Numerical Modelling of the Original and Advanced Version of the TEMKIN-Reactor for Catalysis Experiments in Laboratory Scale

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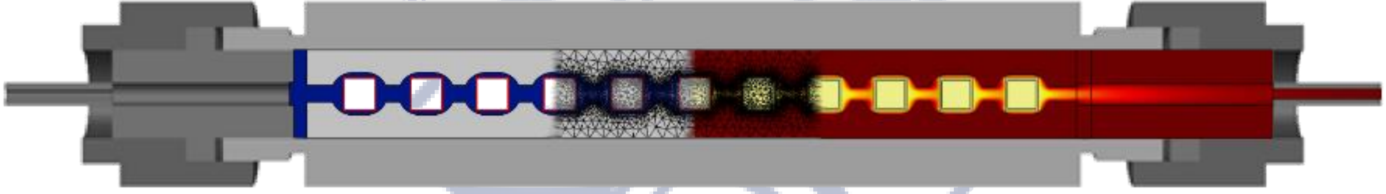
2014 CAMBRIDGE

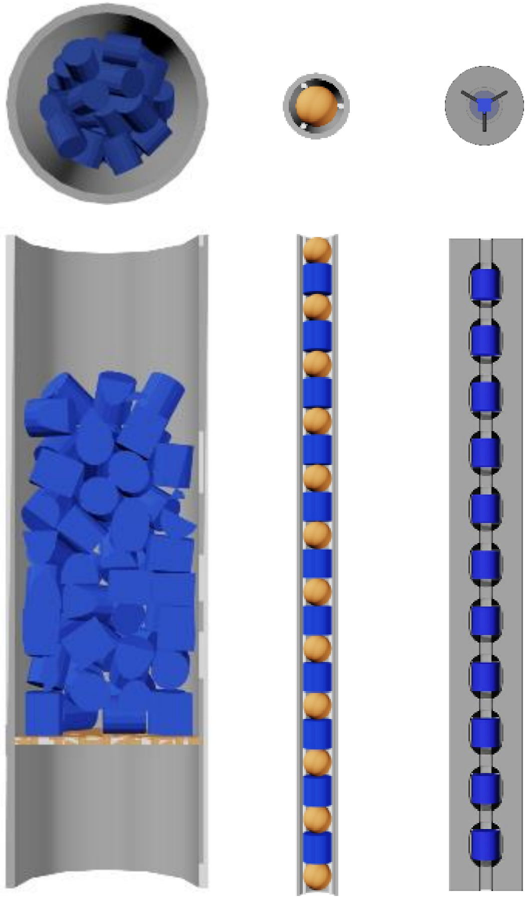
D. Götz, M. Kuhn, P. Claus

TU Darmstadt, Ernst-Berl-Institute for Technical and Makromolekular Chemistry, Alarich-Weiss-Straße 8, D-64287 Darmstadt, Germany



Laboratory Scale Reactors

Testing of Egg-shell Catalysts



- Plug Flow Reactor (PFR)
  - Simple build-up
  - Requirements for ideal behaviour:
    - Reactor radius / pellet radius: min. 10
    - Reactor length / pellet length: min. 30

High catalyst amounts and feed streams
⇨ cost-intensive

- TEMKIN reactor
  - Original: TEMKIN AND COWORKERS
  - Advanced version: CLAUS AND COWORKERS
  - Smaller catalyst amounts and feed streams needed

Complex mass, momentum and heat transport!

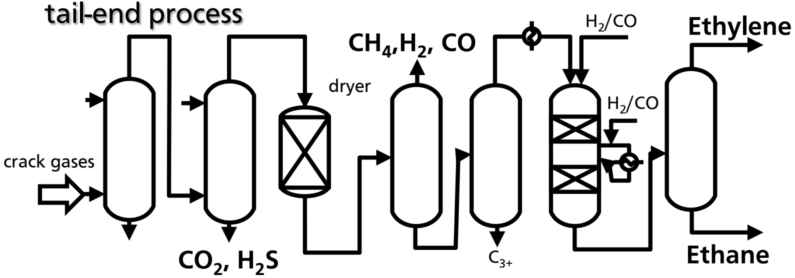
M. Temkin et al., Kulkova, Kinet. Katal **1969**, 10, 461-463.
M. Kuhn, M. Lucas, P. Claus, Chemie Ingenieur Technik, **2014**.
Patent, DE200920003014, **2009**.

