Matteo Maestri & Alberto Cuoci

CatalyticFOAM

first principles multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

HPC enabling of OpenFOAM for CFD applications

25 March 2015
Outline

✓ Introduction and motivation

✓ Development of the catalyticFOAM solver for the OpenFOAM® framework
  ✓ Governing equations
  ✓ Numerical methodology

✓ Validation and examples
  ✓ CPO of CH₄ on platinum gauze (complex 3D geometry)
  ✓ CPO of iso-octane (complex chemistry)
  ✓ Tubular reactor with Raschig rings (complex 3D geometry)
  ✓ Packed bed reactors for industrial applications (complex 3D geometry)

✓ Extensions
  ✓ KMC (Kinetic Monte Carlo)
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- Extensions
  - KMC (Kinetic Monte Carlo)
Chemical reactor engineering

Catalytic reactor design:

✓ Important in chemical industry (~90% of industrial chemical processes are catalytic)

✓ Need for an accurate design to provide high yields (€)

✓ Need for a deep understanding for advanced design
Chemical reactor engineering

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Chemical reactor design

Catalytic FOAM: Heterogeneous catalysis within OpenFOAM
Chemical reactor design

Dominant reaction mechanism:
understanding & design

\[
\begin{align*}
[\text{CO}]_{\text{Rh}} &+ [\text{OH}]_{\text{Rh}} + [\text{H}]_{\text{Rh}} \\
[\text{H}]_{\text{Rh}} + [\text{OH}]_{\text{Rh}} &+ \text{Rh} \\
[\text{H}_2\text{O}]_{\text{Rh}} &+ 2\text{Rh}
\end{align*}
\]
A multiscale phenomenon

Result of the interplay among phenomena at different scales

Microscale

- $\text{COOH}^* + * \rightarrow \text{CO}^* + \text{OH}^*$
- $\text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* + *$
- $\text{COOH}^* + * \rightarrow \text{CO}_2^* + \text{H}^*$
- $\text{CO}^*_2 + \text{H}^* \rightarrow \text{COOH}^* + *$
- $\text{CO}_2^* + \text{H}_2\text{O}^* \rightarrow \text{COOH}^* + \text{OH}^* + \text{H}^*$
- $\text{COOH}^* + \text{OH}^* \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^*$
- $\text{CO}_2^* + \text{H}^* \rightarrow \text{HCOO}^* + *$
- $\text{HCOO}^* \rightarrow \text{CO}_2^* + \text{H}^*$
- $\text{CO}_2^* + \text{OH}^* + * \rightarrow \text{HCOO}^* + \text{O}^*$
- $\text{HCOO}^* + \text{OH}^* \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^*$
- $\text{CH}^* + \text{H}^* \rightarrow \text{CH}_2^* + *$
- $\text{CH}^* + * \rightarrow \text{C}^* + \text{H}^*$
- $\text{C}^* + \text{H}^* \rightarrow \text{CH}^* + *$
- $\text{CH}_3^* + \text{O}^* \rightarrow \text{CH}_2^* + \text{OH}^*$
- $\text{CH}_2^* + \text{OH}^* \rightarrow \text{CH}_3^* + \text{O}^*$
- $\text{CH}^* + \text{OH}^* \rightarrow \text{CH}_2^* + \text{O}^*$
- $\text{CH}_2^* + \text{O}^* \rightarrow \text{CH}^* + \text{OH}^* + *$
- $\ldots$

$\sim 10^2$ potential steps @ different coverages

Macroscale

- $\text{[CO]}_{\text{Rh}} + \text{[OH]}_{\text{Rh}} + \text{[H]}_{\text{Rh}} \rightarrow \text{CO}$
- $\text{[CO]}_{\text{Rh}} + 2\text{[H]}_{\text{Rh}} \rightarrow \text{CO}_2$ + $\text{H}_2\text{O}$
- $\text{[H]}_{\text{Rh}} + \text{[OH]}_{\text{Rh}} + \text{Rh} \rightarrow \text{RDS}$
- $\text{[H}_2\text{O}]_{\text{Rh}} + 2\text{Rh} \rightarrow \text{H}_2$ + $\text{H}_2\text{O}$

Result of the interplay among phenomena at different scales

T catalyser

T gas

Temperature [°C]

Axial length [mm]

400

500

600

700

800

900

1000

1100

0 2 4 6 8 10

mmol/s

Catalytic FOAM: Heterogeneous catalysis within OpenFOAM
A multiscale phenomenon

- **MICROSacle**
  - Making and breaking of chemical bonds
  - Intrinsic functionality

- **MesoScale**
  - Interplay among the chemical events

- **MacroScale**
  - Reactor engineering and transport phenomena

Interplay among scales
Observed functionality

Microkinetic analysis of complex chemical processes at surfaces, M. Maestri - in “New strategy for chemical synthesis and catalysis” Wiley, 2011

Catalytic FOAM: Heterogeneous catalysis within OpenFOAM
Catalysts at work (I)
Catalysts at work (II)

Boundary layer

Film diffusion
Catalysts at work (III)

Boundary layer

Film diffusion

Porous catalyst

Pore diffusion
Catalysts at work (IV)

1. Boundary layer
2. Porous catalyst
3. Active sites
4. Chemical reaction
Catalysts at work (V)

Boundary layer

1. Porous catalyst

2. Active sites

3. Chemical reaction

4. Adsorption/desorption

5. Pore diffusion

6. Film diffusion

A

B
Need of bridging between the scales

**MICROSCALE**
- Making and breaking of chemical bonds
- Intrinsic functionality

**MESOSCALE**
- Interplay among the chemical events

**MACROSSCALE**
- Reactor engineering and transport phenomena

Length [m]
- $10^{-15}$
- $10^{-6}$
- $10^{-3}$
- $10^0$

Time [s]
- $10^{-15}$
- $10^{-6}$
- $10^0$

Microkinetic analysis of complex chemical processes at surfaces, M. Maestri - in “New strategy for chemical synthesis and catalysis” Wiley, 2011
A first-principles approach to CRE

1. **MICROSCALE**
   - Making and breaking of chemical bonds

2. **MESOSCALE**
   - Interplay among the chemical events

3. **MACROSCALE**
   - Reactor engineering and transport phenomena

**Length [m]**

- $10^{-9}$
- $10^{-6}$
- $10^{-3}$
- $10^{0}$

**Time [s]**

- $10^{-15}$
- $10^{-6}$
- $10^{0}$

**Methods**

- Electronic structure theory
- MK/kMC
- CFD
Microkinetic modeling and transport

- **CatalyticFOAM**: Heterogeneous catalysis within OpenFOAM

**MICROSCALE**
- Making and breaking of chemical bonds

**MESOSCALE**
- Interplay among the chemical events

**MACROSCALE**
- Reactor engineering and transport phenomena

**Complex geometries**

- **CFD**: Complex geometries
- **MK/kMC**: Microkinetic modeling

**Length [m]**

- $10^{-9}$
- $10^{-3}$
- $10^0$

**Time [s]**

- $10^{-15}$
- $10^{-6}$
- $10^0$
Need of new numerical tools

MICROSCALE
Making and breaking of chemical bond

MESOSCALE
Interplay among the chemical events

MACROSCALE
Reactor engineering and transport phenomena

Development of a new solver
Need of new numerical tools

MICROSCALE
Detailed kinetic mechanism

MESOSCALE

MACROSSCALE
CFD
OpenFOAM

Interplay among scales

Length [m]

