GHENT UNIVERSITY

LCT

DRIVING CHEMICAL TECHNOLOGY

FACULTY OF ENGINEERING AND ARCHITECTURE

THE 8TH ASIAN-PACIFIC CHEMICAL REACTION ENGINEERING SYMPOSIUM
NOVEMBER 14, 2017, SHANGHAI (CHINA)

CFD BASED DESIGN OF A NOVEL REACTOR TECHNOLOGY FOR THE OXIDATIVE COUPLING OF METHANE

Laurien A. Vandewalle, Patrice Perreault, Kevin M. Van Geem, Guy B. Marin

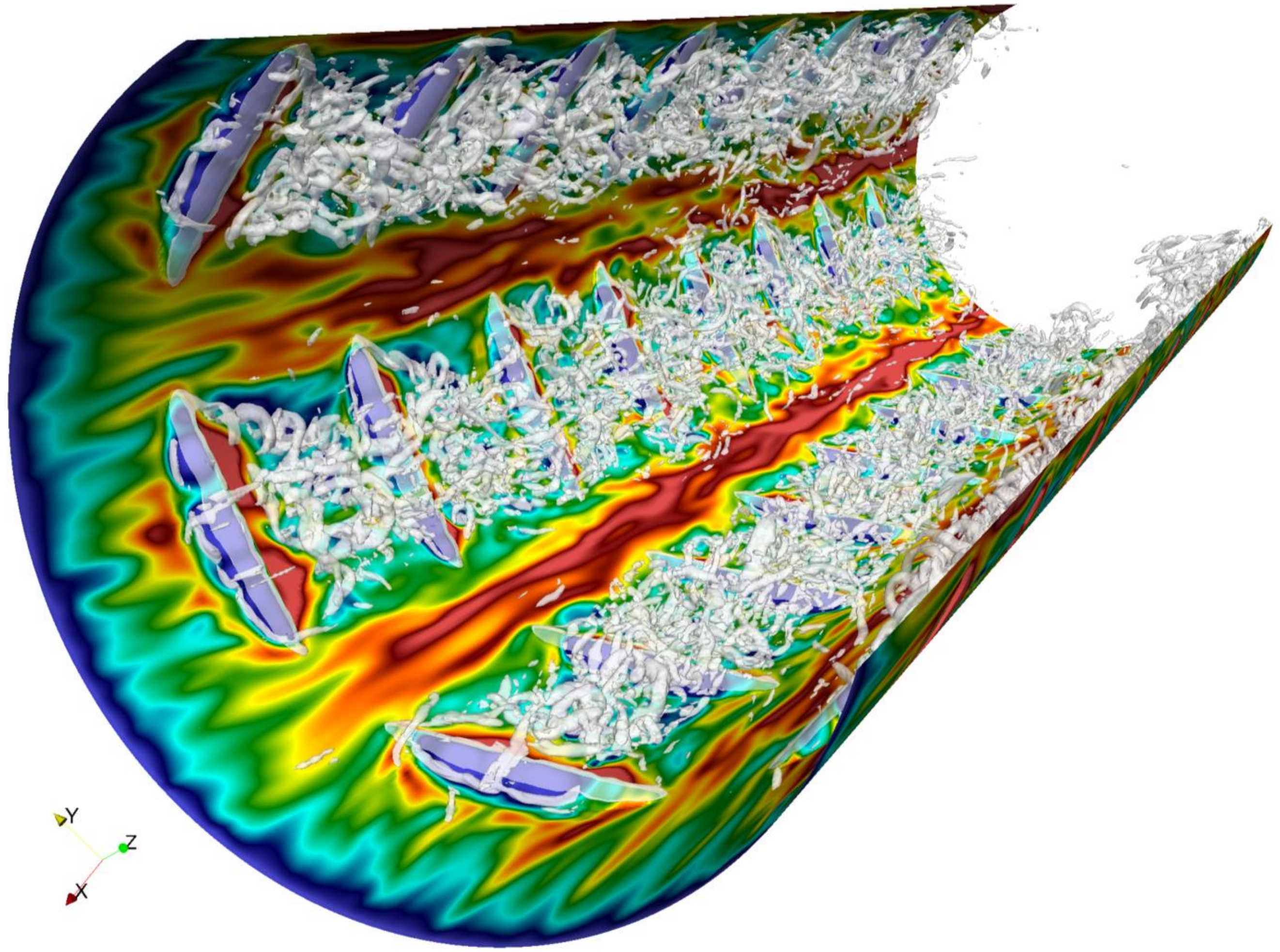
Laboratory for Chemical Technology (Ghent University, Belgium)