Selective Hydrogenation of Acetylene

- Ethylene production in a steam cracker
  - Acetylene impurities in ethylene stream
  - Poisoning of downstream processes

⇨ Selective hydrogenation using Pd-Ag/Al_2O_3 egg shell catalysts

A. Borodzinki, Catal Rev 2006, 48, 91-144.



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- Commercial industrial catalyst

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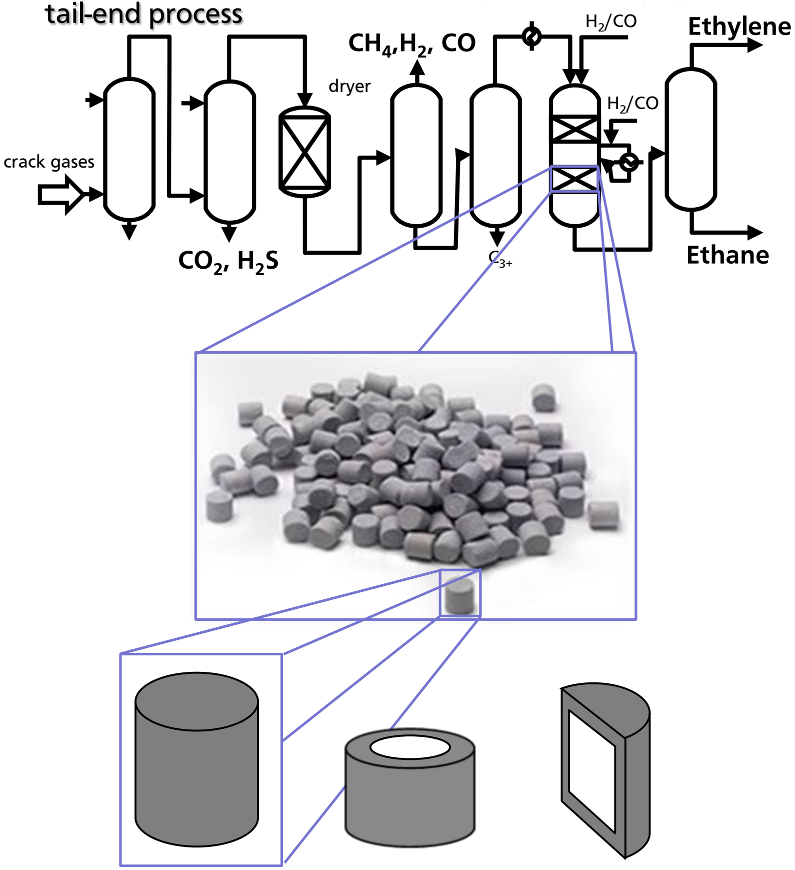

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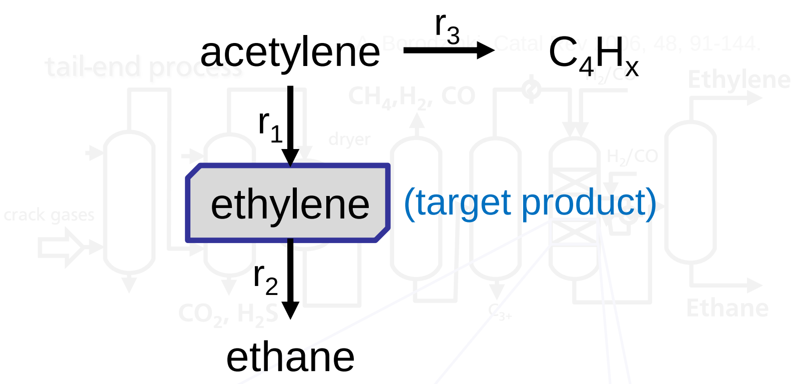


acetylene $\xrightarrow{r_3}$ C_4H_x

r_1 ↓

ethylene (target product)

r_2 ↓

ethane

- Commercial industrial catalyst
  - Kinetics from PFR experiments
    - Two different active sites AS1 and AS2 due to carbon and hydrocarbon deposits
    - Ethylene can only adsorb and react at the bigger active sites
    - Reactions spatially separated

