HYDRODYNAMICS OF GAS-SOLID PACKED BED MILLIREACTORS: EXPERIMENTAL AND NUMERICAL STUDIES

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EUROKIN MEETING 24/02/21

Context

CATALYSTS TESTING

NEW ENERGIES

- Catalysts development:
  - 1. Screening phase
  - 2. Kinetic study

- Laboratory tests on pellets (~mm)
  - Same as in industrial practice

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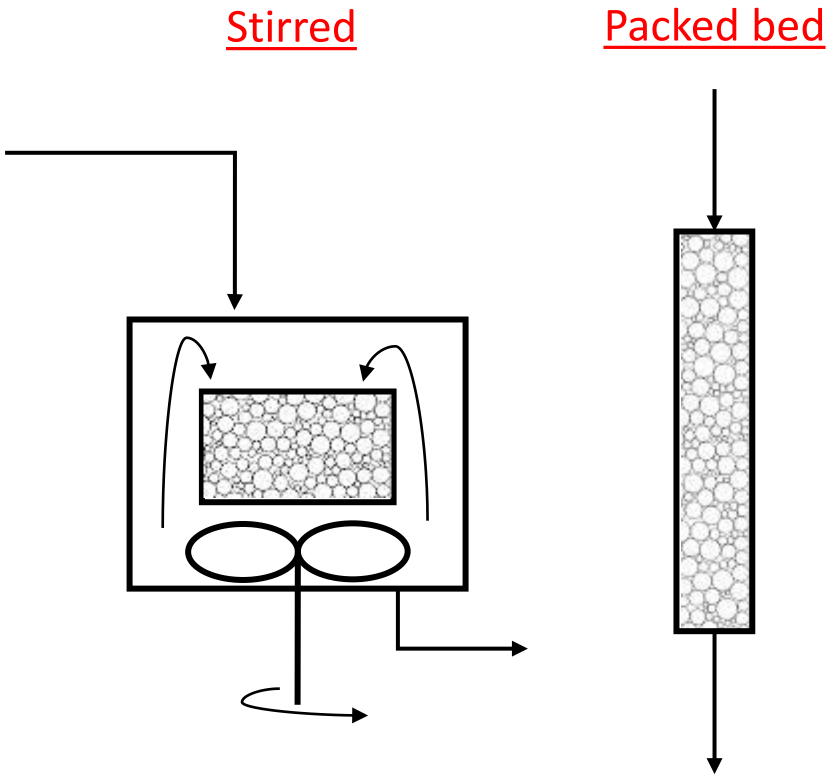
  - Stirred tank reactors
  - Packed beds



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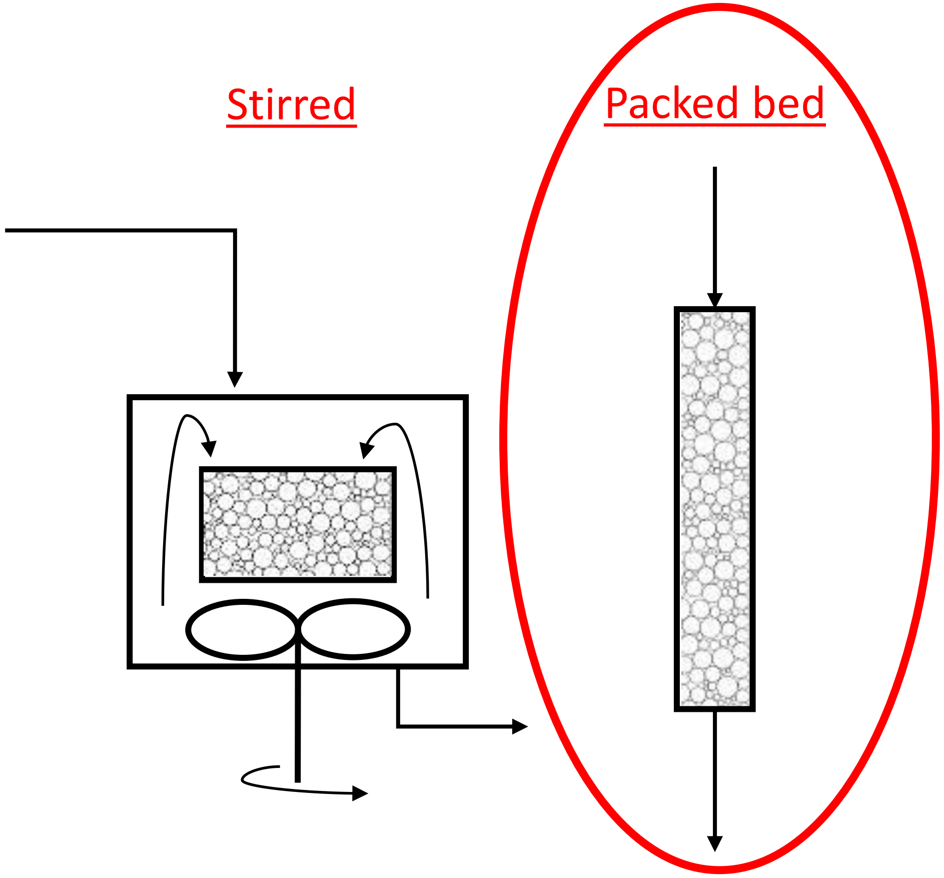
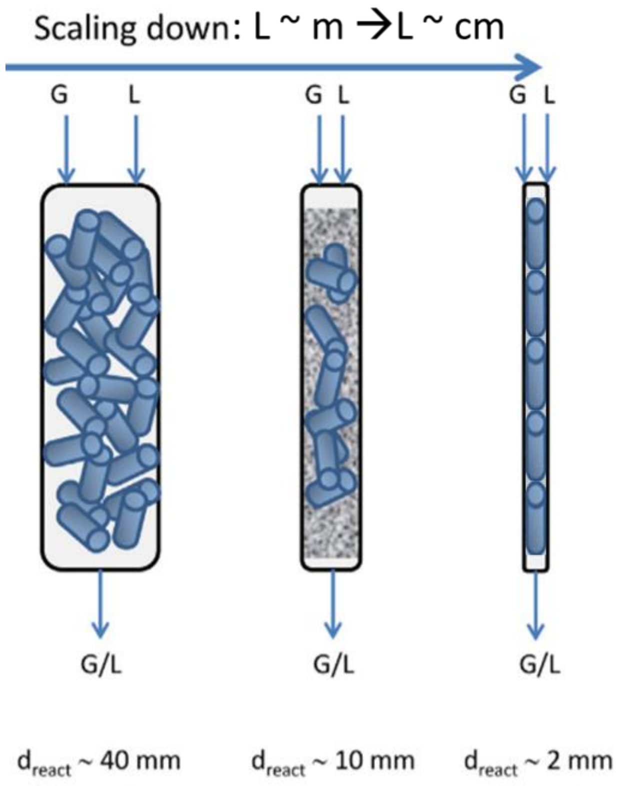


TESTING REACTORS IN HETEROGENEOUS CATALYSIS

- Trend for testing reactors: miniaturization
  - Advantages: cheaper & safer operation
  - Downscaling criterion: keep industrial contact times
  - Lower limit: catalyst size → Packed bed millireactors



[1]

[1] Moulijn J. et al. (2016), Catalysis Today Vol. 259

Context

TESTING REACTORS IN HETEROGENEOUS CATALYSIS

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  - Advantages: cheaper & safer operation
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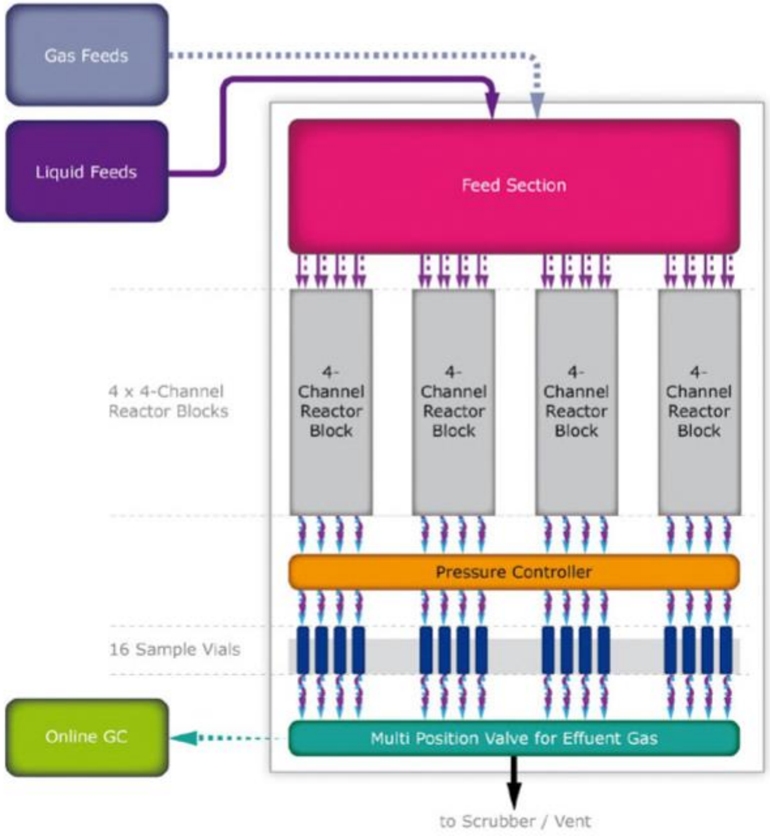
- Easier implementation of parallel reactor systems

- High Throughput Experimentation (HTE):

  Experimentation with packed bed millireactors in parallel
  - Currently used for screening phase



Scheme of an Avantium FLOWRENCE HTE unit

Question: can we use HTE for kinetics?

