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

18th OpenFOAM Workshop (Genoa, Italy, 2023)

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Tonkomo, LLC

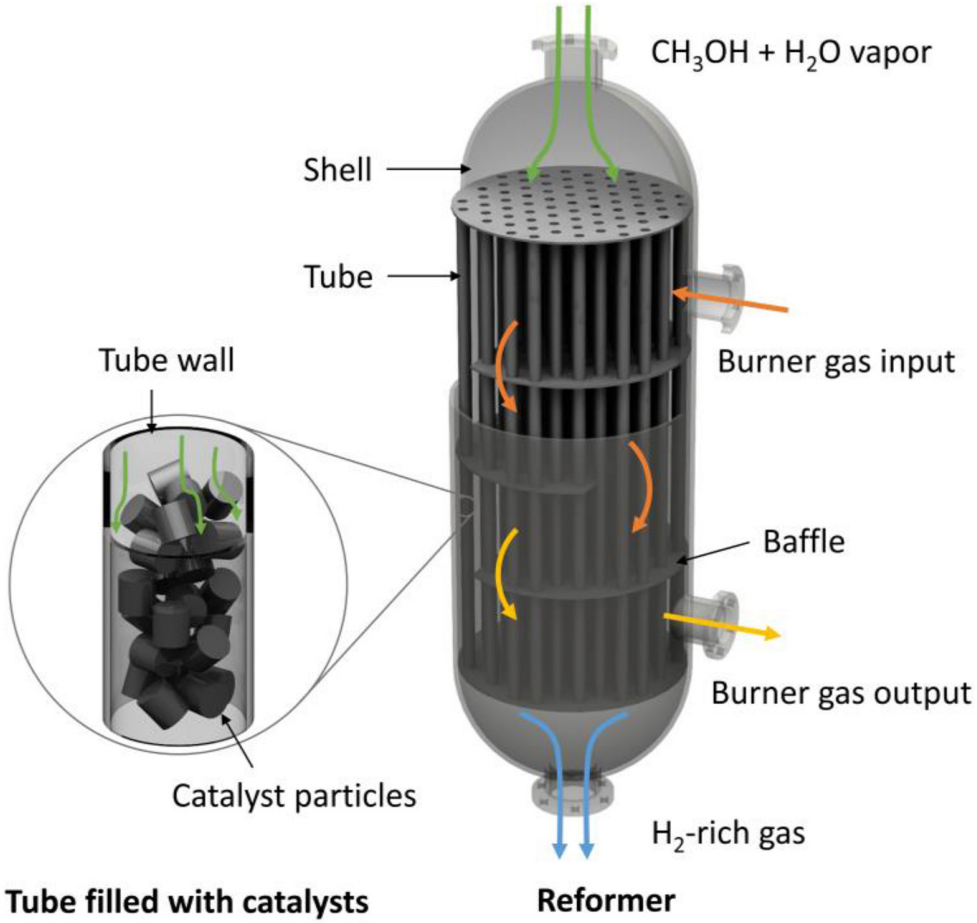
- **Owners:** Lee Tonkovich, PhD & Eric Daymo, PE
  - Reaction engineering expertise with 30+ years of experience (>150 patents)
  - Co-founders of Velocys (microchannel reactors)
  - Experienced with algal bioreactors (Heliae)
  - Now, owners of a small business dedicated to developing innovative solutions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

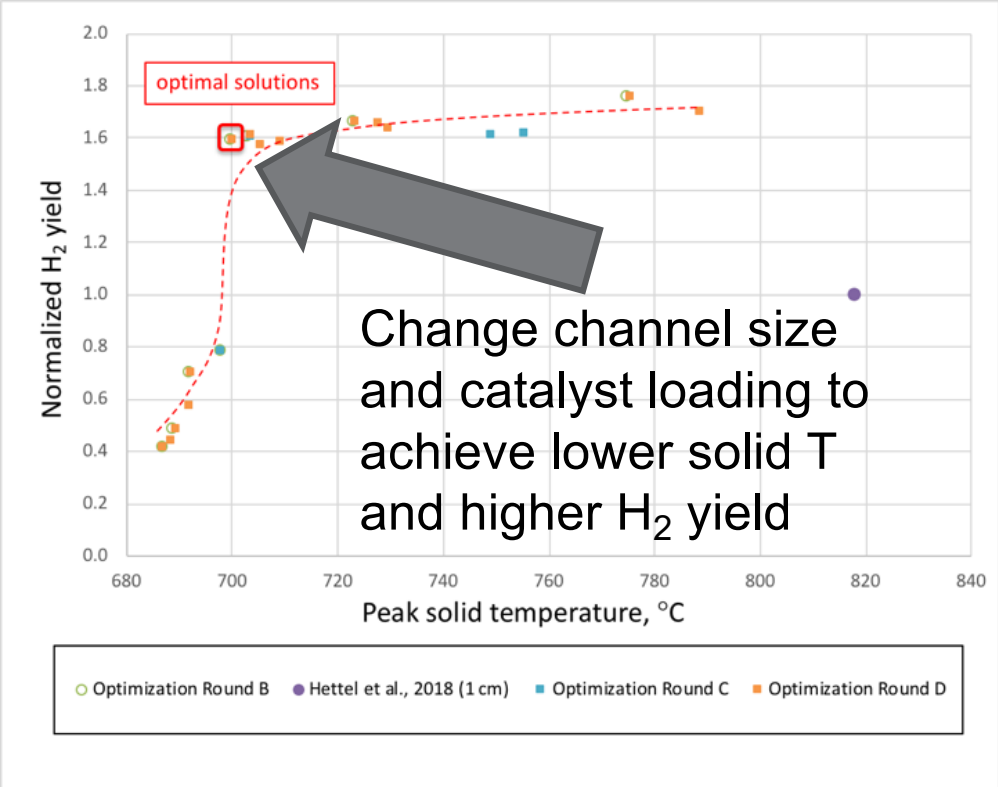
- DETCHEM stands for DETailed CHEMistry
  - Software package for reacting flow simulation
  - www.detchem.com

