# 1D AND 2D POROUS MEDIA FIXED BED REACTOR SIMULATIONS WITH DUO

**18th OpenFOAM Workshop (Genoa, Italy, 2023)**

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**Akash Shirsath (Karlsruhe Institute of Technology)**

# Tonkomo, LLC

- **Owners:** <u>Lee Tonkovich</u>, PhD & <u>Eric Daymo</u>, PE
  - Reaction engineering expertise with 30+ years of experience (>150 patents)
  - Co-founders of Velocys (microchannel reactors)
  - Experienced with algal bioreactors (Heliae)
  - Now, owners of a small business dedicated to developing innovative solutions for **climate** – energy – food – water

- **Motivation**: cost-effective and reliable tools for reaction engineering
  - Commercial is CFD expensive for small businesses
  - OpenFOAM is missing required features for reaction engineers

- **Vision**: Affordable tools that liberate creativity, accelerate commercial product development, and enhance entrepreneurism

# Catalytic Fixed Bed Reactors

- Tubular fixed bed catalytic reactors are the "workhorse" of the chemical industry

- CFD is one tool used to analyze fixed-bed reactor performance

- OpenFOAM does not have extensive built-in tools for such packed bed reactor calculations
  - Surface reactions
  - Packed bed heat transfer
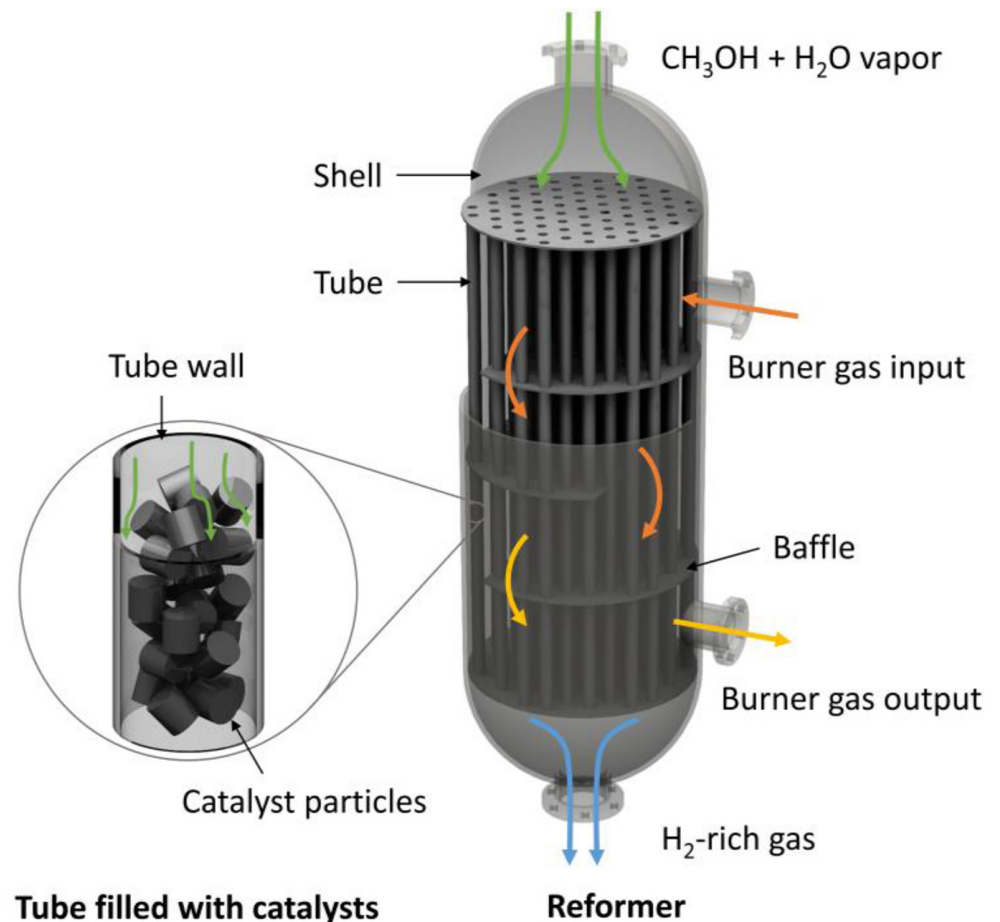


Zhu, J., Cui, X., Araya, S.S. Comparison between 1D and 2D numerical models of a multi-tubular packed-bed reactor for methanol steam reforming, International Journal of Hydrogen Energy 47 issue 54 (2022), 22704-22719

# DETCHEM and DUO
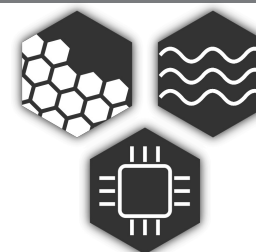
www.detchem.com

- DETCHEM stands for DETailed CHEMistry
  - Software package for reacting flow simulation
  - www.detchem.com

  *Reference: Deutschmann et al. 2022*

- DUO: DETCHEM und OpenFOAM coupling
  - Surface reactions
  - Kinetic theory transport properties
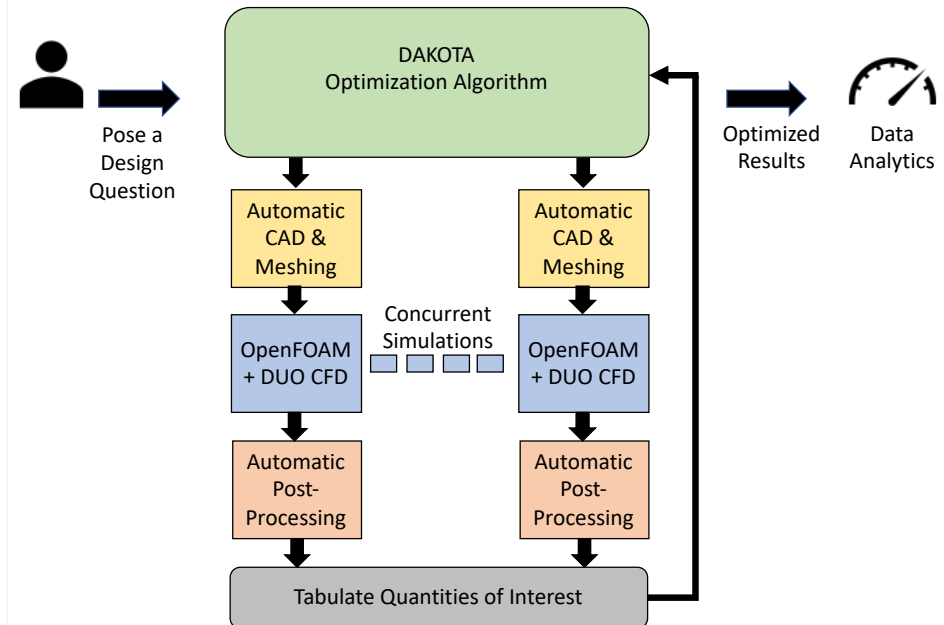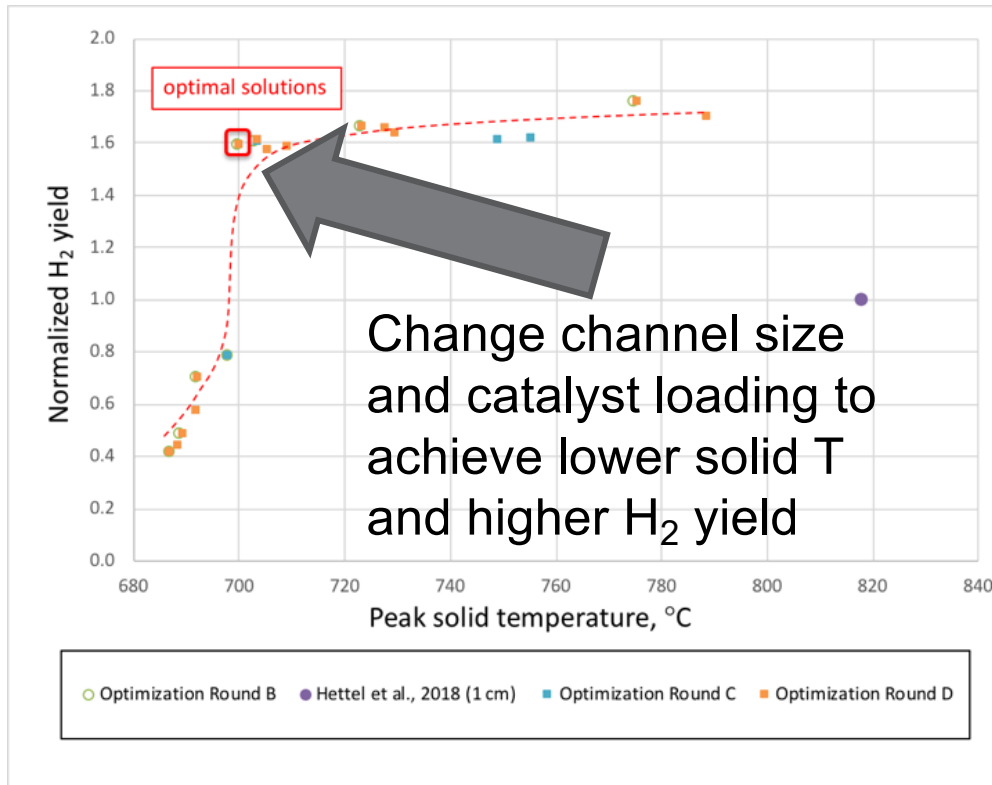  - Mixture/multicomponent diffusion