Time [s]

$10^{-15}$ $10^{-6}$ $10^{0}$

$10^{-9}$ $10^{-6}$ $10^{0}$

$10^{-3}$ $10^{-3}$

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
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Catalysts at work

1. Boundary layer
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5. Adsorption/desorption
6. Pore diffusion
7. Film diffusion

Catalytic FOAM: Heterogeneous catalysis within OpenFOAM
Governing equations

**Continuity**
\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0
\]

**Momentum**
\[
\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \nabla \left[ \mu \left( \nabla \mathbf{v} + \nabla \mathbf{v}^T \right) - \frac{2}{3} \mu \left( \nabla \mathbf{v} \right) \mathbf{l} \right] + \rho \mathbf{g}
\]

**Species**
\[
\frac{\partial (\rho \omega_k)}{\partial t} + \nabla \cdot (\rho \omega_k \mathbf{v}) = -\nabla \cdot (\rho \omega_k \mathbf{v}_k) + \dot{\Omega}_k^{\text{hom}}
\quad k = 1, \ldots, NG
\]

**Energy**
\[
\rho \hat{C}_P \frac{\partial T}{\partial t} + \rho \hat{C}_P \mathbf{v} \nabla T = \nabla \cdot (\lambda \nabla T) - \rho \sum_{k=1}^{NG} \hat{C}_{P,k} \omega_k \mathbf{v}_k - \sum_{k=1}^{NG} \hat{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}}
\]
Boundary conditions

### Non-catalytic walls

\[ \nabla \omega_k \big|_{\text{inert}} = 0 \]
\[ T \big|_{\text{inert}} = f(t,T) \]
\[ \nabla T \big|_{\text{inert}} = g(t,T) \]

### Catalytic walls

\[ \rho \Gamma_{k,\text{mix}} \left( \nabla \omega_k \right) \big|_{\text{catalytic}} = -\alpha_{\text{cat}} \dot{\Omega}^\text{het}_k \quad k = 1, \ldots, NG \]
\[ \lambda \left( \nabla T \right) \big|_{\text{catalytic}} = -\alpha_{\text{cat}} \sum_{j=1}^{NR} \Delta H^\text{het}_j \dot{r}^\text{het}_j \]
\[ \sigma_{\text{cat}} \frac{\partial \theta_i}{\partial t} = \dot{\Omega}^\text{het}_i \quad i = 1, \ldots, NS \]

Adsorbed (surface) species

### Detailed microkinetic models

- \[ \text{COOH}^* + \ast \rightarrow \text{CO}^* + \text{OH}^* \]
- \[ \text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* + \ast \]
- \[ \text{COOH}^* + \ast \rightarrow \text{CO}_2^* + \text{H}^* \]
- \[ \text{CO}_2^* + \text{H}^* \rightarrow \text{COOH}^* + \ast \]
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- \[ \text{COOH}^* + \text{OH}^* \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^* \]
- \[ \text{CO}_2^* + \text{H}^* \rightarrow \text{HCOO}^{**} \]
- \[ \text{HCOO}^{**} \rightarrow \text{CO}_2^* + \text{H}^* \]
- \[ \text{CO}_2^* + \text{OH}^* + \ast \rightarrow \text{HCOO}^{**} + \text{O}^* \]
- \[ \text{HCOO}^{**} + \text{OH}^* \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^* \]
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- \[ \text{C}^* + \text{H}^* \rightarrow \text{CH}^* + \ast \]
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- \[ \text{CH}^* + \text{OH}^* \rightarrow \text{CH}_2^* + \text{O}^* \]
- \[ \text{CH}_2^* + \text{O}^* \rightarrow \text{CH}^* + \text{OH}^* \]

...
Numerical challenges (I)

✓ Dimensions of the system
  • Proportional to the number of species
  • Proportional to the number of cells

$U, T, p, \rho, x$
Numerical challenges (I)

Dimensions of the system
- Proportional to the number of species
- Proportional to the number of cells

Stiffness
- Different temporal scales involved
- Different spatial scales involved
Numerical challenges (I)

- **Dimensions of the system**
  - Proportional to the number of species
  - Proportional to the number of cells

- **Stiffness**
  - Different temporal scales involved
  - Different spatial scales involved

- **Non-linearity**
  - Source term non linear in concentrations and temperature
  - Coverage dependence of activation energy

\[
U, T, p, \rho, x
\]

\[
r_j = A_j \cdot T^\beta_j \cdot \exp \left( - \frac{E_{att,j}(\theta_i)}{RT} \right) \prod_{i=1}^{NC} (c_i)^{\nu_{ij}}
\]
Numerical challenges (II)

- **Dimensions of the system**
  - Proportional to the number of species
  - Proportional to the number of cells

- **Stiffness**
  - Different temporal scales involved
  - Different spatial scales involved

- **Non-linearity**
  - Source term non linear in concentrations and temperature
  - Coverage dependence of activation energy

*segregated approaches are not feasible*
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM®

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Numerical solution

**Fully segregated algorithms**
- Easy to implement and computationally efficient
- Unfeasible when large, stiff kinetic mechanisms are used

**Strong non-linearity of reaction terms**
- High stiffness

**Fully coupled algorithms**
- All the processes and their interactions are considered simultaneously
- Natural way to treat problems with multiple stiff processes
- The resulting system of equations can be extremely large and the computational cost prohibitive

**Operator-splitting methods**
- Usually avoid many costly matrix operations
- Allow the best numerical method to be used for each type of term or process
- The resulting algorithms can be very complex and usually differ from term to term

**Detailed kinetic schemes**
- ~100 species
- ~1000 reactions

**Complex geometries**
Numerical solution

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM

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  - High stiffness

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  - Allow the best numerical method to be used for each type of term or process
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**Detailed kinetic schemes**
- ~ 100 species
- ~ 1000 reactions

**Complex geometries**
Operator-splitting algorithm

After spatial discretization, the original PDE systems is transformed into an ODE system

\[
\frac{\partial \rho \omega_k}{\partial t} = -\nabla \cdot (\rho \omega_k \mathbf{v}) - \nabla \cdot (\rho \omega_k \mathbf{V}_k) + \Omega_k^{\text{hom}} \\
\quad \text{for} \quad k = 1, \ldots, NG \\
\rho \hat{C}_P \frac{\partial T}{\partial t} = -\rho \hat{C}_P \mathbf{v} \nabla T + \nabla \cdot (\lambda \nabla T) - \rho \sum_{k=1}^{NG} \hat{C}_{P,k} \omega_k \mathbf{V}_k - \sum_{k=1}^{NG} \hat{H}_k^{\text{hom}} \Omega_k^{\text{hom}} \\
\sigma_{\text{cat}} \frac{\partial \theta_i}{\partial t} = \tilde{\Omega}_i^{\text{het}} \quad \text{for} \quad i = 1, \ldots, NS
\]

\[
S = \text{terms associated to the stiff processes} \quad \text{(homogeneous and heterogeneous reactions)} \\
M = \text{terms involving transport processes} \quad \text{(convection and diffusion), non stiff and weakly non linear}
\]
Operator-splitting: an example (I)

\[ \frac{\partial \varphi}{\partial t} = S + M \]

Chemistry \rightarrow Diffusion, convection...
Operator-splitting: an example (II)

\[ \frac{\partial \phi}{\partial t} = S + M \]

Chemistry \rightarrow Diffusion, convection...

