Heterogeneous catalysis within OpenFOAM

HPC enabling of OpenFOAM for CFD applications

November, 26th, 2012
Outline

✓ Introduction and motivation

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

✓ 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)

✓ Extensions
  ✓ KMC (Kinetic Monte Carlo)
  ✓ Multi-region solver

✓ Conclusions and future works
✓ **Introduction and motivation**

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✓ Conclusions and future works
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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- Need for an accurate design to provide high yields (€)
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CatalyticFOAM: Heterogeneous catalysis within OpenFOAM

Chemical reactor design

Graphs showing temperature and flow profiles along the axial length of a reactor.
Chemical reactor design

Dominant reaction mechanism: understanding & design

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

RDS

\[ [\text{H}]_{\text{Rh}} + [\text{OH}]_{\text{Rh}} + \text{Rh} \]

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

Result of the interplay among phenomena at different scales

**Microscale**

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

\[ \ldots \]

\[ \sim 10^2 \text{ potential steps @ different coverages} \]

**Macroscale**

\[ \text{[CO]}_{\text{Rh}} + [\text{OH}]_{\text{Rh}} + [\text{H}]_{\text{Rh}} \]

\[ \text{[CO]}_{\text{Rh}} + 2[\text{H}]_{\text{Rh}} \]

\[ \text{[H]}_{\text{Rh}} + [\text{OH}]_{\text{Rh}} + \text{Rh} \]

\[ \text{[H}_2\text{O}]_{\text{Rh}} + 2\text{Rh} \]

\[ \text{CO} \]

\[ \text{H}_2 \]

\[ \text{H}_2\text{O} \]

\[ \text{RDS} \]

\[ \text{CO}_2 \]

\[ \text{H}_2 \]

\[ \text{H}_2\text{O} \]

\[ \text{CH}_4 \]

\[ \text{O}_2 \]

\[ \text{CO} \]

\[ \text{H}_2 \]

\[ \text{H}_2\text{O} \]

\[ \text{CO}_2 \]

\[ \text{T catalyst} \]

\[ \text{T gas} \]

\[ \text{mmol/s} \]

\[ \text{Temperature [°C]} \]

\[ \text{Axial length [mm]} \]
A multiscale phenomenon

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

**MESOSCALE**
- Interplay among the chemical events

**MACROSCALE**
- Mass and energy transport phenomena

---

*Microkinetic analysis of complex chemical processes at surfaces*  
M. Maestri – in "New strategy for chemical synthesis and catalysis" Wiley, 2011
Need of tools for analysis

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

**MESOSCALE**
- Interplay among the chemical events

**MACROSCALE**
- Mass and energy transport phenomena

Interplay among scales

*Time [s]*
- Length [m]

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

10^{-15} 10^{-12} 10^{-9} 10^{-6} 10^{0}

Development of a new solver

Need of tools for analysis

Microscopic 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

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Governing equations

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad \text{continuity}
\]

\[
\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \nabla \cdot \left[ \mu (\nabla \mathbf{v} + \nabla \mathbf{v}^T) - \frac{2}{3} \mu (\nabla \mathbf{v}) I \right] + \rho \mathbf{g} \quad \text{momentum}
\]

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

\[
\rho \hat{C}_P \frac{\partial T}{\partial t} + \rho \hat{C}_P \mathbf{v} \nabla T = \nabla \cdot (\lambda \nabla T) - \rho \sum_{k=1}^{NG} \hat{C}_{P_k} \omega_k \mathbf{V}_k - \sum_{k=1}^{NG} \hat{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}} \quad \text{gas-phase energy}
\]
### 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

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

**Adsorbed (surface) species**

\[ r_j = A_j \cdot T^{r_j} \cdot \exp \left( - \frac{E_{\text{att}}(\theta_i)}{RT} \right) \prod_{i=1}^{NC} (c_i)^{v_{ij}} \]

---

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

\[ U, T, p, \rho, x \]
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM

Numerical challenges

✓ 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

$U, T, p, \rho, x$
Numerical challenges

✓ 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

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

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

✓ Stiffness
  • Different temporal scales involved
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seggregated approaches are not feasible
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Numerical solution

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

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

**Fully segregated algorithms**
- 😊 easy to implement and computationally efficient
- 😞 unfeasible when large, stiff kinetic mechanisms are used

**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

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CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
Numerical solution

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- 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

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
Operator-splitting algorithm

\[
\begin{align*}
\frac{\partial (\rho \omega_k)}{\partial t} &= -\nabla \cdot (\rho \omega_k \mathbf{v}) - \nabla \cdot (\rho \omega_k \mathbf{V}_k) + \dot{\Omega}_k^{\text{hom}} \\
\rho \hat{C}_P \frac{\partial T}{\partial t} &= -\rho \hat{C}_P \mathbf{v} \nabla T + \nabla \cdot (\lambda \nabla T) - \rho \sum_{k=1}^{NG} \hat{C}_{P,k} \omega_k \mathbf{V}_k - \sum_{k=1}^{NG} \hat{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}} \\
\sigma_{\text{cat}} \frac{\partial \theta_i}{\partial t} &= \dot{\Omega}_i^{\text{het}} \\
\end{align*}
\]

\text{PDE}

\text{Stiff reaction terms}

\text{gas-phase species}

\text{gas-phase energy}

\text{adsorbed (surface) species}

Finite volume discretization

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

\[
\begin{align*}
\frac{\partial \omega_k}{\partial t} &= M_k + S_k \\
\frac{\partial T}{\partial t} &= M^T + S^T \\
\frac{\partial \theta_i}{\partial t} &= S_i^{\text{het}} \\
\end{align*}
\]

\text{ODE}

S = terms associated to the stiff processes (homogeneous and heterogeneous reactions)

M = terms involving transport processes (convection and diffusion), non stiff and weakly non linear

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
Strang splitting (I)

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

Chemistry

Diffusion, convection...

