
Ni loading:

7wt% on SiC1

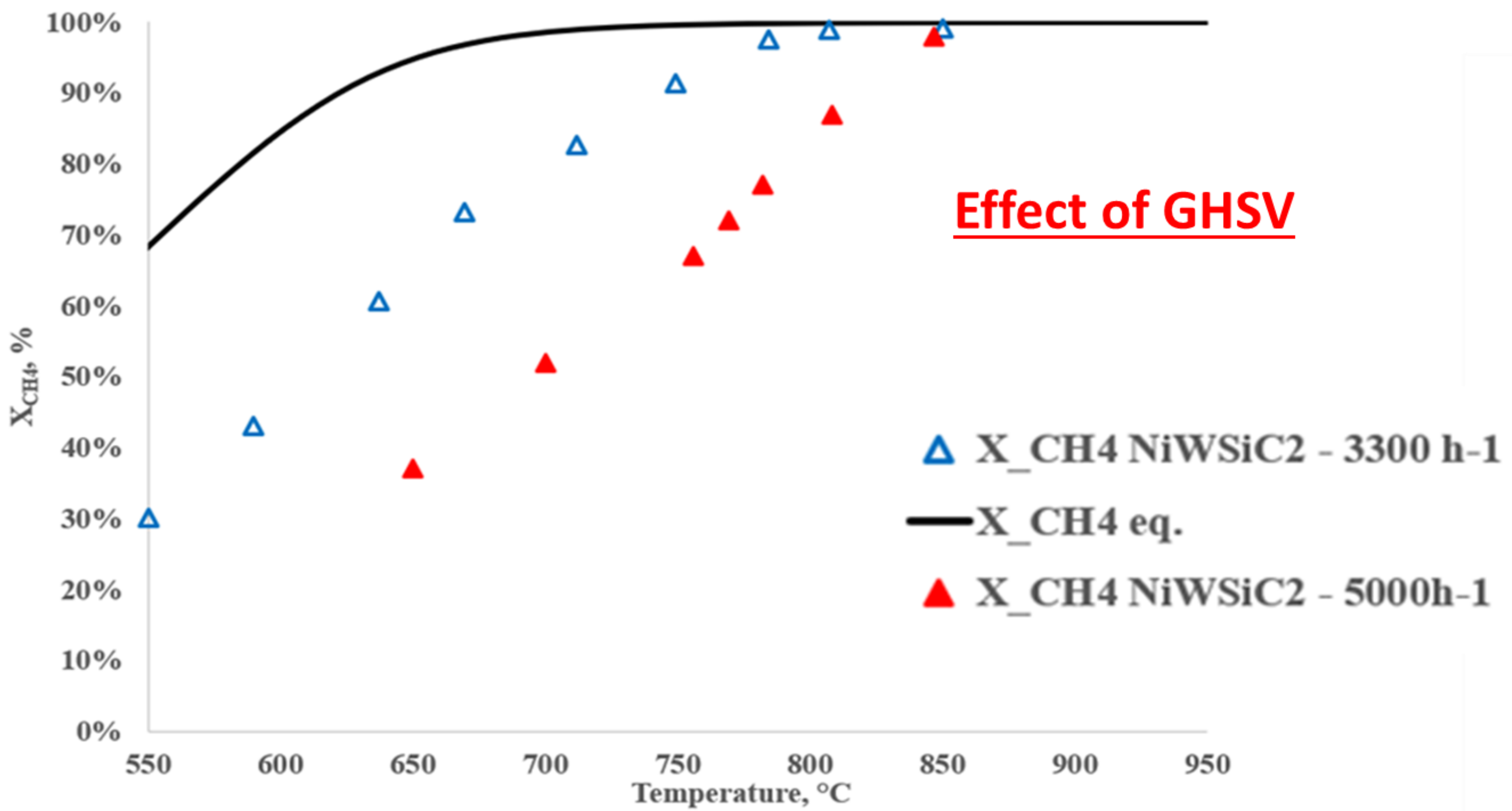


Ni catalysed monolith

15wt% on SiC2



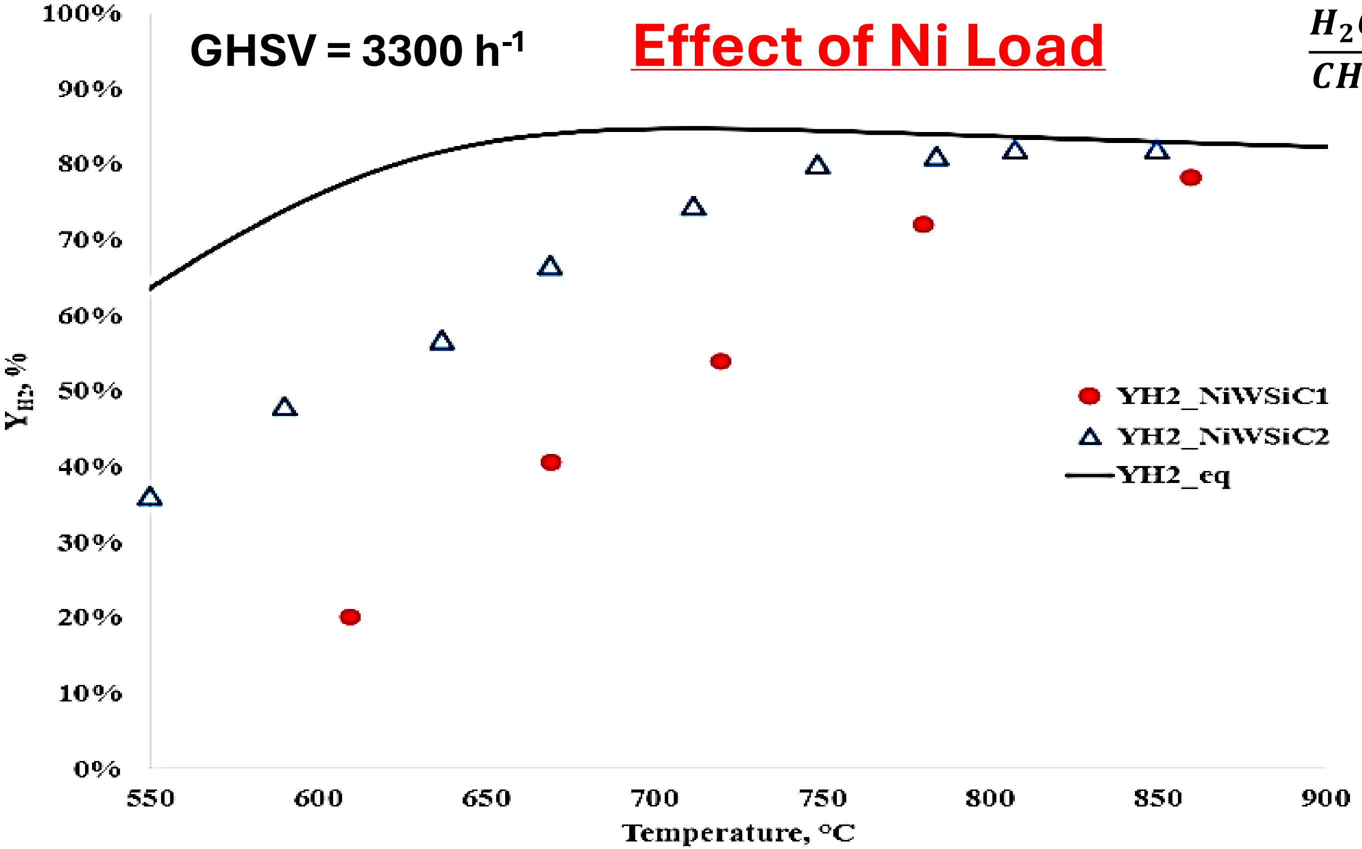
2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)



Effect of GHSV

2

STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)



$$\frac{H_2O}{CH_4} = 3 \qquad Y_{H_2} = \frac{F_{H_2,out}}{4 \cdot F_{CH_4,in}}$$

NiWSiC2 approaches the thermodynamic equilibrium at about 780°C, showing, in whatever case, a H2 Yield very close to the thermodynamic equilibrium for temperature higher than 700°C.

NiWSiC1 showed a significantly lower CH_4 conversion and H2 Yield, and only at about 880°C approached the thermodynamic equilibrium.

2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

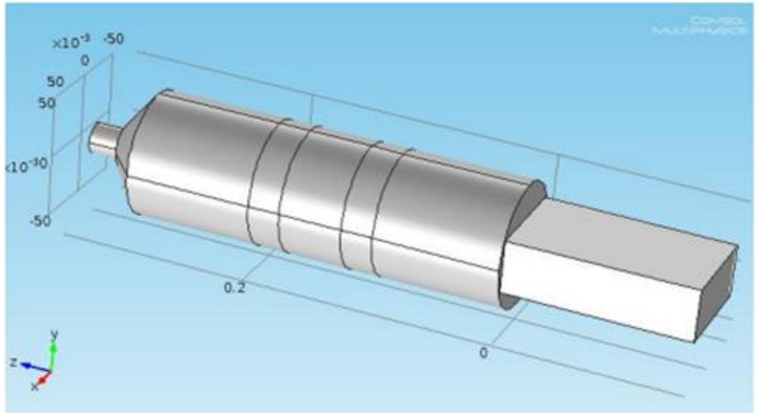
	Energy consumption
Microwave process	$3.8\ \frac{kWh}{Nm^3_{H2}}$

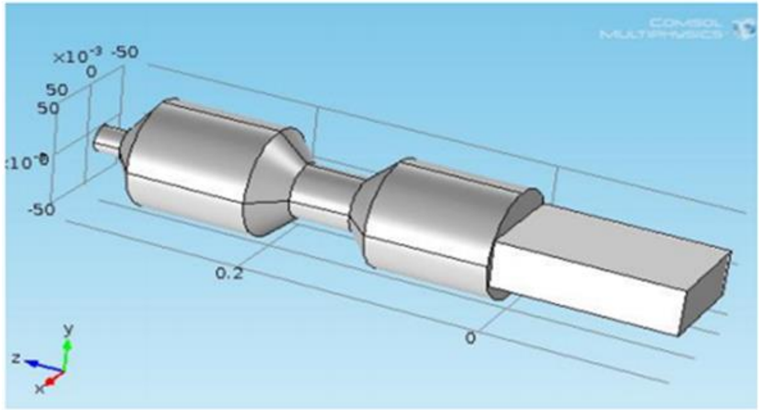
Technology	Conventional alcaline electrolyser	Advanced Alcaline electrolyser	Proton exchange electrolyser	High temperature electrolyser
Efficiency	77-80%	80-90%	85-90%	90-100%
Energy consumption (kWh/Nm$^3_{H2}$)	4.3-4.9	3.8-4.3	4.2-5	3.5

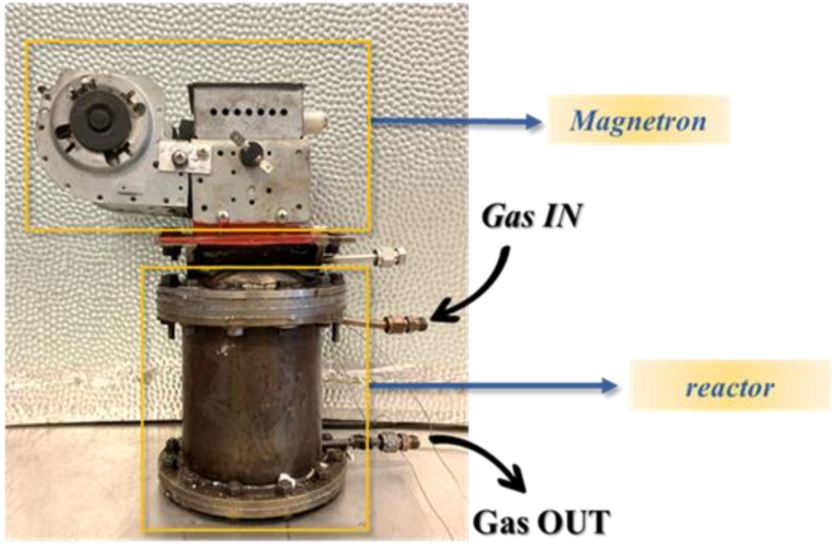
Hydrogen production from water electrolysis:current status and future trends. Proceedings of the IEEE vol. 100 n°2, 2012.