Operator-splitting scheme

Chemical step

\[ \frac{\partial \phi}{\partial t} = S \]

Transport step

\[ \frac{\partial \phi}{\partial t} = M \]
Operator-splitting: an example (III)

\[ \frac{\partial \varphi}{\partial t} = S + M \]

Chemistry \quad \rightarrow \quad \text{Diffusion, convection...}

Chemical step

\[ \frac{\partial \varphi}{\partial t} = S \]

Transport step

\[ \frac{\partial \varphi}{\partial t} = M \]
Operator-splitting: an example (IV)

\[
\frac{\partial \varphi}{\partial t} = S + M
\]

Chemistry \rightarrow Diffusion, convection...

Chemistry

\[
\frac{\partial \varphi}{\partial t} = S
\]
Operator-splitting: an example (V)

\[ \frac{\partial \varphi}{\partial t} = S + M \]

Chemistry \rightarrow Diffusion, convection... \\

Chemistry

\[ \frac{\partial \varphi}{\partial t} = S \]

\[ \frac{\partial \varphi}{\partial t} = M \]
**Operator-splitting: an example (VI)**

\[ \frac{\partial \varphi}{\partial t} = S + M \]

**Chemistry**

**Diffusion, convection...**

**Transport**

\[ \frac{\partial \varphi}{\partial t} = S \]
\[ \frac{\partial \varphi}{\partial t} = M \]
Each computational cell behaves as a chemical reactor in the splitting-operator algorithm (chemical step).

Each reactor is described by a set of stiff ODE, which must be integrated on the time step $\Delta t$. 

- **Semi-batch reactor**
  - $Q_{hom}$
  - $R_{hom}$
  - $R_{het}$
  - $Q_{het}$

- **Batch reactor**
  - $R_{hom}$
  - $Q_{hom}$

---

**Catalytic wall**

**Gas mixture**
Operator-splitting in catalytic FOAM (II)

Homogeneous reactions

Catalytic face

Semi-batch reactor

NF = number of catalytic faces
NG = number of gas-phase species
NS = number of adsorbed (surface) species

Equations: \[ N = NG + 1 + NF \cdot NS \]

\[
\begin{align*}
\rho \frac{d\omega_k}{dt} &= \dot{\omega}^\text{hom}_k + \frac{1}{V} \left\{ \sum_{j=1}^{NF} \alpha_j^{\text{cat}} A_j \dot{\omega}^\text{het}_k - \omega_k \sum_{j=1}^{NF} \alpha_j^{\text{cat}} A_j \sum_{k=1}^{NG} \dot{\omega}^\text{het}_k \right\} \\
\rho \hat{C}_p \frac{dT}{dt} &= -\sum_{k=1}^{NG} \hat{H}^\text{hom}_k \dot{\omega}^\text{hom}_k - \sum_{k=1}^{NS} \hat{H}^\text{het}_k \dot{\omega}^\text{het}_k \\
\sigma_{\text{cat}} \frac{\partial \theta_{i,j}}{\partial t} &= \dot{\omega}^\text{het}_{i,j} \quad i=1,...,NS \quad j=1,...,NF
\end{align*}
\]
Operator-splitting in catalytic FOAM (III)

**Homogeneous reactions**

\[ \text{NF} = \text{number of catalytic faces} \]
\[ \text{NG} = \text{number of gas-phase species} \]
\[ \text{NS} = \text{number of adsorbed (surface) species} \]

**Unknowns**  \[ N = \text{NG} + 1 + \text{NF} \cdot \text{NS} \]

\[ \rho \frac{d \omega_k}{dt} = \dot{\Omega}_k^\text{hom} + \frac{1}{V} \left\{ \sum_{j=1}^{\text{NF}} \alpha_j^\text{cat} A_j \dot{\Omega}_k^\text{het} \right\} + \sum_{k=1}^{\text{NF}} \sum_{j=1}^{\text{NG}} \alpha_j^\text{cat} A_j \dot{\Omega}_k^\text{het} \]

\[ \rho \hat{C}_P \frac{dT}{dt} = -\sum_{k=1}^{\text{NG}} \hat{H}_k^\text{hom} \dot{\Omega}_k^\text{hom} - \sum_{k=1}^{\text{NS}} \hat{H}_k^\text{het} \dot{\Omega}_k^\text{het} \]

\[ \frac{\partial \theta_{i,j}}{\partial t} = \dot{\theta}_{i,j} \]

**Batch reactor**

Gas-phase species

Gas-phase temperature

Adsorbed species
catalyticFOAM structure

- OpenFOAM®
  Complex CFD
- CatalyticSMOKE
  Surface microkinetics
- OpenSMOKE
  Complex gas-phase chemistry
- Numerical library for stiff ODEs system
  (LSODE, RADAU5, CVODE, BzzMath, etc.)

CFD code for reacting flows with heterogeneous reactions
Solution procedure

Main features:

- **Solution of the Navier-Stokes equations** (laminar and turbulent regime)
- **No limit to the number of species and reactions**
- **Isothermal and adiabatic conditions**
while (runTime.run()) loop
{
    #include "readTimeControls.H"
    #include "readPISOControls.H"
    #include "compressibleCourantNo.H"
    #include "setDeltaT.H"

    runTime++;

    #include "rhoEqn.H"  Continuity equation

    for (label ocorr=1; ocorr <= nOuterCorr; ocorr++)
    {
        #include "UEqn.H"  Momentum equations
        #include "chemistry.H"  Chemical step
        #include "properties.H"
        #include "YEqn.H"
        #include "TEqn.H"  Transport step

        for (int corr=1; corr<=nCorr; corr++)  PISO loop
        {
            #include "pEqn.H"
        }
    }

    #include "write.H"  Post-processing
}
Chemical step

Loop over all the reactors
{
    if reactor is catalytic
    {
        assembling ODE initial values
        (gas-phase species, temperature, adsorbed species)

        solving the ODE system

        moving the solution to OpenFOAM
    }

    else
    {
        assembling ODE initial values
        (gas-phase species and temperature)

        solving the ODE system

        moving the solution to OpenFOAM
    }
}

Numerical library for stiff ODE systems
(OpenSMOKE++, CVODE, LSODE, etc.)
Stiff ODE solvers in catalytic FOAM (I)