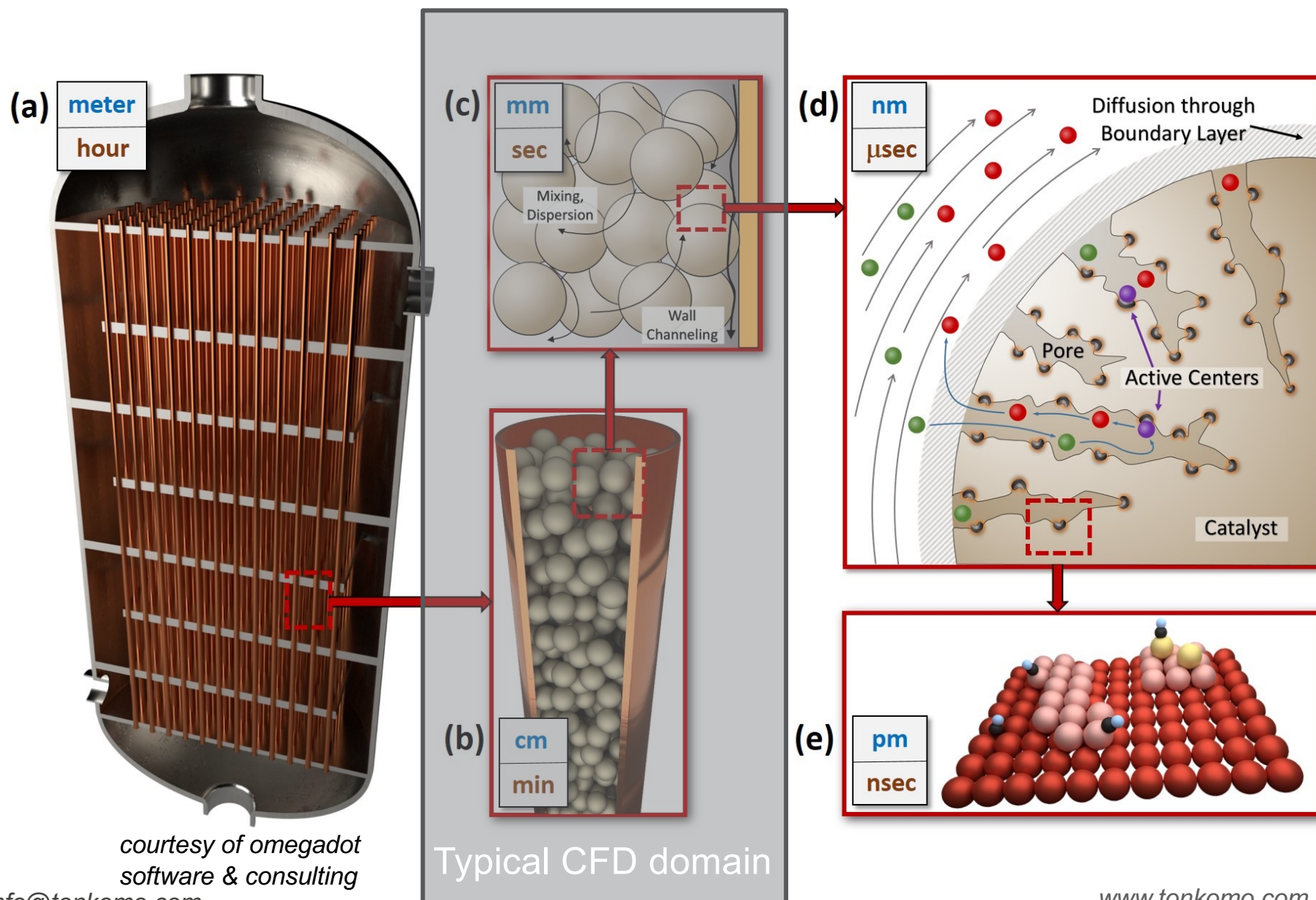| Product | Description |
|---|---|
| Manual | Manual for DETCHEM |
| EQUIL | Equilibrium and adiabatic reactor temperature calculation. |
| GASPROBE | Tool for evaluating the transport and kinetic properties of the chemical species participating in a gas-phase reaction mechanism. |
| SURFPROBE | Tool for evaluating the transient and steady state surface coverages of various chemical species participating in a surface reaction mechanism. |
| BATCH | Reactor model for simulating the behavior of an ideal batch reactor for gas-phase as well as for surface reactions. |
| MPTR | Reactor model for simulating the behaviour of a tank reactor with gas-phase and multiple condensed phases. |
| CSTR | Reactor model for simulating behavior of an continuous stirred tank reactor for gas-phase as well as surface reactions. |
| PLUG | Reactor model for simulating the behavior of an ideal plug flow reactor for gas-phase as well as surface reactions. |
| STAG | Transient one-dimensional model for the simulation of stagnation flow reactors with models for catalytic surface reactions, external and internal diffusion, and gas-phase reactions. |
| PBR | Simulates a packed-bed reactor including a full-featured internal pellet resistance model (e.g., calculate effectiveness factor as a function of reactor length, or calculate internal pellet composition as a function of pore length). PBR is validated against experimental data and accurately captures radial heat transfer effects in a packed bed. |
| CHANNEL | Two dimensional model based on boundary layer equations for simulating the behavior of tubular reactor for gas-phase as well as for surface reactions. |
| MONOLITH | Transient code for simulating catalytic monoliths in 2D and 3D. |
| SOFC | Two-dimensional solid-oxide fuel cell model for the simulation of button cell, planar cells as well as tubular cells for co-flow configuration. |
| RESERVOIR | Transient single channel model. |
| DUO | Interface to OpenFOAM to calculate coupled fluid and solid regions with additional detailed gas-phase or surface chemistry (e.g. coated foams). For the modeling of monoliths the flow in the channels can be handled in 1D or 2D optionally. |

# Why do we need simpler CFD?
# One reason: Optimization and Discovery



Change channel size and catalyst loading to achieve lower solid T and higher $H_2$ yield

Plot: Normalized $H_2$ yield vs Peak solid temperature, °C. Legend: Optimization Round B, Hettel et al., 2018 (1 cm), Optimization Round C, Optimization Round D. "optimal solutions" marked.



Flowchart: Pose a Design Question → DAKOTA Optimization Algorithm → Automatic CAD & Meshing → OpenFOAM + DUO CFD → Automatic Post-Processing → Tabulate Quantities of Interest. Concurrent Simulations. Optimized Results → Data Analytics.