2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

Optimization of the reactor geometry







The reactor geometry was studied in order to INTENSIFY the MW Field in the catalytic volume

2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

CFD Modelling

MODEL EQUATIONS

ELECTROMAGNETIC FIELD

01 $$\nabla * {\mu_r}^{-1} * (\nabla * \boldsymbol{E}) - {k_0}^2 * \left(\varepsilon_r - \frac{j * \sigma}{\omega * \varepsilon_0}\right) * \boldsymbol{E} = 0$$

0A $$S = \frac{\int_{\partial\Omega} (E - E_1) * E_1}{\int_{\partial\Omega} E_1 * E_1}$$

0B $$\mathrm{n} * \boldsymbol{E} = 0$$

LAMINAR FLOW

01 $$\rho * \frac{\partial \mathbf{u}}{\partial t} + \rho * (\boldsymbol{u} * \nabla) * \boldsymbol{u} = \nabla * [-p * \boldsymbol{I} + \boldsymbol{K}] + F$$
$$\rho * \nabla * \mathbf{u} = 0$$

02 $$\rho * \frac{\partial \mathbf{u}}{\partial t} + \rho * (\boldsymbol{u} * \nabla) * \boldsymbol{u} = \nabla * [-p * \boldsymbol{I} + \boldsymbol{K}] + F$$
$$\rho * \nabla * \mathbf{u} = 0$$
$$\mathbf{K} = \mu * (\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^T)$$

0A $$\mathbf{u} = 0$$

0B $$-\int_{\partial\Omega} \rho * (\boldsymbol{u} * \boldsymbol{n}) d_{bc} * dS = m$$

0C $$[-p * \boldsymbol{I} + \boldsymbol{K}] * \boldsymbol{n} = -\widehat{p_0} * \boldsymbol{n}$$
$$\widehat{p_0} \leq p_0$$

HEAT TRANSPORT IN SOLID

01 $$\rho * C_p * \boldsymbol{u} * \nabla T + \nabla * \boldsymbol{q} = Q + Q_{ted}$$
$$q = -k * \nabla T$$

02 $$\rho * C_p * \boldsymbol{u} * \nabla T + \nabla * \boldsymbol{q} = Q + Q_p + Q_{vd}$$
$$\boldsymbol{q} = -k * \nabla T$$
$$\rho = \frac{p_A}{R_s * T}$$

0A $$-\mathbf{n} * \mathbf{q} = 0$$

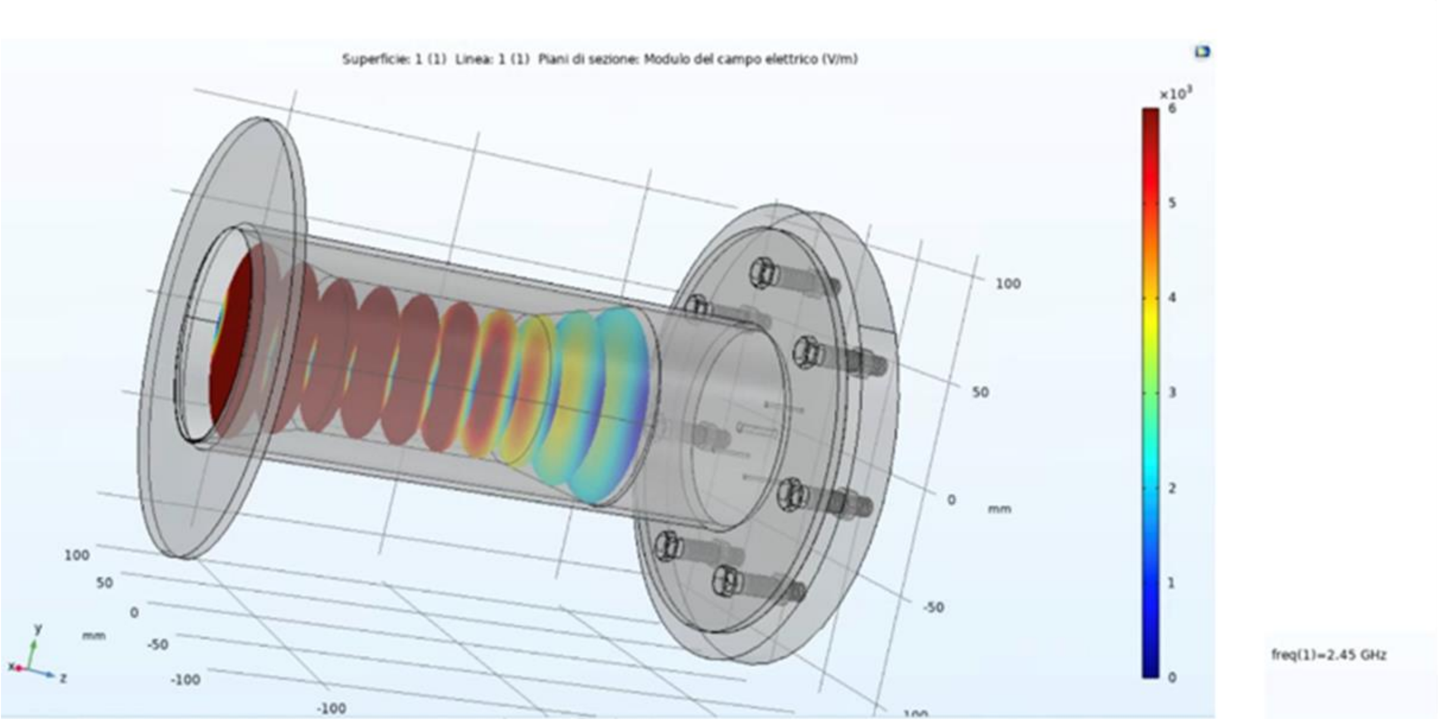
0B $$-\boldsymbol{n} * \boldsymbol{q} = \rho * \Delta_H * u * n$$
$$\Delta_{\boldsymbol{H}} = \int_{\boldsymbol{Tustr}}^{\boldsymbol{T}} C_p * dT$$

0C $$-\mathbf{n} * \mathbf{q} = Q_b$$

COMSOL MULTIPHYSICS®

2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

ELECTROMAGNETIC FIELD IN THE EMPTY WAVE GUIDE

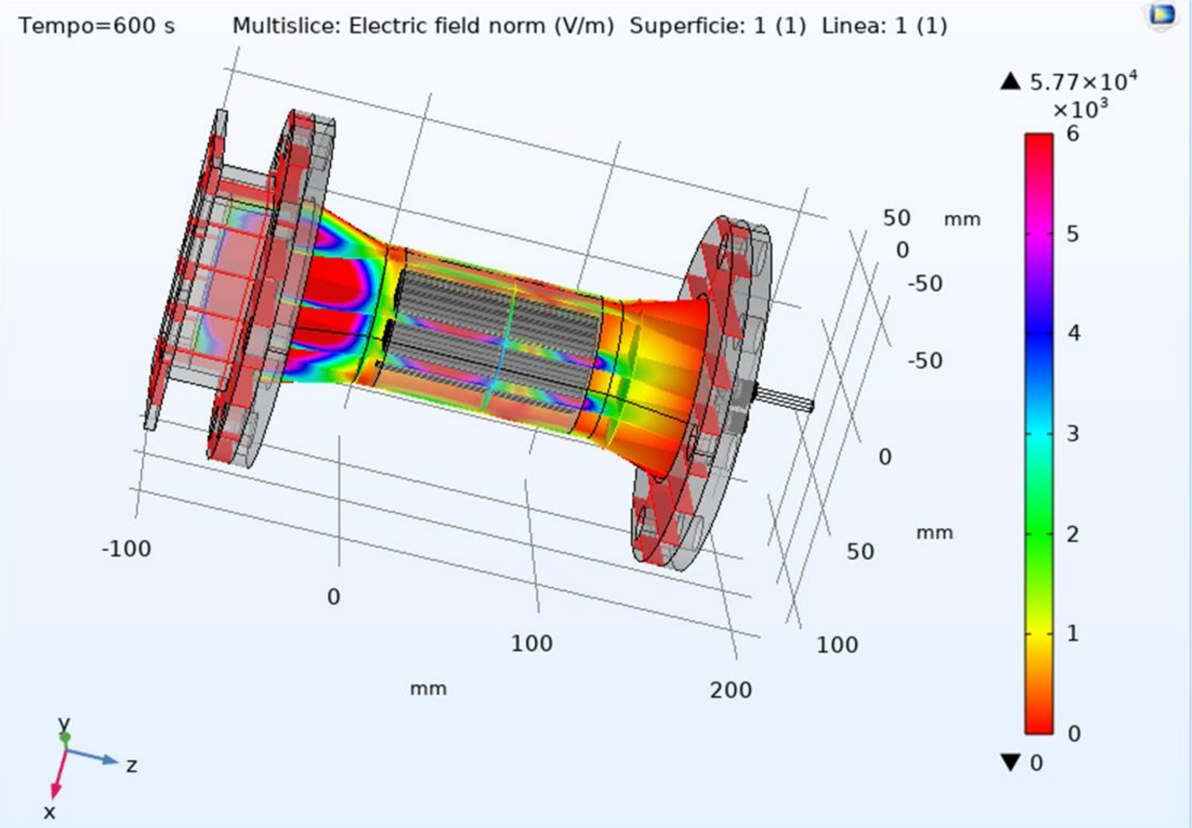


COMSOL MULTIPHYSICS®

CFD Modelling

2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

ELECTROMAGNETIC FIELD IN THE FILLED WAVE GUIDE


Tempo=600 s Multislice: Electric field norm (V/m) Superficie: 1 (1) Linea: 1 (1)

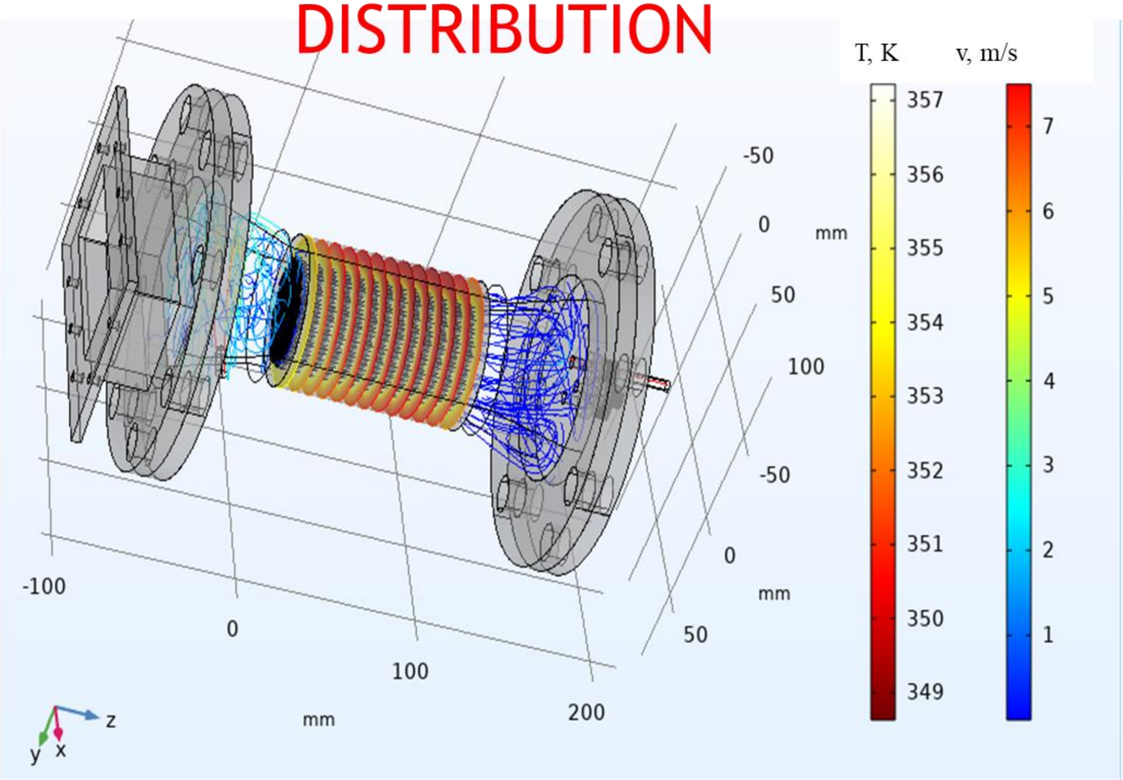
A special geometry with a restriction in the catalytic section seems to **intensify the electromagnetic field in the catalytic bed**.

