

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

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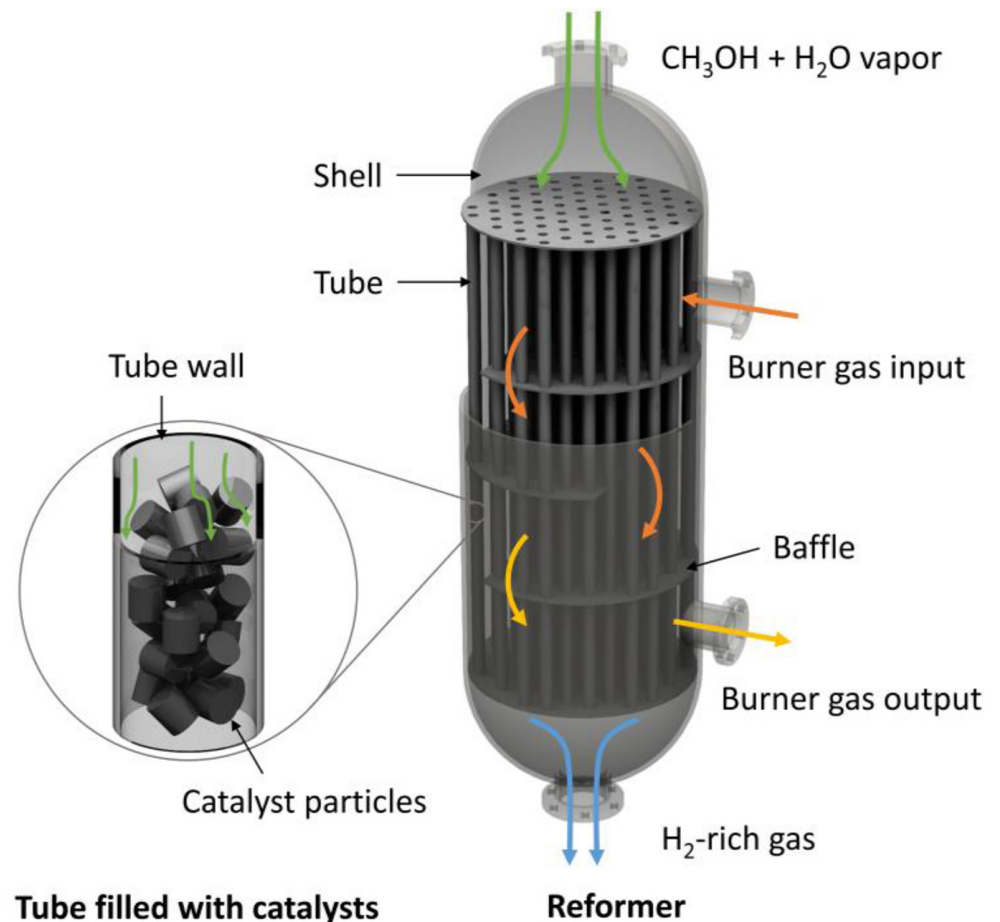
# Tonkomo, LLC

- **Owners:** Lee Tonkovich, PhD & Eric Daymo, 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 entrepreneurship



# Catalytic Fixed Bed Reactors

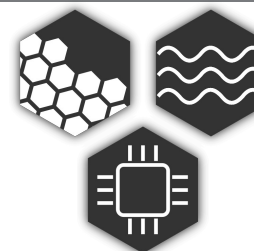
- Tubular fixed bed catalytic reactors are the “workhorse” of the chemical industry
- CFD is one tool used to analyze fixed-bed reactor performance
- OpenFOAM does not have extensive built-in tools for such packed bed reactor calculations
  - Surface reactions
  - Packed bed heat transfer



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](http://www.detchem.com)

- DETCHEM stands for DETailed CHEMistry
  - Software package for reacting flow simulation
  - [www.detchem.com](http://www.detchem.com)

*Reference: Deutschmann et al. 2022*

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

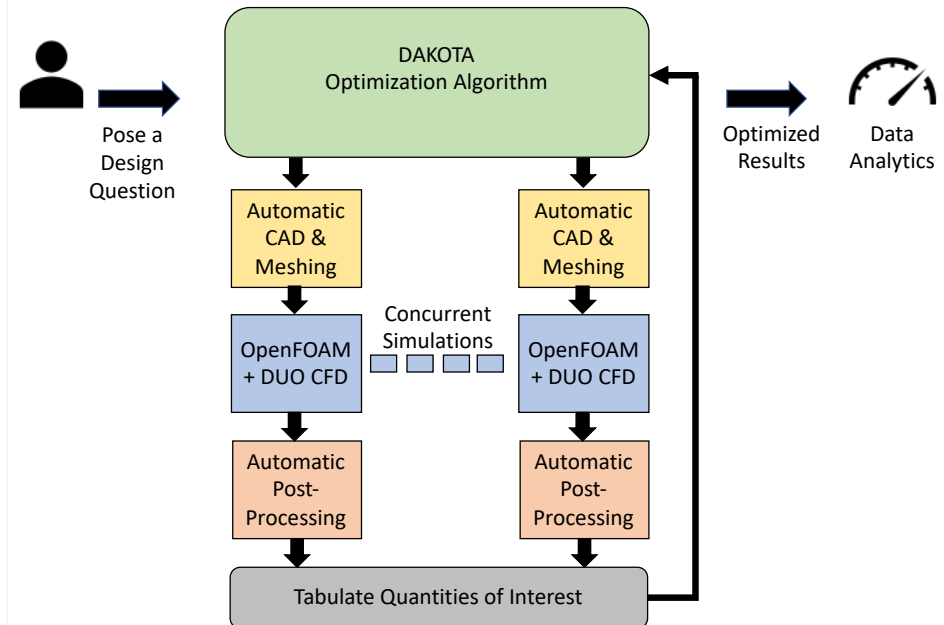
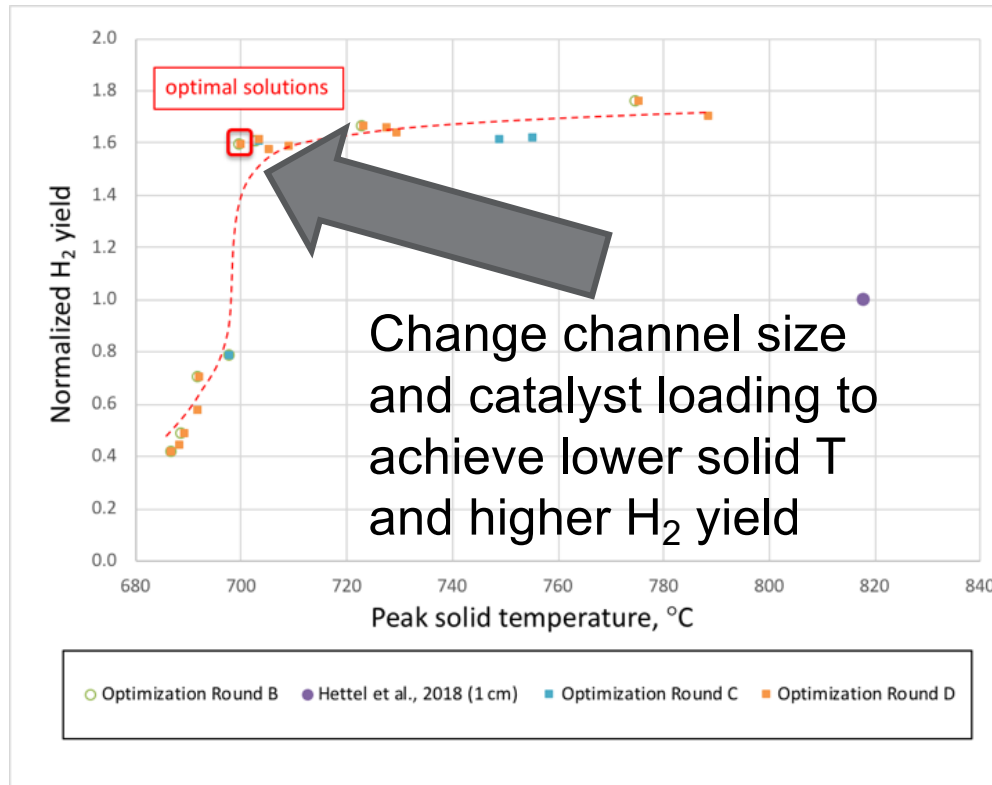