*Optimization: often 10,000's of cases run … need fast results*

Daymo, E., Tonkovich, A., Hettel, M., Guerrero, J. Accelerating Reactor Development with Accessible Simulation and Automated Optimization Tools, *Chemical Engineering and Processing - Process Intensification*, 2019
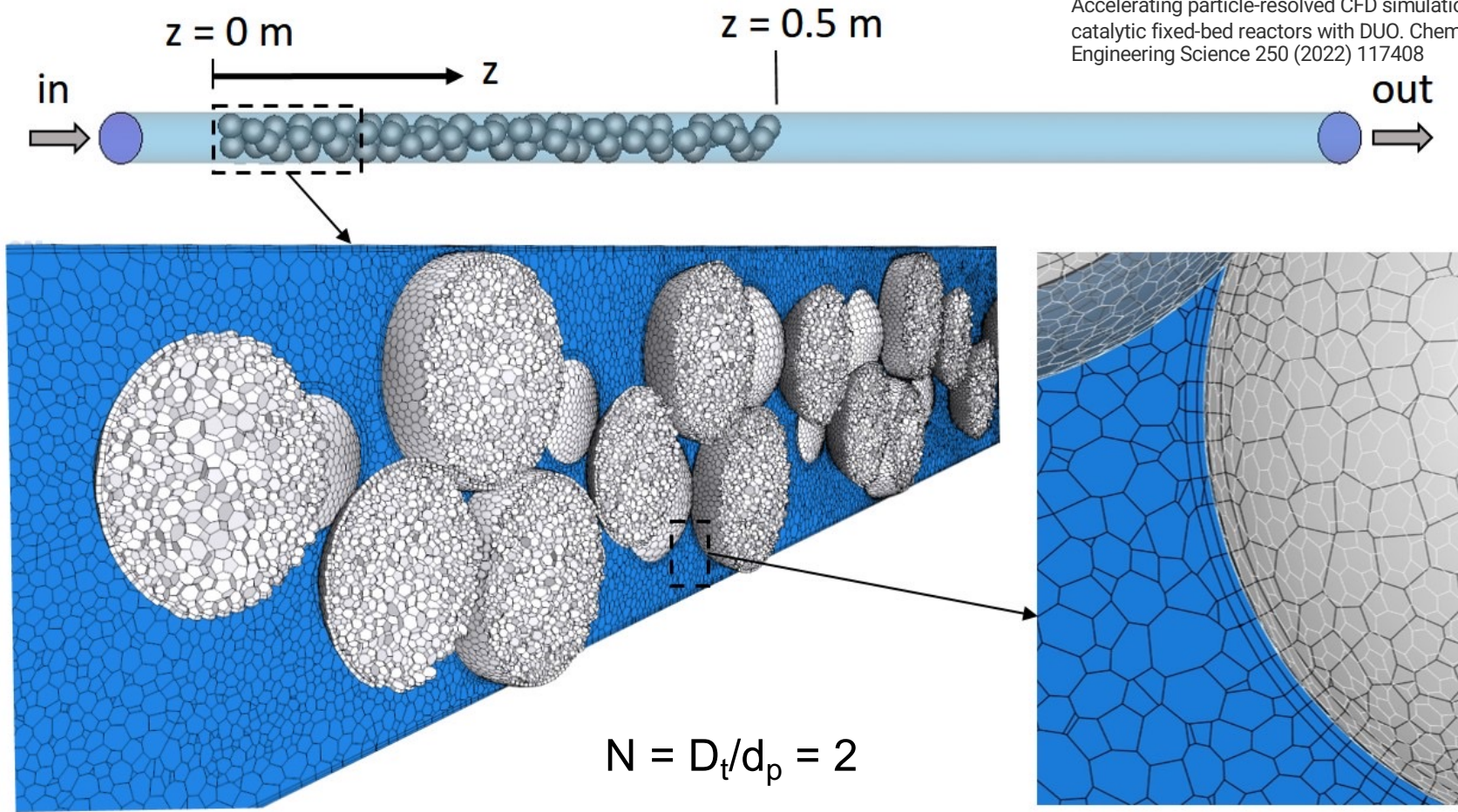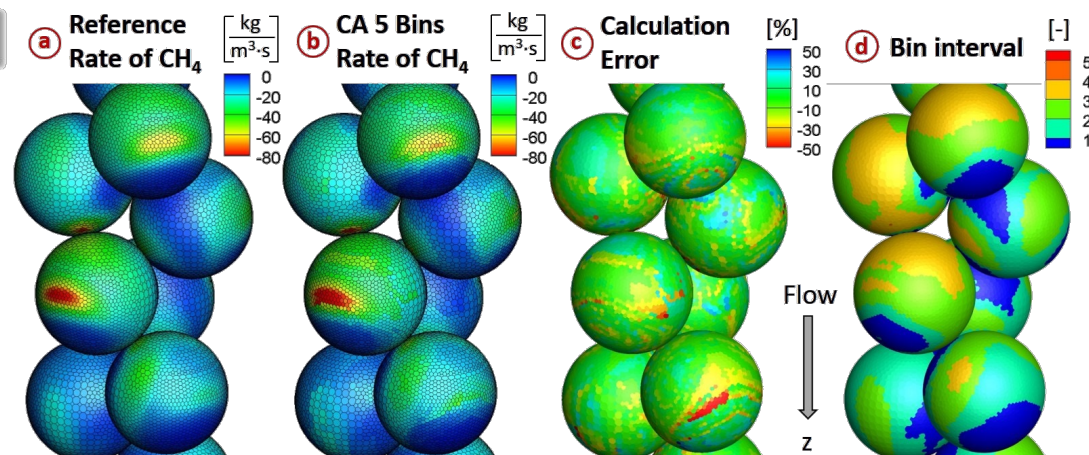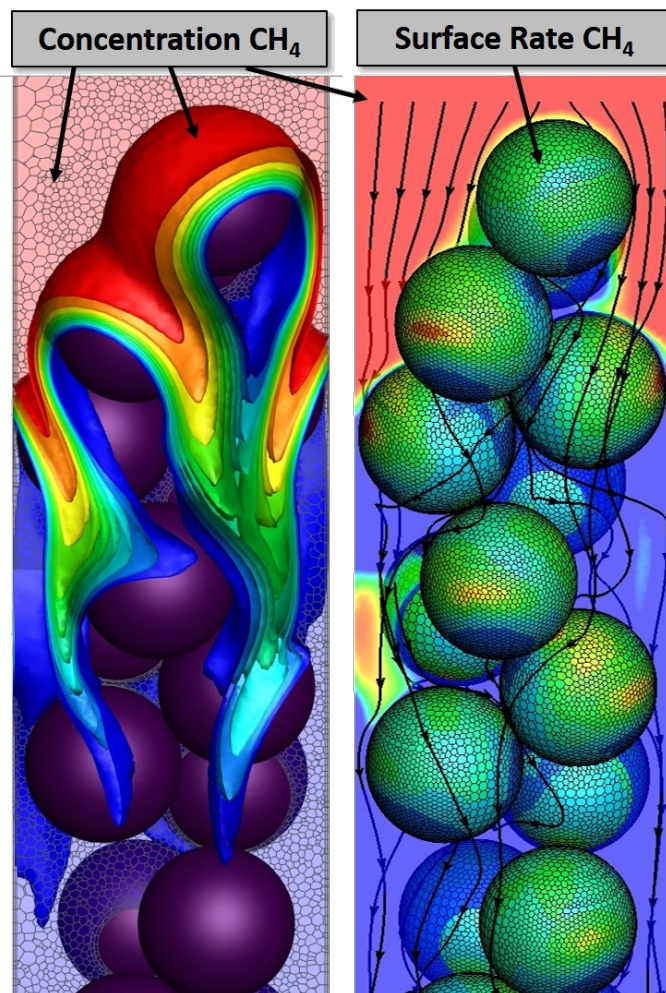
# Inside a fixed bed reactor



(a) meter / hour

(b) cm / min

(c) mm / sec — Mixing, Dispersion; Wall Channeling

(d) nm / μsec — Diffusion through Boundary Layer; Pore; Active Centers; Catalyst

(e) pm / nsec

Typical CFD domain

*courtesy of omegadot software & consulting*

*info@tonkomo.com*

# Particle Resolved CFD (PRCFD)

$$N = D_t/d_p = 2$$

1,559,544 fluid cells, 774,386 cells solid cells
217,810 reactive surface faces

# Particle resolved CFD



**Concentration CH$_4$**

**Surface Rate CH$_4$**

(a) **Reference Rate of CH$_4$** $\left[\frac{kg}{m^3 \cdot s}\right]$

(b) **CA 5 Bins Rate of CH$_4$** $\left[\frac{kg}{m^3 \cdot s}\right]$

(c) **Calculation Error** [%]

(d) **Bin interval** [-]

Flow z

*surface chemistry on individual particles simulated*

*cell agglomeration speeds-up chemistry*

yet even with speedup, calculation of 86 particles required 100's of core hours

Daymo, E., Hettel, M., Deutschmann, O., Wehinger, G. Accelerating particle-resolved CFD simulations of catalytic fixed-bed reactors with DUO. Chemical Engineering Science 250 (2022) 117408
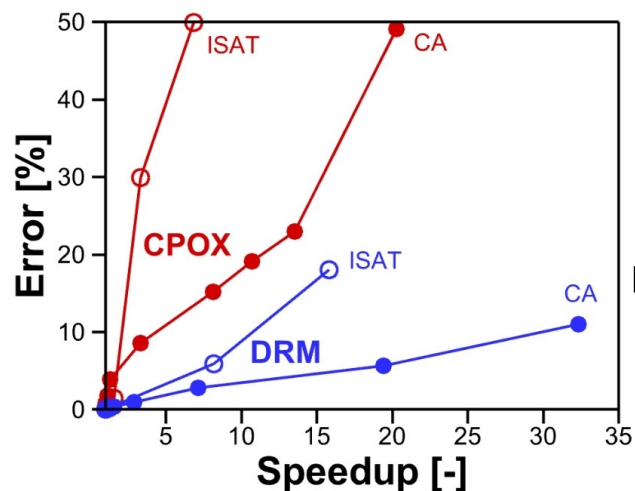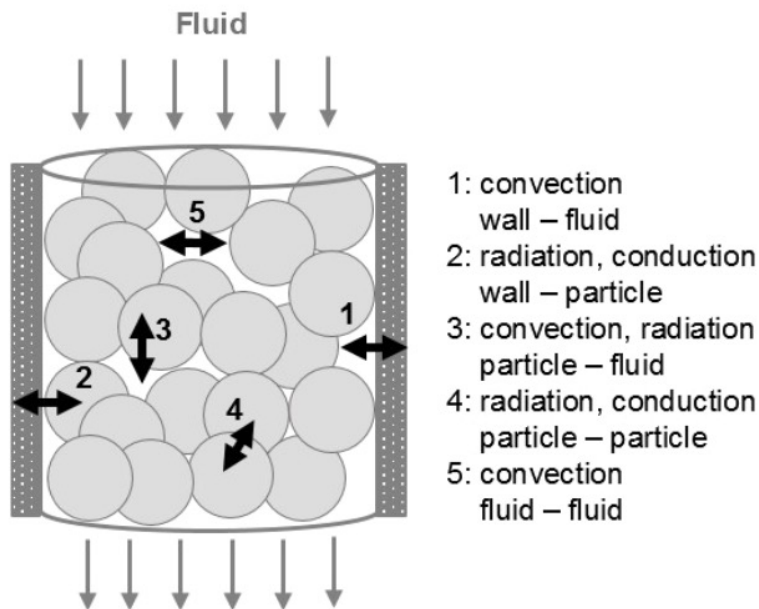
# Continuum Model Options:
# Fixed Bed Reactor Modeling

results presented here
use a single energy equation

- ## Single energy equation for solid and fluid

- ## Separate fluid and solid energy equations

  - Heat transfer resistance between solid and fluid phases
  - OpenFOAM has this capability, but with a fixed fluid-solid heat transfer coefficient
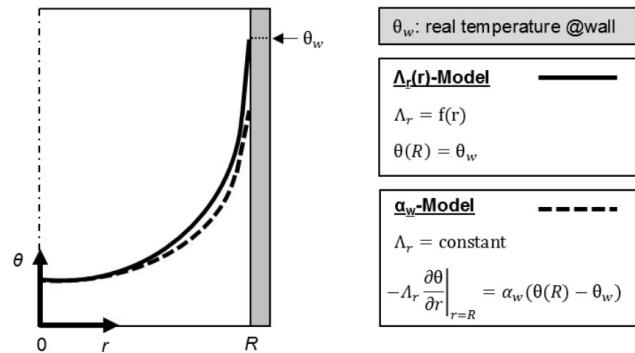
Fluid