PACKED BED MILLIREACTORS

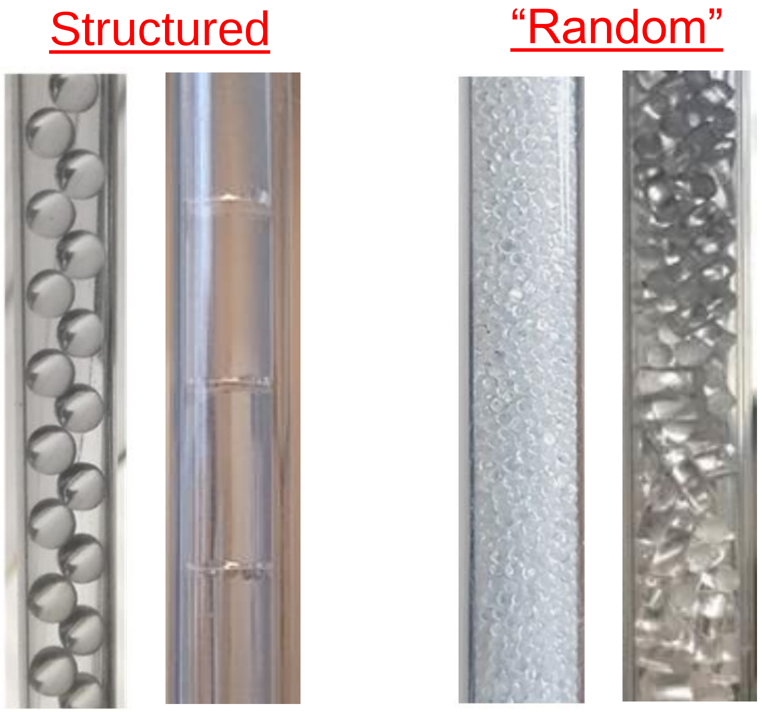
- Packed bed millireactors: packed beds with $D_r < 1$ cm

- Packing governed by reactor/particle diameter ratio:

$$\delta = \frac{D_r}{d_p}$$

  - Typical values: $1 < \delta < 10$

- Two main configurations:
  - Low δ: structured beds
  - Large δ: random beds



Context

PACKED BED MILLIREACTORS

- Risks related to the use of packed bed millireactors
  - 1. Lower superficial velocities *(u)* because of shorter lengths *(L)*
    - $u = L\ /\ \text{contact time}$
    - Effect on fluid dispersion?
    - External mass transfer $\propto u^{0.5}$ [2]

[2] Ranz, W. E. and Marshall, W. R. (1952), Chemical Engineering Progress, Vol. 48

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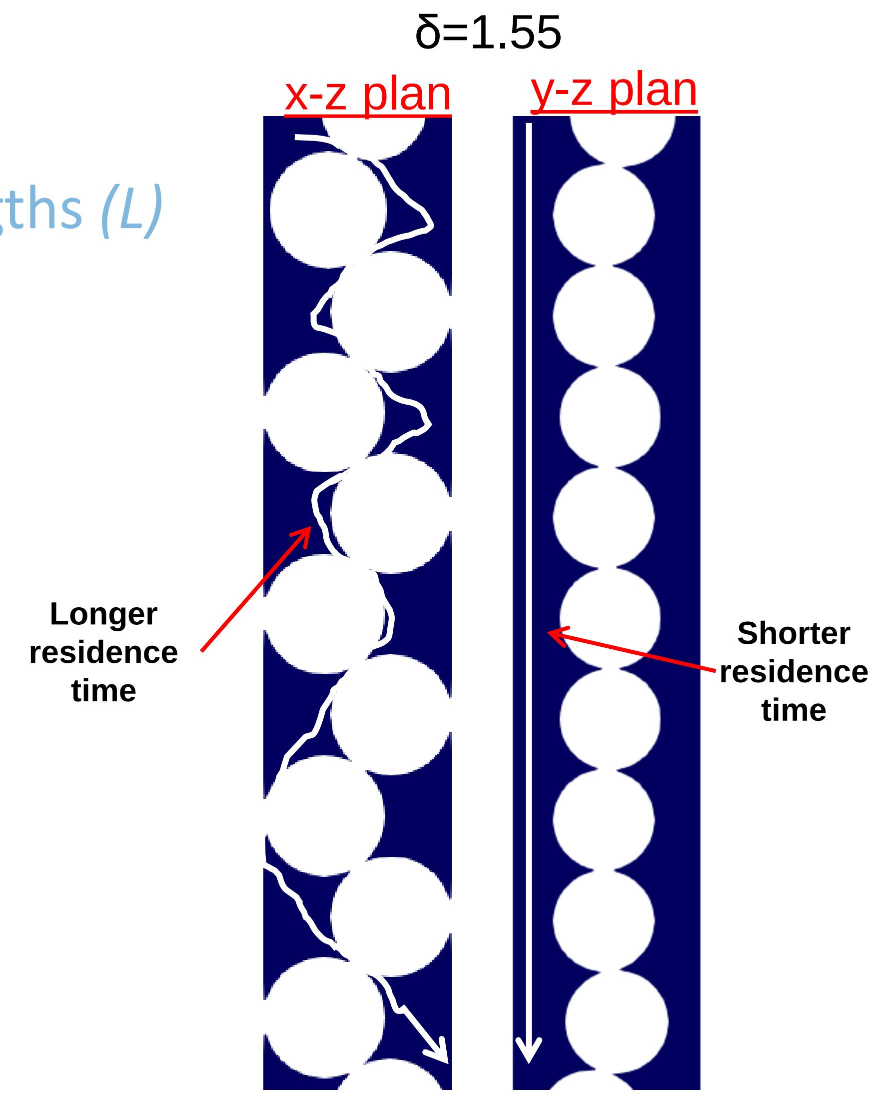
- 2. Channeling near walls → Fluid dispersion
  - Different residence times → Different conversions
    - Mean conversion ≠ Conversion of equal residence times
  - Literature recommends $\delta > 15$ *[3]*



[3] Delgado, J. M. P. Q. (2006), Heat Mass Transfer Vol. 42, No.4

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  - *Pe* number as indicator

$$Pe = \frac{u \cdot L}{\varepsilon \cdot D_{ax}}$$

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  - *Pe* number as indicator
  - Mears-Gierman criterion *[4]*

$$Pe_{min} > 8 \cdot n_r \cdot ln\frac{1}{1-X}$$

Conversion	Pe_{min}*	Application example
50%	5.5	Reforming
70%	9.6	
90%	18.4	Hydrotreatings
95%	24	
99%	36.8	
99.99%	73.7	HDS

*first-order reaction assumed

[3] Delgado, J. M. P. Q. (2006), Heat Mass Transfer Vol. 42, No.4
[4] Gierman (1988), Applied catalysis Vol.43

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PACKED BED MILLIREACTORS

- State of the art on G/S packed bed millireactors (D_r < 1 cm, δ<10):

Parameter	Covered area	Missing
δ	1.125<δ<1.76 [5, 6]	Other δ values
Porosity filler effect	1 CFD study + Hypothetical ideal G/S reaction [6]	Experimental study + size and shape effect + other reactions

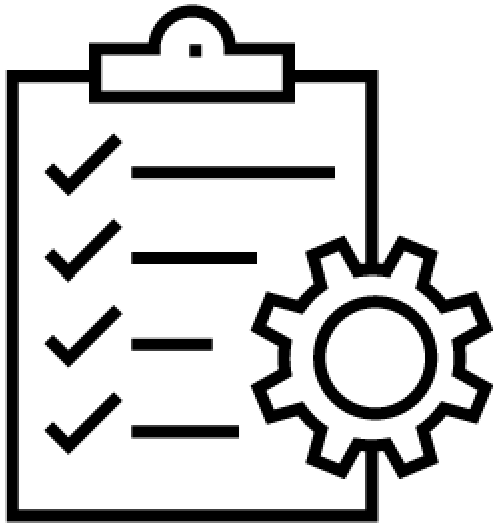
$\delta = D_r/d_p$

[5] Šolcova and Schneider (2004), Chemical Engineering Science Vol. 59
[6] Fernengel et al. (2019), Chemical Engineering Journal Vol.373

PRESENTATION OUTLINE

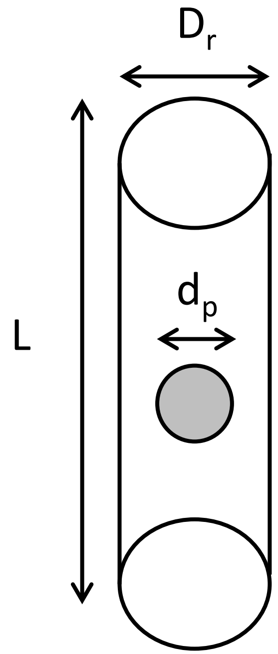
NEW ENERGIES

- Scope and strategy of the study
- Hydrodynamic study
- Reactive experiments
- Conclusions and perspectives



SCOPE OF THE STUDY

- Packed bed millireactors
  - D_r < 8 mm, L = 9-25 cm
  - 1 < δ < 8
  - Particles: cylinders, spheres (mm)
  - With and without fine powder as porosity filler



Powders

Irregularly shaped

Silicon Carbide (SiC)

Spherical

ZirBlast®
60-70% ZrO_2
28-33% SiO_2
<10% Al_2O_3

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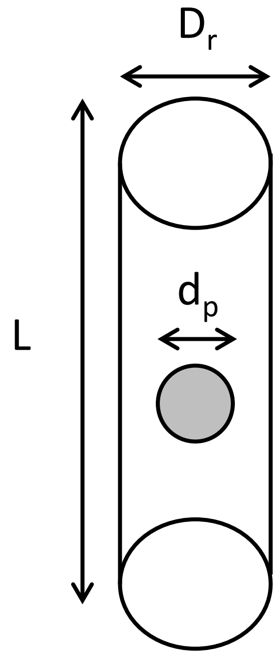
- 1. Fluid dispersion?

- 2. Can mass transfer be improved?



