Process Intensification by 3D printing technologies applied to NO ($\rightarrow NO_2$) oxidation

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H2020: PRINTCR3DIT - Process Intensification through Adaptable Catalytic Reactors made by 3D Printing
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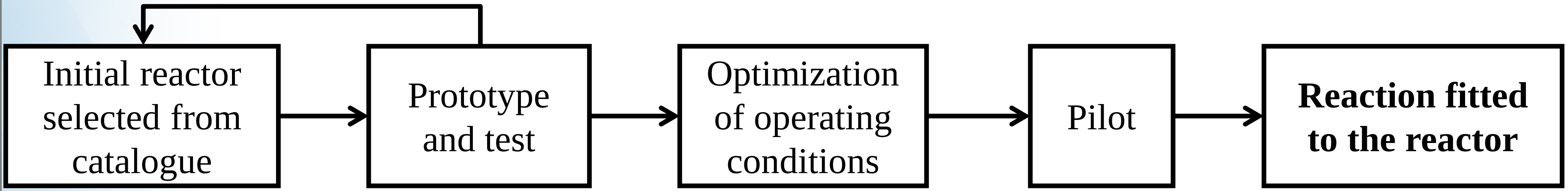
Outline

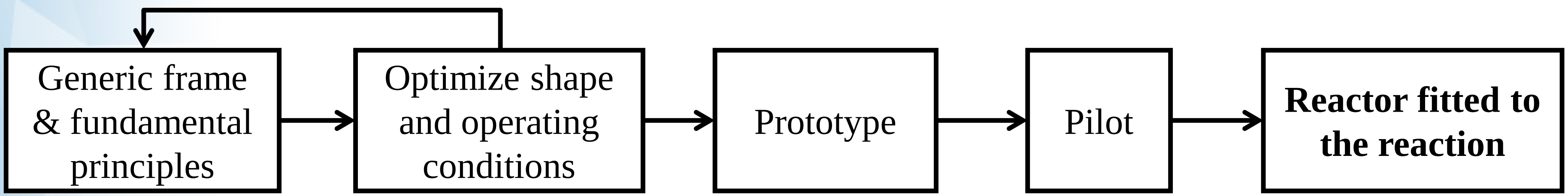
- **Project introduction**
- **NO → NO_2 oxidation**
  - **Technology**
  - **Process intensification concept**
  - **Catalytic approach**
- **Structured catalysts**
  - **Design**
  - **Production**
- **Demonstrator: design & results**
- **Conclusions**
- **Acknowledgments & announcements**

Motivation

Current reactor design & optimization



New paradigm in reactor design & optimization



Design the best reactor for your particular purpose

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Consortium

13 Partners:

Industrial: 4

SME: 4

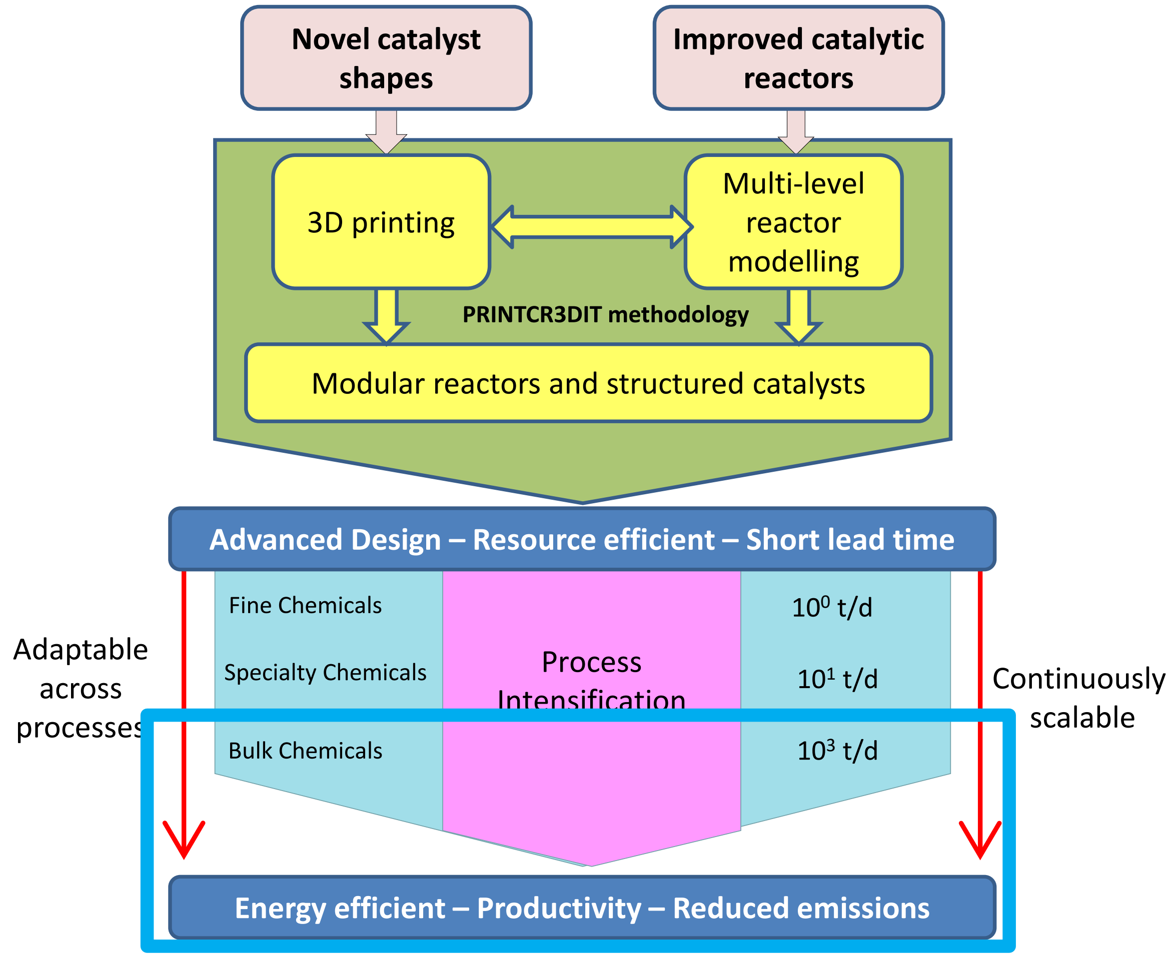
R&D: 4

Academic: 1

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

Budged: 5,493,891 €

PRINTCR3DIT: **Pr**ocess **Int**ensification Through Adaptable **C**atalytic **Re**actors Made By **3D** Printing