1: convection
   wall – fluid
2: radiation, conduction
   wall – particle
3: convection, radiation
   particle – fluid
4: radiation, conduction
   particle – particle
5: convection
   fluid – fluid

**Figure 1.** Heat transport mechanisms in fixed-bed reactors through which gas flows (modified according to [4]).

Stegehake, C., Riese, J., Grünewald. Modeling and validating fixed-bed reactors: A state-of-the-art review. ChemBioEng Rev 2019, 6, No. 2, 28−44
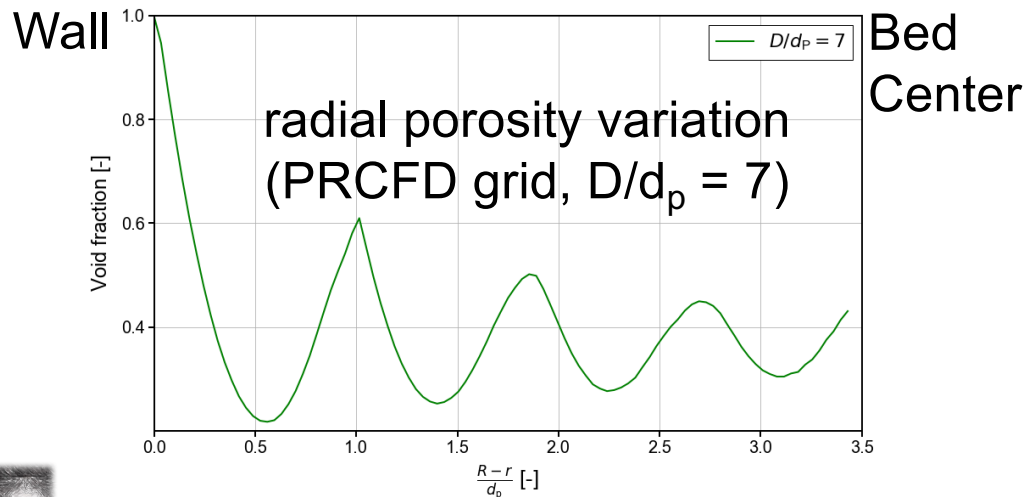
# Continuum Model Options:
## Fixed Bed Reactor Modeling

*results presented here use the $\alpha_w$ model*

$\theta_w$: real temperature @wall

**$\Lambda_r(r)$-Model** ———
$\Lambda_r = f(r)$
$\theta(R) = \theta_w$

**$\alpha_w$-Model** - - - -
$\Lambda_r = \text{constant}$
$-\Lambda_r \left.\frac{\partial \theta}{\partial r}\right|_{r=R} = \alpha_w(\theta(R) - \theta_w)$

Stegehake, C., Riese, J., Grünewald. M., Modeling and validating fixed-bed reactors: A state-of-the-art review. ChemBioEng Rev 2019, 6, No. 2, 28−44

- $\alpha_w$ model
  - BC T(r=R) $\neq$ T$_{wall}$
  - $\varepsilon(r)$ = constant
  - $u(r) = u_{superficial}$

radial porosity variation (PRCFD grid, $D/d_p$ = 7)

Wall — Bed Center

Void fraction [-]

$\frac{R-r}{d_p}$ [-]

$D/d_P = 7$

- $\Lambda_R$ model
  - BC T(r=R) = T$_{wall}$
  - $\varepsilon(r)$ varies
  - $u(r) = \dfrac{u_{superficial}}{\varepsilon(r)}$

# Effective thermal diffusivity

steady state energy balance:

$$\nabla \cdot (\rho \cdot u \cdot h_{s,t}) - \nabla \cdot (\alpha_{eff} \cdot \nabla h_s) = -\sum_i^n h_i^o \cdot R_i - \nabla \cdot \sum_i^n h_i \cdot ((\vec{j_i} + \rho \cdot Y_i \cdot u_c) + \alpha_{eff} \cdot \nabla Y_i))$$

where,
$$\alpha_{eff} = \frac{k_{eff}}{Cp_{eff}} \qquad k_{eff} = k_{rf} + k_{rs} \qquad Cp_{eff} = \frac{Cp_f \rho_f \varepsilon + (1-\varepsilon)Cp_s \rho_s}{\rho_f \varepsilon + (1-\varepsilon)\rho_s}$$

$$k_{rs} = k_f \left( (1 - \sqrt{1-\epsilon}) + \sqrt{1-\epsilon} \left\{ \frac{2}{1 - \frac{k_f}{k_s}B} \left[ \frac{\left(1 - \frac{k_f}{k_s}\right)B}{\left(1 - \frac{k_f}{k_s}B\right)^2} ln\frac{k_s}{k_f B} - \frac{B+1}{2} - \frac{B-1}{1 - \frac{k_f}{k_s}B} \right] \right\} \right) \qquad \text{Solid}$$
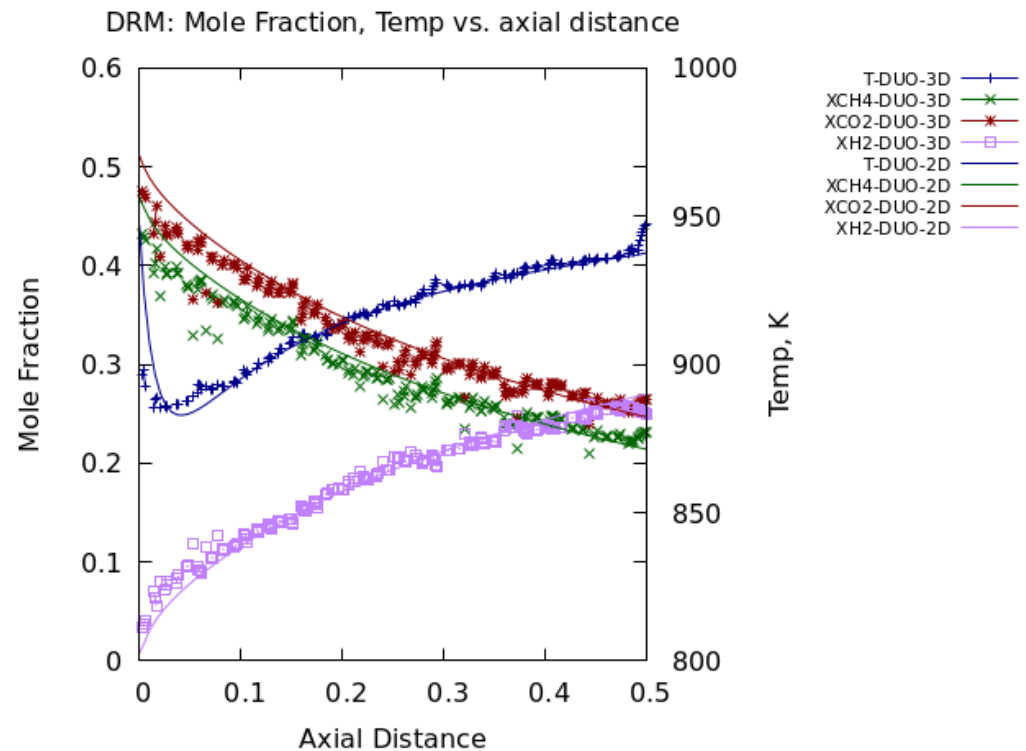
Zehner and Schlünder (1978)

$$k_{rf} = k_f \left[ \frac{RePr}{8.65\left(1 + 19.4\left(\frac{d_p}{d_t}\right)^2\right)} \right] \qquad \text{Fluid}$$

Specchia et al. (1980)

# Porous media: Dry Reforming of Methane CFD 2D vs 3D validation test

- Dry reforming of methane example
  - $CO_2 + CH_4 \Leftrightarrow 2CO + 2H_2$

- 3D DUO PRCFD vs. 2D DUO porous media: *Excellent fit*

  (Wedge geometry, 1000 cells)

- *Note the low N (D/d$_p$) value of 2…*

DRM: Mole Fraction, Temp vs. axial distance

*Legend:*
- T-DUO-3D
- XCH4-DUO-3D
- XCO2-DUO-3D
- XH2-DUO-3D
- T-DUO-2D
- XCH4-DUO-2D
- XCO2-DUO-2D
- XH2-DUO-2D

*Mole Fraction* vs *Axial Distance*, *Temp, K*

**100's - 1000's of core hours for 3D PRCFD, to anywhere from "a few" core hours to minutes for 2D porous media**

# Porous media: Comparison against data Steam Methane Reforming (SMR)

Hoang, D.L., Chan, S.H., Ding. O.L. Kinetic and modelling study of methane steam reforming over sulfide nickel catalyst on a gamma alumina support. Chemical Engineering Journal, 112 issues 1-3 (2005), 1-11.

