CCPC
Consortium for Computational Physics and Chemistry
U.S. DEPARTMENT OF ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Importance of Conjugate Heat Transfer in Modeling of Fixed Bed Reactors for Renewable Fuels and Chemicals

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NETL Multiphase Workshop, Aug 2022

U.S. DEPARTMENT OF ENERGY

COMSOL Packed Bed Reactor Modeling in CCPC

- In 2018, CCPC embarked on a program to model fixed bed reactors for use in BETO funded projects
- COMSOL was selected as the prime modeling software
  - Workstation package, easily deployed
  - Full treatment of mass and heat transfer (MHT) at reactor scale
  - Approximate treatment of diffusion and reaction inside catalyst pellets: the *Reactive Pellet Bed*
    - Pellet interiors are represented in one dimension
    - Spherical equivalent diameters are used
    - Each grid cell can represent N_{pel} pellets. N_{pel} can be >> 1
    - Extra dimension (as opposed to particle discretization) requires some additional subgrid modeling
  - New heat transfer models in COMSOL v6.0 ranging from porous medium to more accurate packed bed model

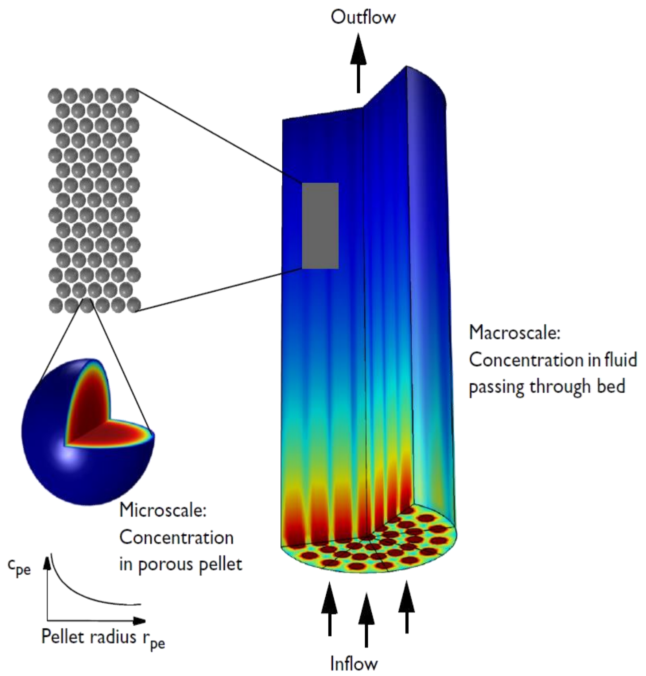
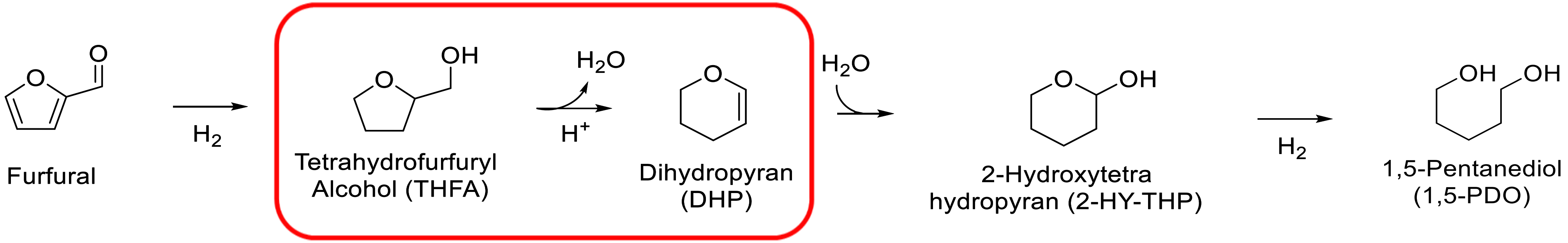


Image made using COMSOL Multiphysics® software and is provided courtesy of COMSOL

PYRAN
The 5-Carbon Company

Catalytic Upgrading of Bio-based Furfural to 1,5-Pentanediol: A New Renewable Monomer for the Coatings Industry



Fixed Bed Catalytic Reactor
Endothermic

BETO DFO Project, CRADA NFE-20-08393

Catalyxx

Guerbet Chemistry

Alcohol dehydrogenation (endothermic)

$$C_{2n}H_{4n+1}OH \rightarrow C_{2n}H_{4n}O + H_2$$

Aldol condensation (exothermic)

$$C_{2m}H_{4m+1}OH + C_{2n}H_{4n}O + H_2 \rightarrow C_{2(m+n)} H_{4(m+n)+1}OH + H_2O$$

Other reactions, including WGS

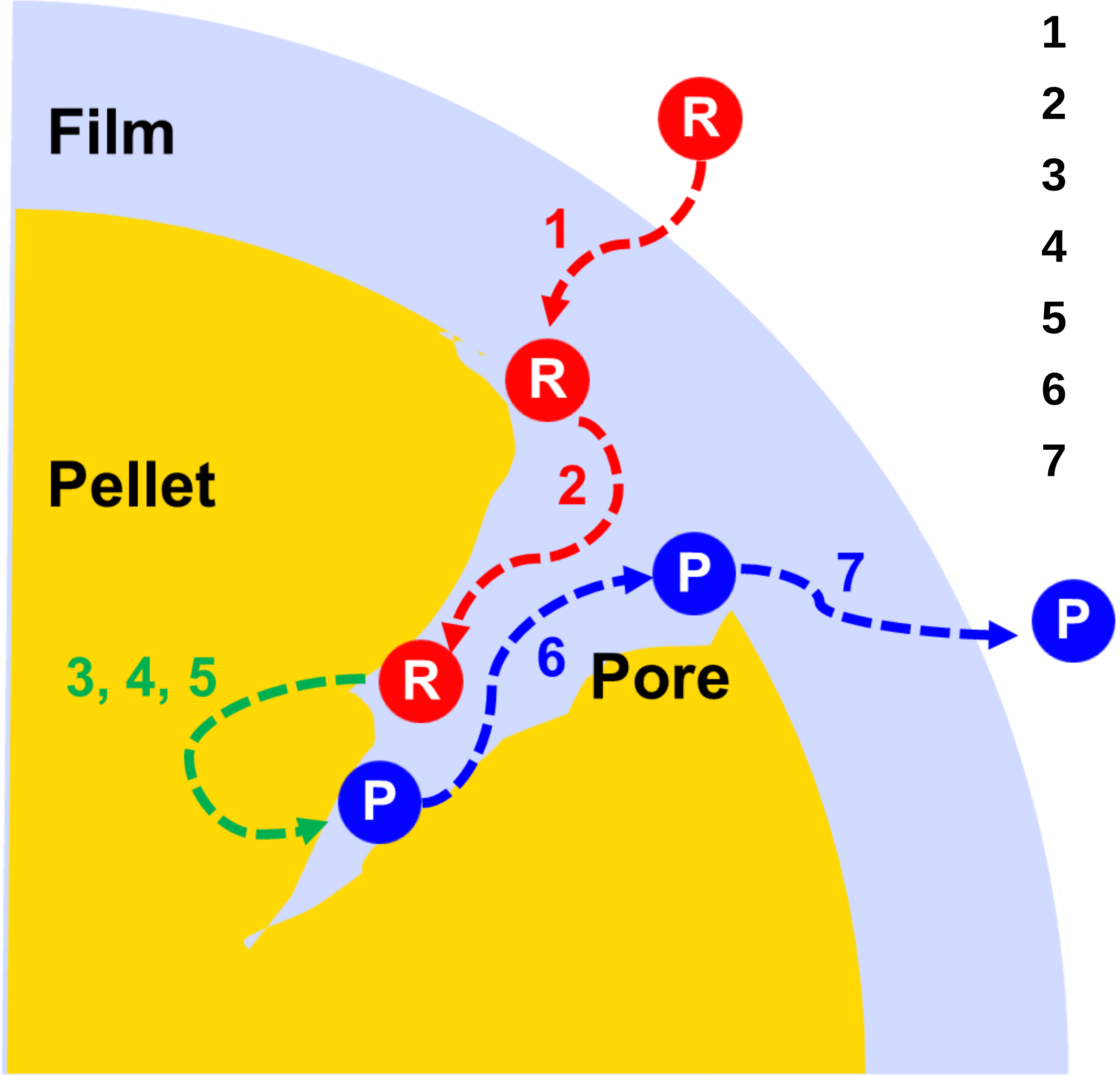
Comple, LHHW-type rate expressions

BETO DFO Project
CRADA NFE-20-08396

26 Species

1. H2
2. H2O
3. CO
4. CO2
5. Methane
6. Ethane
7. Propane
8. MeOH
9. EtOH
10. PrOH
11. BuOH
12. 2-BuOH
13. iBuOH
14. HeOH
15. OcOH
16. DeOH
17. EtBuOH
18. EtHeOH
19. Bual
20. Etal
21. EtAce
22. DodOH
23. TedOH
24. EtOcOH
25. EtDeOH
26. N2

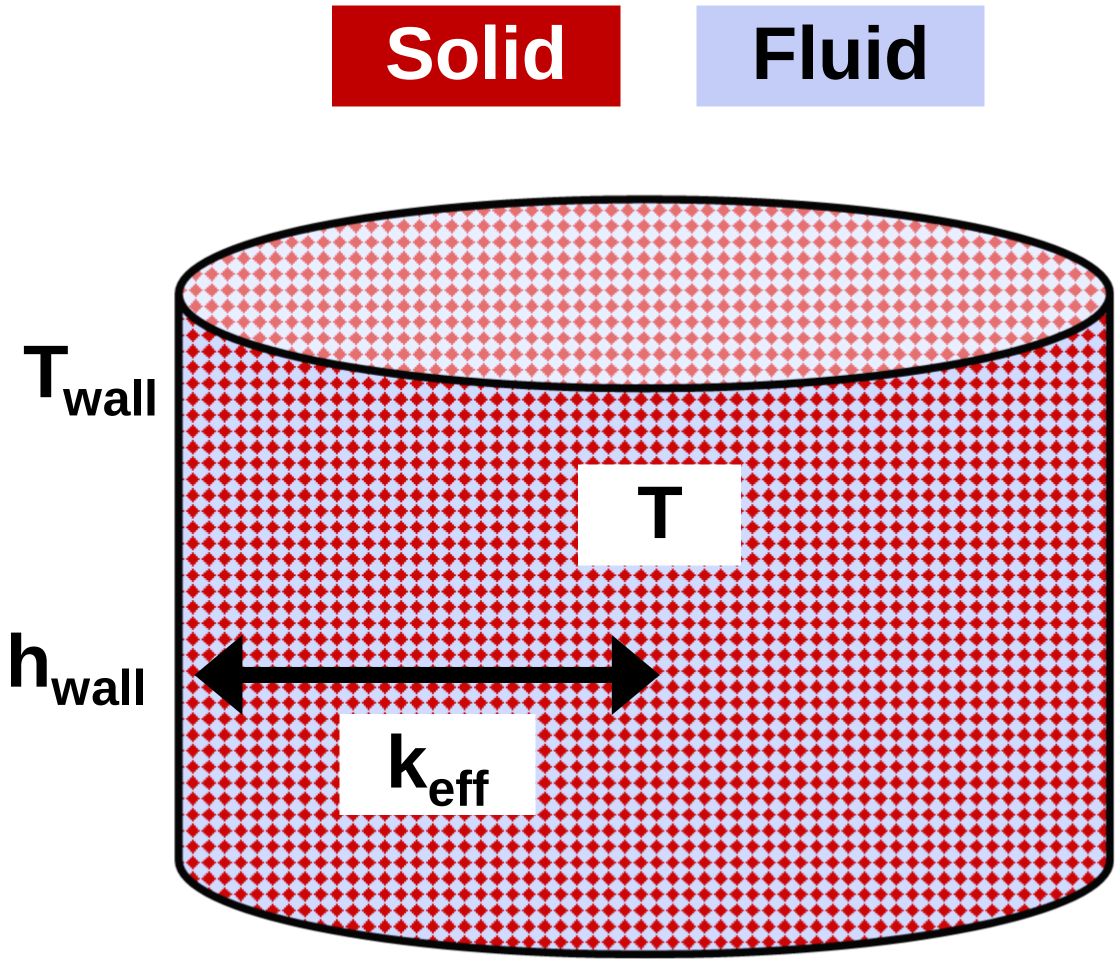
22 Reactions:



