

# PRINTCR3DIT: Process Intensification through Adaptable Catalytic Reactors made by 3D Printing

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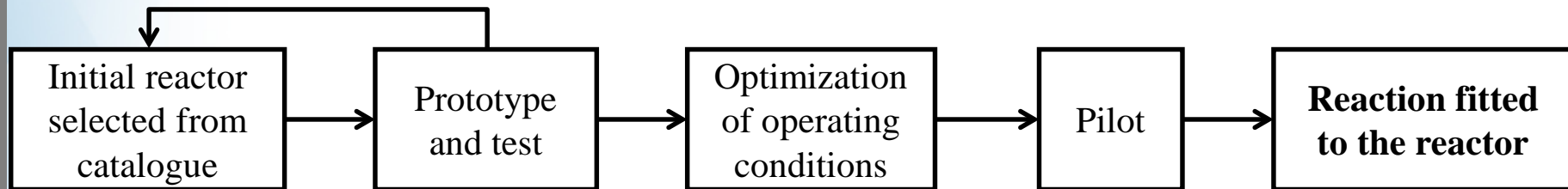
# Outline

- **Project introduction**
- **Application example**
  - Technology
  - Process intensification concept
  - Catalytic approach
- **3D hybrid catalysts**
  - Design
  - Production
- **Demonstrator: design & results**
- **Conclusions**
- **Acknowledgments & announcements**