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
Strang splitting (I)

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

Chemistry \rightarrow Diffusion, convection...

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

Chemical step

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

Transport step

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
Strang splitting (I)

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

Chemistry → Strang splitting scheme → Diffusion, convection...

Chemical step

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

Transport step

\[ \frac{\partial \varphi}{\partial t} = M \]
Strang splitting (II)

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

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

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

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
Strang splitting (II)

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

Chemistry

Diffusion, convection...

Chemistry

Transport

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
Strang splitting (II)

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

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

Diffusion, convection...

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

Transport
Operator splitting algorithm (I)

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

Global system

Jacobian matrix:

- Sparse
- Unstructured
- Blocks
Operator splitting algorithm (II)

Source term

Global system

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

Jacobian matrix:
- Sparse
- Diagonal
- Blocks

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
Operator splitting algorithm (III)

Global system

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

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

Transport term
\[ \frac{\partial \varphi}{\partial t} = M \]

Jacobian matrices:
- Sparse
- Unstructured

N_{\text{cells}}
Operator splitting algorithm (IV)

Global system

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

Source term

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

Using a suitable algorithm for each sub-problem

Transport term

\[ \frac{\partial \varphi}{\partial t} = M \]
Reactor network

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 $\Delta t$
Heterogeneous reactors

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

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

Semi-batch reactor

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

Gas-phase species

Gas-phase temperature

Adsorbed species
Homogeneous reactors

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

Unknowns \( N = NG + 1 + NF \cdot NS \)

Batch reactor

\[
\begin{align*}
\rho \frac{d\omega_k}{dt} &= \dot{\Omega}_k^{\text{hom}} + \frac{1}{V} \left\{ \sum_{j=1}^{NF} \alpha_j^{\text{cat}} A_j \dot{\Omega}_k^{\text{het}} + \sum_{j=1}^{NF} \alpha_j^{\text{cat}} A_j \sum_{k=1}^{NS} \dot{n}_k^{\text{het}} \right\} \\
\rho C_P \frac{dT_k}{dt} &= -\sum_{k=1}^{NG} \dot{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}} - \sum_{k=1}^{NS} \dot{H}_k^{\text{het}} \dot{\Omega}_k^{\text{het}} \\
\sigma_{i,j}^{\text{cat}} \frac{\partial \theta_{i,j}}{\partial t} &= \dot{n}_i^{\text{het}} \\
& \quad \text{for } i=1,\ldots,NS \quad j=1,\ldots,NF
\end{align*}
\]
catalyticFOAM structure

OpenFOAM®
Complex CFD
catalyticFOAM structure

OpenFOAM®
Complex CFD

- Implementation of detailed reaction mechanisms for surface kinetics
- Heterogeneous kinetic models: CHEMKIN® format, UBI-QEP framework

CatalyticSMOKE
Surface microkinetics

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
OpenFOAM®
Complex CFD

✓ Implementation of detailed reaction mechanisms for surface kinetics
✓ Heterogeneous kinetic models: CHEMKIN® format, UBI-QEP framework

CatalyticSMOKE
Surface microkinetics

OpenSMOKE
Complex gas-phase chemistry
catalyticFOAM structure

- **OpenFOAM®**
  - Complex CFD

- **catalyticFOAM**
  - CFD code for reacting flows with heterogeneous reactions

- **CatalyticSMOKE**
  - Surface microkinetics

- **OpenSMOKE**
  - Complex gas-phase chemistry
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
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: BzzMath6, CVODE, DVODE.

Performances of stiff ODE solvers: CPU time

<table>
<thead>
<tr>
<th>Language</th>
<th>Linear system solution</th>
<th>Parallel</th>
<th>Code available</th>
<th>License</th>
</tr>
</thead>
<tbody>
<tr>
<td>BzzMath6</td>
<td>C++</td>
<td>Direct</td>
<td>No</td>
<td>No</td>
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<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td>DVODE</td>
<td>FORTRAN</td>
<td>Direct</td>
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<td>Yes</td>
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<tr>
<td>CVODE</td>
<td>C</td>
<td>Direct/Iterative</td>
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<td>Yes</td>
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<tr>
<td>DLSODE</td>
<td>FORTRAN</td>
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<tr>
<td>MEBDF</td>
<td>FORTRAN</td>
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<td></td>
<td></td>
<td>Free</td>
</tr>
</tbody>
</table>
Details about the C++ implementation

For each solver a common C++ interface was created

**Creation of ODE System objects**

```cpp
ODESystem_BatchReactor_Homogeneous_DVODE *odeSystemObject_Homogeneous;
odeSystemObject_Homogeneous =
    ODESyste_m_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);
ode_Homogeneous.SetAbsoluteTolerance(aTol);
ode_Homogeneous.SetRelativeTolerance(rTol);
ode_Homogeneous.SetInitialValues(t0,Y0);
ode_Homogeneous.Solve(tf);
ode_Homogeneous.Solution(yF);
```
Solution procedure

Main features:

✓ Solution of the Navier-Stokes equations (laminar and turbulent regime)
Solution procedure

Main features:

- Solution of the Navier-Stokes equations (laminar and turbulent regime)
- No limit to the number of species and reactions
Solution procedure

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- Solution of the Navier-Stokes equations (laminar and turbulent regime)
- No limit to the number of species and reactions
- Isothermal and adiabatic conditions
Solution procedure

Navier-Stokes Eqs. (PISO predictor)

Reactor network (Strang predictor)

Properties evaluation

Transport Eqs. (Strang corrector)

Pressure Eqn. Velocity correction (PISO corrector)

$t_{i+1} = t_i + \Delta t$

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())
{
    #include "readTimeControls.H"
    #include "readPISOControls.H"
    #include "compressibleCourantNo.H"
    #include "setDeltaT.H"

    runTime++;
    Info<< "Time = " << runTime.timeName() << nl << endl;

    #include "rhoEqn.H"  continuity

    for (label occr=1; occr <= nOuterCorr; occr++)
    {
        #include "UEqn.H"  momentum
        #include "chemistry.H"
        #include "properties.H"
        #include "YEqn.H"
        #include "TEqn.H"

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

    #include "write.H"  Post-processing
}

...
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
    }
}

...
solverOptions file

```
gasProperties "H2onRh_UBI_MatteoTDC_2008/idealgas.bin";
gasKinetics "H2onRh_UBI_MatteoTDC_2008/reactions.bin";
surfaceProperties "H2onRh_UBI_MatteoTDC_2008/surface.bin";

homogeneousReactions on;  
energyEquation off;  
viscosityMixingLaw Herning;

absoluteTolerance 1.e-12;  
RelativeTolerance 1.e-7;  
AlfaCatalyst 1.5668;
```

Thermodynamics/Transport properties and kinetic schemes

Homogeneous reactions on/off

Gas-phase energy equation on/off

Evaluation of dynamic viscosity

Absolute and relative tolerances (ODE solver)

Specific, catalytic surface (dimensionless)
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✓ Conclusions and future works
Laminar, coflow flames (I)

PolimiC1C16HT kinetic scheme
- 168 species
- 5400 reactions
- Freely available in CHEMKIN format: http://creckmodeling.chem.polimi.it

2D axisymmetric (55x200 mm)
- Computational grid: ~10,000 cells
- Pressure/Velocit coupling: PISO
- Discretization: first order upwind


Measurements along the axis
Laminar, coflow flames (II)

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  ✓ Numerical methodology

✓ 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)

✓ Extensions
  ✓ KMC (Kinetic Monte Carlo)
  ✓ Multi-region solver

✓ Conclusions and future works
The numerical tests have been performed by investigating the combustion of a fuel-rich H\textsubscript{2} over Rh catalyst in an annular reactor (*)

### Operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner radius</td>
<td>0.235 cm</td>
</tr>
<tr>
<td>Outer radius</td>
<td>0.450 cm</td>
</tr>
<tr>
<td>Reactor length</td>
<td>1.5 cm</td>
</tr>
<tr>
<td>H\textsubscript{2} mole fraction</td>
<td>0.04 (-)</td>
</tr>
<tr>
<td>O\textsubscript{2} mole fraction</td>
<td>0.01 (-)</td>
</tr>
<tr>
<td>N\textsubscript{2} mole fraction</td>
<td>0.95 (-)</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>

(*) M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos, 2D detailed modeling of fuel-rich H\textsubscript{2} combustion over Rh/Al\textsubscript{2}O\textsubscript{3} catalyst, Chemical Engineering Science (2008)
Numerical test

✓ Cylindrical symmetry
✓ 2D domain
✓ Low computational effort

Meshes
2D Axisymmetric Mesh from 2,000 to 10,000 cells

- Centered (2\textsuperscript{nd} order) spatial discretization
- Implicit Euler time integration
- Max Courant number 0.1
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM

Kinetic schemes

Heterogeneous kinetics

- **5 Species**: Rh(s), H2O(s), H(s), OH(s), O(s)
- **18 Reactions**

1. \( \text{H}_2 + 2\text{Rh (s)} \rightarrow \text{2H (s)} \)
2. \( 2\text{H (s)} \rightarrow \text{H}_2 + 2\text{Rh (s)} \)
3. \( \text{O}_2 + 2\text{Rh (s)} \rightarrow \text{2O (s)} \)
4. \( \text{2O (s)} \rightarrow \text{O}_2 + 2\text{Rh (s)} \)
5. \( \text{OH (s)} + \text{Rh (s)} \rightarrow \text{H (s)} + \text{O (s)} \)
6. \( \text{H (s)} + \text{O (s)} \rightarrow \text{OH (s)} + \text{Rh (s)} \)
7. \( \text{H}_2\text{O (s)} + \text{Rh (s)} \rightarrow \text{H (s)} + \text{OH (s)} \)
8. \( \text{H (s)} + \text{OH (s)} \rightarrow \text{H}_2\text{O (s)} + \text{Rh (s)} \)
9. \( \text{H}_2\text{O (s)} + \text{O (s)} \rightarrow \text{2OH (s)} \)
10. \( \text{2OH (s)} \rightarrow \text{H}_2\text{O (s)} + \text{O (s)} \)
11. \( \text{OH + Rh (s)} \rightarrow \text{OH (s)} \)
12. \( \text{OH (s)} \rightarrow \text{OH + Rh (s)} \)
13. \( \text{H}_2\text{O + Rh (s)} \rightarrow \text{H}_2\text{O (s)} \)
14. \( \text{H}_2\text{O (s)} \rightarrow \text{H}_2 \text{O + Rh (s)} \)
15. \( \text{H + Rh (s)} \rightarrow \text{H (s)} + \text{Rh (s)} \)
16. \( \text{H (s)} \rightarrow \text{H + Rh (s)} \)
17. \( \text{O + Rh (s)} \rightarrow \text{O (s)} \)
18. \( \text{O (s)} \rightarrow \text{O + Rh (s)} \)