Product	Description
Manual	Manual for DETCHEM
EQUIL	Equilibrium and adiabatic reactor temperature calculation.
GASPROBE	Tool for evaluating the transport and kinetic properties of the chemical species participating in a gas-phase reaction mechanism.
SURFPROBE	Tool for evaluating the transient and steady 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?

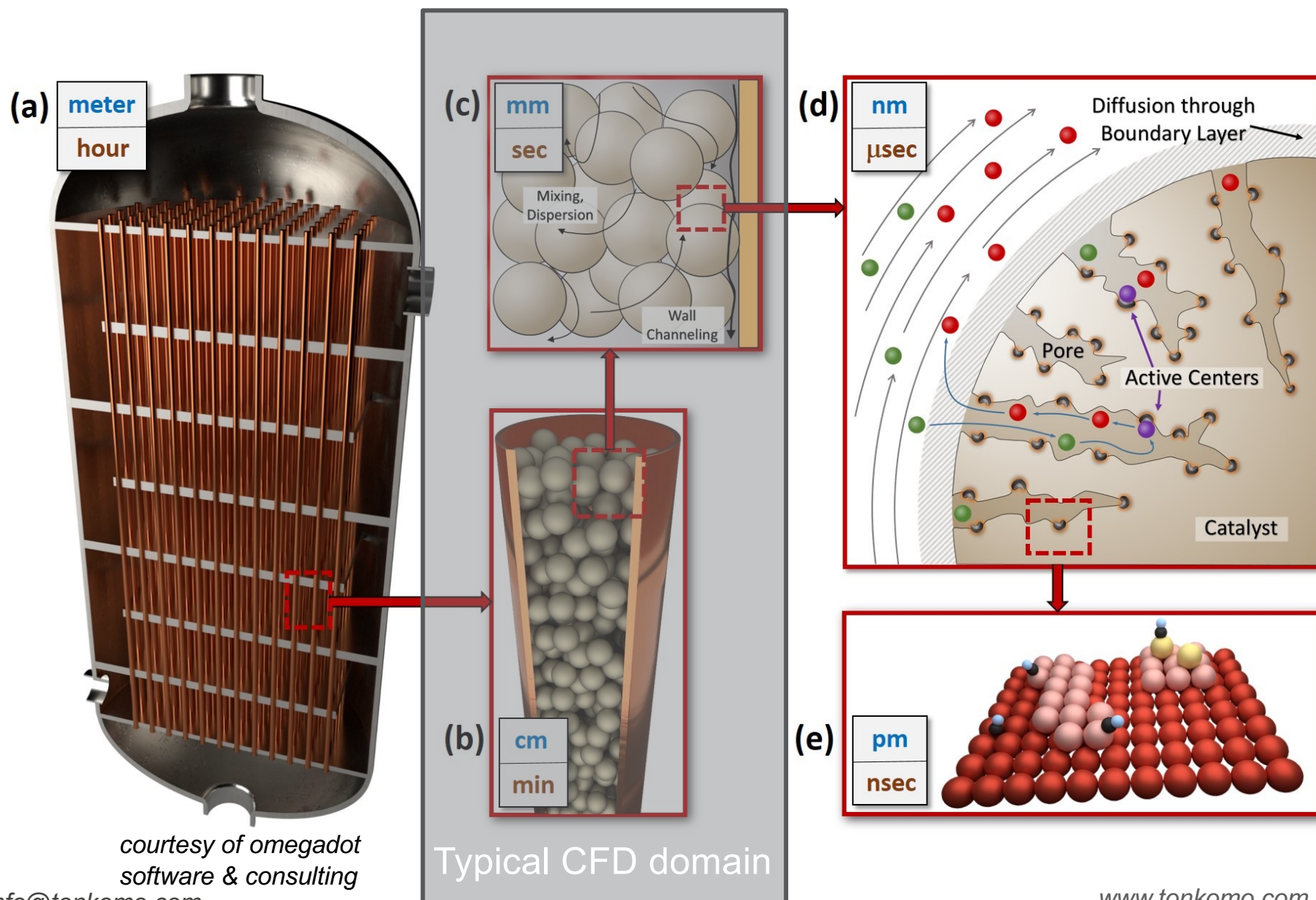
## One reason: Optimization and Discovery