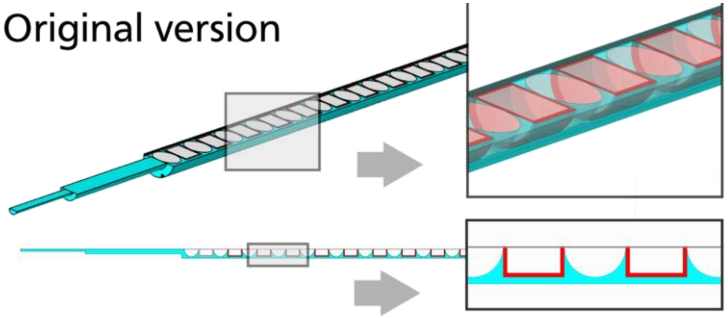
	active site
$r_1 = \frac{k_1 p_A p_{H2}^{\frac{1}{2}}}{(1 + K_{A,13}\, p_A)^2}$	AS 1
$r_2 = \frac{k_2 p_{Ey} p_{H2}}{(1 + K_{A,2}\, p_A)^2}$	AS 2
$r_3 = \frac{k_3 p_A p_{H2}^{\frac{1}{2}}}{(1 + K_{A,13}\, p_A)^2}$	AS 1

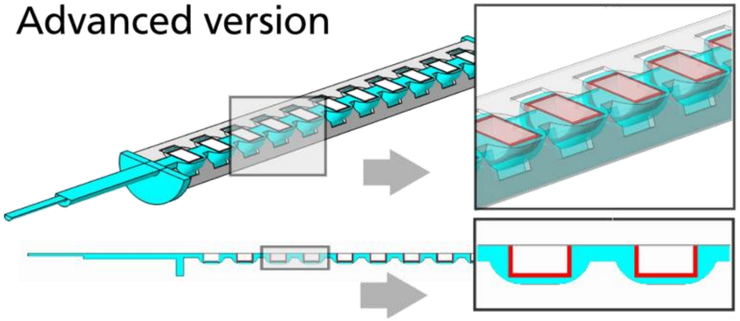
A. Pachulski, R. Schödel, P. Claus, Applied Catalysis A: General 2012, 445-446, 107-120.

Modelling in COMSOL Multiphysics

- Distinguishing between different domains
  - Free gas flow (cyan)

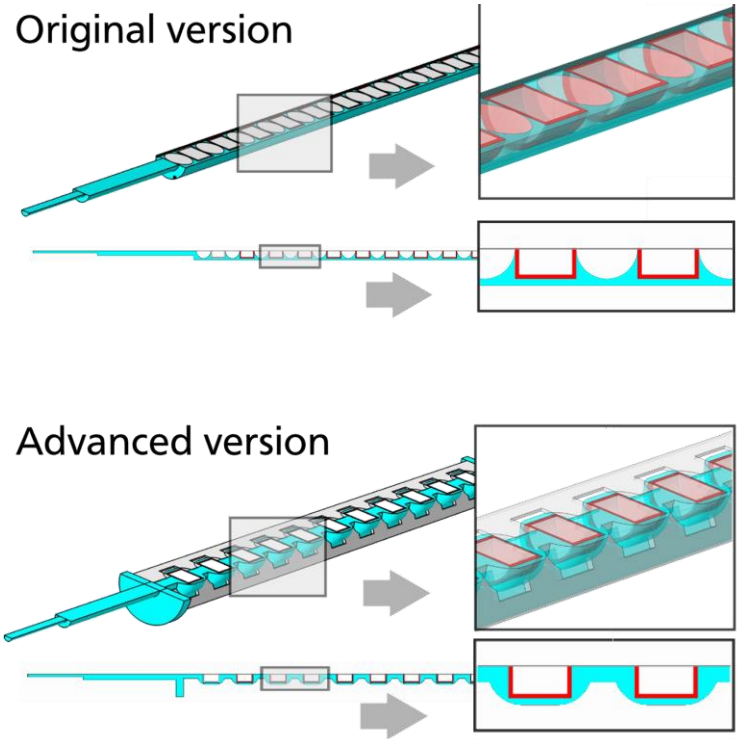
    Modelling of laminar fluid flow coupled with heat and species transport


Original version


Advanced version

Modelling in COMSOL Multiphysics

- Distinguishing between different domains
    - Free gas flow (cyan)
      Modelling of laminar fluid flow coupled with heat and species transport
    - Inert support (white)
      Modelling of species and heat transport in porous media (no convection)