1. $CH_4 + H_2O \Leftrightarrow CO + 3H_2$

$$R_1 = \frac{k_1}{P_{H_2}^{2.5}}\left(P_{CH_4}P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{e1}}\right)\cdot\frac{1}{Q_{SMR}^2}$$

2. $CO + H_2O \Leftrightarrow CO_2 + H_2$

$$R_2 = \frac{k_2}{P_{H_2}}\left(P_{CO}P_{H_2O} - \frac{P_{H_2}P_{CO_2}}{K_{e2}}\right)$$

3. $CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2$

$$R_3 = \frac{k_3}{P_{H_2}^{3.5}}\left(P_{CH_4}P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_{e3}}\right)\cdot\frac{1}{Q_{SMR}^2}$$

$$k_i = k_{0,i}\cdot e^{\left(\frac{-EA_i}{RT}\right)}$$

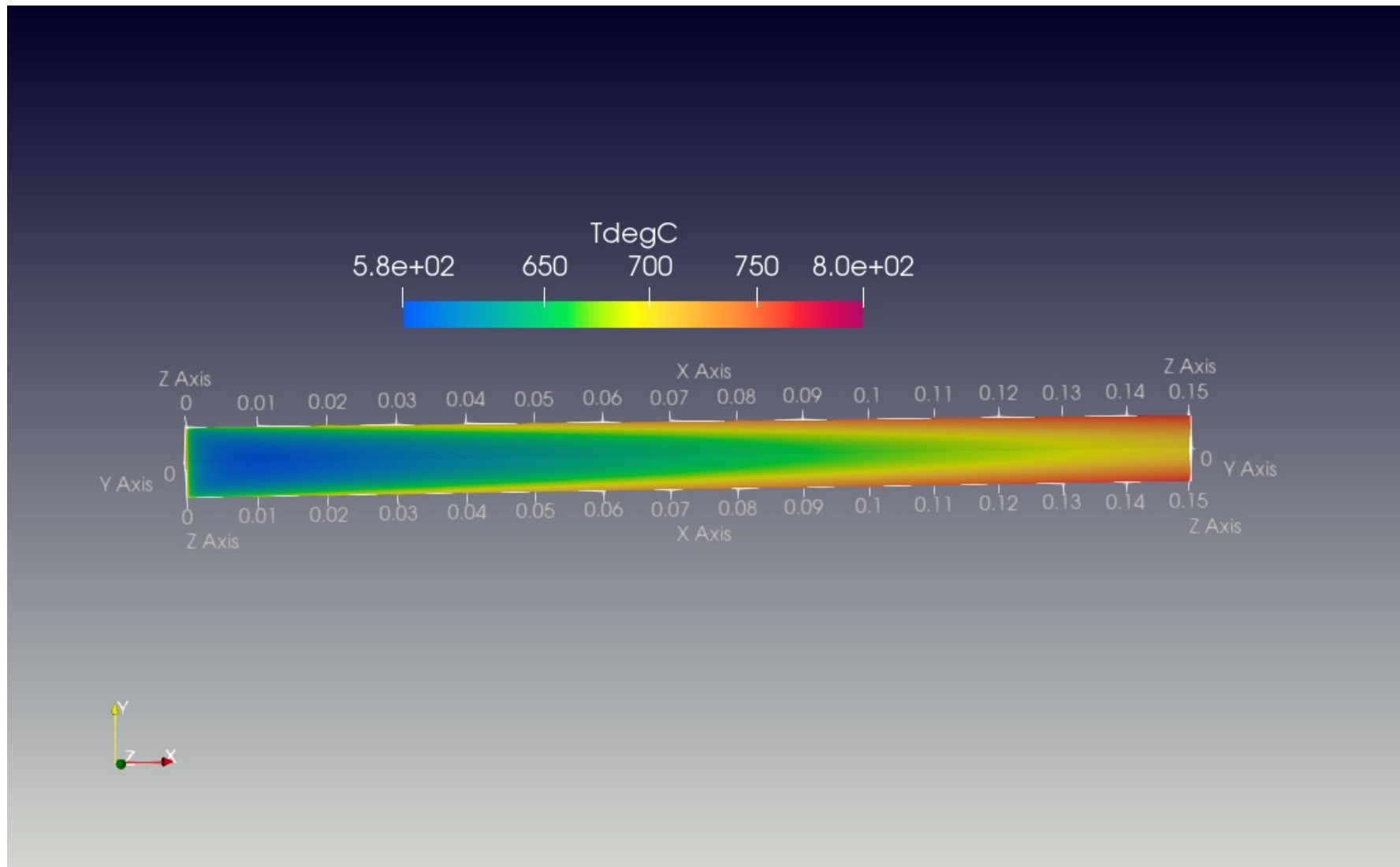$$K_{CH_4} = K_{0,CH_4}\cdot e^{\left(\frac{\Delta H_{CH_4}}{RT}\right)}$$

$$K_{H_2O} = K_{0,H_2O}\cdot e^{\left(\frac{\Delta H_{H_2O}}{RT}\right)}$$

$$K_{e_1} = e^{\left(\frac{-26830}{T}+30.114\right)}$$
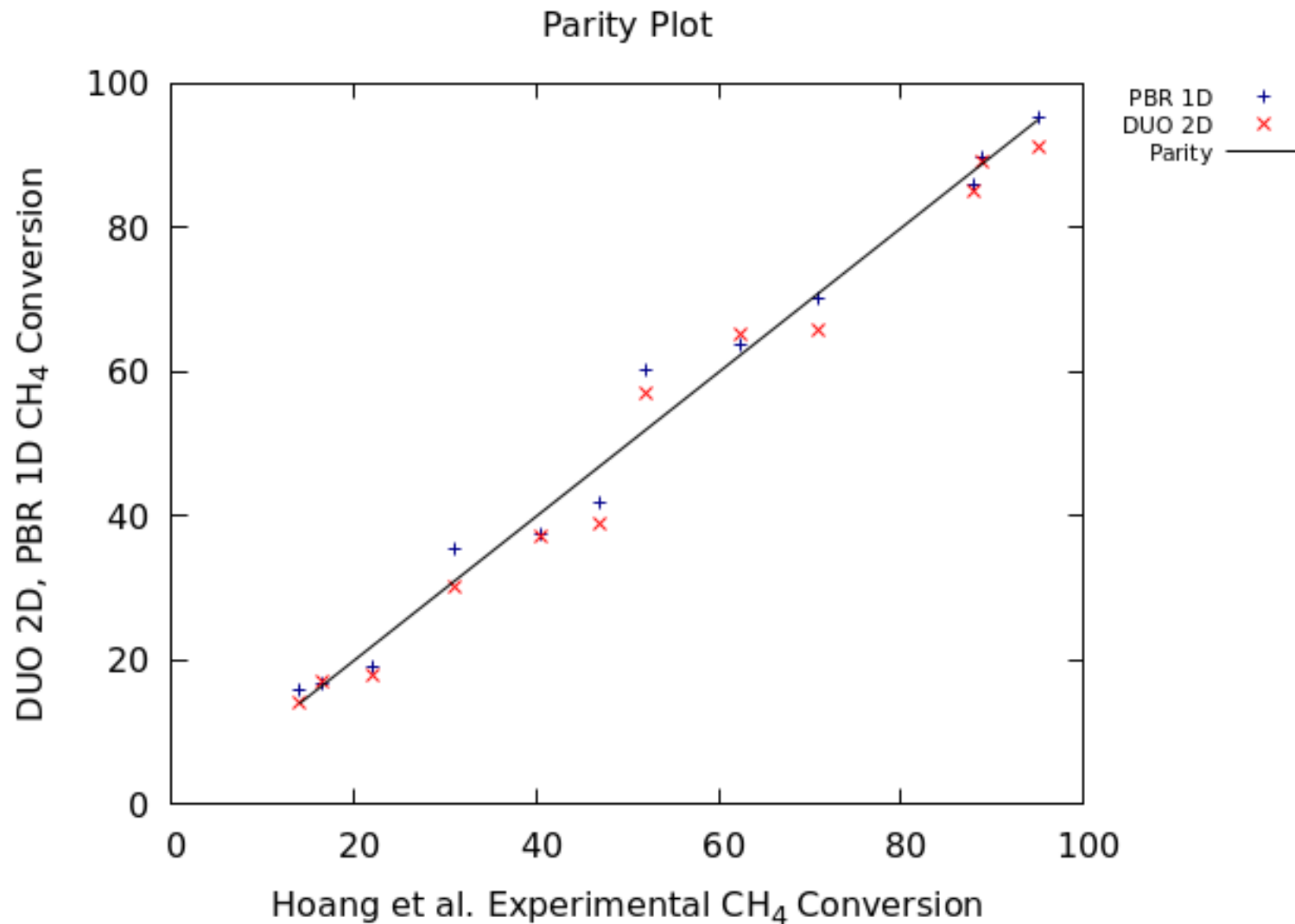
$$K_{e_2} = e^{\left(\frac{4400}{T}-4.036\right)}$$