**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

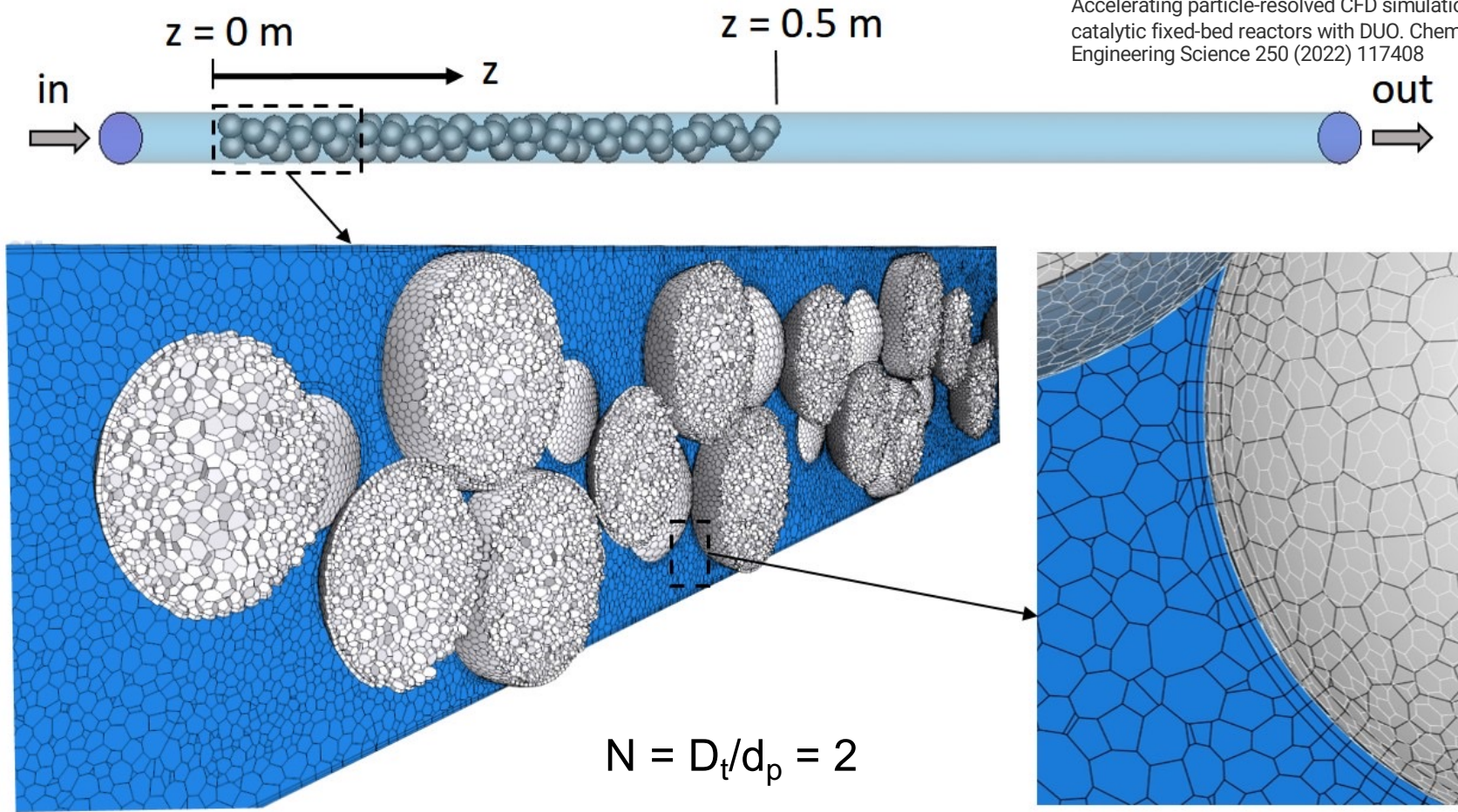
# Inside a fixed bed reactor





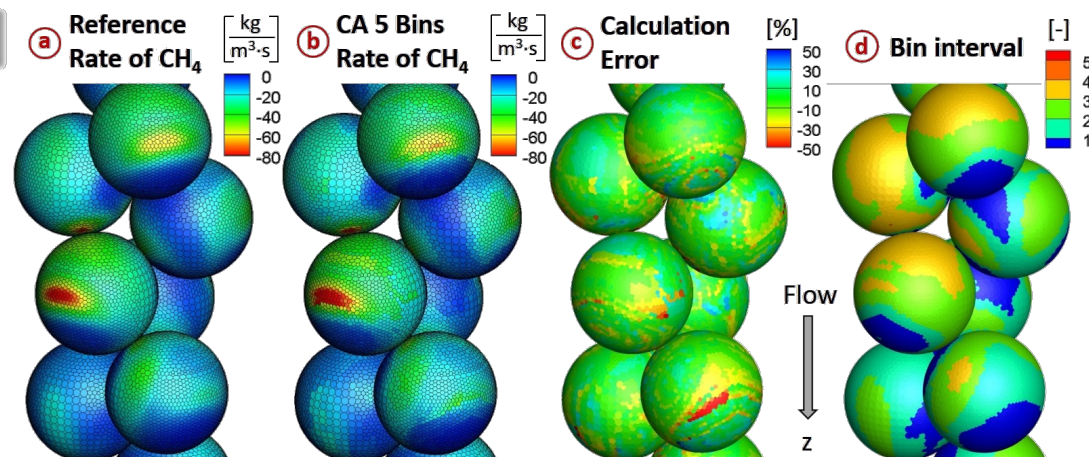
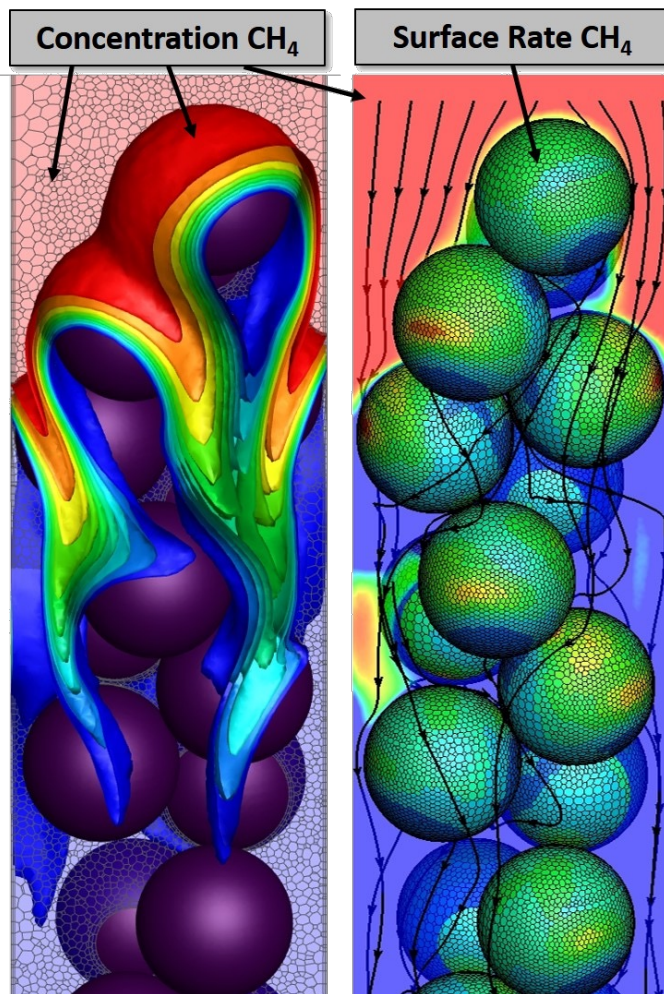
# Particle Resolved CFD (PRCFD)

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



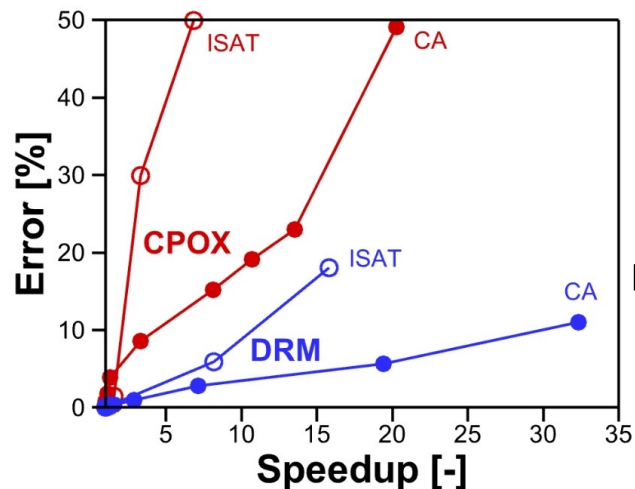
1,559,544 fluid cells, 774,386 cells solid cells  
217,810 reactive surface faces

# Particle resolved CFD



*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

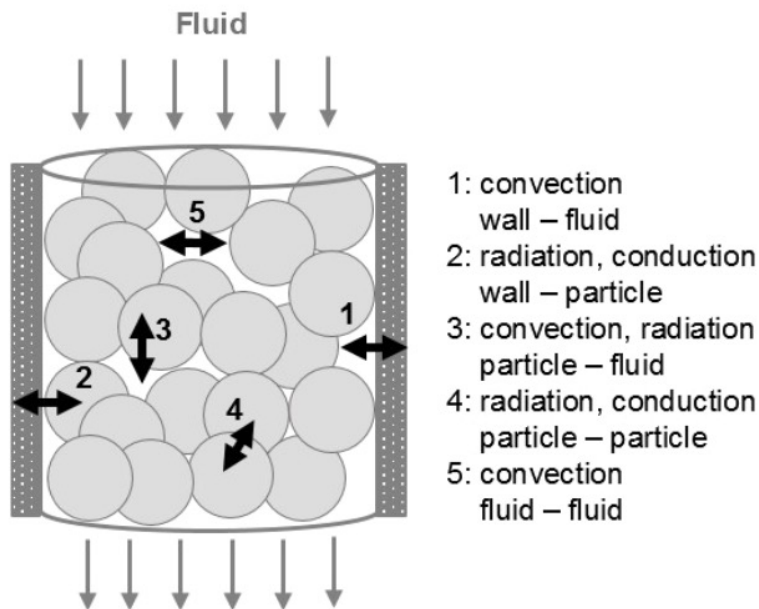
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# Continuum Model Options: Fixed Bed Reactor Modeling