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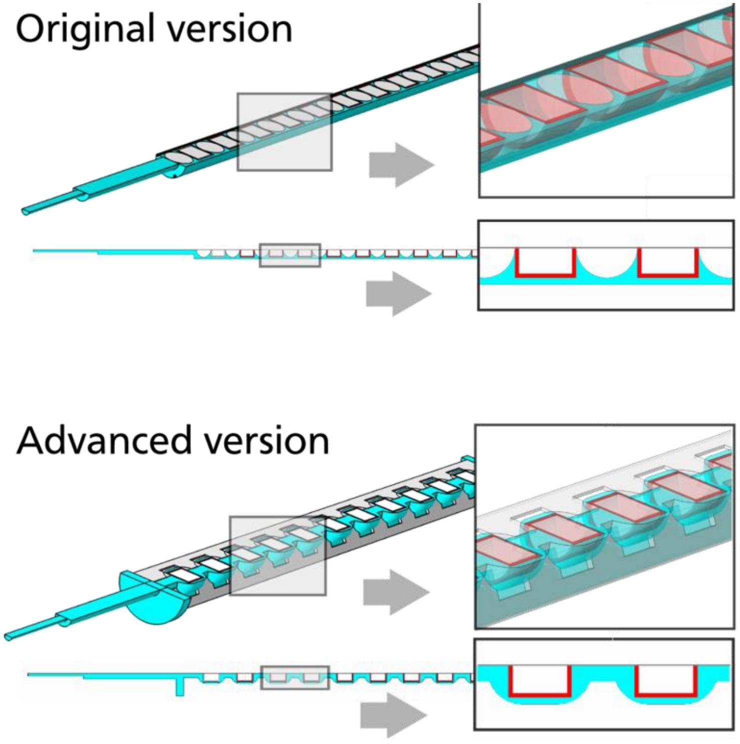
    - Catalytically active shell (red)
      Modelling of species and heat transport in porous media including reaction kinetics



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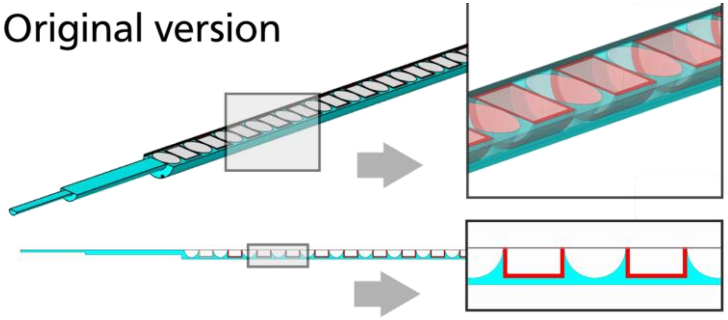
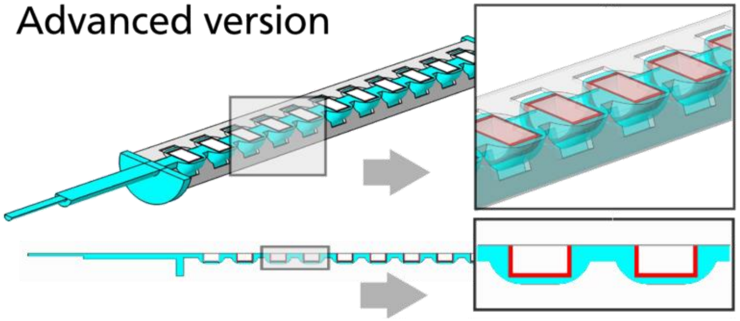
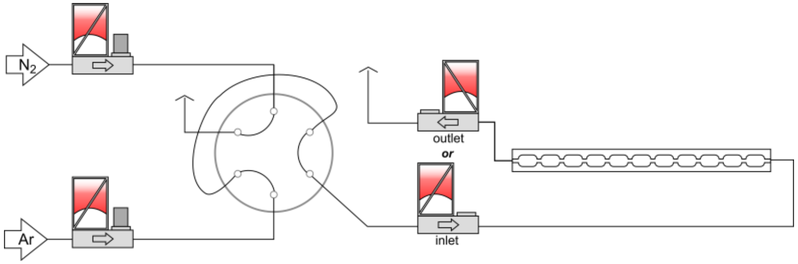
    Modelling of species and heat transport in porous media including reaction kinetics
  - Reactor body (not shown)
    Modelling of heat transport



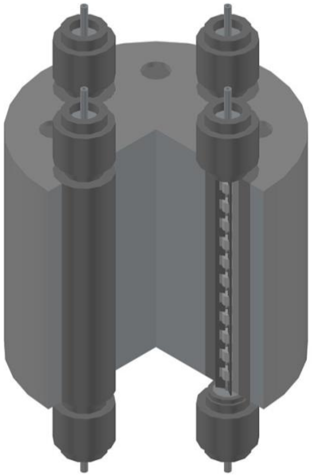


Validation
Experimental setup

- Pulse tagging experiments
  - Pulse injection by pneumatic 6-port valve
  - Pulse detection via sensor unit of a thermal mass flow controller