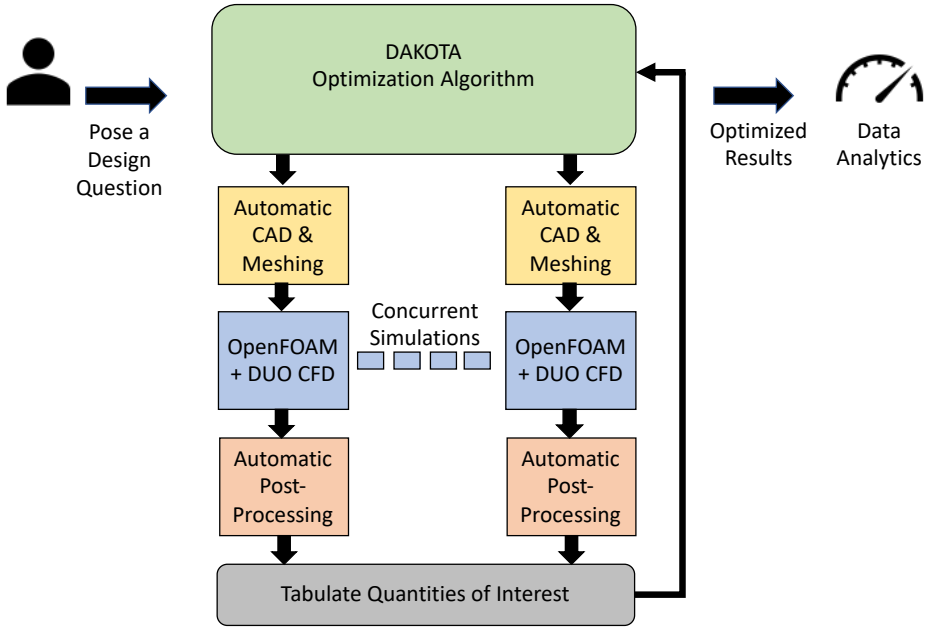
  Reference: Deutschmann et al. 2022

- 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

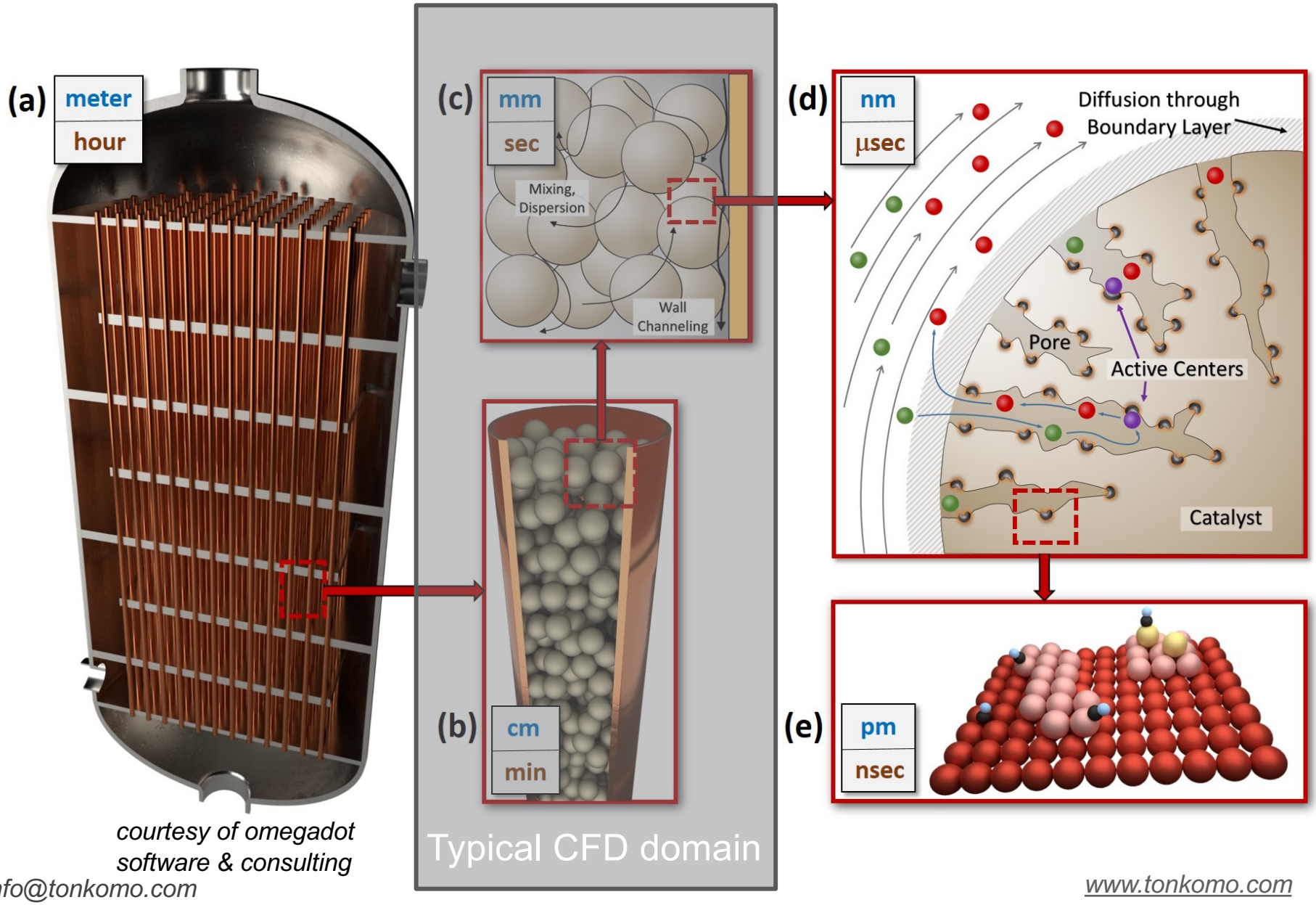




Optimization: often 10,000's of cases run … need fast results

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

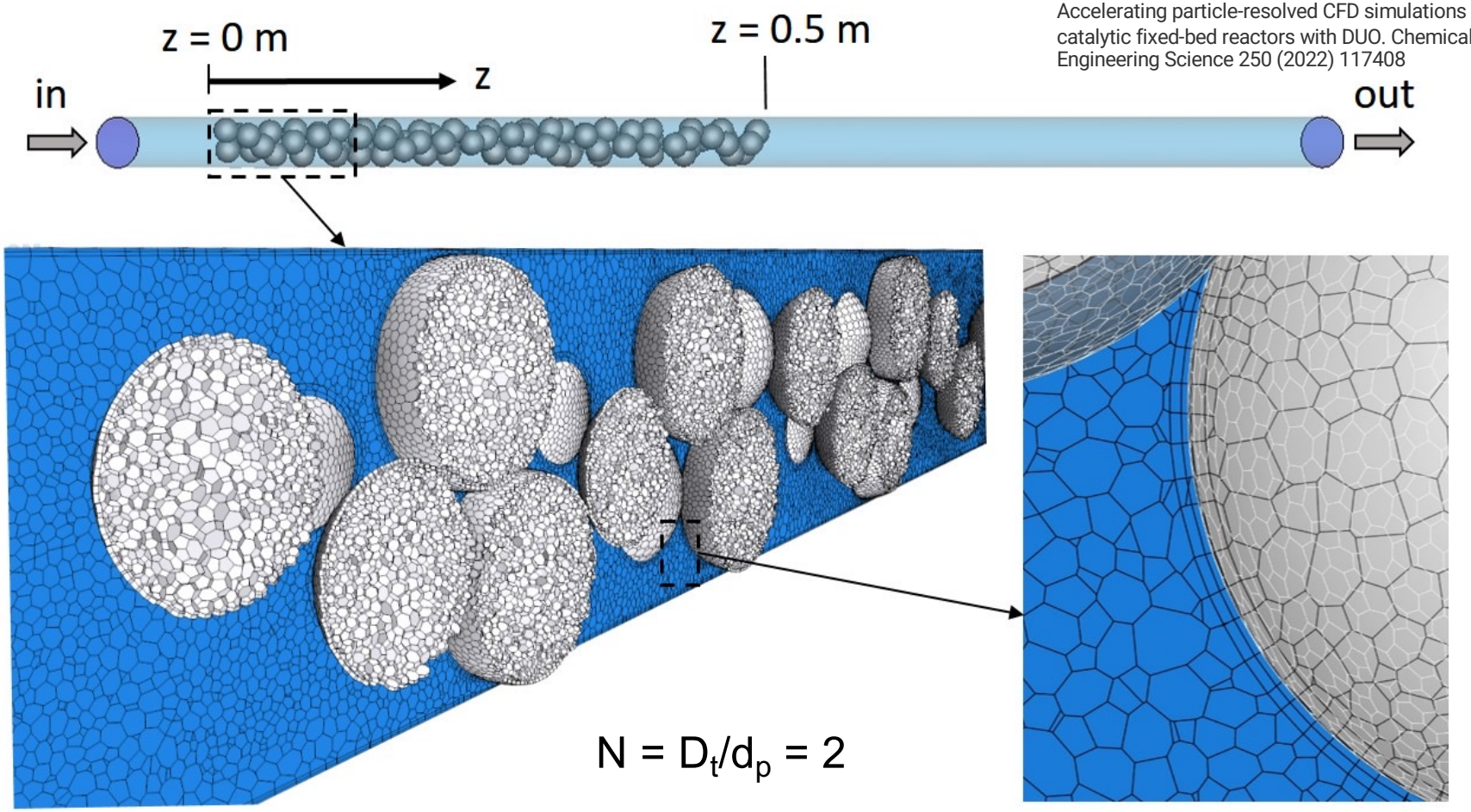