**Microkinetic mechanism**
Maestri et al., 2008
Mhadeshwar and Vlachos, 2005

Homogeneous kinetics

- **10 Species**
- **21 Reactions**

1. \( \text{H + O}_2 \rightarrow \text{OH + O} \)
2. \( \text{O + H}_2 \rightarrow \text{OH + H} \)
3. \( \text{H + O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \)
4. \( \text{H + 2O}_2 \rightarrow \text{HO}_2 + \text{O}_2 \)
5. \( \text{OH + HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \)
6. \( \text{H + HO}_2 \rightarrow \text{2OH} \)
7. \( \text{O + HO}_2 \rightarrow \text{O}_2 + \text{OH} \)
8. \( \text{2OH} \rightarrow \text{O}_2 + \text{H}_2\text{O} \)
9. \( \text{H}_2 + \text{M} \rightarrow \text{2H + M} \)
10. \( \text{O}_2 + \text{M} \rightarrow \text{2O + M} \)
11. \( \text{H + OH + M} \rightarrow \text{H}_2\text{O} + \text{M} \)
12. \( \text{H + HO}_2 \rightarrow \text{H}_2\text{O} + \text{O} \)
13. \( \text{2HO}_2 \rightarrow \text{2H}_2\text{O} + \text{O} \)
14. \( \text{2OH + M} \rightarrow \text{H}_2\text{O}_2 + \text{M} \)
15. \( \text{O + OH + M} \rightarrow \text{HO}_2 + \text{M} \)
16. \( \text{H + H}_2\text{O} \rightarrow \text{H}_2 \text{ + OH} \)
17. \( \text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{OH} \)
18. \( \text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2 \text{ + HO}_2 \)
19. \( \text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH} \)
20. \( \text{OH + HO}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2 \)
21. \( \text{O + HO}_2 \rightarrow \text{OH + HO}_2 \)

**PolimiH2 mechanism** (Frassoldati et al., 2006)
Main results

\[ \alpha_{\text{cat}} = 0 \]

\[ \alpha_{\text{cat}} = \frac{A_{\text{cat}}}{A} = 1.50 \]

H2 mole fraction

O2 mole fraction

H2O mole fraction

473K [0-0.04]

773K [0-0.10]

973K [0-0.05]
Comparison with experimental measurements

- **Flow rate of:**
  - 0.274 Nl/min
  - 0.548 Nl/min
  - 1.096 Nl/min

- **Inlet:**
  - $H_2 = 0.04$
  - $O_2 = 0.01$
  - $N_2 = 0.95$

- **Reactor:**
  - $R_{in} = 0.235$ cm
  - $R_{out} = 0.450$ cm
  - $L = 1.5$ cm

---

Validation

Comparison with experimental measurements

- Flow rate of:
  - 0.274 Nl/min
  - 0.548 Nl/min
  - 1.096 Nl/min

- Inlet:
  - H₂ = 0.04
  - O₂ = 0.01
  - N₂ = 0.95

- Reactor:
  - Rᵢₙ = 0.235 cm
  - Rₒᵤₜ = 0.450 cm
  - L = 1.5 cm

Validation

Comparison with experimental measurements

- Flow rate of:
  - 0.274 Nl/min
  - 0.548 Nl/min
  - 1.096 Nl/min

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  - $\text{N}_2 = 0.95$

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  - $R_{\text{in}} = 0.235 \text{ cm}$
  - $R_{\text{out}} = 0.450 \text{ cm}$
  - $L = 1.5 \text{ cm}$

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Extensions
- KMC (Kinetic Monte Carlo)
- Multi-region solver

Conclusions and future works
Catalytic FOAM: Heterogeneous catalysis within OpenFOAM

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 \times 10^{-9} \text{ mol/cm}^{2}</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

Inlet

Heterogeneous kinetics
• 11 Surface Species
• 36 Surface Reactions

Homogeneous kinetics
• 25 Species
• 300 Reactions

Centered (2nd order) spatial discretization
Implicit Euler time integration
Max Courant number 0.05

www.detchem.com/mechanisms


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

CPO of methane over platinum gauze (III)

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

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 CO2 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)

Comparison with experimental data

- 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
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Extensions
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Conclusions and future works
CPO of iso-octane over rhodium catalyst (I)

### Operating conditions

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<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>$iC_8H_{18}$ mole fraction</td>
<td>0.143 (-)</td>
</tr>
<tr>
<td>$O_2$ mole fraction</td>
<td>0.057 (-)</td>
</tr>
<tr>
<td>$N_2$ 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/cm²</td>
</tr>
<tr>
<td>Catalytic surf.</td>
<td>5 cm⁻¹</td>
</tr>
</tbody>
</table>