<table>
<thead>
<tr>
<th>Solver</th>
<th>Language</th>
<th>Linear system solution</th>
<th>Parallel</th>
<th>Code available</th>
<th>License</th>
</tr>
</thead>
<tbody>
<tr>
<td>OpenSMOKE++</td>
<td>C ++</td>
<td>Direct</td>
<td>No</td>
<td>Yes</td>
<td>Free</td>
</tr>
<tr>
<td>DVODE</td>
<td>FORTRAN</td>
<td>Direct</td>
<td>No</td>
<td>Yes</td>
<td>Free</td>
</tr>
<tr>
<td>CVODE</td>
<td>C</td>
<td>Direct/iterative</td>
<td>Yes</td>
<td>Yes</td>
<td>Free</td>
</tr>
<tr>
<td>DLSODE</td>
<td>FORTRAN</td>
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<td>Free</td>
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<tr>
<td>DLSODA</td>
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<td>No</td>
<td>Yes</td>
<td>Free</td>
</tr>
<tr>
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<td>Yes</td>
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</tr>
<tr>
<td>LIMEX4</td>
<td>FORTRAN</td>
<td>Direct</td>
<td>No</td>
<td>Yes</td>
<td>Free only for academic use</td>
</tr>
<tr>
<td>MEBDF</td>
<td>FORTRAN</td>
<td>Direct</td>
<td>No</td>
<td>Yes</td>
<td>Free</td>
</tr>
</tbody>
</table>

Most of the CPU Time (80-90%) is spent for the numerical integration of the ODE systems corresponding to the homogeneous and heterogeneous reactors.

The best performances are obtained using the following solvers: OpenSMOKE++, CVODE, DVODE.

Performances of stiff ODE solvers: CPU time

Homogeneous reactors (78 species, 1325 reactions)

Heterogeneous reactors (12 species, 38 reactions)
For each solver a common C++ interface was created

**Creation of ODE System objects**

```cpp
ODESystem_BatchReactor_Homogeneous_DVODE *odeSystemObject_Homogeneous;
odeSystemObject_Homogeneous =
    ODESystem_BatchReactor_Homogeneous_DVODE::GetInstance();
```

**Creation of ODE System Solver**

```cpp
OpenSMOKE::OpenSMOKE_DVODE<ODESystem_BatchReactor_Homogeneous_DVODE>
ode_Homogeneous(odeSystemObject_Homogeneous);
```

**Loop on every computational cell**

```cpp
ode_Homogeneous.SetMaximumNumberOfSteps(100000);
ode_Homogeneous.SetAnalyticalJacobian(false);
node_Homogeneous.SetAbsoluteTolerance(aTol);
node_Homogeneous.SetRelativeTolerance(rTol);
node_Homogeneous.SetInitialValues(t0,Y0);
node_Homogeneous.Solve(tf);
node_Homogeneous.Solution(yF);
```
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CPO of methane over platinum gauze (I)

Operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>600 K</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>10 m/s</td>
</tr>
<tr>
<td>Gauze temperature</td>
<td>1000-1200 K</td>
</tr>
<tr>
<td>CH₄ mole fraction</td>
<td>0.143 (-)</td>
</tr>
<tr>
<td>O₂ mole fraction</td>
<td>0.057 (-)</td>
</tr>
<tr>
<td>He mole fraction</td>
<td>0.80 (-)</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.3 bar</td>
</tr>
<tr>
<td>Pt site density</td>
<td>2.72 x 10⁻⁹ mol/cm²</td>
</tr>
<tr>
<td>Catalytic surf.</td>
<td>5 cm⁻¹</td>
</tr>
</tbody>
</table>

CPO of methane over platinum gauze (II)

3D computational mesh
140,000 cells
3,500 catalytic faces

Symmetry planes

Inlet

Outlet

Heterogeneous kinetics
- 11 Surface Species
- 36 Surface Reactions

www.detchem.com/mechanisms


Homogeneous kinetics
- 25 Species
- 300 Reactions

http://creckmodeling.chem.polimi.it/


Centered (2nd order) spatial discretization
Implicit Euler time integration
Max Courant number 0.05
CPO of methane over platinum gauze (III)

\[ T_{\text{inlet}} = 600K \]
\[ T_{gauze} = 1000K \]

The temperature of the mixture becomes uniform at 2-3 wires diameters downstream the gauze

Under the conditions used in these tests the homogeneous reactions are not relevant

Simulations performed with and without the gas-phase reactions exhibit very similar results

The concentration of radical species in the gas phase is negligible

CO and CO\(_2\) are produced on the surface of the catalytic wires, with their maximal yield occurring at the crossing of the wires
CPO of methane over platinum gauze (IV)

- CH₄ and O₂ conversions are not temperature dependent.
- The CO selectivity is strongly influenced by the gauze temperature.
- Mass fraction of main adsorbed species (CO(s), OH(s), etc.) is maximum downstream, where the inlet mixture meet the catalyst wires.

Comparison with experimental data:

- CO selectivity
- O₂ conversion
- CH₄ conversion

Chart showing conversion and selectivity as a function of catalyst temperature [K].
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM®

Outline

✓ Introduction and motivation

✓ Development of the catalyticFOAM solver for the OpenFOAM® framework
  ✓ Governing equations
  ✓ Numerical methodology

✓ Validation and examples
  ✓ CPO of CH₄ on platinum gauze (complex 3D geometry)
  ✓ CPO of iso-octane (complex chemistry)
  ✓ Tubular reactor with Raschig rings (complex 3D geometry)
  ✓ Packed bed reactors for industrial applications (complex 3D geometry)

✓ Extensions
  ✓ KMC (Kinetic Monte Carlo)

**Operating conditions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>1076 K</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>0.90 m/s</td>
</tr>
<tr>
<td>Wall temperature</td>
<td>1076 K</td>
</tr>
<tr>
<td>iC\textsubscript{8}H\textsubscript{18} mole fraction</td>
<td>0.143 (-)</td>
</tr>
<tr>
<td>O\textsubscript{2} mole fraction</td>
<td>0.057 (-)</td>
</tr>
<tr>
<td>N\textsubscript{2} mole fraction</td>
<td>0.80 (-)</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Rh site density</td>
<td>2.49 \times 10^{-9} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>Catalytic surf.</td>
<td>5 cm\textsuperscript{-1}</td>
</tr>
</tbody>
</table>

**Heterogeneous kinetics**

- 17 Surface Species
- 56 Surface Reactions

www.detchem.com/mechanisms

**Homogeneous kinetics**

- 168 Species
- 5,400 Reactions

http://creckmodeling.chem.polimi.it/
Catalytic FOAM: Heterogeneus catalysis within OpenFOAM

Gas-phase main species
2D mesh (4,000 cells)

- **iC8H18**
  - Color bar: 0 to 0.046
  - The catalytic surface reaction is very fast in the entrance (first 1 mm)

- **CO**
  - Color bar: 0 to 0.05
  - Strong back-diffusion of H2: importance of diffusion coefficients

- **CO2**
  - Color bar: 0 to 0.0001
  - Strong radial gradient are present in the first mm of the reactor

- **H2O**
  - Color bar: 0 to 0.05

- **O2**
  - Color bar: 0 to 0.153
  - The concentration of iC8H18 and O2 on the surface is practically zero, which means that catalytic reactions are mass-transfer limited

- **H2**
  - Color bar: 0 to 0.15

4 days of calculation on 12 cores
CPO of iso-octane over rhodium catalyst (III)

Catalytic FOAM
2D mesh (5,000 cells)

M. Hartmann, et al., Combustion and Flame 157 (2010) 1771-1782

M. Hartmann, et al., Combustion and Flame
157 (2010) 1771-1782
Outline

- Introduction and motivation
- Development of the catalyticFOAM solver for the OpenFOAM® framework
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  - Numerical methodology
- Validation and examples
  - CPO of CH₄ on platinum gauze (complex 3D geometry)
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- Extensions
  - KMC (Kinetic Monte Carlo)
Catalytic FOAM: Heterogeneous catalysis within OpenFOAM

Tubular reactor with Raschig rings (I)

- Operating conditions:
  - Internal diameter: 1 cm
  - Total length: 15 cm
  - CH₄ mole fraction: 0.100 (-)
  - O₂ mole fraction: 0.056 (-)
  - N₂ mole fraction: 0.844 (-)
  - Temperature: 873.15 K
  - Residence time: 0.15 s

- No homogeneous reactions!