courtesy of omegadot software & consulting

info@tonkomo.com

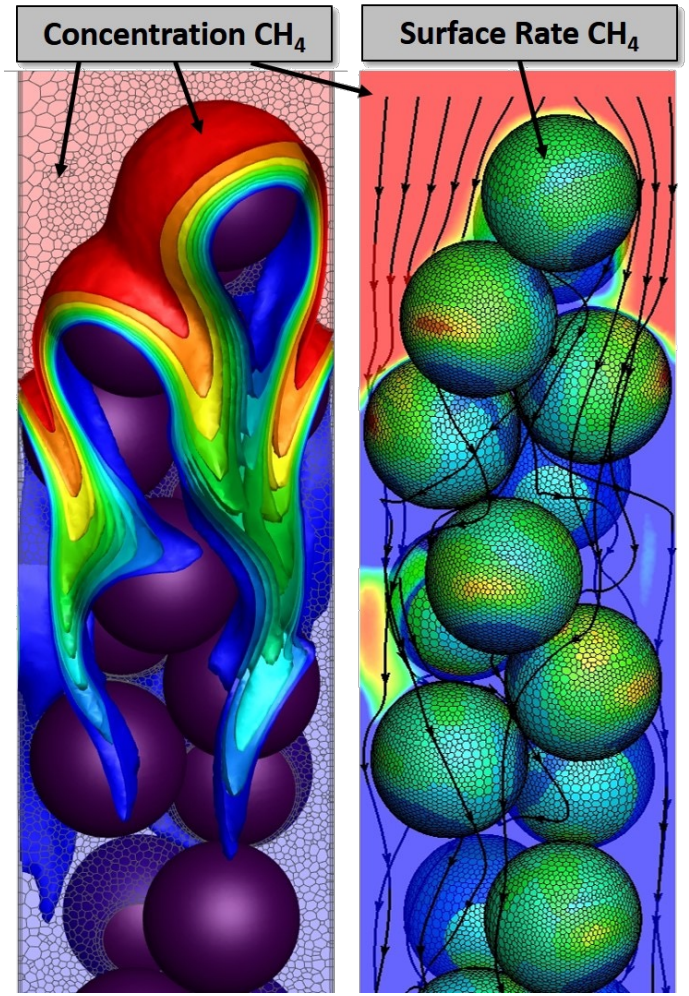
Particle Resolved CFD (PRCFD)

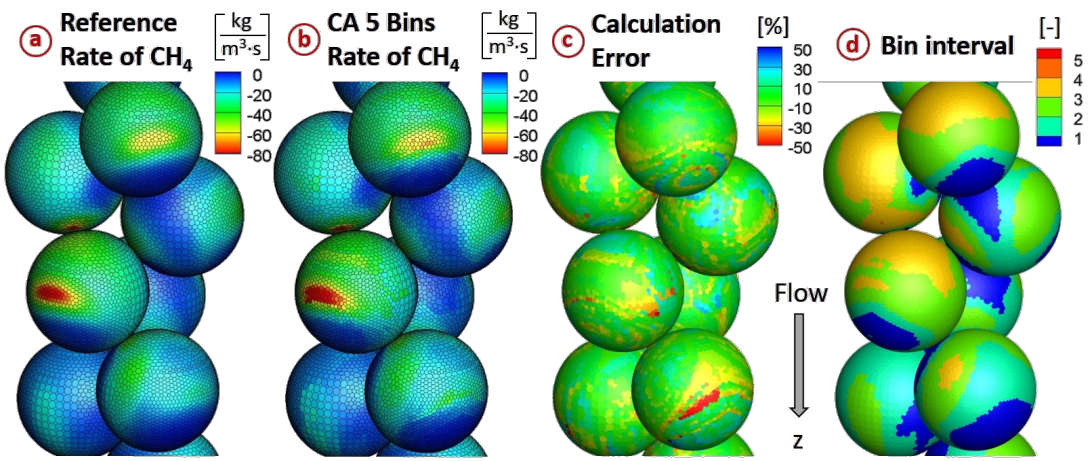
Daymo, E., Hettel, M., Deutschmann, O., Wehinger, G. Accelerating particle-resolved CFD simulations of catalytic fixed-bed reactors with DUO. Chemical Engineering Science 250 (2022) 117408