1 Diffusion of R through boundary film
2 Diffusion of R into pores
3 Adsorption of R on catalyst surface
4 Reaction R → P
5 Desorption of P from catalyst surface
6 Diffusion of P out of pores
7 Diffusion of P through boundary film

- Film thickness is a function of local conditions: composition, velocity, T & p
- COMSOL v6.0 Packed Bed Model allows all of these steps to be modeled
- Typically, we combine steps 3-5 into rate expressions in eg LHHW form

Porous Medium Conjugate Heat Transfer Models in COMSOL v6.0



- **Local thermal equilibrium: one temperature field**
- **Use skeletal matrix as solid phase, and total fluid (pores plus voids) as fluid phase**

$$\varepsilon_p = \varepsilon_{rxr} = \varepsilon_{void} + \theta_{bed} \cdot \varepsilon_{pore}$$

$$\theta_s = \theta_{rxr} = 1\text{-}\ \varepsilon_{rxr}$$

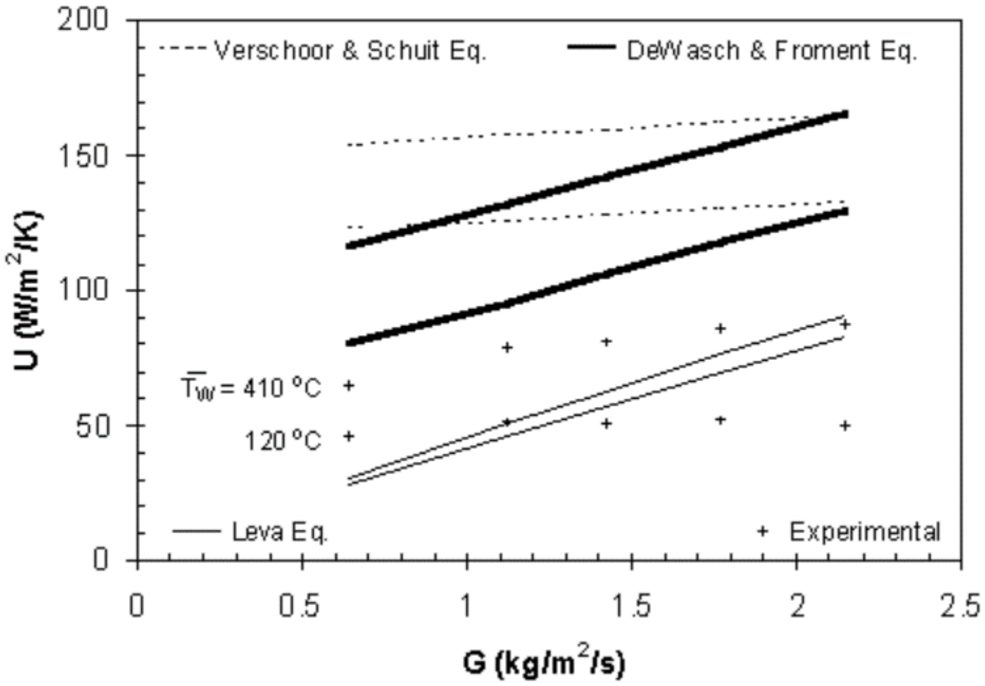
- **Typical:**

$$\varepsilon_{rxr} = 0.81$$

$$\theta_{rxr} = 0.19$$

Heat Transfer Parameters of Packed Beds

Wall Heat Transfer Coefficient, h_{wall}



L. Jorge et.al, "Evaluation of heat transfer in catalytic fixed bed reactors: a review", *Braz. J. Chem. Eng.* ***4****, 16 (1999)*

Effective Skeletal Solids Thermal Conductivity, k_{skel}

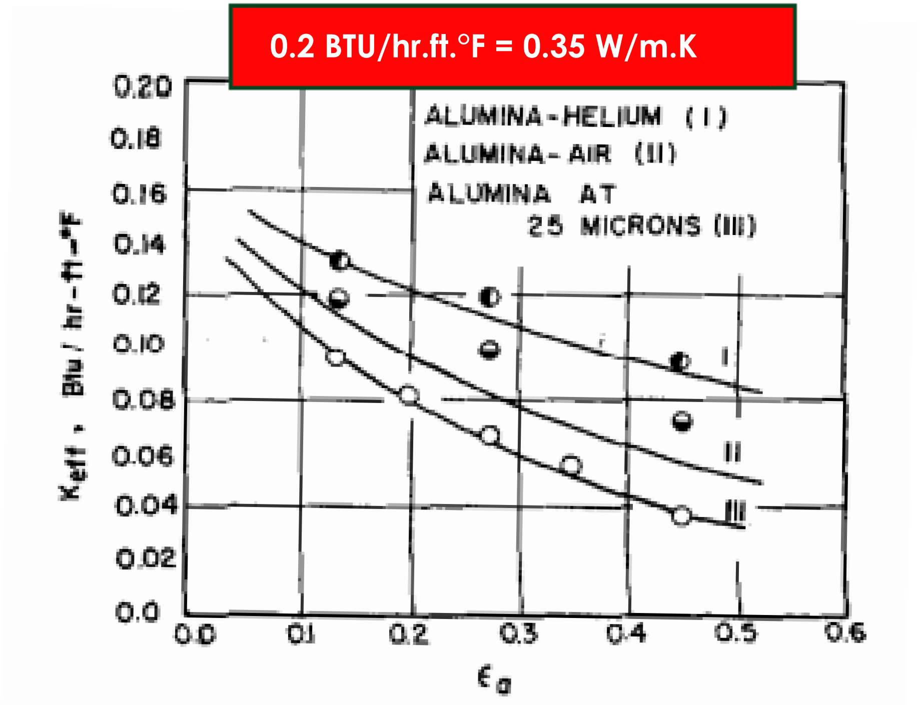
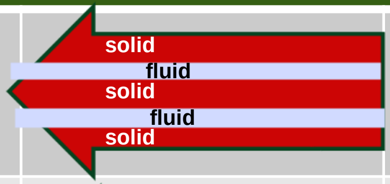
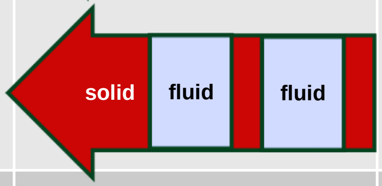
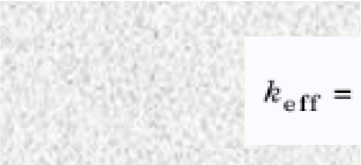
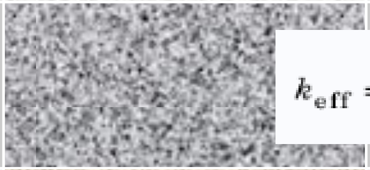
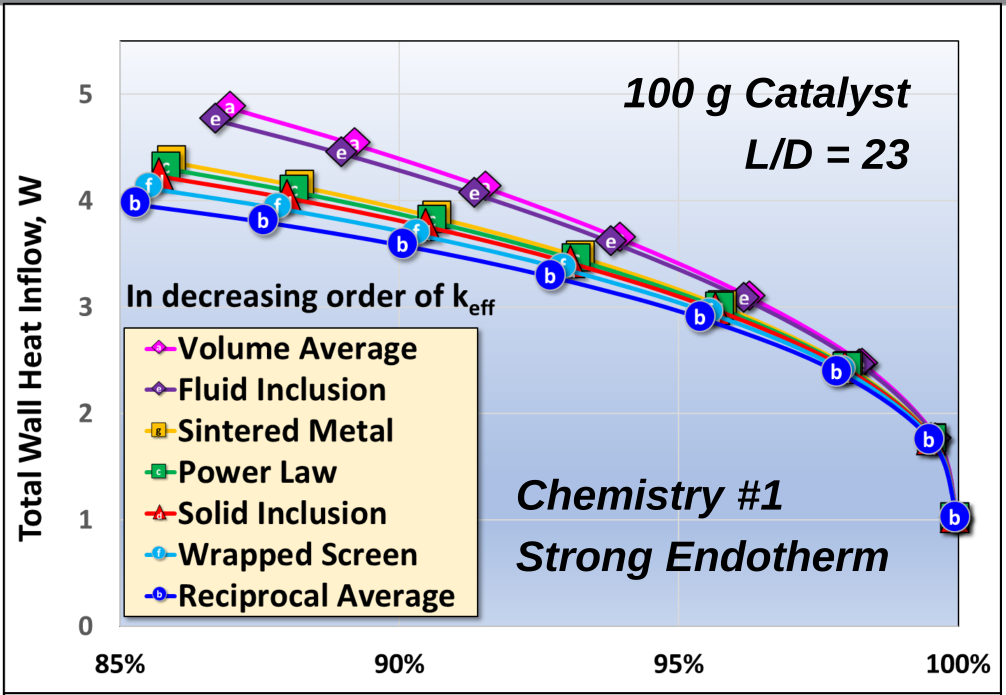


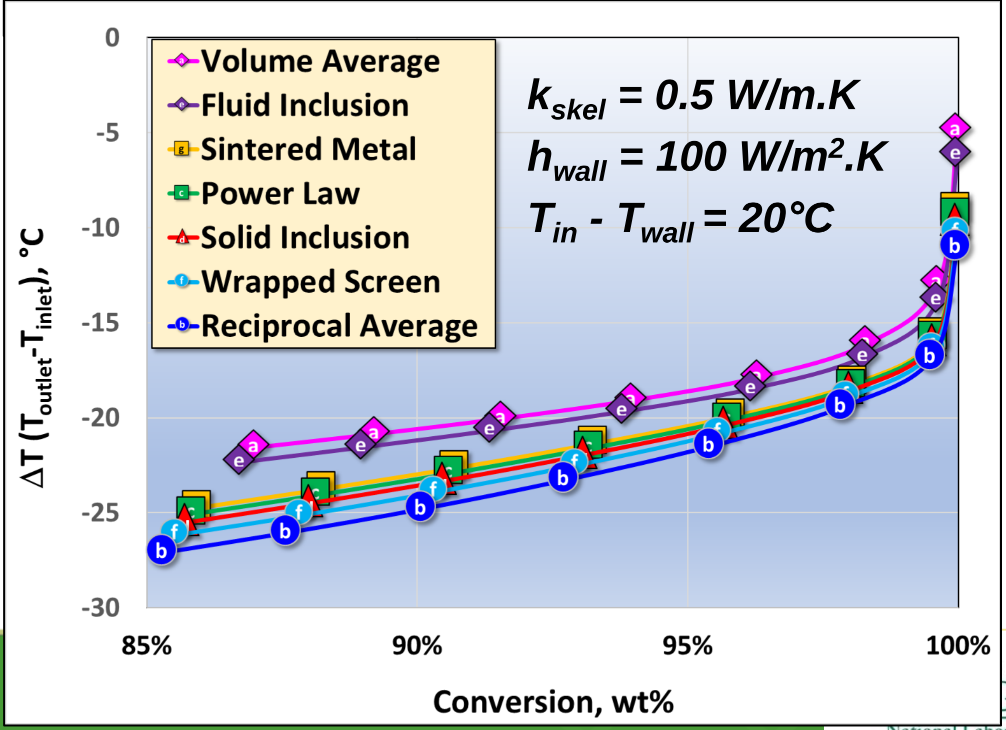
Fig. 2. Prediction of thermal conductivity: alumina-air, alumina-helium 120°F. (11).