### Heterogeneous kinetics
- 17 Surface Species
- 56 Surface Reactions

### Homogeneous kinetics
- 168 Species
- 5,400 Reactions


Sketch of a single channel (circular section)

reactants → Rhodium catalyst → products

www.detchem.com/mechanisms

http://creckmodeling.chem.polimi.it/
CPO of iso-octane over rhodium catalyst (II)

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

The catalytic surface reaction is very fast in the entrance (first 1 mm)

Strong back-diffusion of H2: importance of diffusion coefficients

Strong radial gradient are present in the first mm of the reactor

The concentration of iC8H18 and O2 on the surface is practically zero, which means that catalytic reactions are mass-transfer limited
CPO of iso-octane over rhodium catalyst (III)

CatalyticFOAM
2D mesh (5,000 cells)

DETCHEM CHANNEL
www.detchem.com

M. Hartmann, et al., Combustion and Flame
157 (2010) 1771-1782
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM

Outline

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  ✓ Multi-region solver

✓ Conclusions and future works
**Tubular reactor with Raschig rings (I)**

**Operating conditions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal diameter</td>
<td>1 cm</td>
</tr>
<tr>
<td>Total length</td>
<td>15 cm</td>
</tr>
<tr>
<td>CH$_4$ mole fraction</td>
<td>0.100 (-)</td>
</tr>
<tr>
<td>O$_2$ mole fraction</td>
<td>0.056 (-)</td>
</tr>
<tr>
<td>N$_2$ mole fraction</td>
<td>0.844 (-)</td>
</tr>
<tr>
<td>Temperature</td>
<td>873.15 K</td>
</tr>
<tr>
<td>Residence time</td>
<td>0.15 s</td>
</tr>
</tbody>
</table>

**Velocity Field**

**3D Unstructured Mesh: ~250,000 cells**

- Homogeneous reactors: 240,000
- Heterogeneous reactors: 10,000

**No homogeneous reactions!**

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)

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
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A “first-principles” approach

**MICROSCALE**
Making and breaking of chemical bond

**MESOSCALE**
Interplay among the chemical events

**MACROSCALE**
Mass and energy transport phenomena

Interplay among scales

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

**MICROSSCALE**
- Making and breaking of chemical bond

**MESOSCALE**
- Interplay among the chemical events

**MACROSSCALE**
- Mass and energy transport phenomena

Interplay among scales

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

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

“Effective” bridging between the scales

- 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.

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: Ru₂O

Computational details
Mesh: unstructured, ~90,000 cells
Discretization: 2nd 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

66%
50%
34%
18%

time [s]
Outline

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  ✓ Multi-region solver

✓ Conclusions and future works
**Motivation**

In the original version of catalyticFOAM the catalyst morphology is not detailed.

The presence of the catalyst was accounted for by as 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)
How to couple the regions?

Coupling at the boundary interface:
- Conjugate heat transfer
- Conjugate mass transfer

Partitioned Approach
- Governing equations are solved in each zone with the appropriate BCs.
- Mixed BCs for a PDE indicates that different BCs are used on different parts of the boundary of the domain of the equation.
- The resulting conditions have to be used for each region, according to the updated values in the neighboring one.
The partitioned approach

Solid Interface Cells
\[
\begin{align*}
\frac{d}{dt} (\rho_{\text{mix}} Y_i) &= \nabla (\rho_{\text{mix}} D_{\text{mix,i}} \nabla (Y_i)) \\
\frac{d}{dt} (\rho_{\text{mat}} c_p T) &= \nabla (k \nabla (T))
\end{align*}
\]
with the mixed BCs on the interface:
\[
\begin{align*}
T_{\text{LSOL}} &= \frac{k_{\text{SOL}} T_{\text{SOL}} + k_{\text{FLU}} T_{\text{FLU}}}{\Delta_{\text{SOL}} + \Delta_{\text{FLU}}} \\
C_{\text{LSOL}} &= \frac{D_{\text{SOL}} C_{\text{SOL}} + D_{\text{FLU}} C_{\text{FLU}}}{\Delta_{\text{SOL}} + \Delta_{\text{FLU}}}
\end{align*}
\]

Fluid Interface Cells
\[
\begin{align*}
\frac{d}{dt} (\rho_{\text{mix}} Y_i) &= \nabla (\rho_{\text{mix}} D_{\text{mix,i}} \nabla (Y_i)) - \nabla (\Phi Y_i) \\
\frac{d}{dt} (\rho_{\text{mat}} c_p T) &= \nabla (k \nabla (T))
\end{align*}
\]
with the mixed BCs on the interface:
\[
\begin{align*}
T_{\text{LFLU}} &= \frac{k_{\text{FLU}} T_{\text{FLU}} + k_{\text{SOL}} T_{\text{SOL}}}{\Delta_{\text{FLU}} + \Delta_{\text{SOL}}} \\
C_{\text{LFLU}} &= \frac{D_{\text{FLU}} C_{\text{FLU}} + D_{\text{SOL}} C_{\text{SOL}}}{\Delta_{\text{FLU}} + \Delta_{\text{SOL}}}
\end{align*}
\]

Convergence Criteria
\(\rightarrow\) Residuals must be lower than user given absolute and relative tolerances:
\[
\begin{align*}
|T^{(k)} - T^{(k-1)}| &\leq \text{absTol}_T \\
|T^{(k)} - T^{(k-1)}| + |T^{(k-1)}| &\leq \text{relTol}_T \\
|Y_i^{(k)} - Y_i^{(k-1)}| &\leq \text{absTol}_Y \\
|Y_i^{(k)} - Y_i^{(k-1)}| + |Y_i^{(k-1)}| &\leq \text{relTol}_Y
\end{align*}
\]