GHENT UNIVERSITY

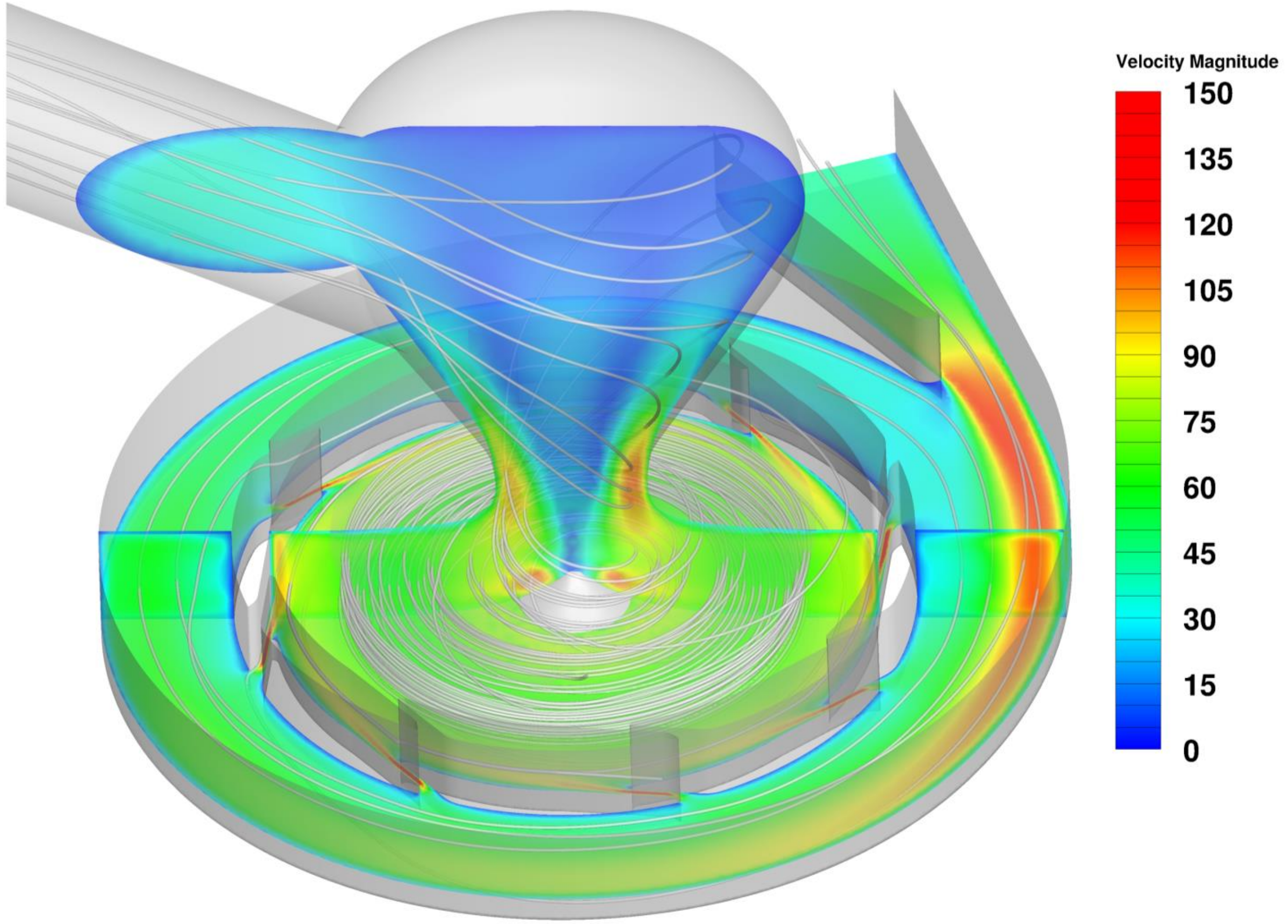
LCT DRIVING CHEMICAL TECHNOLOGY

3D reactor technology: the new standard

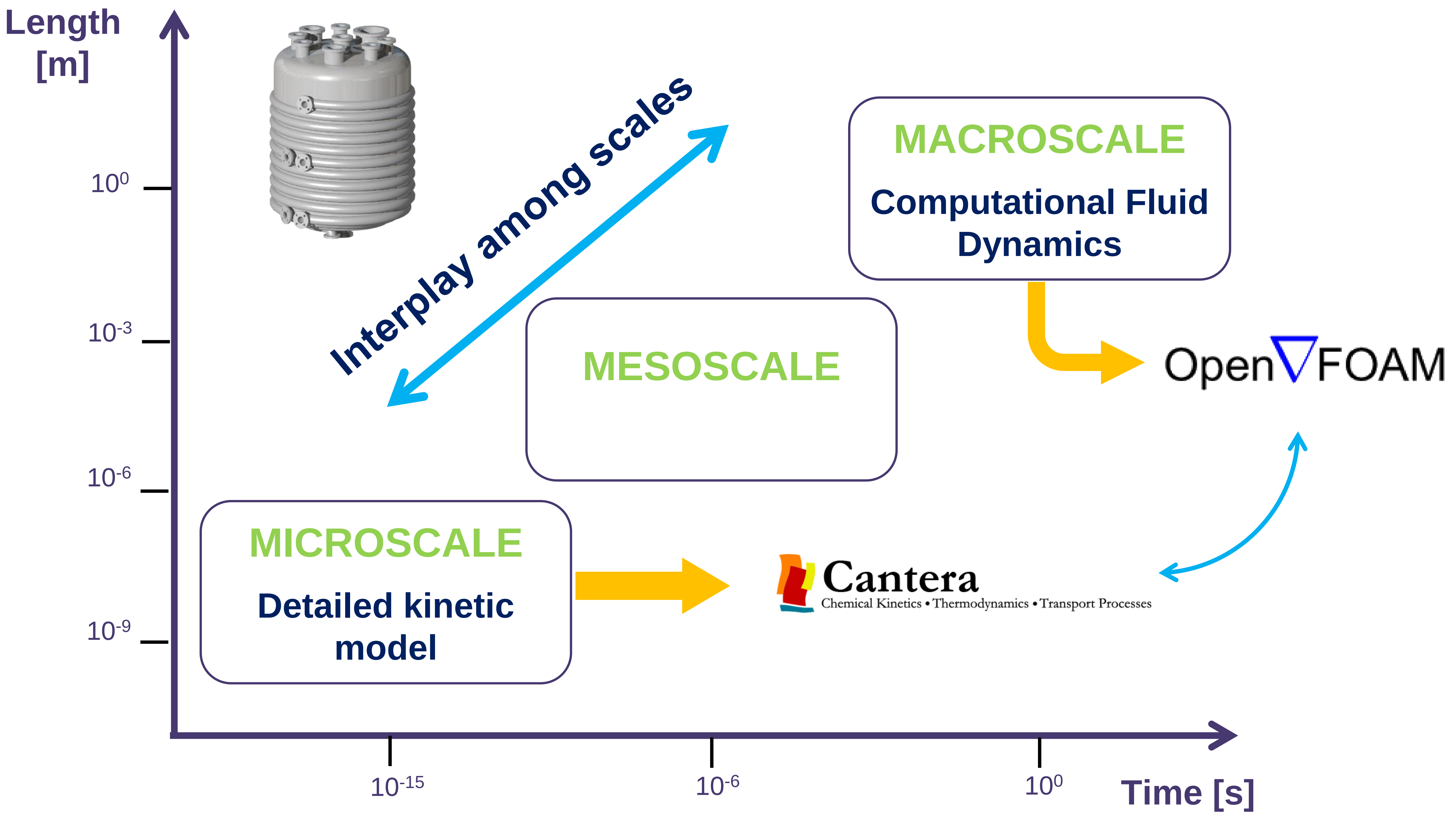
TURBULATOR REACTOR



ROTOR REACTOR



Design: multiscale modeling framework

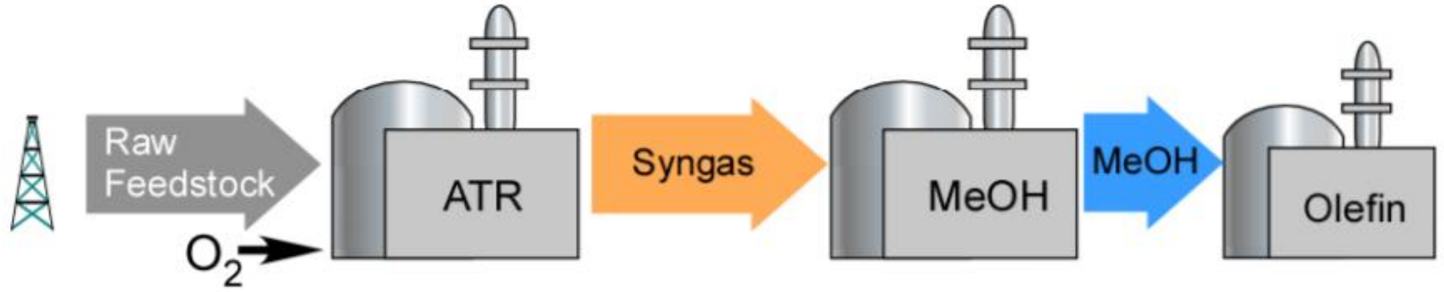


New trends in olefin production

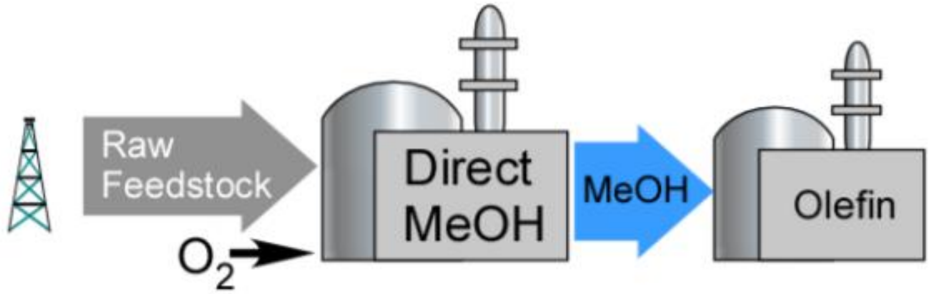
Abundancy of cheap methane from shale gas and stranded gas

→ Develop processes to **valorize methane** to higher hydrocarbons

Syngas / MeOH

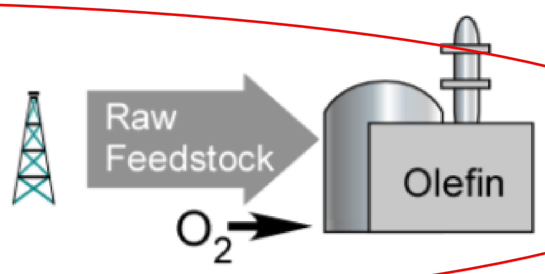


Avoid syngas



Oxidative coupling of methane

Avoid intermediates



Oxidative coupling of methane (OCM)

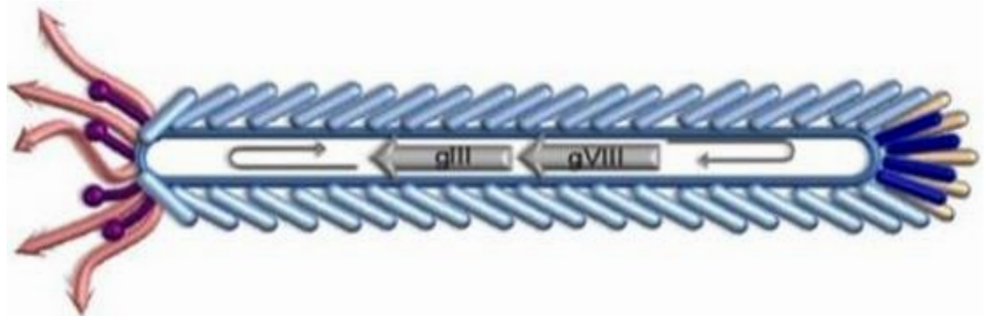
Recent history

1982 Keller and Bhasin: pioneering work

2008 DOW Chemical awards "methane challenge grants"

2013 Small firms are developing technologies for converting natural gas to fuel and chemicals

April 2015 Siluria technologies anounces successful start-up of demonstration plant for OCM



Demonstration unit for OCM in La Porte (TX)

Key challenges

- Strongly **exothermic** reaction(s)
- Inverse relationship between C2 hydrocarbon selectivity and CH_4 conversion: **low C2 yields**

} Catalyst design & <u>Reactor design</u>

OCM research at LCT

Microkinetics of **Methane Oxidative Coupling**
(Sun et al. 2008)

Catalyst design based on microkinetic models: **Oxidative Coupling of Methane**
(Thybaut et al. 2011)

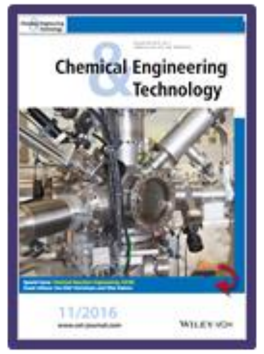
Oxidative Coupling of Methane: a microkinetic model accounting for intraparticle surface-intermediates concentration profiles
(Kechagiopoulos et al. 2014)

Oxidative Coupling of Methane: catalytic behaviour assessment via comprehensive microkinetic modelling
(Alexiadis et al. 2014)

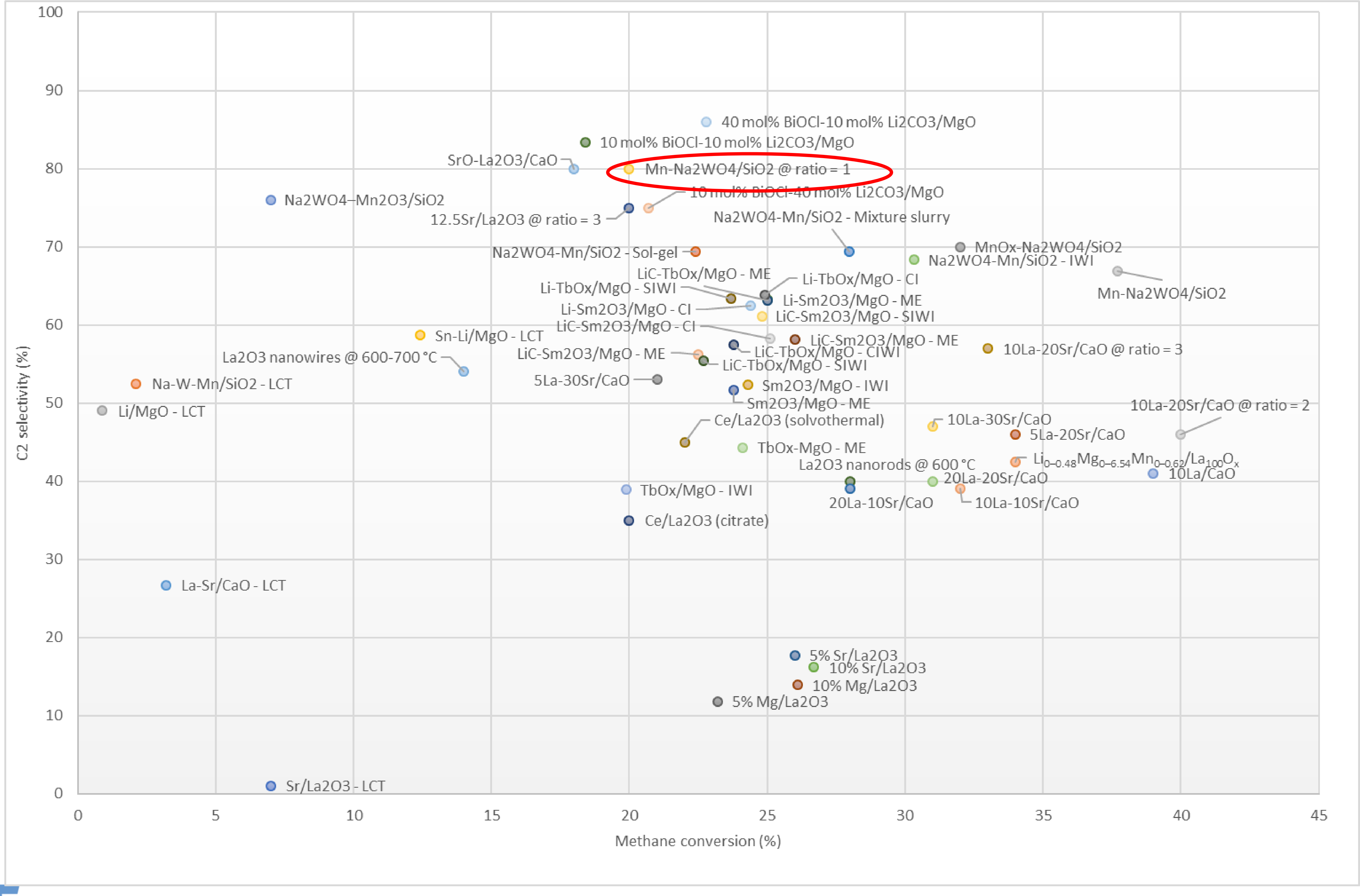
A novel technology for Natural Gas conversion by means of integrated **Oxidative Coupling** and Dry Reforming of **Methane**
(Thybaut et a. 2014)

Quantitative screening of an extended **Oxidative Coupling of Methane** catalyst library
(Alexiadis et al. 2016)

Oxidative Coupling of Methane: opportunities for microkinetic model-assisted process implementations
(Obradović et al. 2016)