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



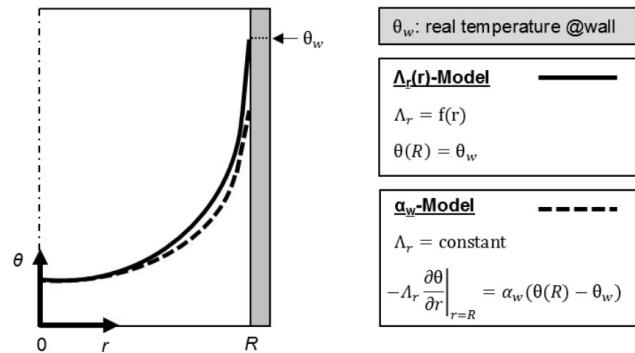
**Figure 1.** Heat transport mechanisms in fixed-bed reactors through which gas flows (modified according to [4]).

Steghake, C., Riese, J., Grünwald. Modeling and validating fixed-bed reactors: A state-of-the-art review. ChemBioEng Rev 2019, 6, No. 2, 28–44



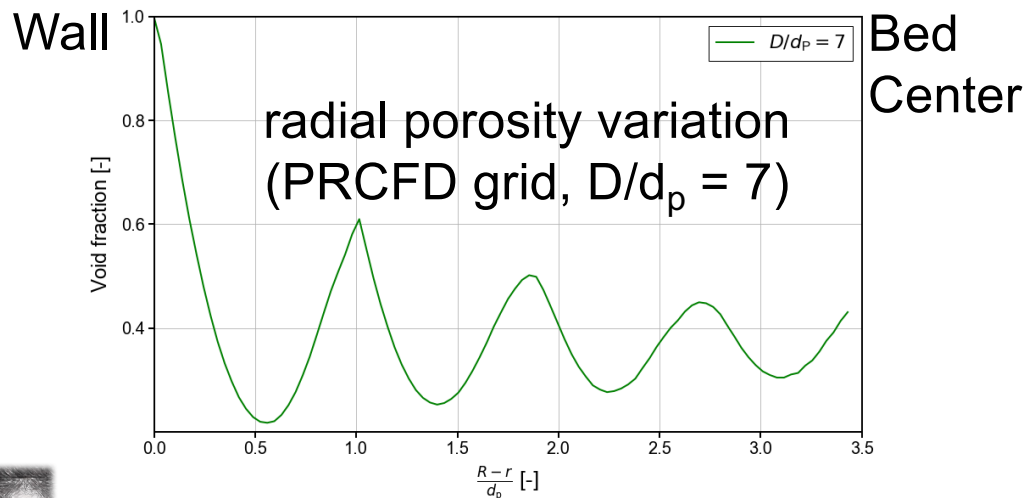
# Continuum Model Options: Fixed Bed Reactor Modeling

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



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  $T(r=R) \neq T_{\text{wall}}$
  - $\varepsilon(r) = \text{constant}$
  - $u(r) = u_{\text{superficial}}$



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

# 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,

$$\alpha_{eff} = \frac{k_{eff}}{Cp_{eff}}$$

$$k_{eff} = k_{rf} + k_{rs}$$

$$Cp_{eff} = \frac{C\rho_f\rho_f\varepsilon + (1-\varepsilon)C\rho_s\rho_s}{\rho_f\varepsilon + (1-\varepsilon)\rho_s}$$

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

Zehner and Schlünder (1978)

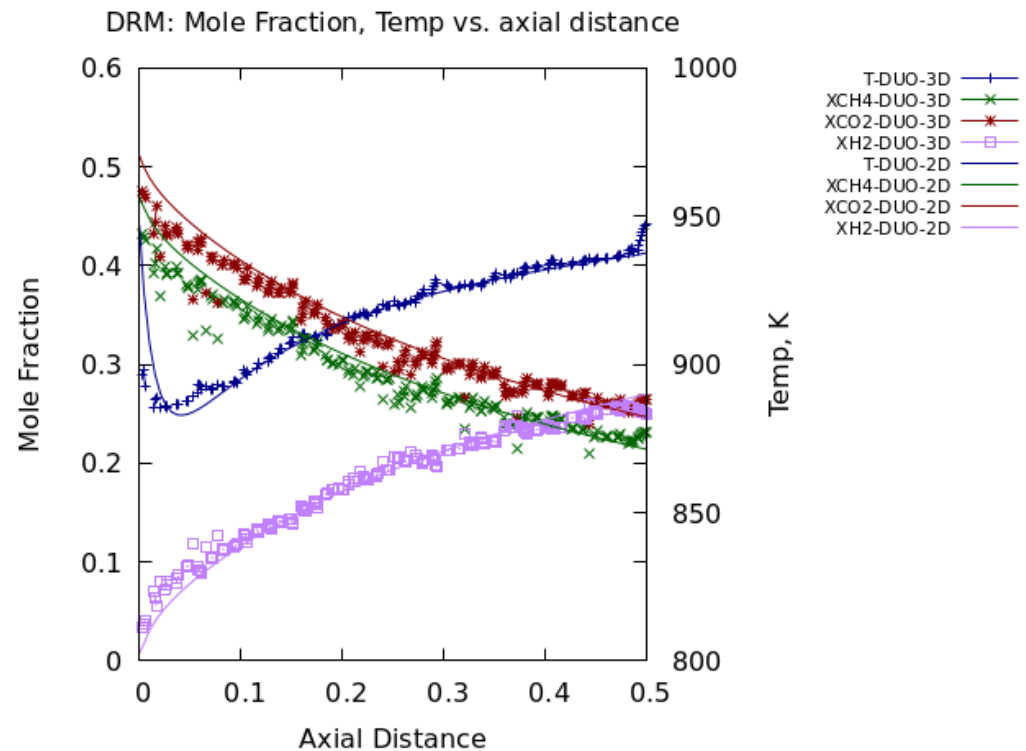
$$k_{rf} = k_f \left[ \frac{RePr}{8.65 \left( 1 + 19.4 \left( \frac{d_p}{d_t} \right)^2 \right)} \right] \quad \text{Fluid}$$

Specchia et al. (1980)

# Porous media: Dry Reforming of Methane

## CFD 2D vs 3D validation test

- Dry reforming of methane example
  - $\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2\text{CO} + 2\text{H}_2$
- 3D DUO PRCFD vs. 2D DUO porous media:  
*Excellent fit*  
(Wedge geometry, 1000 cells)
- *Note the low  $N$  ( $D/d_p$ ) value of 2...*