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

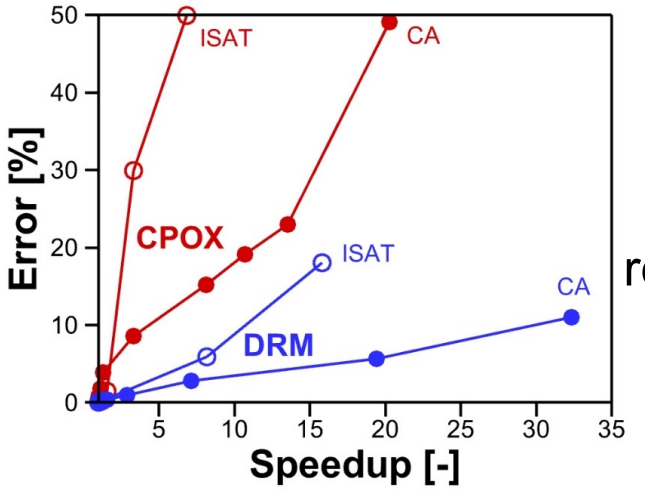
Particle resolved CFD





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

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

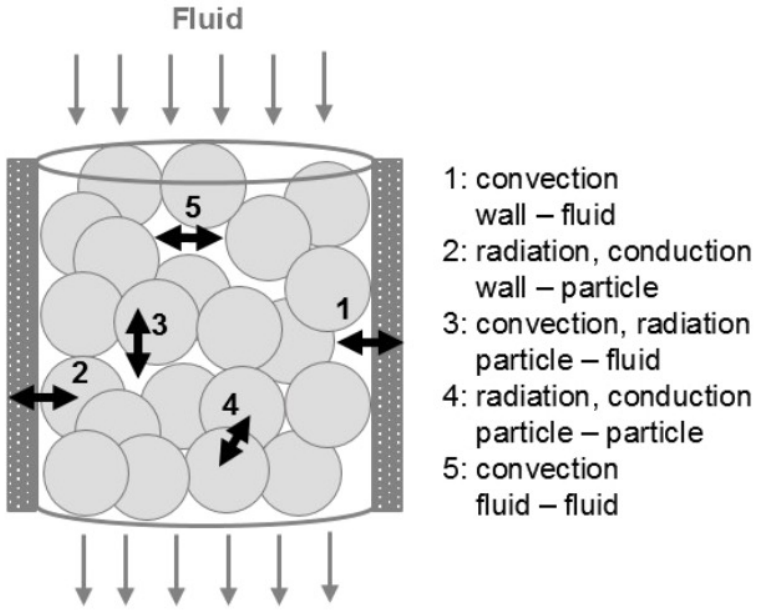


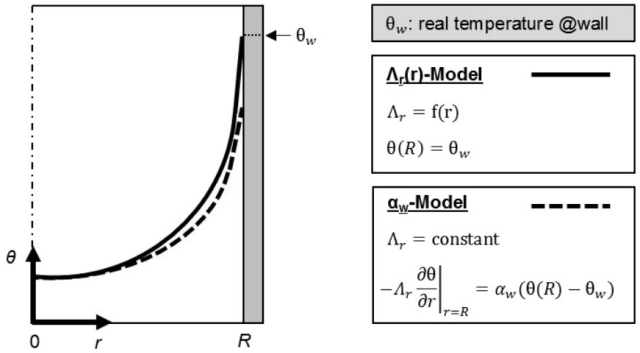
Figure 1. Heat transport mechanisms in fixed-bed reactors through which gas flows (modified according to [4]).

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

- 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

Continuum Model Options:
Fixed Bed Reactor Modeling

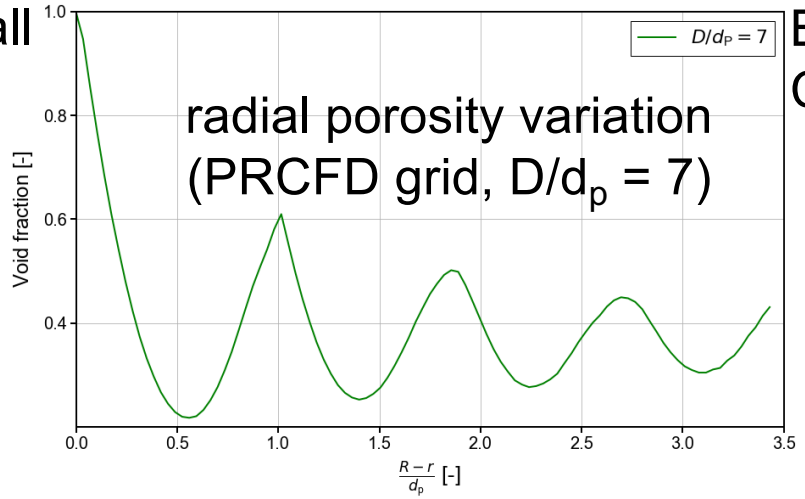
results presented here use the α_w model



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

- α_w model
  - BC T(r=R) ≠ T_{wall}
  - ε(r) = constant
  - $u(r) = u_{superficial}$

Wall



Bed Center

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

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, $\alpha_{eff} = \frac{k_{eff}}{Cp_{eff}}$ $\quad k_{eff} = k_{rf} + k_{rs}$ $\quad Cp_{eff} = \frac{C\rho_f\rho_f\varepsilon + (1-\varepsilon)C\rho_s\rho_s}{\rho_f\varepsilon + (1-\varepsilon)\rho_s}$

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

Solid

Zehner and Schlünder (1978)

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

Fluid

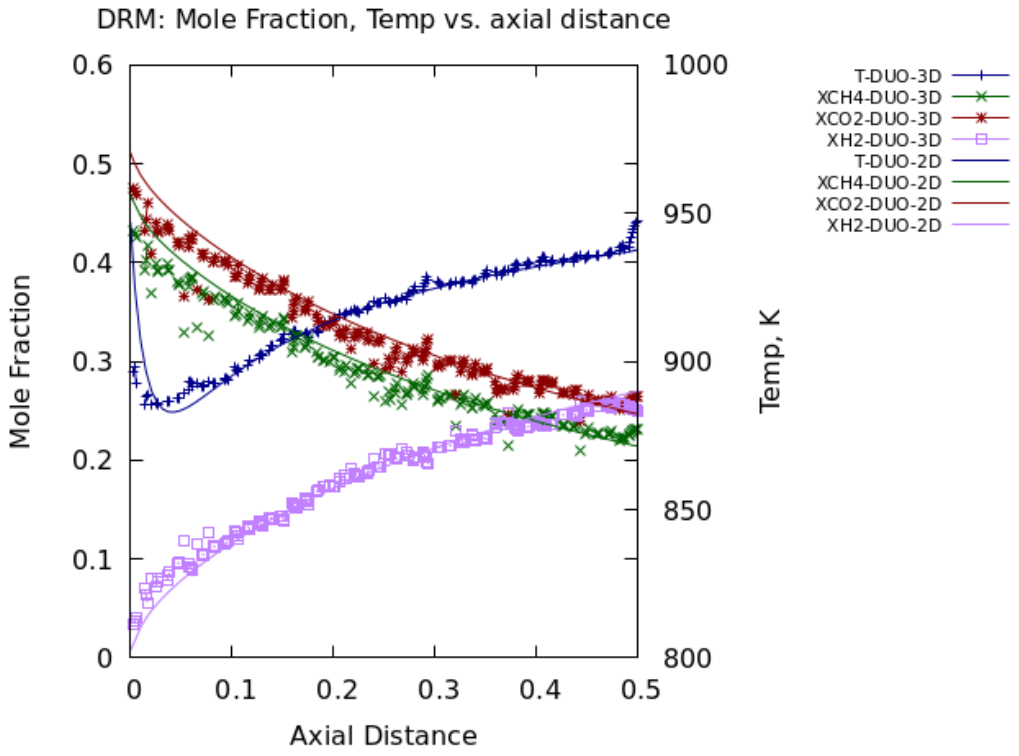
Specchia et al. (1980)