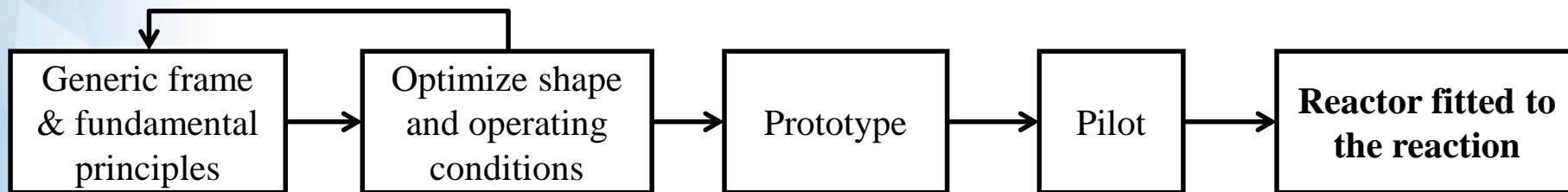


# Motivation

Current reactor design & optimization



New paradigm in reactor design & optimization



**Design the best reactor for your particular purpose**

# Consortium



## 13 Partners:

Industrial: 4



SME: 4



R&D: 4

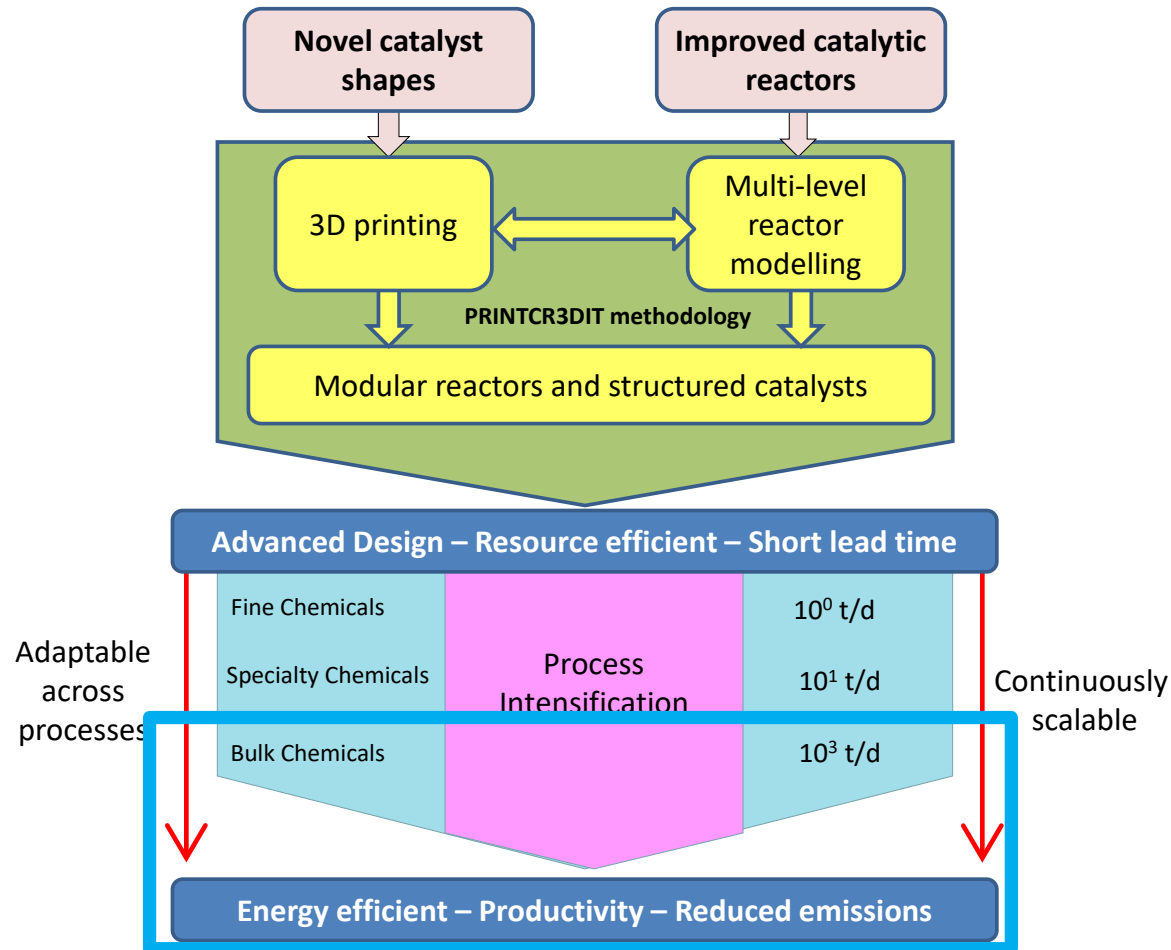
Academic: 1

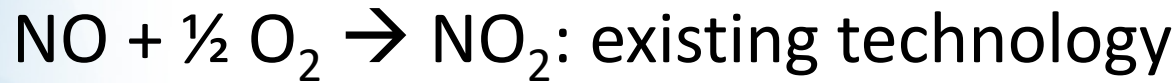


Duration: 36 months, 1/10/2015 – 30/9/2018

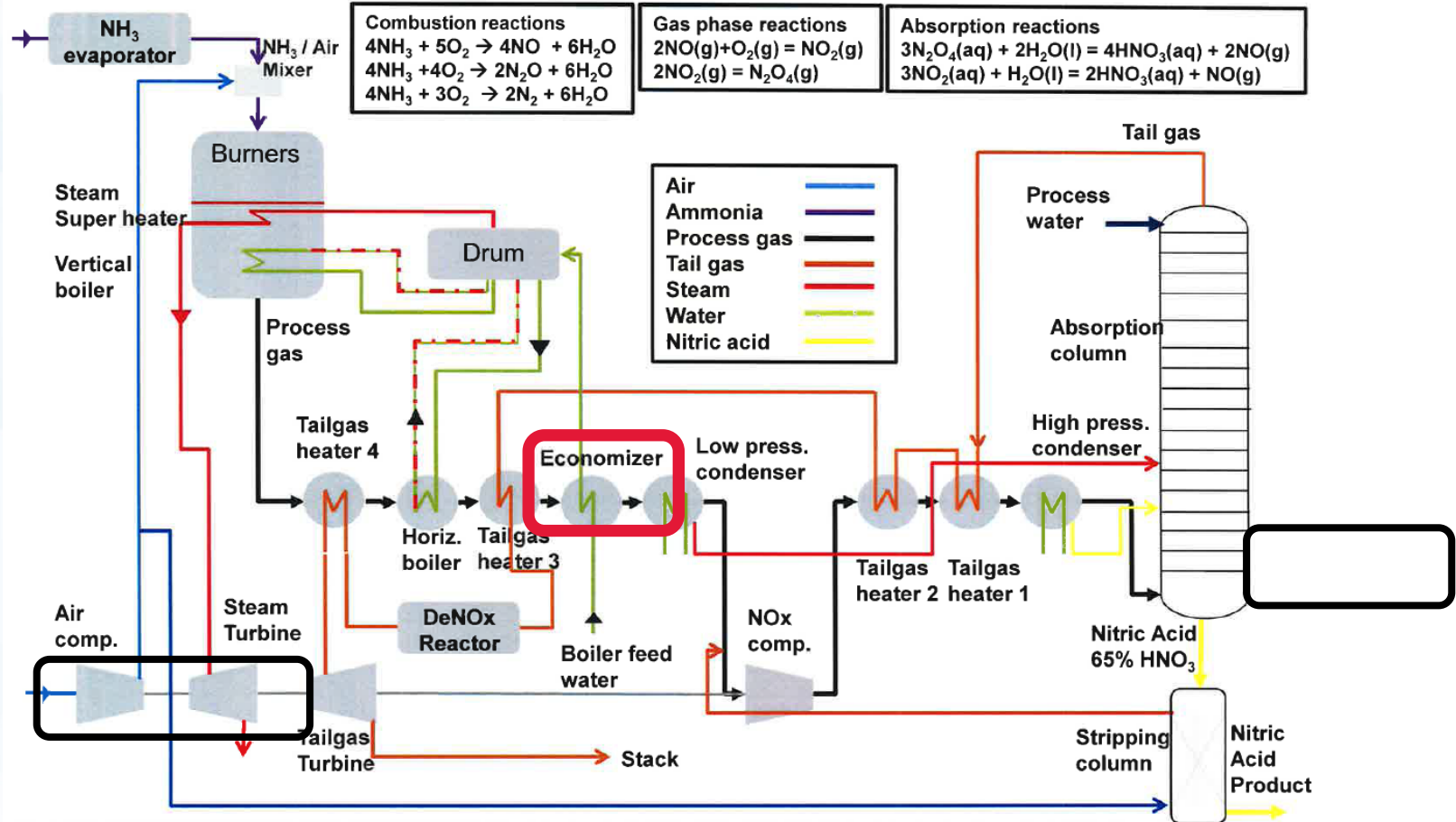
Budged: 5,493,891 €

# PRINTCR3DIT: Process Intensification Through Adaptable Catalytic Reactors Made By 3D Printing





### Modern Medium Dual Pressure Process



$\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2$ : existing technology

### Economizer: heat-exchange reactor

$\text{NO} + \text{N}_2 +$   
 $\text{H}_2\text{O} + \text{O}_2$

300 °C

1-10 bar,

$\sim 20 \text{ m/s}$

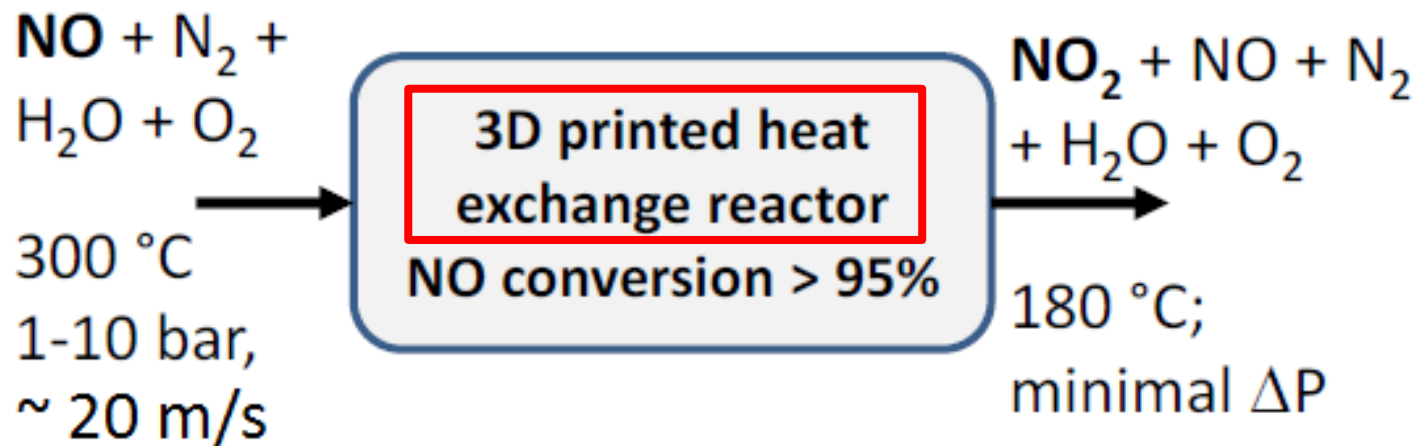
Non-catalytic  
Horizontal boiler  
NO conversion  $\sim 24\%$

$\text{NO}_2 + \text{NO} + \text{N}_2$   
 $+ \text{H}_2\text{O} + \text{O}_2$

180 °C;  $\Delta P \approx 0$



Mass transfer rate is slower than heat transfer rate. We want to increase NO conversion at high temperature to recover the energy of oxidation (-114 kJ/mol) at higher temperatures.