**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.



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



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



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

$$Q_{SMR} = 1 + K_{CH_4} P_{CH_4} + K_{H_2O} P_{H_2O}$$

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

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

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

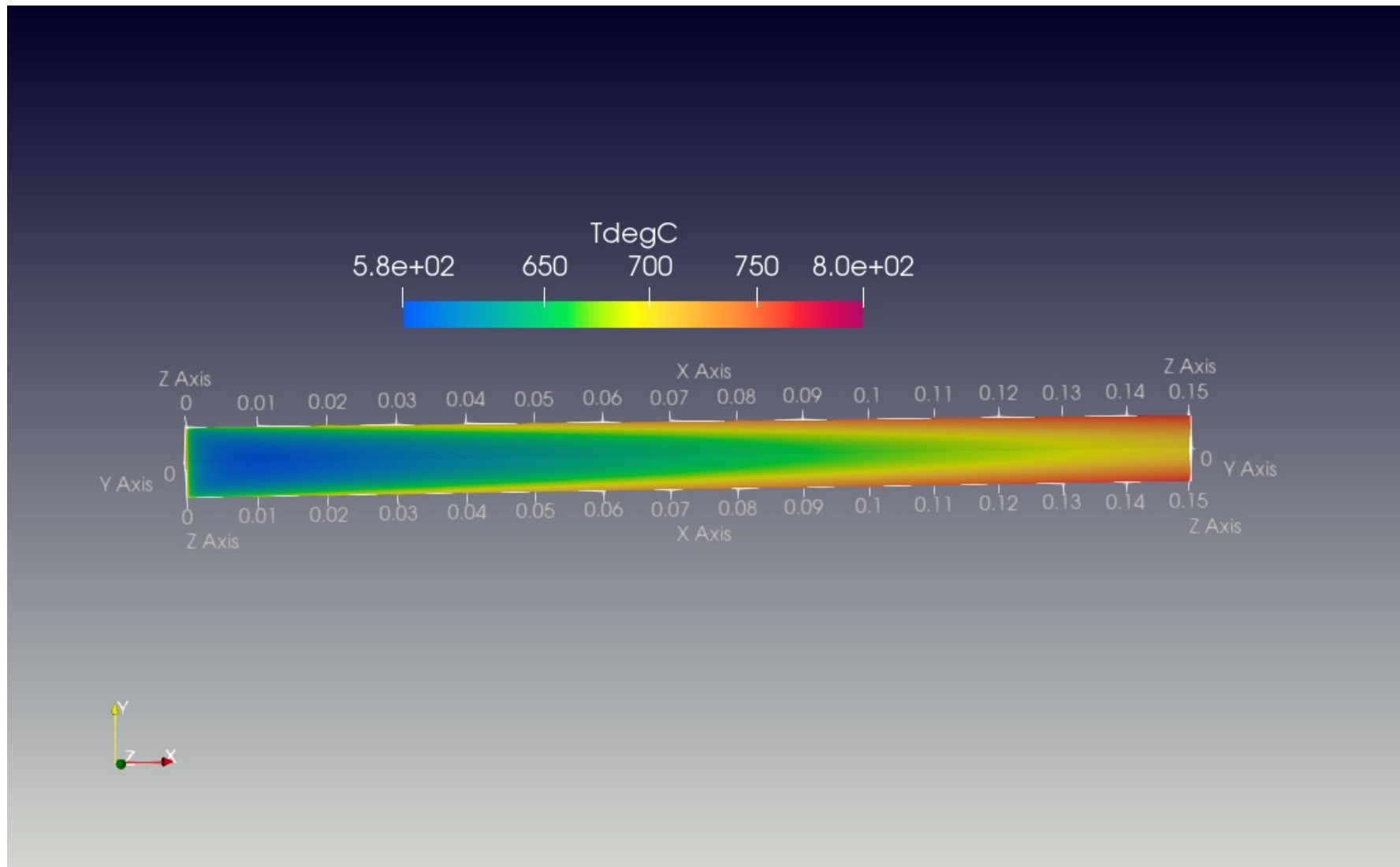
$$K_{e1} = e^{\left(\frac{-26830}{T} + 30.114\right)}$$