J. Butt,, "Thermal conductivity of porous catalysts", *AIChE Journal 106 (1965)*

Porous Medium Heat Transfer Models in COMSOL v6.0
k_{eff} of Solid + Fluid Phases

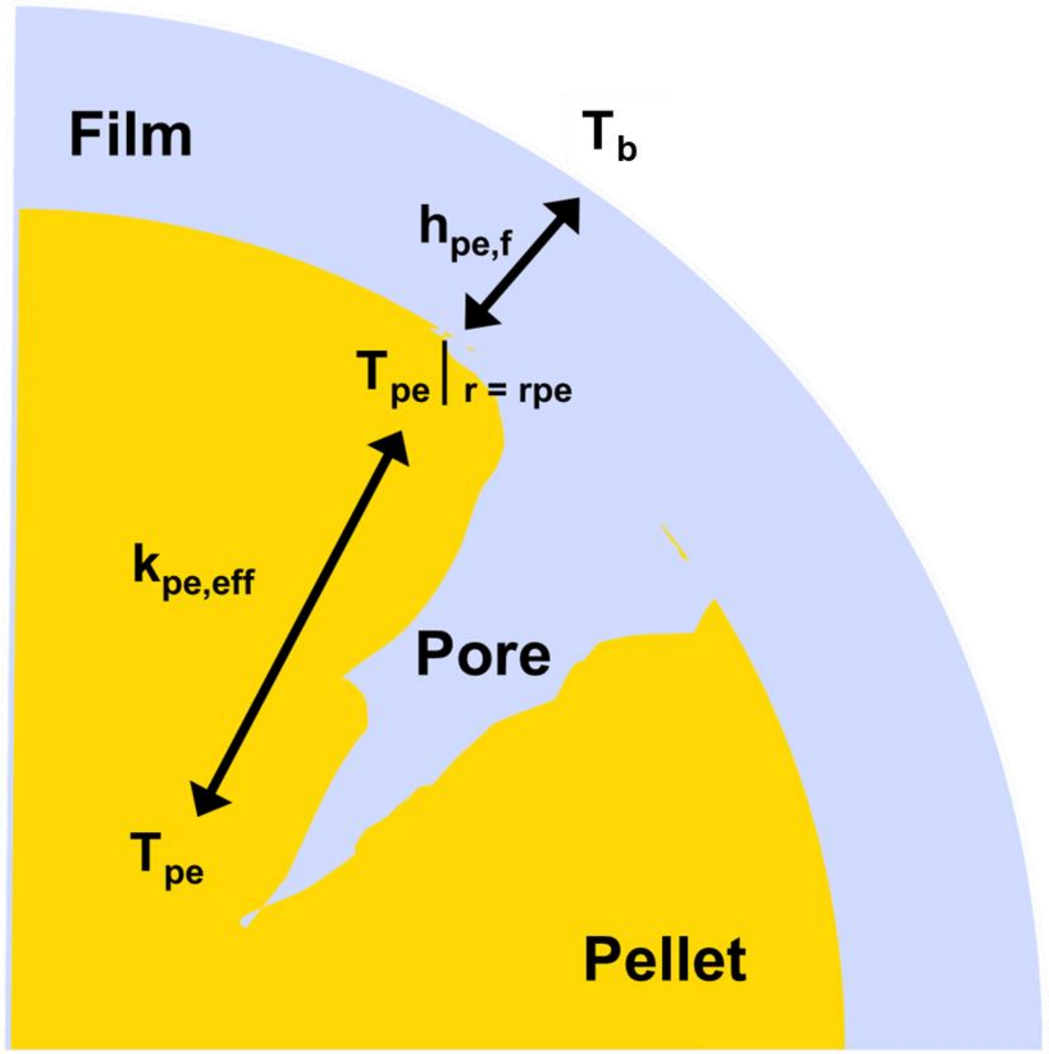
Model	Illustration	Equation
Plane layers parallel to heat flow (volume average)		$k_{eff} = \theta_s k_s + \varepsilon_p k_f$
Plane layers perpendicular to heat flow (reciprocal average)		$\frac{1}{k_{eff}} = \frac{\theta_s}{k_s} + \frac{\varepsilon_p}{k_f}$
Power law (geometric mean)		$k_{eff} = k_s^{\theta_s} \cdot k_f^{\varepsilon_p}$
Solid spherical inclusions		$k_{eff} = k_f \frac{2k_f + k_s - 2(k_f - k_s)\theta_s}{2k_f + k_s + (k_f - k_s)\theta_s}$
Fluid spherical inclusions		$k_{eff} = k_s \frac{2k_s + k_f - 2(k_s - k_f)\varepsilon_p}{2k_s + k_f + (k_s - k_f)\varepsilon_p}$
Wrapped screen		$k_{eff} = k_f \frac{k_f + k_s - (k_f - k_s)\theta_s}{k_f + k_s + (k_f - k_s)\theta_s}$
Sintered metal fibers		$k_{eff} = \varepsilon_p^2 k_f + \theta_s^2 k_s + \frac{4\varepsilon_p \theta_s k_f k_s}{k_f + k_s}$





Packed Bed Heat Transfer Model in COMSOL v6.0

- Local thermal nonequilibrium: two interspersed temperature fields
  - T_f = temperature in bulk fluid in voids
  - T_{pe} = temperature inside pellets = f(r)
- No pellet-pellet heat transfer: all heat transfer occurs between pellets and fluid
- Two important options:
  - RV = Reaction Volume. Total (pellet) volume or pore volume
  - HV = Heated Volume. Heat of reaction can be invoked separately for pellet solid volume and pellet fluid volume



Local Thermal Nonequilibrium Packed Bed Model: LTN-PB

Macroscopic heat transfer in bed voids

$$\varepsilon_b \rho_f C_{p,f} \frac{\partial T_b}{\partial t} + \rho_f C_{p,f} \boldsymbol{u} \cdot \nabla T_b + \nabla \cdot \boldsymbol{q_f} = Q_{pe,f} + \varepsilon_b Q_f$$

$$\boldsymbol{q_f} = -\varepsilon_b Q_{pe,f} k_f \nabla T_b$$

Microscopic heat transfer inside pellet

$$\left(\rho C_p\right)_{pe,eff} \frac{\partial T_{pe}}{\partial t} + \frac{1}{\left(r \cdot r_{pe}\right)^2} \frac{\partial}{\partial r}\left(-r^2 k_{pe,eff} \frac{\partial T_{pe}}{\partial r}\right) = Q_{pe}$$

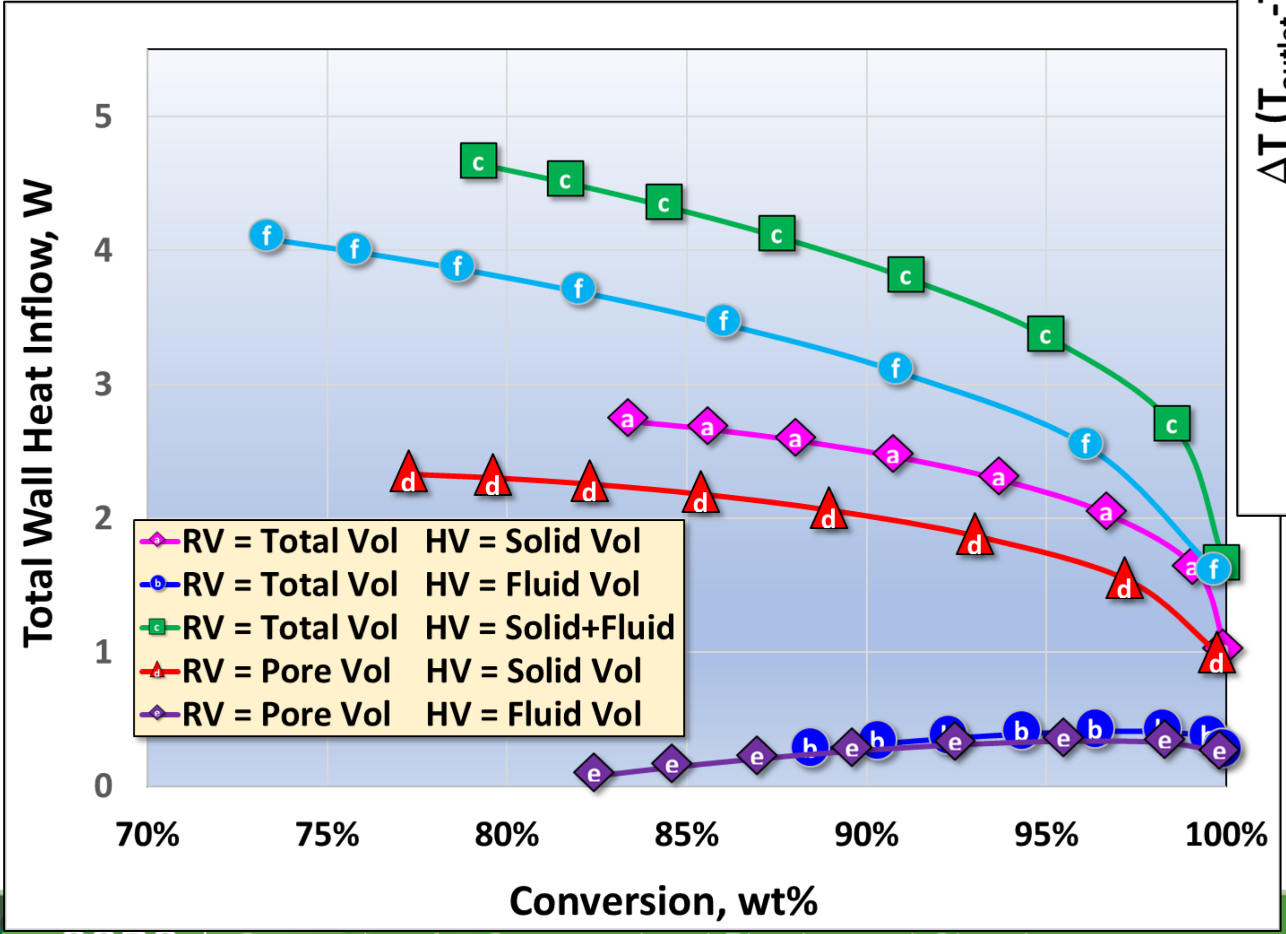
$$\left(\rho C_p\right)_{pe,eff} = \left(1 - \varepsilon_{pe}\right)\rho_{pe} C_{p,pe} + \varepsilon_{pe} \rho_f C_{p,f}$$