Catalyst for OCM

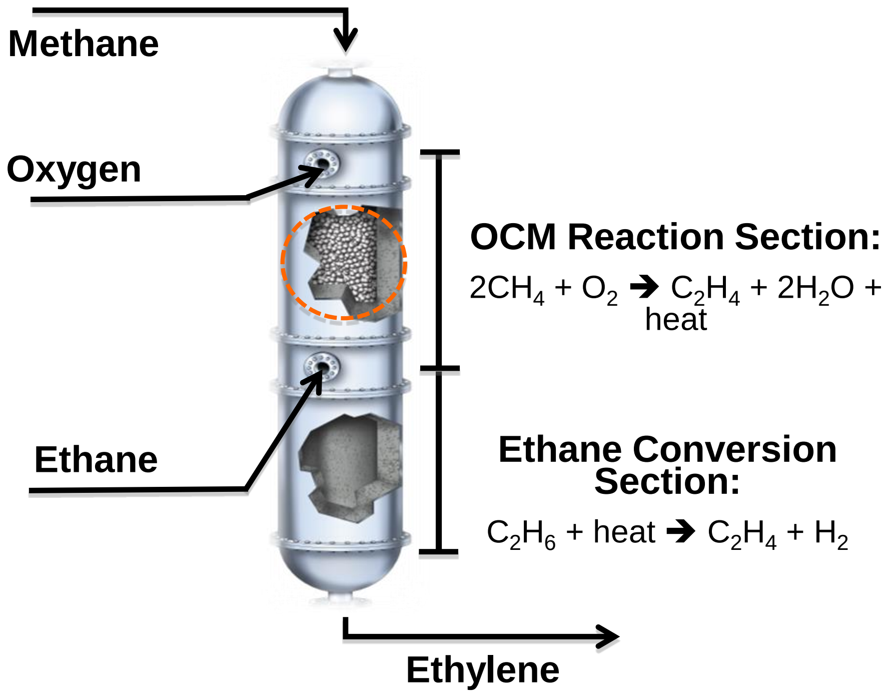


GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

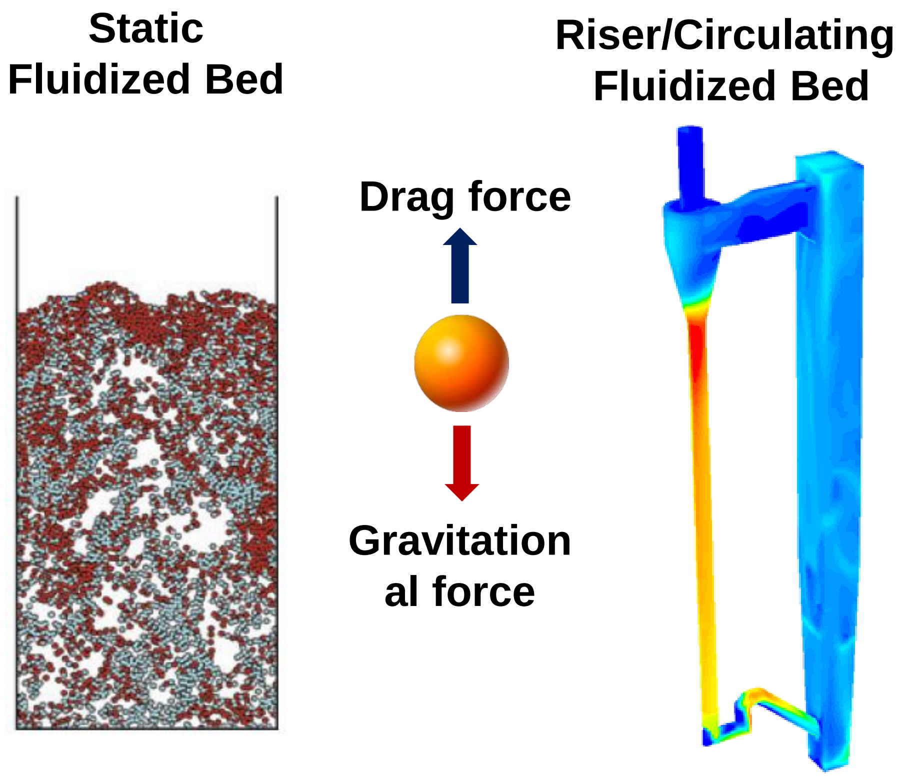
Reactor design for OCM

Conventional Fixed Bed



Limitations:
- Thermal control difficult:
- Potential formation of hotspots

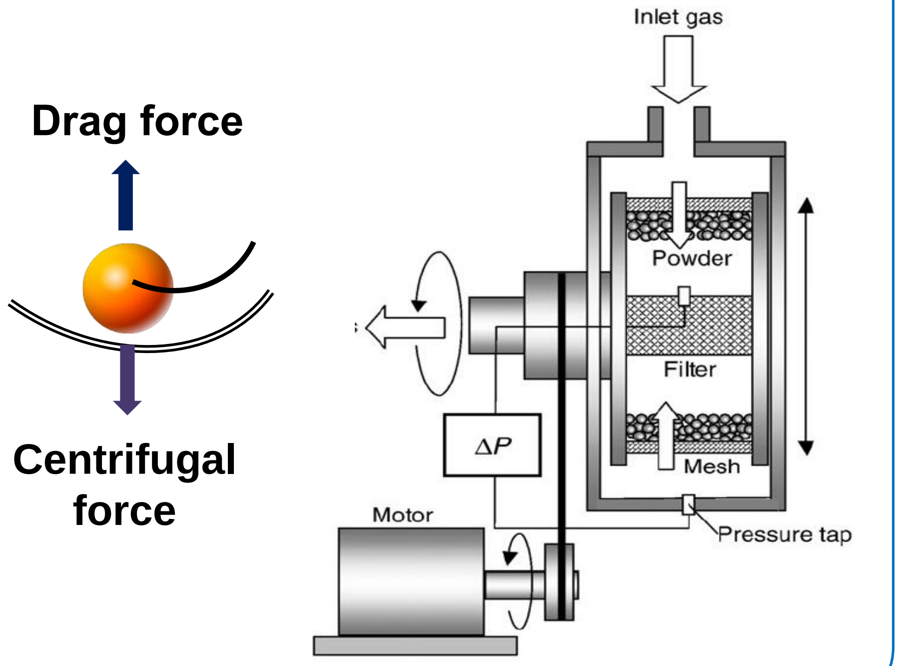
Gravitational fluidized bed



Advantages:
- Better heat and mass transfer

Limitations:
- Limited slip velocities (~ 1 m s^{-1})
- Entrainment of particles at high gas flow rates

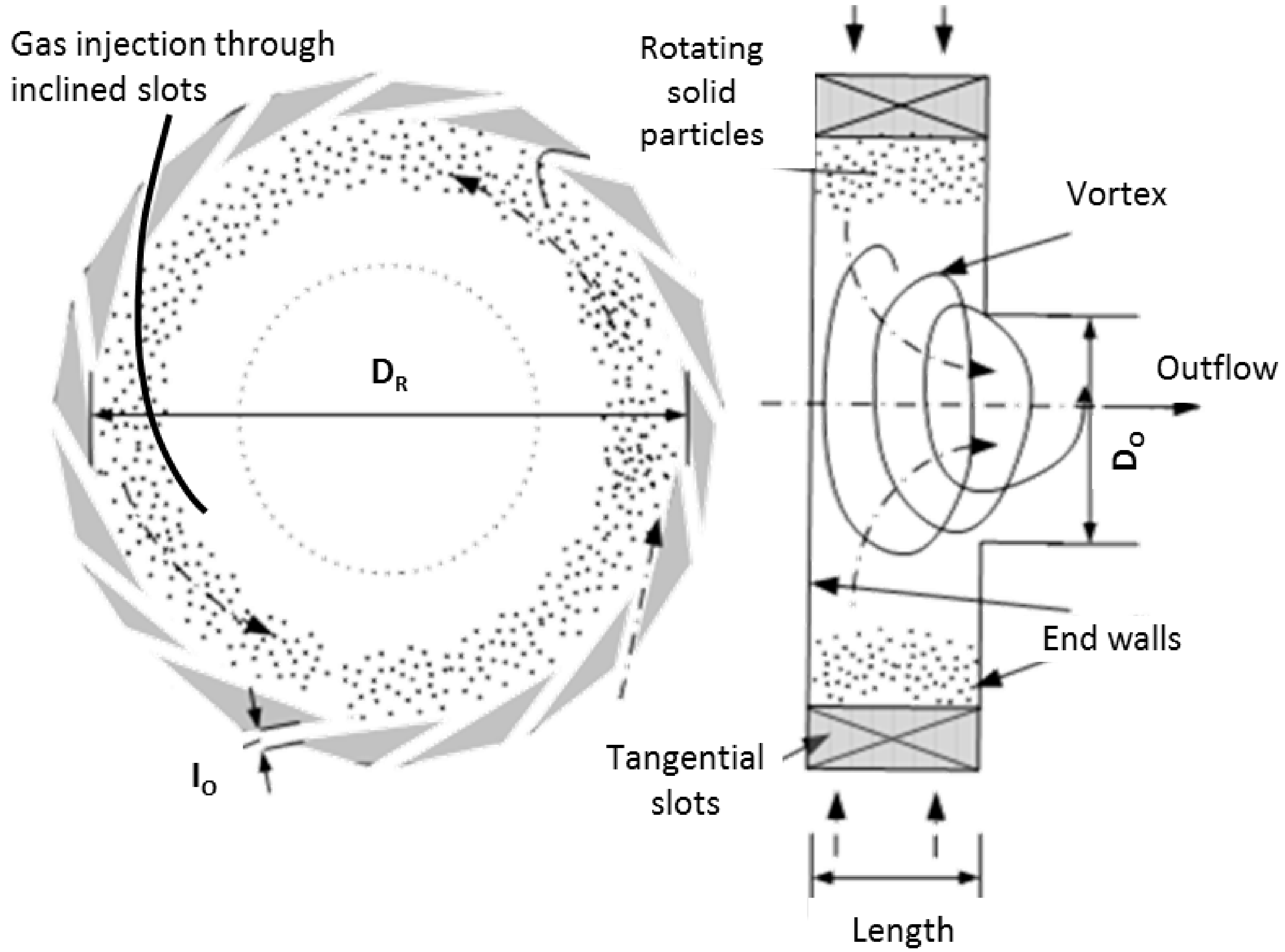
Rotating fluidized bed

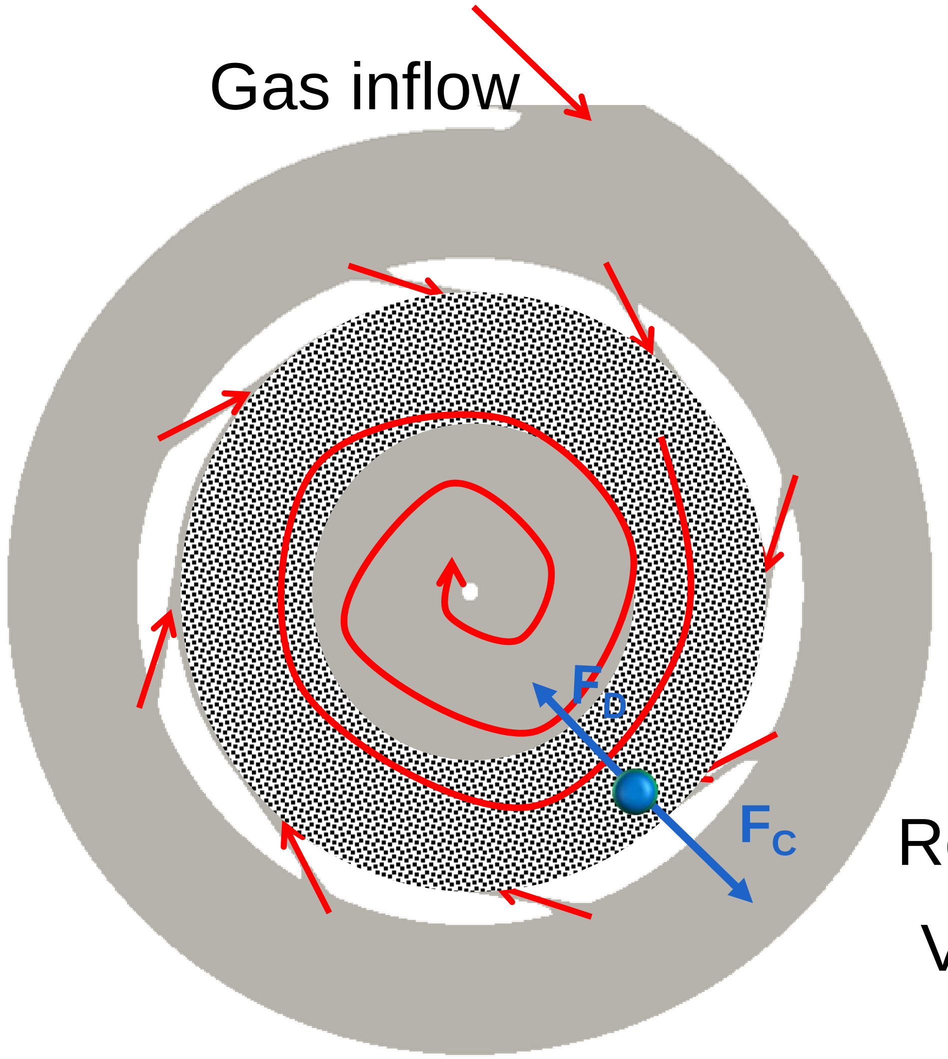


Advantages:
- Dense particle bed
- High gas feed flow rates
- Higher slip velocity → *better heat & mass transfer*