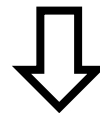




# Challenge No. 1



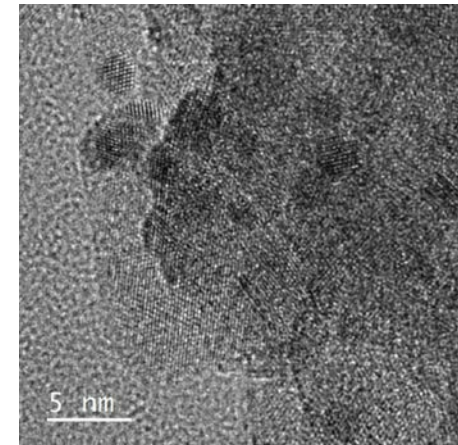
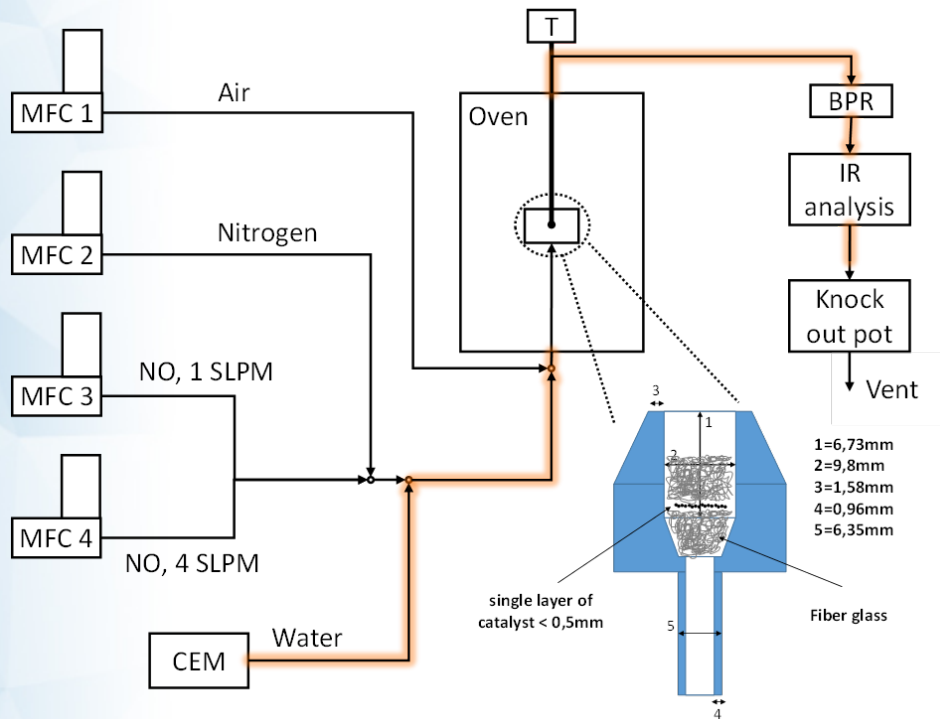
Lack of normative: No entity is qualifying 3D printed reactors.



Solution: design the internals (catalyst) and use in standard reactor

# Challenge No. 2

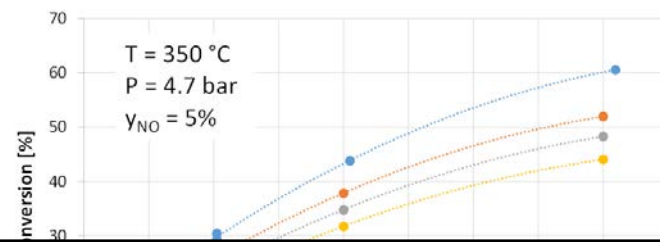
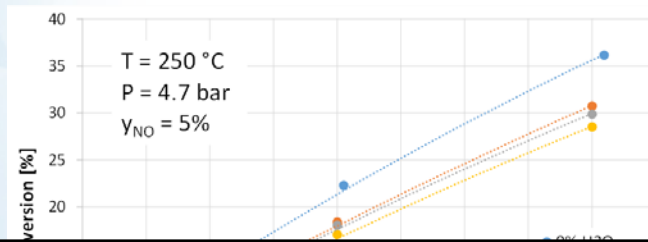
NO oxidation mechanisms known only at the ppm level (not %)




**VERY CORROSIVE REACTION!!!**

# Catalytic results

We have measured 819 points to determine the kinetic equation





**Article**

[pubs.acs.org/IECR](https://pubs.acs.org/IECR)

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Cite This: *Ind. Eng. Chem. Res.* 2018, 57, 10180–10186

## Process Intensification in Nitric Acid Plants by Catalytic Oxidation of Nitric Oxide

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# 3D printing

## Simplified description of 3D printing techniques (by 2015)

### Fuse deposition

Xy + z motors with a "dispenser". Catalyst can be embedded in a polymer or in a slurry. Heat required to remove the polymer. Low-medium accuracy.

