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Paper #124E

Computational Fluid Dynamics based design of a novel reactor technology for oxidative coupling of methane

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

Laboratory for Chemical Technology, Ghent University

http://www.lct.UGent.be

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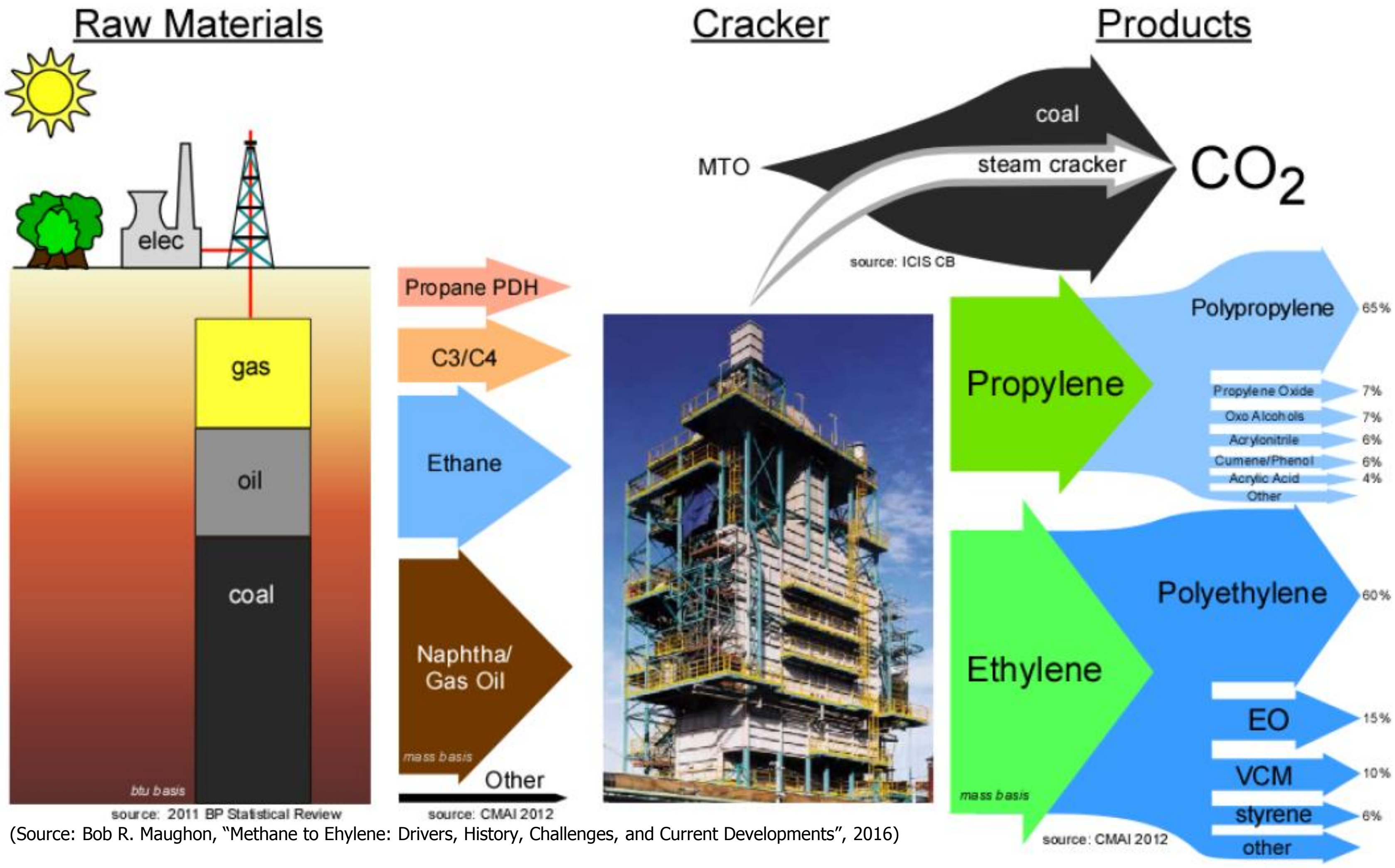
29th Ethylene Producers' Conference

The chemical industry today

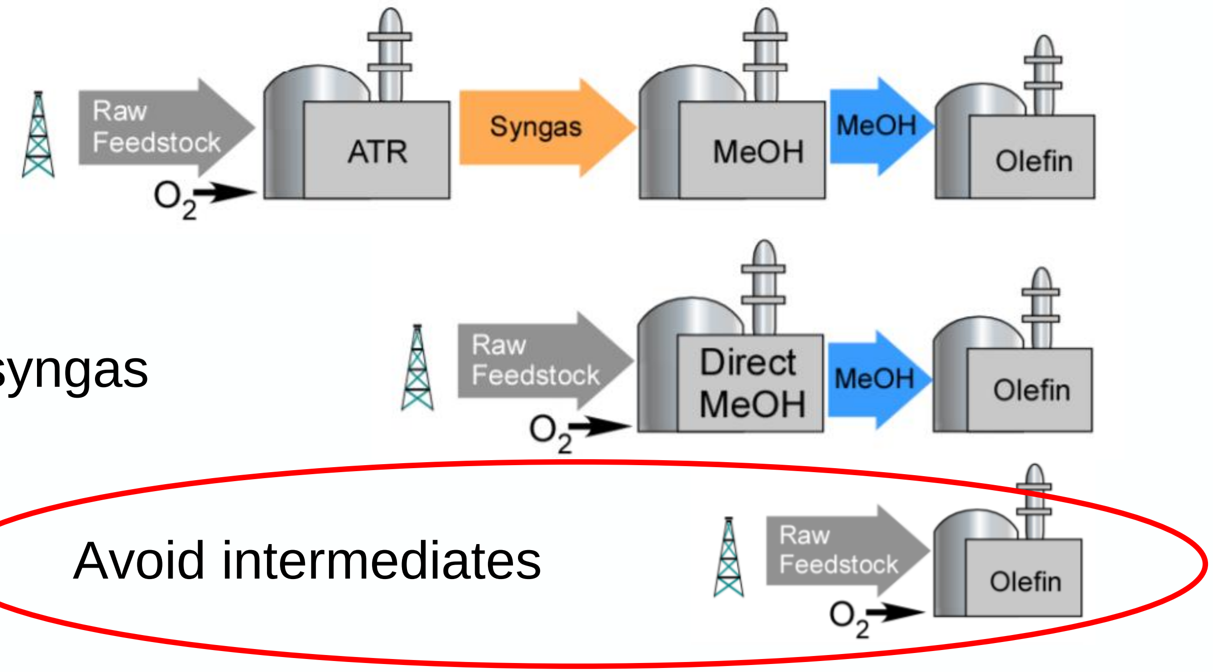


(Source: Bob R. Maughon, “Methane to Ehylene: Drivers, History, Challenges, and Current Developments”, 2016)

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

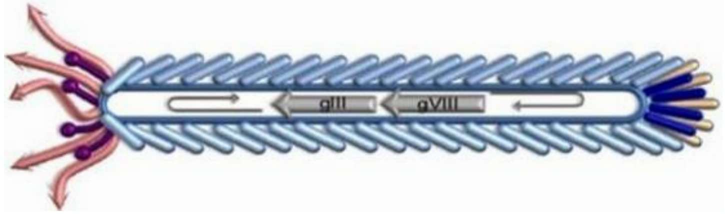
Success for implementation will require:
- ✓ Breakthrough in catalysis, reactor design, separation processes
- ✓ Fundamental technology development
- ✓ Industry / government / academic partnerships

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 technology for converting natural gas to fuel and chemicals
- **April 2015** Siluria Technologies announces successful start-up of demonstration plant for OCM

Demonstration unit for OCM in La Porte, Texas



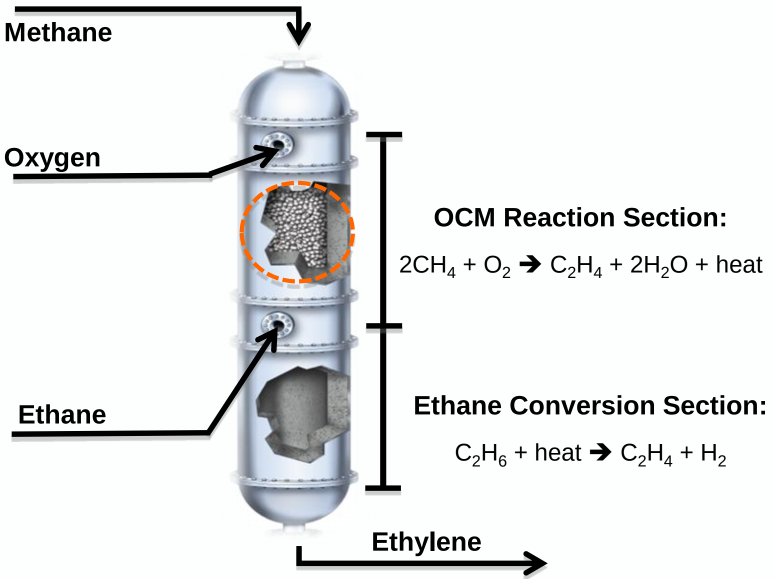
Key challenges

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

} Reactor design!