$$K_{e2} = e^{\left(\frac{4400}{T} - 4.036\right)}$$

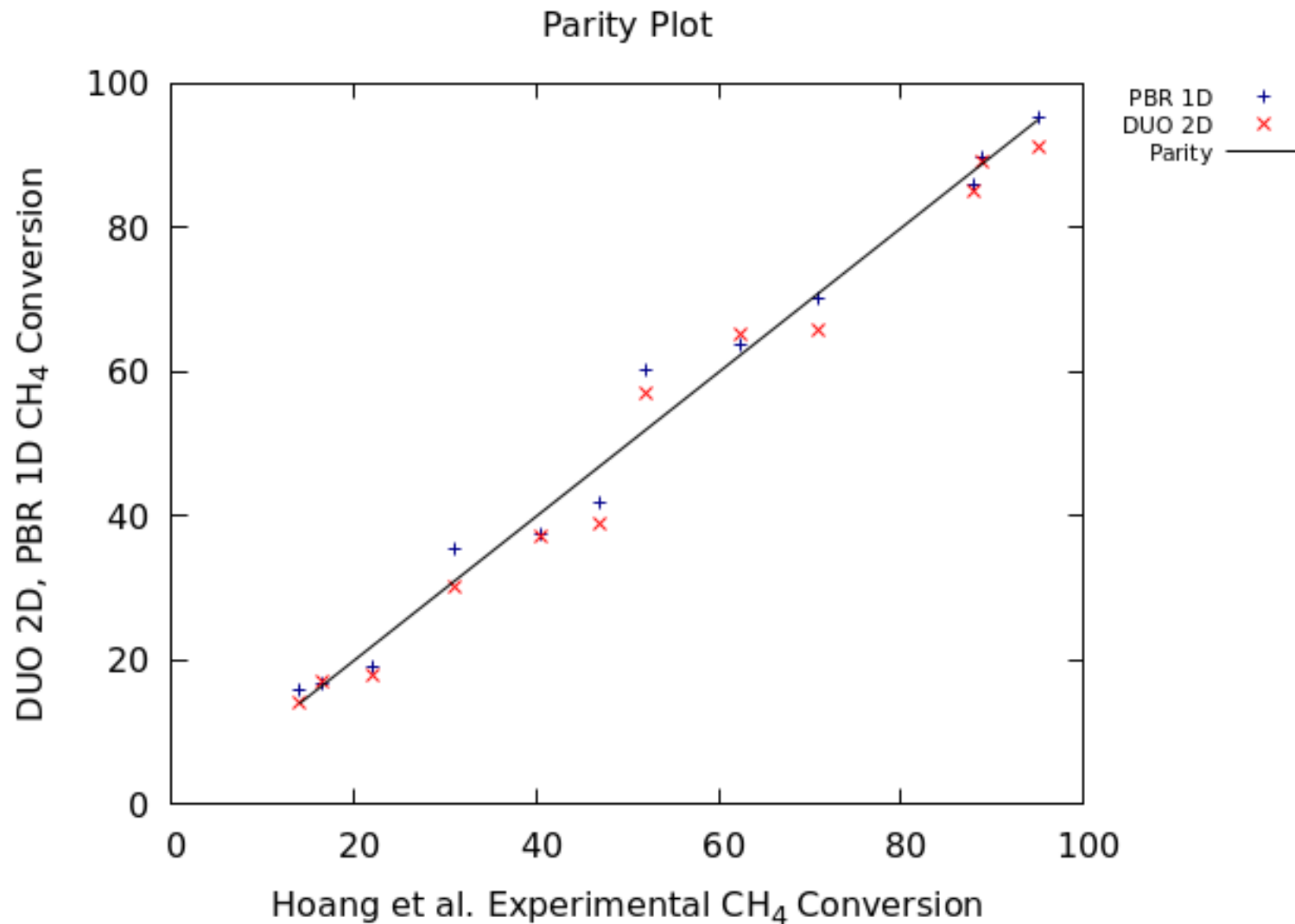
$$K_{e3} = K_{e1} K_{e2}$$



# Radial temperature gradients are $> 200^{\circ}\text{C}$

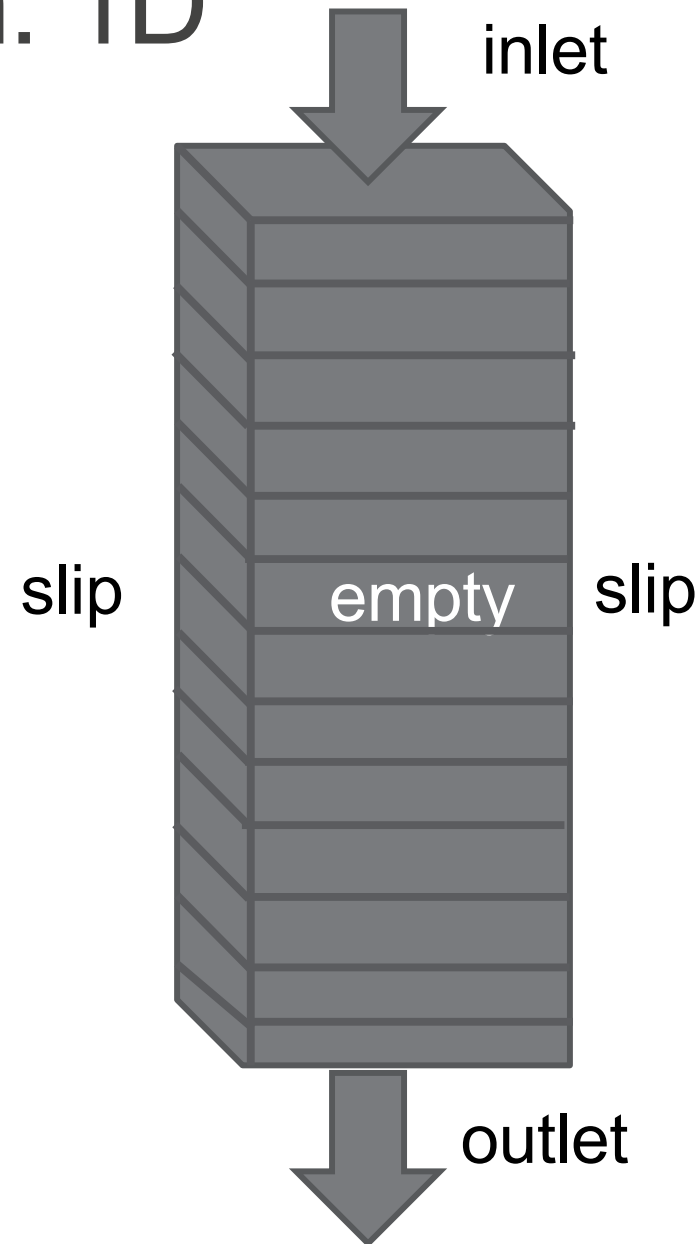


# Parity plot: Porous media vs. Expt.



# 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

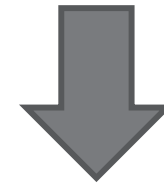




# 1D Packed Bed Reactor

*Energy balance with overall heat transfer coefficient term*

$$\begin{aligned} & \nabla \cdot (\rho \cdot u \cdot h_{s,t}) - \nabla \cdot (\alpha_{eff} \cdot \nabla h_s) \\ = & \frac{\partial p}{\partial t} - \sum_i^n h_i^o \cdot R_i - \nabla \cdot \sum_i^n h_i \cdot ((\vec{j}_i + \rho \cdot Y_i \cdot u_c) + \alpha_{eff} \cdot \nabla Y_i)) + U \frac{4}{d_t} (T - T_w) \end{aligned}$$



EEqn.H

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

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

*Many correlations are involved... including...*

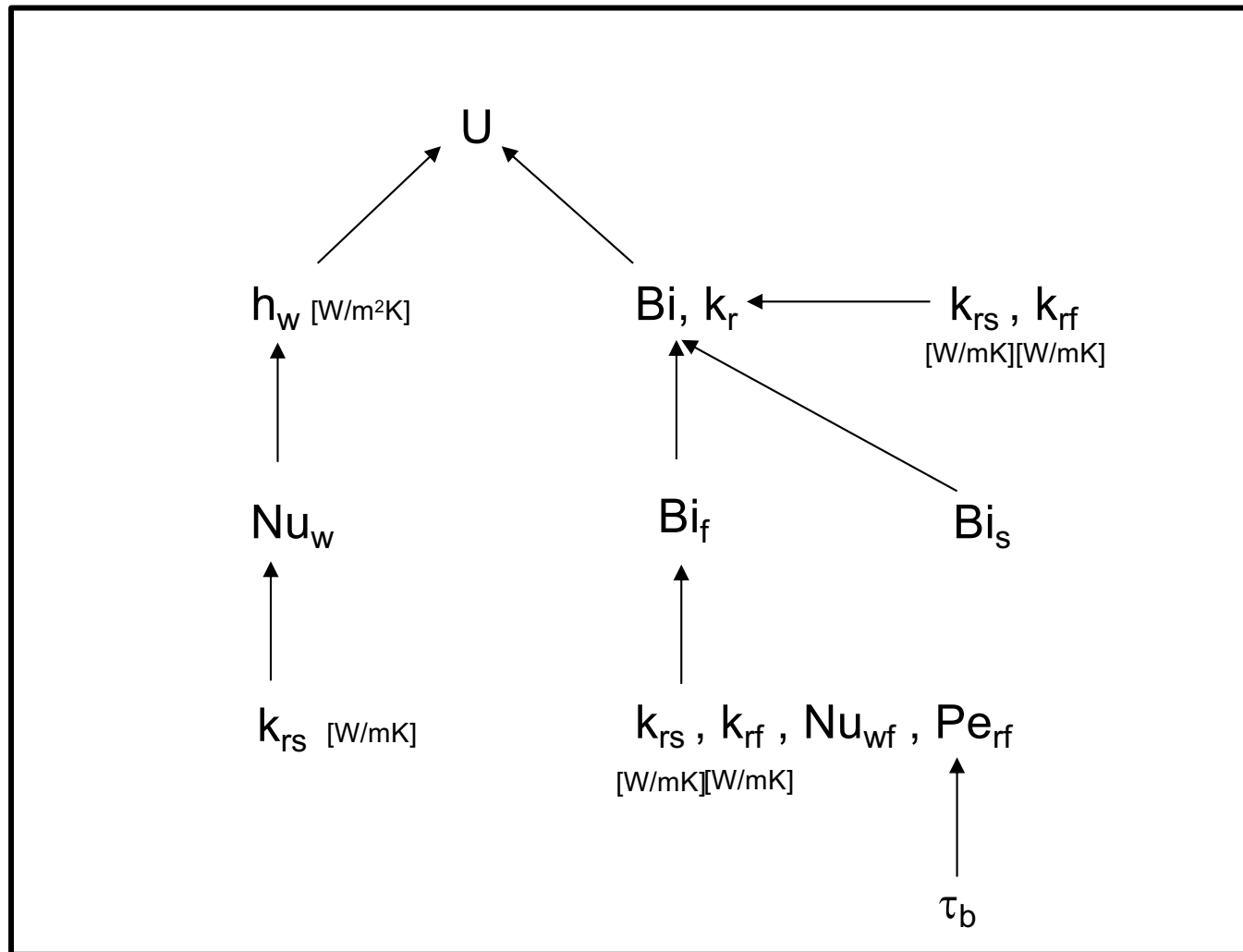
$$\frac{1}{U} = \frac{1}{h_w} + \frac{R_t}{3k_{eff}} \frac{Bi+3}{Bi+4}$$