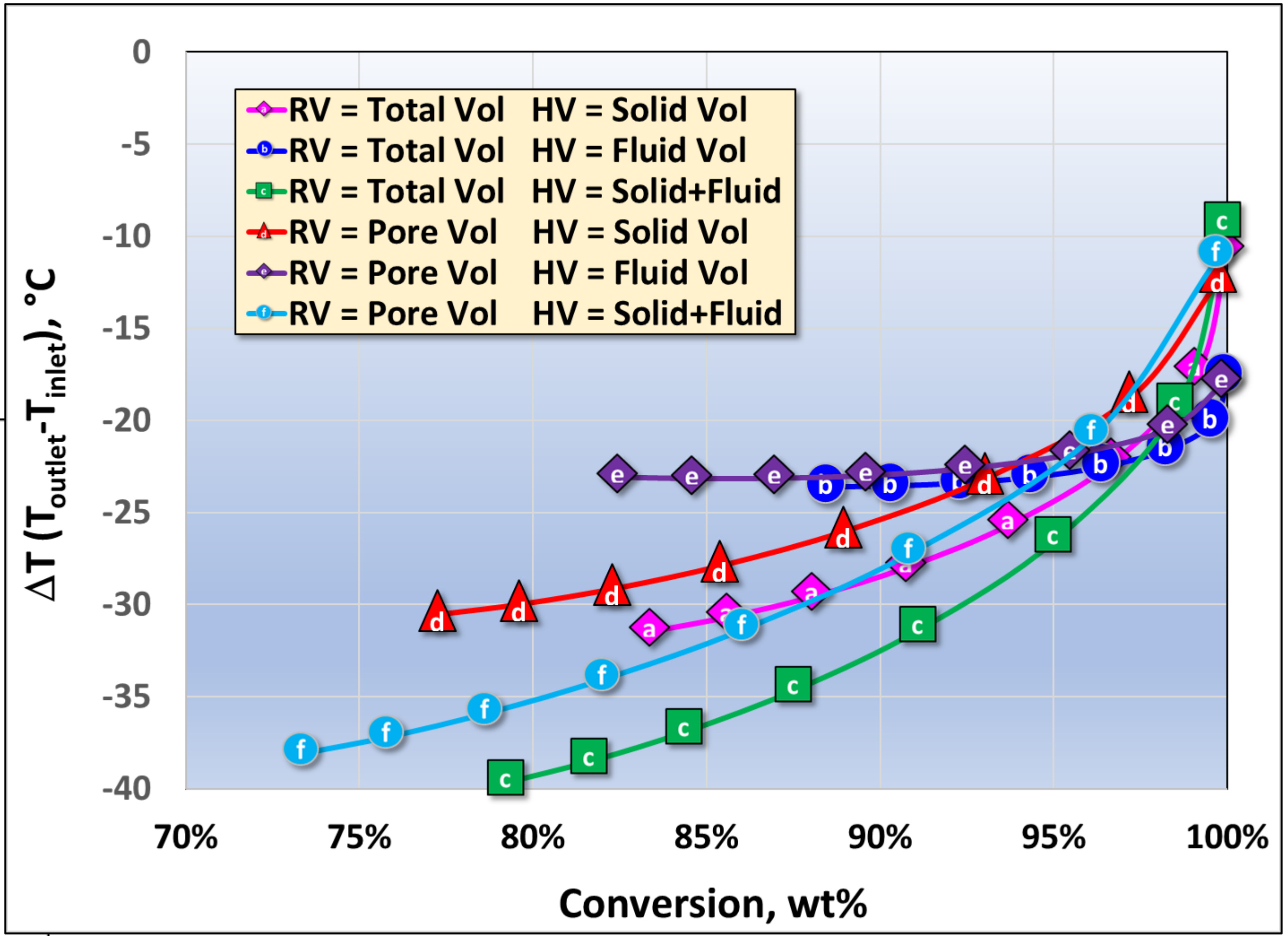
Coupling condition at pellet-fluid interface

$$q_{pe|_{r=rpe}} = h_{pe,f}\left(T_f - T_{pe|_{r=rpe}}\right)$$

$$h_{pe,f} = \frac{1}{\left[d_{pe}\left(\frac{1}{k_f Nu} + \frac{1}{10\, k_{pe,eff}}\right)\right]}$$

LTN-PB Options for Reaction Volume (RV) and Heated Volume (HV): Which are Correct?