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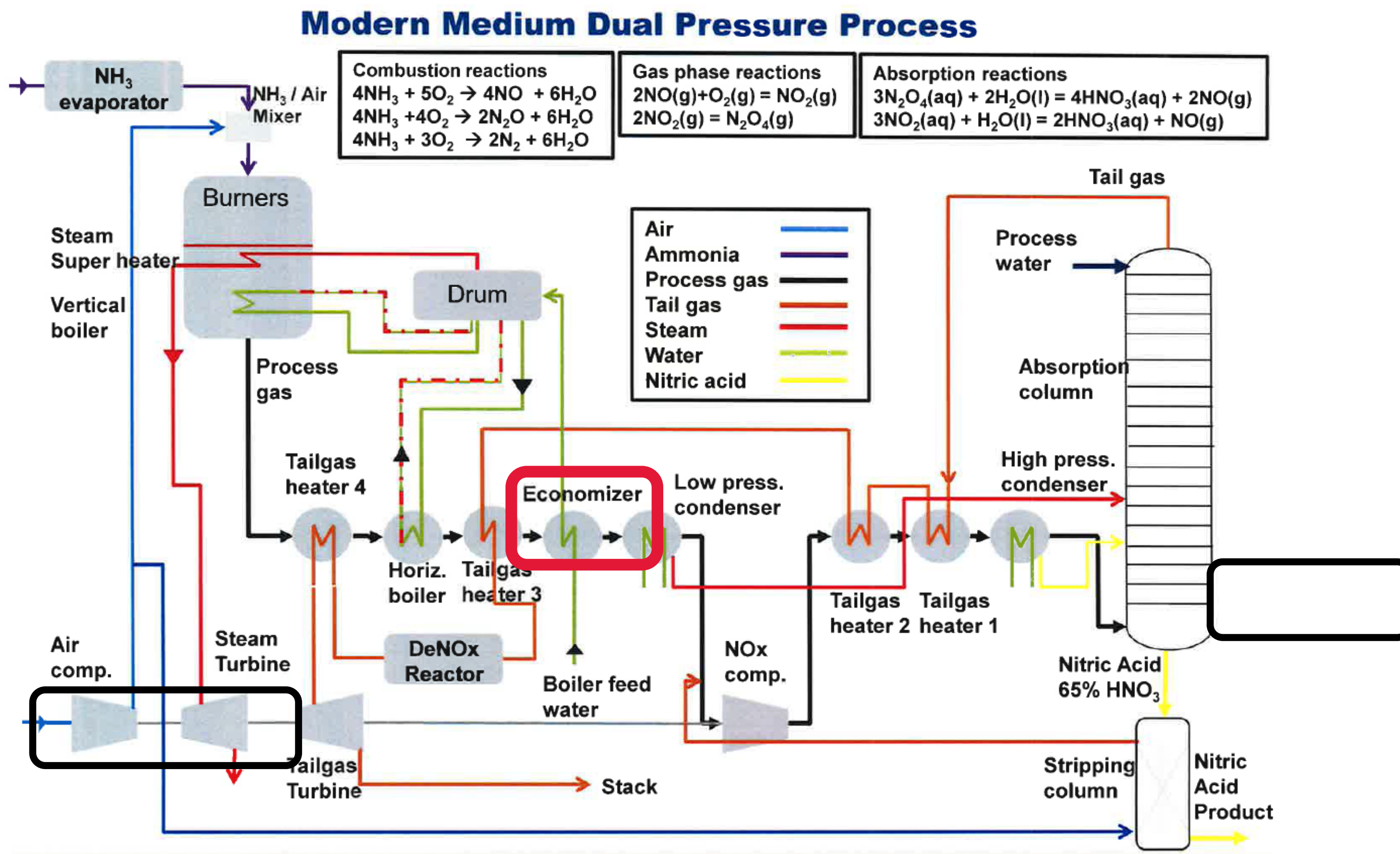
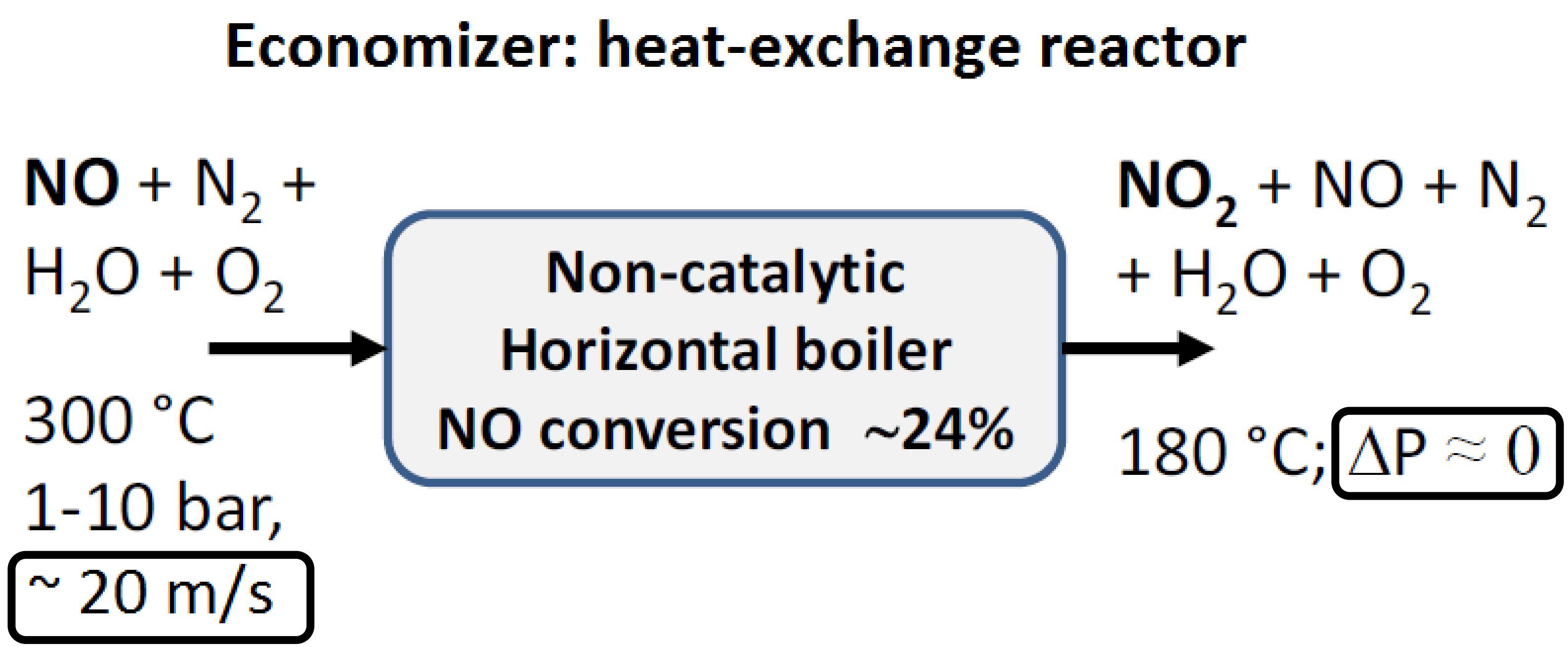
$NO + ½ O_2 \rightarrow NO_2$: existing technology