COMSOL MULTIPHYSICS®

CFD Modelling

2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

FLOW AND TEMPERATURE DISTRIBUTION

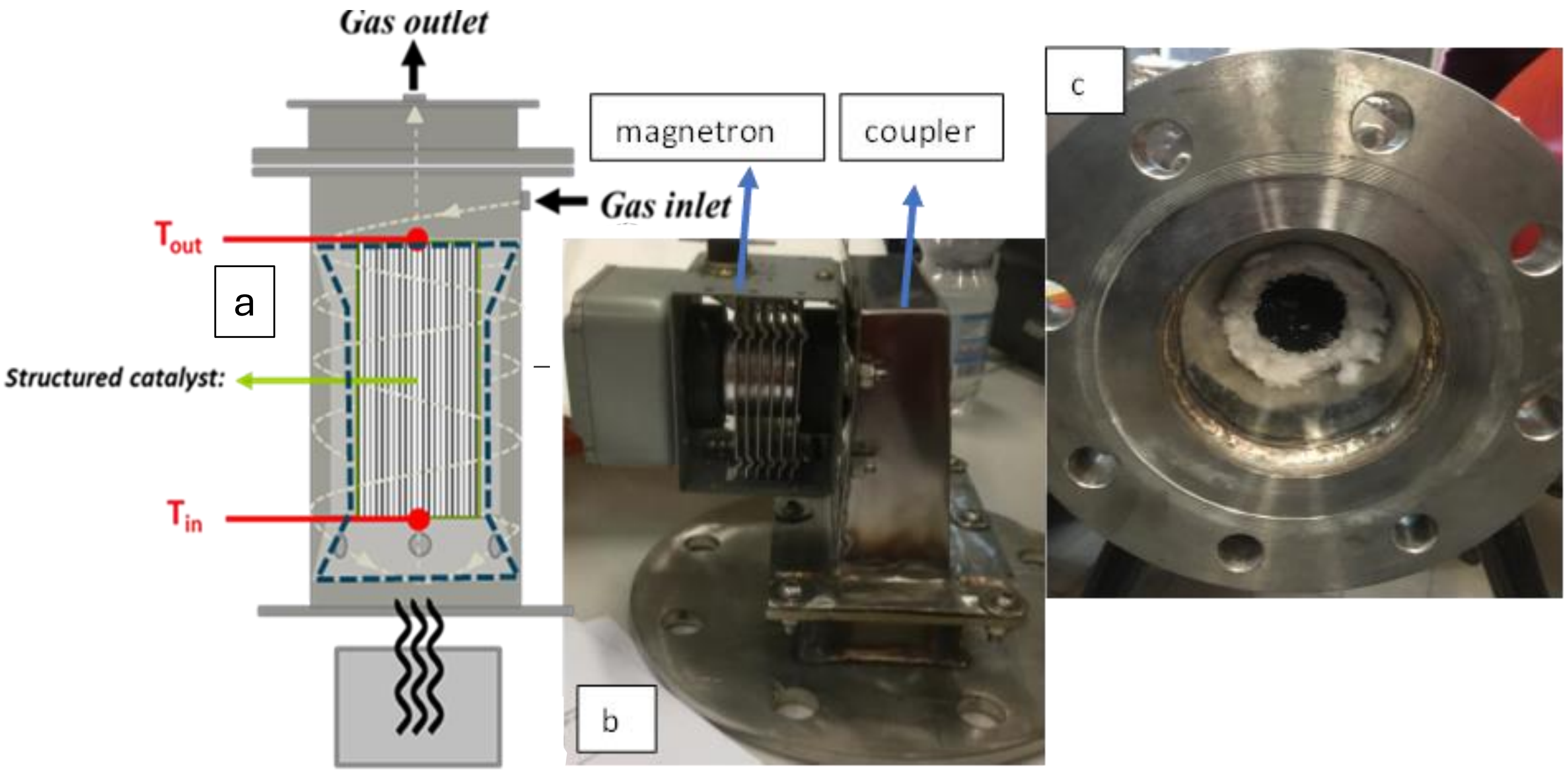


COMSOL MULTIPHYSICS®

CFD Modelling

2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

Microwave reactor optimized configuration



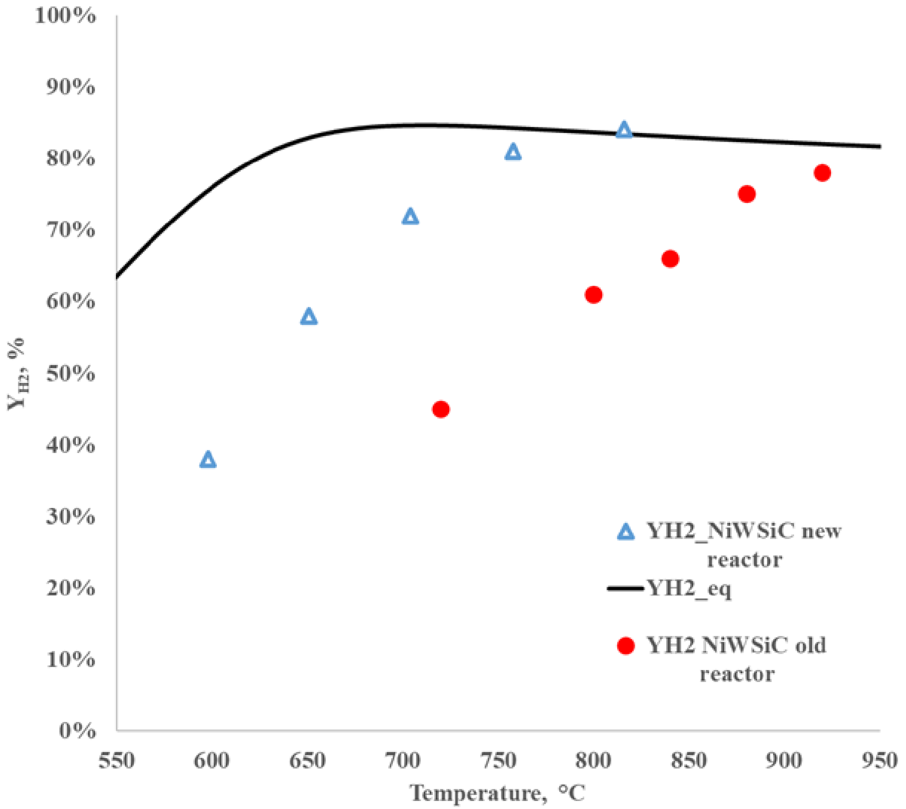
2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

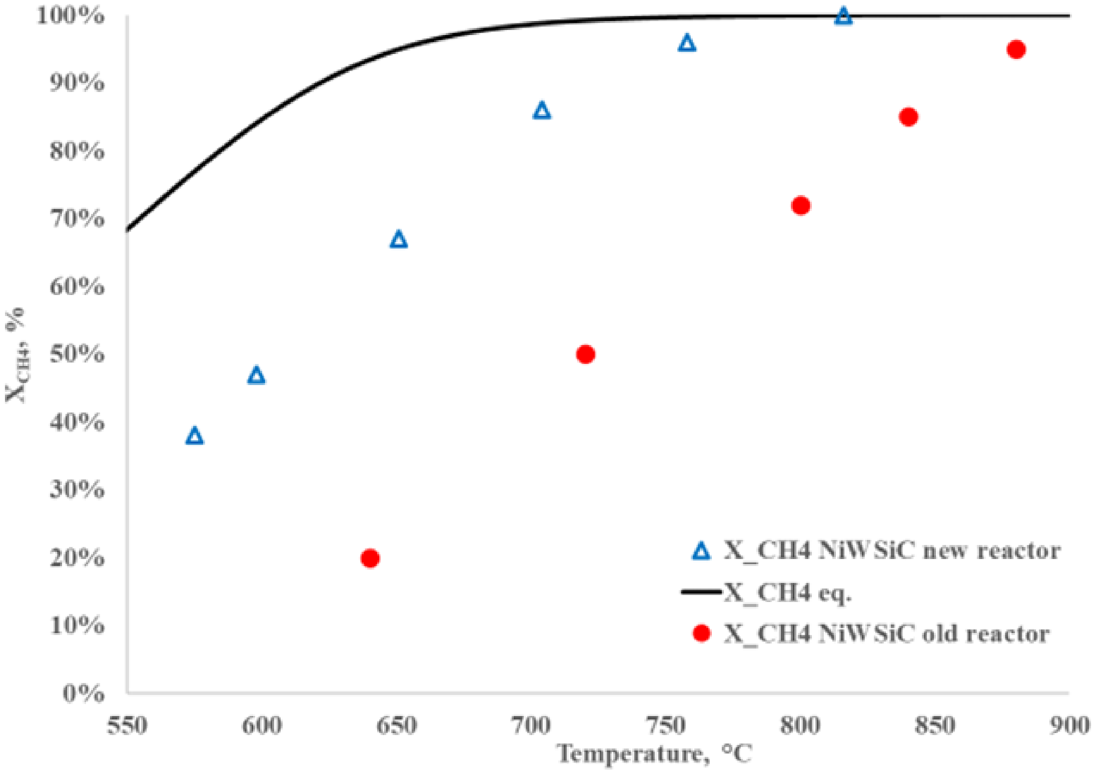
GHSV = 5000 h^{-1}

$$\frac{H_2O}{CH_4} = 3 \qquad \frac{N_2}{CH_4} = 3$$

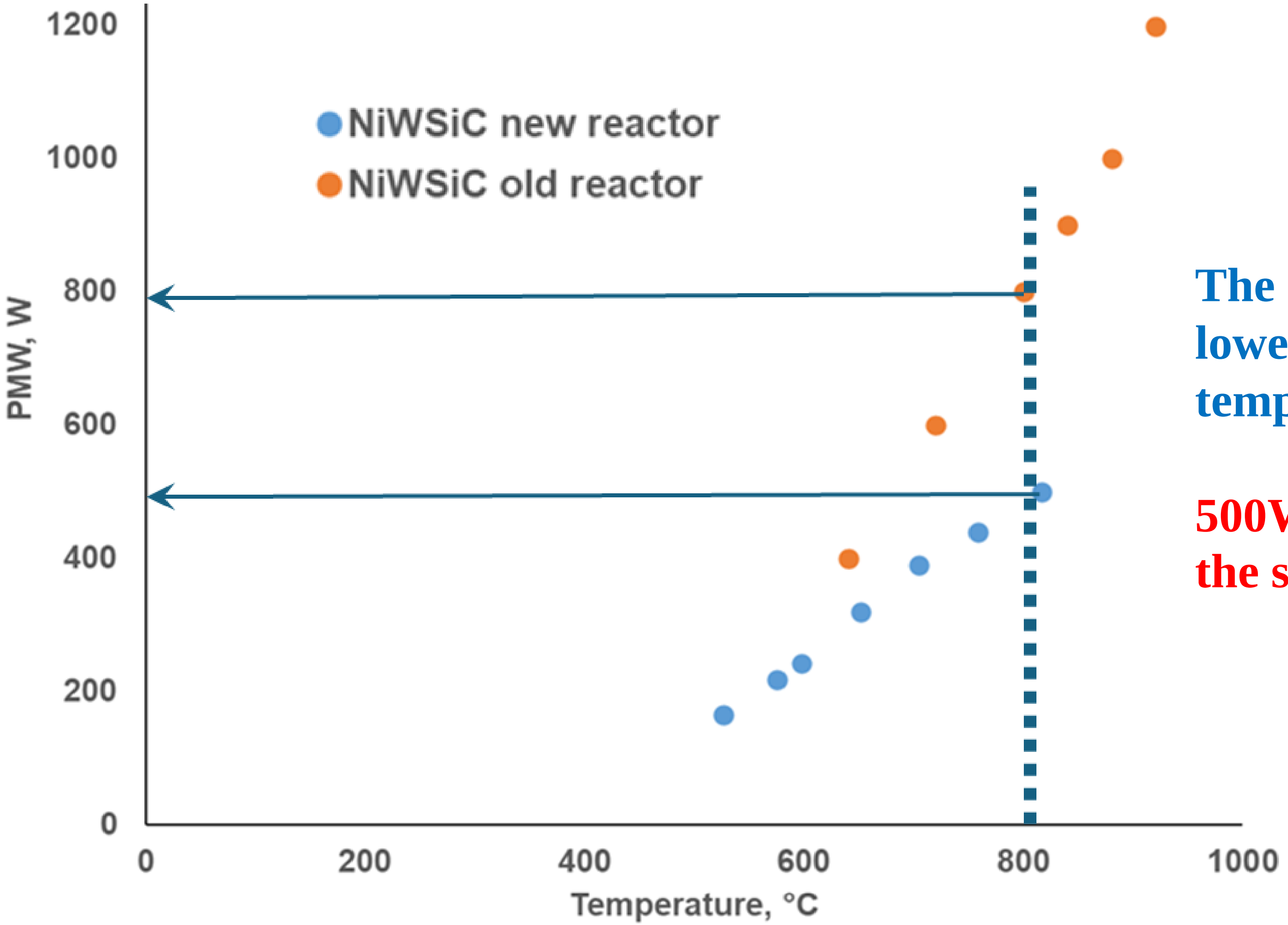
$$X_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}}$$

$$Y_{H_2} = \frac{F_{H_2,out}}{4 \cdot F_{CH_4,in}}$$





2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)



GHSV = 5000 h^{-1}

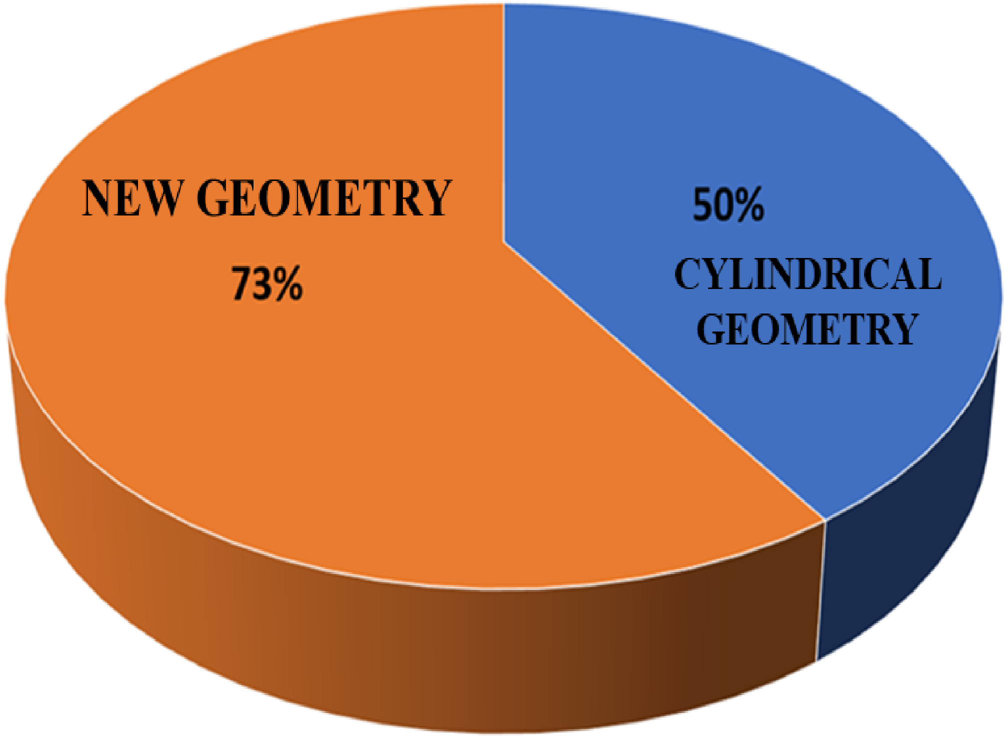
The new reactor configuration resulted in a lower MW power needed to reaching the same temperature.

500W instead of 800W are needed for having the same temperature of 800°C.

2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

By applying the thermal balance, the energy efficiency of the MW-assisted tests can be calculated.

$$(F_{CH4,in}\cdot cp_{CH4,in} + F_{\mathrm{N2},in}\cdot cp_{\mathrm{N2},in})\cdot(T_{gas,in} - T_{\mathrm{rif}}) + F_{H2O,in}\cdot cp_{H2O,in}\cdot(T_{H2O,in} - T_{\mathrm{rif}}) - (F_{CH4,\mathrm{out}}\cdot cp_{CH4,\mathrm{out}} + F_{\mathrm{N2,out}}\cdot cp_{\mathrm{N2,out}} + F_{H2O,\mathrm{out}}\cdot cp_{H2O,\mathrm{out}} + F_{CO2,out}\cdot cp_{\mathrm{C}O2,\mathrm{out}} + F_{CO,out}\cdot cp_{\mathrm{C}O,\mathrm{out}} + F_{H2,\mathrm{out}}\cdot cp_{H2,\mathrm{out}})\cdot(T_{gas,\mathrm{out}} - T_{\mathrm{rif}}) - (F_{CH4,in} - F_{CH4,out})\cdot\Delta H^{\circ}_{\mathrm{R,Trif,}}SR + (F_{\mathrm{CO2},in} - F_{\mathrm{CO2},out})\cdot\Delta H^{\circ}_{\mathrm{R,Trif,}}\mathrm{WGS} + Q_{MW} - Q_{diss} = 0$$



2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

	Energy consumption
Microwave process	$2.5\ \frac{\mathbf{kWh}}{\mathbf{Nm}^3_{H2}}$

Technology	Conventional alcaline electrolyser	Advanced Alcaline electrolyser	Proton exchange electrolyser	High temperature electrolyser
Efficiency	77-80%	80-90%	85-90%	90-100%
Energy consumption (kWh/Nm^3_{H2})	4.3-4.9	3.8-4.3	4.2-5	3.5

Hydrogen production from water electrolysis: current status and future trends. Proceedings of the IEEE vol. 100 n°2, 2012.