Chemistry #1

Strong Endotherm

100 g Catalyst

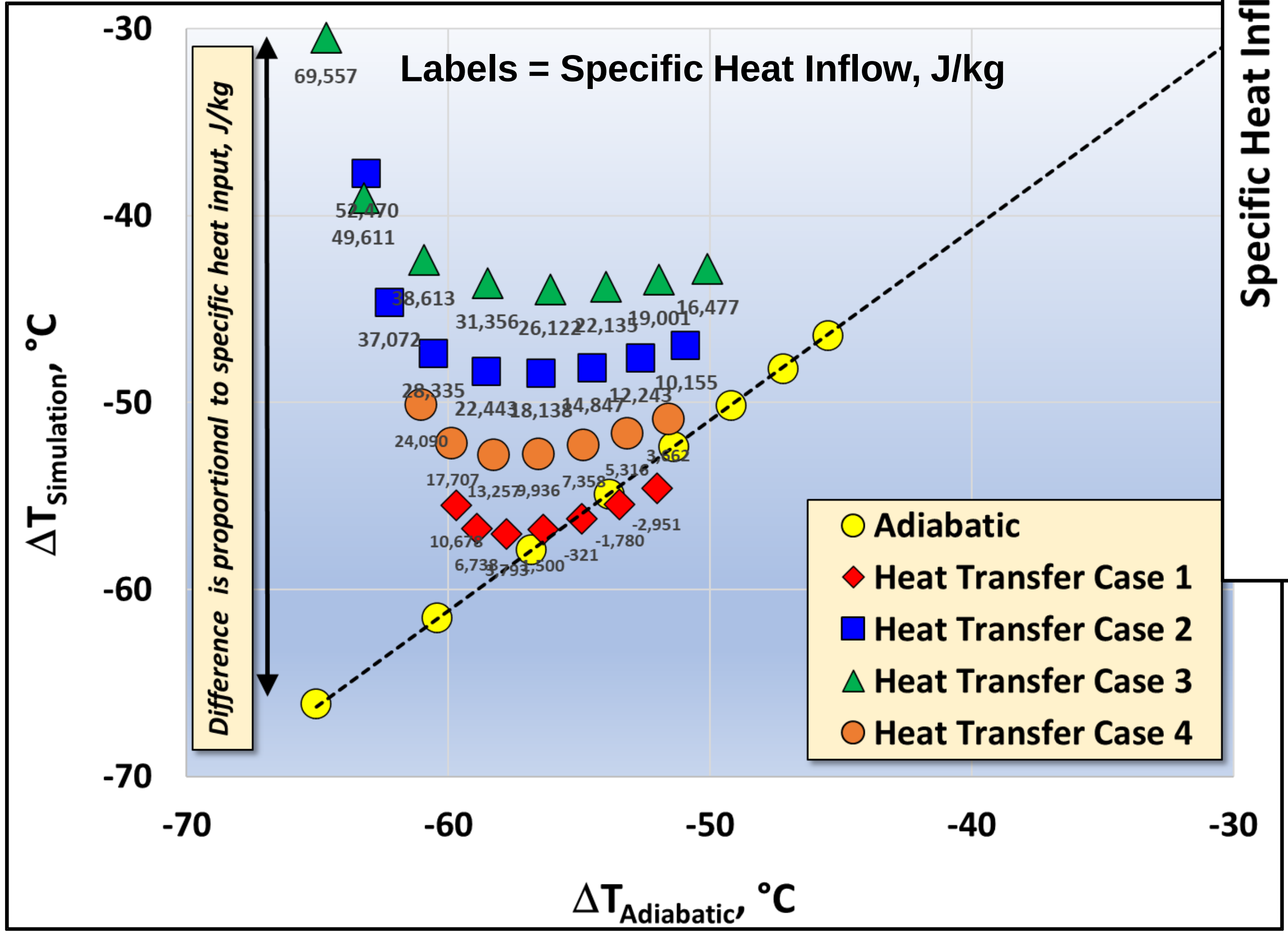
L/D = 23

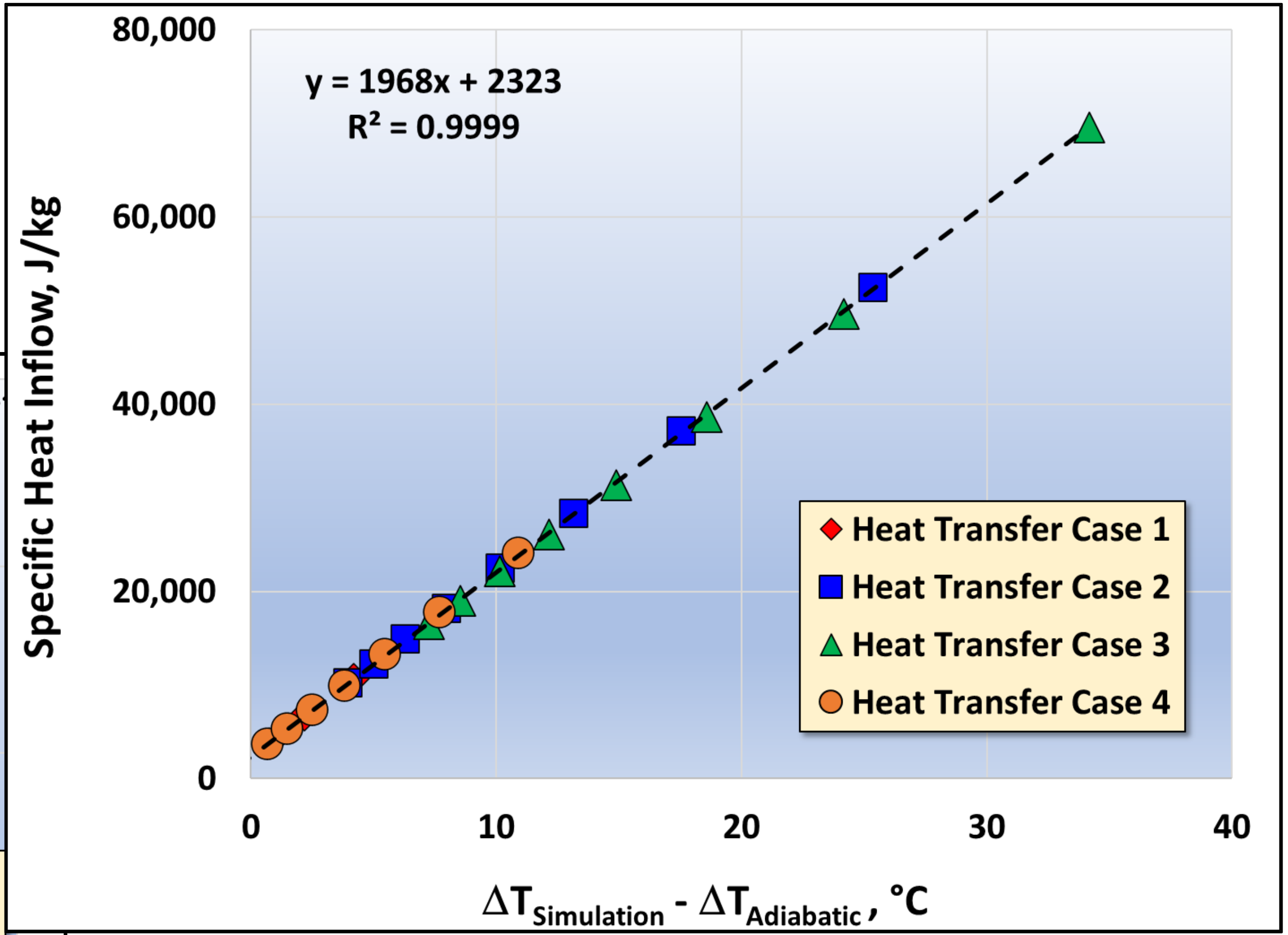
$k_{skel} = 0.5$ W/m.K

$h_{wall} = 100$ W/m^2.K

$T_{in} - T_{wall} = 20$°C

Manual Heat Balance Check: Calculate $\Delta T_{Adiabatic}$



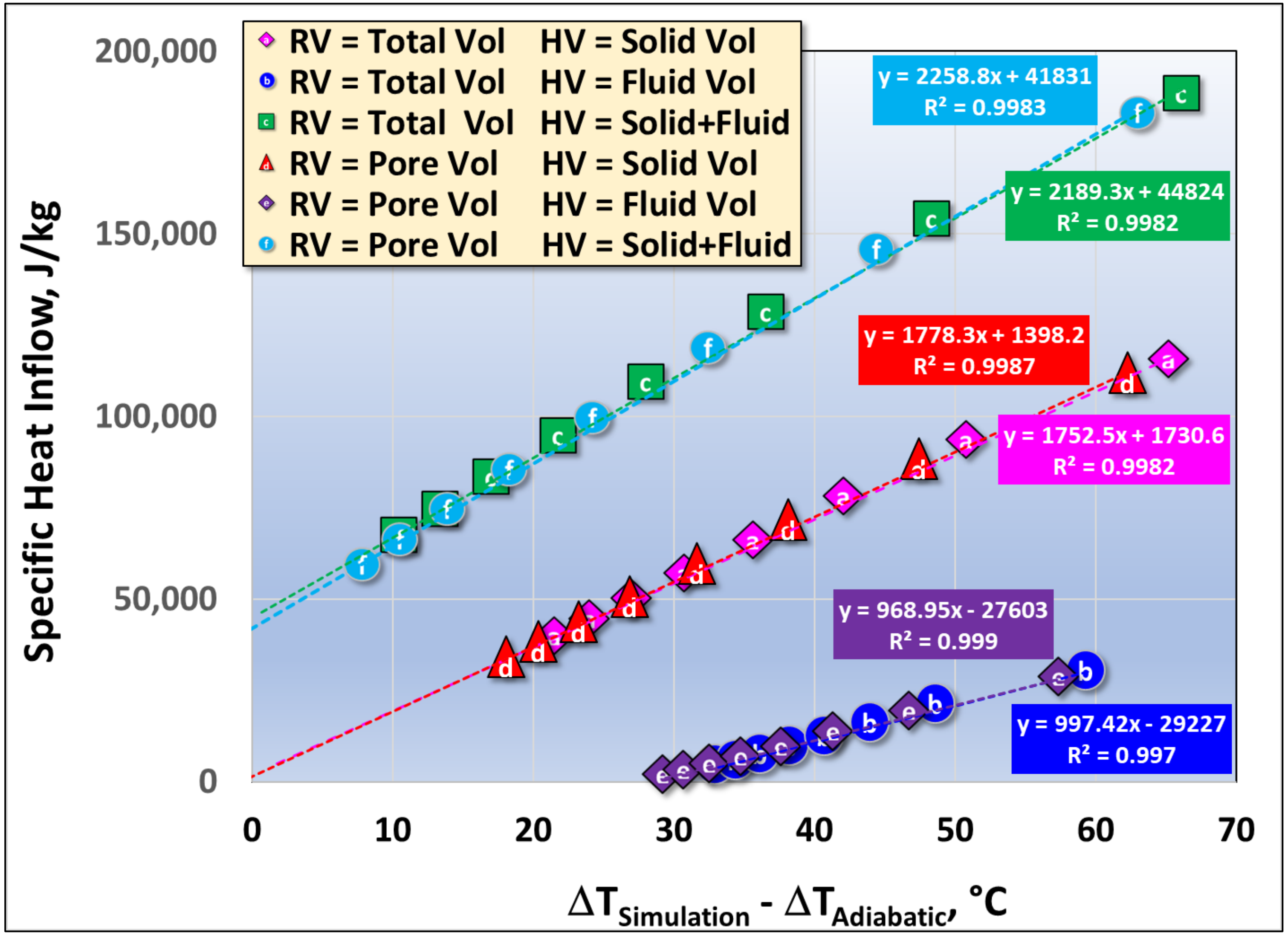


- **Slope is the average heat capacity of this group of chemical species**
- **In principle, this can be used to estimate wall heat flow from experimental data**

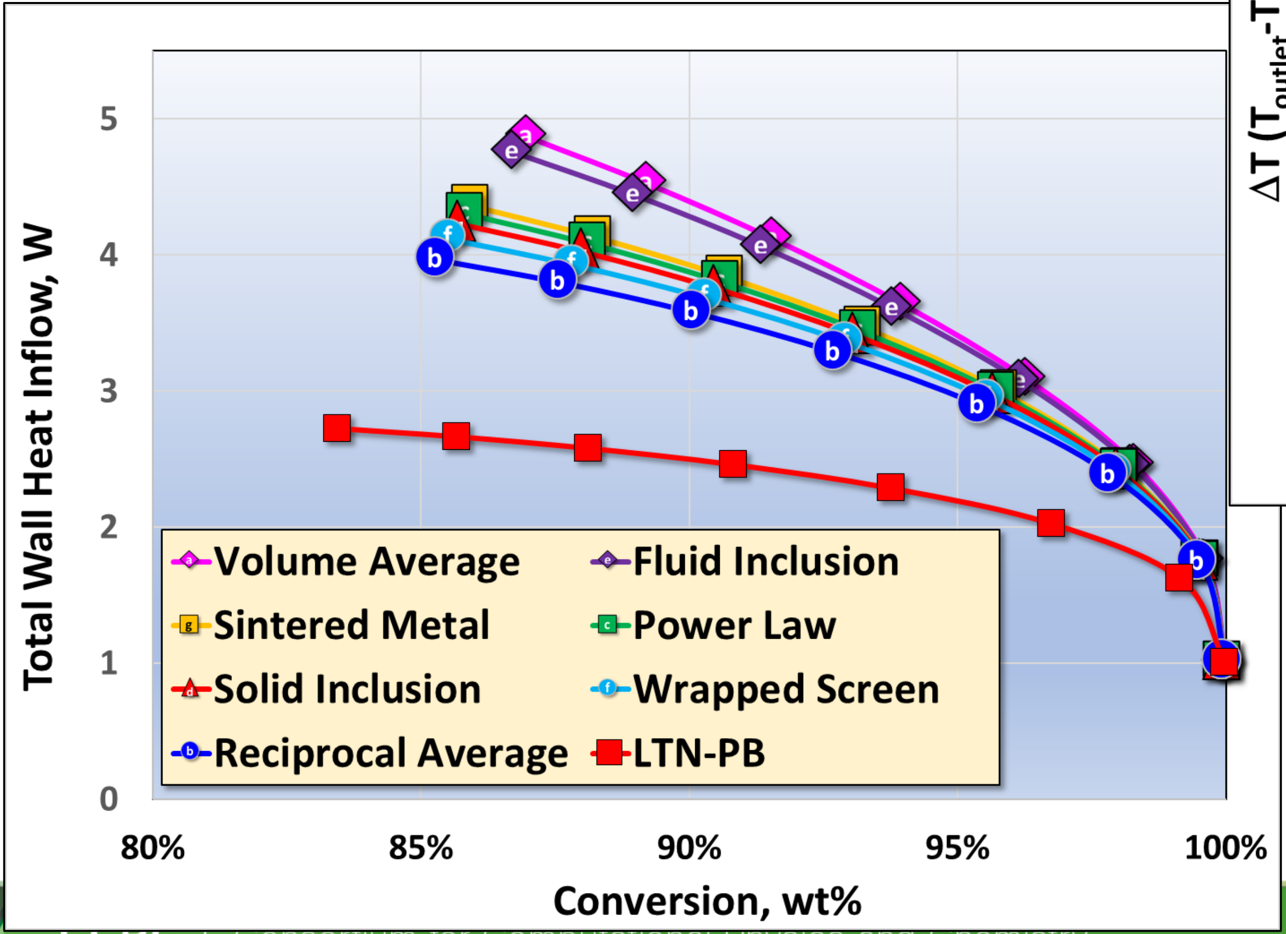
Manual Heat Balance Check of LTN-PB Options