$$Q_{SMR} = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}}$$

$$K_{e_3} = K_{e_1}K_{e_2}$$

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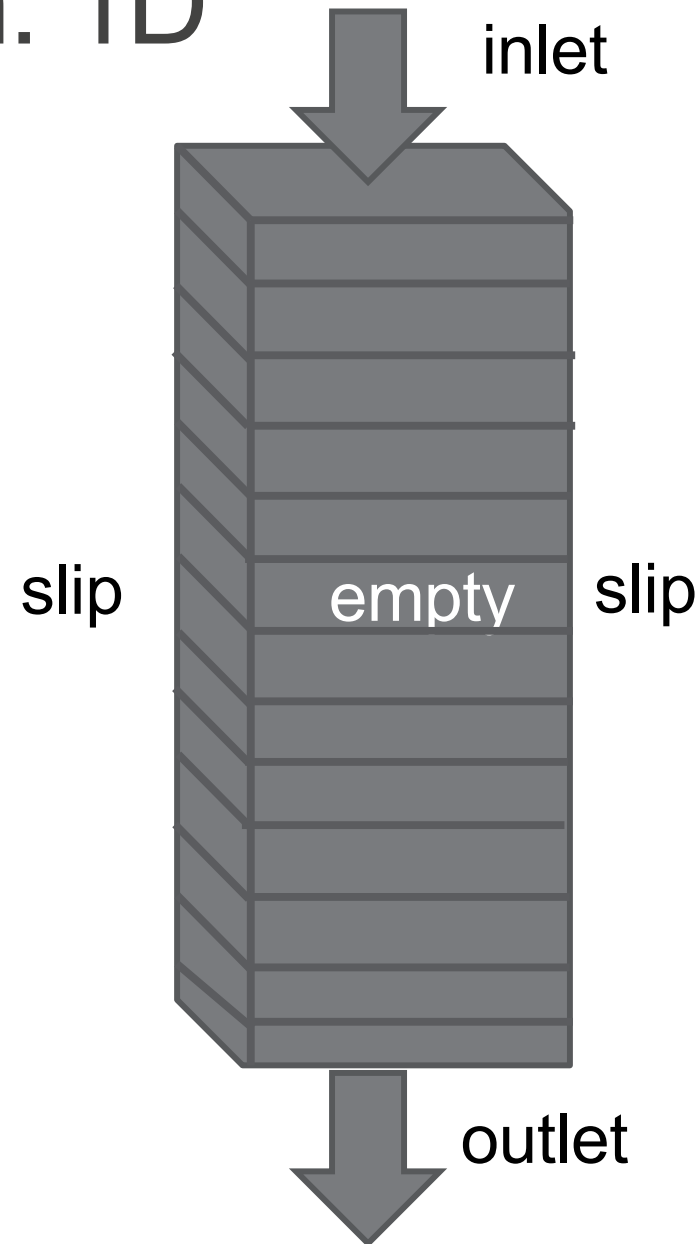# Radial temperature gradients are > 200°C

# Parity plot: Porous media vs. Expt.

# Further acceleration: 1D

- 1D grid
- OpenFOAM can simulate isothermal or adiabatic reactor
- What about non-isothermal, non-adiabatic? e.g.,
  - Constant wall T
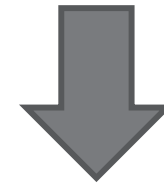  - Temperature inside reactor can vary

inlet

slip    empty    slip

outlet

# 1D Packed Bed Reactor

*Energy balance with overall heat transfer coefficient term*

$$\nabla \cdot \left( \rho \cdot u \cdot h_{s,t} \right) - \nabla \cdot \left( \alpha_{eff} \cdot \nabla h_s \right)$$

$$= \frac{\partial p}{\partial t} - \sum_i^n h_i^o \cdot R_i - \nabla \cdot \sum_i^n h_i \cdot \left( \left( \vec{j_i} + \rho \cdot Y_i \cdot u_c \right) + \alpha_{eff} \cdot \nabla Y_i \right) + U \frac{4}{d_t} \left( T - T_w \right)$$

$T_w$ = wall temperature
$d_t$ = tube diameter

> **EEqn.H**
>
> ```
> if (useOverallU) {
> EEqn += - overallU*Tdiff*4/(dtube);}
> ```

*Many correlations are involved… including…*

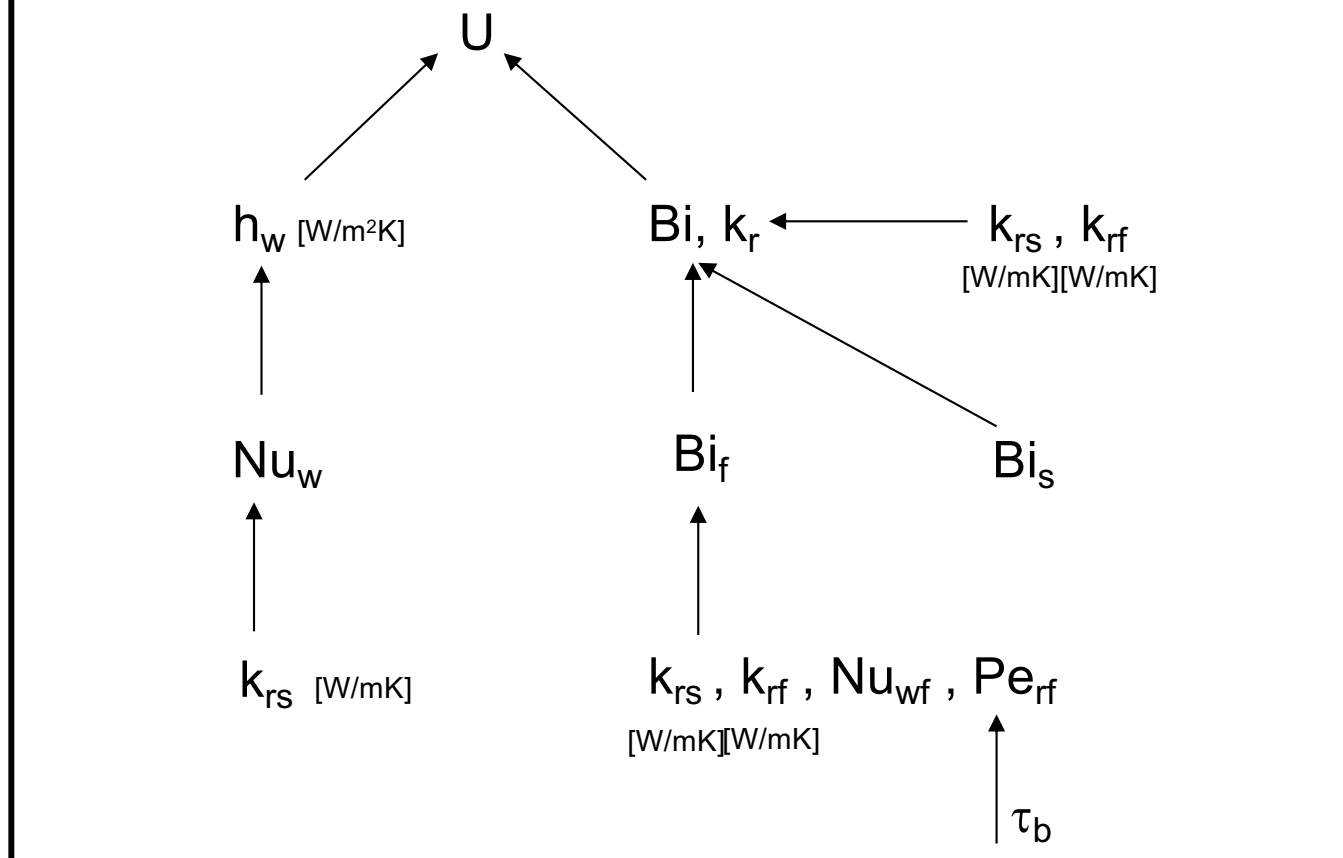$$\frac{1}{U} = \frac{1}{h_w} + \frac{R_t}{3k_{eff}} \frac{Bi+3}{Bi+4}$$

Dixon (1996)

$$Nu_w = \left( 1.3 + \frac{5}{N} \right) \frac{k_{rs}}{k_f} + 0.19 Pr^{1/3} Re^{3/4}$$

Martin & Nilles (1993)

# Additional Equations
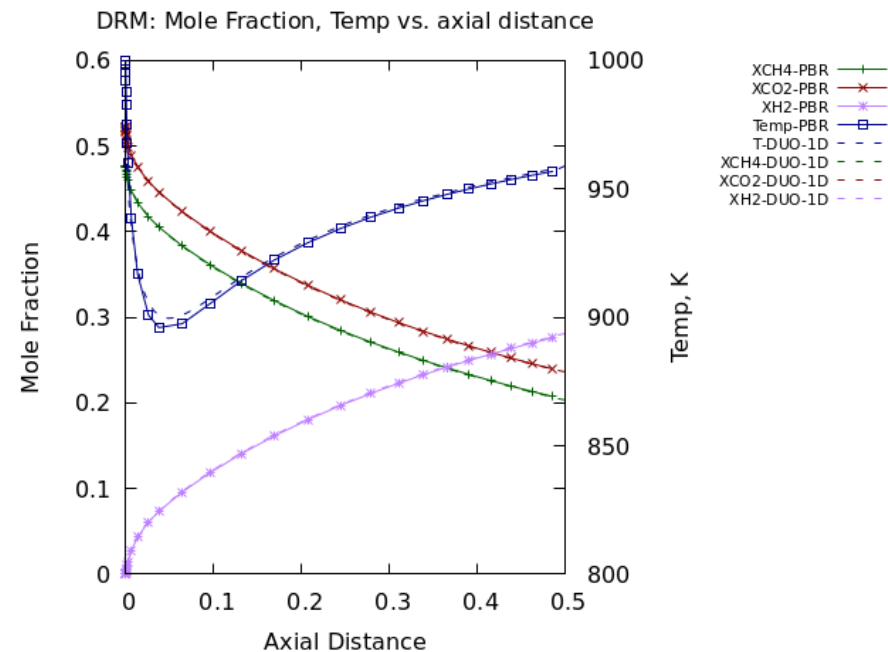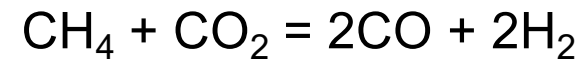
For calculations presented in this presentation…

$$U$$

$$h_w \text{ [W/m}^2\text{K]} \qquad Bi, k_r \longleftarrow k_{rs}, k_{rf}$$
$$\text{[W/mK][W/mK]}$$

$$Nu_w \qquad Bi_f \qquad Bi_s$$

$$k_{rs} \text{ [W/mK]} \qquad k_{rs}, k_{rf}, Nu_{wf}, Pe_{rf}$$
$$\text{[W/mK][W/mK]}$$

$$\tau_b$$

NOTE: On GitHub repository different *Bi* correlation used than shown above: $Bi = \dfrac{h_w d_t}{2\, k_r}$, so $Bi_f$, $Bi_s$ are not needed