Limitation:
- Mechanical moving parts (abrasion)

Gas-solid vortex reactor (GSVR)





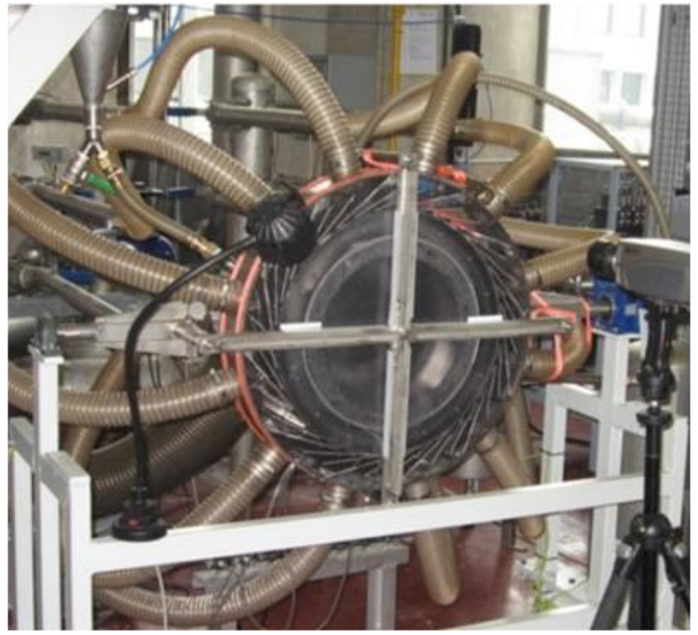
Rotating bed in Vortex reactor

- Dense particle bed → reduced reactor volume
- High gas feed flow rates → shorter gas residence time
- Higher gas-solid slip velocity → better gas-solid heat and mass transfer

✓ **Momentum, heat and mass transfer intensification**

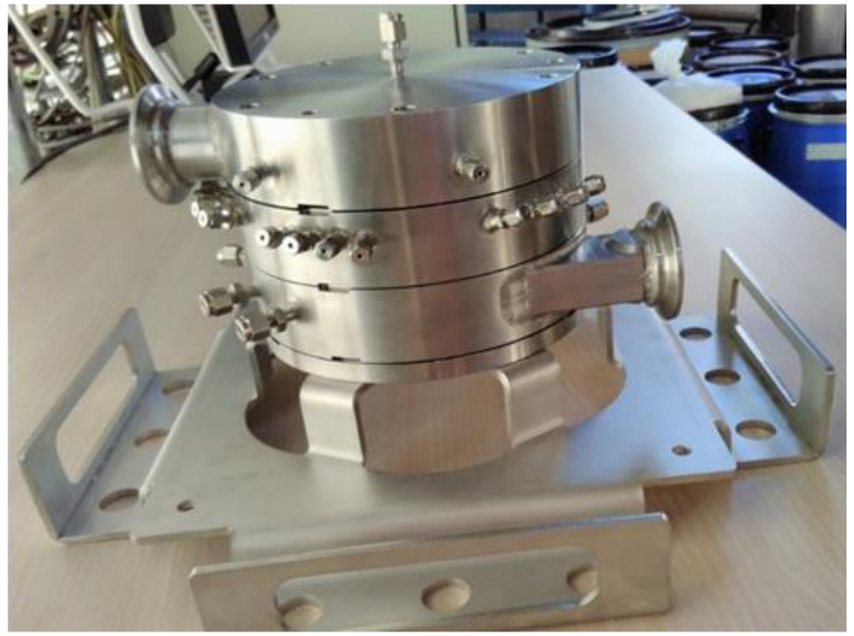
GSVR technology at LCT

Cold flow unit

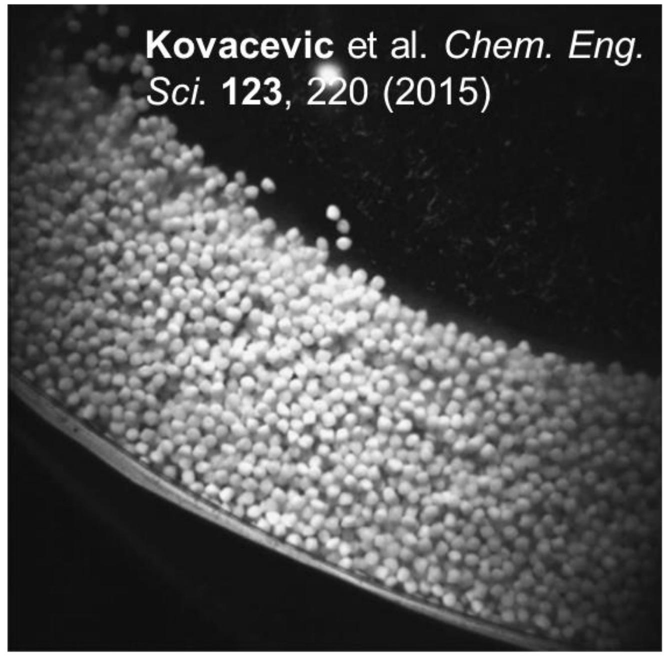


Hot flow unit

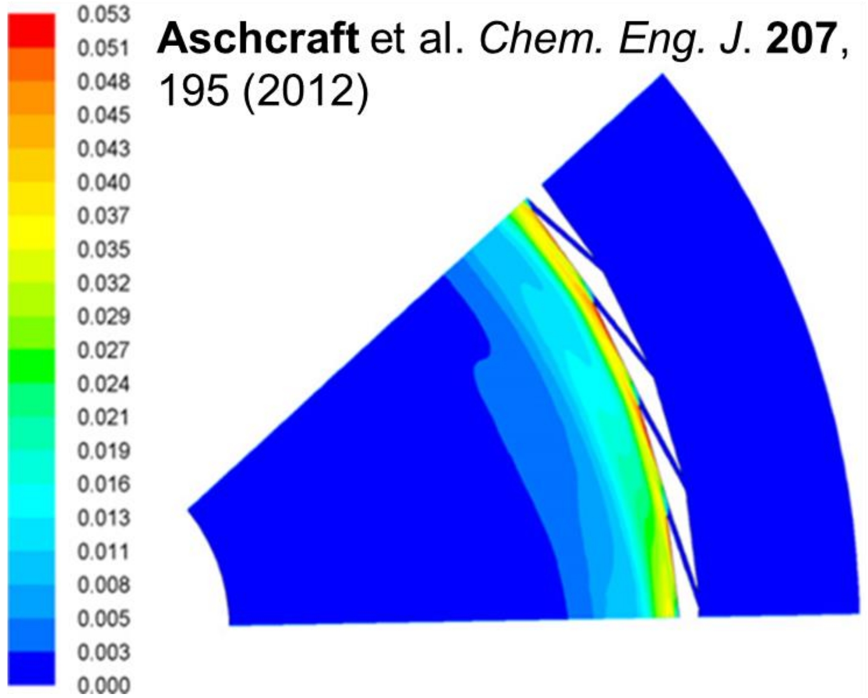
Reactive unit



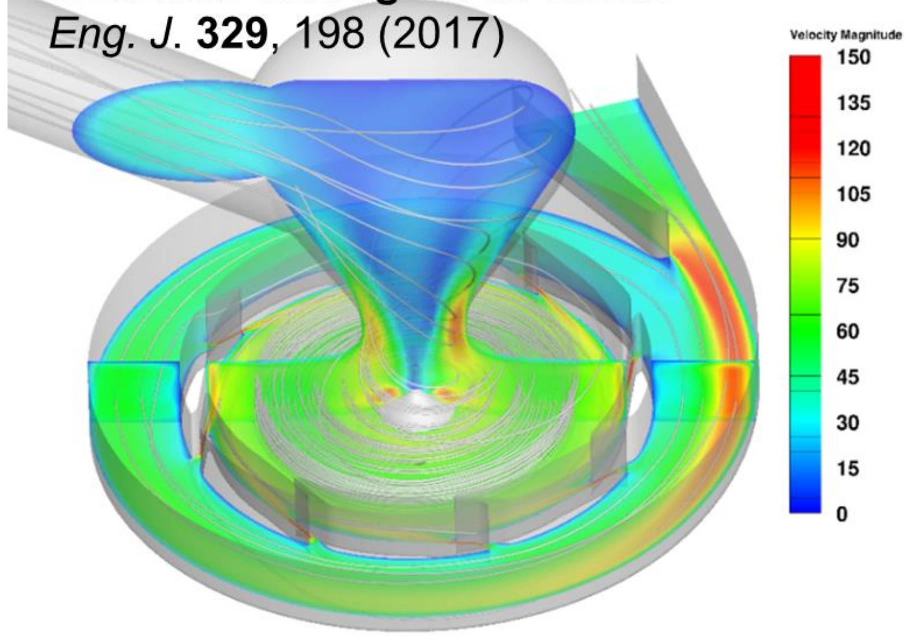
Experiments & CFD simulations



Kovacevic et al. *Chem. Eng. Sci.* **123**, 220 (2015)



Aschcraft et al. *Chem. Eng. J.* **207**, 195 (2012)



Gonzalez-Quiroga et al. *Chem. Eng. J.* **329**, 198 (2017)

GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

GSVR technology at LCT

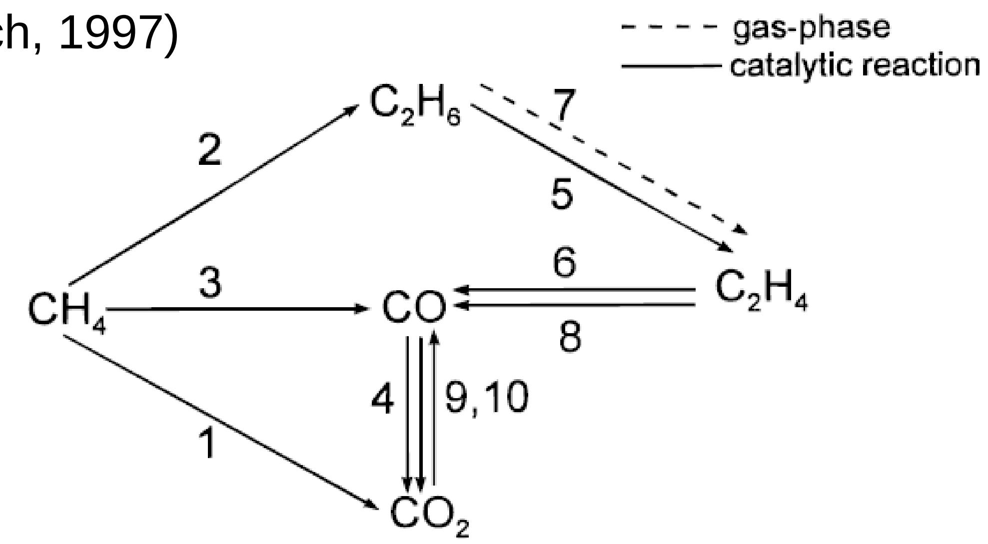
Developed for biomass fast pyrolysis

- Lignocellulosic biomass conversion to bio-oil & chemicals
- High interphase heat transfer demands
- Very small vapor residence time
- Temperature ~ 800 K