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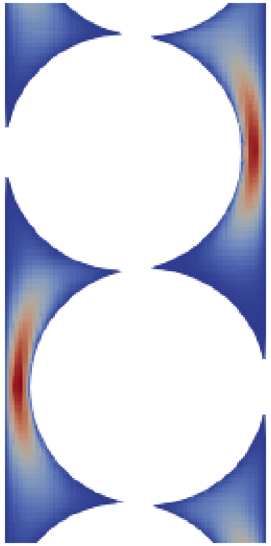
- 1. Hydrodynamic study: RTD experiments + CFD simulations
  - Target: characterize fluid dispersion at different operating conditions



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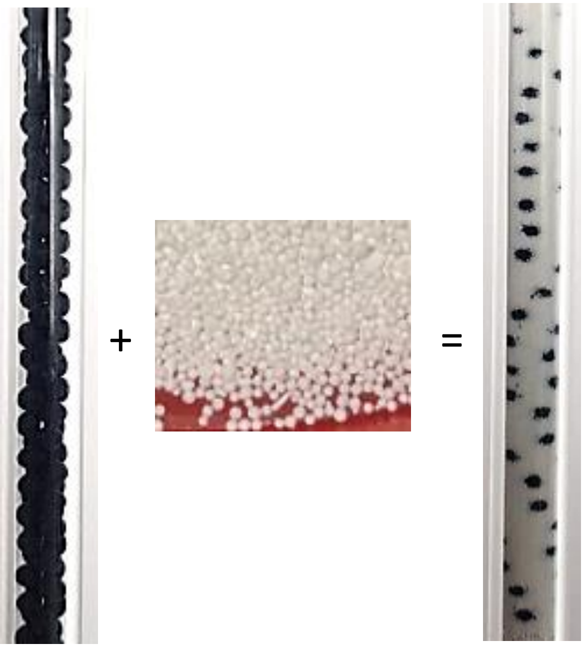
- 2. Reactive tests
  - Target: explore mass transfer changes induced by porosity filler presence



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PRESENTATION OUTLINE

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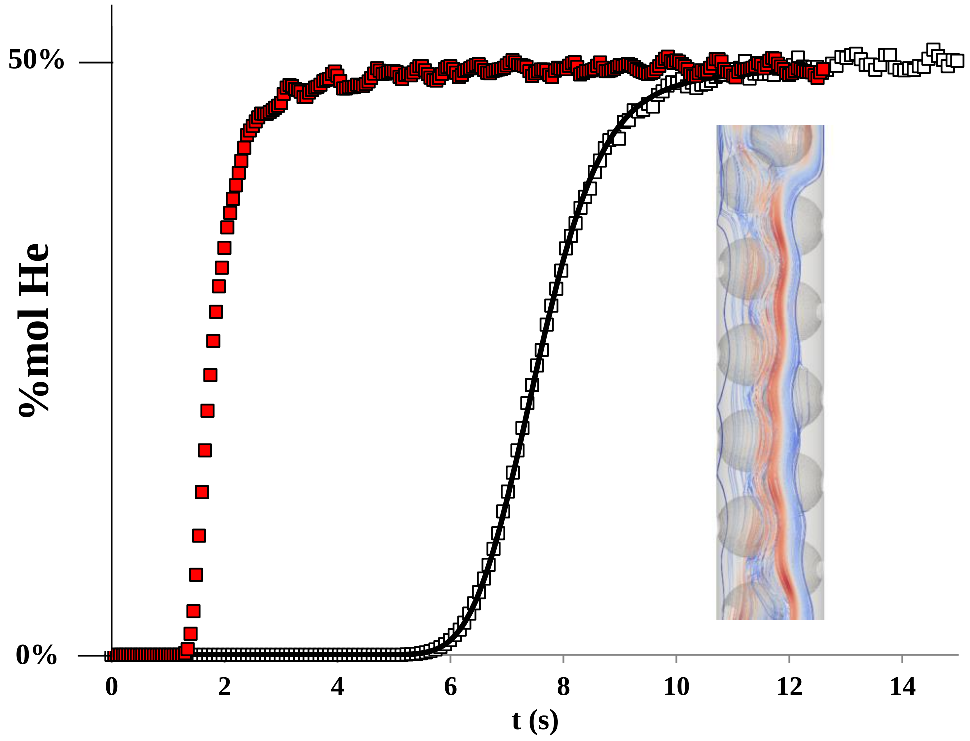
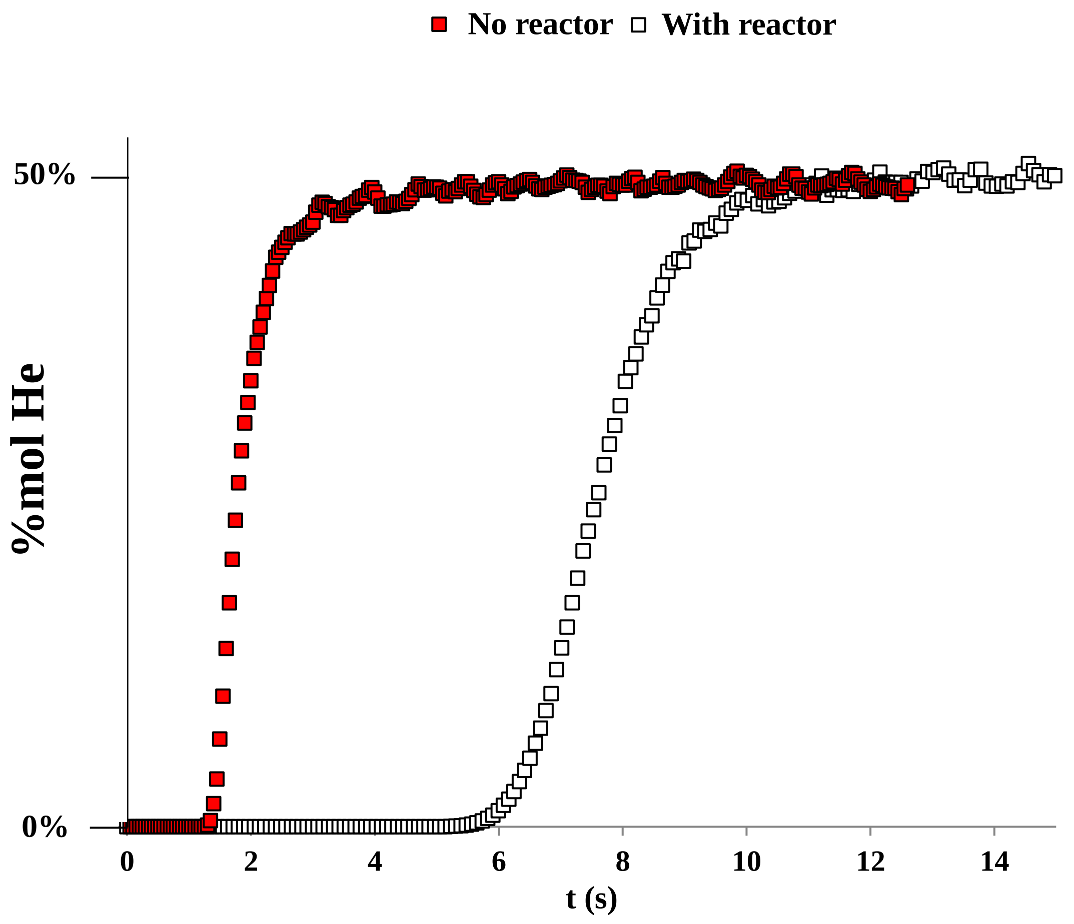
- General conclusions and perspectives



HYDRODYNAMIC STUDY: METHODS

- RTD experiments:
  - N_2-He step change
    - Mass spectrometer for measurements



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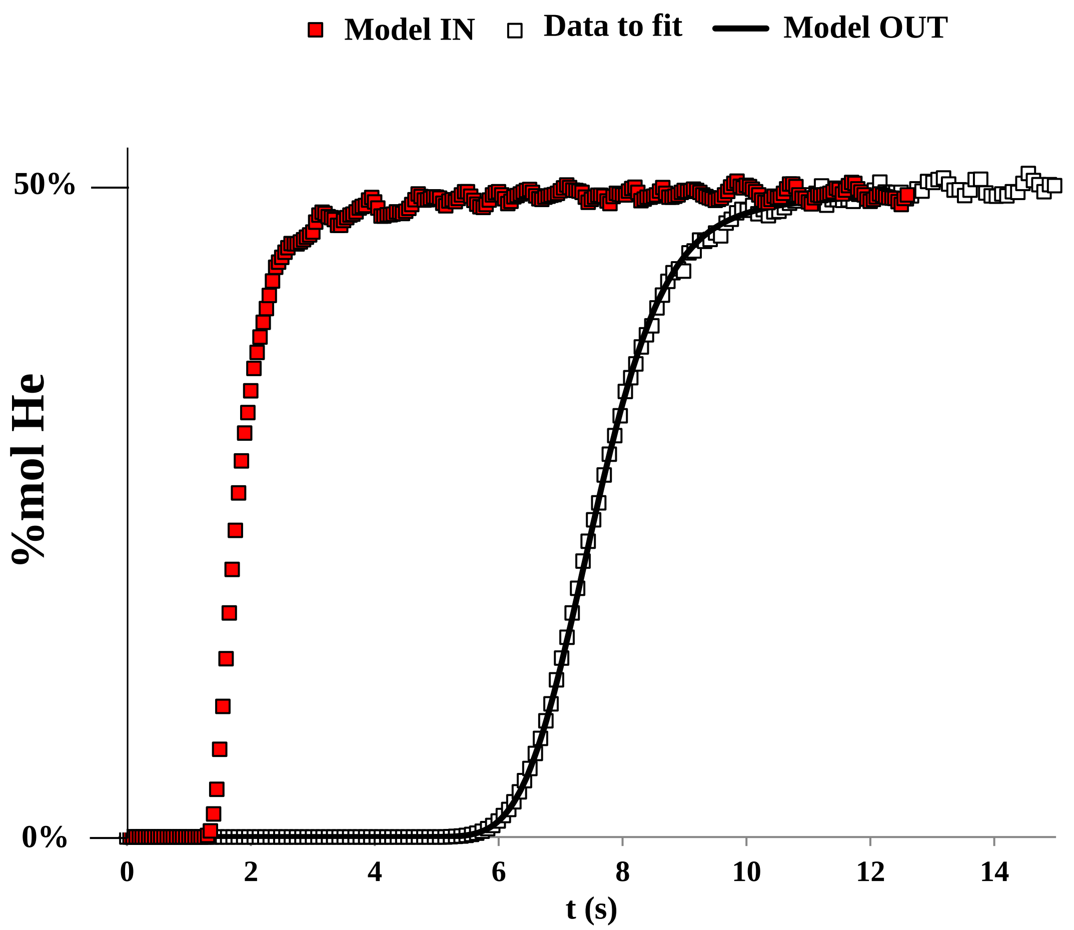
Accumulation — Dispersion — Convection

$$\frac{\partial C}{\partial t} = D_{ax}\frac{\partial^2 C}{\partial z^2} - \frac{u}{\varepsilon}\frac{\partial C}{\partial z}$$

$$Pe = \frac{1}{\varepsilon}\cdot\frac{u \cdot L}{D_{ax}}$$



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- CFD: simulation workflow
  - 1. Grains3D DEM code to obtain the packing