2 STEAM REFORMING: process intensification by means of structured catalysts active for the reaction and susceptible to microwaves (MW)

MW-ASSISTED REFORMING PROCESSES

Process	Catalyst	MW input	Operating Condition	X_{CH4}; X_{CO2}	Energy Consumption kWh $Nm^{-3}H_2$	Reference
MDR	$7Ru/SrTiO_3$	P = 36.99 kW	CO_2/CH_4=1 T=940 °C.	X_{CH4}= 99.5% X_{CO2}= 94%	18.6	Gangurde et al., 2018
MDR	$La_xSr_{2-x}CoO_{4}$ - Mn	P = 140 W	CO_2/CH_4=1 WHSV = 10 L h^{-1} g^{-1}	X_{CH4}= 80% X_{CO2}= 80%	4.0	Marin et al., 2021
MSR	15%Ni/CeO_2-Al_2O_3 on a SiC monolith	P = 800 W @ GHSV = 3300 h^{-1} P = 1000 W @ GHSV = 5000 h^{-1}	GHSV = 3300 and 5000 h^{-1} T = 550 – 950 °C P = 1 bar S/C = 3	CH_4 equilibrium conversion T = 800 °C – GHSV = 3300 h^{-1} T = 850 °C – GHSV = 5000 h^{-1}	3.8	Meloni et al., 2021
MSR	7%Ni/CeO_2-Al_2O_3 on a SiC monolith	P = 400 W	GHSV = 5000 h^{-1} T = 550 – 800 °C P = 1 bar S/C = 3	CH_4 equilibrium conversion @ T = 750 °C	**2.5**	**Meloni et al., 2022**

MICROWAVE ASSISTED CHEMICAL PROCESSES

CASE STUDIES

1 METHANE DRY REFORMING

2 METHANE STEAM REFORMING

3 **DEHYDROGENATION OF PROPANE**

3 MW assisted dehydrogenation of propane to propylene

$$C_3H_8 \rightleftarrows C_3H_6 + H_2 \qquad \Delta H^\circ_{r,\,298K} = 124.3\ kJ/mol$$

Critical aspects

- High operating temperatures
- <u>Homogeneous side reactions favored at high temperatures</u>
- <u>Coke formation and frequent catalyst regeneration cycles</u>

Hydrogenolysis of propane $C_3H_8 + H_2 \rightleftarrows C_2H_6 + CH_4$

Cracking of propane $C_3H_8 \rightleftarrows C_2H_4 + CH_4$

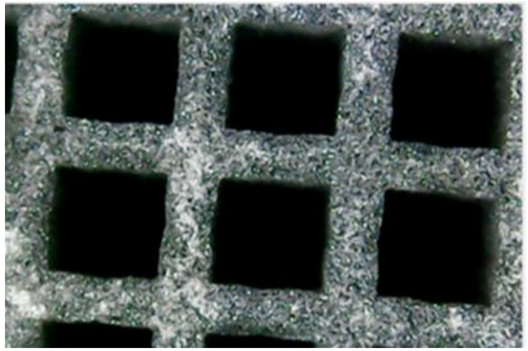
Deep dehydrogenation $C_3H_6 \rightleftarrows C_3H_4 + H_2$

Process intensification

- Study and preparation of a Pt-Sn-based catalyst supported over MgO-modified alumina
- Transfer of the catalytic formulation over a SiC monolith to obtain a MWs susceptible structured catalyst
- Testing of the structured catalyst both with conventional and MW heating technique

3 MW assisted dehydrogenation of propane to propylene

Catalyst preparation



Bare SiC

Al_2O_3 washcoat

Al_2O_3/SiC

Dip-coating

Up to **30 wt%** load

+ MgO

MgAlO/SiC

Wet impregnation

Up to **30 wt%** load with respect to Al_2O_3

+ Pt

Pt/MgAlO/SiC

Wet impregnation

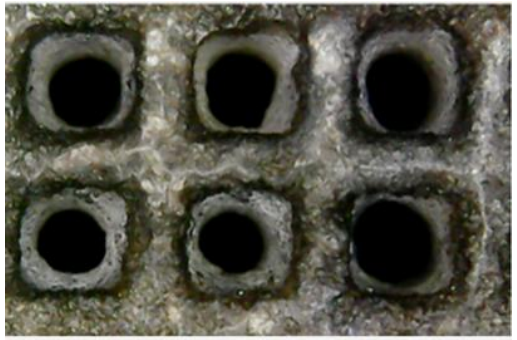
Up to **0.5 wt%** load with respect to Al_2O_3 + MgO

+ Sn

Pt-Sn/MgAlO/SiC

Wet impregnation

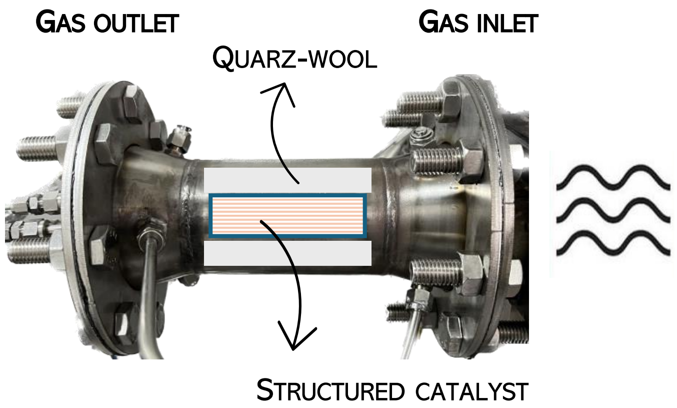
Up to **0.7 wt%** load with respect to Al_2O_3 + MgO