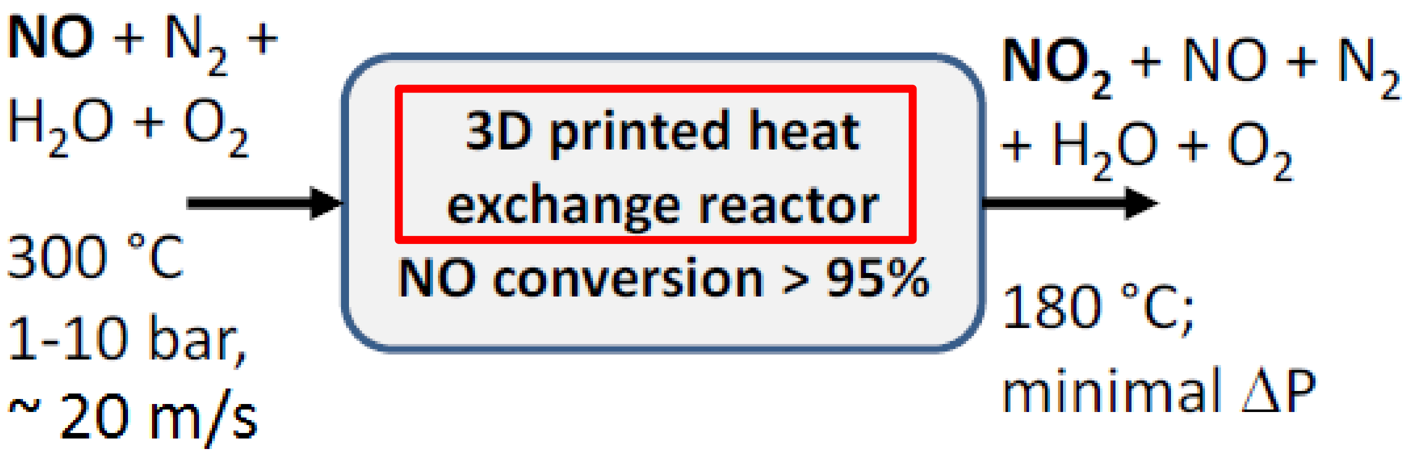


$NO + ½ O_2 \rightarrow NO_2$: existing technology



$NO + ½ O_2 \rightarrow NO_2$: process intensification

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

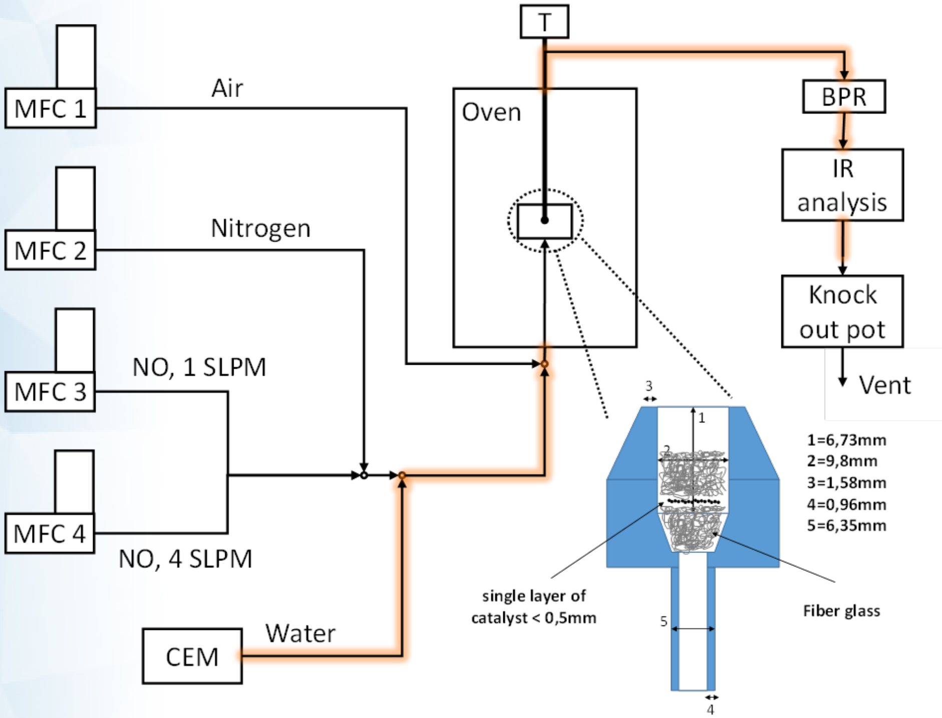
Lack of normative: No entity is qualifying 3D printed reactors.