# Validation test: 1D DUO vs 1D DETCHEM$^{PBR}$ Dry Reforming of Methane

- Microkinetic surface model

- 1D DUO vs 1D DETCHEM$^{PBR}$

- Perfect match with DETCHEM$^{PBR}$

$$CH_4 + CO_2 = 2CO + 2H_2$$

DRM: Mole Fraction, Temp vs. axial distance

Legend:
- XCH4-PBR
- XCO2-PBR
- XH2-PBR
- Temp-PBR
- T-DUO-1D
- XCH4-DUO-1D
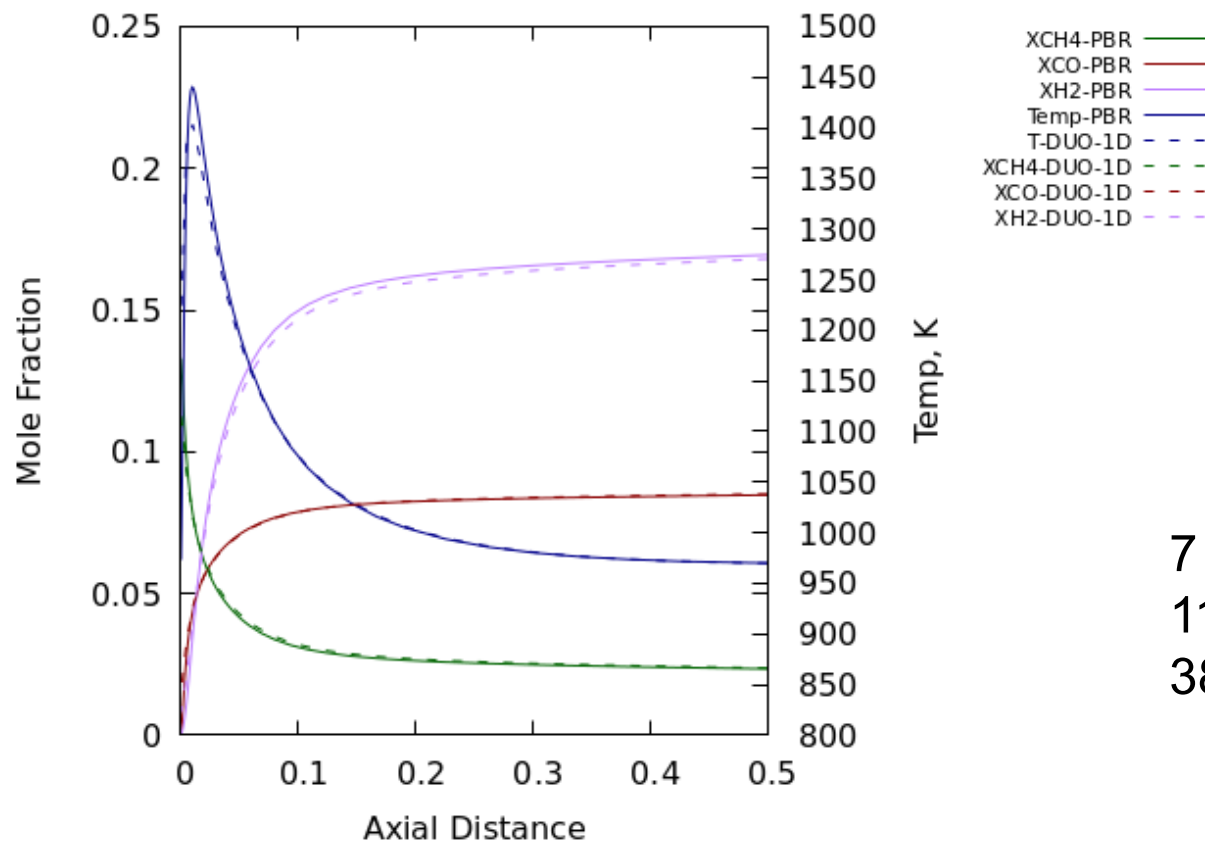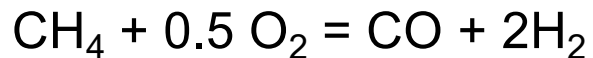- XCO2-DUO-1D
- XH2-DUO-1D

6 gas phase species
13 surface species
52 surface reactions
(200 cells)

# Validation test: 1D DUO vs 1D DETCHEM$^{PBR}$ Catalytic Partial Oxidation of Methane

$CH_4 + 0.5\ O_2 = CO + 2H_2$



7 gas phase species
11 surface species
38 reactions (microkinetics)