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…*



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

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

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

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

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

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

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

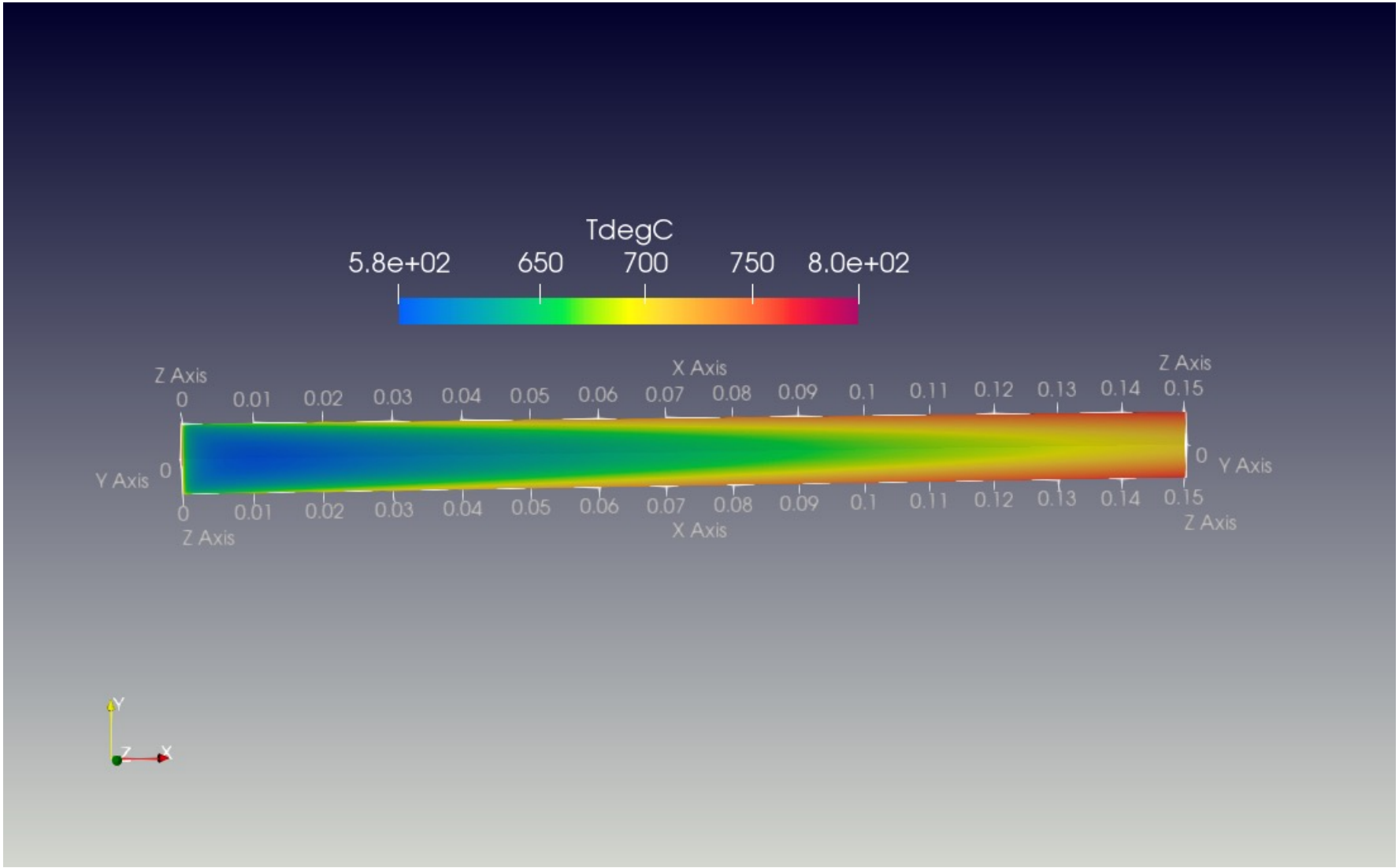
$$K_{e_1} = e^{\left(\frac{-26830}{T}+30.114\right)}$$

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

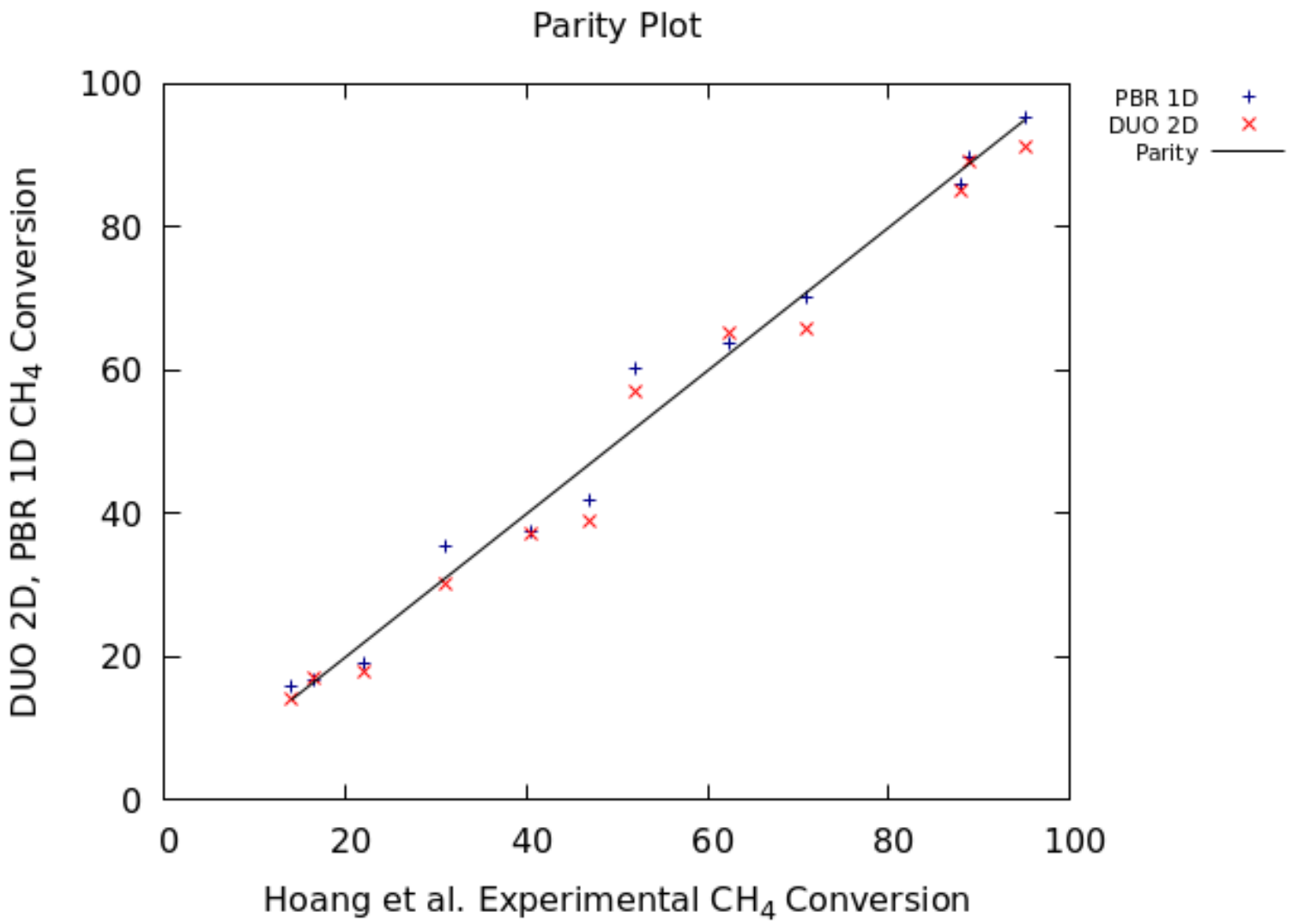
$$K_{e_2} = e^{\left(\frac{4400}{T}-4.036\right)}$$