- Catalysis experiments
  - 4 reactor modules in series in a temperated aluminium block
  - Typical industrial reaction conditions
    - GHSV = 4000 h^{-1}
    - Pressure = 11 bar
    - Temperature = 45 °C
    - Hydrogen, acetylene, propane (internal standard): 1 Vol-% each; ethylene: 30 Vol-%; argon: 67 Vol-%,
  - Online-gas chromatography connectors between reactor modules

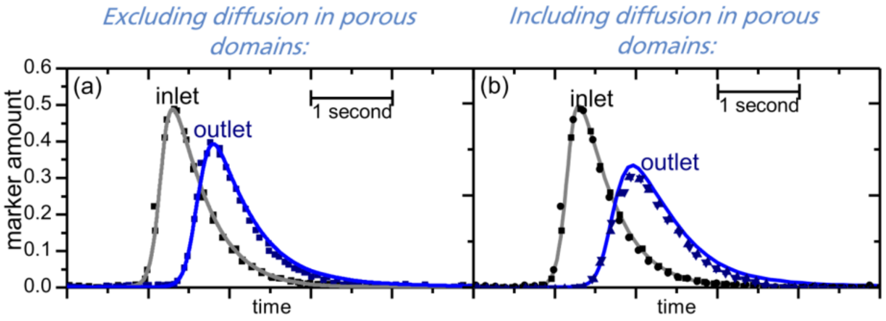


details published in
M. Kuhn, M. Lucas, P. Claus, Chemie Ingenieur Technik, 2014.

Validation

Pulse Tagging Experiments

- Good agreement between simulated and measured pulse experiments


Excluding diffusion in porous domains:

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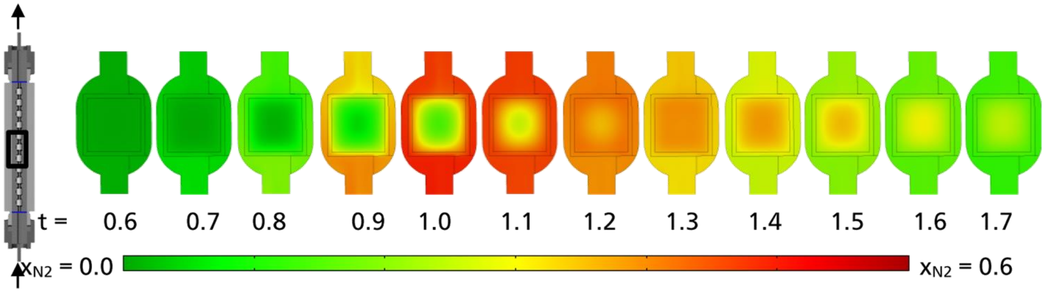
- Diffusion into the porous pellets leads to increasing residence times



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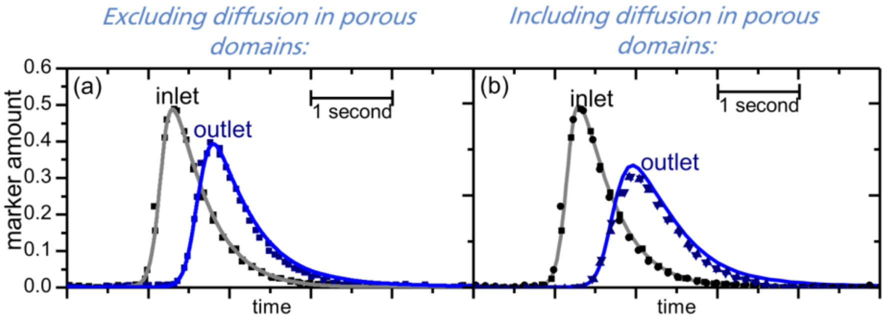