Reactor design for OCM

Conventional Fixed Bed



OCM Reaction Section:

$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O + \text{heat}$

Ethane Conversion Section:

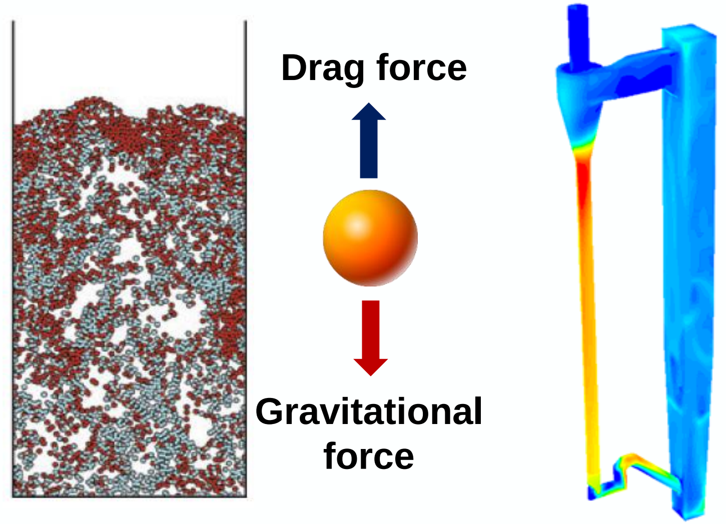
$C_2H_6 + \text{heat} \rightarrow C_2H_4 + H_2$

Limitations:

- Thermal control of the reactor is difficult:
- Potential formation of hotspots

Static Fluidized Bed

Riser/Circulating Fluidized Bed



Advantages:

- Better heat and mass transfer

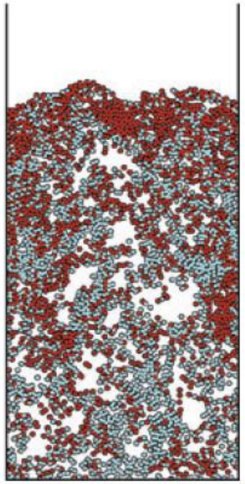
Limitations:

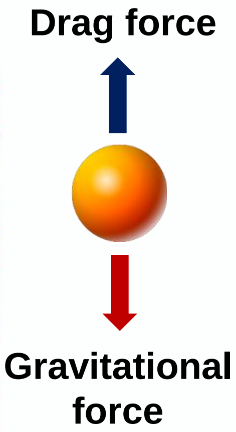
- Limited slip velocities (~ 1 m s^{-1})
- Entrainment of particles at high gas flow rates

Reactor design for OCM

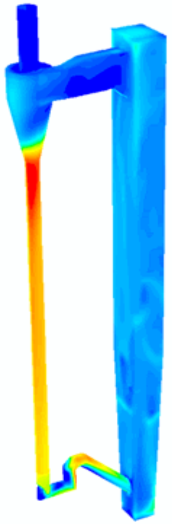
Centrifugal instead of gravitational force field → Process intensification

Static Fluidized Bed





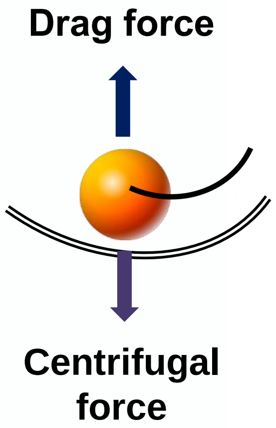
Riser/Circulating Fluidized Bed

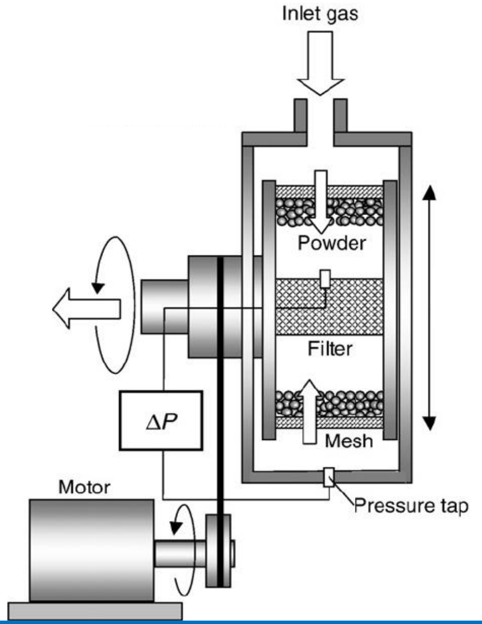


Limitations:

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

Rotating Fluidized Bed





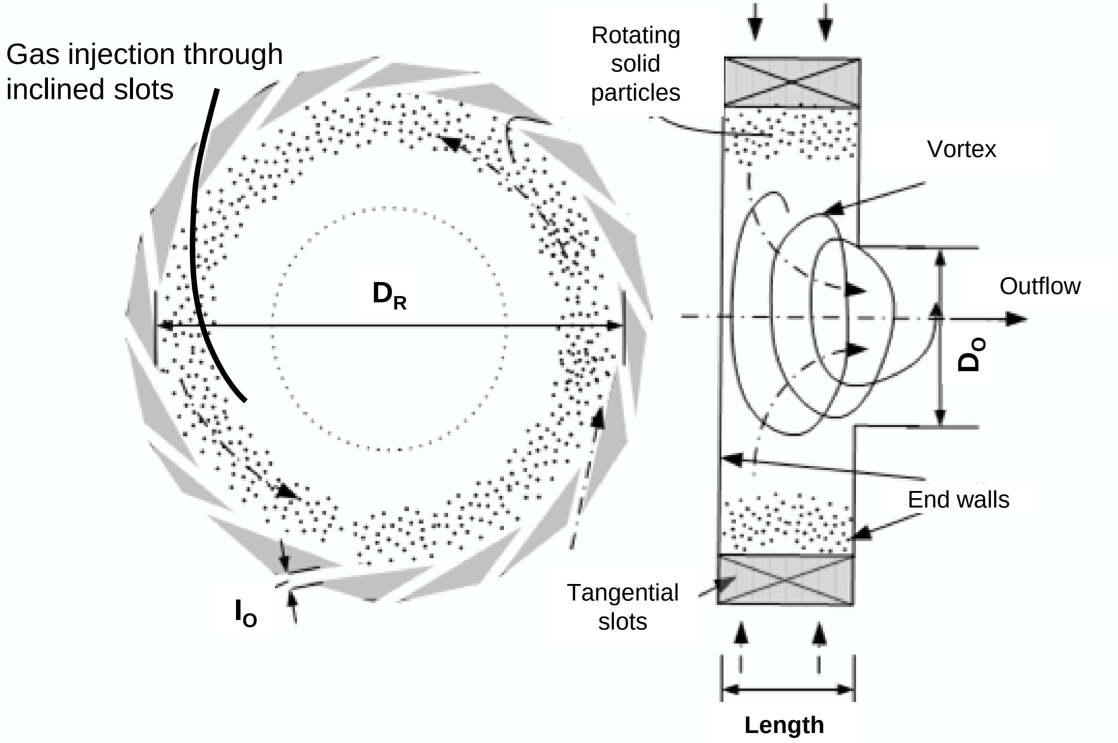
Advantages:

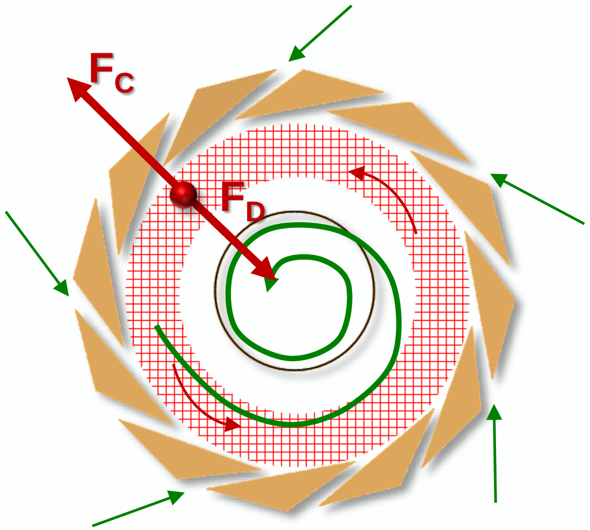
- Dense particle bed
- High gas feed flow rates
- Higher slip velocity → *better heat & mass transfer*

Limitation:

- Mechanical moving parts (abrasion)

Gas-Solid Vortex Reactor (GSVR)





Fluidized Bed in Vortex Reactor

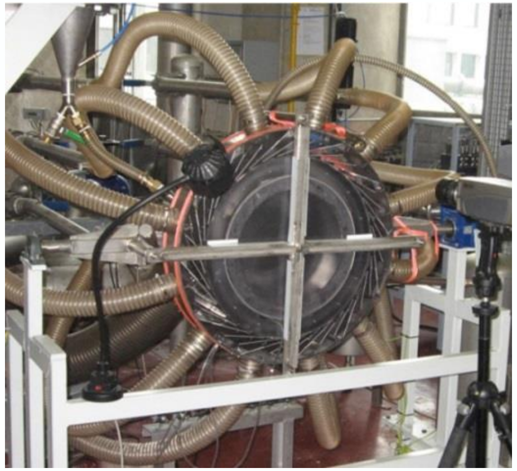
Advantages:

- Dense particle bed
- High gas feed flow rates → *high throughput operation*
- Higher slip velocity → *better heat & mass transfer*

GSVR emerges as an excellent reactor choice to demonstrate the OCM process

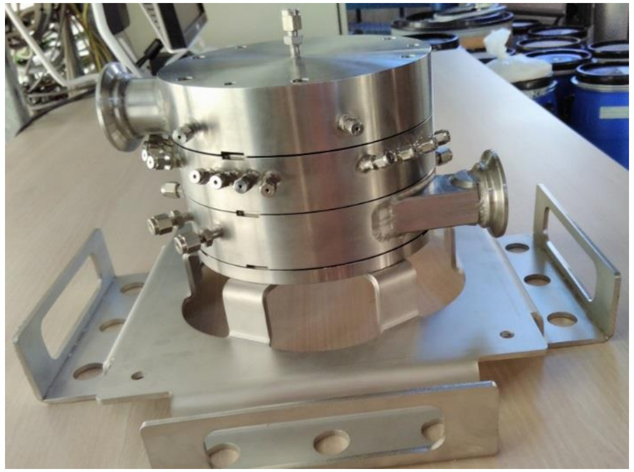
GSVR Research at LCT (Laboratory for Chemical Technology)

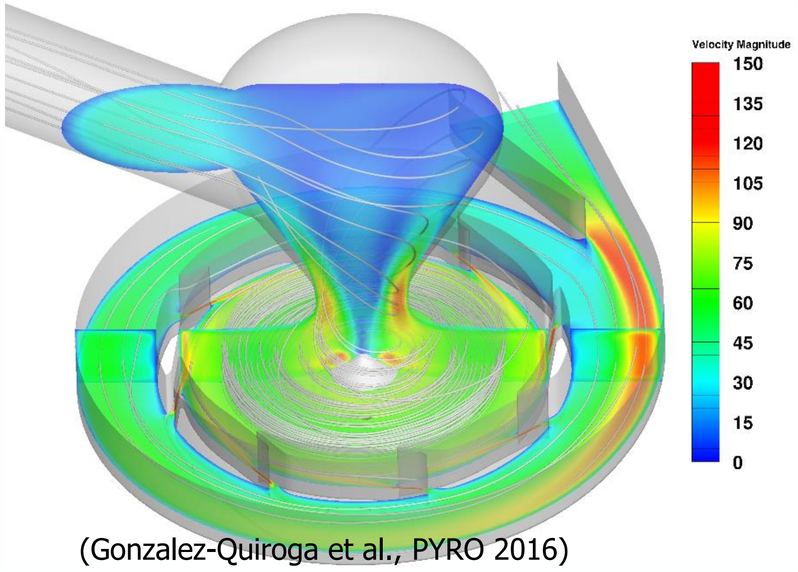
Cold flow unit



Hot flow unit

Reactive unit





(Gonzalez-Quiroga et al., PYRO 2016)

Optimize GSVR for OCM… A lot of **degrees of freedom**!

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

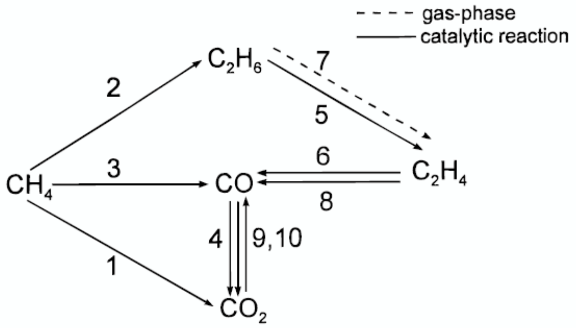
Catalysts and kinetics

Comparison of catalysts using a simple isothermal **plug flow reactor** model, which is an *ideal* representation of an isothermal **fixed bed reactor**

La_2O_3/CaO (Stansch, 1997) ***– $Mn/Na_2WO_4/SiO_2$*** (Danespayeh, 2009)

Comprehensive 10-step kinetic model

(1 gas-phase, 9 catalytic reactions)



Sr/La_2O_3 – Sn-Li/MgO (Alexiadis, 2014)

Detailed microkinetic model developed at the LCT

(39 gas-phase, 26 catalytic reactions)

Remark

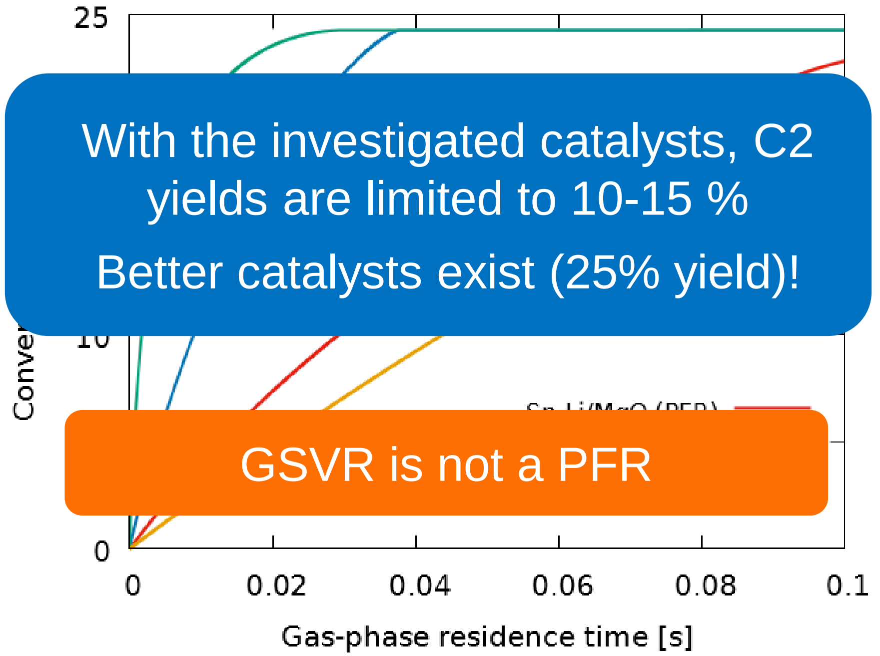
Homogeneous and heterogeneous reactions simultaneously ➔ Two space times

For the presented simulations, the bed density has been kept constant (40%) and only the gas phase residence time has been varied