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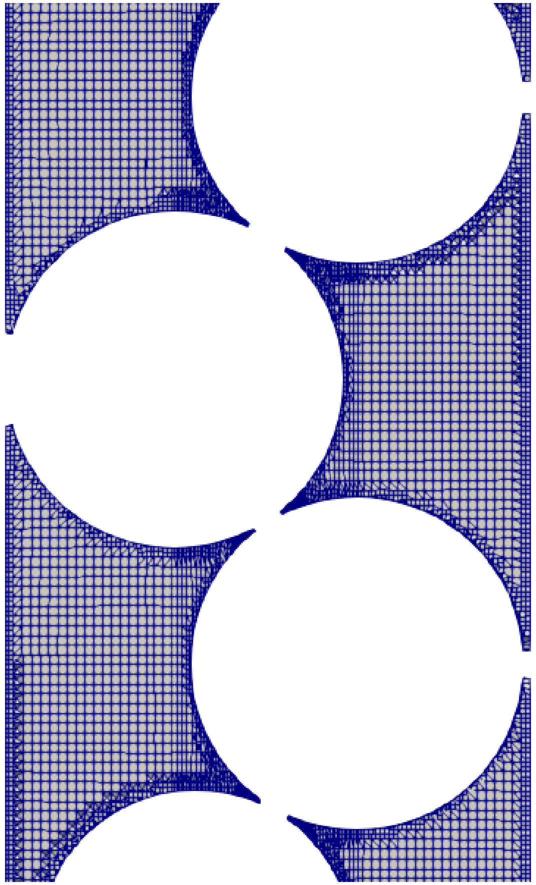

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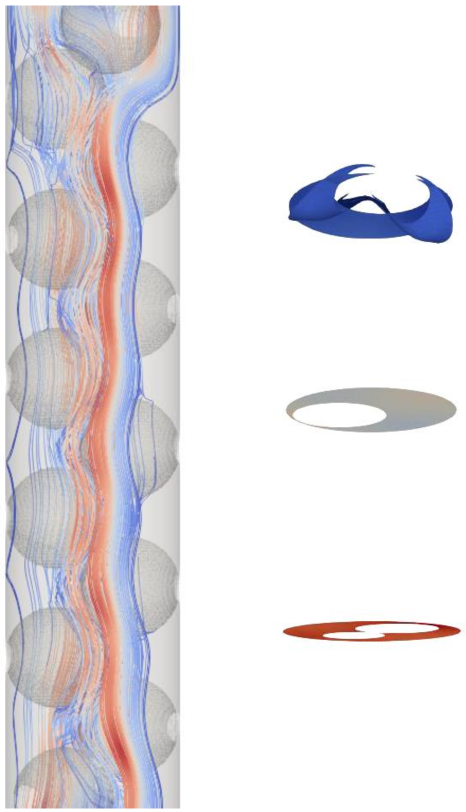

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Convection Diffusion Generation

1. $\nabla.(\mathbf{v}M_n) = \nabla.(D_m \nabla M_n) + nM_{n-1}$, n>1

- CFD: simulation workflow
  - 1. Grains3D DEM code to obtain the packing
  - 2. `blockMesh` and `snappyHexMesh` OpenFOAM® utilities to create the mesh
  - 3. `SimpleFoam` OpenFOAM® solver computes the flow
    - Steady state transport equations for M_1 and M_2 [7]

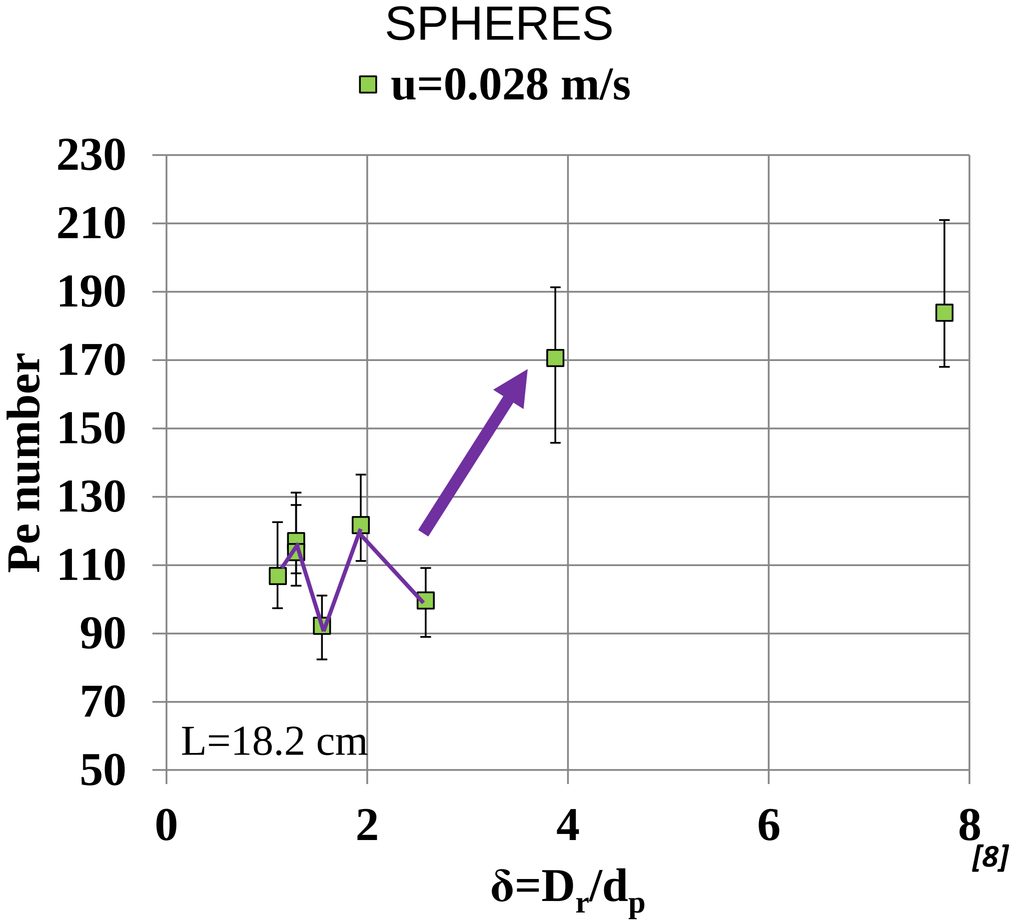
2. $Pe = 2\frac{\left(M_{1,out} - M_{1,in}\right)^2}{\left(M_{2,out} - M_{1,out}^2\right) - \left(M_{2,in} - M_{1,in}^2\right)}$

[7] Liu and Tilton (2010), AIChe Journal Vol. 56 No.10

HYDRODYNAMIC STUDY: RESULTS

- Complex behavior of *Pe* number with *δ*
  - Spheres
    - Higher values for *δ* > 3 → Random beds

RTD DATA



[8]

