Modeling of NO Oxidation in a 3D-Printed Catalytic Foam Reactor

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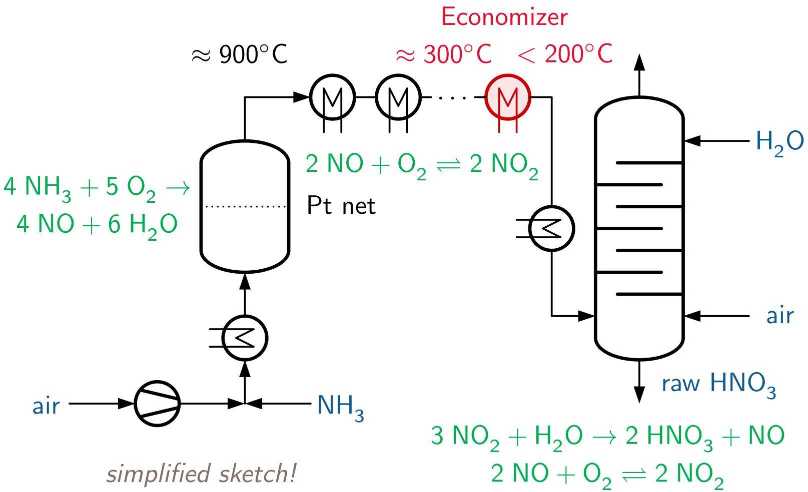
Introduction

- Context:
  - Ostwald process for nitric acid production
  - EU funded project PRINTCR3DIT (Horizon 2020, Spire)
- Focus: *Economizer* cooler and reactor
  - Equilibrium reaction $2\,NO + O_2 \rightleftharpoons 2\,NO_2$
  - Equilibrium shift to NO_2 for low temperature
  - Cooling from $\approx 300^\circ C$ to $< 200^\circ C$
  - Conversion close to equilibrium
  - Heat recovery
  - *Pressure drop constraint*
  - Economizer design goal:
    Tube bundle reactor, 3D printed structured catalyst carrier

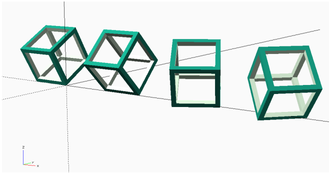
Economizer Position in Ostwald Process

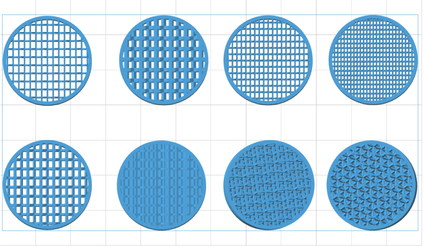
Economizer is a cooler and NO oxidation reactor in Ostwald process.



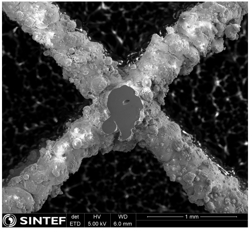
simplified sketch!

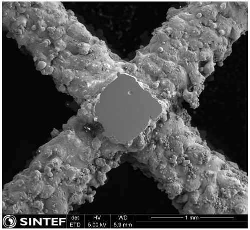
3D Printed Catalyst Carrier



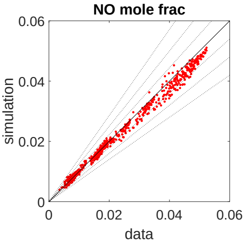


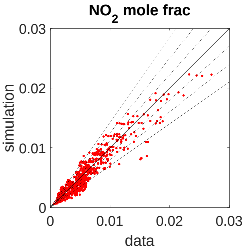
3D printed iso-reticular support





Reaction Kinetics





- Isothermal ideal PFR experiments (SINTEF)
- Main reaction: $2\ \mathrm{NO} + \mathrm{O}_2 \rightleftharpoons 2\ \mathrm{NO}_2$
- Rate equation:

$$r = k \cdot \exp\left(-\frac{E_A}{RT}\right) \cdot \frac{p_{\mathbf{NO}}^2 \cdot p_{\mathbf{O_2}} - p_{\mathbf{NO_2}}^2 / K_{\mathbf{eq}}}{\left(1 + K_{\mathbf{NO_2}} \cdot p_{\mathbf{NO_2}} + K_{\mathbf{H_2O}} \cdot p_{\mathbf{H_2O}}\right)^2}$$