⇩

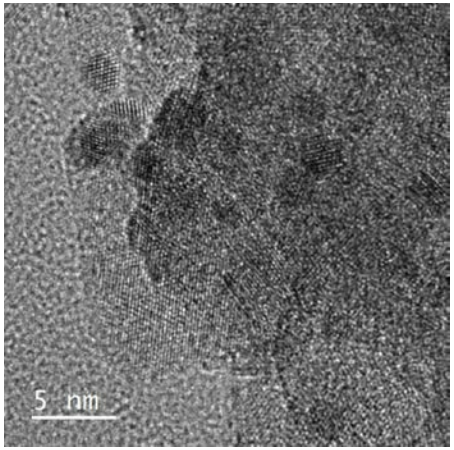
Solution: design the internals (catalyst) and use in standard reactor

Challenge No. 2

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



$Pt – Al_2O_3$



VERY CORROSIVE REACTION!!!

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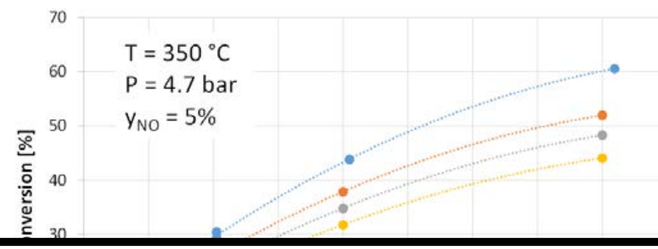
Catalytic results

We have measured 819 points to determine the kinetic equation



I&EC research
Industrial & Engineering Chemistry Research

Article

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

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3D printing

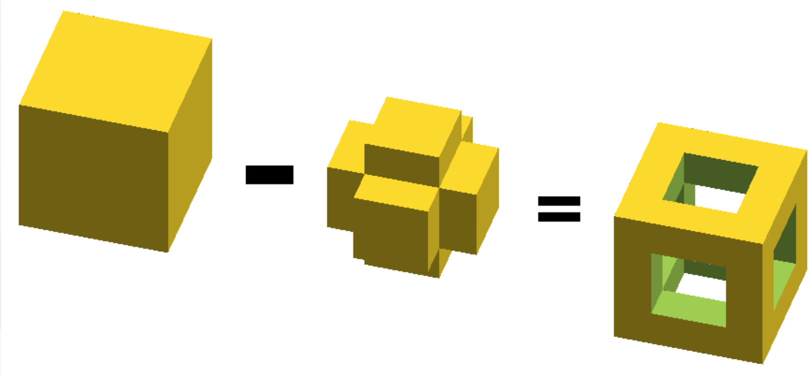
Simplified description of 3D printing techniques (by 2015)

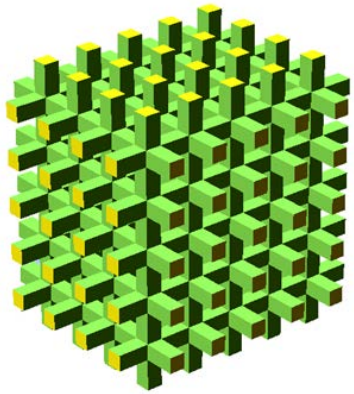
Fuse deposition	Laser sintering	Stereolithography
Xy + z motors with a "dispenser". Catalyst can be embedded in a polymer or in a slurry. Heat required to remove the polymer. Low-medium accuracy.	Heat used to sinter particles. Extremelly high T for ceramic materials. Non porous materials. Print with very high accuracy.	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: macro-level control

Design of iso-reticular (perfect) foams.
Make one cell at the time with mathematical operations. Then replicate over space.