Comparison catalysts

Isothermal plug flow reactor model

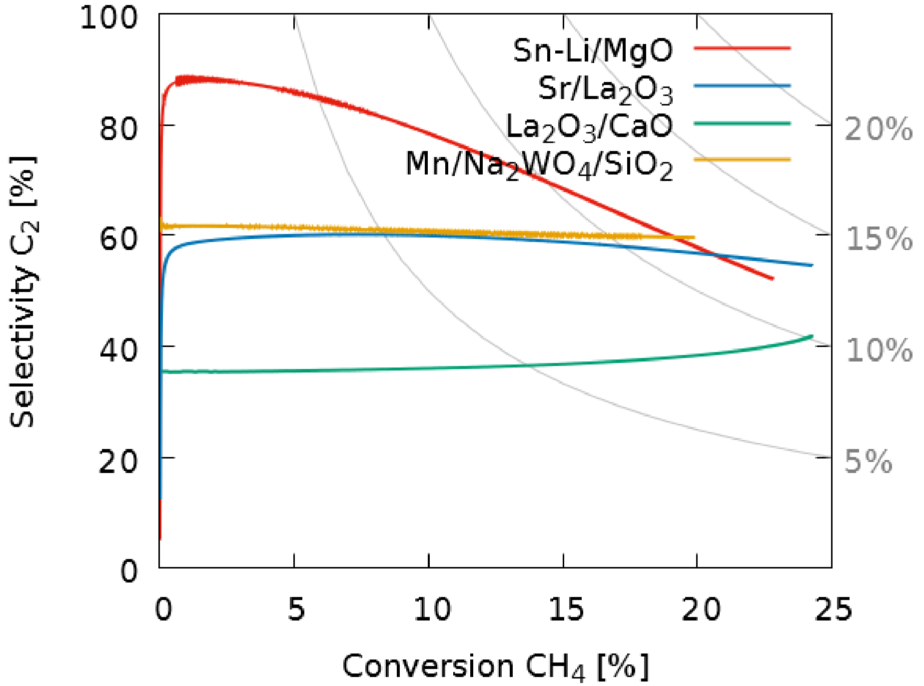
Conditions: CH_4/O_2=4, T=1023K, p=1.1bara, ϵ_b=0.6



With the investigated catalysts, C2 yields are limited to 10-15 %

Better catalysts exist (25% yield)!

GSVR is not a PFR



For the investigated conditions, the **Sr/La_2O_3** catalyst is most interesting.

From simulations at different temperature:

residence time ~ 20-50 ms ➔ 10-25% methane conversion, 5-15% C2 yield

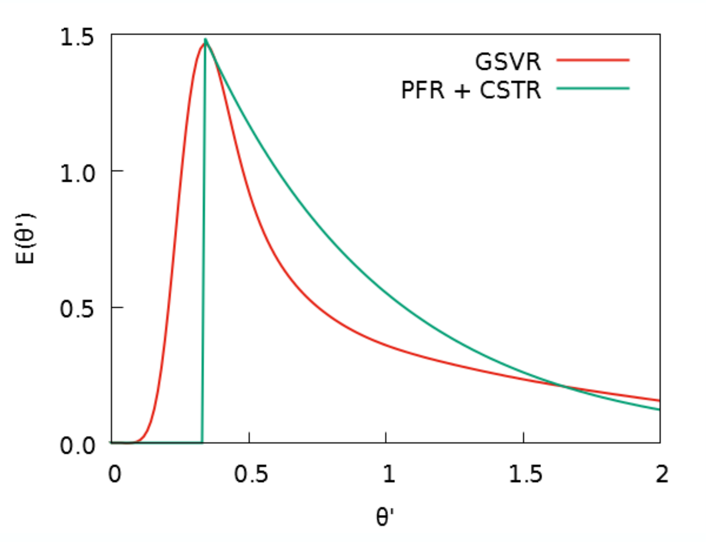
Non-ideal behavior of the GSVR

The GSVR is fundamentally different from a fixed bed reactor, hence it cannot be modeled by an ***~~ideal plug flow~~*** reactor model

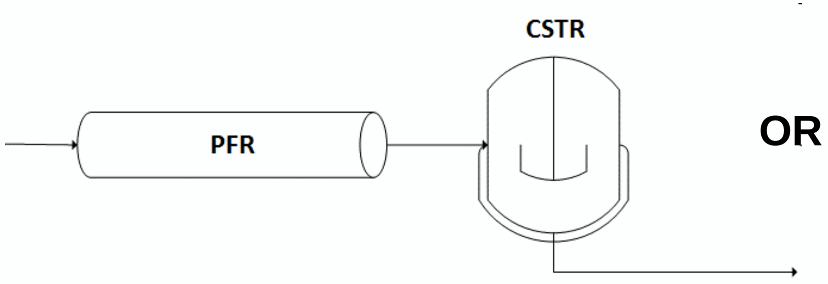
↓

Get information about the ***non-ideal*** behavior by constructing the **residence time distribution**

✓ Scaled residence time distribution from **tracer experiment/simulation**



GSVR can be modeled as a combination of a plug flow reactor and CSTR



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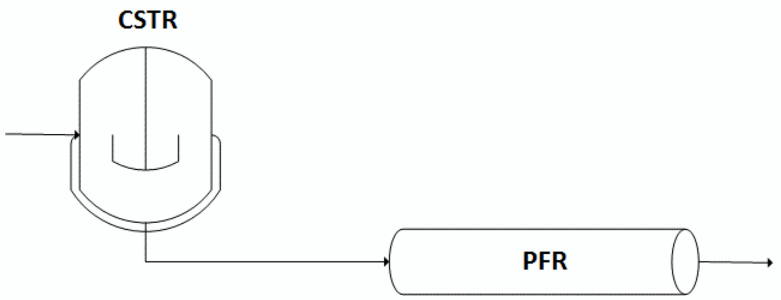


*PFR = Plug Flow Reactor, CSTR = Continuously Stirred Tank Reactor

Adiabatic reactor operation

Non-ideal behavior is important during adiabatic reactor operation !

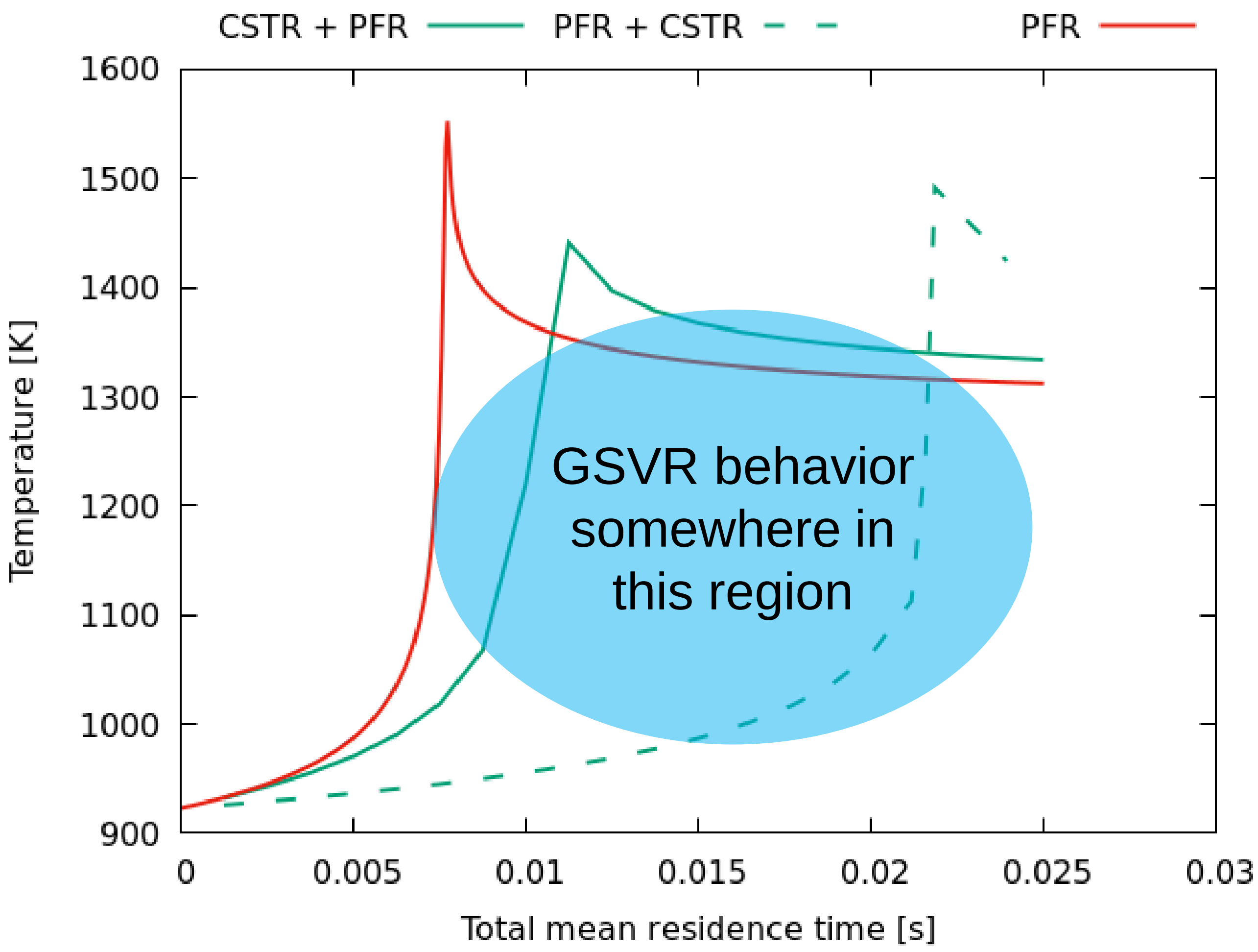
Thermal control of the reactor !