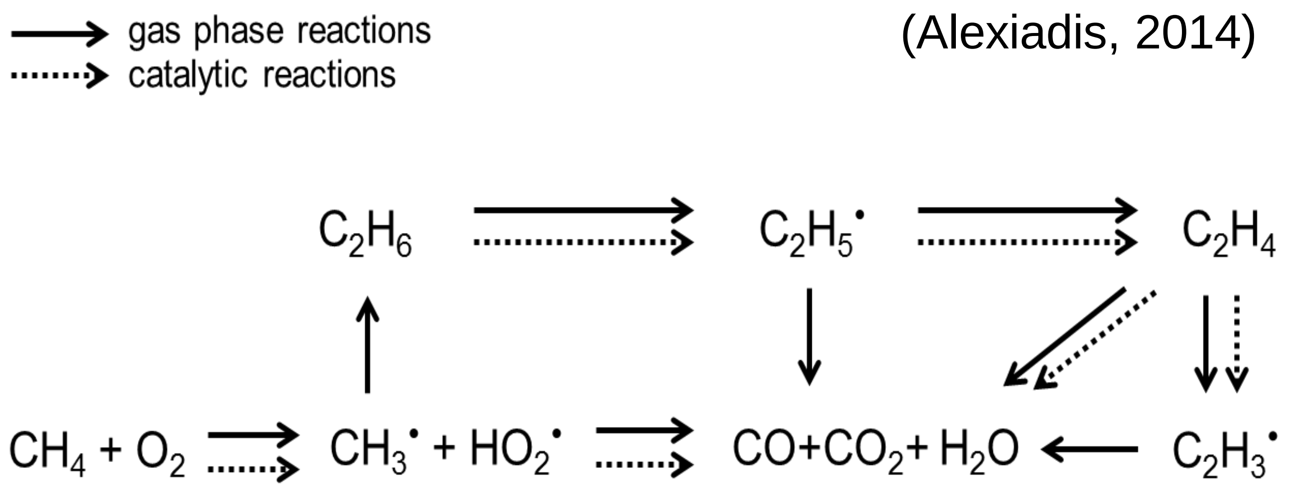
GSVR modifications for OCM

Direct conversion of methane to ethylene: substantially faster rates

(Stansch, 1997)



(Alexiadis, 2014)



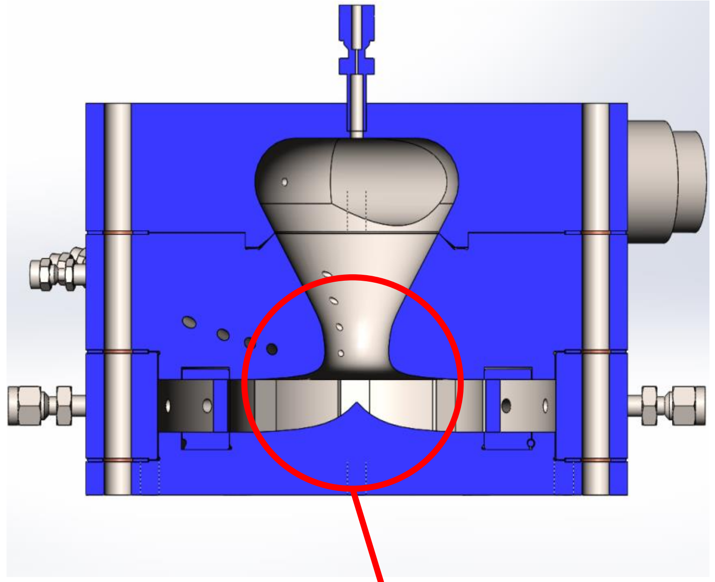
Reactive GSVR

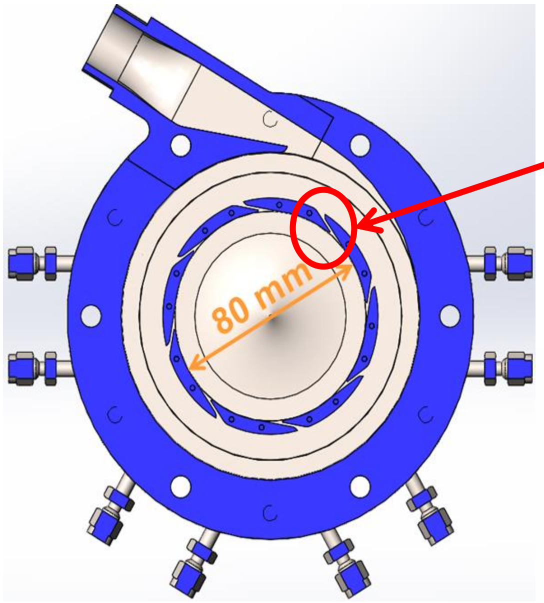
- ✓ Proof-of-concept unit: world's first reactive GSVR for biomass fast pyrolysis and OCM
- ✓ Design based on preliminary calculations and CFD simulations
- ✓ Flexible unit: number and angle of inlet slots can easily be adjusted

OCM-related issues:

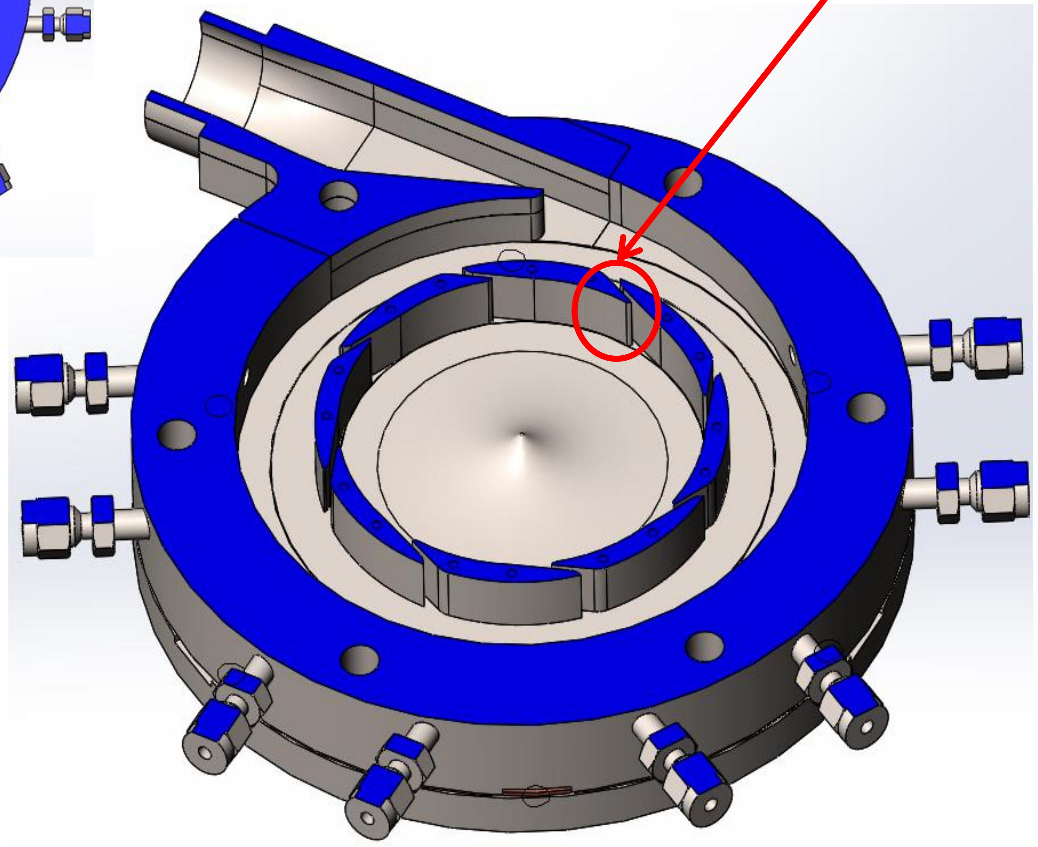
- ✗ Heat management is important due to highly exothermic OCM reactions: using N_2 and/or catalyst diluent might be required
- ✗ Catalyst attrition in the GSVR is limited due to the dense rotating bed with rather uniform velocity

Reactive GSVR: current design



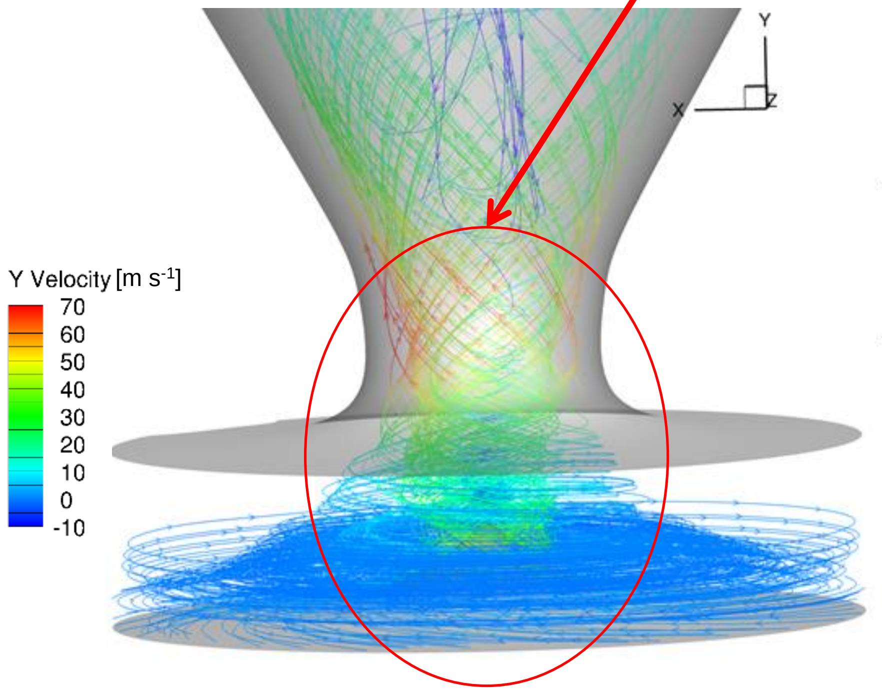


✓8 inlet slots
✓10° with respect to the tangent
✓1 mm width
✓Gas inlet velocity 60-140 m/s



- ✓ Diverging side wall shape
- ✓ Reduced backflow
- ✓ Recovery of kinetic energy of the swirl into pressure