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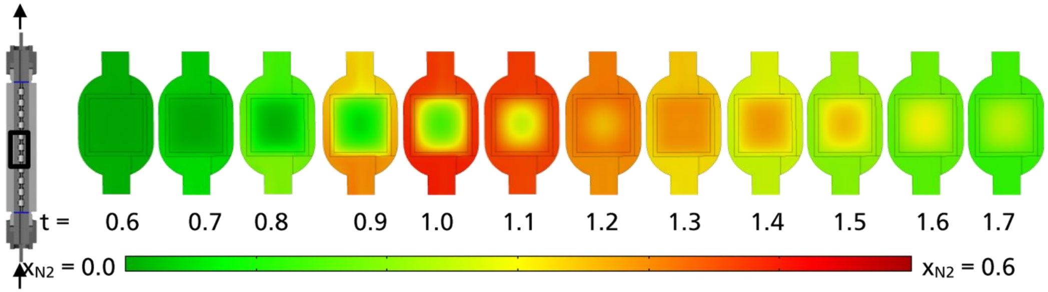
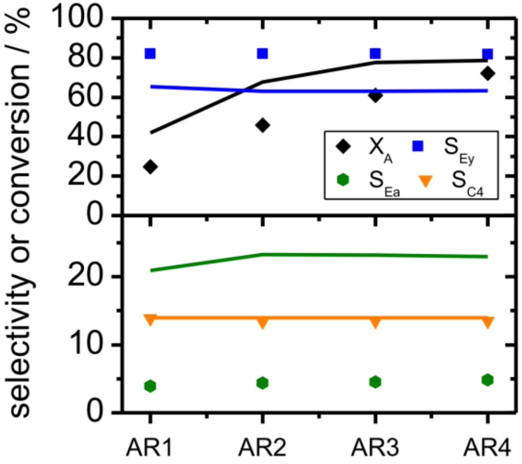


⇨ **Simple reactor models fail due to complex mass transfer**

Validation

Catalysis Experiments

- PFR results differ from TEMKIN results



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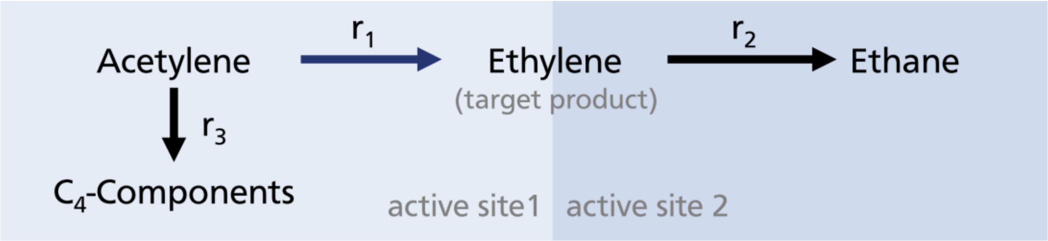
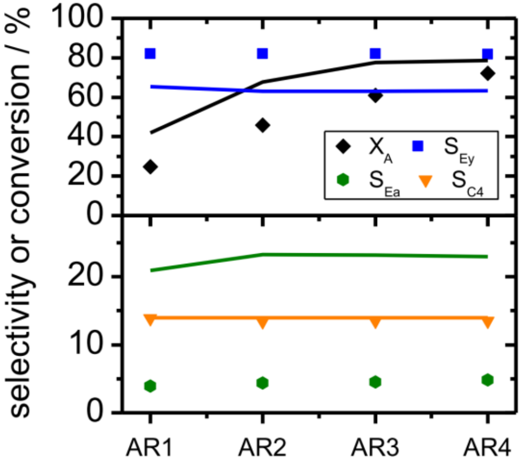
Catalysis Experiments

- PFR results differ from TEMKIN results
- Different densities of the two active sites
    - e.g. due to hotspots in PFR





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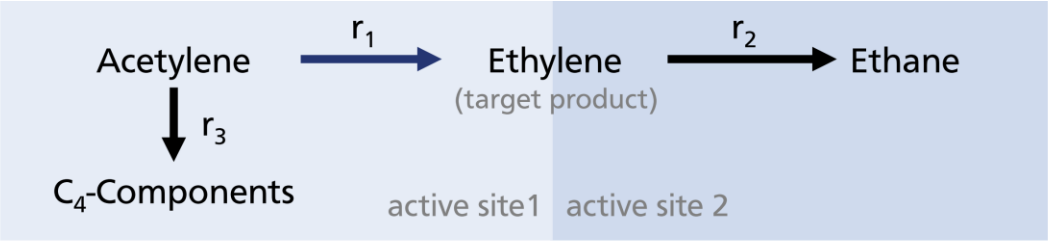


Acetylene $\xrightarrow{r_1}$ Ethylene (target product) $\xrightarrow{r_2}$ Ethane