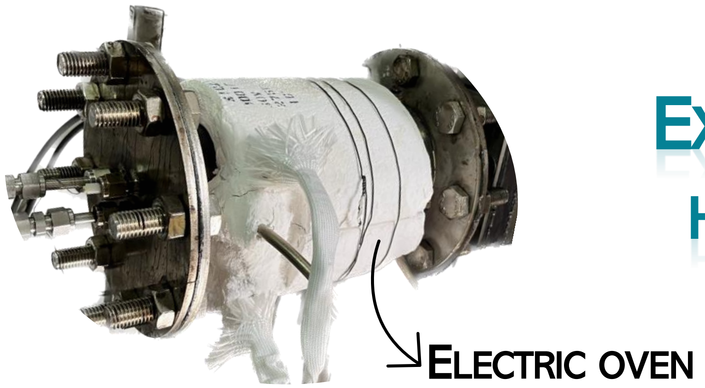


Final catalyst

2 MW assisted dehydrogenation of propane to propylene

MW HEATING





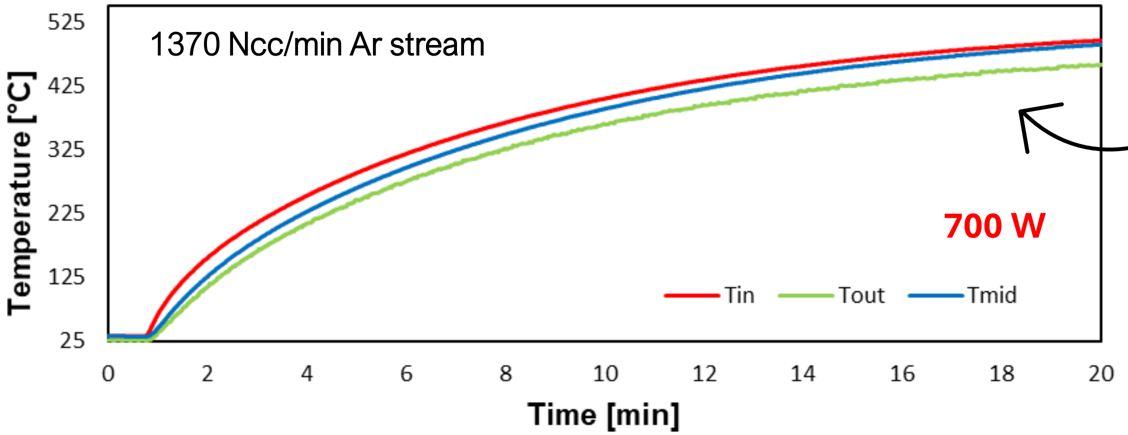
EXTERNAL HEATING

DIFFERENT HEATING METHOD

SAME REACTOR

3 MW assisted dehydrogenation of propane to propylene

BARE SIC MONOLITH

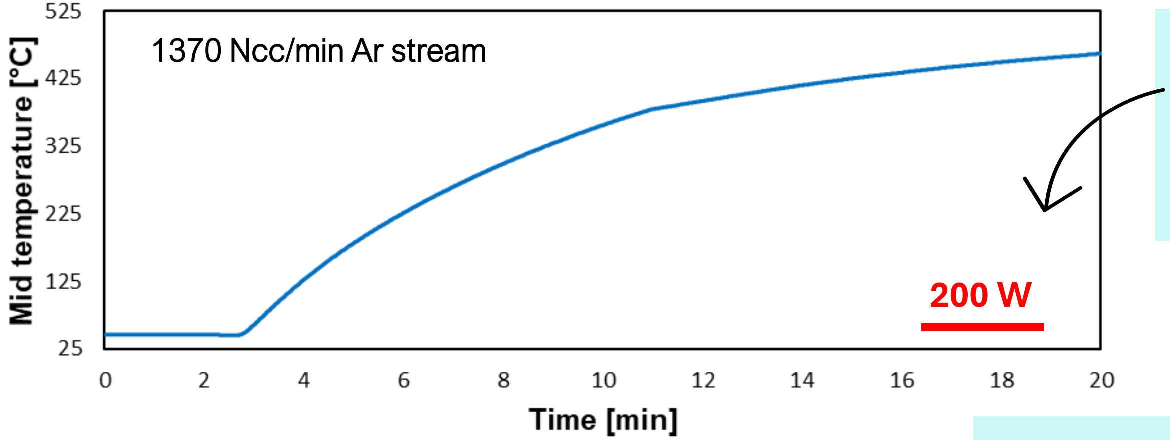


② **AXIAL TEMPERATURE PROFILE**

THE MW HEATING ASSURED A HOMOGENEOUS TEMPERATURE DISTRIBUTION OF THE MONOLITH

CATALYTIC SIC MONOLITH

Sn/Pt/Mg Al O/SiC



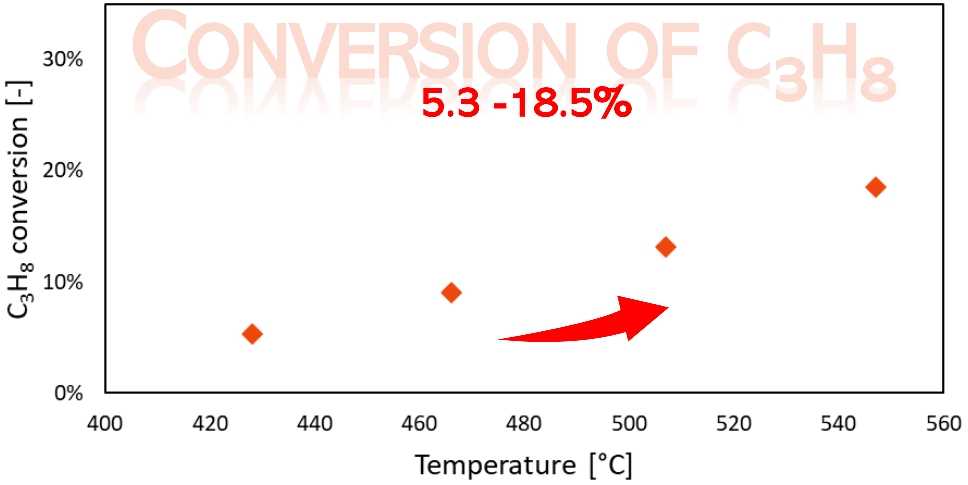
③ **LOWER MW GENERATOR POWER**

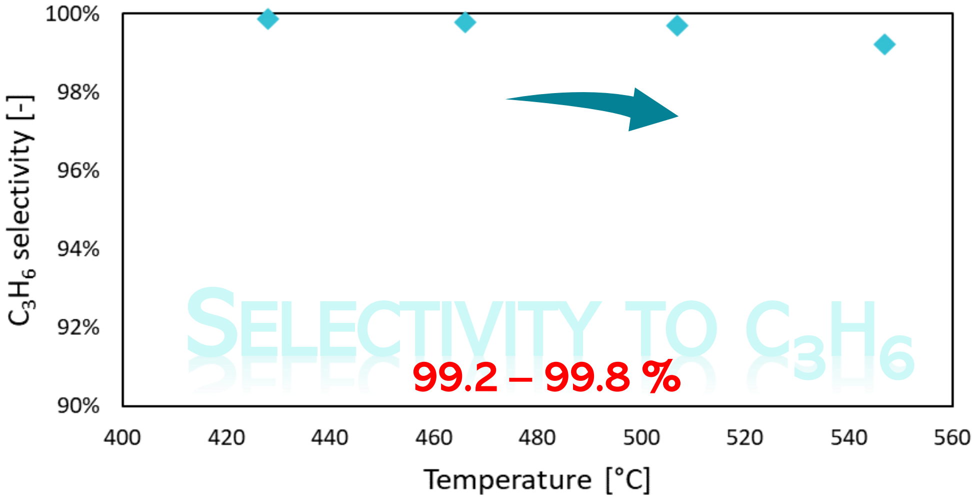
THE ACTIVE PHASE INCREASE THE MW HEATING CAPACITY OF THE SIC MONOLITH

① **RAPID AND EASY HEATING OF THE CATALYTIC ZONE**

AFTER 20 MINUTES THE CATALYST REACHED 470 °C

3 MW assisted dehydrogenation of propane to propylene

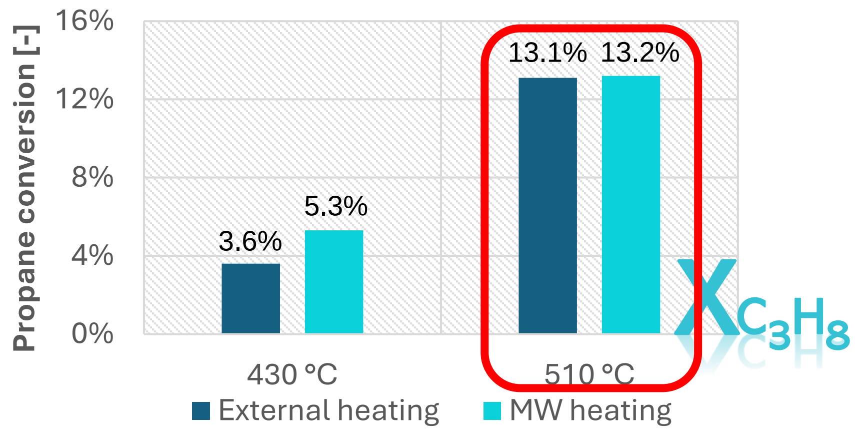


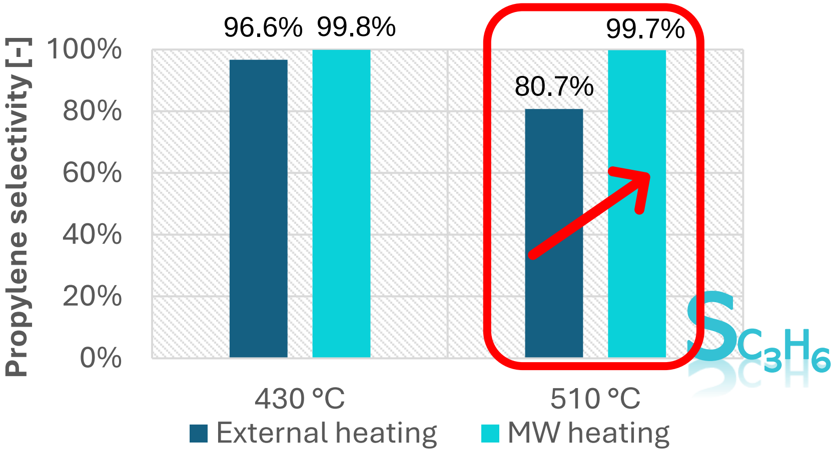


OPERATIVE CONDITIONS

REACTANTS MIXTURE	80 VOL% C_3H_8	20 VOL% He
TEMPERATURE RANGE	450 – 600 °C	
PRESSURE	1 BAR	
SPACE VELOCITY (WHSV)	6 h^{-1}	

3 MW assisted dehydrogenation of propane to propylene





REACTOR CAVITY AFTER THE ACTIVITY TEST

EXTERNAL HEATING

MW HEATING

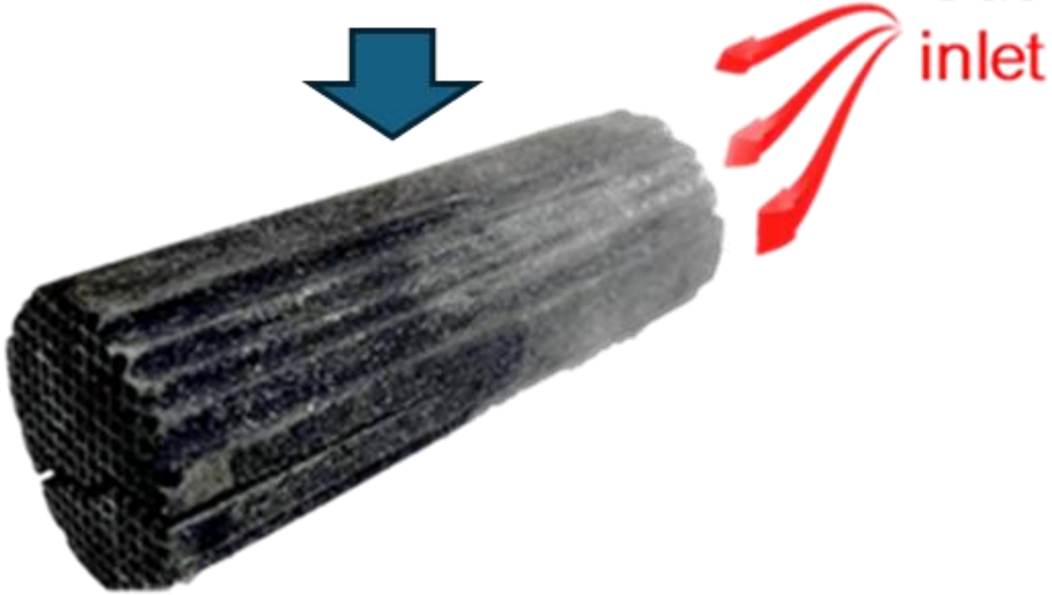
CARBON BALANCE	■ External heating	■ MW heating
C_{out}/C_{in}	0.90 – 0.87	1.02 – 1.03

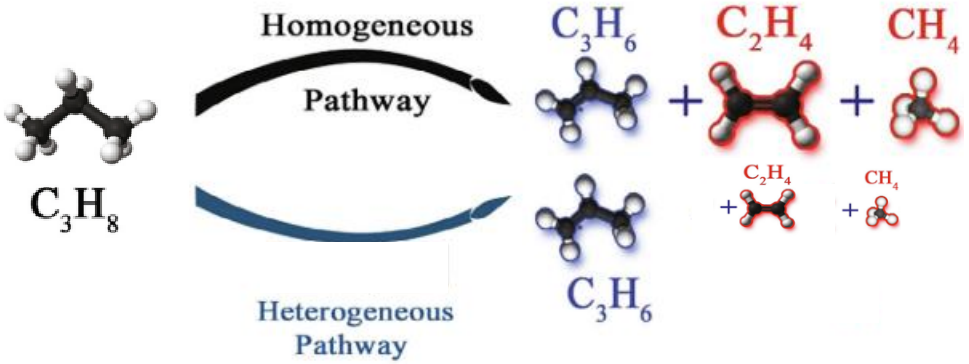
3 MW assisted dehydrogenation of propane to propylene

EFFECT OF MW ELECTRIFICATION ON PDH

- Reverse of the heat flux assured by the MW heating
- Limited coke formation and improved propylene selectivity

Coke formation in the outlet zone



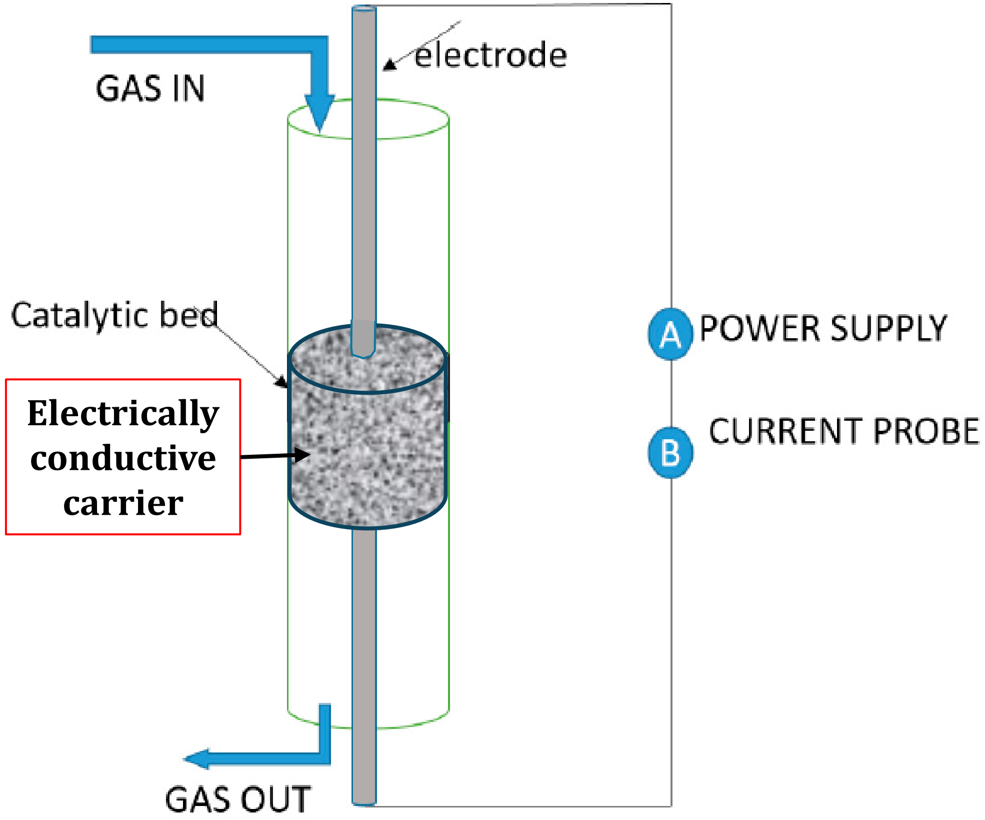


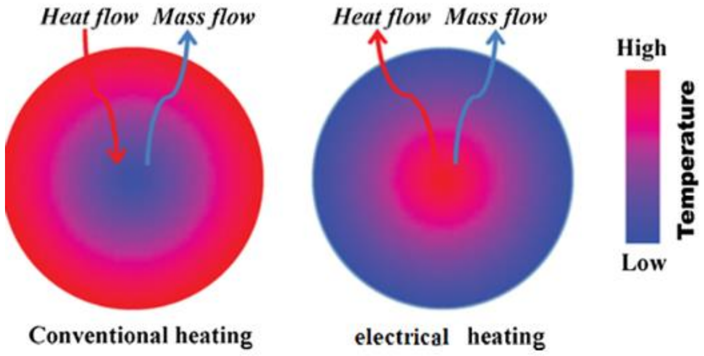
- Selective MW heating of the catalyst
- Reduced homogeneous reactions
- Higher selectivity towards the desired products

JOULE/OHMIC HEATING

JOULE HEATING TECHNOLOGY

allows to perform electricity-driven process





$$P = \frac{V^2}{R}\ [W]$$

OHMIC CHEMICAL PROCESSES

CASE STUDIES

1. METHANE DRY REFORMING: Electrically driven SiC-based structured catalyst
2. METHANE DRY REFORMING: Ni-catalyzed Si-SiC foam
3. METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam

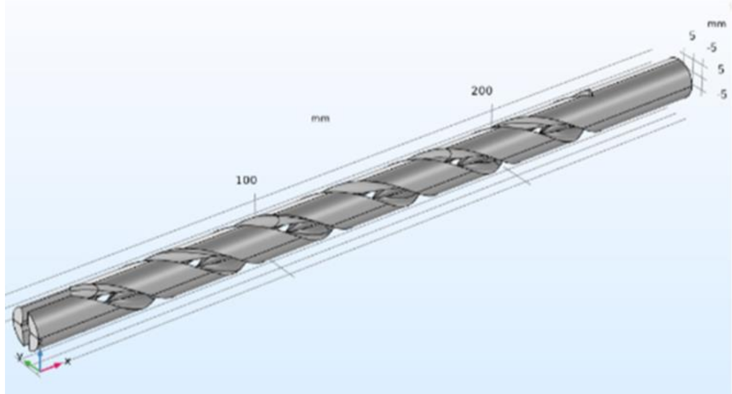
OHMIC CHEMICAL PROCESSES

CASE STUDIES

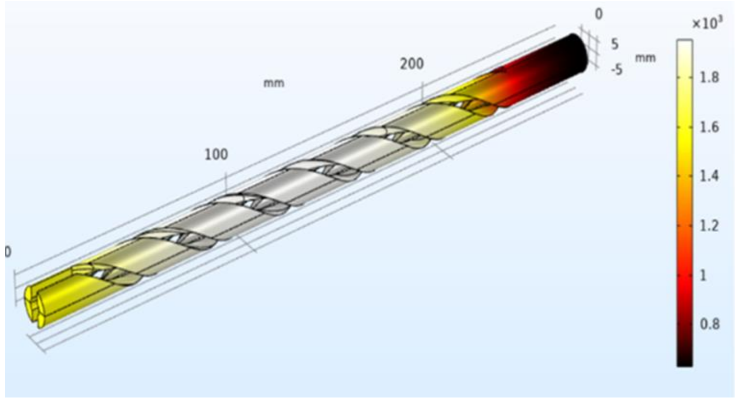
1. **METHANE DRY REFORMING: Electrically driven SiC-based structured catalyst**
2. METHANE DRY REFORMING: Ni-catalyzed Si-SiC foam
3. METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam

1 METHANE DRY REFORMING: Electrically driven SiC-based structured catalyst

Preparation of a catalyst directly on the surface of a commercial heating element



Conductive SiC element

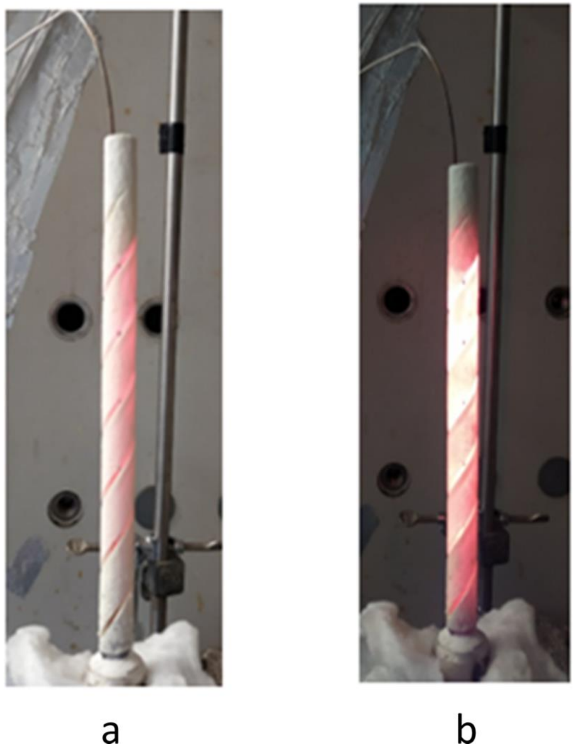


Temperature profile along the SiC element as a consequence of the Joule effect

SiC parameters used for the "heat transfer in solids" physics.