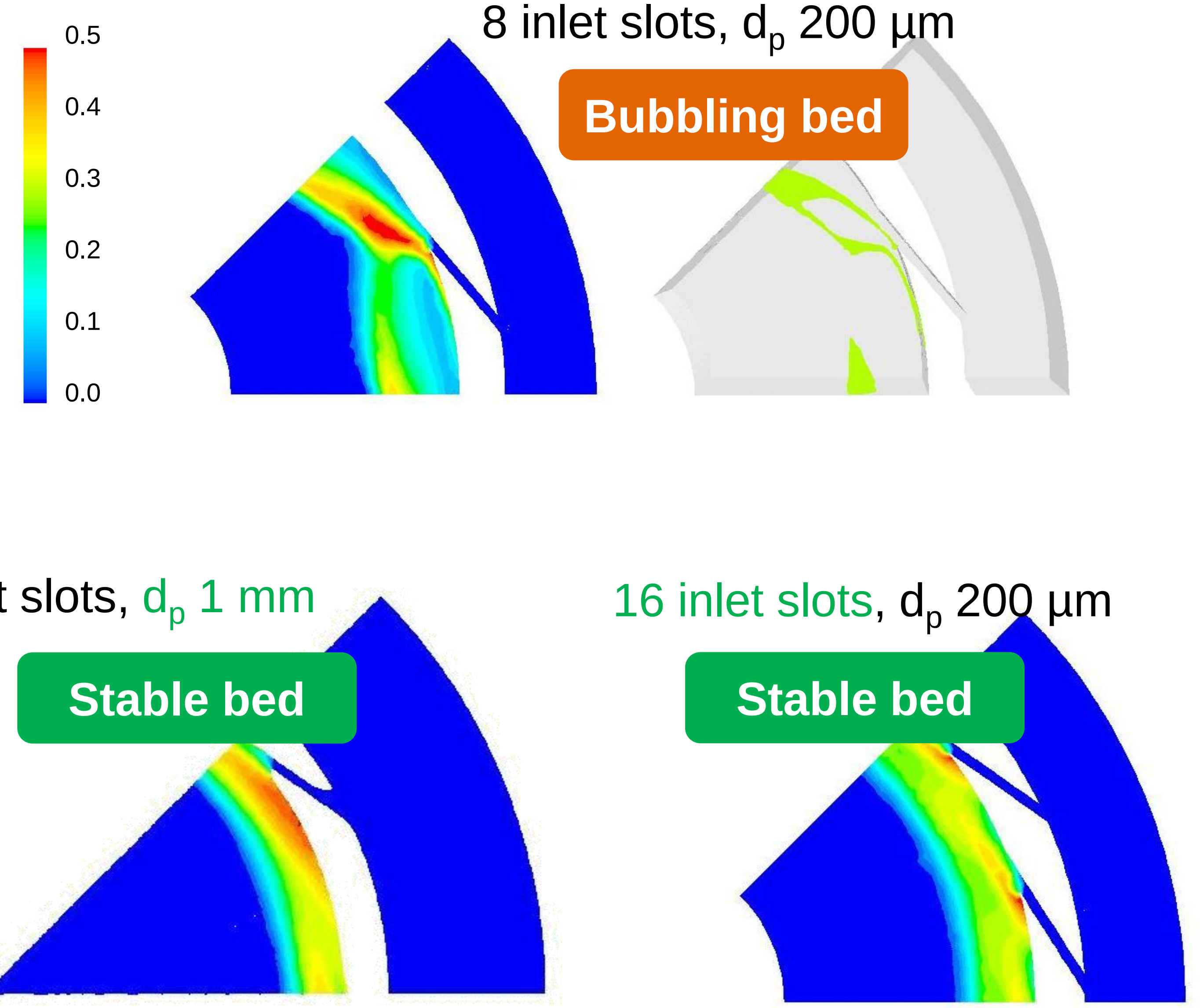
Backflow is minimized and displaced upwards towards the outlet



Gas only CFD simulation; N_2 mass flow: 6.67 g s^{-1}
Inlet temperature: 842K; Turbulence model: RSM

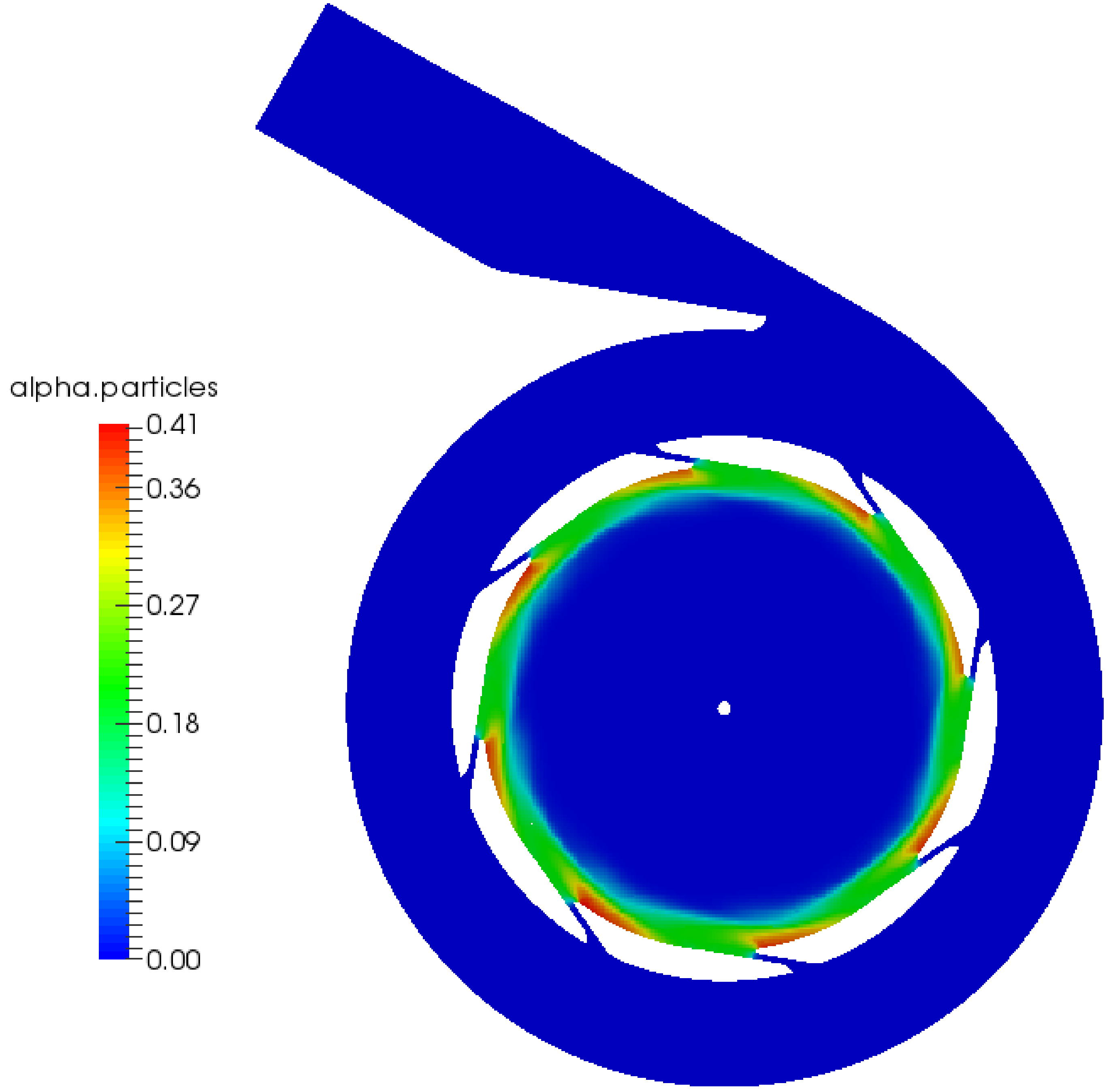
Non-reactive gas-particle simulations

Optimize design/operating conditions to obtain a stable bed



Nitrogen feed: 30 Nm³/hr, 923 K

16 g particles (density 2300 kg/m³)



Air feed: 40 Nm³/hr, 290 K

10 g particles (density 2700 kg/m³, d_p 500 µm)

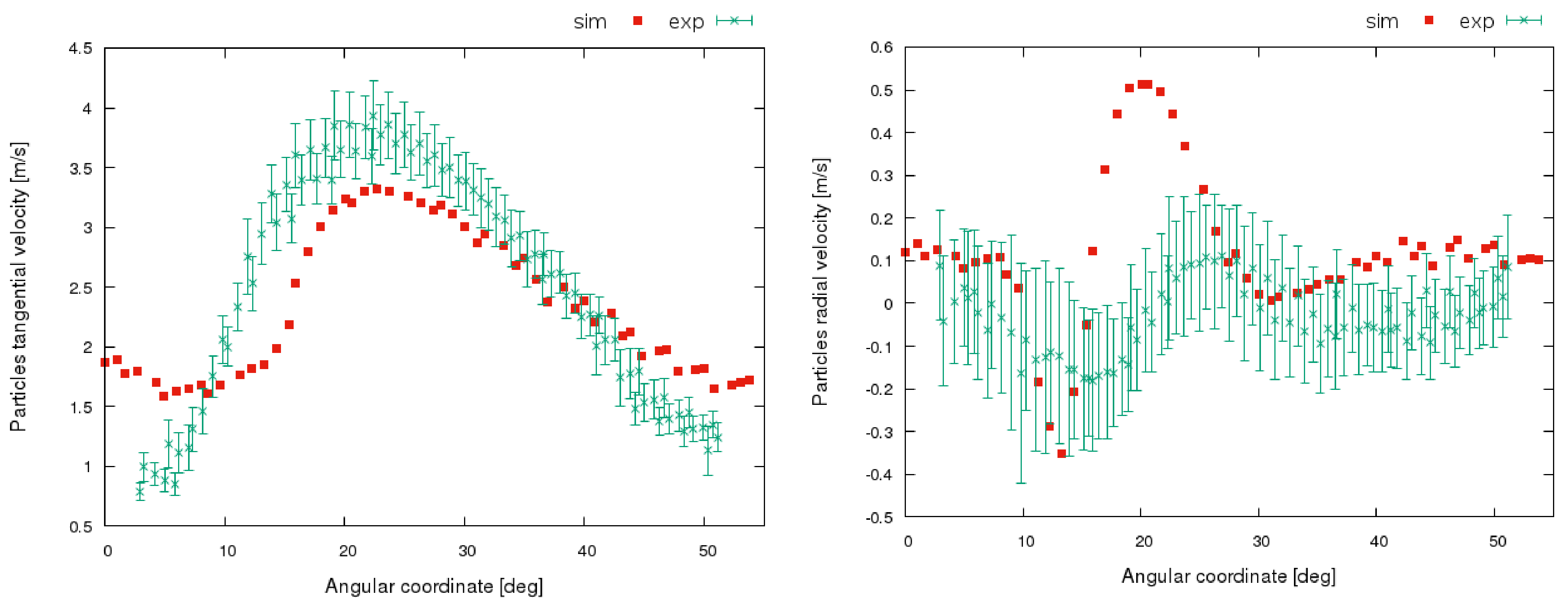
GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