PIMPLE Method
\(\rightarrow\) For each time step, given a maximum number of iterations, solve alternatively for every cell of the 2 coupled regions
\(\rightarrow\) Check for convergence: when it is reached, proceed to the next time step
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM

Multi-domain code

Solve Solid

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

Mass Transfer Eq.

\[
\frac{d(\rho_{\text{mat}} c_{p,\text{mat}} T)}{dt} = \nabla (k_{\text{mat}} \nabla (T))
\]

Heat Transfer Eq.

\[
m_{\text{tot}} \frac{dY_i}{dt} = \frac{R_{\text{hom},i}}{\rho_{\text{mix}}} + \left( R_{\text{gas},i} MW_{i} - dm_{\text{cat},i} \right) \xi \delta_{\text{mil}}
\]

Fluid Chemistry

\[
dT = \frac{Q_{\text{hom}} + Q_{\text{het}}}{\rho_{\text{mix}} c_{p,\text{mix}}}
\]

\[
d\theta_i = \frac{R_{\text{surf},i}}{T_{\text{mil}}}
\]

Update Solid Properties

Solve Fluid

\[
\frac{d\rho_{\text{mix}}}{dt} + \nabla \Phi = 0
\]

Rho Eq.

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

Mass Transfer Eq.

\[
\frac{d(\rho_{\text{mat}} c_{p,\text{mat}} T)}{dt} = \nabla \left( k_{\text{mat}} \nabla (T) \right) - c_p \nabla (\Phi T)
\]

Heat Transfer Eq.

\[
\frac{dY_i}{dt} = \frac{R_{\text{hom},i}}{\rho_{\text{mix}}}
\]

Solid Chemistry

Update Fluid Properties

\[
\frac{d(\tilde{U} \rho_{\text{mix}})}{dt} + \nabla (\tilde{U} \Phi) - \nabla (\mu \nabla \tilde{U}) - \nabla (\mu \text{dev}_2(\nabla \tilde{U})^T) = \rho \ddot{g}
\]

U Eq.

\[
\nabla \left( \frac{\nabla P}{\alpha_p} \right) = \nabla v^*
\]

Pressure Eq.
The numerical tests have been performed by investigating the combustion of a fuel-rich H₂ over Rh catalyst in an annular reactor (*). 

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<td>O₂ mole fraction</td>
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</tr>
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Numerical simulations take into account the solid phase (catalytic layer) in order to model the diffusive limitations and correctly capture the experimental measurements.

The mesh is thus highly refined near the catalytic wall in the radial direction.
Example: annular reactor (II)

Numerical simulations take into account the solid phase (catalytic layer) in order to model the diffusive limitations and correctly capture the experimental measurements.

The mesh is thus highly refined near the catalytic wall in the radial direction.
Example: annular reactor (IV)

O₂ mass fraction in radial direction in the solid phase

strong influence of diffusive intra-phase limitations inside the 50 μm thick catalytic solid phase in the middle range of temperatures

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM
What we have done...

- Numerical procedure adopted
- Development of the catalyticFOAM solver for the OpenFOAM® framework
- Numerical tests
- Validation tests
- Show-case

→ Splitting scheme
→ Implementation of the solution procedure
→ Optimization of spatial and temporal discretization
→ Reliable description of the system
→ Wide applicability
What we are doing/planning to do...

✓ Description of the solid-phase:
  ✓ Energy transport within the solid and with the environment
  ✓ Mass transport within the solid (diffusion and reaction problem, i.e., detailed assessment of internal mass limitations)

✓ Validation and extension to turbulent flow

✓ Kinetic Monte Carlo

✓ Parallelization of the calculation

✓ Storage/retrieval methods (e.g. ISAT) for fast numerical integration of ODE systems
The catalyticFOAM software is fully compatible with OpenFOAM version 2.1.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 will be released under the L-GPL license through an independent website: www.catalyticfoam.polimi.it
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM

Acknowledgements

Students involved in the project:

CatalyticFOAM@polimi.it
Conclusions

✓ C++ library for homogeneous and heterogeneous chemistry (complex kinetics, thermodynamics, transport properties)

✓ Development of the catalyticFOAM solver for the OpenFOAM® framework

✓ Validation tests (lab-scale systems)
  ✓ Annular reactor (simple chemistry)
  ✓ CPO of CH$_4$ on platinum gauze (complex 3D geometry)
  ✓ CPO of iso-octane (complex chemistry)
  ✓ Tubular reactor with Raschig rings
**Perspectives**

**Validation**
- ✔ Realistic reactors

**Chemistry and Physics**
- ✔ Extension to turbulent flow

**Numerics**
- ✔ Storage/retrieval methods (e.g. ISAT) for fast numerical integration of ODE systems
- ✔ Steady state problems: more efficient strategies
- ✔ Improvement of parallel performances
Acknowledgements

Matteo Calonaci

Federica Furnari

Sandro Goisis

Alessandra Osio

Thank you for your attention!

www.catalyticfoam.polimi.it
catalyticfoam@polimi.it
Show case

Any geometry with arbitrary complexity can be investigated with catalyticFOAM.