Formation of hotspots unavoidable in fixed bed reactor (PFR)

CSTR characteristics

→ better mixing

→ delay / smoothing of hot spots



$CH_4/O_2=4$, T=923K, p=1.1bara, $\epsilon_b=0.6$, Sr/La_2O_3

*PFR = Plug Flow Reactor, CSTR = Continuously Stirred Tank Reactor

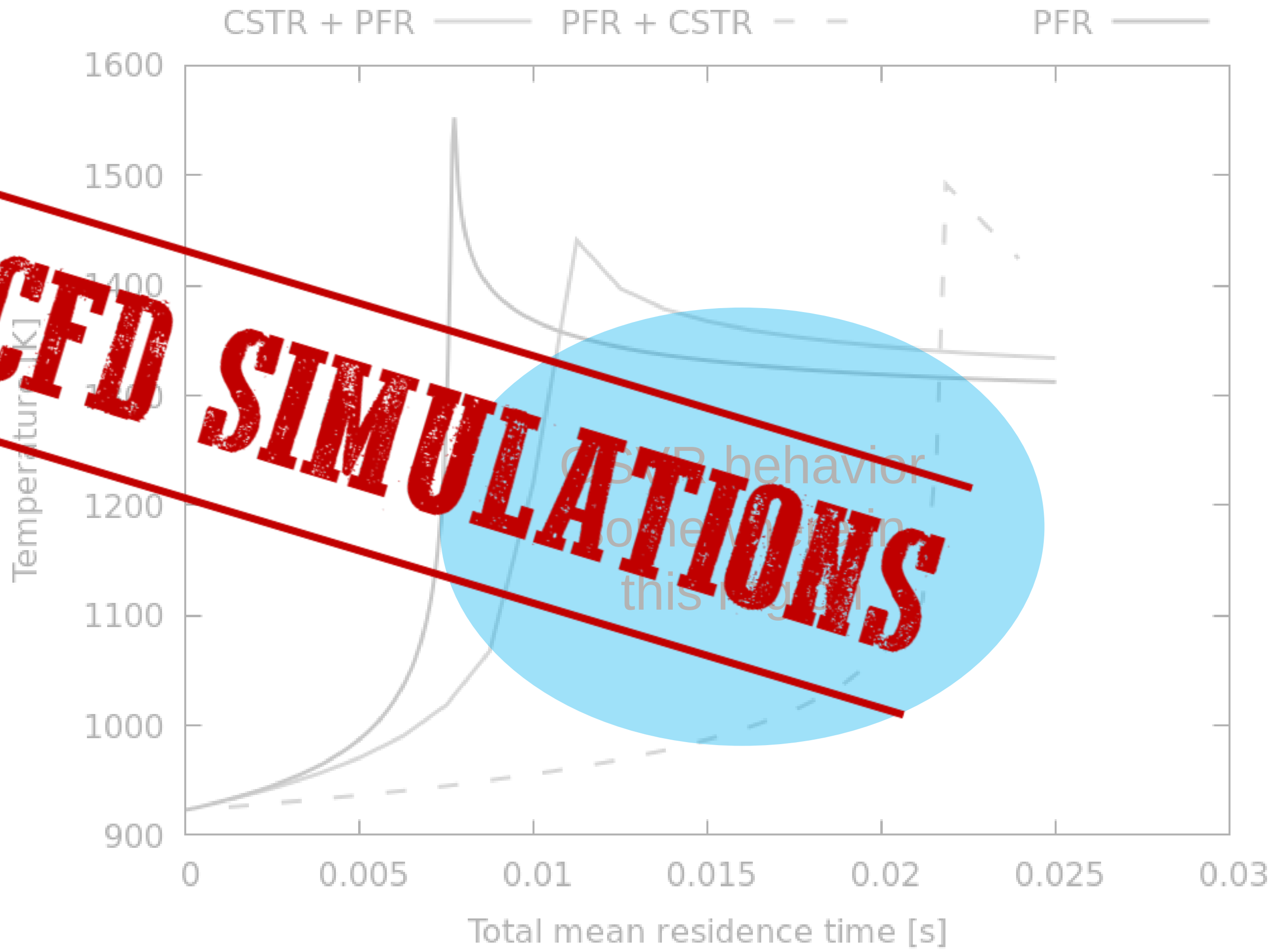
Adiabatic reactor operation

Non-ideal behavior is important during adiabatic reactor operation !

Thermal control of the reactor !

Formation of hotspots highly probable in fixed bed reactor (PFR)

CSTR characteristics
→ better mixing
→ delay / smoothing of hot spots



CSTR behavior somewhere in this region

WANTED: CFD SIMULATIONS

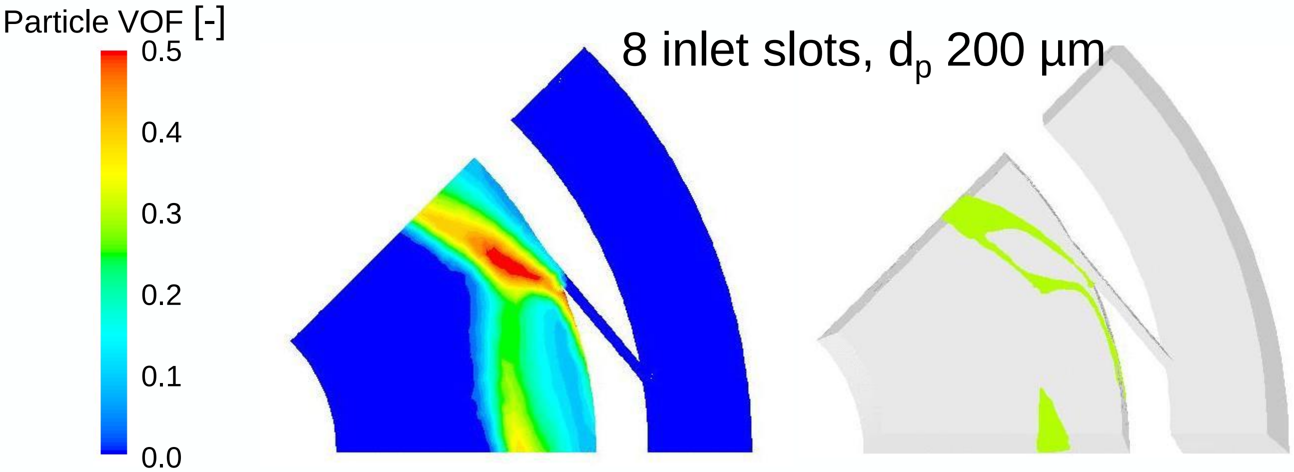
CH_4/O_2=4, T=923K, p=1.1bara, ϵ_b=0.6, Sr/La_2O_3