### Laser sintering

Heat used to sinter particles. Extremely high T for ceramic materials. Non porous materials. Print with very high accuracy.

### Stereolithography

Low-power laser or light to make a polymerization. Ceramic in the slurry. Heat required to remove the polymer. Very high accuracy.

We want high accuracy for design!

# Catalyst design: multiple functionalities

Body of aluminum → fast heat transfer

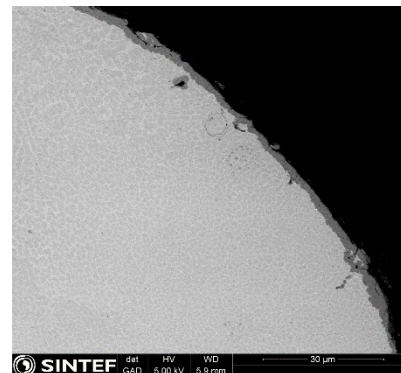


Fast mass transfer

Low pressure drop

Fast heat transfer

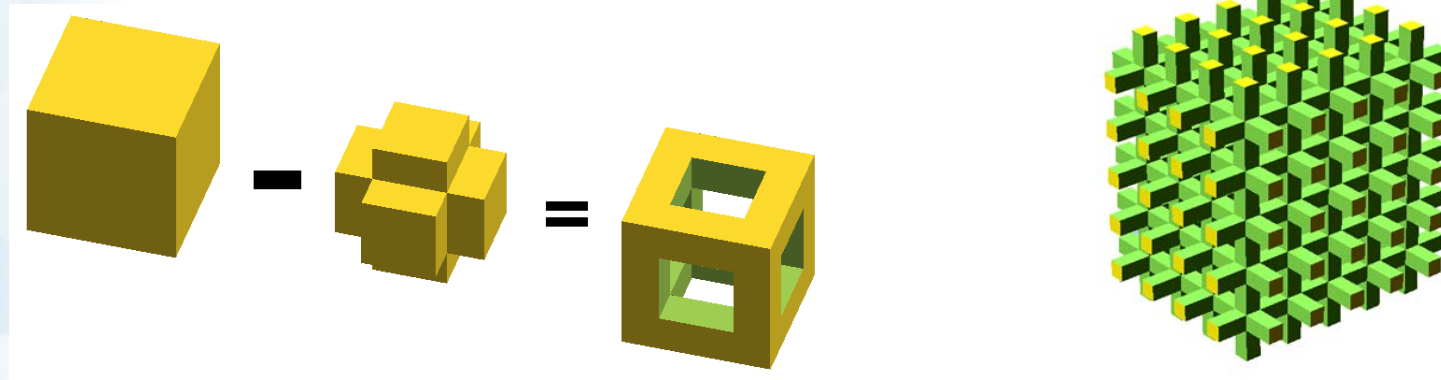
Heart of alumina → fast diffusion; low  $\Delta P$



# Catalyst design: macro-level control

Design of iso-reticular (perfect) foams.

Make one cell at the time with mathematical operations. Then replicate over space.

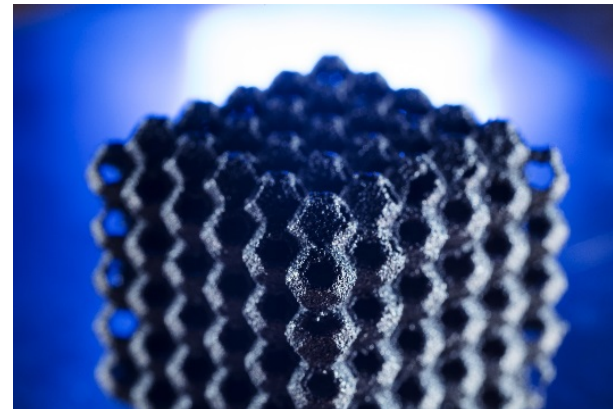
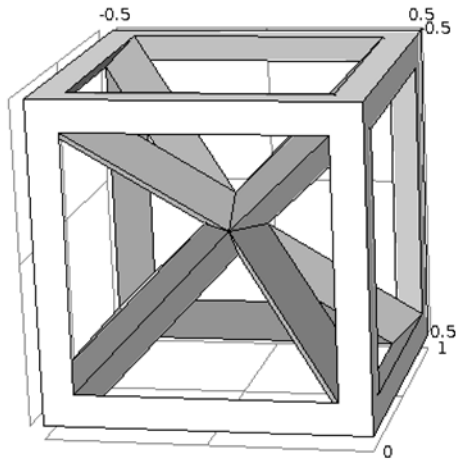
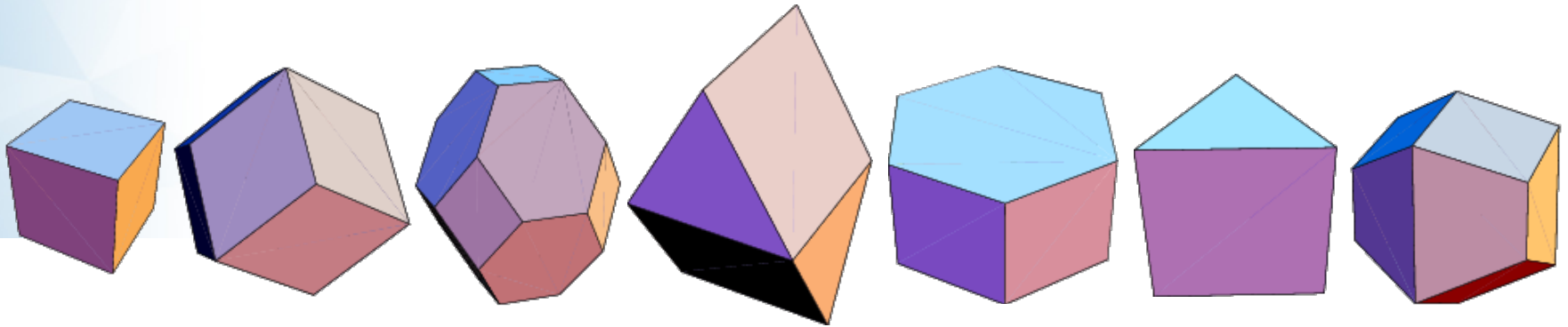