- K_{eq} from thermodynamics
- 4 adapted parameters: k, E_A, K_{NO}, $K_{\mathrm{H_2O}}$
- Data base: 825 experimental runs
- Parameter fit: Inhouse software
- Reasonable fit, all parameters significant

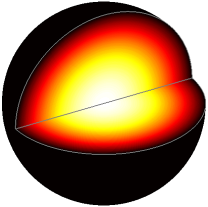
Pore Diffusion Pellet/Cat Layer Model

- Pore diffusion model based on modified *dusty gas model*
- Stefan-Maxwell diffusion, Knudsen diffusion and convection:

$$c \cdot \nabla x_i + \frac{x_i}{R \cdot T} \cdot \left(1 + \frac{B_0 \cdot p}{\eta \cdot D_{K,i}}\right) \cdot \nabla p = \sum_j \frac{x_i \cdot j_j - x_j \cdot j_i}{D_{ij}} - \frac{j_i}{D_{K,i}}$$

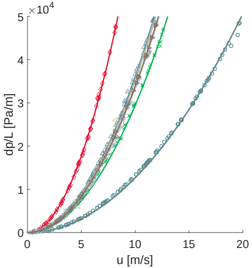
- Small pore size ($D_K \ll D_{ij}$): $\rightarrow$ Knudsen diffusion, independent species flux, full rank equation system
- Large pore size ($D_K \gg D_{ij}$, $B_0 \rightarrow \infty$):
  → Stefan-Maxwell diffusion, momentum conserved, rank deficient system:
  Solve for $N_{\text{comp}} - 1$ components $+$ bootstrap condition
- Practical cases: mathematically full rank, but bad condition
- *DGM equations are numerically difficult to solve.*

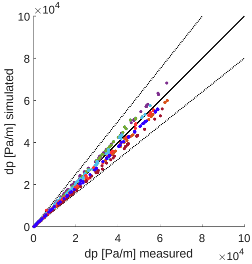
Pore Diffusion Pellet/Cat Layer Model



- Alternative: Simplification
  - Neglect pellet pressure profile
  - Remove pressure-flow coupling
  - Replace with total mass flux = zero
- Well defined rank $N_{\mathrm{comp}} - 1$ for all pore sizes
- Closing condition: $\dot{m}_{\mathrm{total}} = 0$
- Full rank well conditioned equation system
- Linear in fluxes
- Limiting cases satisfied (SM for large, Knudsen for small pores)
- Very efficient numerical solution

Bed Pressure Drop





- Individual Δp curves
- One equation for each structure
- Geometry optimization not feasible

- Common Δp eq. for *all* foams with parametrized geometry

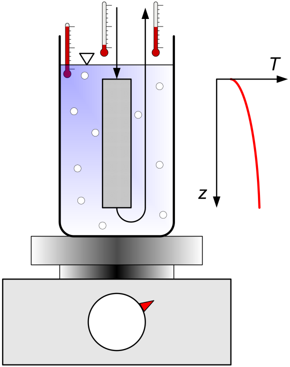
$$Eu = \frac{4}{3} \cdot \frac{-\frac{\partial p}{\partial z} \cdot D}{\rho \cdot u^2} \cdot \frac{\epsilon^2}{1-\epsilon}$$

$$Eu = \frac{k}{\epsilon \cdot \sqrt{1-\epsilon}}$$

[1] *Pressure drop and heat transfer properties of cubic iso-reticular foams*, Chem. Eng. and Processing - Process Intensification, acccepted for publication 9.3.18

Wall Heat Transfer

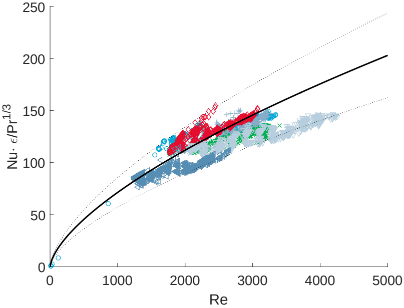
SINTEF experiment:



(principal sketch)

Modeling:

- α from temperature increase
- Generalized: dimensionless variables
- $Nu = f(Re, Pr, \epsilon)$



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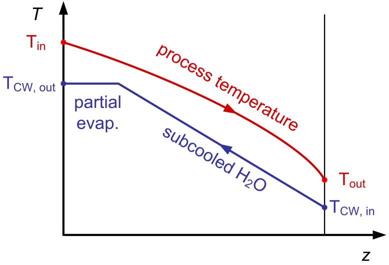
Reactor Cooling Concept

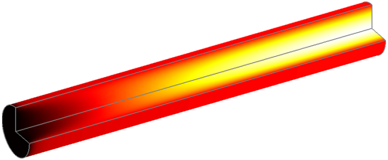
- Water/Steam?
  - $T_{\text{boil}} < T_{\text{process outlet}}$
  - High ΔT near inlet
  - Fast process T drop
  - Low reaction rates at low temperature
- Thermo oil?
  - Safety issue (NO_2 + Hydrocarbons)
  - Not available on Yara site
- Cooling Water?
  - $p_{\text{vap}}(300^\circ\text{C}) > 80$ bar
  - Not available on Yara site
- BFW, partially evaporated
  - Subcooled BFW
  - Countercurrent flow
  - Partial evaporation
  - Steam system available
  - Limited p and ΔT
  - Good heat recovery



2D Fixed Bed Reactor Model

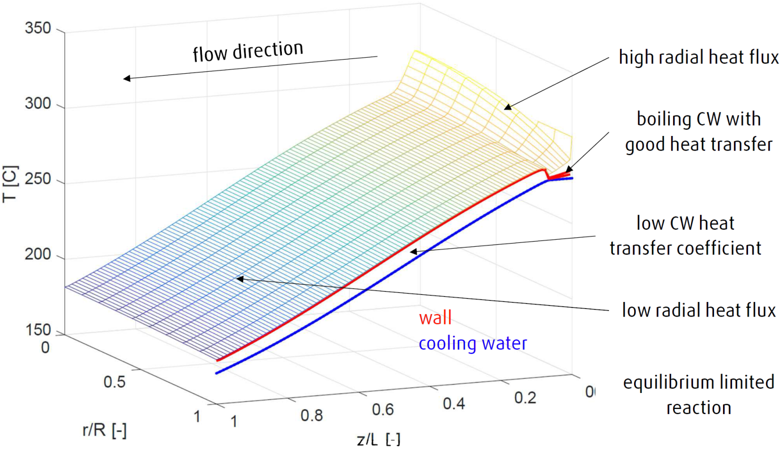
- 2D model including axial and radial gradients
- Full 2D resolution of all variables
- Convective and diffusive fluxes
- Finite volume discretization
  - Mass and heat balances
  - Momentum balance
- C++ code for fast and stable numerical solution
- ≈ 10 s calc. time

- Model input
  - Inlet flow
  - Tube wall boundary
  - Kinetics
  - Properties
  - Heat transfer
  - Eff. heat conductivity
  - Irreversible Δp



Simulation Results – Example T Profile

Reactor model is able to predict the fixed bed profiles.



high radial heat flux

boiling CW with good heat transfer

low CW heat transfer coefficient

low radial heat flux

equilibrium limited reaction

Conclusion

- Model is able to predict reactor operating point
- Trade-off between conversion, reactor volume and Δp
  - Fine foam: high surface, high pressure drop
  - Coarse foam: less surface, less pressure drop, bigger reactor volume
  - Low velocity: lower pressure drop, high number of tubes
- Spherical particle bed not feasible due to excessive Δp
- Reduced pressure drop with printed foam design
- Next step: pilot plant at Yara site

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The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 680414.

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> “*Perfection is attained, not when there is nothing left to add, but when there is nothing left to take away.*”
>
> Antoine de St. Exupéry (1900-1944)

Thank you!

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