*PFR = Plug Flow Reactor, CSTR = Continuously Stirred Tank Reactor

Non-reactive CFD simulations

Example: optimize design / conditions for stable bed formation
(N_2 feed: 10 g/s, 923 K; catalyst particles: 2300 kg/m³, 16 g total)

Bubbling bed

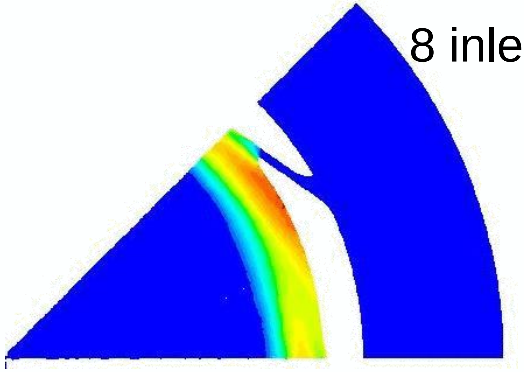


8 inlet slots, d_p 200 µm

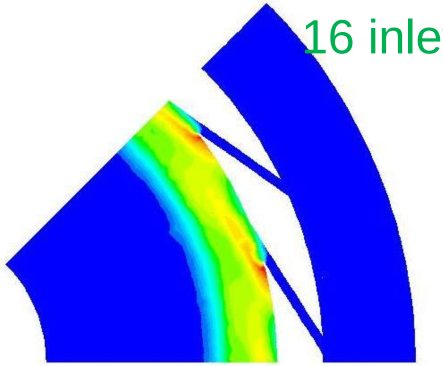
Bubbling bed not optimal for OCM

➔ Increase particle diameter OR increase number of inlet slots

Stable bed



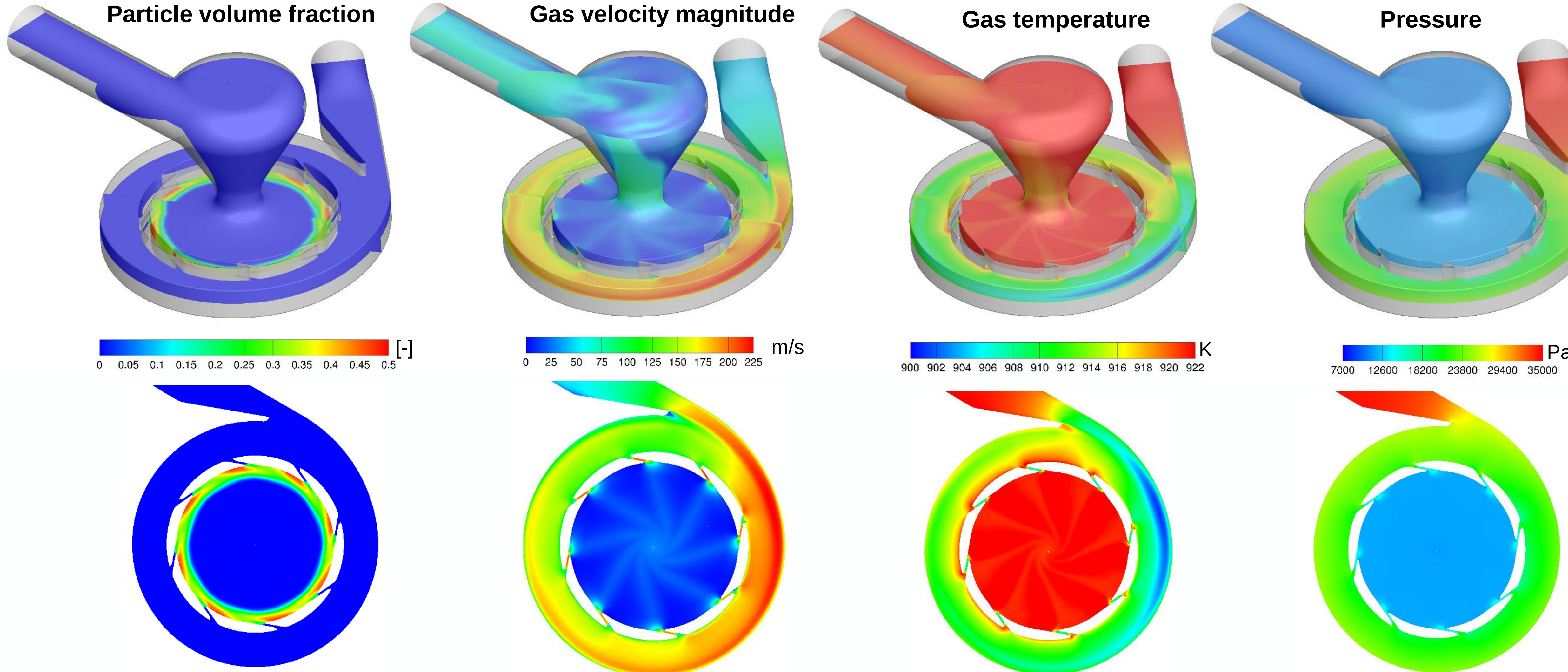
8 inlet slots, d_p 1 mm



16 inlet slots, d_p 200 µm

Non-reactive CFD simulations

Nitrogen feed: 10 g/s, 923 K
Catalyst particles: 2300 kg/m³, 16 g, ⌀1 mm



Particle volume fraction

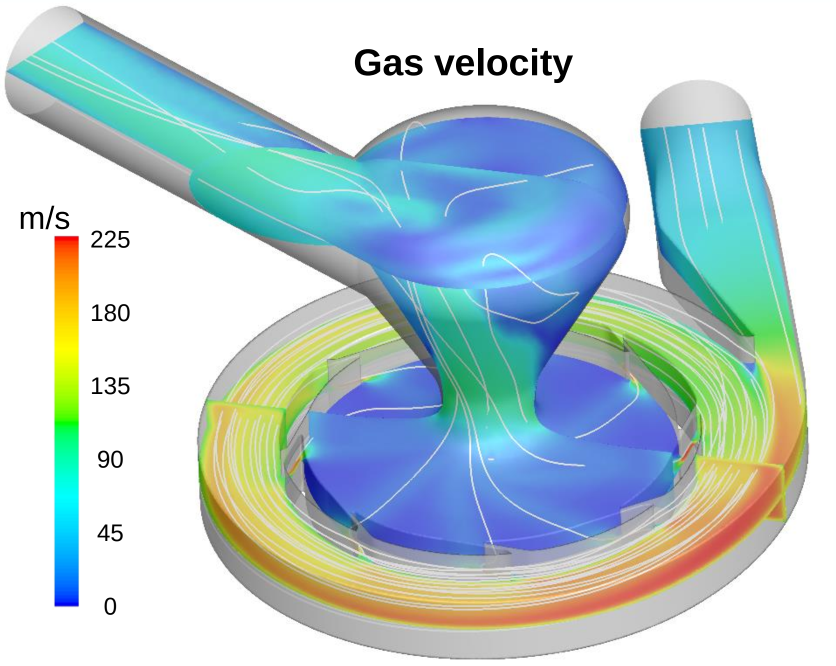
Gas velocity magnitude

Gas temperature

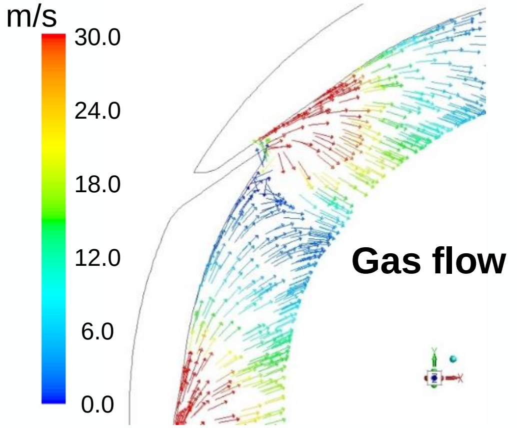
Pressure

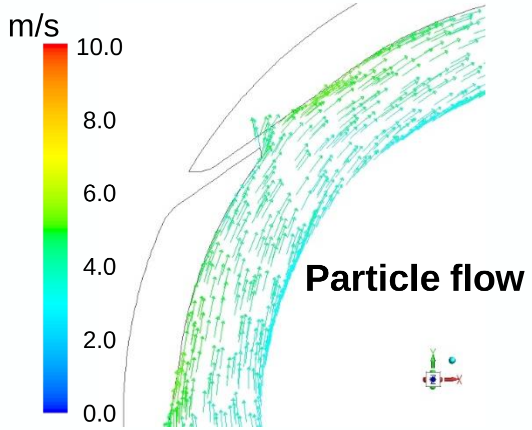
Non-reactive CFD simulations

Nitrogen feed: 10 g/s, 923 K
Catalyst particles: 2300 kg/m³, 16 g, ⌀1 mm



Mean gas-phase residence time in the bed: ~**1 ms**





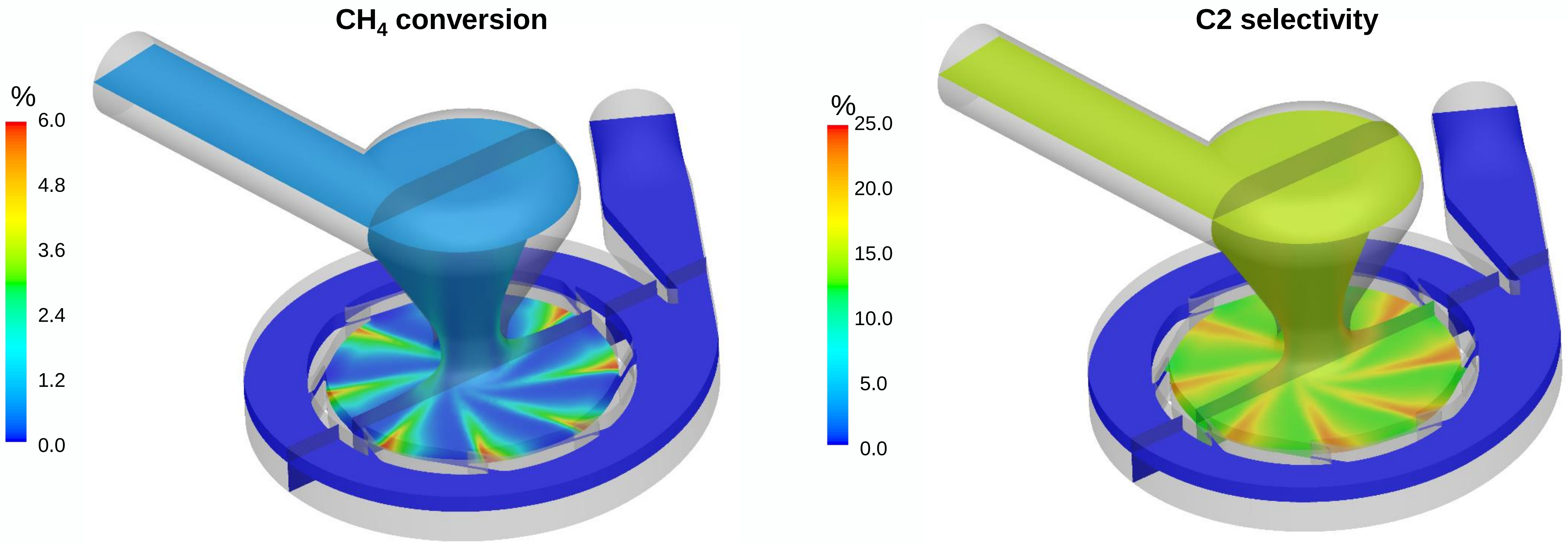
With simulated conditions: **very low** gas phase residence times in the bed (probably too low to obtain significant conversions and yields for OCM)

Reactive CFD simulations

La_2O_3/CaO catalyst
Stansch kinetics: 10-step mechanism

CH_4/O_2 feed: ratio 4, 10 g/s, 923 K
Catalyst particles: 2300 kg/m³, 16 g, ⌀1 mm