# Dramatic time reduction...

3D PRCFD            100's/1000's of core hours

2D Porous Media     < 1 to "a few" core hours

1D Porous Media     Core **seconds** to **minutes**

# Example code (OpenFOAM 10)

- https://github.com/TonkomoLLC/OFW18

```
forAll(cellsZone, cI)
{
    if (cellsZone[cI] == celli)
    {
        // Effective radial solid thermal conductivity, Zhener and Schlunder
        scalar kfks = kappaCells[celli] / kappaSolid;
        scalar kskf = kappaSolid / kappaCells[celli];
        scalar Cterm = 1.25;        // setup for spheres!
        scalar Bterminner = (1-porosity)/porosity;
        scalar Bterm = Cterm*pow(Bterminner,10./9.);
        scalar Bterm2 = 1 - kfks*Bterm;
        scalar Bterm3 = (1 - kfks)*Bterm;
        scalar term0 = 1 - sqrt(1-porosity);
        scalar term1 = sqrt(1-porosity);
        scalar term2 = 2.0/Bterm2;
        scalar term3 = Bterm3 / pow(Bterm2,2.0);
        scalar term4 = log(kskf/Bterm);
        scalar term5 = (Bterm+1)/2;
        scalar term6 = (Bterm - 1) / Bterm2;
        scalar kappaEffSolid = kappaCells[celli]*(term0 + term1*(term2*(term3*term4-term5-term6)));

        // Effective radial fluid thermal conductivity, Specchia et al.
        scalar ReNum = thermoMixture.rho(pCells[celli], TCells[celli])*USuperficial*diamParticle/muCells[celli];
        scalar PrNum = CpCells[celli] * muCells[celli]/kappaCells[celli];
        scalar Re_a = ReNum;
        scalar Nnum = diamParticle/diamTube;
        scalar B_Specchia = 1 + 19.4 * pow(Nnum,2.0);
        scalar Pe_H = 8.65*B_Specchia;
        scalar kappaEffConvection = kappaCells[celli]*(Re_a*PrNum/Pe_H);

        kappaCells[celli] = kappaEffSolid + kappaEffConvection;

        // Effective heat capacity
        scalar rhoCelli = thermoMixture.rho(pCells[celli], TCells[celli]);
        scalar rhoAverageCelli = porosity*rhoCelli + (1 - porosity)*rhoSolid;
        scalar cPCelli = ((CpCells[celli] * porosity * rhoCelli)
                + ((1 - porosity)*cPSolid*rhoSolid))/rhoAverageCelli;
        scalar cPFactor = CpCells[celli] / cPCelli;

        kappaCells[celli] *= cPFactor;
    }
}
```

```
kappaEffSolid.correctBoundaryConditions();
kappaEff.correctBoundaryConditions();

// Calculate wall heat transfer coefficient
// H. Martin and M. Nilles. Radiale Warmeleitung in durchstromten Schuttungsrohren. Chem. Ing. Tech. 65 (1993), 14681477.
volScalarField Nuw = (1.3 + 5./Nfactor)*(kappaEffSolid/thermo.kappa()) + 0.19*pow(PrNum,0.33333)*pow(Rep,0.75);
volScalarField hw = Nuw * thermo.kappa() / (diamParticle*UnitLength);

// Bi_s = solid Biot number
// A.G. Dixon. Wall and particle-shape effects on heat transfer in packed beds.
// Chemical Engineering Communications, 71:1 (1988), 217-237.
scalar Bi_s_power = (diamTube/diamParticle)-1.0;
scalar Bi_s = 2.41+(0.156*(std::pow(Bi_s_power,2.0)));

// Bi_f = fluid Biot number
// A.G. Dixon. Wall and particle-shape effects on heat transfer in packed beds.
// Chemical Engineering Communications, 71:1 (1988), 217-237.
scalar Pe_rf_infinity = 12.0; // sphere
volScalarField Nu_wf = 0.523*(1.0-diamParticle/diamTube)*pow(PrNum,1./3.)*pow(Rep,0.738);
scalar tortuosity = 1.5-(0.5*porosity);
volScalarField Pe_rf = (1.0/(((porosity*tortuosity)/(PrNum*Rep))+(1./Pe_rf_infinity)));
volScalarField Bi_f = Nu_wf*diamTube/(2.0*diamParticle)*(Pe_rf/(Rep*PrNum));

// Overall tube Biot number
// D.L. Cresswell and A. G. Dixon, Theoretical prediction of effective heat transfer parameters in packed beds.
// AIChE J. 25 (1979), 663.

// Overall heat transfer coefficient
// A.G. Dixon. An improved equation for the overall heat transfer coefficient in packed beds.
// Chemical Engineering and Processing 35 (1996), 323-331.

forAll(rho, celli)
{
    forAll(cellsZone, cI)
    {
        if (cellsZone[cI] == celli)
        {
            if (Rep[celli] < 10.)
            {
                //alphaEff[celli] = kappaEff[celli]/CpEff[celli];
```
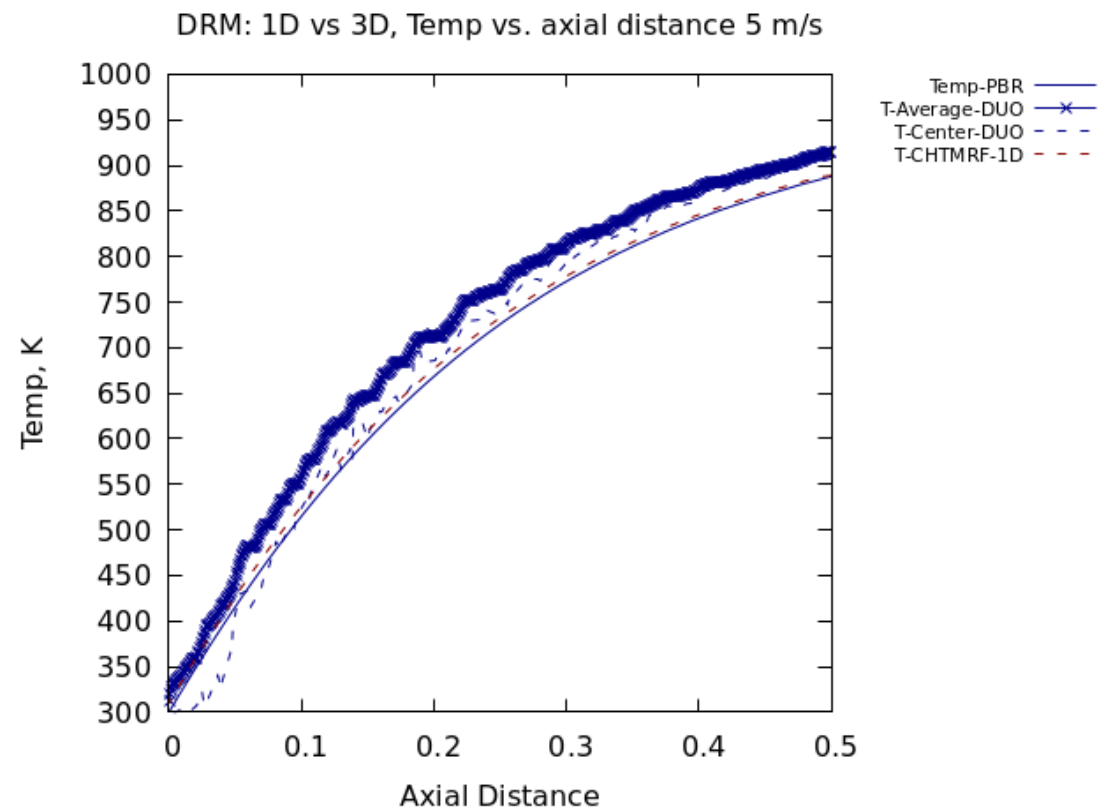
*heRhoThermoPorous*
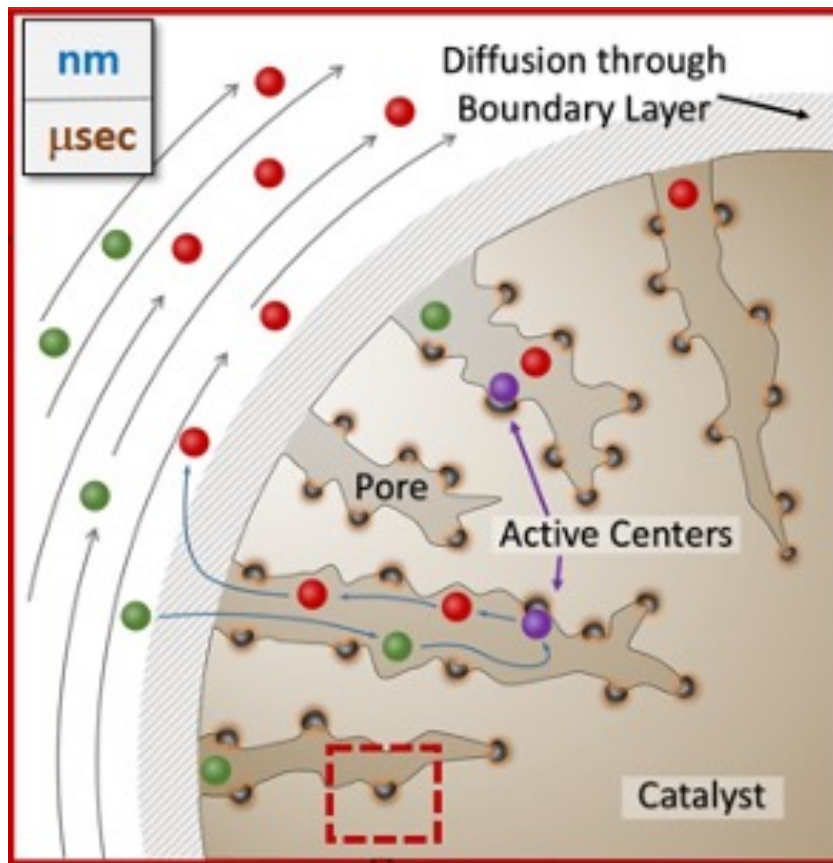Suitable for 2D porous heat transfer

*chtMultiRegionFoam-porous1D*
Includes overall U calculation

# Example Case

- 1D DUO
- 1D DETCHEM$^{PBR}$
- 3D DUO
  (86 particles)
- Heat Transfer Only
  (DRM feed)

DRM: 1D vs 3D, Temp vs. axial distance 5 m/s

Temp, K

Axial Distance

Temp-PBR
T-Average-DUO
T-Center-DUO
T-CHTMRF-1D

# Intra-particle diffusion



*courtesy of omegadot
software & consulting*

- DETCHEM has a built-in "washcoat Models"
  1. Solve for effectiveness factor, $\eta$

  $$\eta = \frac{\tanh(\phi)}{\phi} \quad \phi = L\sqrt{\frac{k}{D_{eff,i}}}$$
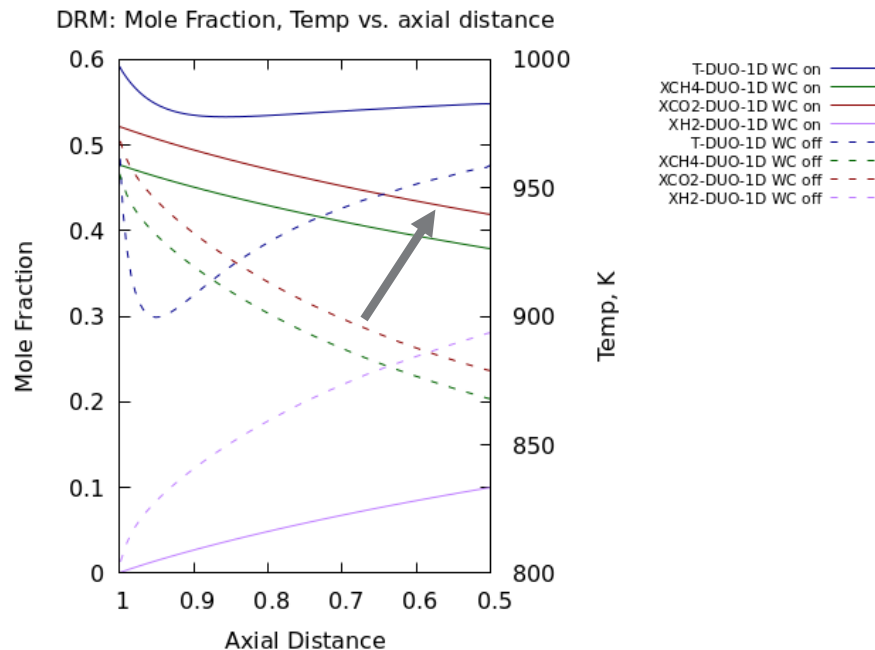
  2. Solve reaction diffusion equation

  $$-\nabla \cdot \left( \rho \cdot D_{i,m} \cdot \nabla Y_i \right) = R_i$$

# Dry Reforming
# Pore Diffusion Effect



DRM: Mole Fraction, Temp vs. axial distance

- thickness = $d_p/2$ = 6.325 mm

- internal porosity= 0.5

- tortuosity = 3

- pore diameter = 1 $\mu$m

Pore diffusion: here, substantially lowers conversion
38% conversion without pore diffusion
12% conversion with pore diffusion

# Why use DUO for 1D PBR models?

**OpenFOAM brings…**

- OpenFOAM handles FVM calculus for axial conduction, diffusion effects

- Wide range of numerical options

- Supporting infrastructure

**DETCHEM brings…**

- Kinetic theory transport properties (via DETCHEM)

- Microkinetic surface reaction models

- Intraparticle diffusion models

- "UDF" format for complex reaction kinetics expressions

# Summary

- Faster simulations: 3D → 2D → 1D

- 1D and 2D reactor simulations oftentimes adequately model tubular reactor performance

- Porous media simulations of packed bed reactors
  - Combined solid and fluid energy balance
  - Effective thermal conductivity combines solid and fluid effects

- 1D non-isothermal, non-adiabatic reactors can be simulated implementing an overall heat transfer coefficient

# Thank you for your attention!



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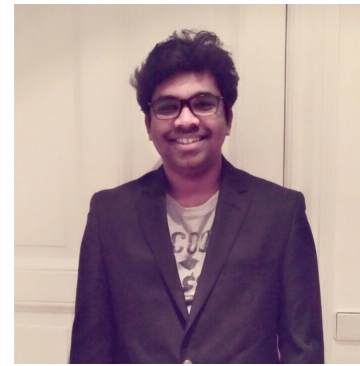
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*Accelerate solutions to real problems with accessible reactive CFD,* ***how can we help?***