Experimental validation

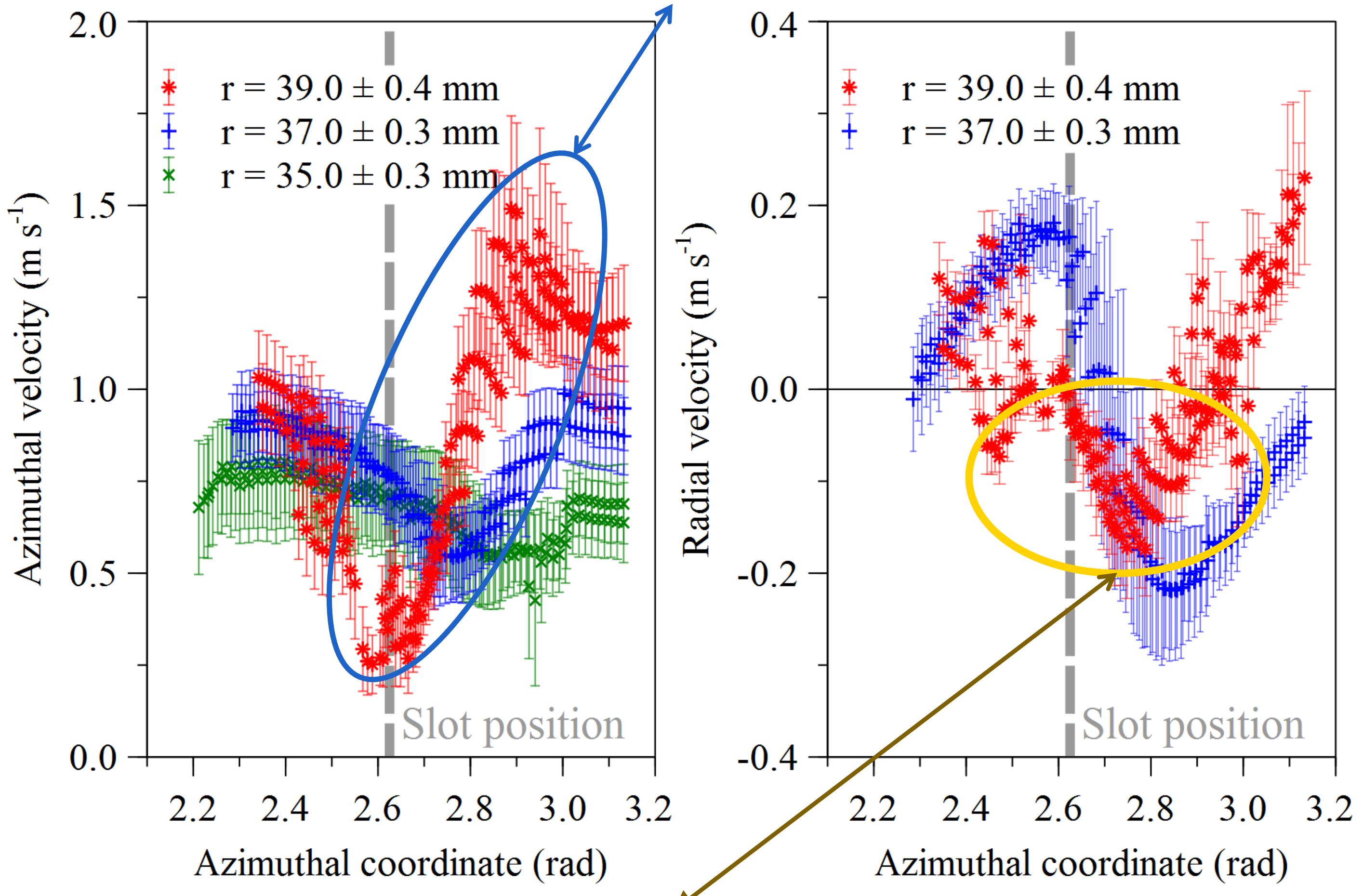
Particle image velocimetry (PIV)

- ✓ Measuring particle velocity profile to validate and finetune hydrodynamic models
- ✓ Improve reactor geometry: number and shape of inlet slots affects velocities and wall friction (attrition!)



The simulated particle velocities resemble the PIV data qualitatively

Higher acceleration-deceleration near the circumferential wall indicates significant frictional losses at that location

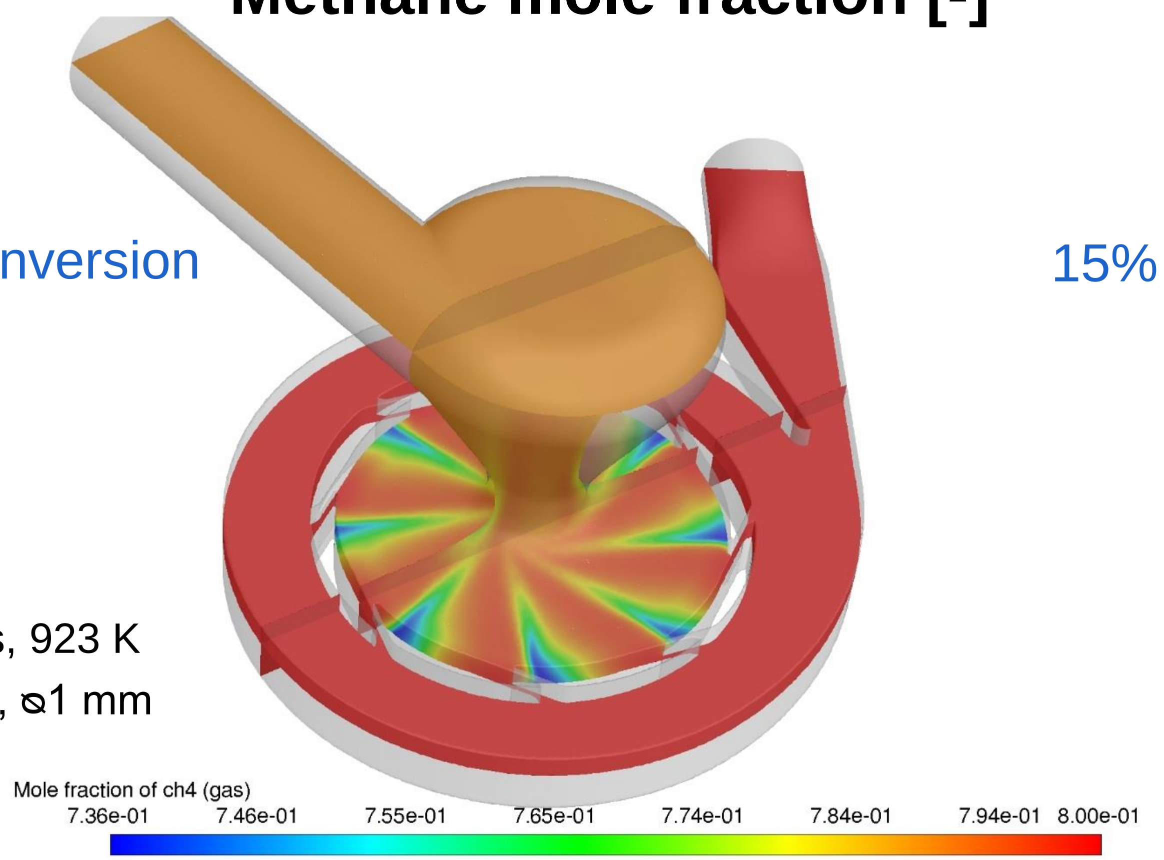


Negative radial velocities indicate where particles touch the wall

Reactive CFD simulations

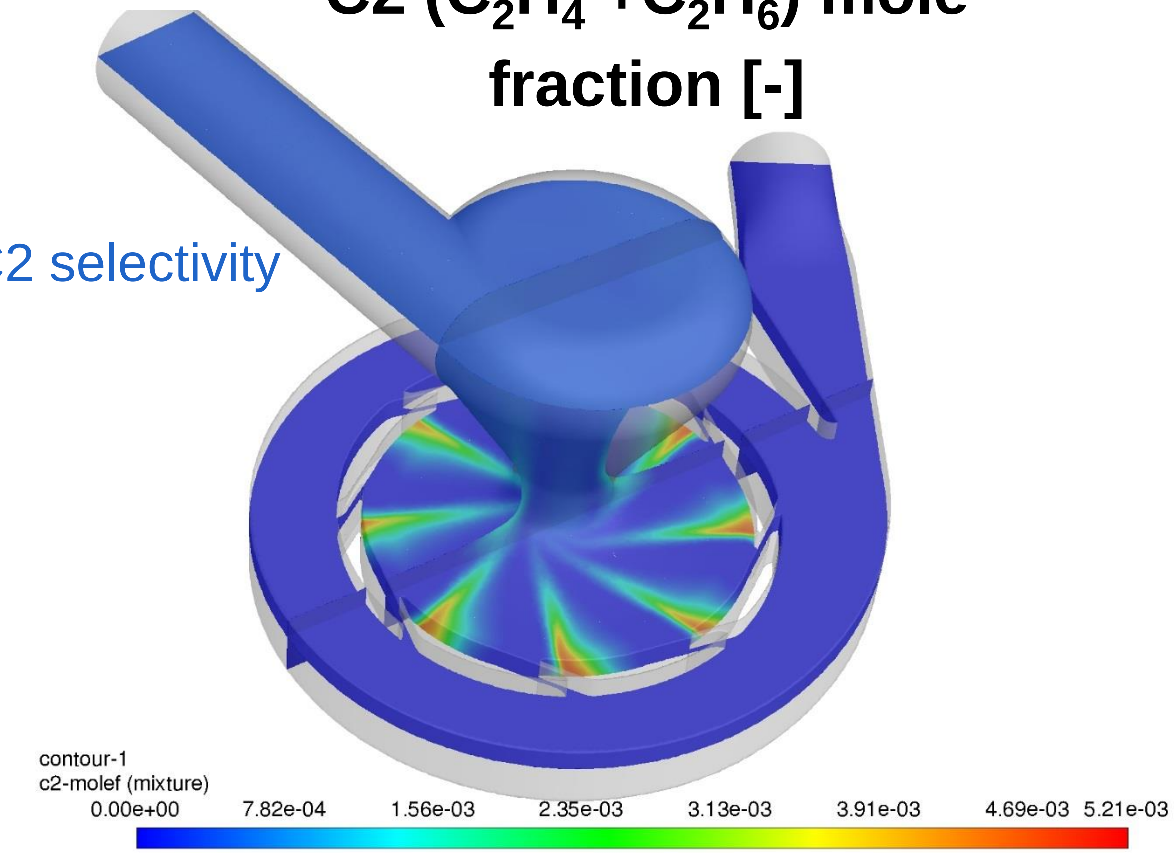
Methane mole fraction [-]

2.5% methane conversion



C2 (C_2H_4 +C_2H_6) mole fraction [-]