<table>
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<th>Operating conditions</th>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
<td>Eccentricity</td>
<td>50 %</td>
</tr>
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(*) 2D detailed modeling of fuel-rich $\text{H}_2$ combustion over Rh/Al$_2$O$_3$ catalyst. M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos – CES 2008
Show case

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<tr>
<td>Slope (y-axis)</td>
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(*) 2D detailed modeling of fuel-rich \(H_2\) combustion over \(Rh/Al_2O_3\) catalyst.
Show case

The possible eccentricity of the annulus in experimental apparatus has been investigated with catalyticFOAM.

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Show case

Identification of the calculation domain

✓ Eccentricity of 50%
✓ Planar symmetry

Show case

Identification of the calculation domain

3D mesh

Effect of eccentricity on the $O_2$ conversion at different temperatures

(*) 2D detailed modeling of fuel-rich $H_2$ combustion over $Rh/Al_2O_3$ catalyst.
Show case

Any geometry with arbitrary complexity can be investigated with catalyticFOAM.

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Show case

The case of cylinders with incident axis has been studied with catalyticFOAM

3D mesh
Show case

O₂ conversion at different temperatures for cylinders with incident axis

Square channel with catalytic spheres

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel Side</td>
<td>0.30 cm</td>
</tr>
<tr>
<td>Channel length</td>
<td>1.50 cm</td>
</tr>
<tr>
<td>Sphere diameter</td>
<td>1.00 cm</td>
</tr>
<tr>
<td>CH\textsubscript{4} mole fraction</td>
<td>0.10</td>
</tr>
<tr>
<td>O\textsubscript{2} mole fraction</td>
<td>0.056</td>
</tr>
<tr>
<td>N\textsubscript{2} mole fraction</td>
<td>0.844</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Temperature</td>
<td>873 K</td>
</tr>
<tr>
<td>Inlet velocity</td>
<td>2 m/s</td>
</tr>
<tr>
<td>Residence Time</td>
<td>7.5 ms</td>
</tr>
<tr>
<td>Reynolds Number</td>
<td>130</td>
</tr>
<tr>
<td>Rh site density</td>
<td>2.49 \times 10^{-9} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>Catalytic surface</td>
<td>1.566 (\cdot)</td>
</tr>
</tbody>
</table>
Heterogeneous kinetics

- 13 Species
- 82 Reactions

*Maestri et al., 2009*
*Mhadeshwar and Vlachos, 2005*

Homogeneous kinetics

- 23 Species
- 84 Reactions

*DRM19 Kinetic Mechanism*

Meshes

- 2X: 696 cells (58 x 12)
- 3X: 2784 cells (116 x 24)
- 4X: 11136 cells (232 x 48)

Numerical details

- Centered (2\textsuperscript{nd} order) spatial discretization
- Implicit Euler time integration
- Max Courant number 0.1
Main results (steady-state)

Mole fractions

<table>
<thead>
<tr>
<th>Species</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>(0.08-0.10)</td>
</tr>
<tr>
<td>O2</td>
<td>(0.01-0.56)</td>
</tr>
<tr>
<td>CO2</td>
<td>(0-0.018)</td>
</tr>
<tr>
<td>CO</td>
<td>(0-0.006)</td>
</tr>
<tr>
<td>H2O</td>
<td>(0-0.027)</td>
</tr>
<tr>
<td>H2</td>
<td>(0-0.0008)</td>
</tr>
</tbody>
</table>

Adsorbed species (mass fractions)

Effect of specific catalytic surface

- $\alpha = 0.75$
- $\alpha = 3.00$
The calculation mesh is divided in structured and unstructured zones

### Operating conditions

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Channle thickness</td>
<td>0.8 cm</td>
</tr>
<tr>
<td>Channel length</td>
<td>6 cm</td>
</tr>
<tr>
<td>CH₄ mole fraction</td>
<td>0.100 (-)</td>
</tr>
<tr>
<td>O₂ mole fraction</td>
<td>0.056 (-)</td>
</tr>
<tr>
<td>N₂ mole fraction</td>
<td>0.844 (-)</td>
</tr>
<tr>
<td>Temperature</td>
<td>873.15 K</td>
</tr>
<tr>
<td>MESH</td>
<td>27,000 cells</td>
</tr>
</tbody>
</table>
Channel with catalytic, toroidal elements

3D Mesh: ~450,000 cells
- Homogeneous reactors: 445,000
- Heterogeneous reactors: 5,000

No homogeneous reactions!
CPU time per heterogeneous reactor: 0.75 ms

This time is weakly dependent on the specific features of the investigated case.
The numerical tests have been performed by investigating the combustion of a fuel-rich $\text{H}_2$ over Rh catalyst in an annular reactor (*).

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(* M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos, 2D detailed modeling of fuel-rich $\text{H}_2$ combustion over Rh/Al$_2$O$_3$ catalyst, Chemical Engineering Science (2008)
It is then possible to investigate also the underestimation of conversion values occurring at high temperatures: the “conversion enhancing mechanism” observed in the experimental data cannot be due homogeneous gas phase chemistry playing a role at high temperatures, as the fraction of H* which is predicted to desorb in the gas phase at 500°C is many order of magnitudes lower than the one identified as necessary to trigger gas-phase chemistry.
It is then possible to investigate also the underestimation of conversion values occurring at high temperatures: the “conversion enhancing mechanism” observed in the experimental data cannot be due homogeneous gas phase chemistry playing a role at high temperatures, as the fraction of H* which is predicted to desorb in the gas phase at 500°C is many order of magnitudes lower than the one identified as necessary to trigger gas-phase chemistry.
A possible explanation for this has been formulated by Maestri et al. (2008), in terms of **additional zones** of low catalytic activity outside the catalytic bed.