3D Unstructured Mesh: ~250,000 cells
- Homogeneous reactors: 240,000
- Heterogeneous reactors: 10,000

CPU time per heterogeneous reactor: 0.75 ms
**Tubular reactor with Raschig rings (II)**

Adsorbed species (mass fractions)

- Rh(s) (0.37-1.0)
- H(s) (0.001-0.006)
- CO(s) (0.-0.57)
- CO2(s) (0.-4·10^-9)

Gas-phase species (mole fractions)

- CH4 (0.-0.10)
- O2 (0.-0.056)
- H2O (0.-0.054)
- H2 (0.-0.006)

**C1 microkinetic model on Rh**

- 82 reaction steps
- 13 adsorbed species
- UBI-QEP and DFT refinement

M. Maestri et al., AIChE J., 2009

Catalytic FOAM: Heterogeneous catalysis within OpenFOAM
Tubular reactor with Raschig rings (III)

Adsorbed species at the catalyst surface

Inlet mixture

Catalytic FOAM: Heterogeneous catalysis within OpenFOAM
Tubular reactor with Raschig rings (IV)

Dynamics of the system
Outline

✓ Introduction and motivation

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✓ Extensions
  ✓ KMC (Kinetic Monte Carlo)
Analysis of performances

Investigated structures
- Cylinders
- Rings
- Spheres

Same catalytic area

<table>
<thead>
<tr>
<th>A_{single element} [m^2]</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>1.13 \times 10^{-4}</td>
</tr>
<tr>
<td>Ring</td>
<td>1.88 \times 10^{-4}</td>
</tr>
<tr>
<td>Cylinder</td>
<td>1.57 \times 10^{-4}</td>
</tr>
</tbody>
</table>

36 cylinders
30 rings
50 spheres
Global kinetic scheme

Micro-kinetic model

step 1 \[ O_2 + 2^* \leftrightarrow 2O^* \]
step 2 \[ C_2H_4 + ^* \leftrightarrow C_2H_4^* \]
step 3 \[ O^* + C_2H_4^* \leftrightarrow C_2H_4O^* + ^* \]
step 4 \[ C_2H_4O^* \leftrightarrow C_2H_4O + ^* \]

Global kinetic scheme

Suljo Linic and Mark A. Barteau, Construction of a reaction coordinate and a microkinetic model for ethylene epoxidation on silver from DFT calculations and surface science experiments, November 2002, Journal of catalyst, pag 200-213

KINETIC MODEL PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>9.85E5 1/(atm m³ s)</td>
</tr>
<tr>
<td>( E_{att} )</td>
<td>15 Kcal/mol</td>
</tr>
<tr>
<td>( m )</td>
<td>0.65</td>
</tr>
<tr>
<td>( n )</td>
<td>0.71</td>
</tr>
</tbody>
</table>

\[
r = k_{overall} (P_{O_2})^n (P_{C_2H_4})^m
\]

\[
k_{overall} = Ae^{-\frac{E_{att}}{RT}}
\]
### OPERATING CONDITIONS

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt; Molar Fraction</strong></td>
<td>35.0 %</td>
</tr>
<tr>
<td><strong>O&lt;sub&gt;2&lt;/sub&gt; Molar Fraction</strong></td>
<td>5.0 %</td>
</tr>
<tr>
<td><strong>CH&lt;sub&gt;4&lt;/sub&gt; Molar Fraction</strong></td>
<td>60.0 %</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>15 atm</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>432 – 550 K</td>
</tr>
<tr>
<td><strong>Inlet Velocity</strong></td>
<td>1 m/s</td>
</tr>
</tbody>
</table>

- Oxygen based process
- Methane as inert component
- Isothermal simulations at 432 K, 490 and 550 K
- Adiabatic simulations at 432 K
- Multiregion simulations at 490 K
The behaviour of the three packed beds is almost the same.

3 days on 8 cores
Isothermal simulations: 550 K

Spheres at high temperature can guarantee the higher conversion.
**Isothermal simulations**

**C$_2$H$_4$ Conversion vs Temperature**

![Graph showing C$_2$H$_4$ conversion vs temperature for Cylinder, Sphere, and Ring with data points at 432 K, 490 K, and 550 K.]

<table>
<thead>
<tr>
<th></th>
<th>432 K</th>
<th>490 K</th>
<th>550 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinders</td>
<td>3.5 %</td>
<td>15.5%</td>
<td>25.0%</td>
</tr>
<tr>
<td>Spheres</td>
<td>3.6 %</td>
<td>16.7%</td>
<td>27.0%</td>
</tr>
<tr>
<td>Rings</td>
<td>3.5 %</td>
<td>14.1%</td>
<td>22.8%</td>
</tr>
</tbody>
</table>
**Extension to multiregion**

**Multiregion Mesh:** The spheres have been meshed with the same level of refinement of the bulk phase - conformal mesh.

**Adiabatic simulations**
Need to have very fine meshes close to the reactor wall.
Outline

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  ✓ CPO of CH₄ on platinum gauze (complex 3D geometry)
  ✓ CPO of iso-octane (complex chemistry)
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  ✓ Packed bed reactors for industrial applications (complex 3D geometry)

✓ Extensions
  ✓ KMC (Kinetic Monte Carlo)
**Extension to kinetic Monte Carlo**

In collaboration with: K. Reuter and S. Matera (TUM)

**MICROSCALE**
- Making and breaking of chemical bonds

**MESOSCALE**
- Interplay among the chemical events

**MACROSCALE**
- Reactor engineering and transport phenomena

**Electronic structure theory**

**CFD**

- CFD

- MK/kMC

- TUM

- CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
**First-principles kinetic Monte Carlo**

- Evaluate the statistical interplay of large number of elementary processes
- Open non-equilibrium system → need to explicitly follow the time evolution
- Rare event dynamics → Molecular Dynamics simulations unsuitable. Map on a lattice model → Markov jump process description

\[
\frac{d}{dt} P(x, t) = \sum_y k(x, y) P(y, t) - \sum_y k(y, x) P(x, t)
\]

- Each site \( a \) has own entry in \( x \) denoting its adsorbate state \( x_a \)
- Simulate trajectories \( x(t) \) (kinetic Monte Carlo)