Shape	Porosity	Strut width
Cubic cell	$\epsilon_f = \frac{[3(L - P)P^2 - 2P^3]}{L^3}$	$(L - P)$



# Catalyst design: macro-level control

To change the porosity vs strut dimension, change the solid.



Description / title **Method for manufacturing a porous foam support, and porous foam supports for catalytic reactors, adsorption processes and energy storage**

Status In force ⓘ  
 Legal status 2017.11.20 Granted  
 Detailed status 2017.11.10 Granted (B1)

Patent number 341465

Application number 20160738

Filed 2016.05.03

Priority None

Case type National

Effective date 2016.05.03

Expiry date 2036.05.03

Publicly available 2017.11.06

Granted 2017.11.20

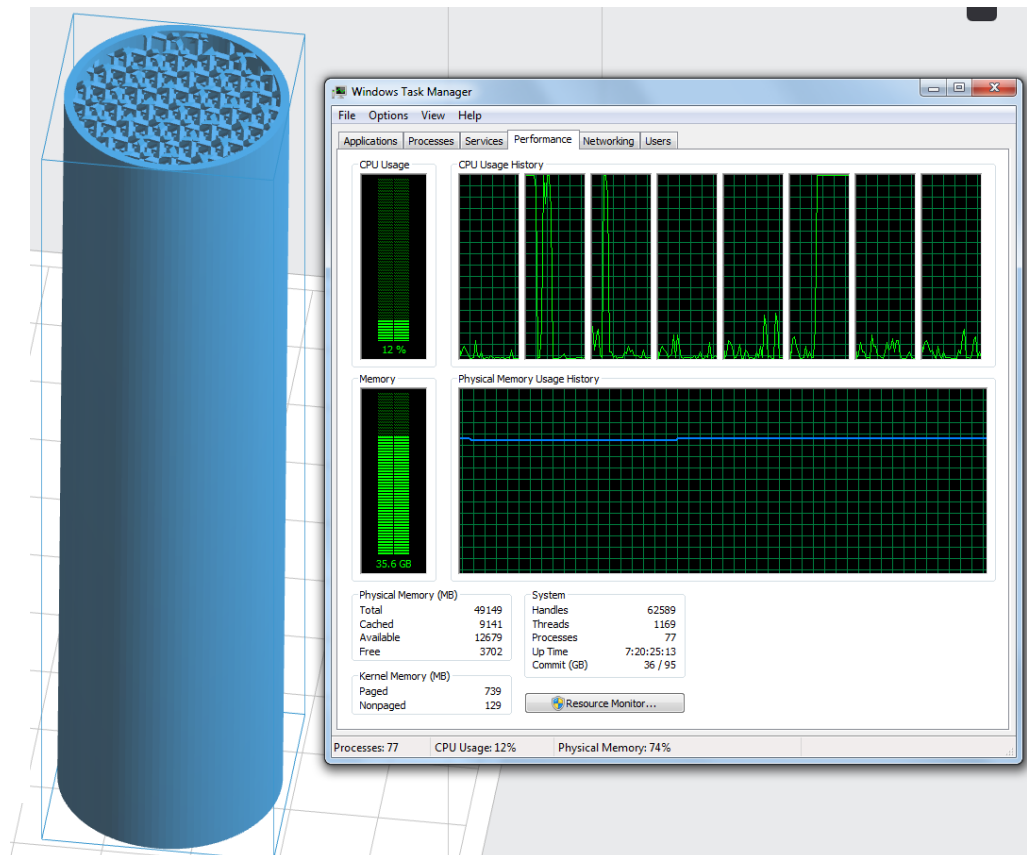
Applicant Sintef TTO AS (NO)

Owner Sintef TTO AS (NO)

Inventor Carlos Grande (NO)