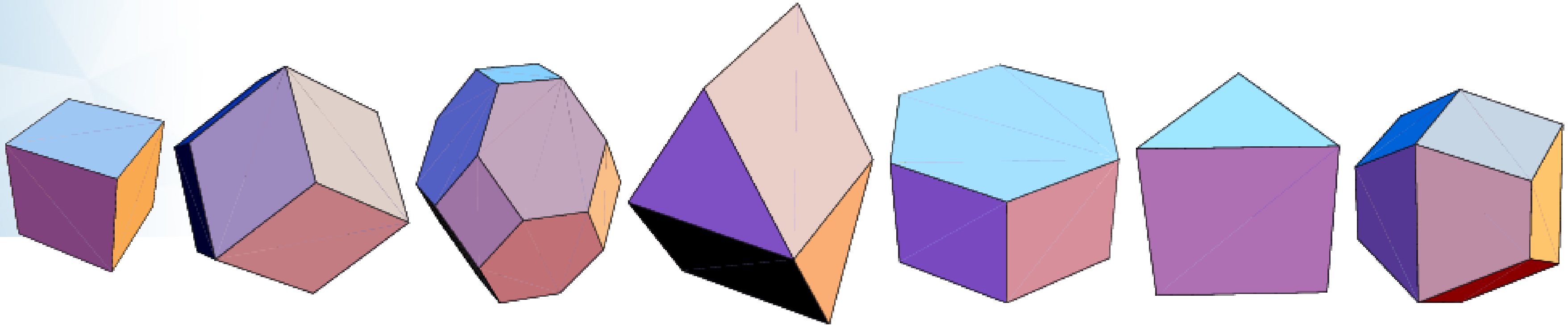


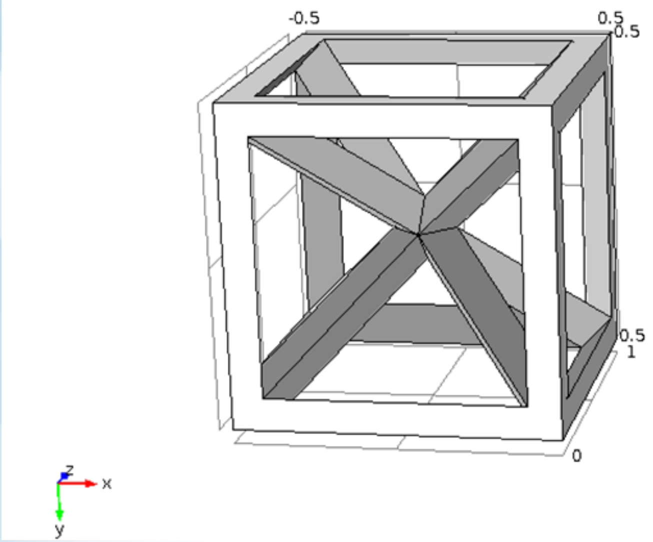


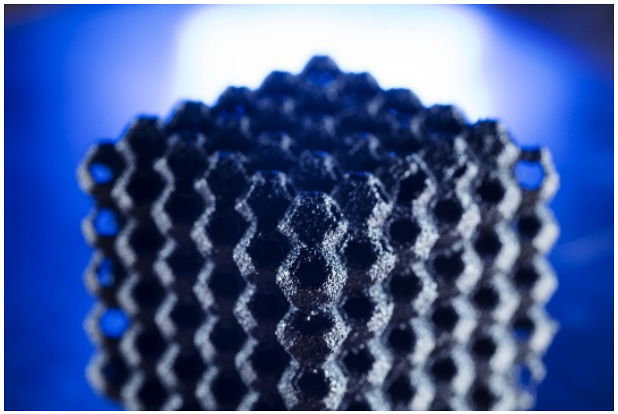
Shape	Porosity	Strut width
Cubic cell	$\varepsilon_f = \frac{[3(L-P)P^2 - 2P^3]}{L^3}$	$(L-P)$

Catalyst design: macro-level control

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







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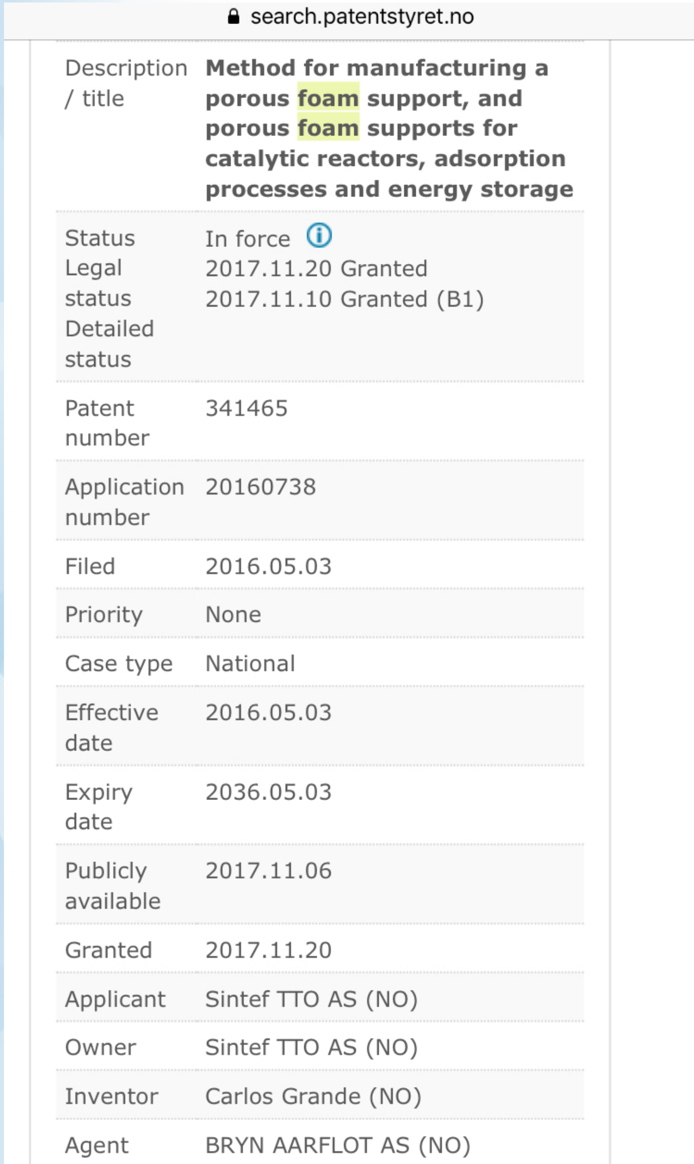
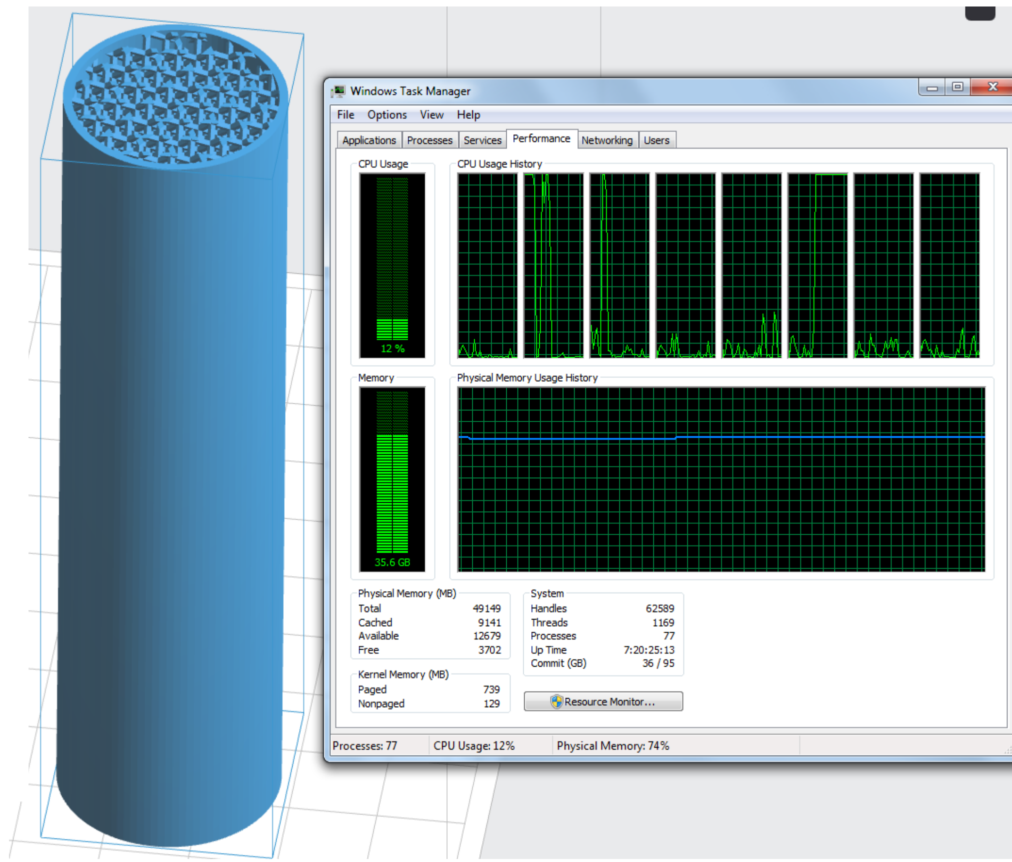
ro-level control