Continuum equations need boundary conditions for the mass fluxes $j^\alpha$ at the surface:

$$j^\alpha_n = v^\alpha M^\alpha \text{TOF}$$

**Coupled problem**: to determine the TOF with 1p-kMC the pressures at the surface are needed, but the pressure field depends on the TOF

**kMC too expensive** for direct coupling to the flow solver

Run kMC beforehand and interpolate (Modified Shepard)

Very efficient

Easily extendable to more complex geometries

---

T_s = 600K, $p_s$(O_2) = 1atm

An example: The reactor STM (I)

The Reactor STM

CO oxidation on Ru$_2$O

Rate constants $k(x,y)$ from DFT and harmonic Transition State Theory

Model system

✓ CO oxidation on RuO$_2$(110)
✓ 2 types of sites, bridge and cus


Rasmussen, Hendriksen, Zeijlemaker, Ficke, Frenken,
An example: The reactor STM (II)

Operating conditions
T: 600 K
P: 1 atm
Inlet: CO + O2 (66%, 34% Vol)
Inlet velocity: 5 cm/s

Catalytic Wall
Catalyst: Ru$_2$O

The reactor STM (II)

Inlet
CO + O$_2$

Catalytic wall

Outlet

d = 2 mm

Computational details
Mesh: unstructured, ~90,000 cells
Discretization: 2$^{nd}$ order, centered
Max time step: $10^{-4}$ s
CPU time: ~2 s per time step
An example: The reactor STM (III)

Steady-state results

Strong recirculations
Dynamic results

Operating conditions
T: 600 K
P: 1 atm
Inlet: CO + O2 (66%, 34% Vol)
Inlet velocity: 5 cm/s

Initial conditions:
CO + O2 (66%, 34% Vol)

The CO mole fraction in the inlet stream increases during the time

CO mole fraction

0 1 2 3 time [s]

18% 34% 50% 66%

Dynamic results
An example: the catalytic gauze (I)

- Rate constants \( k(x,y) \) from DFT and harmonic Transition State Theory
- Model system: CO oxidation on Pd(100):

Original gauze structure

Detail of wire intersections

Computational domain
An example: the catalytic gauze (II)
An example: the catalytic gauze (III)

DFT → kMC → CFD
The catalyticFOAM Group

Matteo Maestri
heterogeneous catalysis, multiscale modeling, microkinetic modeling

Alberto Cuoci
CFD, numerical methods

Stefano Rebuhini (PhD Student)
Hierarchical analysis of complex reacting systems

Mauro Bracconi (PhD student)
ISAT, complex geometries

Former Students

Sandro Goisis and Alessandra Osio
Development of numerical methodology

Tiziano Maffei
Improvement of multi-region solver

Giancarlo Gentile and Filippo Manelli
Development of multi-region solver
The catalyticFOAM web-site

The catalyticFOAM code can be freely downloaded from our web site:

http://www.catalyticfoam.polimi.it/

Statistics since April 2013

Unique visitors: 2,500
Visits: 4,200 (~6 per day)
Visits from 76 different countries

About 200 registered users
The catalytic FOAM software is fully compatible with OpenFOAM version 2.3.x.

Nevertheless, it is not approved or endorsed by ESI/OpenCFD, the producer of the OpenFOAM software and owner of the OPENFOAM® and OpenCFD® trade marks.

Software is released under the L-GPL license through an independent website: www.catalyticfoam.polimi.it
Publications on international journals


Outline

✓ Introduction and motivation

✓ Development of the catalytic FOAM solver for the OpenFOAM® framework
  ✓ Governing equations
  ✓ Numerical methodology
  ✓ Extension to the multi-region modeling

✓ Validation and examples
  ✓ Annular reactor (simple chemistry)
  ✓ CPO of CH₄ on platinum gauze (complex 3D geometry)
  ✓ CPO of iso-octane (complex chemistry)
  ✓ Tubular reactor with Raschig rings (complex 3D geometry)
  ✓ Packed bed reactors for industrial applications (complex 3D geometry)
  ✓ Micro-channel reactors (Hierarchical analysis)

✓ Extensions
  ✓ KMC (Kinetic Monte Carlo)

✓ Conclusions and future works
In the original version of catalyticFOAM the catalyst morphology is not detailed.

The presence of the catalyst was accounted for by a boundary condition imposing continuity between the reactive flux and the diffusive flux to and from the catalytic surface.

This approach does not account for diffusive limitations in the solid phase or in general for the intra-solid transport phenomena.

Need of a Multi-Region Solver (gas phase + solid phases)
Internal transport phenomena

1. Boundary layer
2. Porous catalyst
3. Active sites
4. Chemical reaction
5. Adsorption/desorption
6. Pore diffusion
7. Film diffusion
Internal transport phenomena

Gas Phase

\[
\frac{\partial (\rho \omega_i)}{\partial t} + \nabla (\rho U \omega_i) = \nabla (\rho D_i \nabla \omega_i) + \sum_j R_j \nu_{ij} MW_i
\]

\[
c_p \frac{\partial (\rho T)}{\partial t} + c_p \nabla (\rho UT) = \nabla (k \nabla T) + \sum_j R_j \Delta H_j
\]

\[
\frac{\partial (\rho U)}{\partial t} + \nabla (\rho U U) = -\nabla p + \nabla (\mu \nabla U) + \rho g
\]

\[
\frac{\partial \rho}{\partial t} + \nabla (\rho U) = 0
\]

Solid Phase

\[
\frac{\partial (\rho^{\text{mix}} \omega_i)}{\partial t} = \nabla (\rho^{\text{mix}} D_{\text{eff},i} \nabla \omega_i) + \left( \sum_j R_{\text{het},j} \nu_{ij} MW_i \right) \cdot a_{\text{cat}}
\]

\[
c_{p,\text{sol}} \frac{\partial (\rho_{\text{sol}} T)}{\partial t} = \nabla (k_{\text{eff}} \nabla T) + \sum_j R_{\text{het},j} \Delta H_j \cdot a_{\text{cat}}
\]

\[
\Gamma_{\text{site}} \frac{\partial \vartheta_i}{\partial t} = R_{i,\text{surf}}
\]
Multiple meshes for multiple regions
Multiple meshes for multiple regions

Mesh 1: Fluid Region

Mesh 2: Solid Region 1

Mesh 3: Solid Region 2
Multiple meshes for multiple regions

- Mesh 1: Fluid Region
- Mesh 2: Solid Region 1
- Mesh 3: Solid Region 2

- Multiple meshes
- Different properties for each region
- Separate governing equations on each cell
Linking the regions

How to couple at the interface?
How to couple at the interface?

\[
\begin{align*}
  k_{OWN,I} \nabla T_{OWN(I)} &= k_{NBR,I} \nabla T_{NBR(I)} \\
  T_{OWN,I} &= T_{NBR,I}
\end{align*}
\]

\[
\begin{align*}
  D_{OWN} \nabla C_{OWN(I)} &= D_{NBR} \nabla C_{NBR(I)} \\
  C_{OWN,I} &= C_{NBR,I}
\end{align*}
\]
Linking the regions

\[ T_{OWN,I} = T_{NBR,I} \Rightarrow T_{OWN} = \frac{k_{OWN} \cdot T_{OWN}}{\Delta_{OWN}} + \frac{k_{NBR} \cdot T_{NBR}}{\Delta_{NBR}} \]

\[ C_{OWN,I} = C_{NBR,I} \Rightarrow C_{OWN} = \frac{D_{OWN} \cdot C_{OWN}}{\Delta_{OWN}} + \frac{D_{NBR} \cdot C_{NBR}}{\Delta_{NBR}} \]