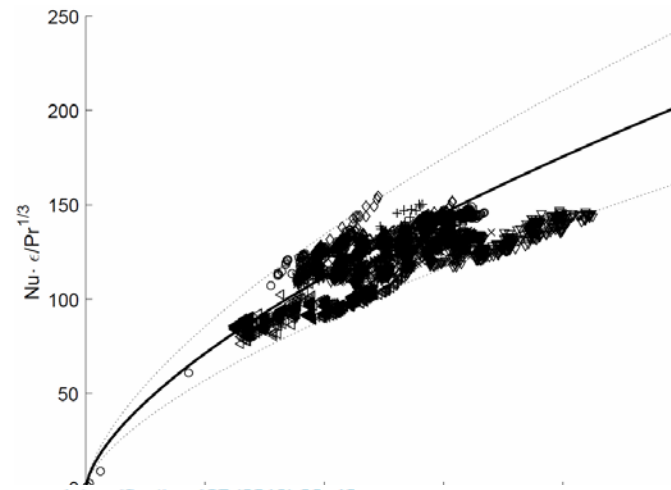
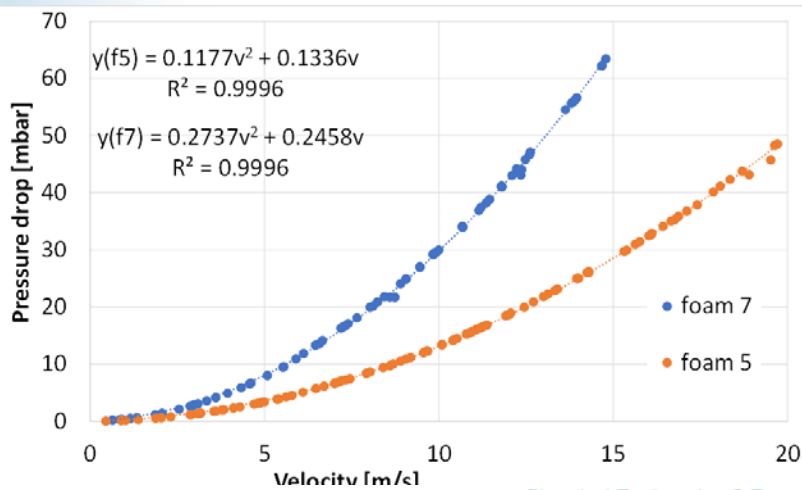
Agent BRYN AARFLOT AS (NO)

pro-level control  
 as strut dimension, change the solid.





# Pressure drop & heat transfer



Chemical Engineering & Processing: Process Intensification 127 (2018) 36–42



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Contents lists available at ScienceDirect

## Chemical Engineering & Processing: Process Intensification

journal homepage: [www.elsevier.com/locate/cep](http://www.elsevier.com/locate/cep)



### Pressure drop and heat transfer properties of cubic iso-reticular foams

Núria F. Bastos Rebelo<sup>a</sup>, Kari Anne Andreassen<sup>a</sup>, Luis I. Suarez Ríos<sup>b</sup>, Juan C. Piquero Cambor<sup>b</sup>, Hans-Jörg Zander<sup>c</sup>, Carlos A. Grande<sup>a,\*</sup>

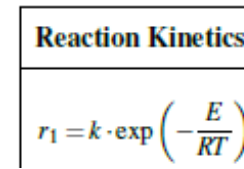
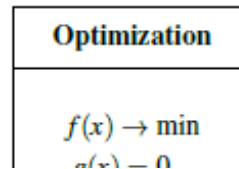
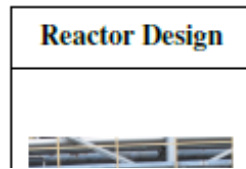
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# Reactor modelling: problem approach



$$\text{div } \dot{n}_i = \sum_j v_{ij} \cdot r_j \quad (\text{species mass balance})$$

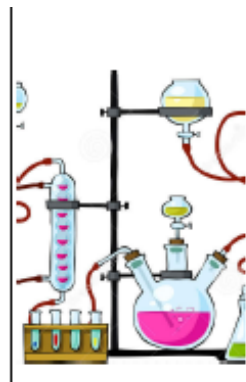
$$\text{div } \dot{q} = 0 \quad (\text{heat balance})$$

$$\text{div} (\rho \cdot u \cdot u_i) = -\text{div}(p \cdot e_i) + \rho \cdot g_i + \left. \frac{\partial p}{\partial x_i} \right|_{\text{irrev.}} \quad (\text{momentum balance})$$

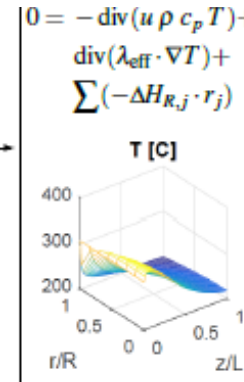
$$\rho = f(p, T, x_i) \quad (\text{state equation})$$

$$h = f(p, T, x_i) \quad (\text{thermal state equation})$$

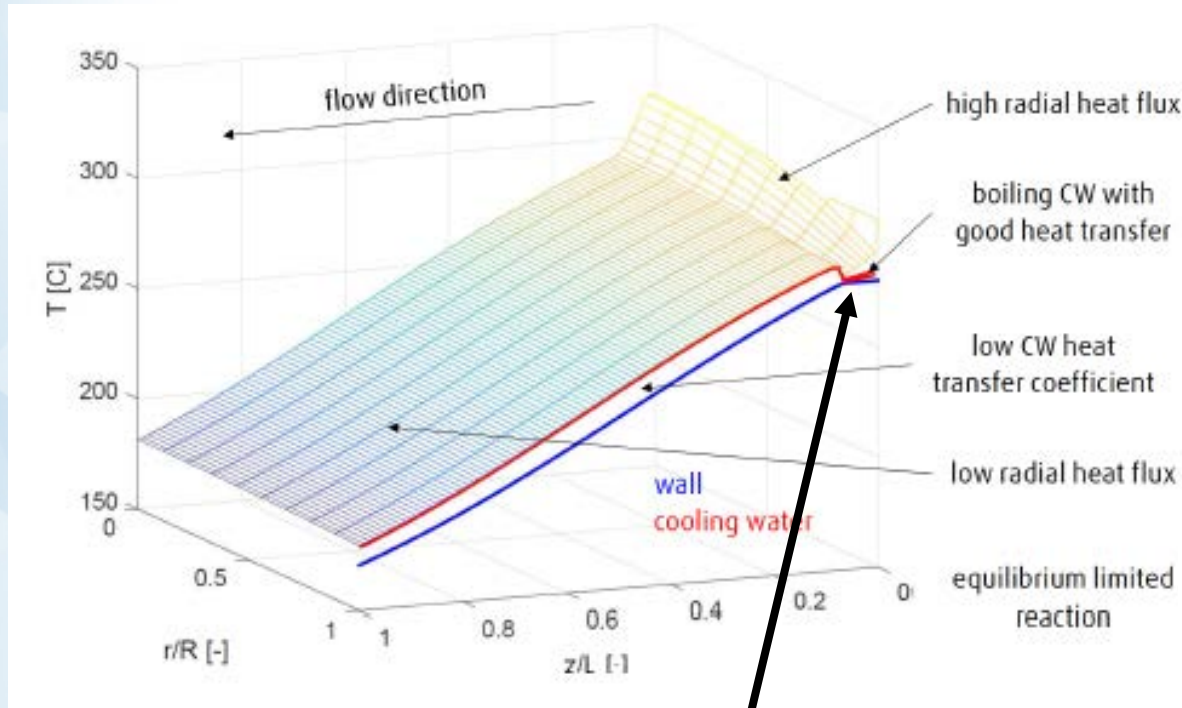
$$r_j = f(p, T, x_i) \quad (\text{reaction rates})$$