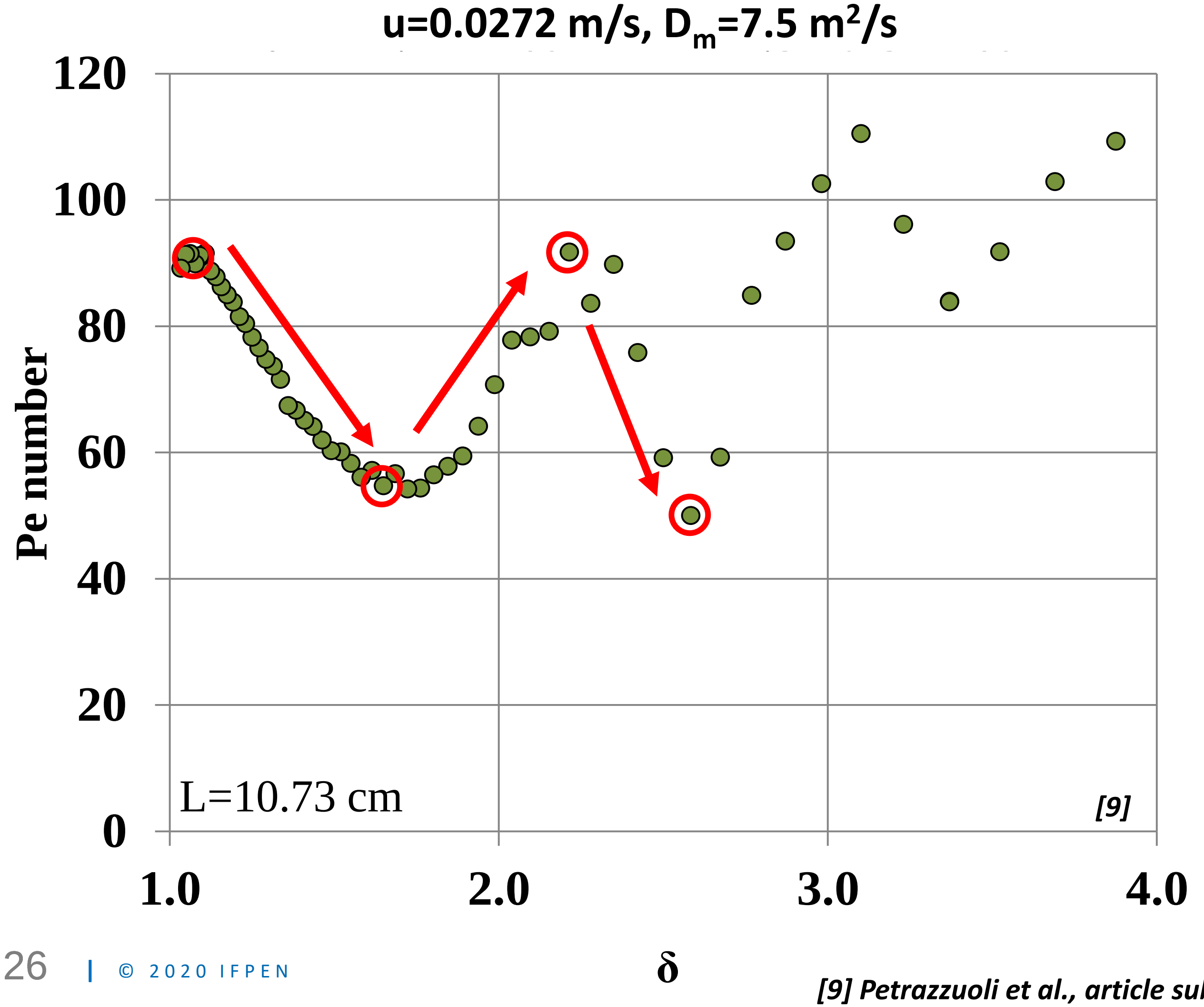
EXPLORED MORE IN DETAIL by CFD

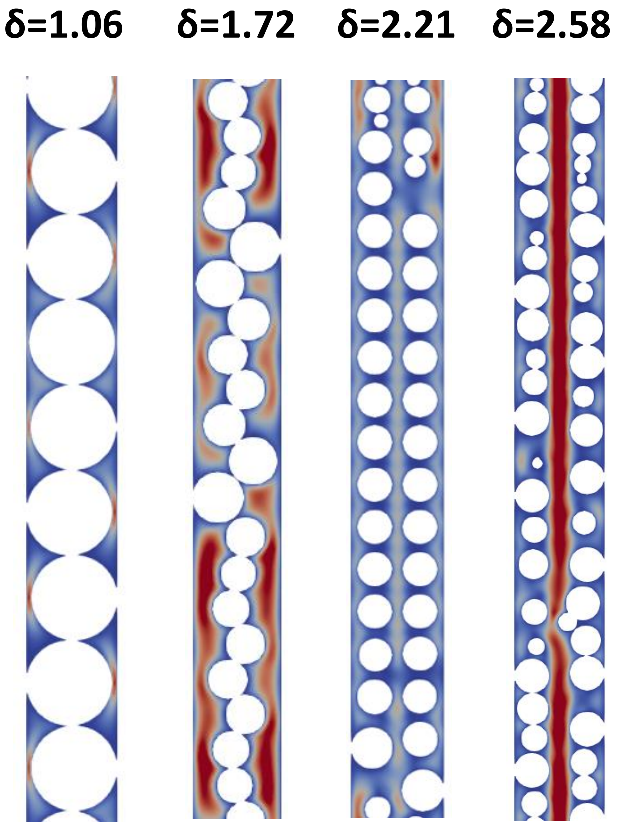
[8] Petrazzuoli et al. (2021), Chemical Engineering Science Vol.231