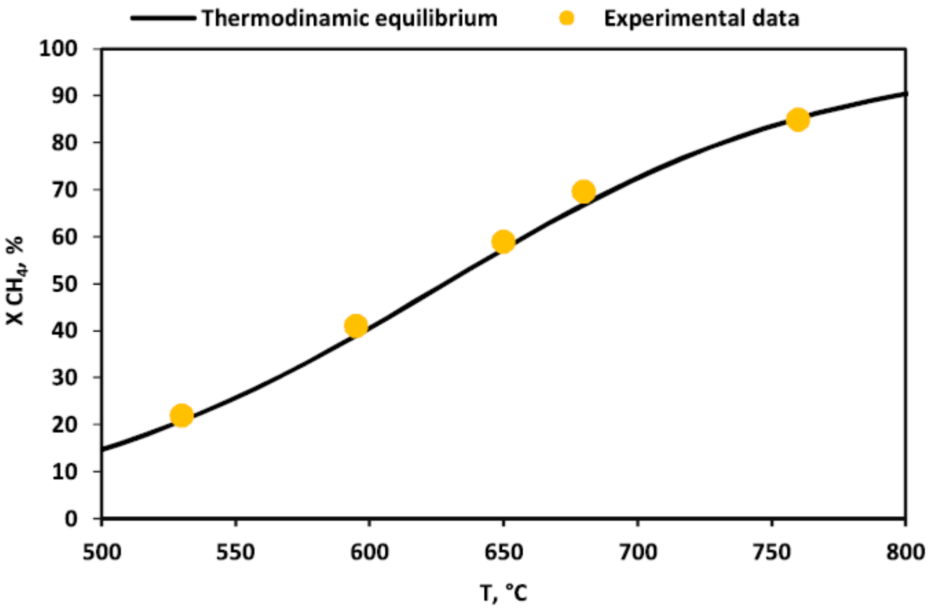
Property	Measure unit	Value
electrical conductivity	$S\ m^{-1}$	$1{*}10^3$
Specific heat (Cp)	$J\ (Kg{*}K)^{-1}$	1200
Relative permittivity	1	10
Density	$Kg\ m^{-3}$	3200
Thermal conductivity	$W\ (m{*}K)^{-1}$	450
Superficial emittivity	1	0.5
Seebeck coefficient	$V\ K^{-1}$	$750{*}10^{-6}$

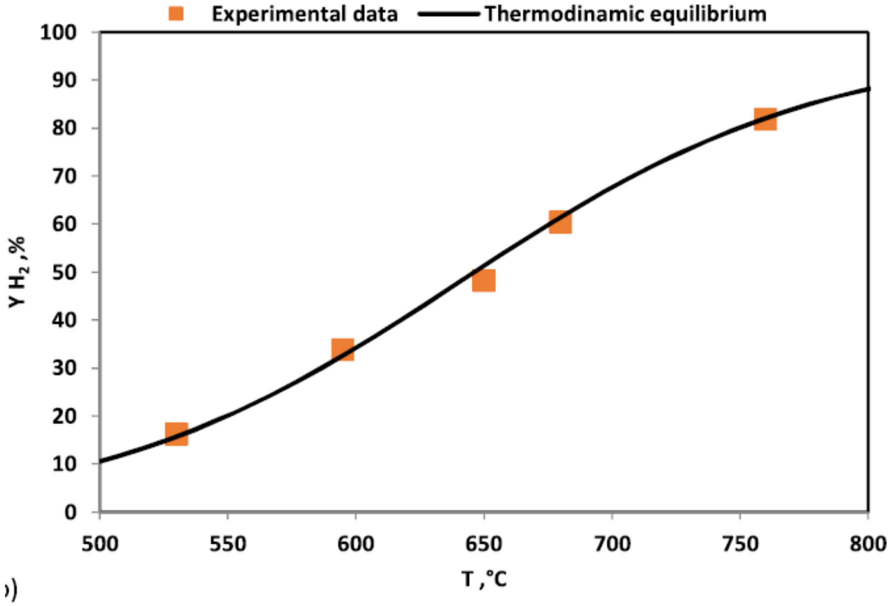
Final Ni-based Catalyst



SiC heating element after washcoat and Ni deposition during the drying and calcination steps. a) T =600 °C, b) T =900 °C

1 METHANE DRY RERFORMING: Electrically driven SiC-based structured catalyst





$$X_{CH_4} = \frac{F_{CH_{4,in}} - F_{CH_{4,out}}}{F_{CH_{4,in}}}$$

$$Y_{H_2} = \frac{F_{H_{2,out}}}{2 \cdot F_{CH_{4,in}}}$$

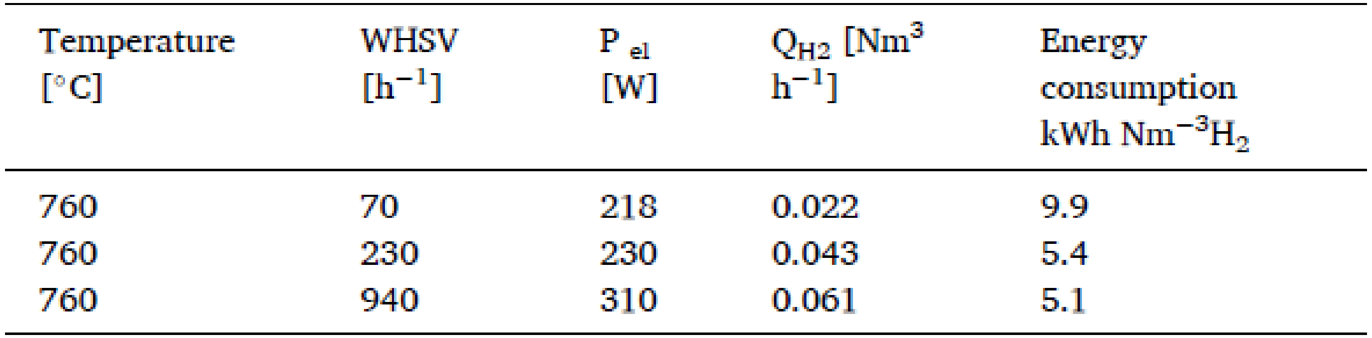
Temperature [°C]	P_{el} [W]
440	58
530	84
595	115
650	143
680	170
760	217

CO_2/CH_4 = 1; WHSV =70 h^{-1}

The experimental data approach the thermodynamic equilibrium profile even at low temperatures (at 760°C a CH_4 conversion equal to 84 % and a H_2 yield equal to 75 % were obtained). The obtained values are higher than the ones reported in literature for catalysts with a comparable Ni loading.

1 METHANE DRY RERFORMING: Electrically driven SiC-based structured catalyst

Properly designed MDR experimental tests have been performed, at the WHSV values of 70, 230 and 940 h^{-1}, with the aim to evaluate the energy consumption of the system.



Temperature [°C]	WHSV [h^{-1}]	P_{el} [W]	Q_{H2} [Nm^3 h^{-1}]	Energy consumption kWh $Nm^{-3}H_2$
760	70	218	0.022	9.9
760	230	230	0.043	5.4
760	940	310	0.061	5.1

- **The system works fine and is able to reach the Equilibrium composition in the overall T and SV investigated.**
- **The energy efficiency is not optimised, even if the results improved at higher SV.**
- **The higher energy consumption at the lower SV values can be explained considering the lab scale of the reactor, where the heat dissipation have a big role.**

Limitations of this study: Carrier Geometry, Support Materials, Not optimized catalyst formulation

OHMIC CHEMICAL PROCESSES

CASE STUDIES

1 METHANE DRY REFORMING: Electrically driven SiC-based structured catalyst

2 **METHANE DRY REFORMING: Ni-catalyzed Si-SiC foam**

3 METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam

2 METHANE DRY REFORMING: Ni-catalyzed Si-SiC foam

ELETTRICALLY CONDUCTIVE SUPPORT

Catalyst preparation

Si-SiC foam

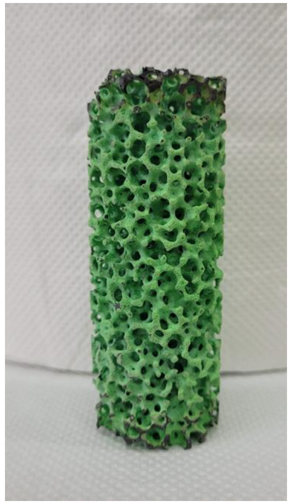
Dip-coating

30 wt% of γ-Al_2O_3

Wet impregnation

15 wt% of CeO_2

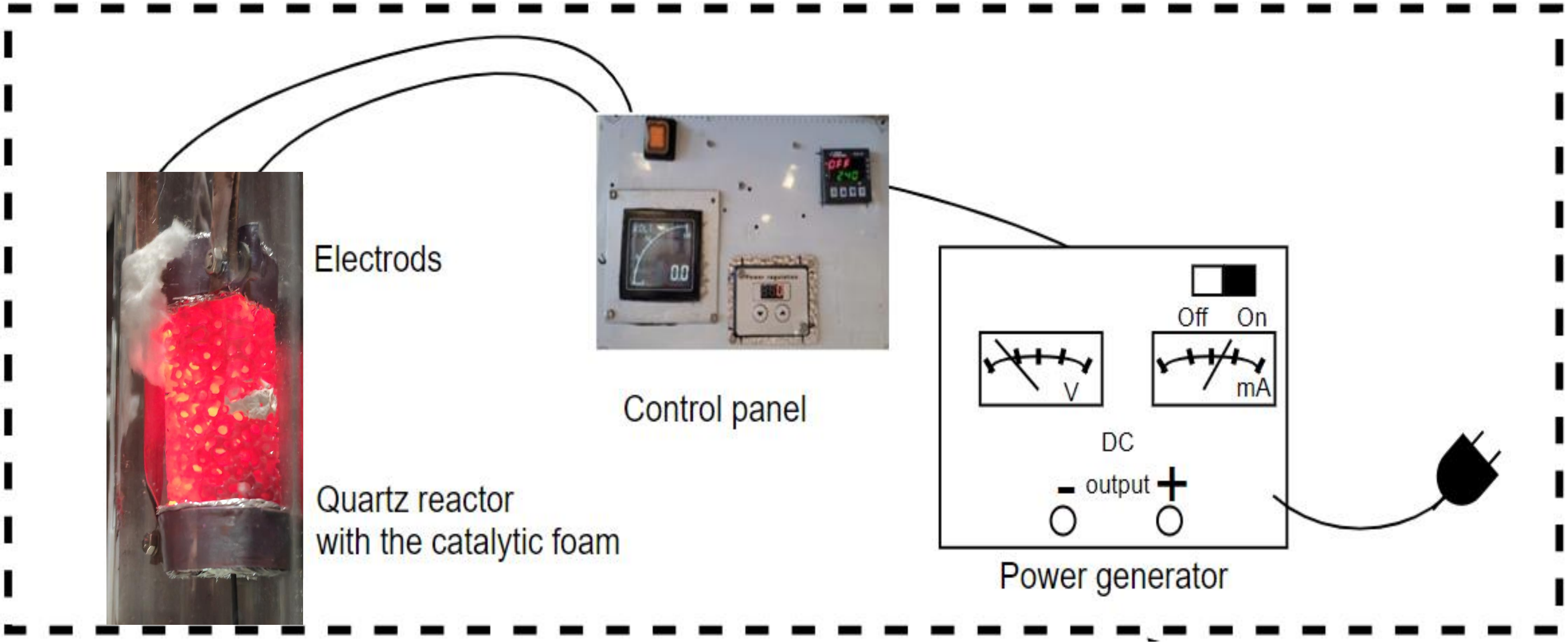
Wet impregnation



10 wt% of NiO

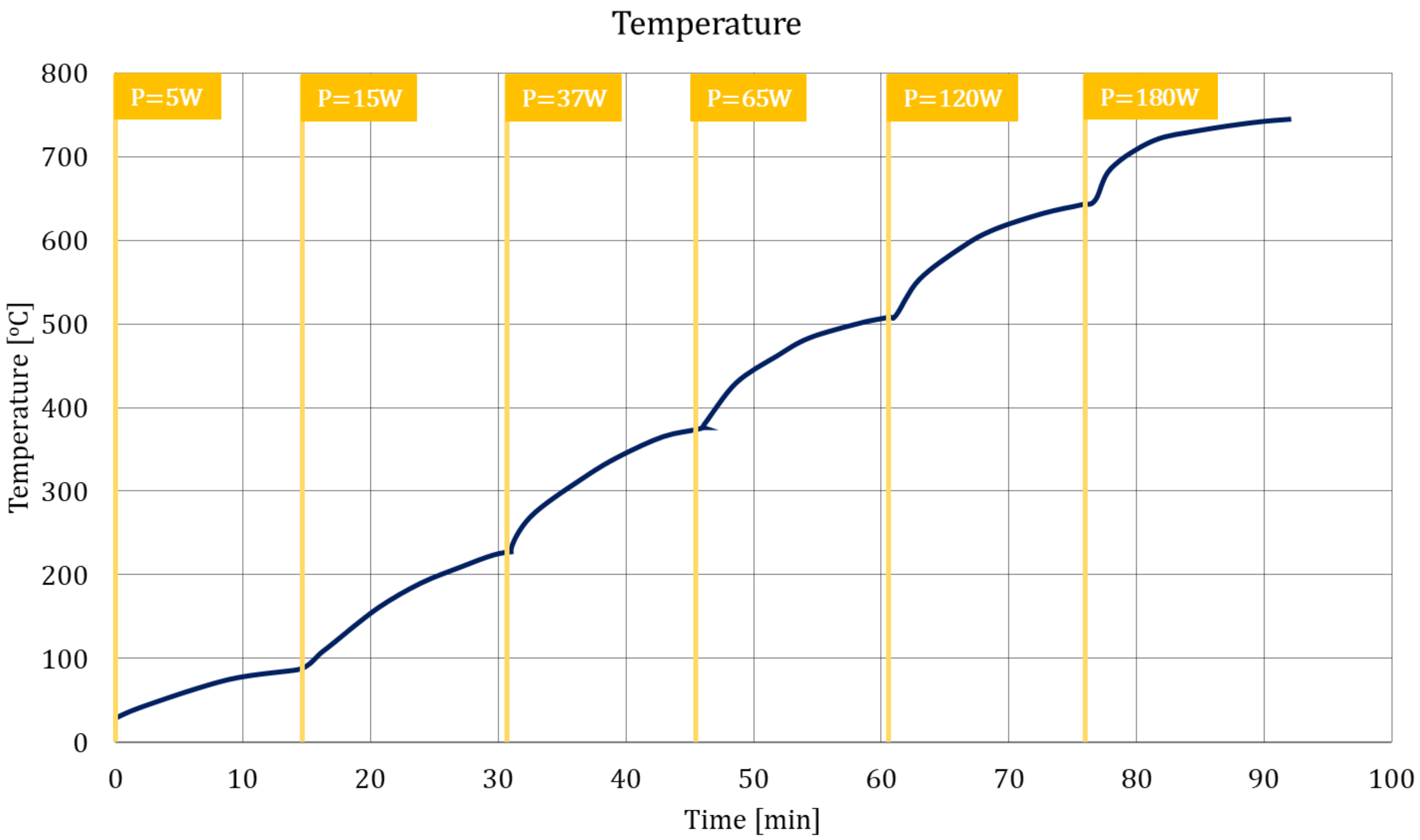
2 METHANE DRY REFORMING: Ni-catalyzed Si-SiC foam