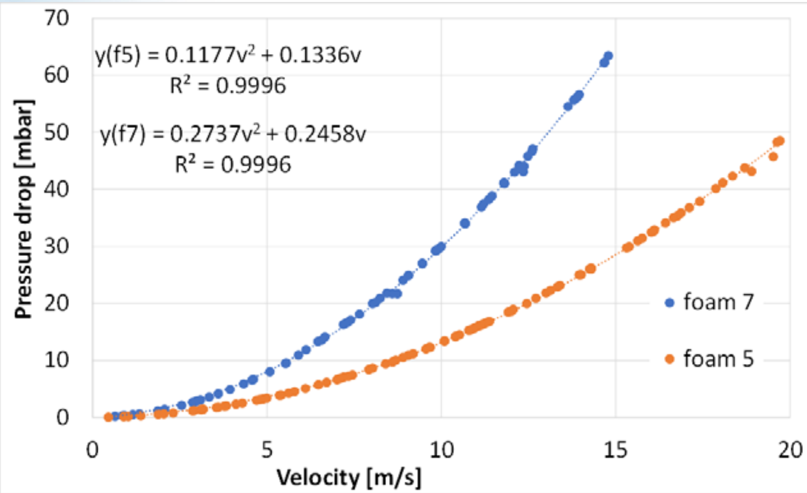
s strut dimension, change the solid.

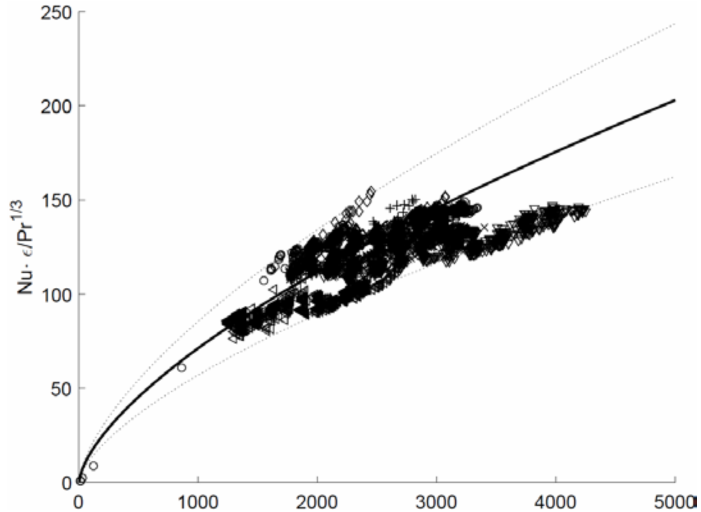

search.patentstyret.no

Description / title	**Method for manufacturing a porous foam support, and porous foam supports for catalytic reactors, adsorption processes and energy storage**
Status Legal status Detailed status	In force 2017.11.20 Granted 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)



Pressure drop & heat transfer





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

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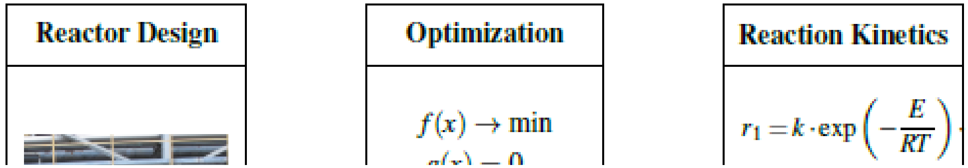
Reactor modelling: problem approach



$$\operatorname{div} \dot{n}_i = \sum_j \nu_{ij} \cdot r_j \qquad \text{(species mass balance)}$$