HYDRODYNAMIC STUDY: RESULTS

NEW ENERGIES

○ CFD results: *Pe* number different flow patterns



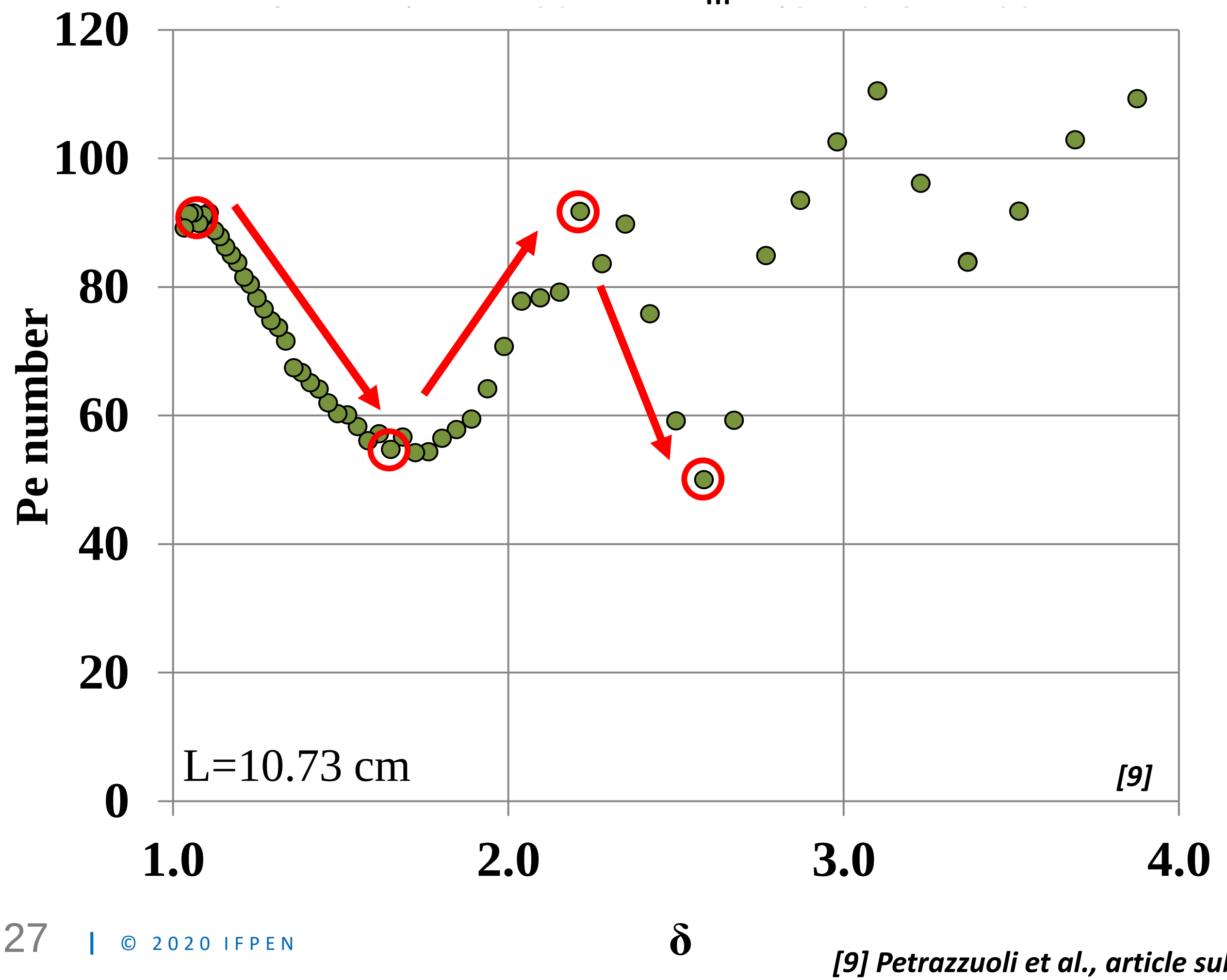


[9] Petrazzuoli et al., article submitted to Chemical Engineering Science

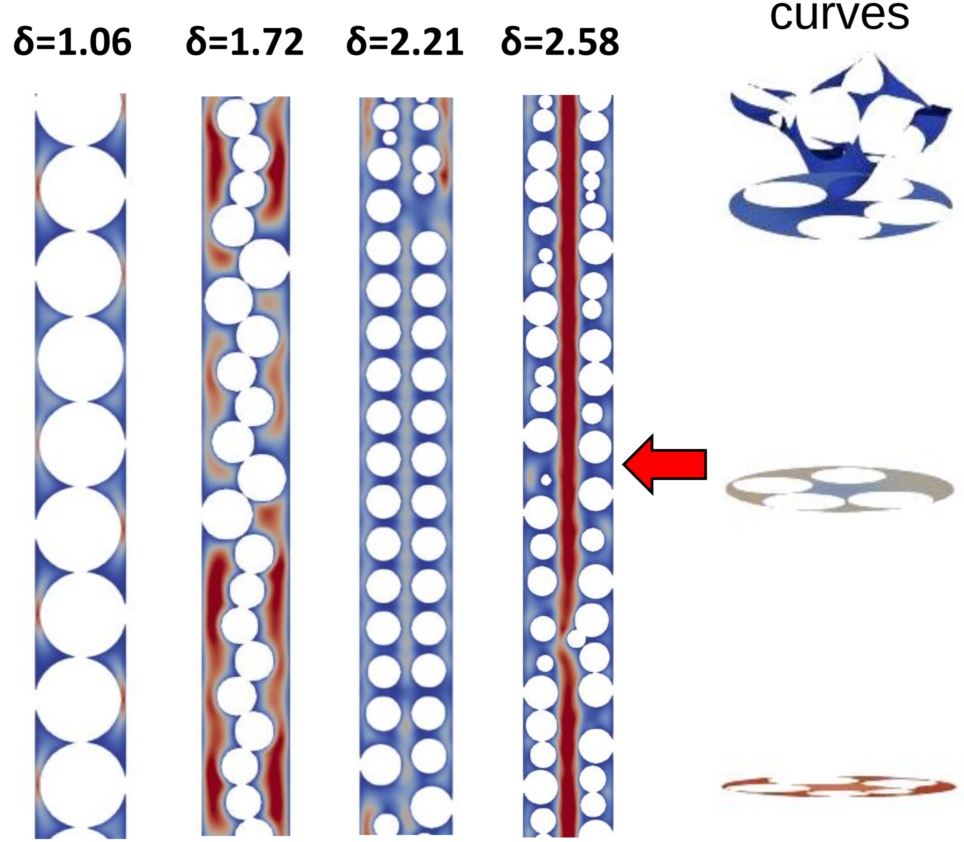
HYDRODYNAMIC STUDY: RESULTS

○ CFD results: *Pe* number different flow patterns

u=0.0272 m/s, D_m=7.5 m²/s



IsoM1 curves



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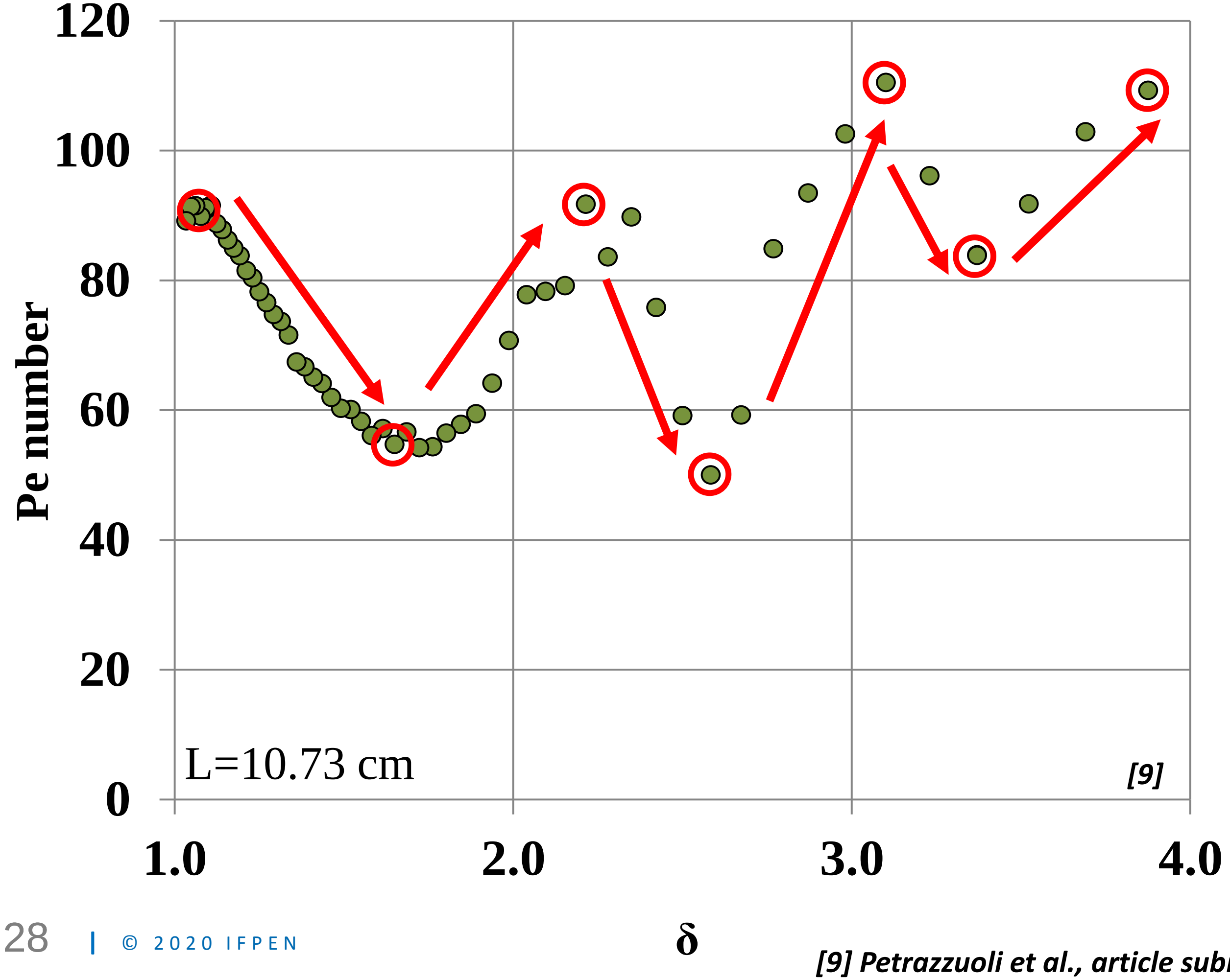

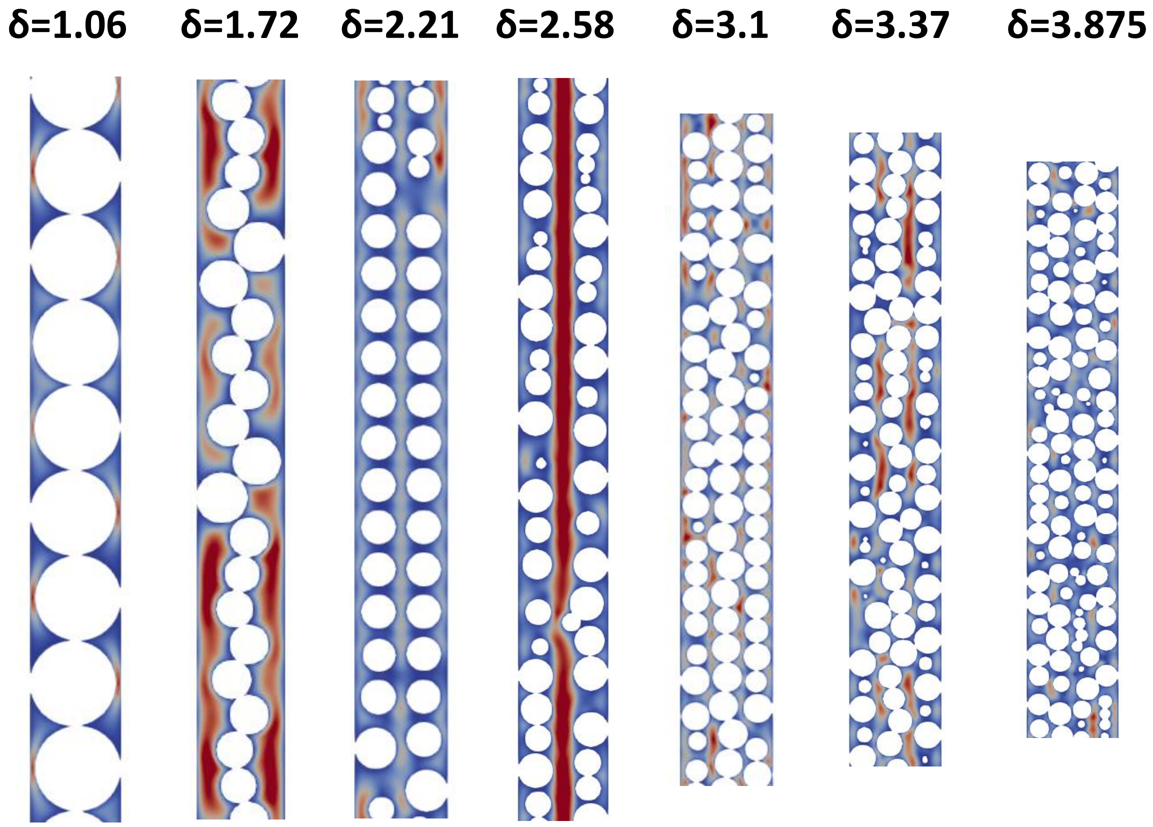

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IFP Energies nouvelles

HYDRODYNAMIC STUDY: RESULTS

- Complex behavior of *Pe* number with δ
  - Spheres
    - Higher values for $\delta > 3$ → Random beds
    - *Pe* number influenced by preferential passages

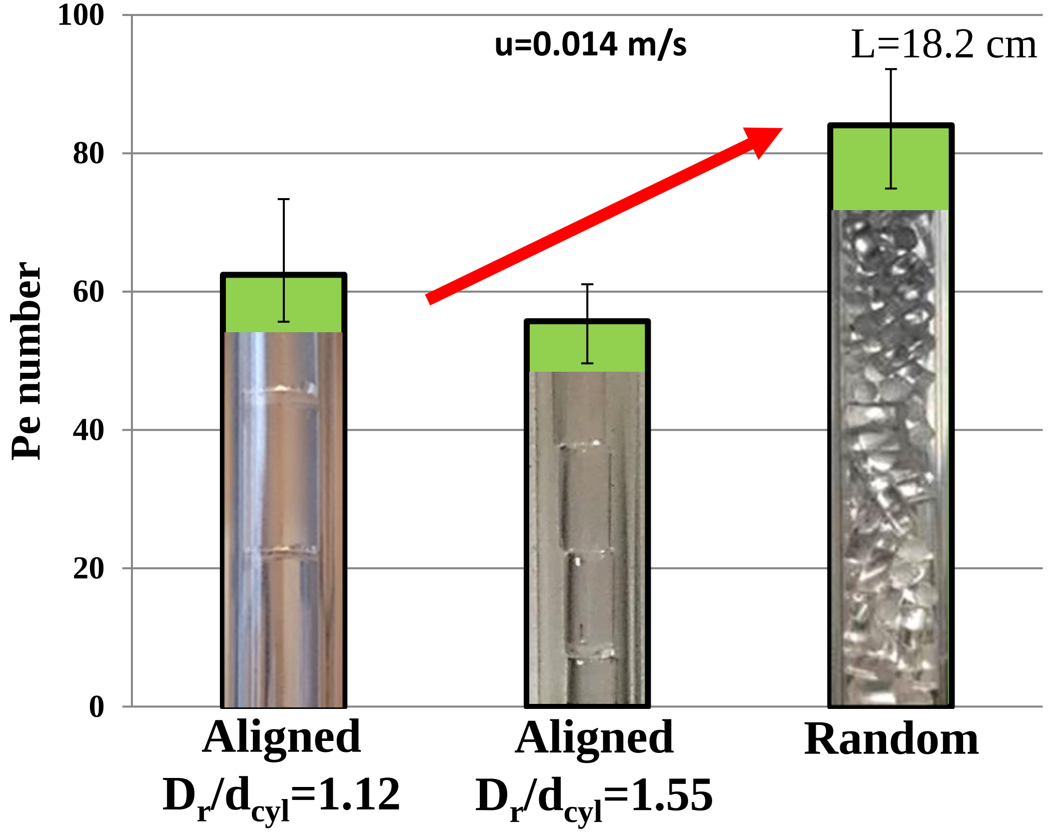
HYDRODYNAMIC STUDY: RESULTS

NEW ENERGIES

- **Complex behavior of *Pe* number with δ**
  - Spheres
    - Higher values for $\delta > 3$ → Random beds
    - *Pe* number influenced by preferential passages
  - Cylinders
    - Higher values for random beds