Ohmic heated reactor configuration



2 METHANE DRY REFORMING: Ni-catalyzed Si-SiC foam

Preliminary heating test



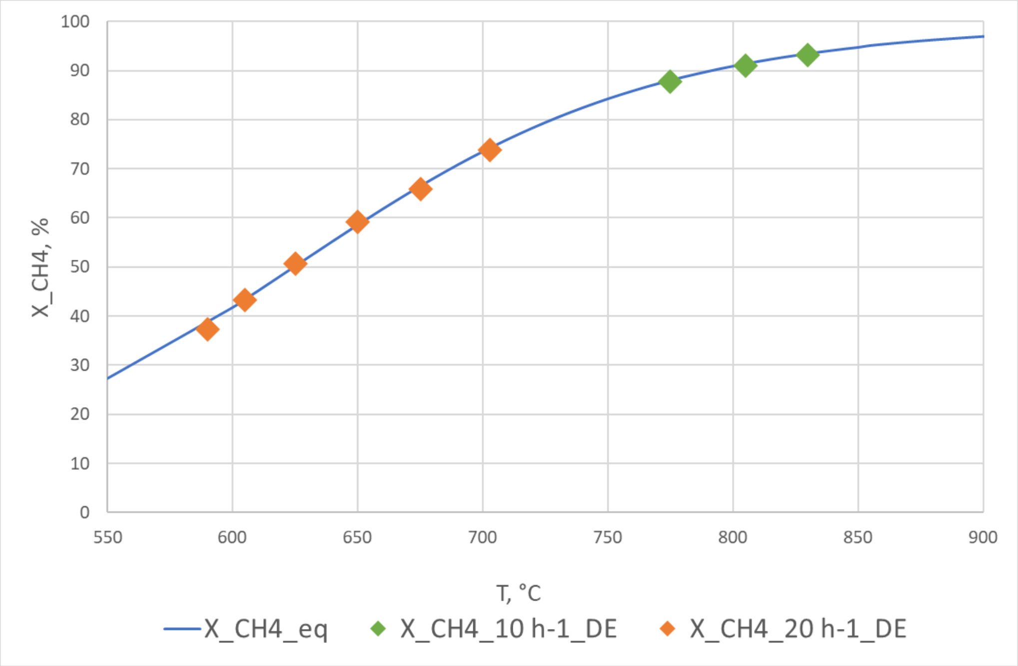
Power Input [%]	Power Supply [W]
5	5
10	15
15	37
20	65
25	120
30	180

The reaction temperature is reached by using a power of 180 W.

2 METHANE DRY REFORMING: Ni-catalyzed Si-SiC foam

Electrically heated activity tests at two different WHSV

WHSV [h^{-1}]	T [°C]	X_CH_4	H_2 produced [Nm^3/h]	Energy supplied [kW]	Energy consumption [kWh/Nm^3H_2]	Theorical limit value of energy consumption [kWh/Nm^3H_2]
10	750	87.7%	0.049	0.195	**4.10**	1.90
20	700	73.8%	0.081	0.210	**2.60**	



$$X_{CH_4} = \frac{F_{CH_4}^{IN} - F_{CH_4}^{OUT}}{F_{CH_4}^{IN}}$$

$$F_i [=] mol/min$$

PROMISING RERSULTS

The experimental results approached the thermodynamic equilibrium data

The energy consumption is close to the theoretical one

2 METHANE DRY REFORMING: Ni-catalyzed Si-SiC foam

Energy consumption comparison with other electrified reforming studies

Technology	Energy consumption, kWh*Nm^{-3}H$_2$
Conventional alcaline electrolyser [1]	4.3-4.9
Advanced Alcaline electrolyser [1]	3.8-4.3
Proton exchange electrolyser [1]	4.2-5
High temperature electrolyser [1]	3.5
Microwave-assisted MSR [1]	3.8
Microwave-assisted MSR [2]	2.5
Microwave-assisted MDR [3]	4.6
Microwave-assisted MDR [4]	18.58
Microwave-assisted MDR [5]	3.98
Microwave-assisted MDR [6]	4.3
Indirect electrification MDR [6]	2.6
Electrically-driven (SiC) MSR [7]	4.8
Electrically-driven (Electric Field) MSR [8]	3.21-3.98
Electrically-driven (SiC) MDR [7]	5.1
Electrically-driven (Electric Field) MDR [9]	18
Electrically-driven (FeCrAlloy) MDR [10]	Not available
Electrically-driven (SiSiC foam) MSR [11]	2

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OHMIC CHEMICAL PROCESSES

CASE STUDIES

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2. METHANE DRY REFORMING: Ni-catalyzed Si-SiC foam
3. **METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam**

3 METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam

With no electrically conductive properties

Main goals

- Identification of the optimal coating procedure and catalytic active phases dispersion
- Adding the Joule heating functionality by applying resistive elements
- Perform the catalytic activity test
- Evaluation of the overall Energy efficency at different operative conditions

3 METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam

Catalyst preparation

WashCoating the structured carrier

20 ppi SiC open foam
annular shaped
OD 60mm and ID 20mm

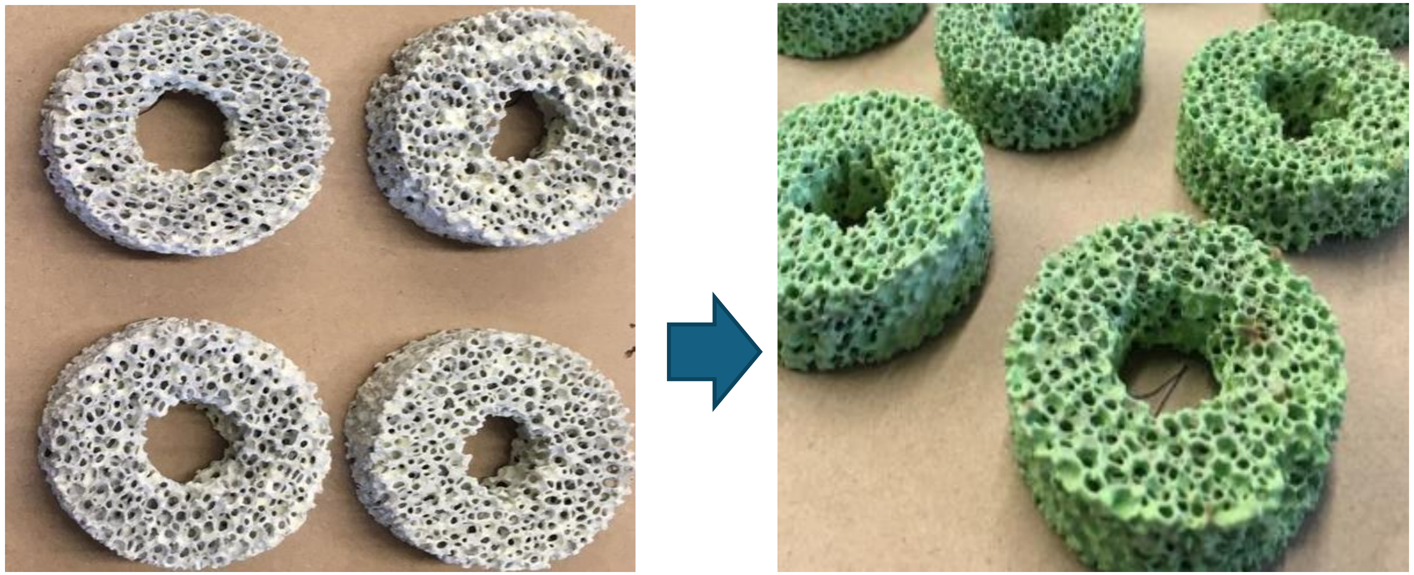
- **High thermal conductivity**
- **High Temperature resistance**
- **Low pressure drop**
- **High Surface to volume ratio**

γ-Al_2O_3 (15%wt)
WASHCOATED FOAM

3 METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam

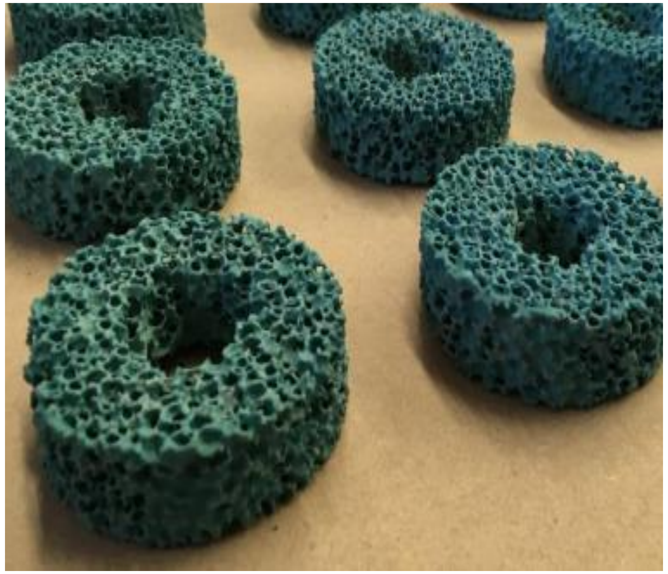
Catalyst preparation

Ceria and Ni addition



Ɣ-Al2O3 COATED FOAM

CeO2/Ɣ-Alumina FOAM



Ni(10%wt)/CeO2/Ɣ-Al2O3 Catalytic FOAM

3 METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam

Combining the heating functionality **Catalyst electrification**

- **Internal heating element (SiC)**
- **Catalytic foams**

- 10 Foams assembled together
- Covered by insulating cement
- Adding the external heating element in Kanthal

Catalyst Volume

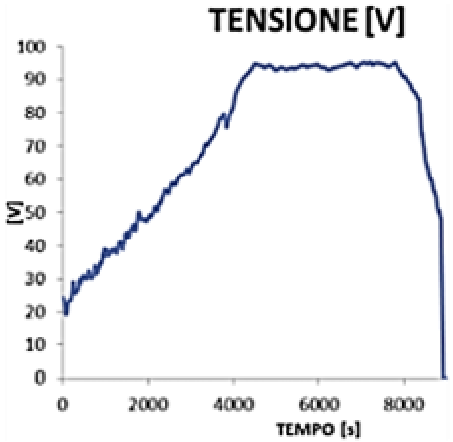
0,3 dm^3

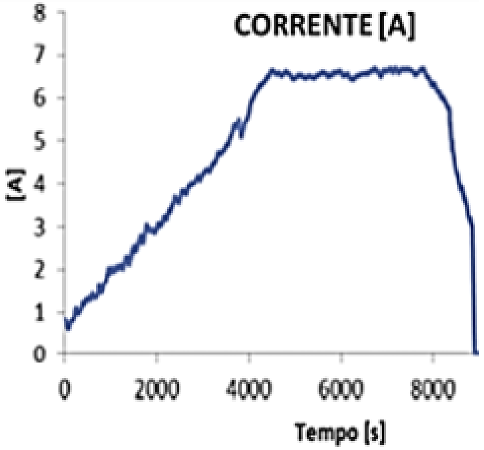
Ohmic values:

- **Ext. 29 Ohm**
- **Int. 8 Ohm**

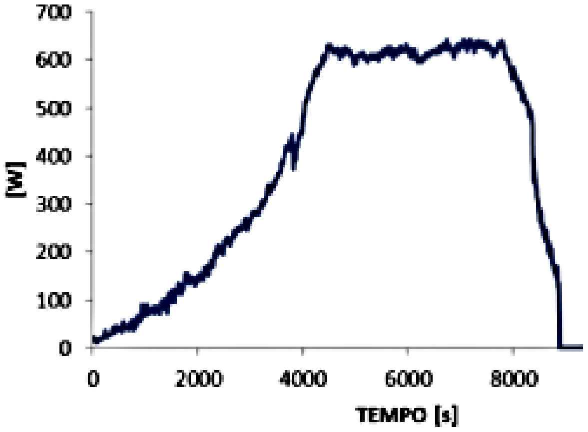
3 METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam

Electrically driven CATALYST HEATING

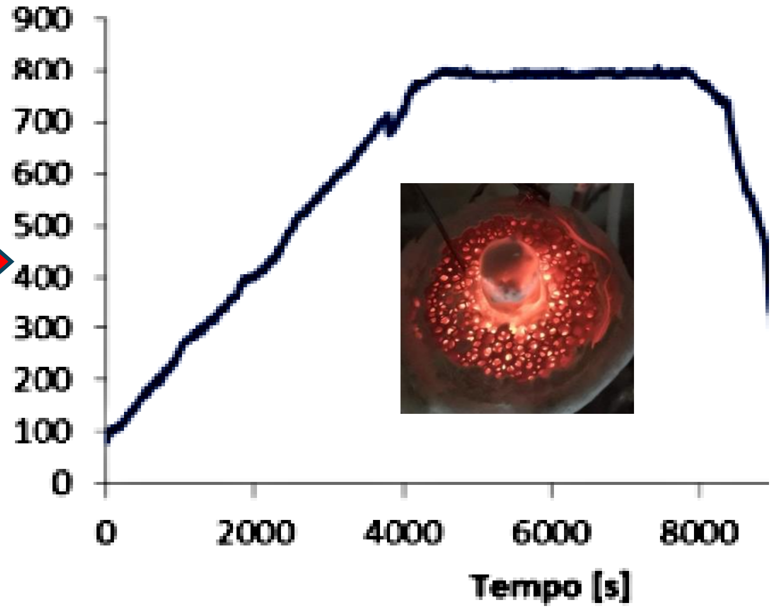




Power (W)



Catalyst Temperature (°C)



During a test we are able to control the catalyst temperature by controlling instantaneously the watts applied to the electrified catalyst by changing the Voltage and the current.