Very low C2 selectivity and CH_4 conversion



Selectivity too low → Use different catalyst / kinetic model

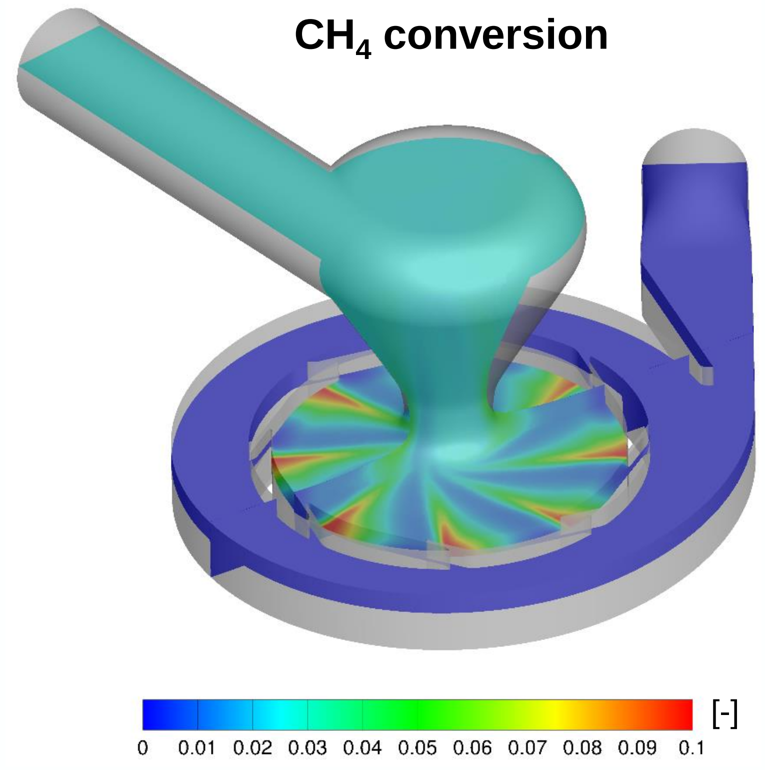
Reactive CFD simulations

State-of-the art catalysts can reach C2 selectivity ~ 80%

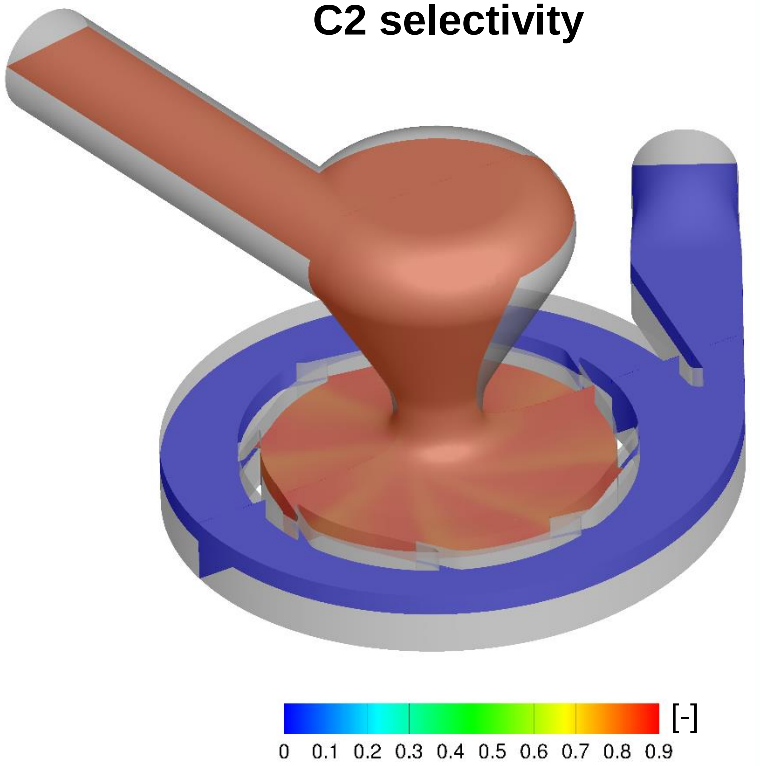
➔ Modified kinetic model

CH_4/O_2 feed: ratio 4, 10 g/s, 873 K

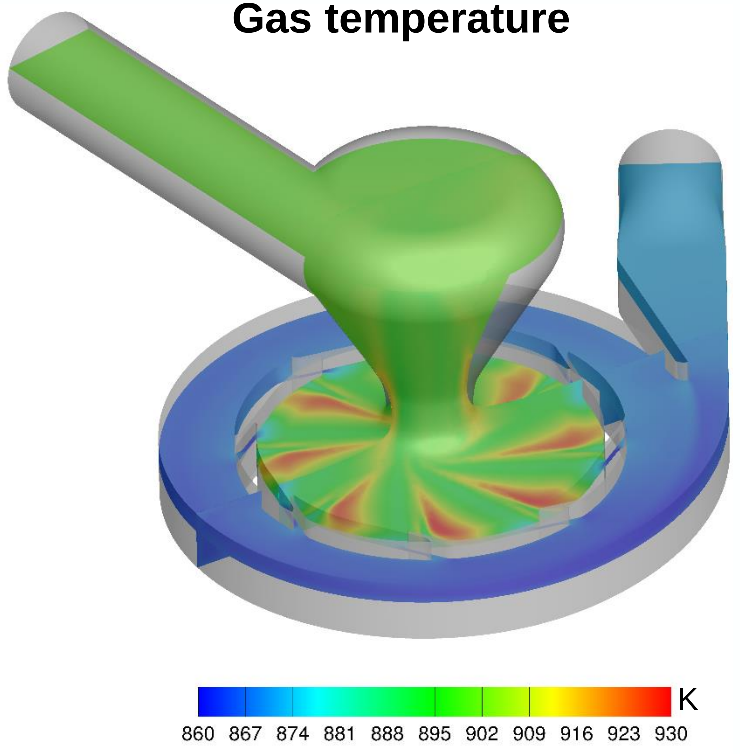
Catalyst particles: 2300 kg/m³, 16 g, ⌀1 mm



CH_4 conversion



C2 selectivity



Gas temperature

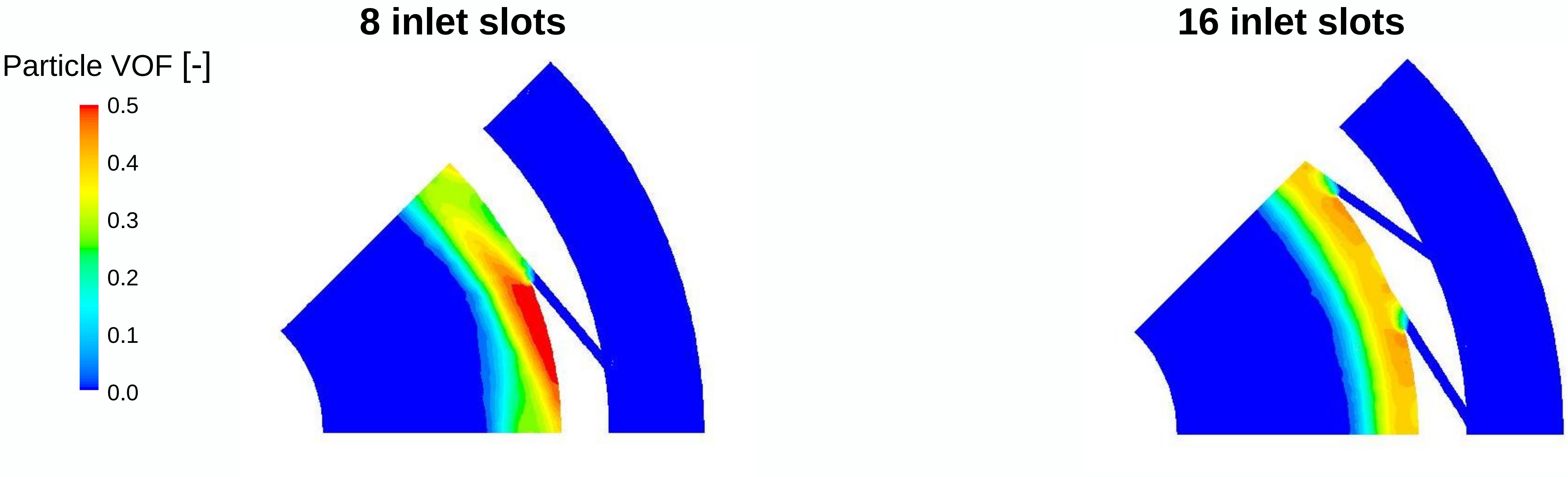
✓ Conversion low (~3%) → Increase residence time

✓ Non-uniform temperature profile → Increase number of inlet slots

Reactive CFD simulations

Number of inlet slots influences bed uniformity

CH_4/O_2 feed: ratio 4, 10 g/s, 873 K
Catalyst particles: 2300 kg/m³, 16 g, ⌀1 mm


8 inlet slots

16 inlet slots

Increasing the number of inlet slots increases bed uniformity

✓ Less bypassing of the bed: higher conversion and C2-yields