RTD DATA

CYLINDERS



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- Complex behavior of *Pe* number with δ
  - Spheres
    - Higher values for $\delta > 3$ → Random beds
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  - Cylinders
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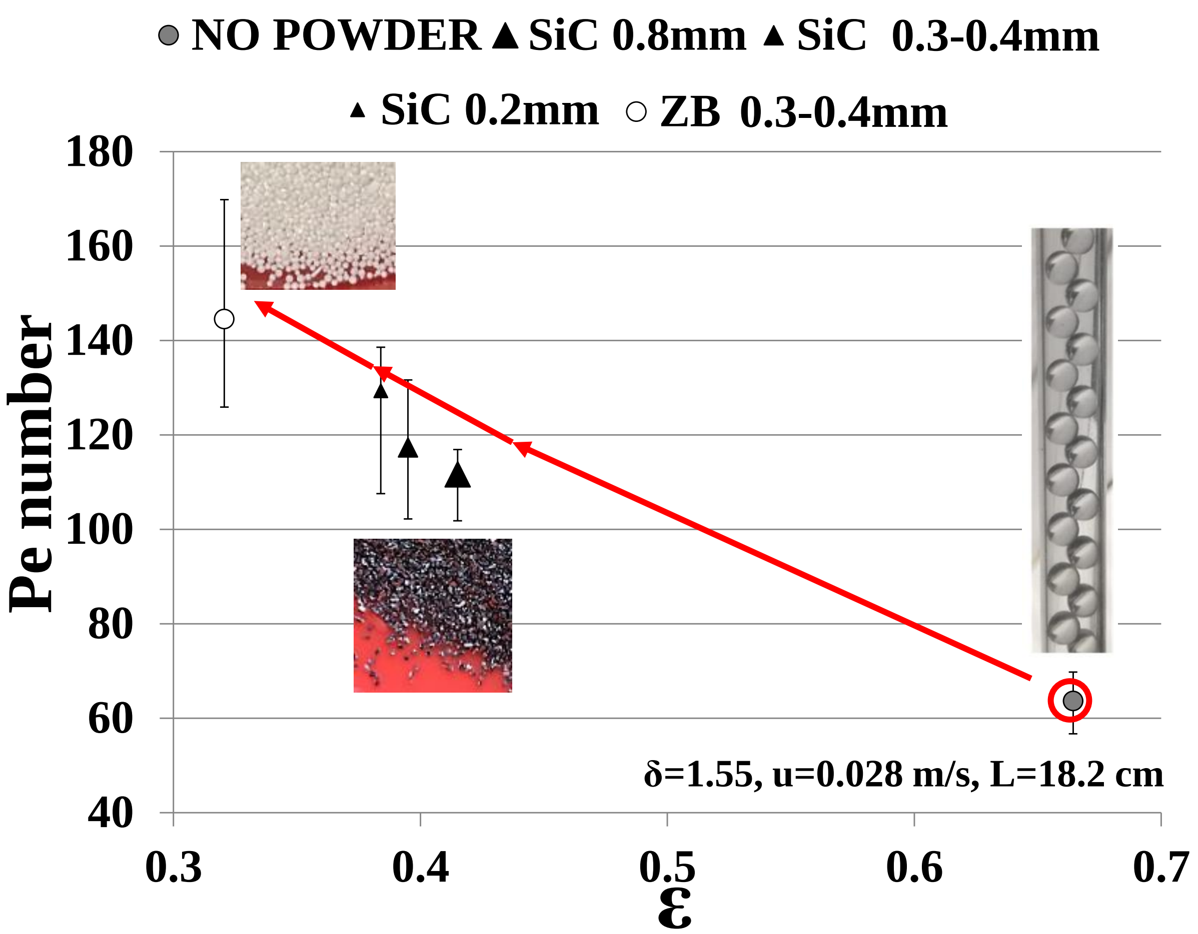
- Positive effect of porosity fillers
  - Lower reactor porosity → Higher *Pe* number
    - Smaller powders preferred
    - Spherical powders fill better the porosity



High Pe numbers without porosity filler

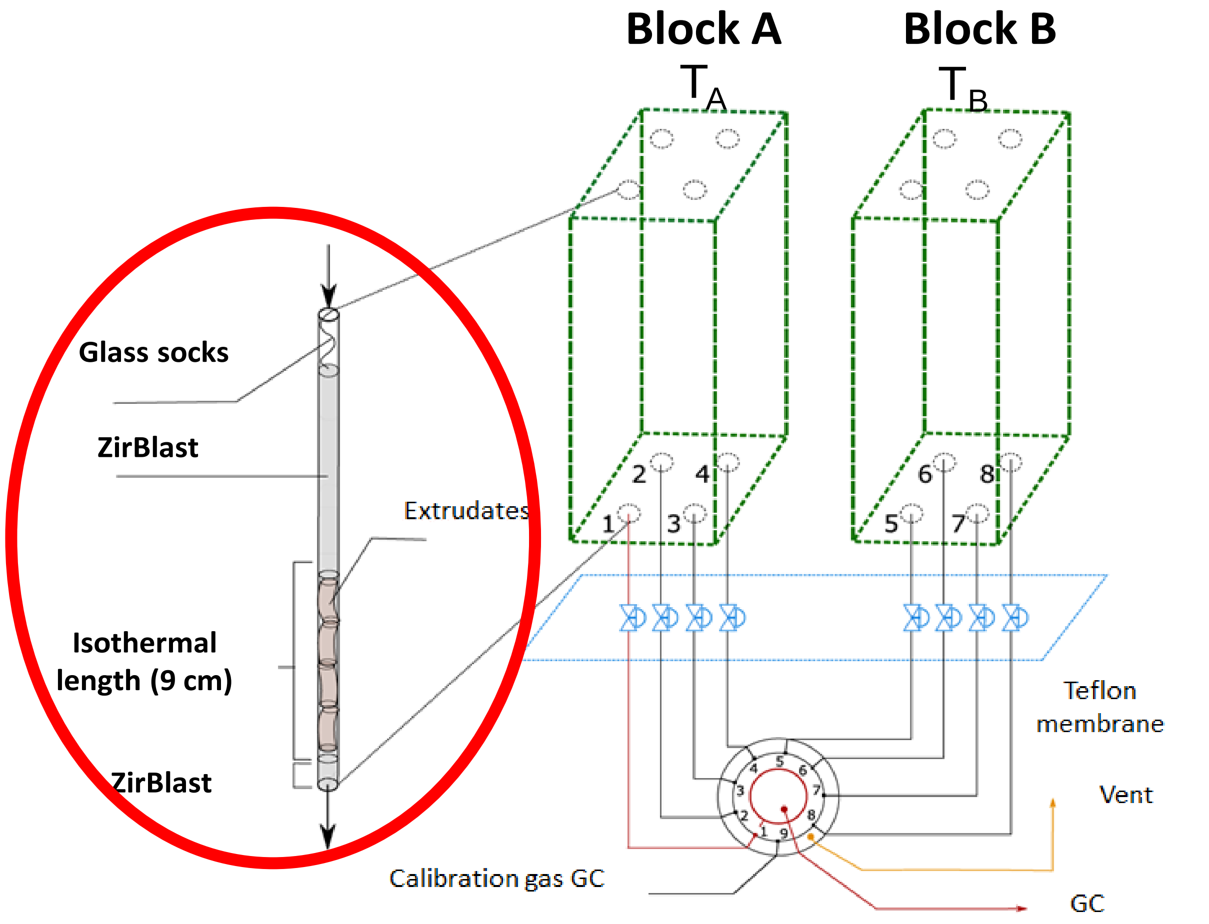
PRESENTATION OUTLINE

NEW ENERGIES

REACTIVE TESTS: UNIT PRESENTATION

NEW ENERGIES

- Tests performed on an Avantium FLOWRENCE HTE unit:
  - 8 parallel reactors
  - Same inlet gas and liquid flow
  - Same inlet pressure
  - GC analysis per single reactor



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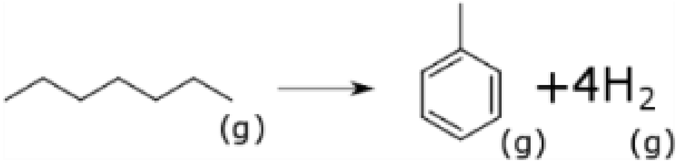
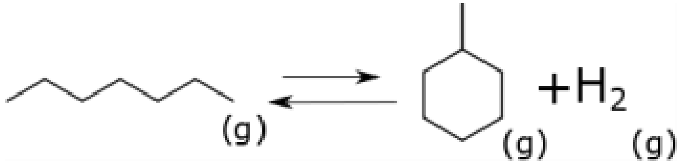
REACTIVE TESTS: METHODS

- 2 reactions tested:
  - *n*-heptane reforming, low ΔH

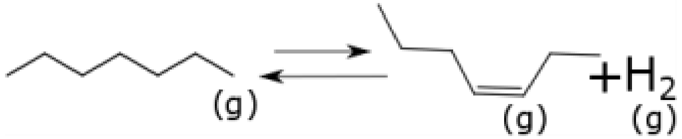
dehydrocyclization



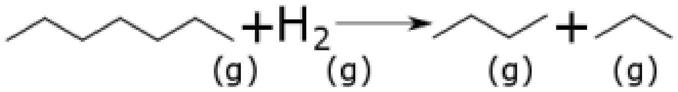
cyclization



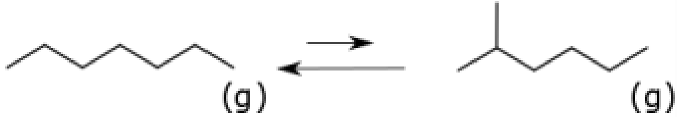
dehydrogenation



hydrocracking



isomerization



<u>Explored operating conditions:</u>

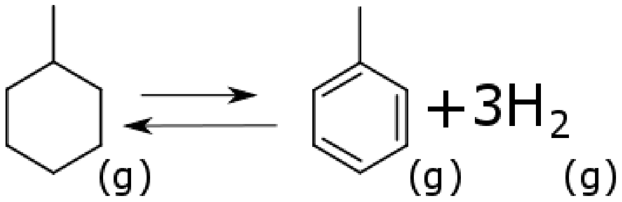
P=10 barg

470 < T < 515 °C

Contact times: 0.2-0.067 g_{cat}·h/g_{HC}

REACTIVE TESTS: METHODS

- 2 reactions tested:
  - *n*-heptane reforming, low ΔH
  - methylcylohexane dehydrogenation, ΔH = 204 kJ/mol



methylcyclohexane toluene

Explored operating conditions:
P=10 barg
330 < T < 350 °C
Contact times: 0.15-0.057 $g_{cat}\cdot h/g_{HC}$

REACTIVE TESTS: METHODS

- 2 reactions tested:
  - *n*-heptane reforming, low ΔH
  - methylcylohexane dehydrogenation, $\Delta H = 204$ kJ/mol
- Different reactor diameters tested
  - 2 to 4 mm
- Different catalyst particles tested
  - Extrudate cylinders and spheres