Two sections with low catalytic activity up-stream and down-stream the catalytic bed are added to the simulations. A catalyst layer of 2 mm is then added upward the main bed. Another one is added downstream, with a length of 7 mm. The **catalytic activity** of these beds is fixed equal to 1% of that of the main bed.
The additional low activity sections (working in chemical regime due to the low amount of catalyst), lead to an increase of the conversion. At low temperatures, on the other hand, the contribution is almost negligible.
Governing equations

Gas-phase

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad \text{continuity} \]

\[ \frac{\partial}{\partial t} (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla \rho + \nabla \cdot \left[ \mu (\nabla \mathbf{v} + \nabla \mathbf{v}^T) - \frac{2}{3} \mu (\nabla \mathbf{v}) \mathbf{I} \right] + \rho \mathbf{g} \quad \text{momentum} \]

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

\[ \rho \hat{C}_p \frac{\partial T}{\partial t} + \rho \hat{C}_p \mathbf{v} \nabla T = \nabla \cdot (\lambda \nabla T) - \rho \sum_{k=1}^{\text{NG}} \hat{C}_{p,k} \omega_k \mathbf{V}_k - \sum_{k=1}^{\text{NG}} \hat{H}_k^\text{hom} \dot{\Omega}_k^\text{hom} \quad \text{gas-phase energy} \]
Boundary conditions

Non-catalytic walls
\[
\nabla \omega_k \bigg|_{\text{inert}} = 0
\]
\[
T \bigg|_{\text{inert}} = f(t, T)
\]
\[
\nabla T \bigg|_{\text{inert}} = g(t, T)
\]

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

Adsorbed (surface) species

Detailed microkinetic models

- \( \text{COOH}^{\ast} + \ast \rightarrow \text{CO}^{\ast} + \text{OH}^{\ast} \)
- \( \text{CO}^{\ast} + \text{OH}^{\ast} \rightarrow \text{COOH}^{\ast} + \ast \)
- \( \text{COOH}^{\ast} + \ast \rightarrow \text{CO}_2^{\ast} + \text{H}^{\ast} \)
- \( \text{CO}_2^{\ast} + \text{H}^{\ast} \rightarrow \text{COOH}^{\ast} + \ast \)
- \( \text{CO}_2^{\ast} + \text{H}_2\text{O}^{\ast} \rightarrow \text{COOH}^{\ast} + \text{OH}^{\ast} \)
- \( \text{COOH}^{\ast} + \text{OH}^{\ast} \rightarrow \text{CO}_2^{\ast} + \text{H}_2\text{O}^{\ast} \)
- \( \text{CO}_2^{\ast} + \text{H}^{\ast} \rightarrow \text{HCOO}^{\ast} \)
- \( \text{HCOO}^{\ast} \rightarrow \text{CO}_2^{\ast} + \text{H}^{\ast} \)
- \( \text{CO}_2^{\ast} + \text{OH}^{\ast} + \ast \rightarrow \text{HCOO}^{\ast} + \text{O}^{\ast} \)
- \( \text{HCOO}^{\ast} + \text{OH}^{\ast} \rightarrow \text{CO}_2^{\ast} + \text{H}_2\text{O}^{\ast} \)
- \( \text{CH}^{\ast} + \text{H}^{\ast} \rightarrow \text{CH}_2^{\ast} + \ast \)
- \( \text{CH}^{\ast} + \ast \rightarrow \text{C}^{\ast} + \text{H}^{\ast} \)
- \( \text{C}^{\ast} + \text{H}^{\ast} \rightarrow \text{CH}^{\ast} + \ast \)
- \( \text{CH}_3^{\ast} + \text{O}^{\ast} \rightarrow \text{CH}_2^{\ast} + \text{OH}^{\ast} \)
- \( \text{CH}_2^{\ast} + \text{OH}^{\ast} \rightarrow \text{CH}_3^{\ast} + \text{O}^{\ast} \)
- \( \text{CH}^{\ast} + \text{OH}^{\ast} \rightarrow \text{CH}_2^{\ast} + \text{O}^{\ast} \)
- \( \text{CH}_2^{\ast} + \text{O}^{\ast} \rightarrow \text{CH}^{\ast} + \text{OH}^{\ast} \)

\[
r_j = A_j \cdot T^{\beta_j} \cdot \exp \left( -\frac{E_{\text{att}}(\theta_i)}{RT} \right) \prod_{i=1}^{\text{NC}} (c_i)^{V_{ij}}
\]

M. Maestri, Microkinetic analysis of complex chemical processes at surface, in “New strategy for chemical synthesis and catalysis”, Wiley-VCH (2012)
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM

CPU time

Homogeneous reactors

- PolimiC1C3HT 80 species 1412 reactions
- GRI30 53 species 325 reactions
- DRM19 23 species 84 reactions

Heterogeneous reactors

- PolimiC1C3HT 80 species 1412 reactions
- GRI30 53 species 325 reactions
- DRM19 23 species 84 reactions

Heterogeneous chemistry: 12 species 38 reactions

% total CPU Time spent for heterogeneous reactors

CPU time [%]

- 23 Species
- 53 Species
- 80 Species

Total CPU Time [%]

- 80 Species
- 53 Species
- 23 Species

Heterogeneous chemistry

Homogeneous chemistry

Transport