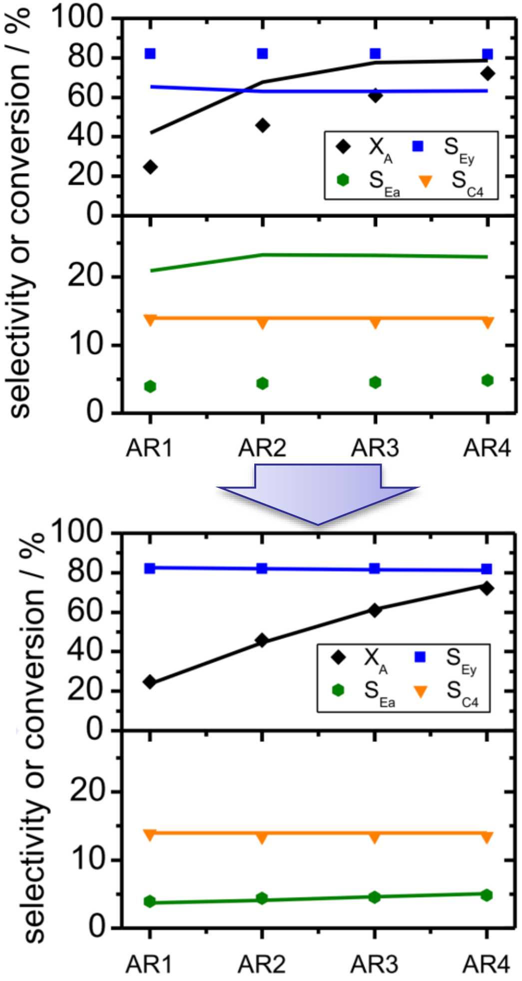
Acetylene $\xrightarrow{r_3}$ C_4-Components

active site1

active site 2

- Adjustment of active site densities AS1 and AS2

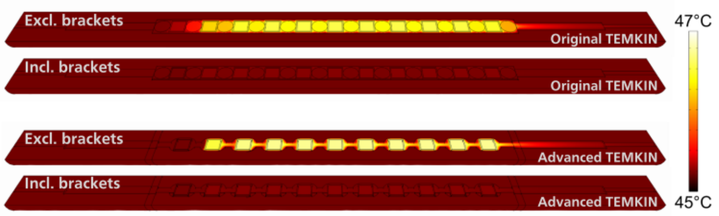
⇨ **Good agreement between experiment and simulation**



Performance Evaluation

Original vs Advanced Version

- Thermal conditions inside the reactor
  - Good heat transfer via pellet holders
  - Nearly ideal isothermal behaviour



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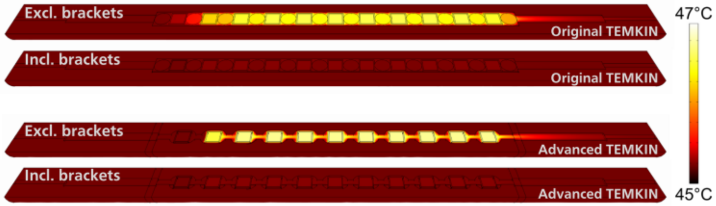
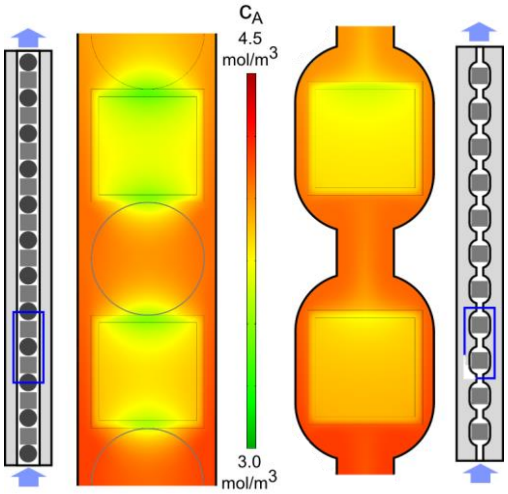


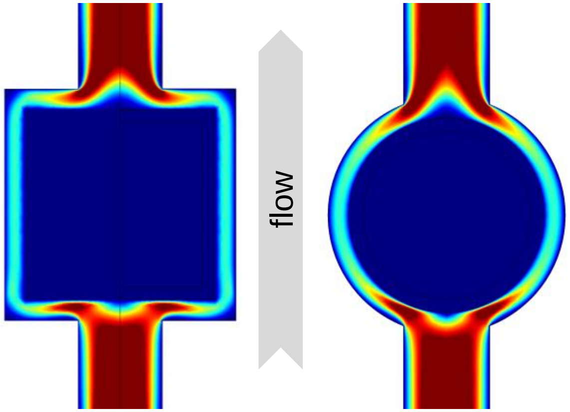
- Mass transfer under reaction conditions
  - Slow mass transfer due to dead zones
    - Original version: *Large dead zones before and after each catalyst pellet*
    - Advanced version: *Only small dead zones after each catalyst pellet*