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

Radial temperature gradients are > 200°C

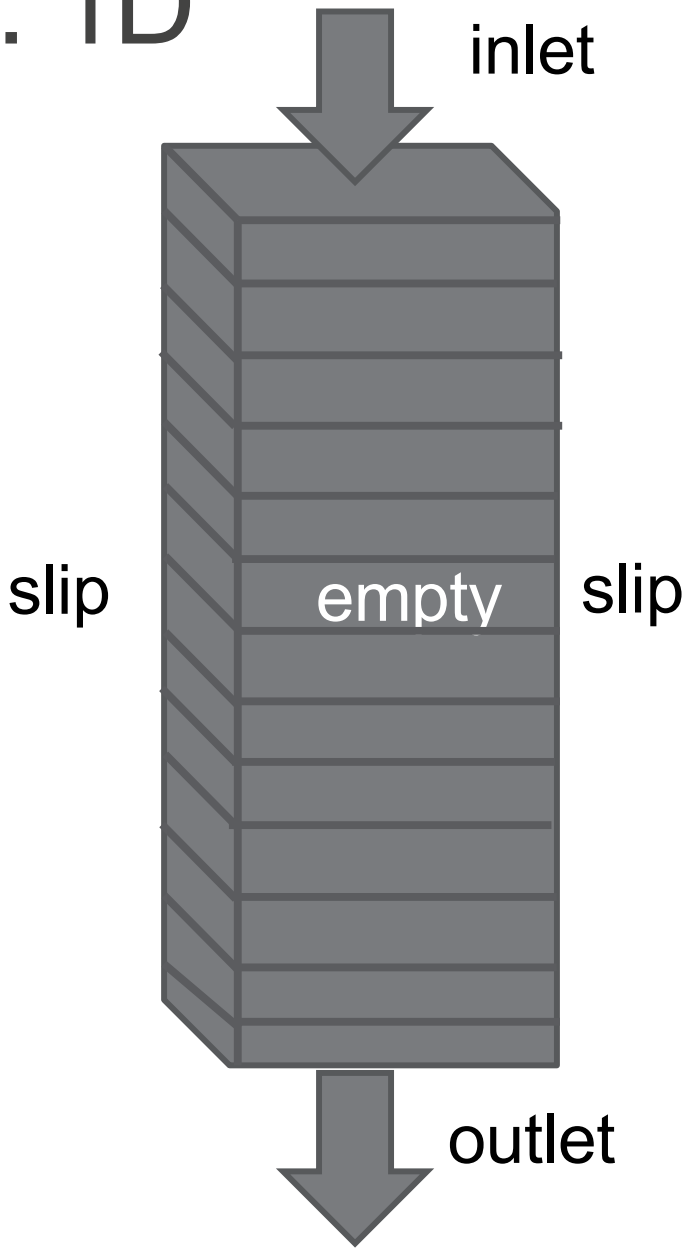


Parity plot: Porous media vs. Expt.



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



1D Packed Bed Reactor

Energy balance with overall heat transfer coefficient term

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

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

EEqn.H

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

T_w = wall temperature
d_t = tube diameter

Many correlations are involved… including…

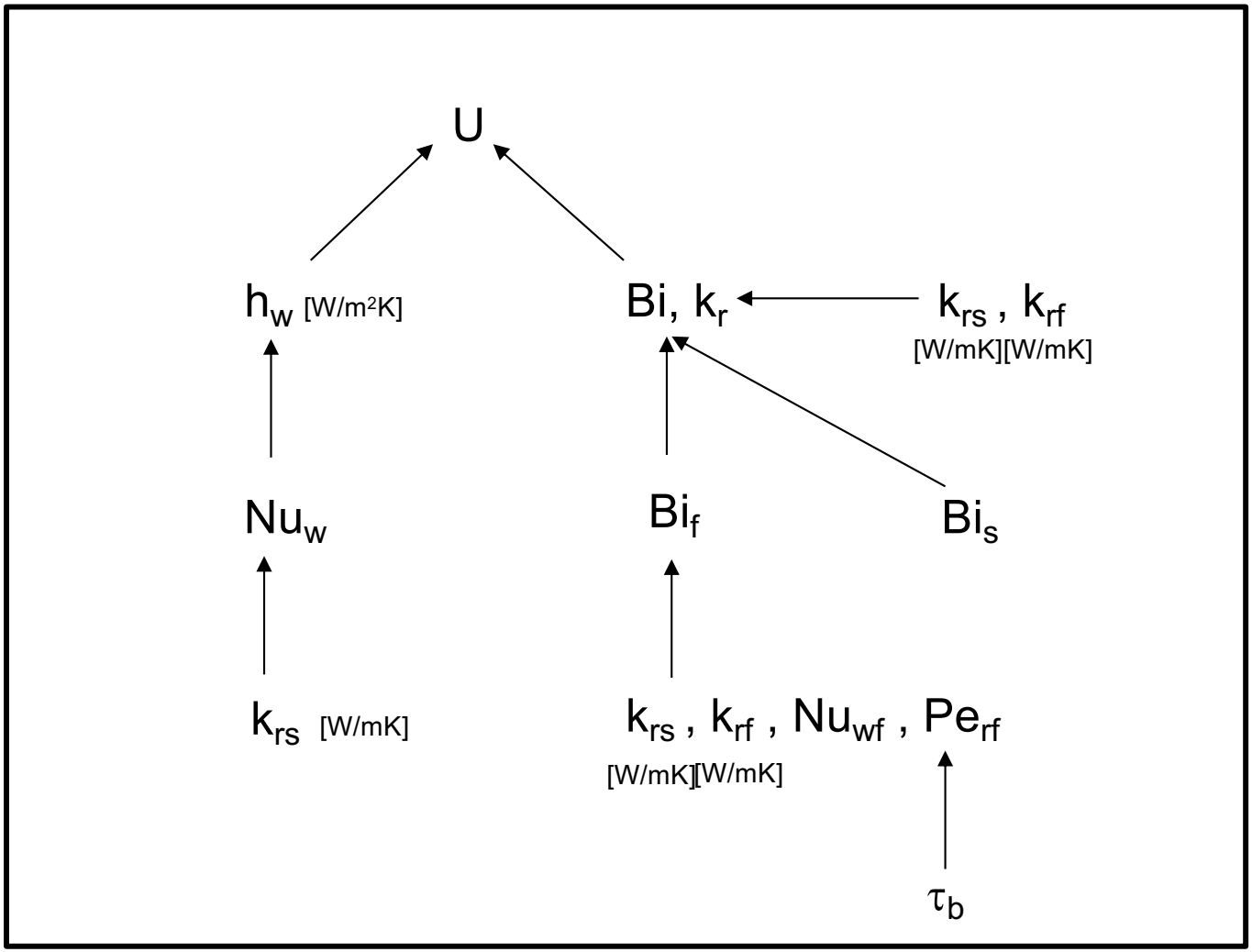
$$\frac{1}{U} = \frac{1}{h_w} + \frac{R_t}{3k_{eff}} \frac{Bi+3}{Bi+4}$$