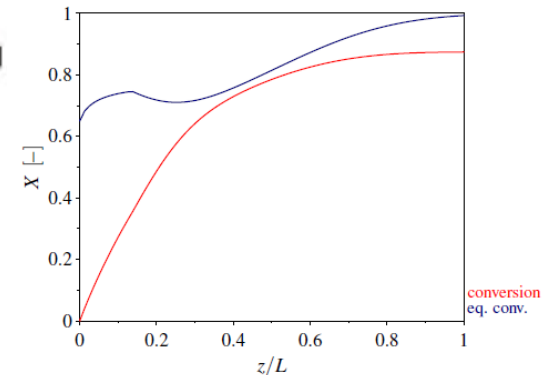
$$\begin{aligned} Nu &= \frac{\alpha \cdot L}{\lambda} \\ Nu &= f(Re, Pr) \\ \Lambda &= \frac{\lambda_{\text{eff}}}{\rho \cdot c_p \cdot u \cdot L} \\ \Lambda &= f(Re) \\ \zeta_L &= \frac{dp/dz \cdot L}{\frac{1}{2} \cdot \rho \cdot u^2} \\ \zeta_L &= f(Re) \end{aligned}$$



# Reactor modelling: results → learning for design



Boiling of water!



## Scale-up & demo decisions

- The demo will replicate 1 tube of the multi-tubular economizer.
  - Length: 7.5m. Diameter: 1 inch external.
- Performance will be monitored in different configurations
  - The length will be divided into 4 tubes of 1.85m
- The heat transfer fluid is pressurized water.
  - It can boil so the sections will be slightly tilted.
- The system will have real feed gas coming from another demo
  - Many variables monitored and gas returned to main unit



## Catalyst scale-up

- All the catalyst support was printed in the same run.
- Not problem-free
  - The length – diameter ratio complicates the printing.
- Powder cleaning had to be solved.