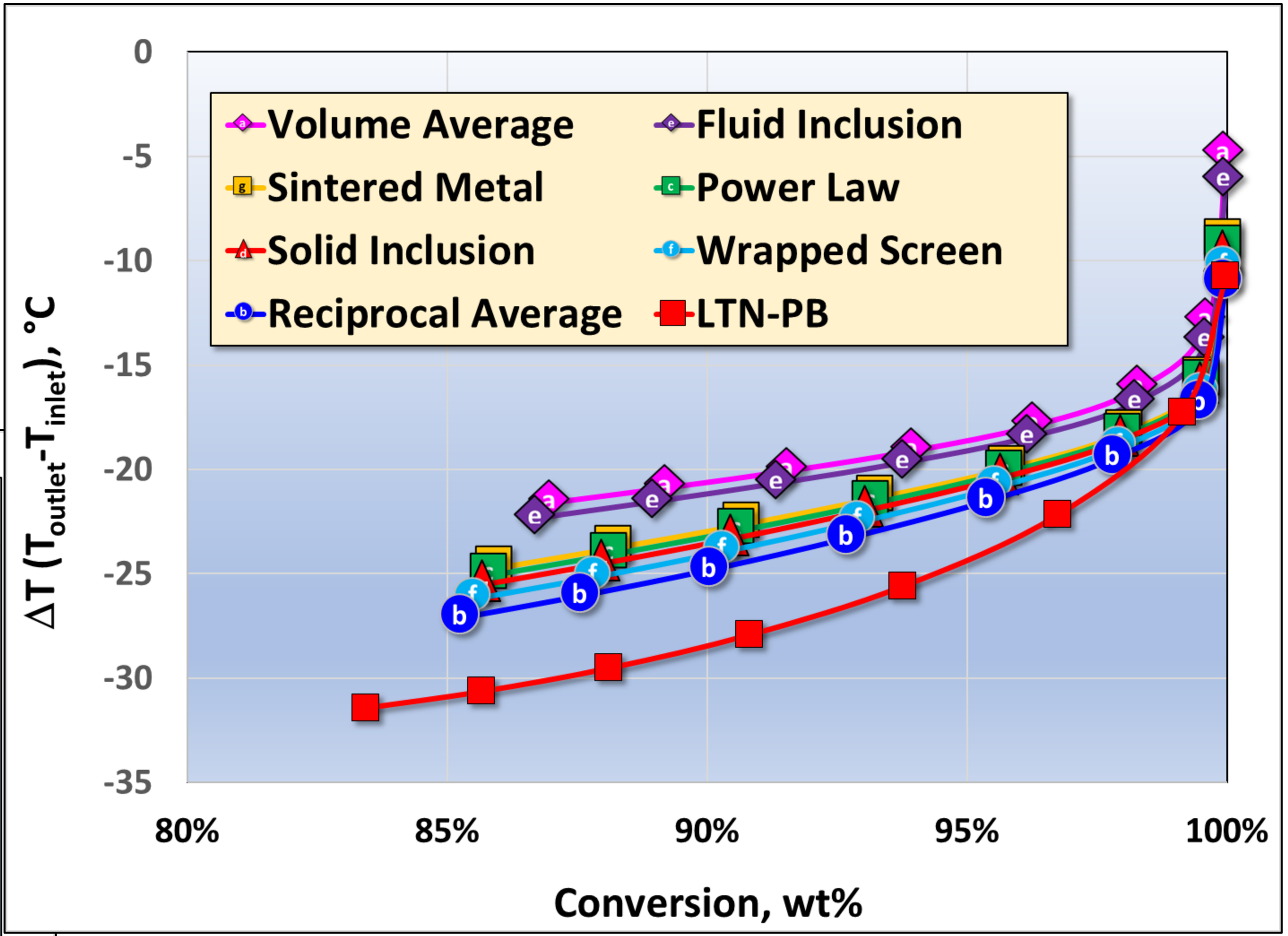
- **Reaction Volume (RV): depends on basis of rate constants. If rate constants are based on total mass or volume of catalyst (like here):**
  RV = total volume

- **Heated Volume (HV): lines (a) and (d) are closest to line shown on previous slide:**
  HV = solid volume only



Packed Bed Model LTN-PB Predicts Less Heat Transfer than Porous Medium Models





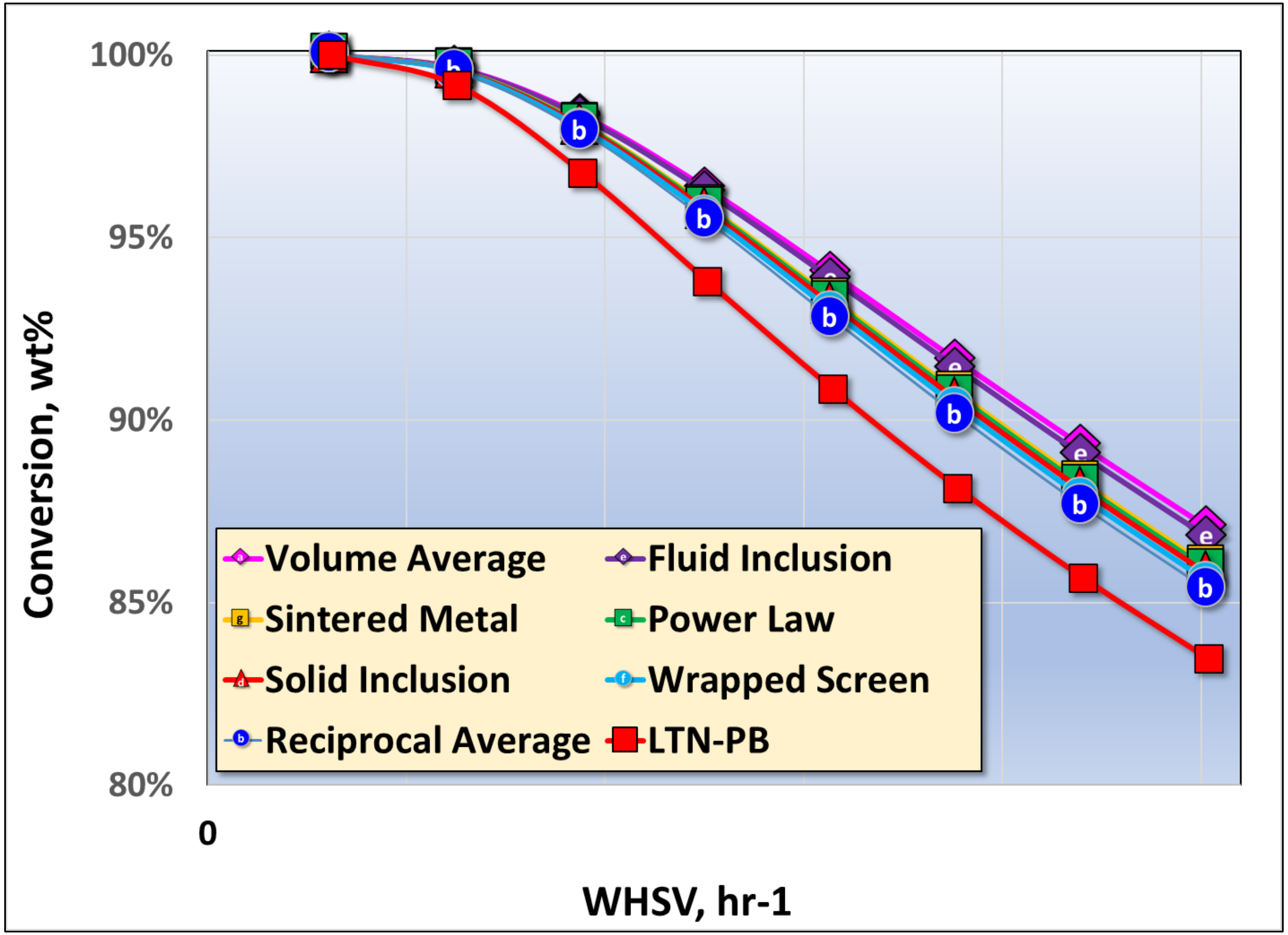
Chemistry #1
Strong Endotherm
100 g Catalyst
L/D = 23

$k_{skel} = 0.5$ W/m.K
$h_{wall} = 100$ W/m^2.K
$T_{in} - T_{wall} = 20$°C

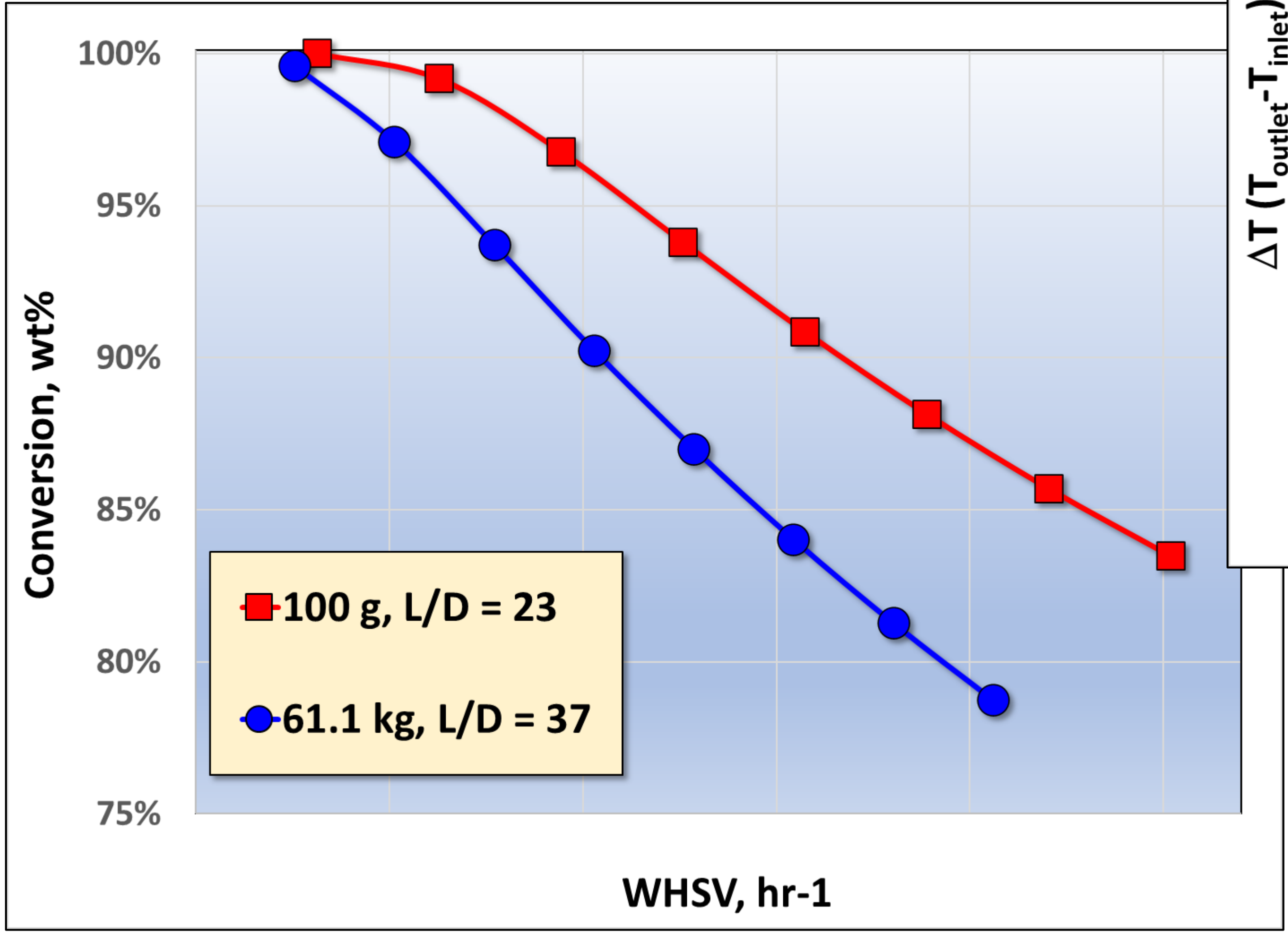
Heat Transfer Significantly Affects Conversion at Lab Scale