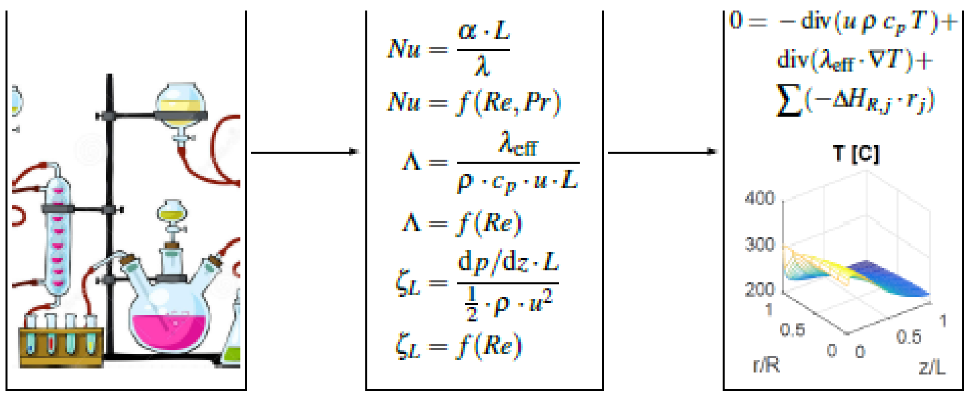
$$\operatorname{div} \dot{q} = 0 \qquad \text{(heat balance)}$$

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

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

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

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



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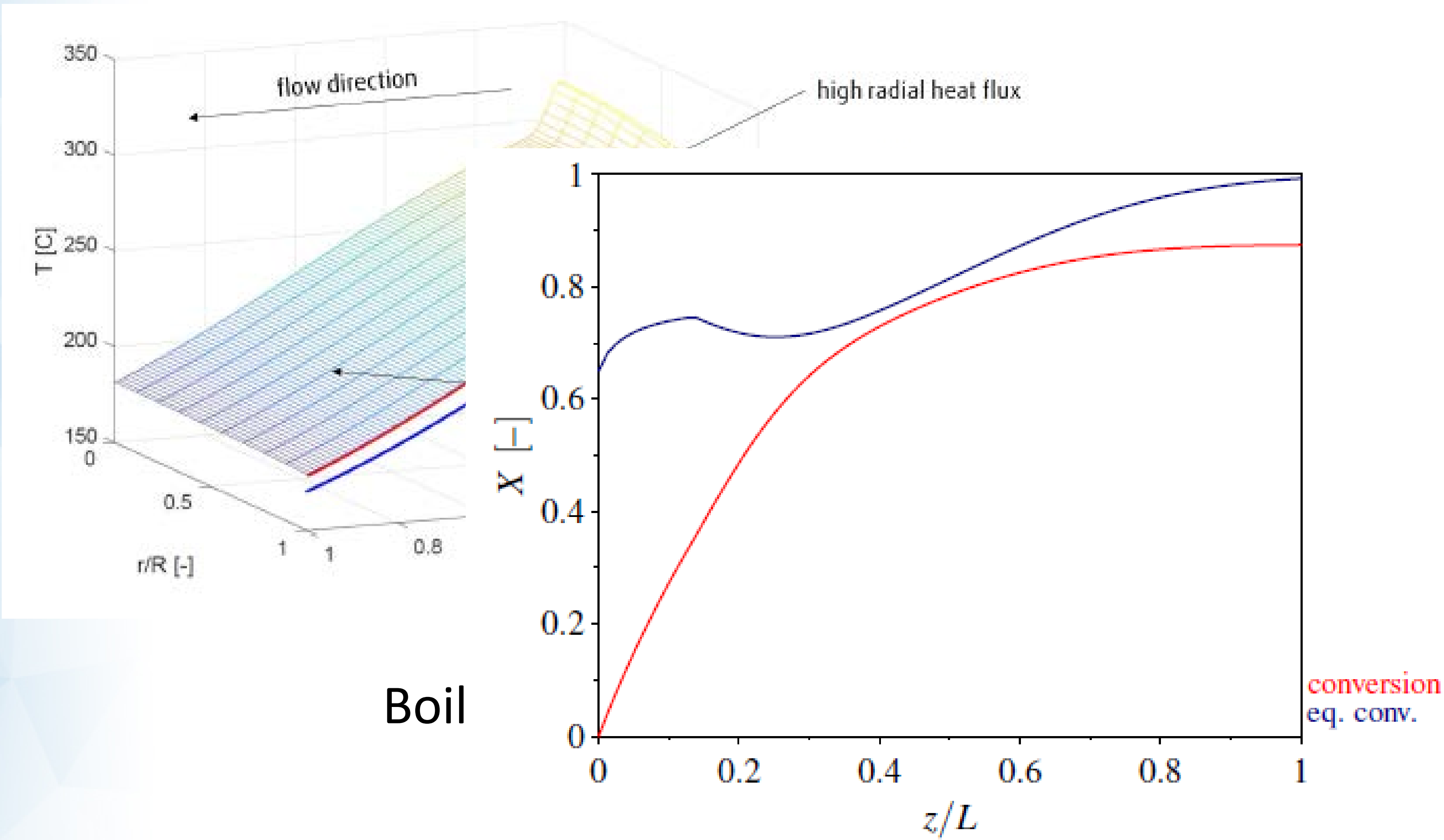
Reactor modelling: results → learning for design