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)

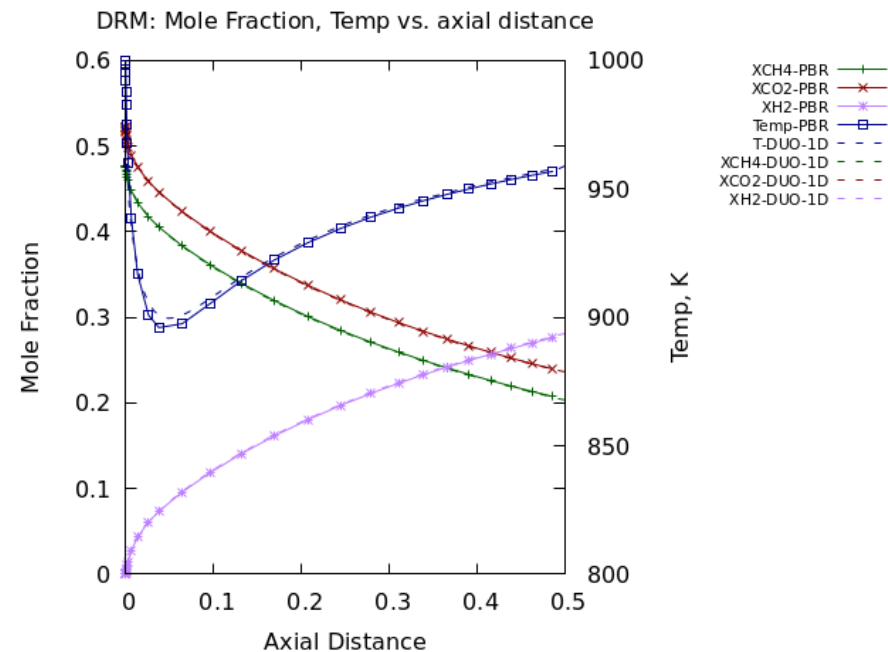
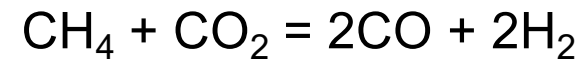
# Additional Equations



# Validation test: 1D DUO vs 1D DETCHEM<sup>PBR</sup>

## Dry Reforming of Methane

- Microkinetic surface model
- 1D DUO vs 1D DETCHEM<sup>PBR</sup>
- Perfect match with DETCHEM<sup>PBR</sup>

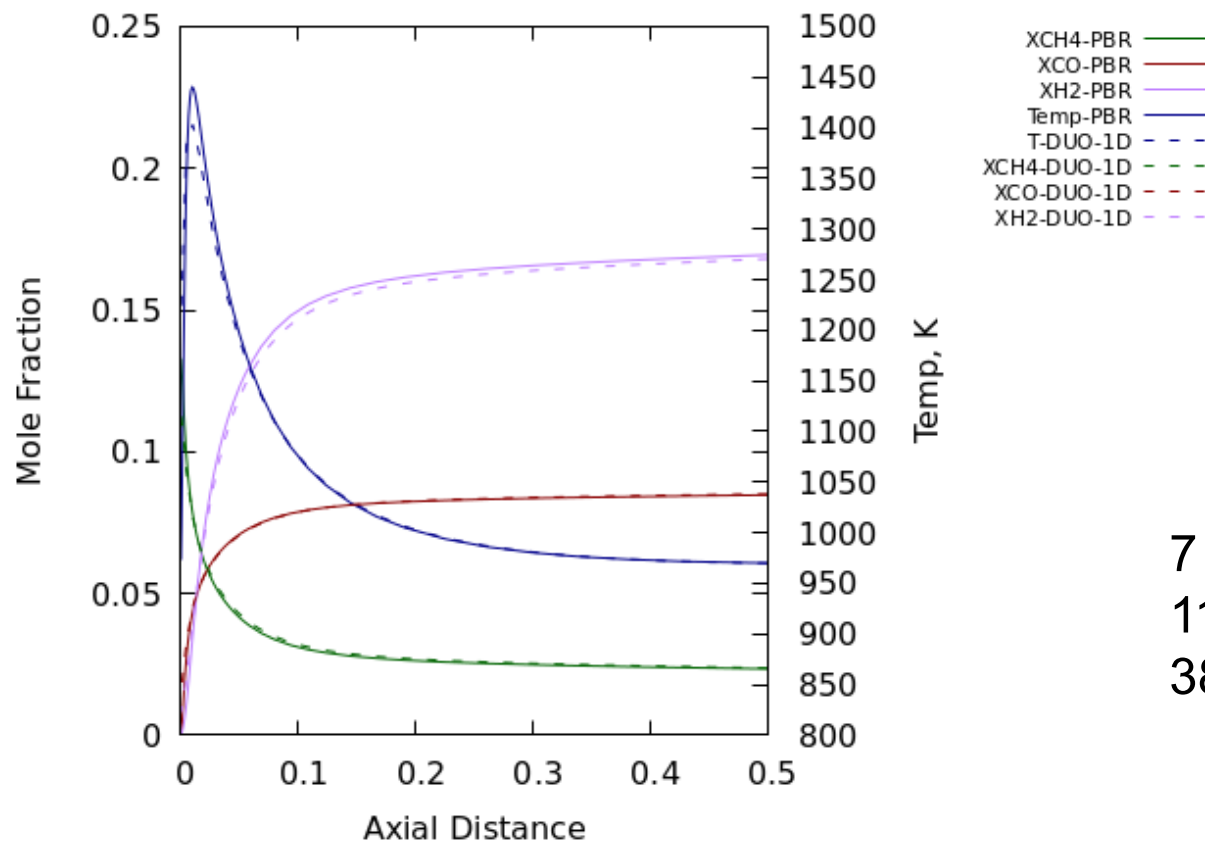
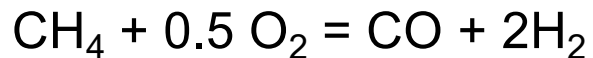


6 gas phase species  
 13 surface species  
 52 surface reactions  
 (200 cells)



# Validation test: 1D DUO vs 1D DETCHEM<sup>PBR</sup>

## Catalytic Partial Oxidation of Methane



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 <b>seconds</b> to <b>minutes</b>



# 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 Warmlleitung in durchstromten Schuttingsrohren. 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]/CoEff[cellI];
            }
        }
    }
}