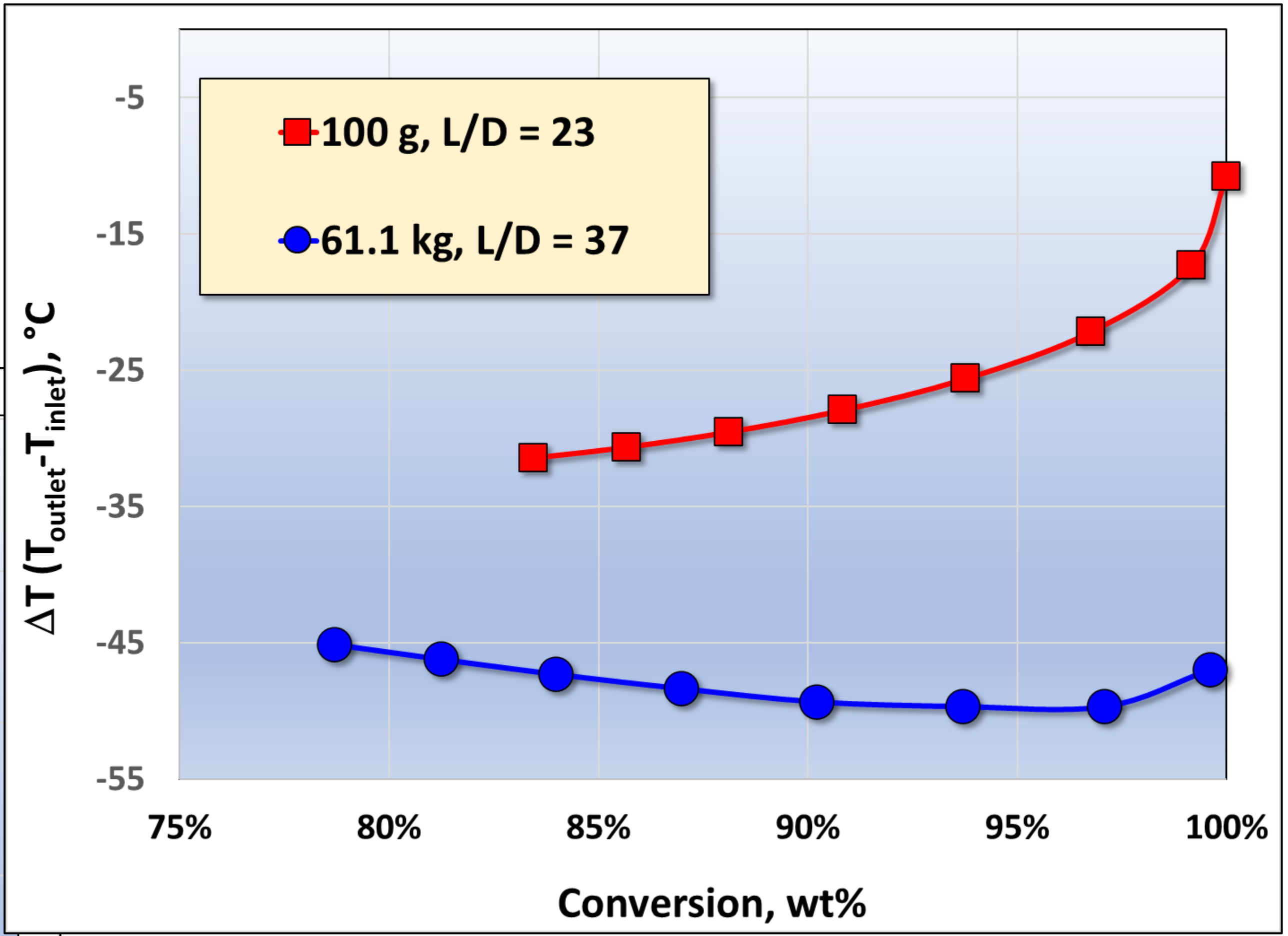
Chemistry #1
Strong Endotherm
100 g Catalyst
L/D = 23

k_{skel} = 0.5 W/m.K
h_{wall} = 100 W/m^2.K
T_{in} - T_{wall} = 20°C



Packed Bed Model LTN-PB Shows Large Differences in Lab and "Pilot+" Scales





Chemistry #1
Strong Endotherm

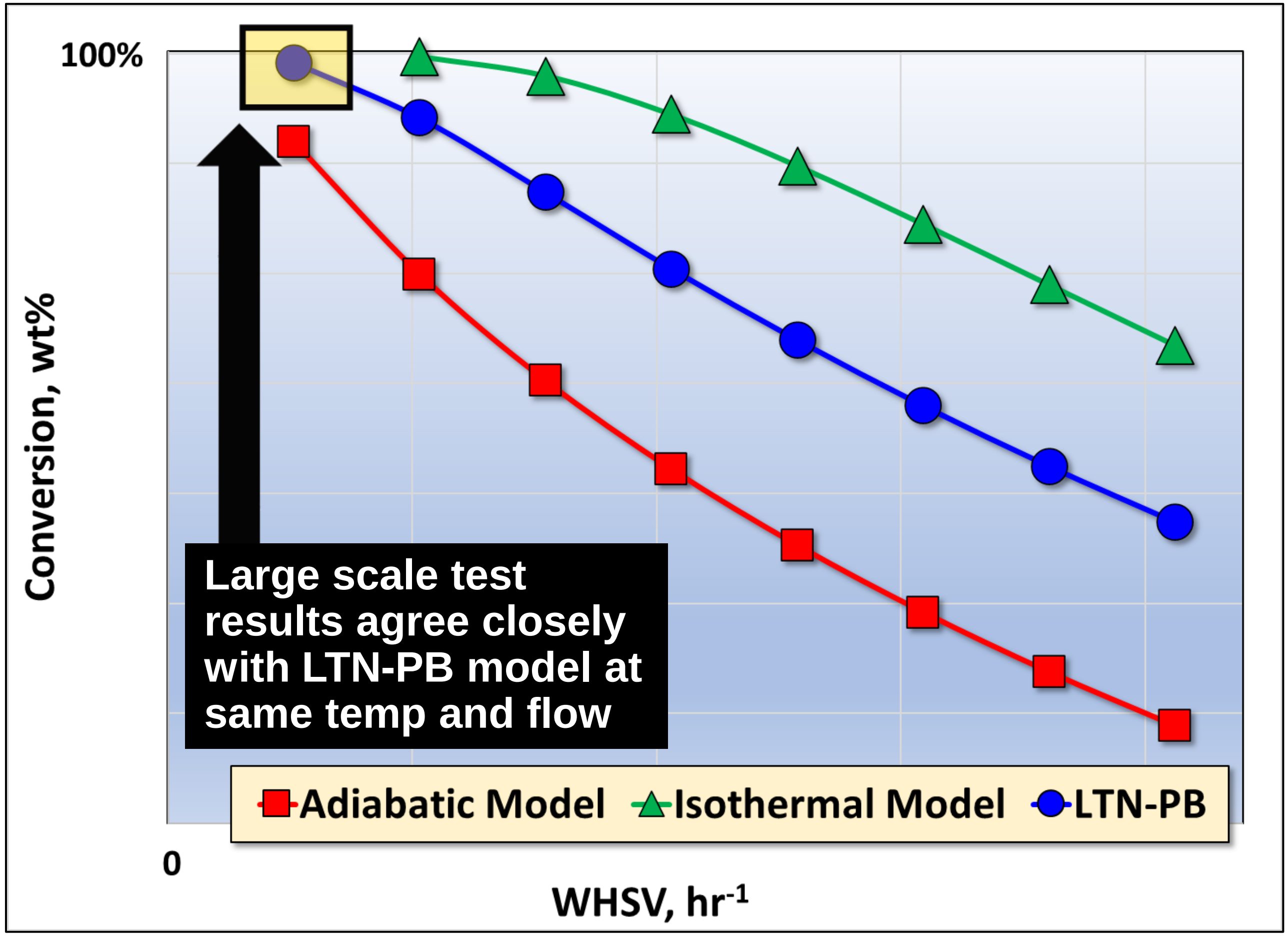
k_{skel} = 0.5 W/m.K
h_{wall} = 100 W/m^2.K
T_{in} = Base + 20°C
T_{wall} = Base

Test: LTN-PB Model Supports Scaleup Step of ~1,000X!!

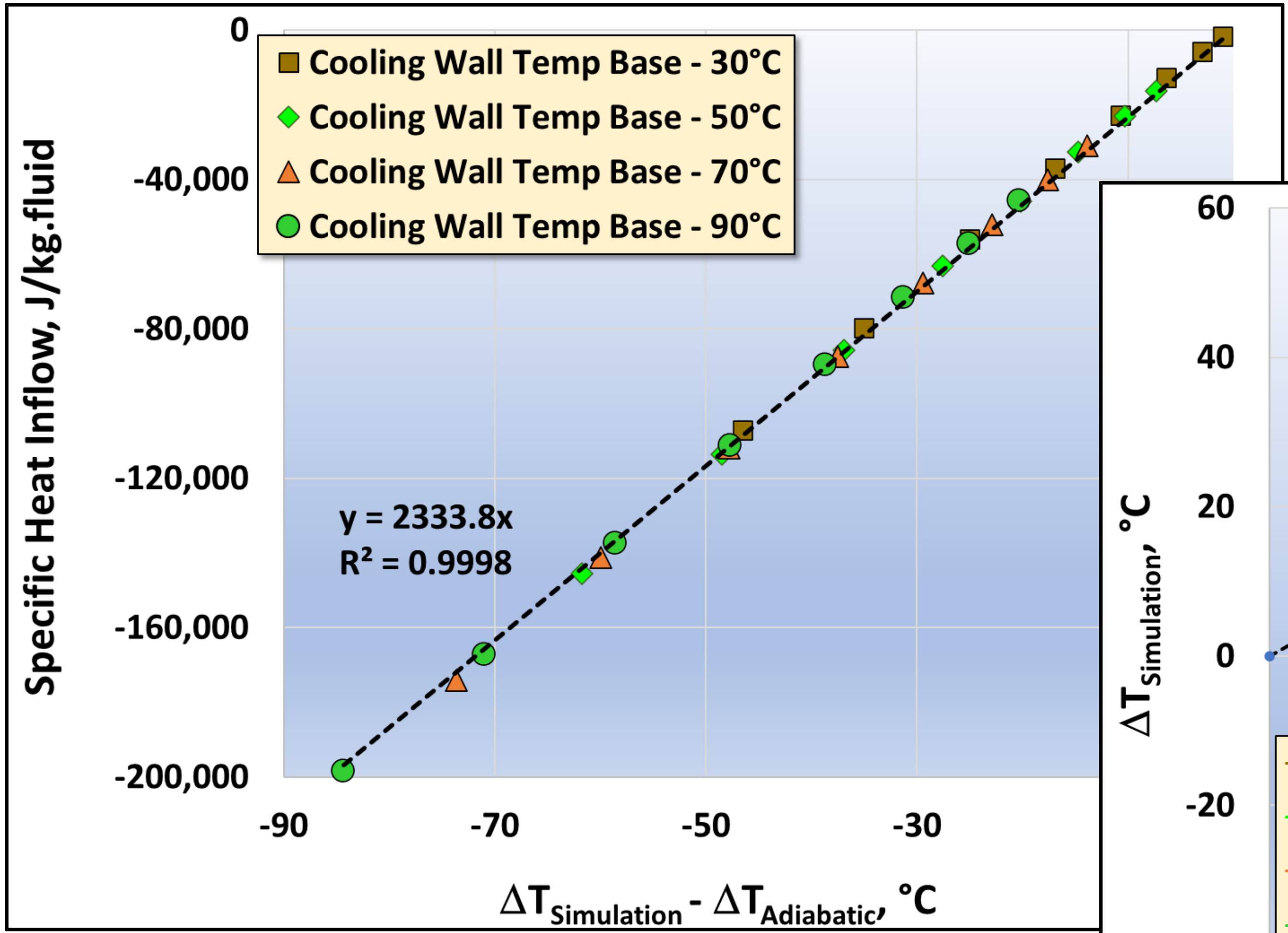
Multiple reactor system holds 100's of kgs of catalyst