15% C2 selectivity



8 slots GSVR reactor

Gas feed: CH_4:O_2:N_2 = 4:1:0, 10 g/s, 923 K

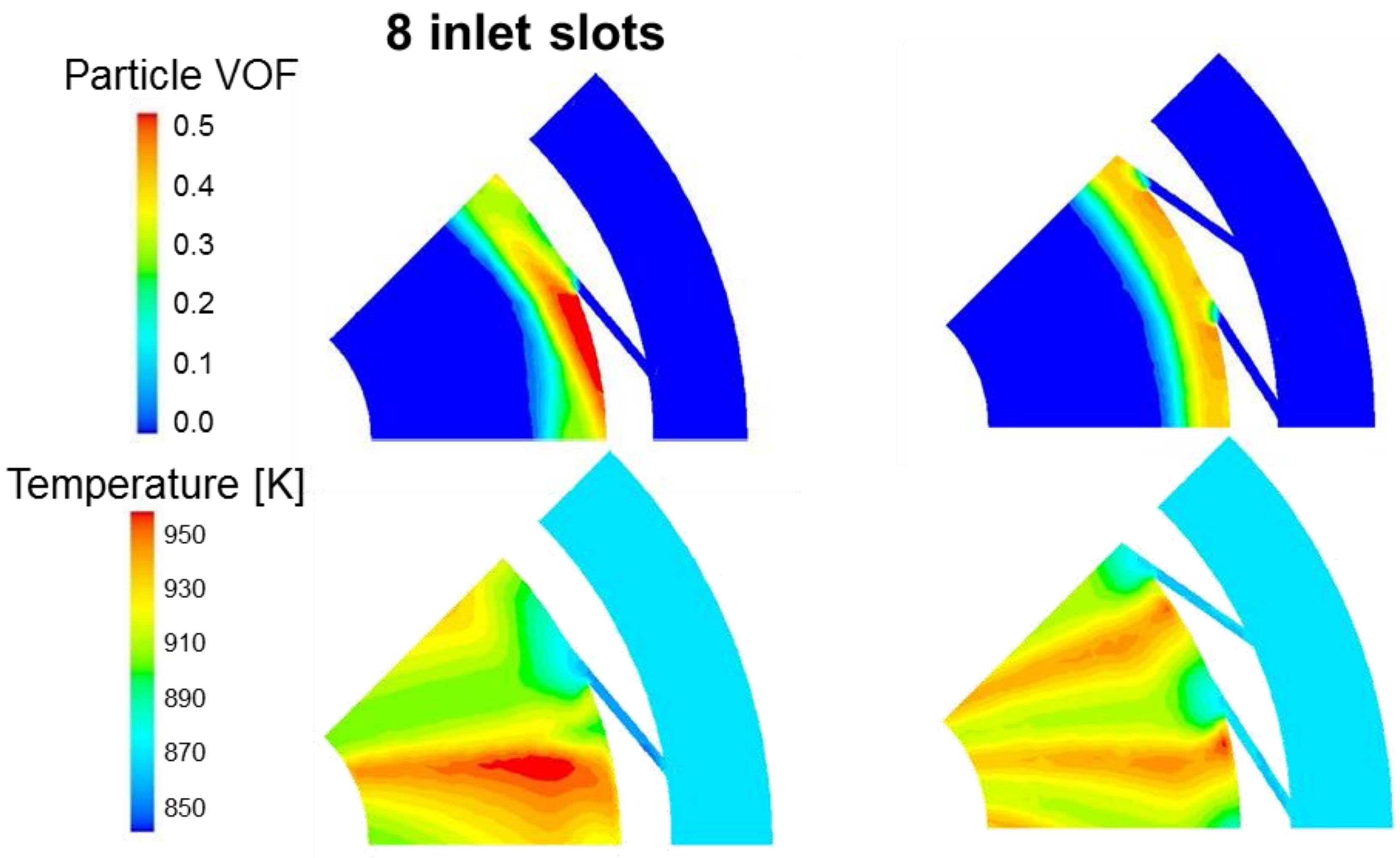
Catalyst particles: 2300 kg/m³, 16 g, ⌀1 mm

C2 selectivity and CH_4 conversion can be increased by adjusting

- Bed density, solid loading
- Gas-phase residence time (flow rate)
- Type of catalyst (!)
- Particle diameter
- Temperature, pressure
- CH_4/O_2 ratio

A lot of degrees of freedom!

Reactive CFD simulations

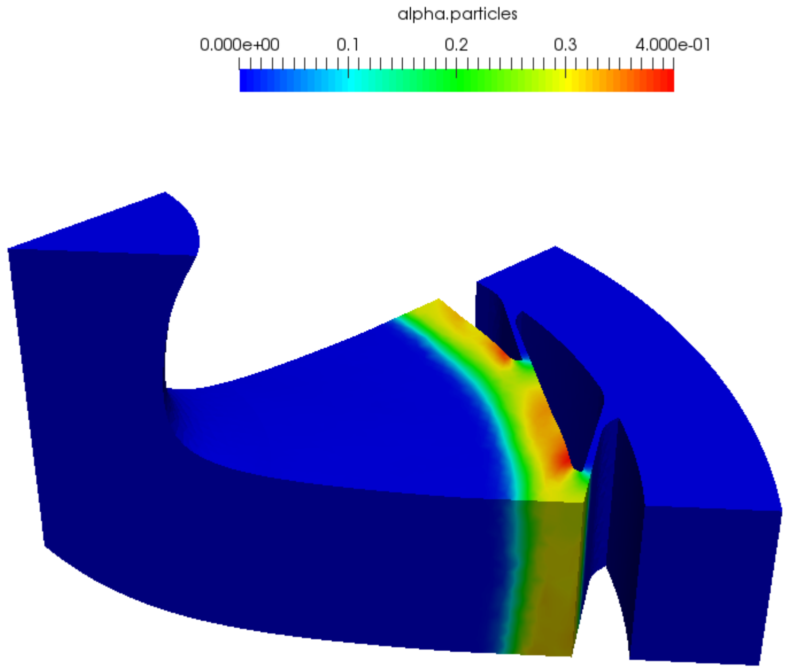


- ✓ Increasing the number of inlet slots increases the bed uniformity
- ✓ Less bypassing of the bed: higher conversion and C2-yields
- ✓ More uniform temperature profile

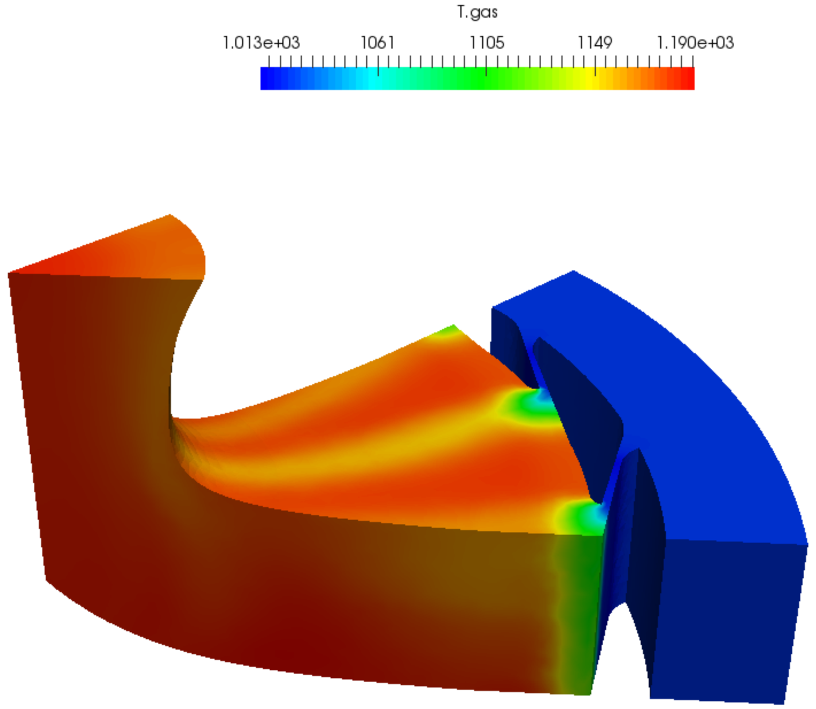
8 vs 16 slots GSVR reactor
Gas feed: CH_4:O_2:N_2 = 4:1:0, 10 g/s, 873 K
Catalyst particles: 2300 kg/m³, 16 g, ø1 mm

Reactive CFD simulations

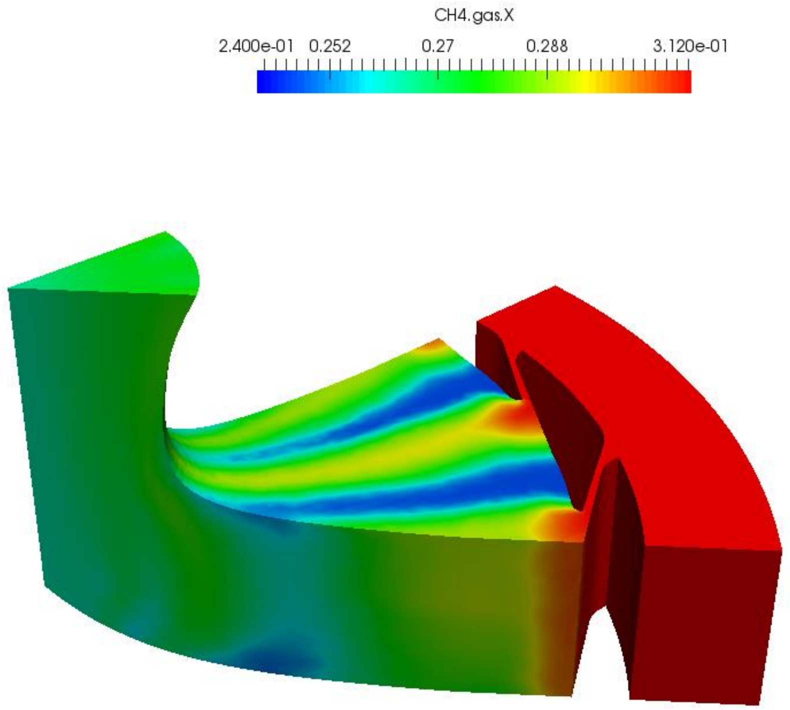
Catalyst volume fraction [-]



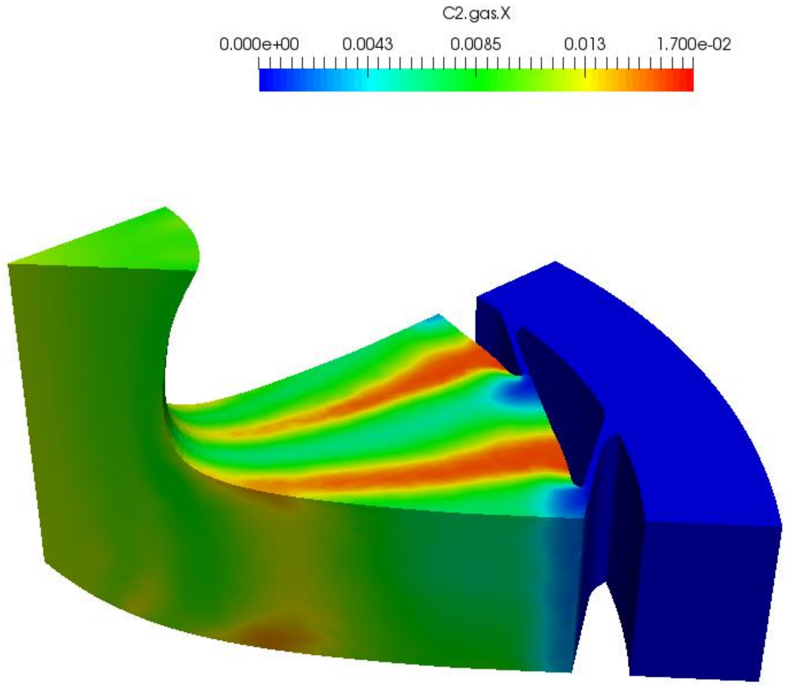
Temperature [K]



Methane mole fraction [-]



C2 (C_2H_4 +C_2H_6) mole fraction [-]



16 slots GSVR reactor

Gas feed: CH_4:O_2:N_2 = 5:1:10, 7 g/s, 1023 K

Catalyst particles: 1173 K, 2300 kg/m³, 11.5 g, ⌀0.5 mm

12.75% methane conversion

49.4% C2 selectivity

Reasonable conversion, but more selective catalyst required

GHENT UNIVERSITY LCT DRIVING CHEMICAL TECHNOLOGY

Conclusions

- GSVR emerges as a promising reactor technology for OCM
- Fluidization in a centrifugal field with particle inertial forces exceeding gravitational force
  - Much higher gas-solid slip velocities compared to conventional fluidized beds: **process intensification**
  - Improved bed uniformity and gas distribution: **temperature control**
  - Short gas residence time and possibility for improving selectivity towards C2 products
- Suitable catalyst must be selected for achieving high C2 yields

Acknowledgements

Colleagues @ LCT

Thank you for your attention