Mixed boundary conditions at the interface
Partitioned Approach

1) Solve in each zone with mixed BCs
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM

Partitioned Approach

1) Solve in each zone with mixed BCs
2) Update interface values and solve in the neighboring region

Mixed boundary conditions at the interface

\[
\begin{align*}
\{ & k_{\text{OWN,I}} \nabla T_{\text{OWN}(I)} = k_{\text{NBR,I}} \nabla T_{\text{NBR}(I)} \\
& T_{\text{OWN,I}} = T_{\text{NBR,I}} \}
\end{align*}
\]

\[
T_{\text{LOWN}} = \frac{k_{\text{OWN}} \cdot T_{\text{OWN}} + k_{\text{NBR}} \cdot T_{\text{NBR}}}{\Delta_{\text{OWN}} \over \Delta_{\text{OWN}}} + \frac{k_{\text{NBR}} \cdot T_{\text{NBR}}}{\Delta_{\text{NBR}}}
\]

\[
\begin{align*}
\{ & D_{\text{OWN}} \nabla C_{\text{OWN}(I)} = D_{\text{NBR}} \nabla C_{\text{NBR}(I)} \\
& C_{\text{OWN,I}} = C_{\text{NBR,I}} \}
\end{align*}
\]

\[
C_{\text{LOWN}} = \frac{D_{\text{OWN}} \cdot C_{\text{OWN}} + D_{\text{NBR}} \cdot C_{\text{NBR}}}{\Delta_{\text{OWN}} \over \Delta_{\text{OWN}}} + \frac{D_{\text{NBR}} \cdot C_{\text{NBR}}}{\Delta_{\text{NBR}}}
\]
Partitioned Approach

1) Solve in each zone with mixed BCs
2) Update interface values and solve in the neighboring region
3) Iterate till convergence is reached
Fluid Region

\[
\begin{align*}
\frac{d(\rho_{\text{mix}} Y_i)}{dt} &= \nabla \left( \rho_{\text{mix}} D_{\text{mix},i} \nabla (Y_i) \right) - \nabla (\Phi Y_i) \\
\frac{d(\rho_{\text{mat}} c_p T)}{dt} &= \nabla (k \nabla (T)) - C_{\text{mix}}^{\text{mix}} \nabla (\Phi T)
\end{align*}
\]

with the mixed BCs on the interface:

\[
T_{i,\text{FLU}} = \frac{k_{\text{FLU}} \cdot T_{\text{FLU}} + k_{\text{SOL}} \cdot T_{\text{SOL}}}{A_{\text{FLU}} + A_{\text{SOL}}}
\]

\[
C_{i,\text{FLU}} = \frac{D_{\text{FLU}} \cdot C_{\text{FLU}} + D_{\text{SOL}} \cdot C_{\text{SOL}}}{A_{\text{FLU}} + A_{\text{SOL}}}
\]
Coupling structure

Solid Region

\[ \frac{d(\rho_{mix} Y_i)}{dt} = \nabla(\rho_{mix} D_{mix,i} \nabla(Y_i)) \]
\[ \frac{d(\rho_{mat} c_p T)}{dt} = \nabla(k \nabla(T)) \]

with the mixed BCs on the interface:

\[ T_{1,\text{SOL}} = \frac{k_{\text{SOL}} \cdot T_{\text{SOL}} + k_{\text{FLU}} \cdot T_{\text{FLU}}}{A_{\text{SOL}} + A_{\text{FLU}}} \]
\[ C_{1,\text{SOL}} = \frac{D_{\text{SOL}} \cdot C_{\text{SOL}} + D_{\text{FLU}} \cdot C_{\text{FLU}}}{A_{\text{SOL}} + A_{\text{FLU}}} \]

Fluid Region

\[ \frac{d(\rho_{mix} Y_i)}{dt} = \nabla(\rho_{mix} D_{mix,i} \nabla(Y_i)) - \nabla(\Phi Y_i) \]
\[ \frac{d(\rho_{mat} c_p T)}{dt} = \nabla(k \nabla(T)) - C_{\text{mix}}^{\text{mix}} \nabla(\Phi T) \]

with the mixed BCs on the interface:

\[ T_{1,\text{FLU}} = \frac{k_{\text{FLU}} \cdot T_{\text{FLU}} + k_{\text{SOL}} \cdot T_{\text{SOL}}}{A_{\text{FLU}} + A_{\text{SOL}}} \]
\[ C_{1,\text{FLU}} = \frac{D_{\text{FLU}} \cdot C_{\text{FLU}} + D_{\text{SOL}} \cdot C_{\text{SOL}}}{A_{\text{FLU}} + A_{\text{SOL}}} \]
**Solid Region**

\[
\frac{d(\rho_{\text{mix}} Y_i)}{dt} = \nabla(\rho_{\text{mix}} D_{\text{mix,i}} \nabla(Y_i))
\]

\[
\frac{d(\rho_{\text{mat}} c_p T)}{dt} = \nabla(k \nabla(T))
\]

with the mixed BCs on the interface:

\[
T_{1,\text{SOL}} = \frac{k_{\text{SOL}} \cdot T_{\text{SOL}} + k_{\text{FLU}} \cdot T_{\text{FLU}}}{A_{\text{SOL}} + A_{\text{FLU}}}
\]

\[
C_{1,\text{SOL}} = \frac{D_{\text{SOL}} \cdot C_{\text{SOL}} + D_{\text{FLU}} \cdot C_{\text{FLU}}}{A_{\text{SOL}} + A_{\text{FLU}}}
\]

**Fluid Region**

\[
\frac{d(\rho_{\text{mix}} Y)}{dt} = \nabla(\rho_{\text{mix}} D_{\text{mix,i}} \nabla(Y)) - \nabla(\Phi Y)
\]

\[
\frac{d(\rho_{\text{mat}} c_p T)}{dt} = \nabla(k \nabla(T)) - c_p^{\text{mix}} \nabla(\Phi T)
\]

with the mixed BCs on the interface:

\[
T_{1,\text{FLU}} = \frac{k_{\text{FLU}} \cdot T_{\text{FLU}} + k_{\text{SOL}} \cdot T_{\text{SOL}}}{A_{\text{FLU}} + A_{\text{SOL}}}
\]

\[
C_{1,\text{FLU}} = \frac{D_{\text{FLU}} \cdot C_{\text{FLU}} + D_{\text{SOL}} \cdot C_{\text{SOL}}}{A_{\text{FLU}} + A_{\text{SOL}}}
\]

**Convergence Criteria**

\[
|T^{(k)} - T^{(k-1)}| \leq \text{absTol}_T \quad |T^{(k)} - T^{(k-1)}| \div T^{(k-1)} \leq \text{relTol}_T
\]

\[
|Y_i^{(k)} - Y_i^{(k-1)}| \leq \text{absTol}_y \quad |Y_i^{(k)} - Y_i^{(k-1)}| \div Y_i^{(k-1)} \leq \text{relTol}_y
\]

**Coupling Method**

- Solve alternatively for every cell of the 2 coupled regions
- Check for convergence: if reached, proceed to next time step

**Coupling Loop**
Multi-region solver architecture

Solve Solid

for each time step...