Performance Evaluation

Benefits from Numerical Simulations

- Quick check and optimisation for new reactor or catalyst geometries



Performance Evaluation
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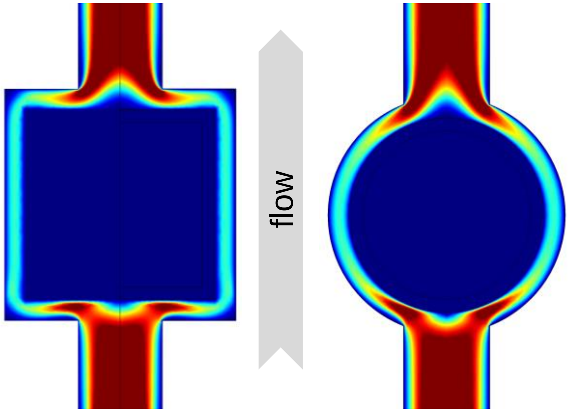
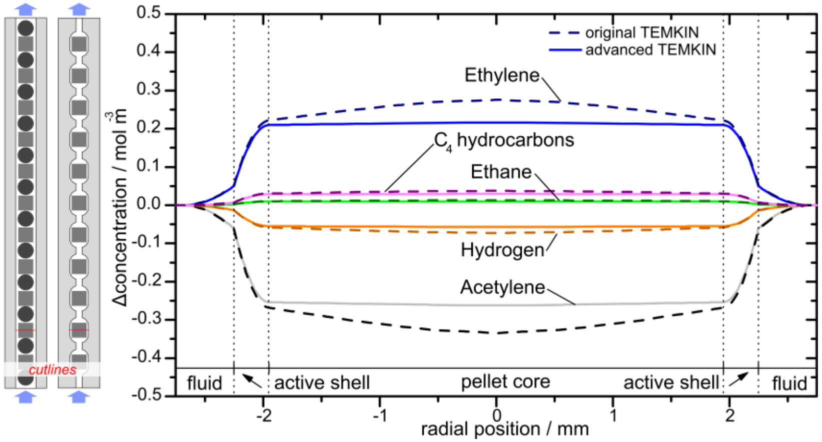
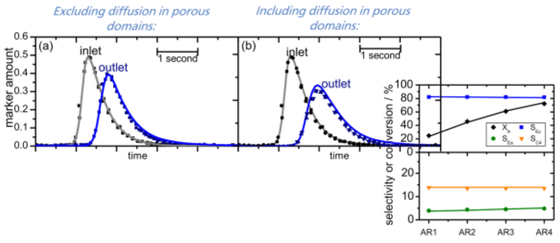


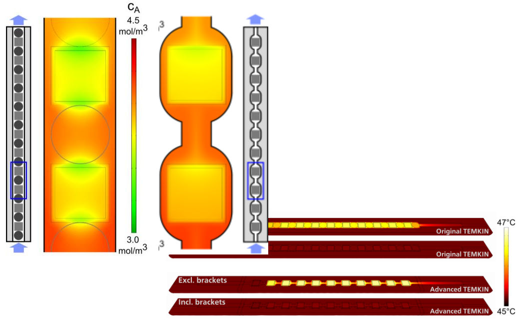
- Checking the interaction between mass transport and kinetics under reaction conditions

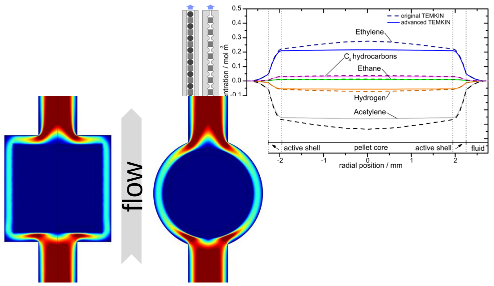


Conclusions

- Good agreement between experiment and simulation
- Simulations clearly confirms the benefits of our advanced reactor version
- COMSOL Multiphysics® is a powerful tool for the development of new laboratory reactor systems







Thank you for your attention!

reacion engineering

catalysis

kinetics

synthesis

- Catalysis - Chemical Reaction Engineering - New Technologies -

with the Claus group

http://www.chemie.tu-darmstadt.de/claus/