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)

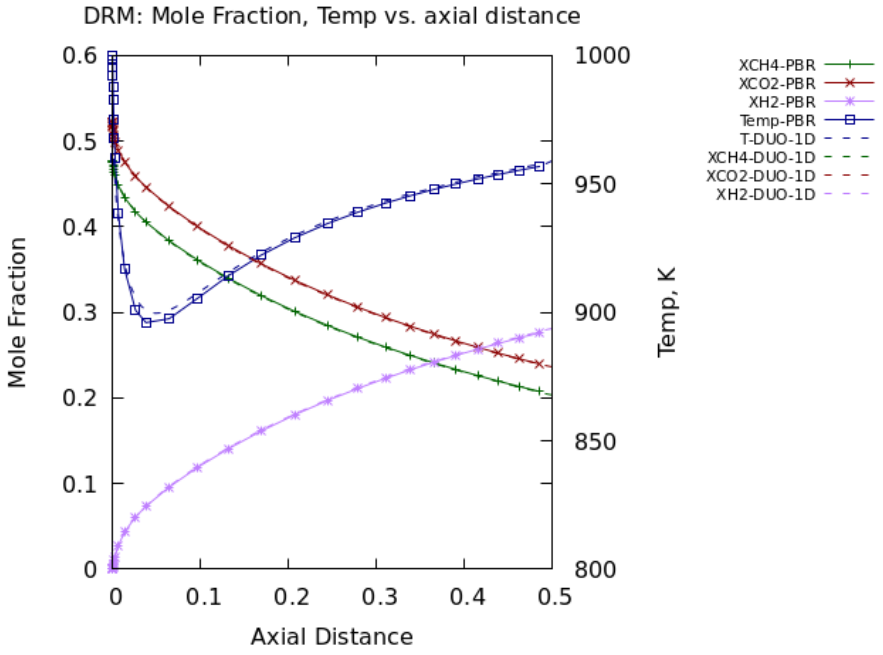
Additional Equations



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

- Microkinetic surface model
- 1D DUO vs 1D DETCHEM^{PBR}
- Perfect match with DETCHEM^{PBR}