Boil

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

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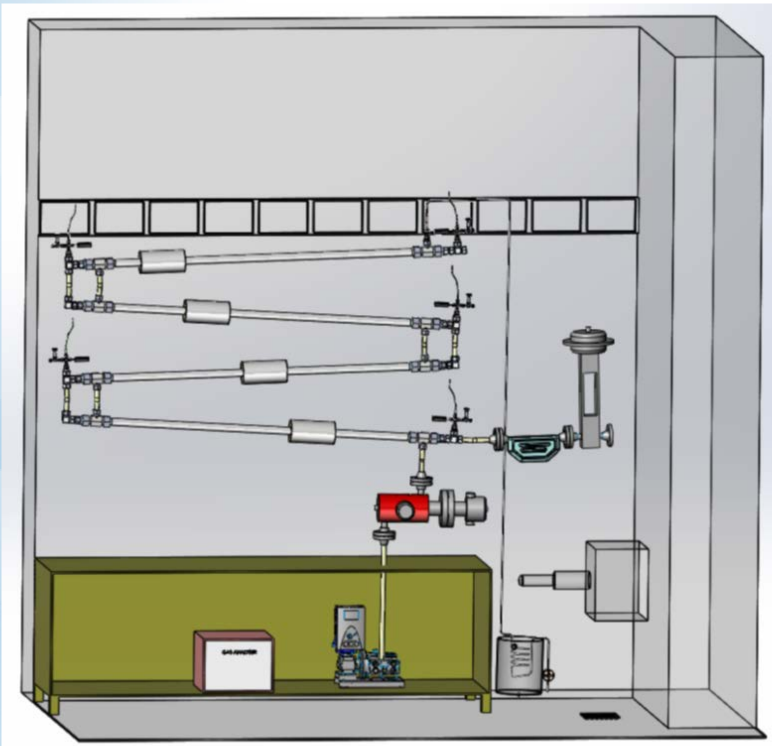
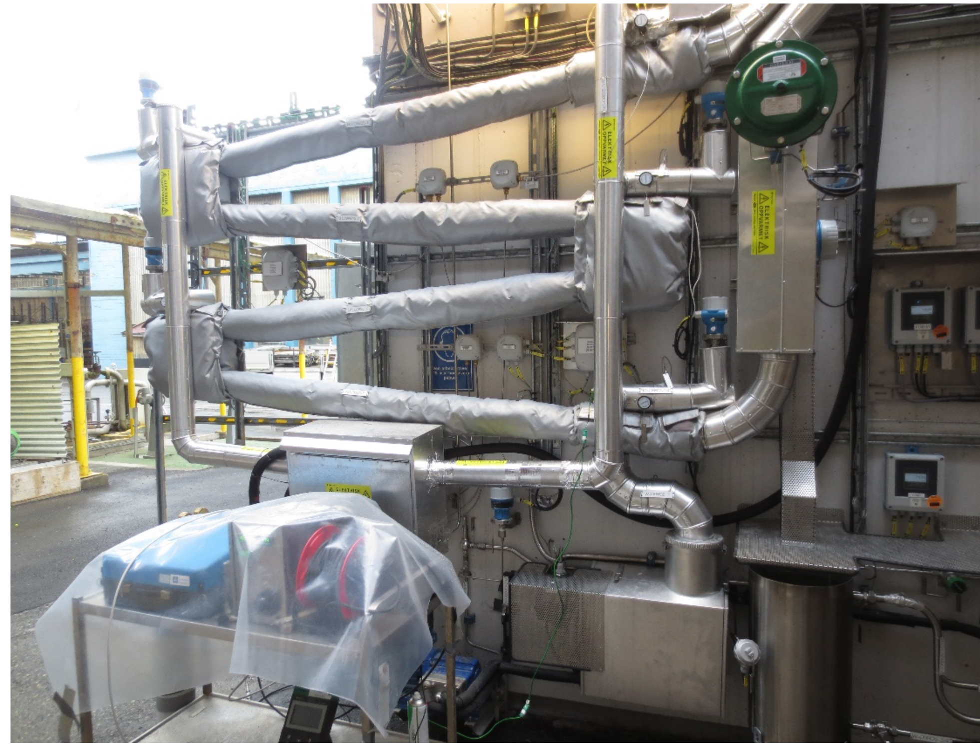
Demo unit



Design



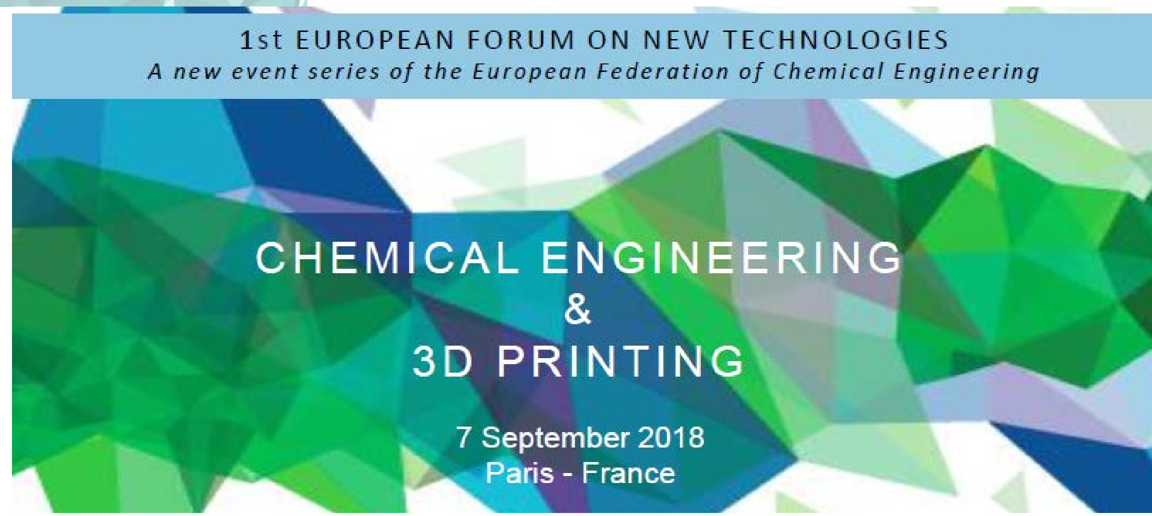
The unit

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.

Announcements

www.printcr3dit.eu



PRINT CR3DIT

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