3 METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam

Electrically driven CATALYTIC TESTS

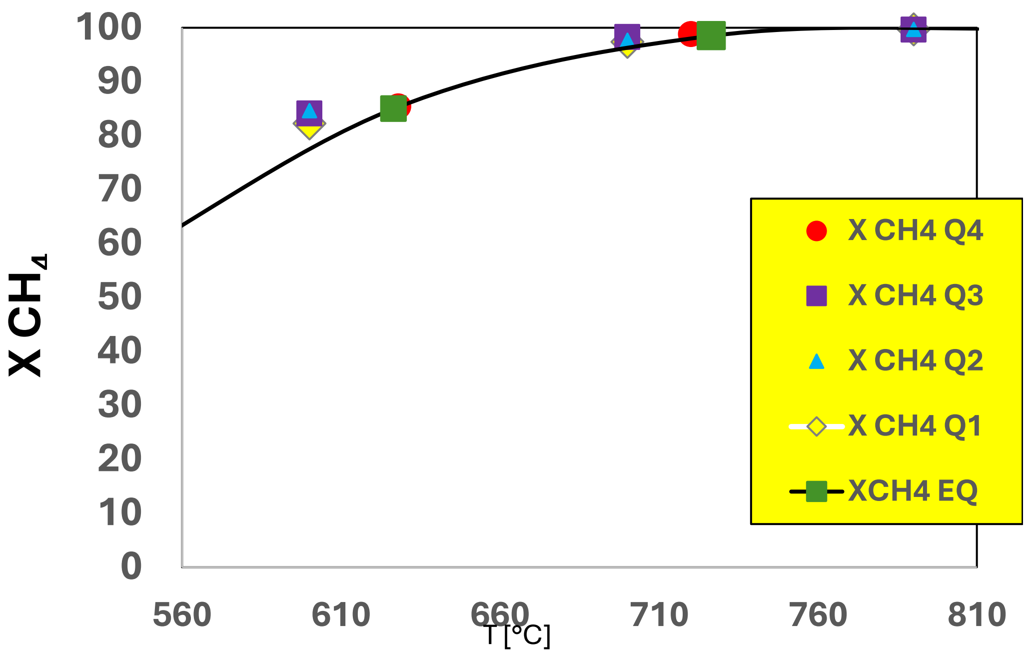
Tests at different GHSV was obtained @ 1 bar by changing the total gas flow rate entering the catalytic bed.

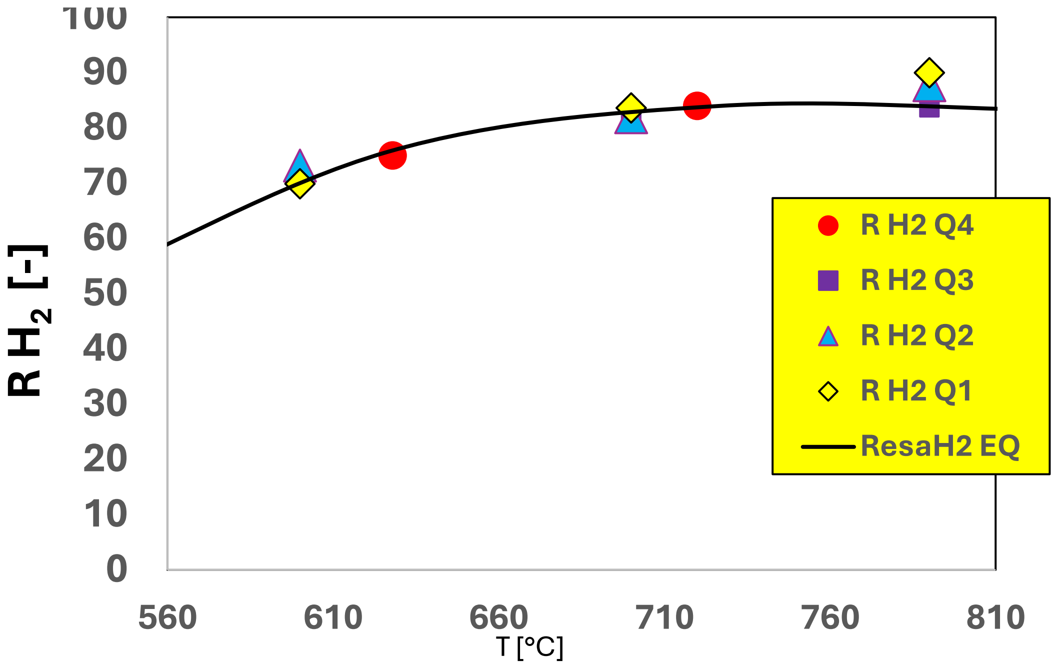
- $Q_1 = 1{,}6$ L/min
- $Q_2 = 3{,}2$ L/min
- $Q_3 = 5{,}3$ L/min
- $Q_4 = 8{,}0$ L/min

Steam/C = 3

Reactions: $CH_4 + H_2O \leftrightarrows CO + 3H_2$

$CO + H_2O \leftrightarrows CO_2 + H_2$





3 METHANE STEAM REFORMING: Ni-catalyzed OBSiC foam

Energetic evaluations at different operating conditions

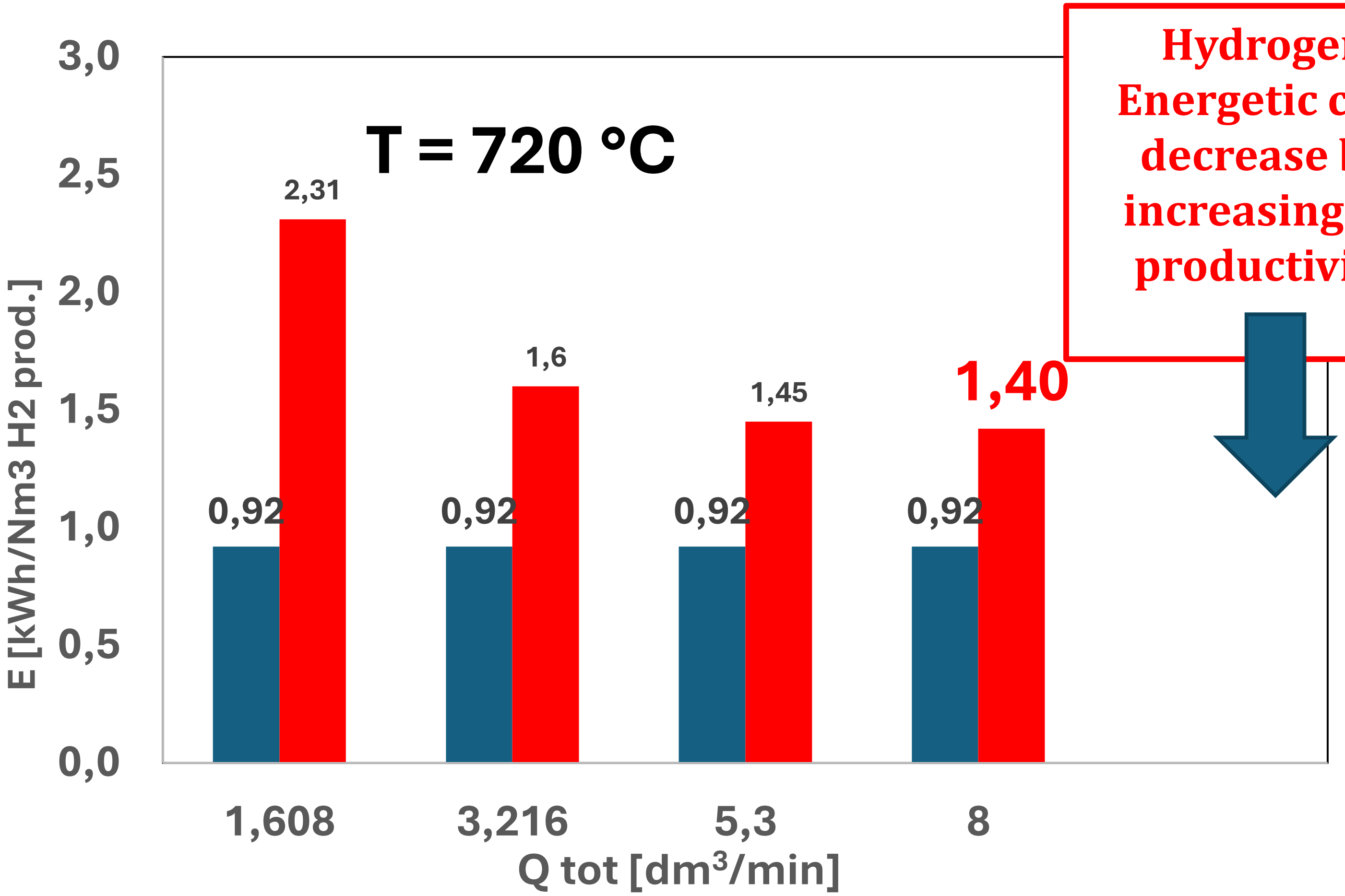
Hydrogen produced:

- Q_1 = 1,6 L/min Q_{H_2} = 0,08 m^3/h
- Q_2 = 3,2 L/min Q_{H_2} = 0,15 m^3/h
- Q_3 = 5,3 L/min Q_{H_2} = 0,26 m^3/h
- Q_4 = 8,0 L/min Q_{H_2} = 0,5 m^3/h

Ideal Energy to produce 1 m^3/h of H_2 calculated by considering entaly changes in a ideal system:

- T_{IN} = 450°C T_{OUT} = 720°C
- S/C = 3
- Equilibrium comp. @ 720°C

Specific energy decrease at higher SV



Hydrogen Energetic cost decrease by increasing its productivity

3 METHANE DRY REFORMING: Ni-catalyzed Si-SiC foam

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This work: 1.40 kWh*Nm^{-3}H$_2$

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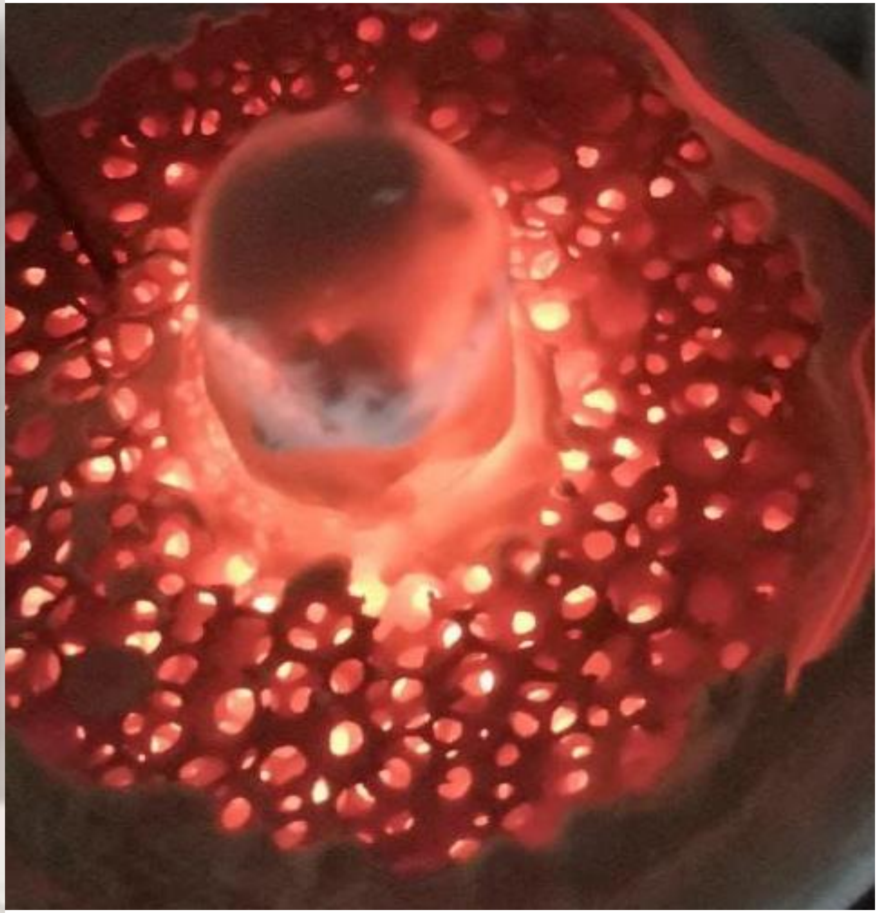
JOULE HEATING TECHNOLOGY

Some examples



COMPARISON AMONG THE STUDIED HEATING METHODS

MICROWAVE ASSISTED HEATING		OHMIC HEATING	
ADVANTAGES	DISASVANTAGES	ADVANTAGES	DISADVANTAGES
• **Inversion of heat flux** • **Selective catalyst heating** • **Elimination of the solid-solid heat transfer limits** • **Possibility of using renewable energy**	• **Difficulty in scaling-up operation;** • **Low Magnetron efficiency (50-60%)**	• **Inversion of heat flux** • **Very high heat flux rate** • **Very high energy transfer efficiency** • **Possibility of using renewable energy** • **Precise control of the T profile**	• Problems of adhesion and stability of the catalytic film over the electrically conductive carriers • Necessity for a specific redesign to optimize catalyst performance • Possible side negative effect of structured substrate

WHAT'S TO REMEMBER

- **The** catalysts and membrane **coupling can be optimized by electrifying** high conductive **structured catalyst**
- **The microwave heating and joule/ohmic heating are two promising electrification methods**
- **Suitable materials** (**MW susceptor and hi-conductive carrier**) must be chosen for the catalyst
- **Reactor geometry** is the key to magnifying the electromagnetic field **in the MW heating application**
- **Energy consumption results have shown values close or lower than that reported for other electrified processes, including the modern electrolysers**

Pro ceed LAB
Processes & Catalysis for Energy & Environment depollution

THE TEAM

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Thank you for you kind attention