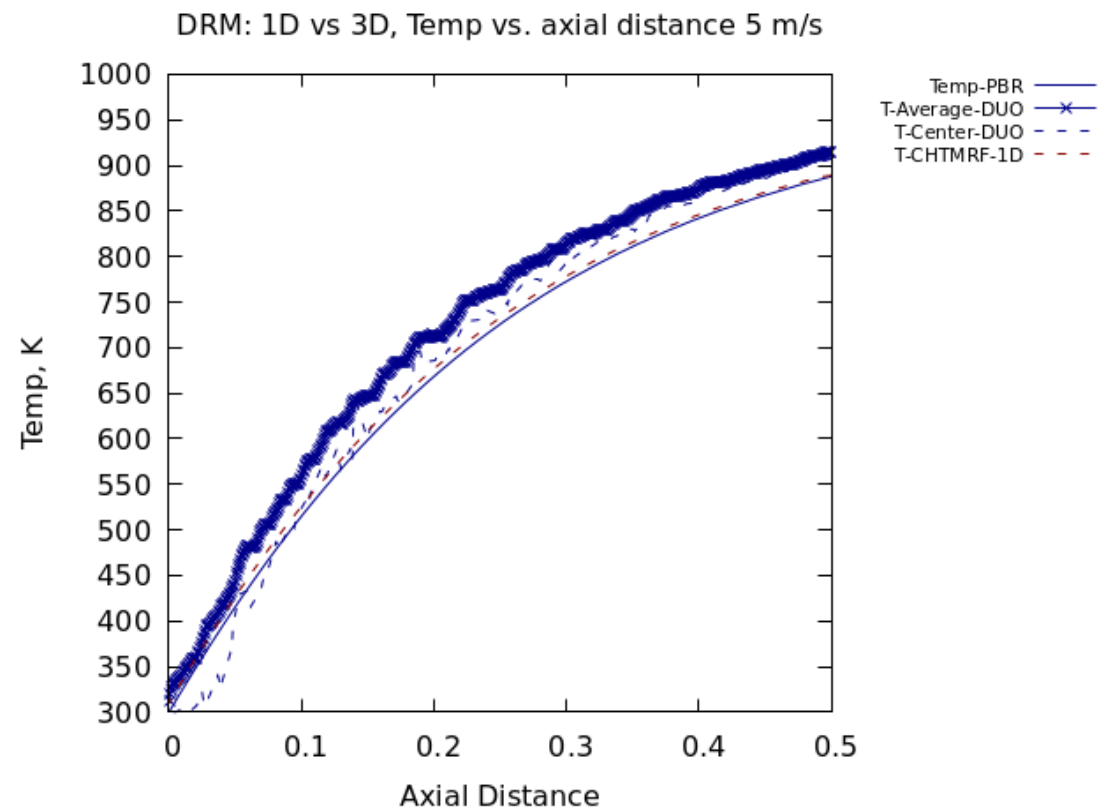
```

*heRhoThermoPorous*  
Suitable for 2D porous heat transfer

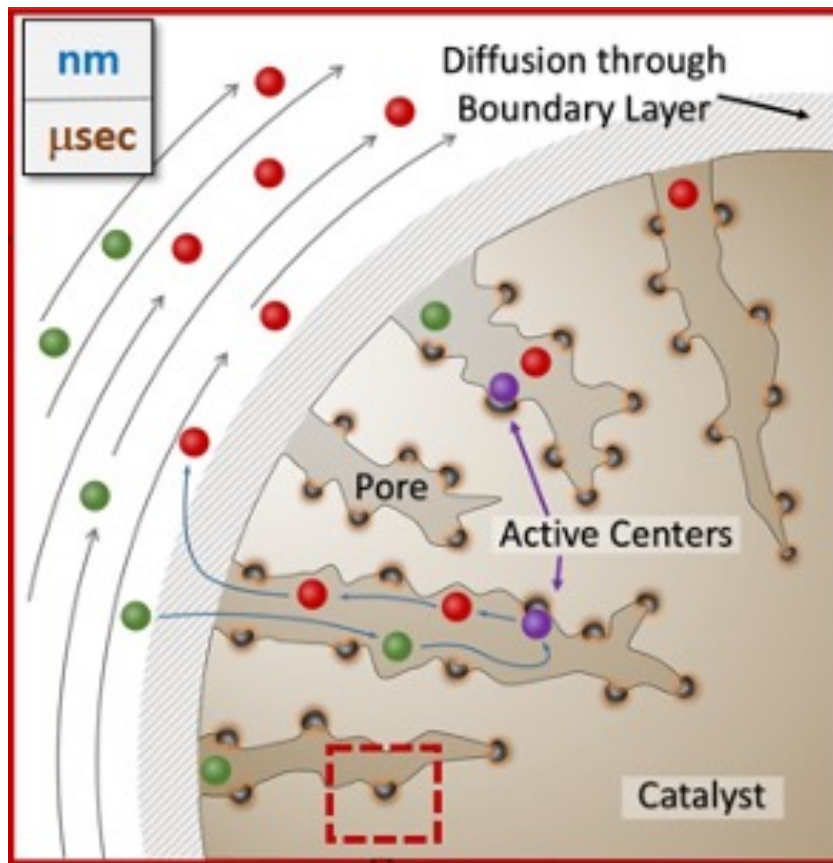
*chtMultiRegionFoam-porous1D*  
Includes overall U calculation

# Example Case

- 1D DUO
- 1D DETCHEM<sup>PBR</sup>
- 3D DUO  
(86 particles)
- Heat Transfer Only  
(DRM feed)



# Intra-particle diffusion



*courtesy of omegadot  
software & consulting*

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

$$\eta = \frac{\tan(\phi)}{\phi} \quad \phi = L \sqrt{\frac{k}{D_{eff,i}}}$$

2. Solve reaction diffusion equation

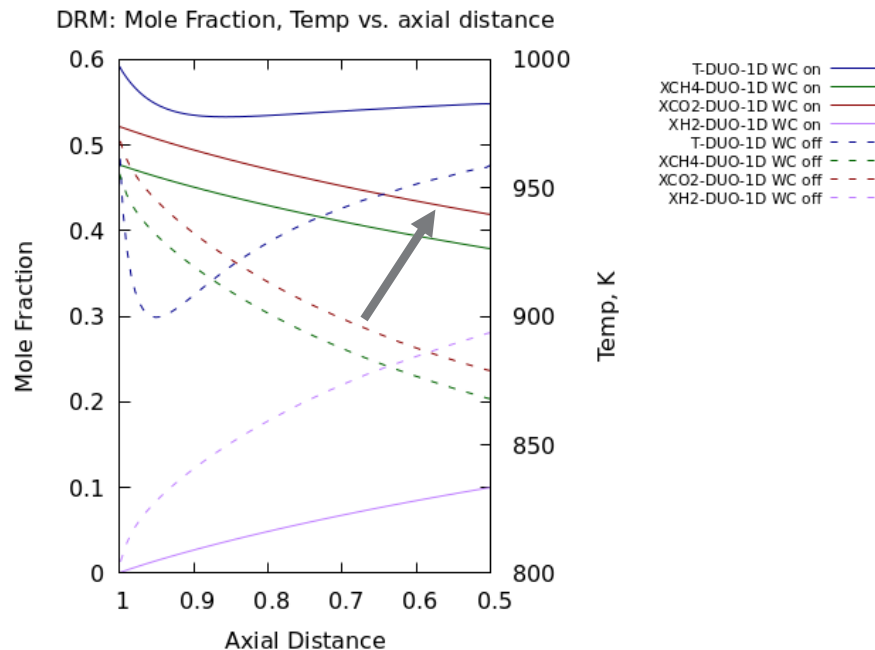
$$-\nabla \cdot (\rho \cdot D_{i,m} \cdot \nabla Y_i) = R_i$$





# Dry Reforming

## Pore Diffusion Effect



- thickness =  $d_p/2 = 6.325$  mm
- internal porosity = 0.5
- tortuosity = 3
- pore diameter =  $1 \mu\text{m}$

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
- Transient calculations
- Wide range of numerical options

## 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  $\rightarrow$  2D  $\rightarrow$  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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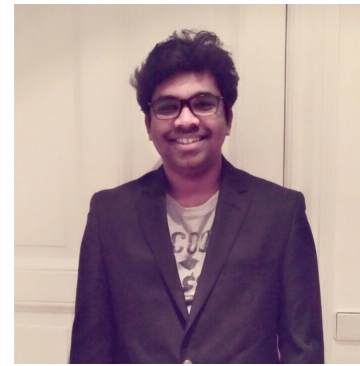
Twitter: @TonkomoLLC



Lee Tonkovich



Matthias Hettel



Akash Shirsath

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