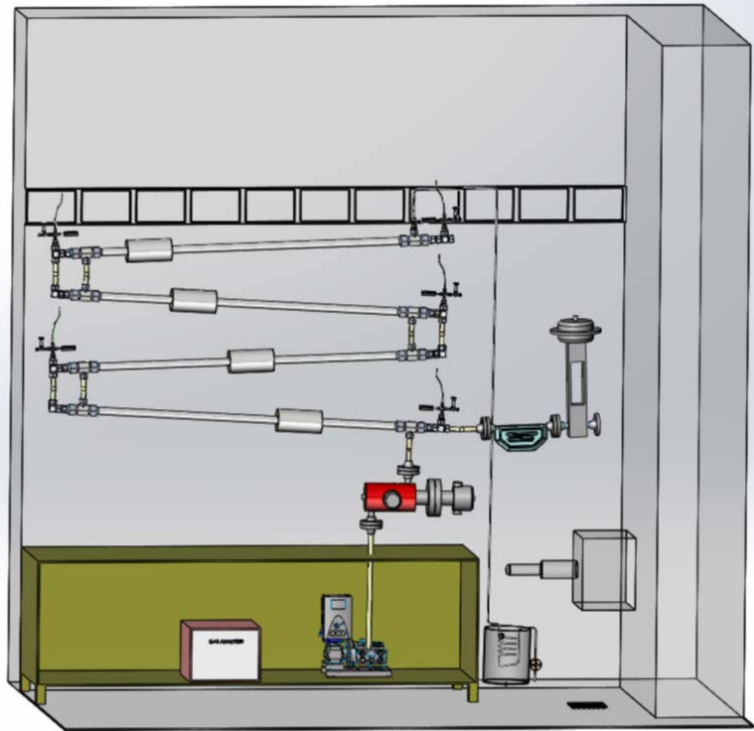
Catalyst



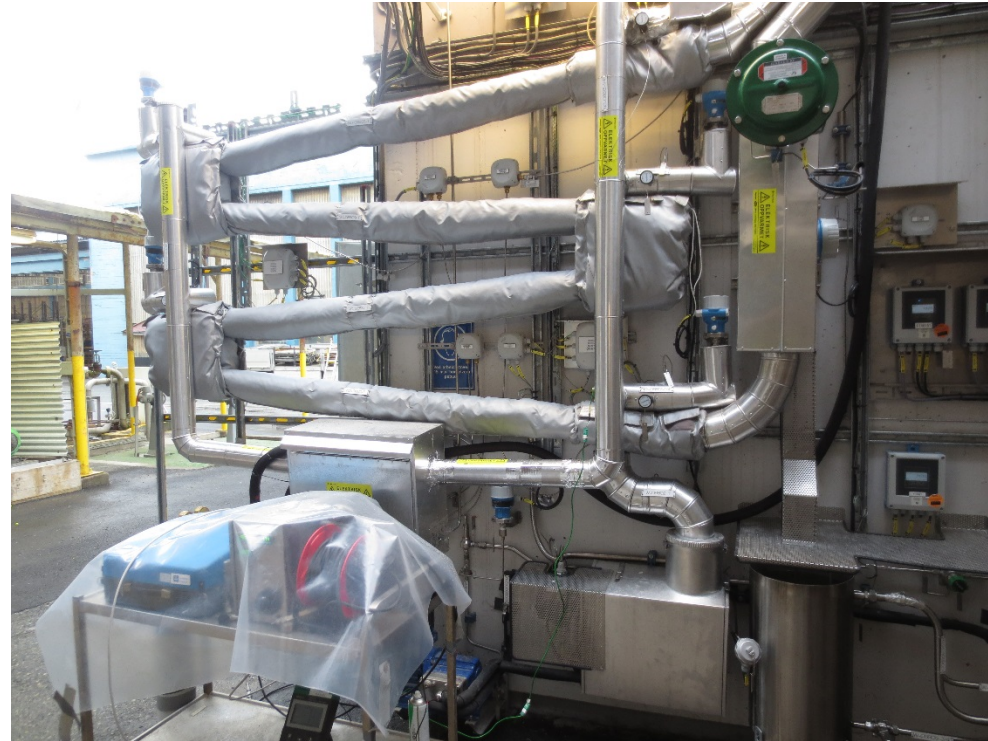
As received



# Demo unit



Design



The unit

# Results

Tests in course. We will evaluate:

- 1- The equipment
- 2- The effect of heat transfer
- 3- The effect of 3D printing
- 4- The catalyst preparation



# Conclusions

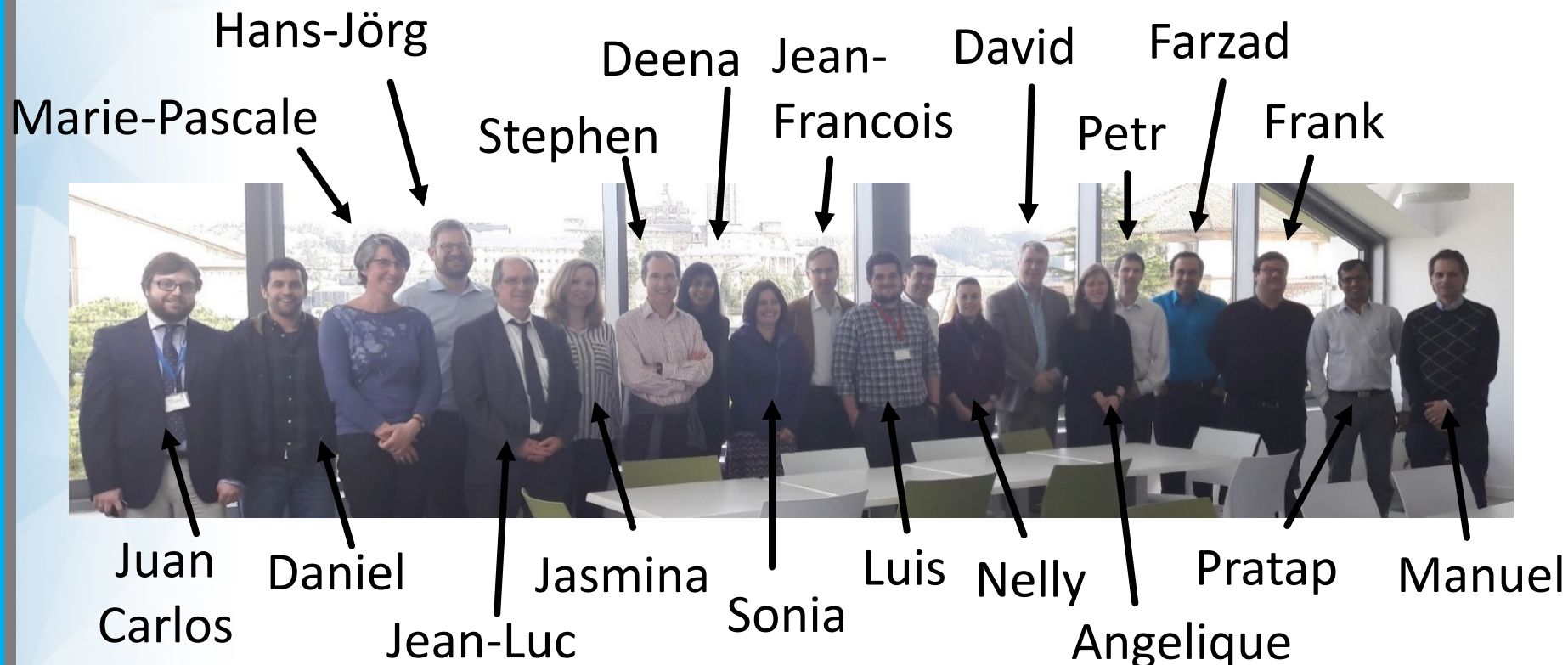
- Normative should be the next step
- Is possible to produce a multi-functional catalyst
- The initial tests confirm that a catalytic process can work
- Using 3D printing is possible to obtain new shapes that can unlock new operation modes of processes. This statement is valid for new process design or for retrofitting.





The project leading to this application has received funding from the *European Union's Horizon 2020 research and innovation programme* under grant agreement No 680414.

The project belongs to the SPIRE programme [www.printcr3dit.eu](http://www.printcr3dit.eu).



# Announcement

[www.printcr3dit.eu](http://www.printcr3dit.eu)

THE FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION  
HORIZON 2020

YARA

SINTEF

SPRE  
Sustainable Process Industry through  
Resource and Energy Efficiency

20 SEP | 9 AM  
Skjærgården Hotel,  
Porsgrunn, Norway

**PRINTCR3DIT: DEMO OF FIRST  
3D PRINTED CATALYSTS**