Solve Fluid
Multi-region solver architecture

for each time step...

Solve Solid

Solve Fluid

Continuity Equation

Navier-stokes Equations

Pressure Corrector

PISO predictor-corrector loop
Multi-region solver architecture

Solve Solid

for each time step...

Solve Fluid

- Continuity Equation
- Mass Transfer Equation
- Heat Transfer Equation
- Fluid Chemistry
  - Homogeneous reactions
- Update Fluid Properties
- Navier-stokes Equations
- Pressure Corrector

Catalytic FOAM: Heterogeneous catalysis within OpenFOAM
Multi-region solver architecture

for each time step...

Solve Solid

- Mass Transfer Equation
- Heat Transfer Equation
- Solid Chemistry
  - Homogeneous and heterogeneous reactions
  - Site species conservation
- Update Solid Properties

Solve Fluid

- Continuity Equation
- Mass Transfer Equation
- Heat Transfer Equation
- Fluid Chemistry
  - Homogeneous reactions
- Update Fluid Properties
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Coupling Loop

PISO predictor-corrector loop

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
Validation with analytical solution

\[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dC_A}{dr} \right) = k_r C_A \]

\[ C_A = C_{A,s} \frac{\sinh \left( \phi \frac{r}{R} \right)}{\frac{r}{R} \sinh (\phi)} \]
Outline

✓ Introduction and motivation

✓ Development of the catalyticFOAM solver for the OpenFOAM® framework
  ✓ Governing equations
  ✓ Numerical methodology
  ✓ Extension to the multi-region modeling

✓ Validation and examples
  ✓ Annular reactor (simple chemistry)
  ✓ CPO of CH₄ on platinum gauze (complex 3D geometry)
  ✓ CPO of iso-octane (complex chemistry)
  ✓ Tubular reactor with Raschig rings (complex 3D geometry)
  ✓ Packed bed reactors for industrial applications (complex 3D geometry)
  ✓ Micro-channel reactors (Hierarchical analysis)

✓ Extensions
  ✓ KMC (Kinetic Monte Carlo)

✓ Conclusions and future works
Micro-channel technology (I)

Development and intensification of processes which involve high exothermic reactions

Improved heat transfer in the honeycomb matrix

Improved mass transfer in the packed bed channel
Micro-channel technology (II)

How “unconventional” geometry influences the mass transfer in micro-channel reactors?

Can literature correlations (developed for industrial reactors) describe mass transfer phenomena in micro-channel reactors?
Micro-channel reactor generation

Two-step Monte Carlo process based on the algorithm of Soppe[1]

H. J. Freund, Erlangen Universität, DE

Investigated micro-channel reactors

300 μm spheres

600 μm spheres

<table>
<thead>
<tr>
<th></th>
<th>Green channel</th>
<th>Blue channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle diameter [m]</td>
<td>300 x 10^{-6}</td>
<td>600 x 10^{-6}</td>
</tr>
<tr>
<td>Reactor length [m]</td>
<td>12.5 x 10^{-3}</td>
<td>12.5 x 10^{-3}</td>
</tr>
<tr>
<td>Tube diameter [m]</td>
<td>4 x 10^{-3}</td>
<td>4 x 10^{-3}</td>
</tr>
</tbody>
</table>
Pressure drops: 600 μm (blue channel)

Particle Reynolds number

\[ \text{Re} = \frac{\rho \cdot v \cdot D_{\text{Particle}}}{\mu} \]

Tube-to-particle diameter ratio describes wall effects

\[ N = \frac{D_{\text{Tube}}}{D_{\text{Particle}}} \]
Pressure drops: a comparison

Pressure drops in the reactor with 600 μm sphere diameter are controlled by wall effects.

Pay attention: same tube-to-particle diameter ratio of the previous micro-channel reactor studied.

Pressure drops in micro-channel reactor with 300 μm sphere diameter are high and wall effects are negligible.
### Mass transfer coefficient (I)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>653</td>
<td>K</td>
</tr>
<tr>
<td>Outlet pressure</td>
<td>101325</td>
<td>Pa</td>
</tr>
<tr>
<td>Inlet molar fraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen (N₂)</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>0.036</td>
<td></td>
</tr>
</tbody>
</table>

- Irreversible first-order kinetics model at the catalytic wall \( (Da \approx 100) \)
- Identical condition within each channel
- Isothermal condition
- Laminar flow \((10 < Re < 90)\)
- Characteristic length: \( D_{Particle} \)

![Mass transfer regime](image)
The mass transfer coefficient is higher for the micro-channel reactor with the sphere diameter of 300 μm.

Mass transfer coefficient estimated with Integral Mass Balance (IMB) method:

\[ K_{mat,i} = \frac{-u_{in} \ln(1 - \chi)}{a_v L} \]
### Sherwood number: 600 μm

**Sherwood number**

- **Reynolds number**
  - Yoshida et al.\(^{[2]}\)
  - Wakao and Funazkri
  - Micro-channel: 600 μm

**Equation**

\[
J_m = \frac{0.91}{Re^{0.51}} \psi
\]

**Particle Reynolds number**

- Yoshida Reynolds number
- Schmidt number

\[
Sh = 2 + 1.1Re^{0.6} Sc^{1/3}
\]

**References**

Why the difference?

This comparison shows that the different Sherwood number depends on the tube-to-particle diameter ratio

\[ N = \frac{D_{\text{Tube}}}{D_{\text{Particle}}} \]

and NOT on micro-dimensions.

<table>
<thead>
<tr>
<th></th>
<th>Particle diameter [m]</th>
<th>Tube diameter [m]</th>
<th>Tube-to-particle diameter ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro-channel</td>
<td>600 \times 10^{-6}</td>
<td>4 \times 10^{-3}</td>
<td>6.7</td>
</tr>
<tr>
<td>Conventional packed bed</td>
<td>6 \times 10^{-3}</td>
<td>40 \times 10^{-3}</td>
<td>6.7</td>
</tr>
</tbody>
</table>
Why the difference?

The Sherwood number depends on the tube-to-particle diameter ratio:

\[ N = \frac{D_{\text{Tube}}}{D_{\text{Particle}}} \]

<table>
<thead>
<tr>
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<th>Tube diameter [m]</th>
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</thead>
<tbody>
<tr>
<td>Micro-channel</td>
<td>600 x 10^{-6}</td>
<td>4 x 10^{-3}</td>
<td>6.7</td>
</tr>
<tr>
<td>Micro-channel</td>
<td>300 x 10^{-6}</td>
<td>4 x 10^{-3}</td>
<td>13.3</td>
</tr>
</tbody>
</table>
The higher mass transfer coefficient for micro-channel with 300 μm depends on the lower influence of the wall effects.

The mass transfer coefficient is reduced by wall effects also in the micro-channel with 300 μm.