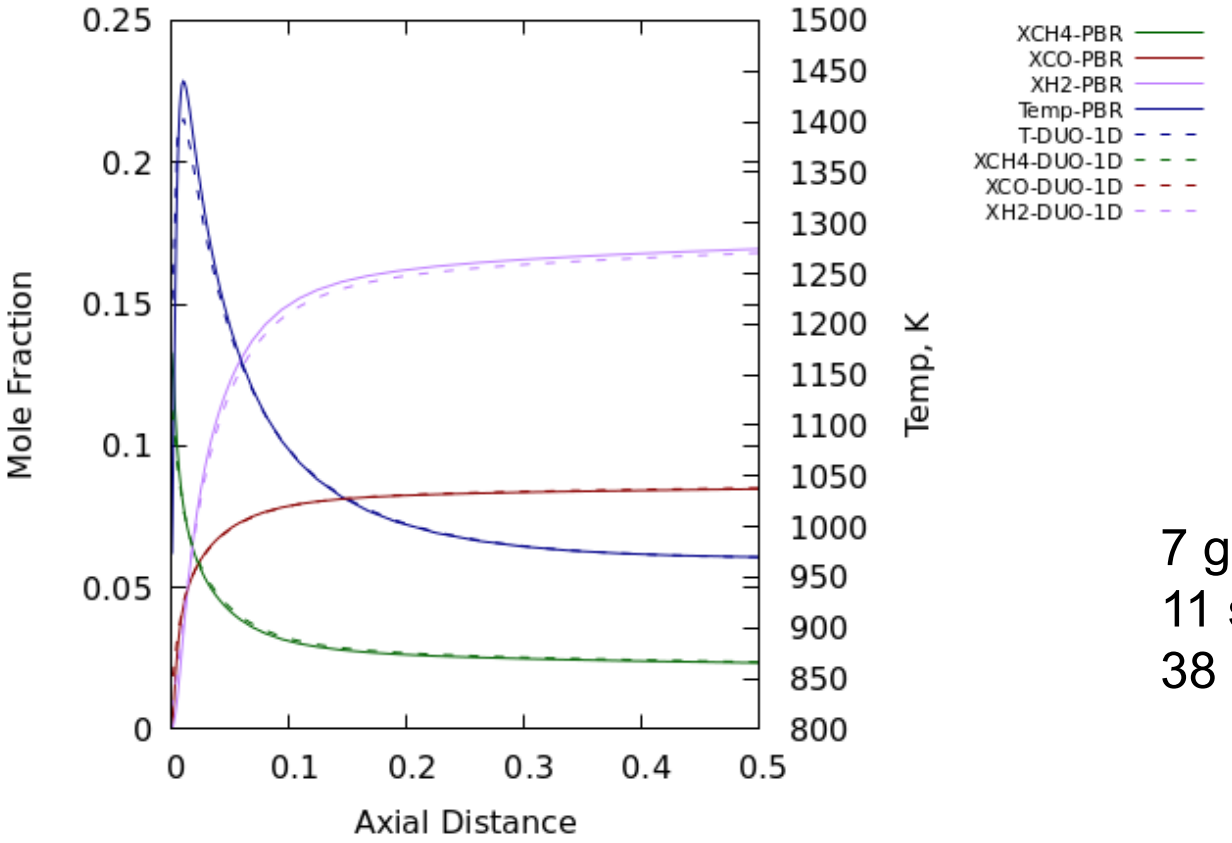
$CH_4 + CO_2 = 2CO + 2H_2$



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;
    }
}
```

heRhoThermoPorous

Suitable for 2D porous heat transfer

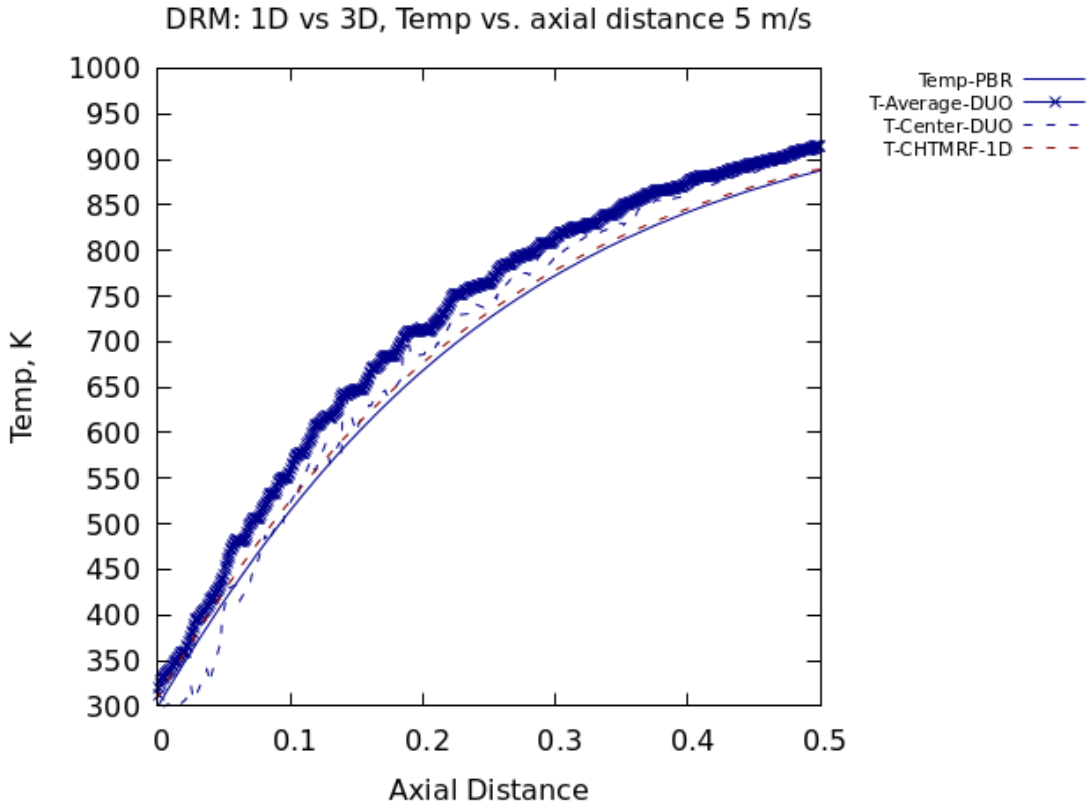
```
kappaEffSolid.correctBoundaryConditions();
kappaEff.correctBoundaryConditions();

// 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];
```

chtMultiRegionFoam-porous1D

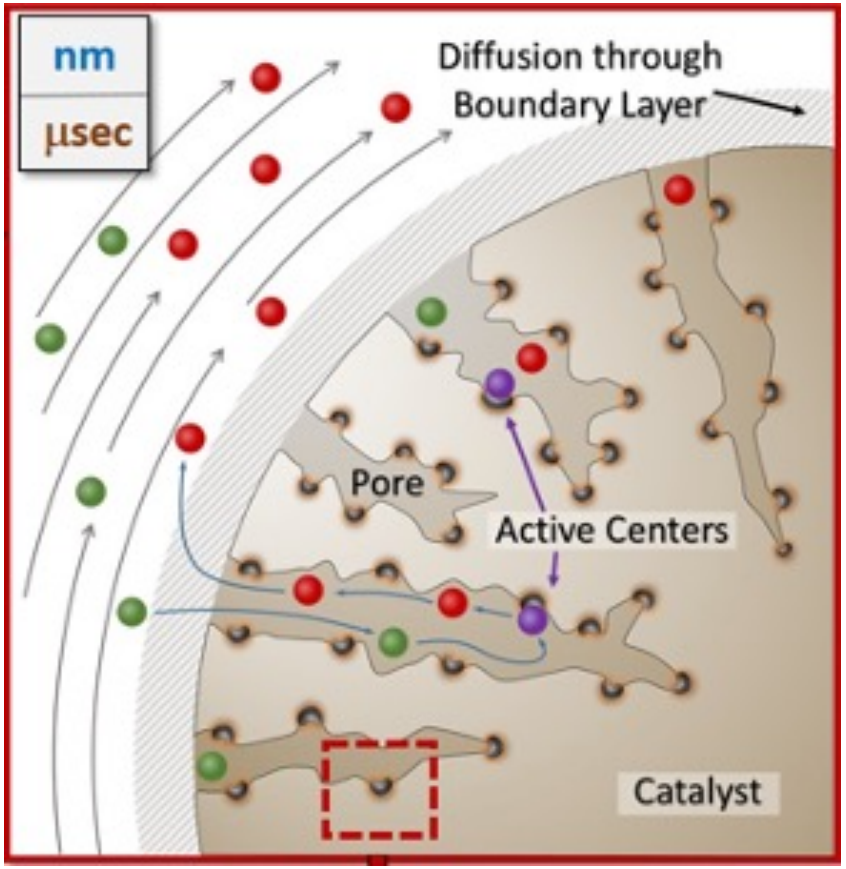
Includes overall U calculation

Example Case

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



Intra-particle diffusion



courtesy of omegadot software & consulting

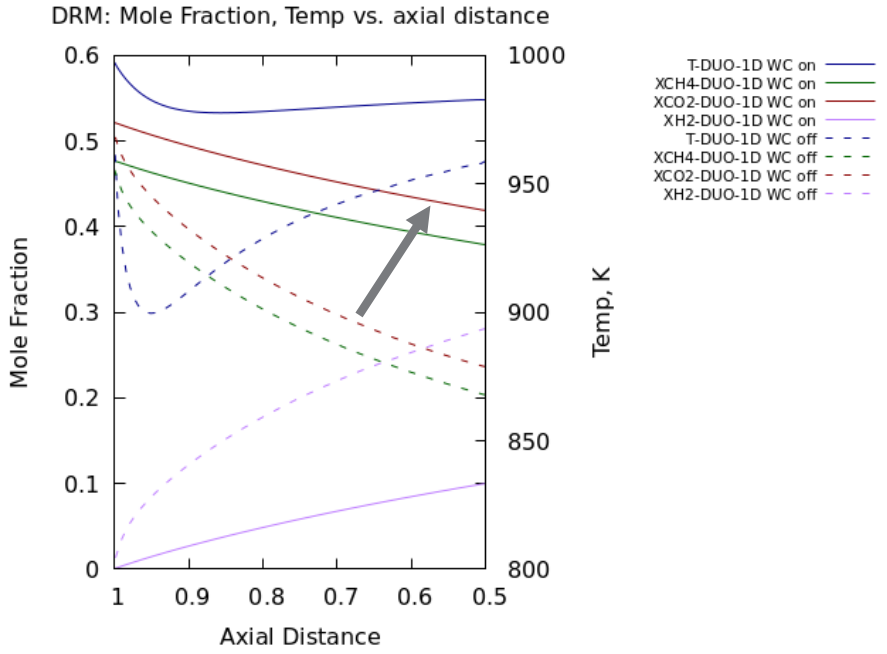
- DETCHEM has a built-in "washcoat Models"
  1. Solve for effectiveness factor, η

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

  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



- thickness = $d_p/2$ = 6.325 mm
- internal porosity= 0.5
- tortuosity = 3
- pore diameter = 1 μm

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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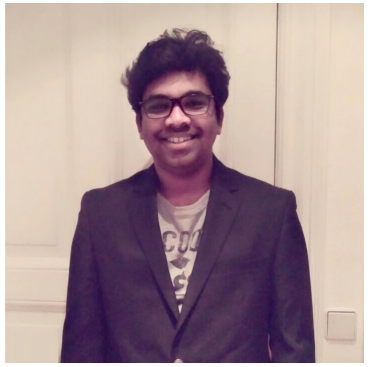

Akash Shirsath

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