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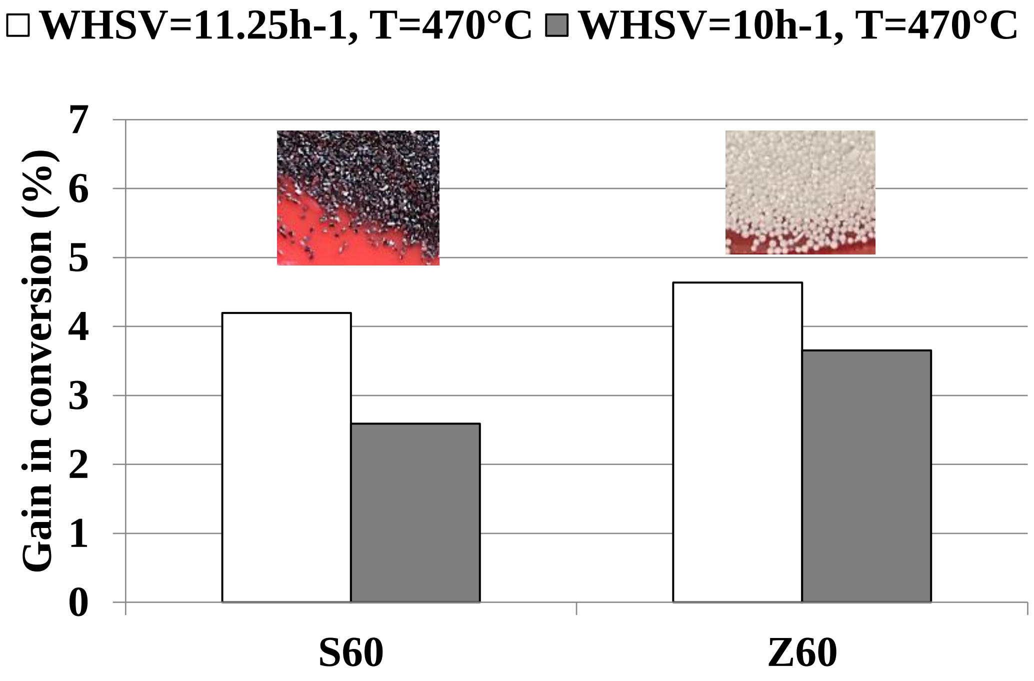
  - methylcylohexane dehydrogenation, ΔH = 204 kJ/mol
- Different reactor diameters tested
  - 2 to 4 mm
- Different catalyst particles tested
  - Extrudate cylinders and spheres
- Different porosity fillers tested
  - Size and shape

SiC	60 µm	150-200 µm	300-400 µm
ZirBlast®	60 µm	150-200 µm	300-400 µm

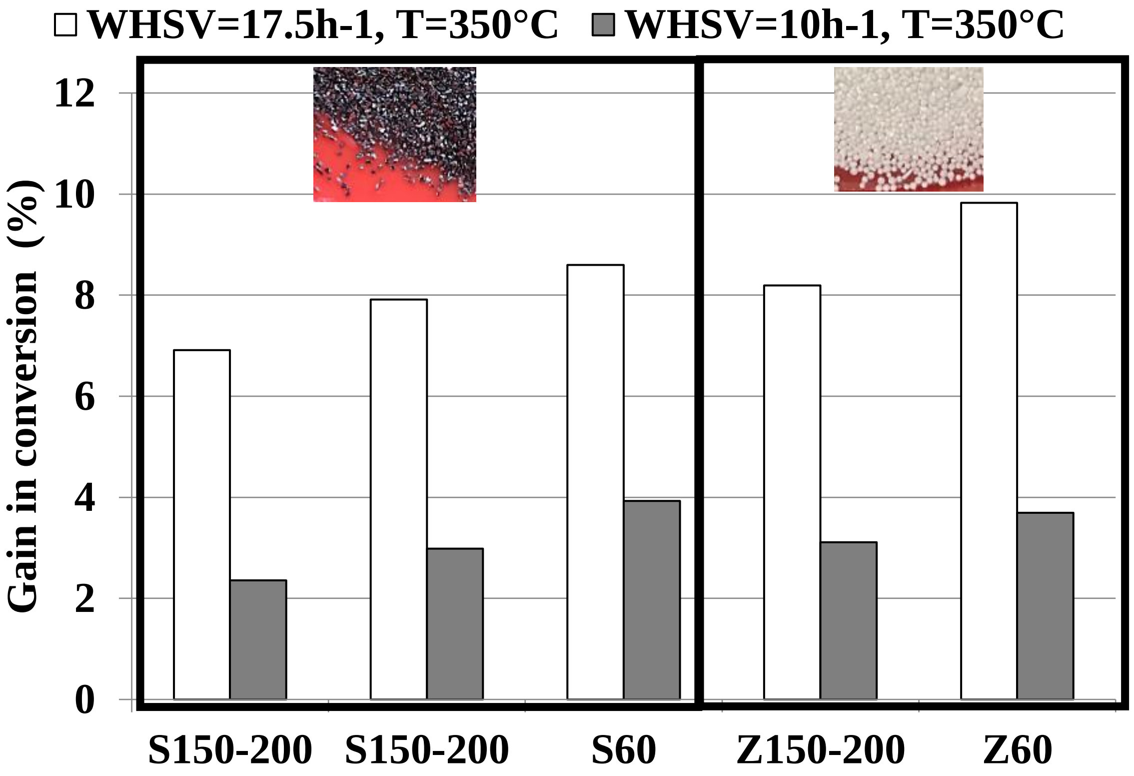
REACTIVE TESTS: RESULTS

- Porosity filler change mass transfer properties → Effect on conversions?
  - Gain in conversion: conversion with porosity filler / conversion without porosity filler

nC7 reforming, D_r= 3 mm catalyst extrudates, P=10 barg



MCH dehydrogenation, D_r=2 mm catalyst extrudates, P=10 barg



Higher WHSV → Higher u → Higher effect

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REACTIVE TESTS: RESULTS

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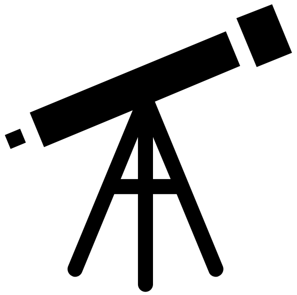
SUMMARY OF THE RESULTS

Porosity filler effect	Reason	Best shape	Best size	Packing repeatability	Recommendation
Slightly positive	+ mass transfer	 Slightly	60, 150-200 µm	Good	Use the largest powder that fills the porosity best

↑ Higher gas interstitial velocity

PRESENTATION OUTLINE



GENERAL CONCLUSIONS AND PERSPECTIVES

Packed bed millireactors

Questions:

- 1. Fluid dispersion?
- 2. Can mass transfer be improved?

- **Main conclusions:**
  - Fluid dispersion:
    - Low fluid dispersion
    - More fluid dispersion when large passages are present ($\delta \approx 1.7, 2.6, 3.4$)
  - Mass transfer slightly improved by porosity fillers
- **Further conclusion:**
  - DEM-CFD workflow accurate and fast

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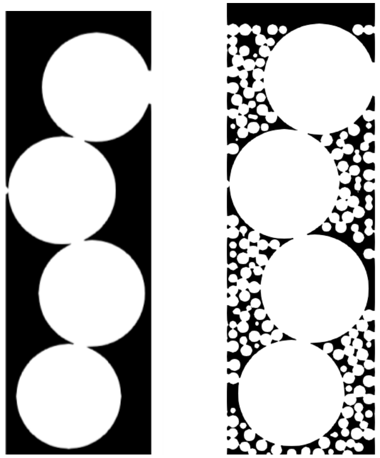
    - More fluid dispersion when large passages are present ($\delta \approx 1.7, 2.6, 3.4$)
  - Mass transfer slightly improved by porosity fillers
- **Other conclusions:**
  - DEM-CFD workflow accurate and fast

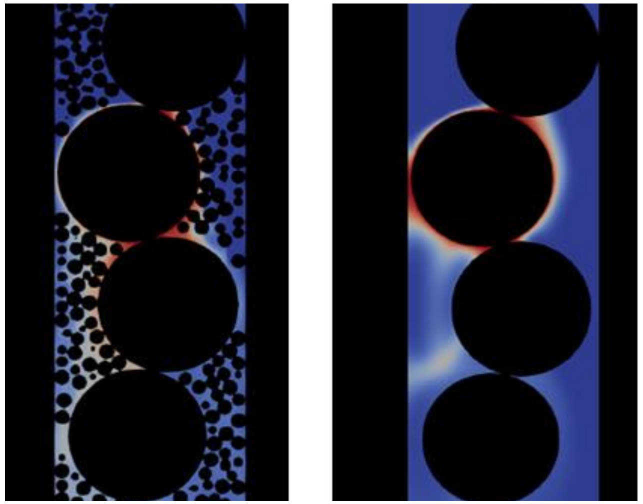
- **Recommendations:**
  - Millireactors suitable for G/S applications
  - Geometries with large preferential passages (or holes) should be avoided
  - Increase bed length as much as possible
  - Use porosity fillers if possible
    - The largest size that correctly fills the porosity

GENERAL CONCLUSIONS AND PERSPECTIVES

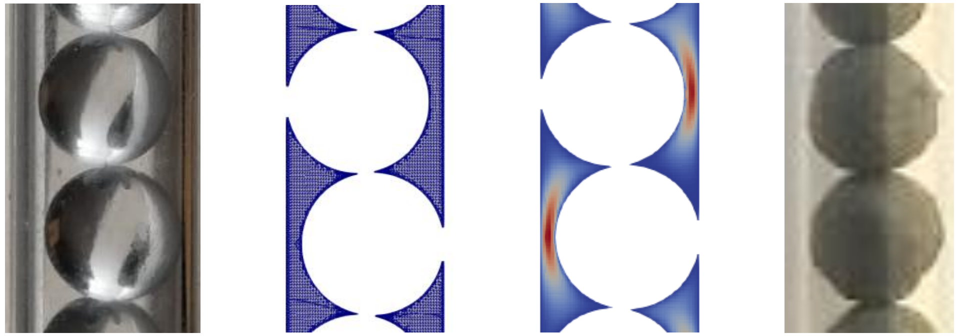


- **Perspectives:**
  - CFD with porosity filler
    - Explore size and shape effect
    - DEM costly → Geometrical methods
  - Estimate mass transfer coefficients
    - Experimentally and through CFD
  - Study polydispered packings hydrodynamics

Concentration fields



THANK YOU FOR YOUR ATTENTION!



IRCELYON

IFP Energies nouvelles

