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

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!*

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$_2$O$_3$ egg shell catalysts

Selective Hydrogenation of Acetylene

- Ethylene production in a steam cracker
  - Acetylene impurities in ethylene stream
  - Poisoning of downstream processes
- Selective hydrogenation using Pd-Ag/Al₂O₃ egg shell catalysts
- Commercial industrial catalyst
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$_2$O$_3$ egg shell catalysts

- 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

\[
\begin{align*}
r_1 &= \frac{k_1 p_{\text{AcH}}^2}{(1 + K_{A,13} p_A)^2} & \text{AS 1} \\
r_2 &= \frac{k_2 p_{\text{Ey}} p_{\text{H2}}}{(1 + K_{A,2} p_A)^2} & \text{AS 2} \\
r_3 &= \frac{k_3 p_{\text{P}} p_{\text{H2}}}{(1 + K_{A,13} p_A)^2} & \text{AS 1}
\end{align*}
\]

Modelling in COMSOL Multiphysics

- Distinguishing between different domains
  - Free gas flow (cyan)
  
  *Modelling of laminar fluid flow coupled with heat and species transport*

![Diagram showing original and advanced versions of the model.](image)
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)
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)
  - Catalytically active shell (red)
    Modelling of species and heat transport in porous media including reaction kinetics
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)
  - Catalytically active shell (red)
    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

Validation
Pulse Tagging Experiments

- Good agreement between simulated and measured pulse experiments

- Diffusion into the porous pellets leads to increasing residence times
Validation
Pulse Tagging Experiments

- Good agreement between simulated and measured pulse experiments

- Diffusion into the porous pellets leads to increasing residence times

⇒ Simple reactor models fail due to complex mass transfer
Validation
Catalysis Experiments

- PFR results differ from TEMKIN results
Validation
Catalysis Experiments

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

\[ \text{Acetylene} \xrightarrow{r_1} \text{Ethylene (target product)} \xrightarrow{r_2} \text{Ethane} \]

C\textsubscript{4}\,- Components

17.09.2014 | TU Darmstadt | Ernst-Berl-Institute | Prof. Dr. P. Claus | Dominik Götz, M.Sc. | 6
Validation
Catalysis Experiments

- PFR results differ from TEMKIN results

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

- 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
Performance Evaluation
Original vs Advanced Version

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

- 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
Benefits from Numerical Simulations

- Quick check and optimisation for new reactor or catalyst geometries

- 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!

- Catalysis - Chemical Reaction Engineering - New Technologies -
with the Claus group

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