✓ More uniform temperature profile

Conclusions

- New reactor technology for OCM: gas-solid vortex reactor (GSVR)
  - Uniform, dense particle beds
  - High gas throughput
  - Very good heat transfer and mixing

- A PFR+CSTR model can be used as a quick screening tool for catalysts and operating conditions

- CFD simulations are required to design and optimize the GSVR

  Residence times need to be increased to obtain acceptable CH_4 *conversions and C2 yields.*

  Adjust design (number of inlet slots) to improve uniformity and increase yields.

Acknowledgements

- FWO Flanders

fwo Research Foundation Flanders
Opening new horizons

- The Long Term Structural Methusalem Funding by the Flemish Government

Long Term Structural Methusalem Funding of the Flemish Government

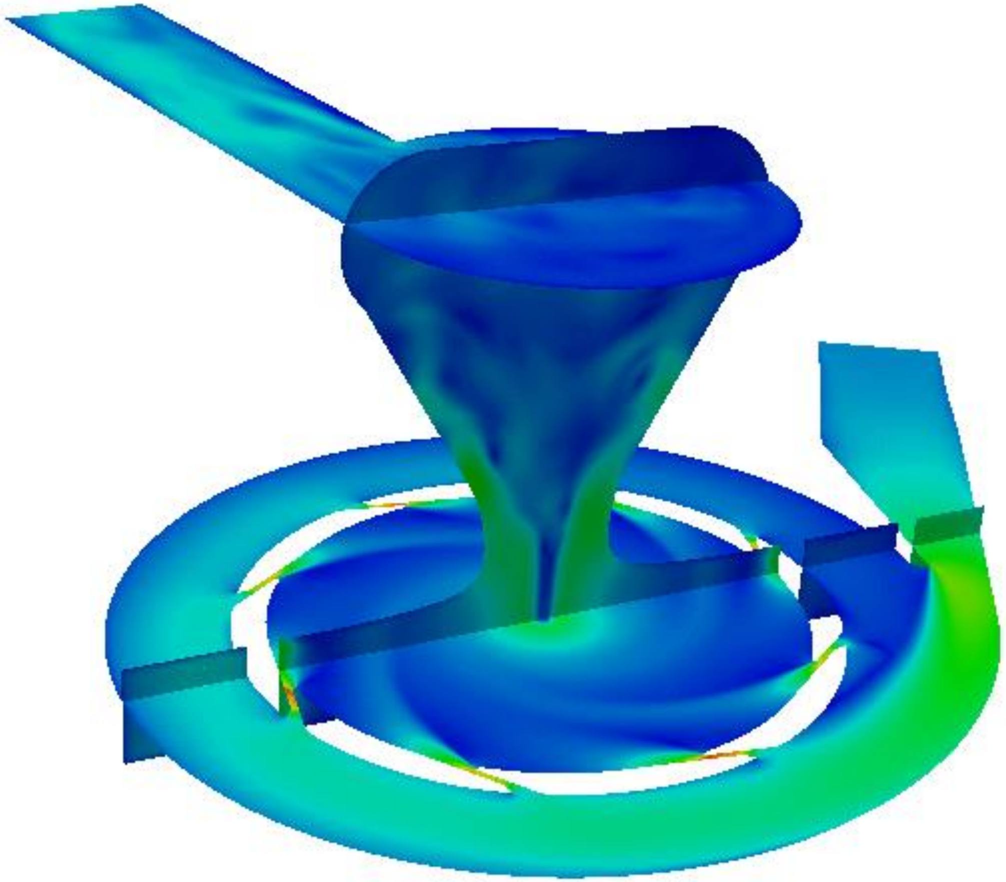
M2dRc

- STEVIN Supercomputer Infrastructure & Vlaams Supercomputer Centrum

HPC UGENT

VSC Vlaams Supercomputer Centrum

Thank you for your attention!



Any questions?