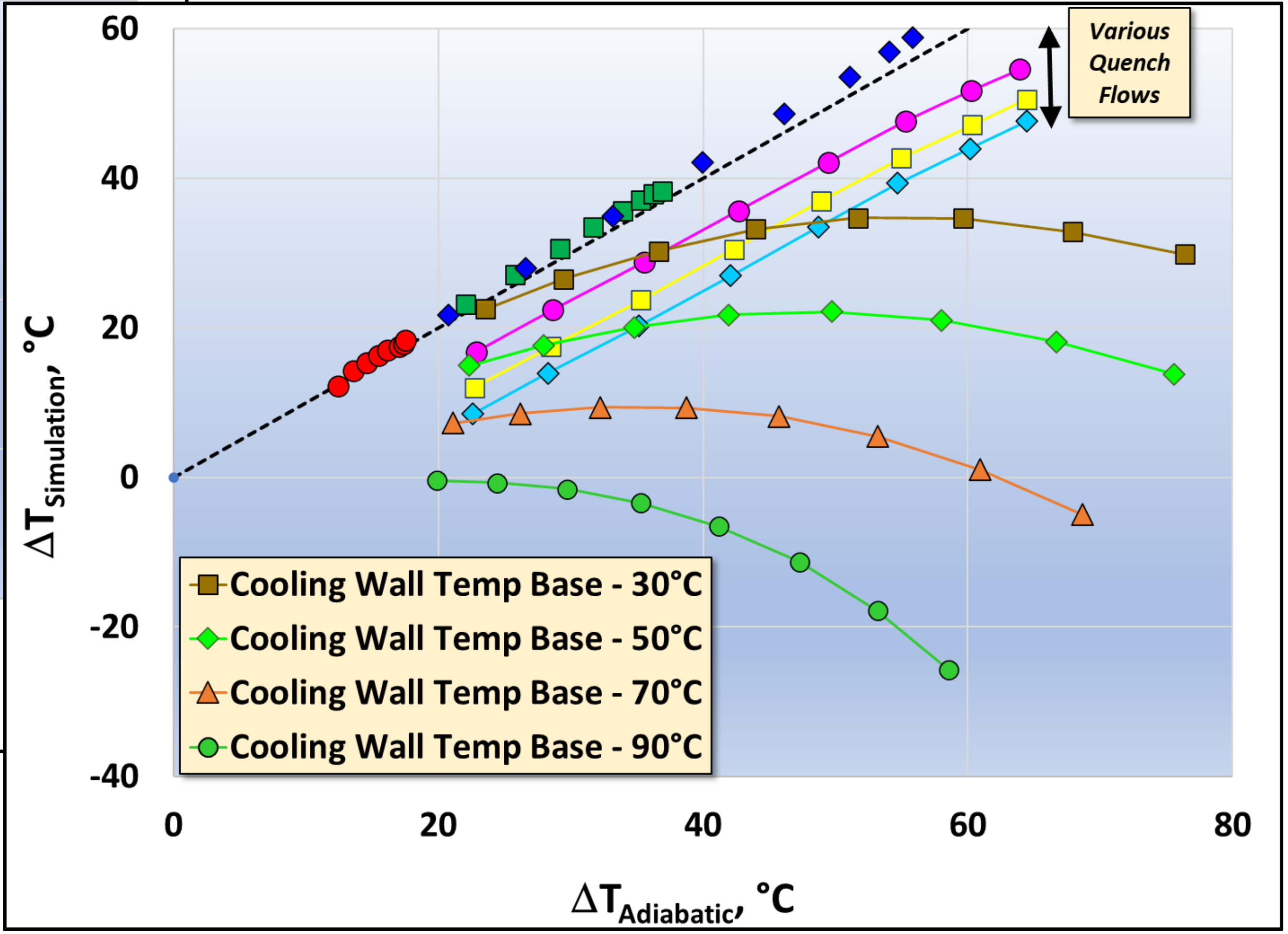
PYRAN The 5-Carbon Company

RPD Technologies



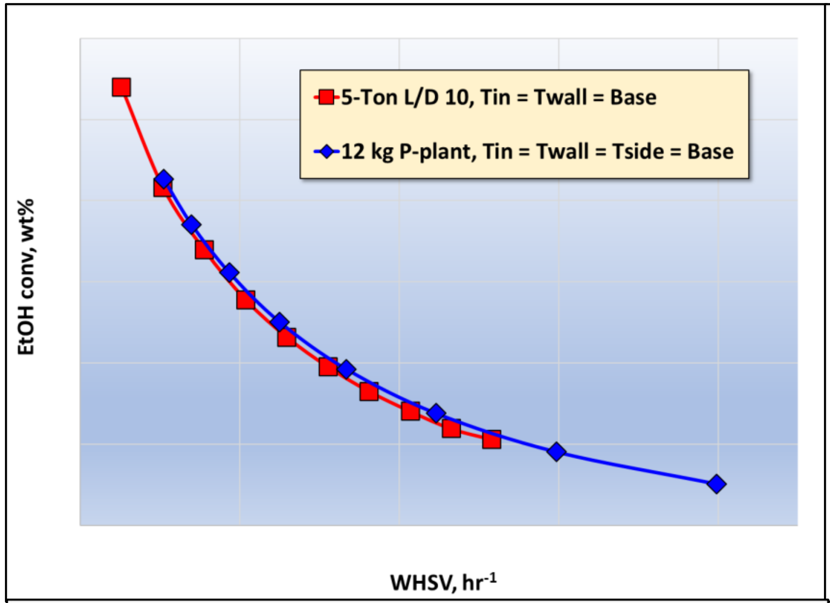
Catalyxx: Heat Balance Cross-Check Works, Even With Complex Thermo

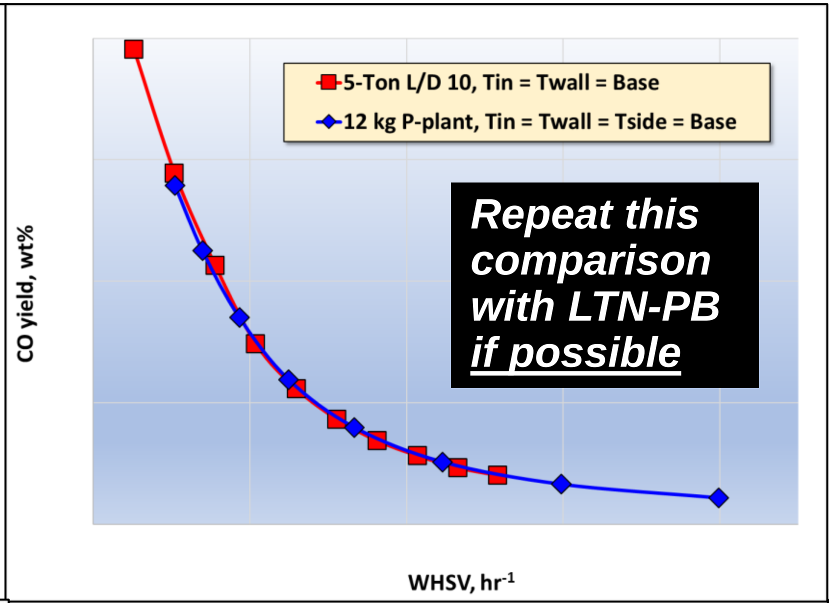




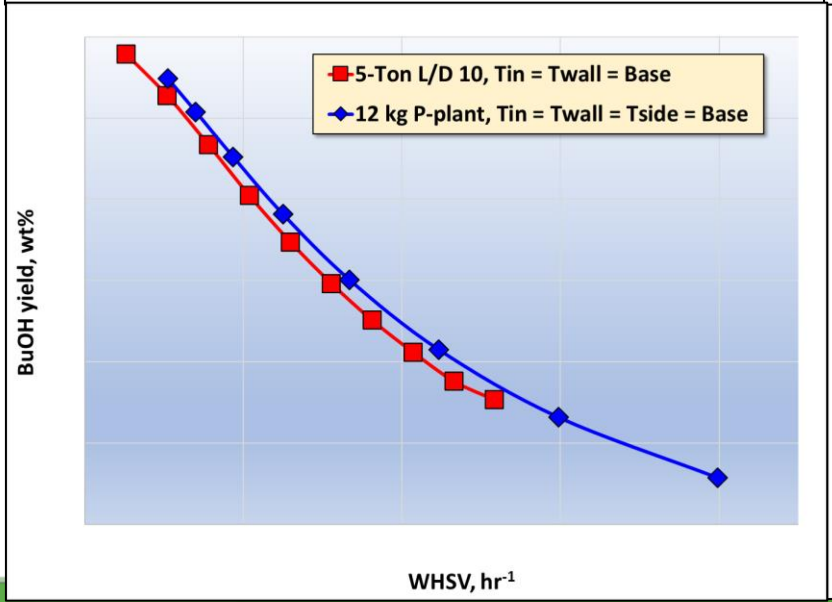
Catalyxx

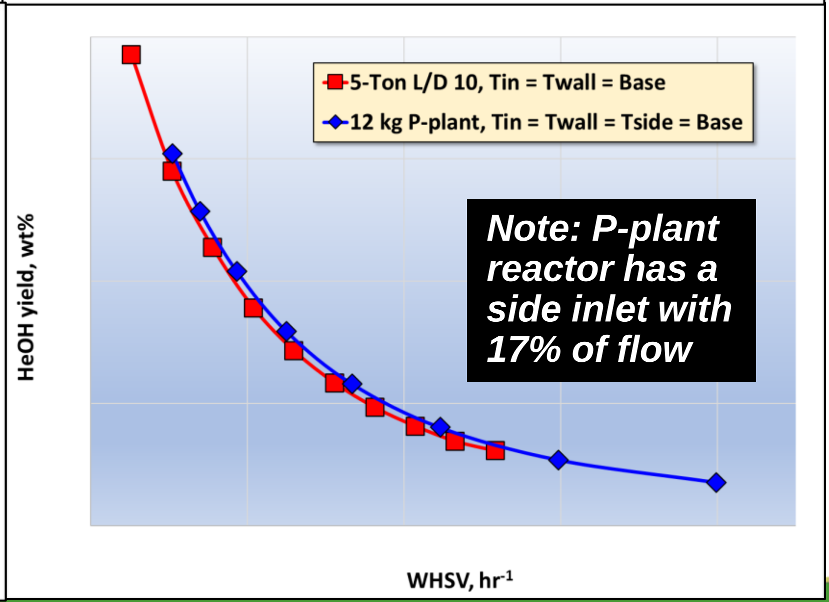
Comparison of 12 kg P-plant and 5-Ton Bed (Volume Average Model)



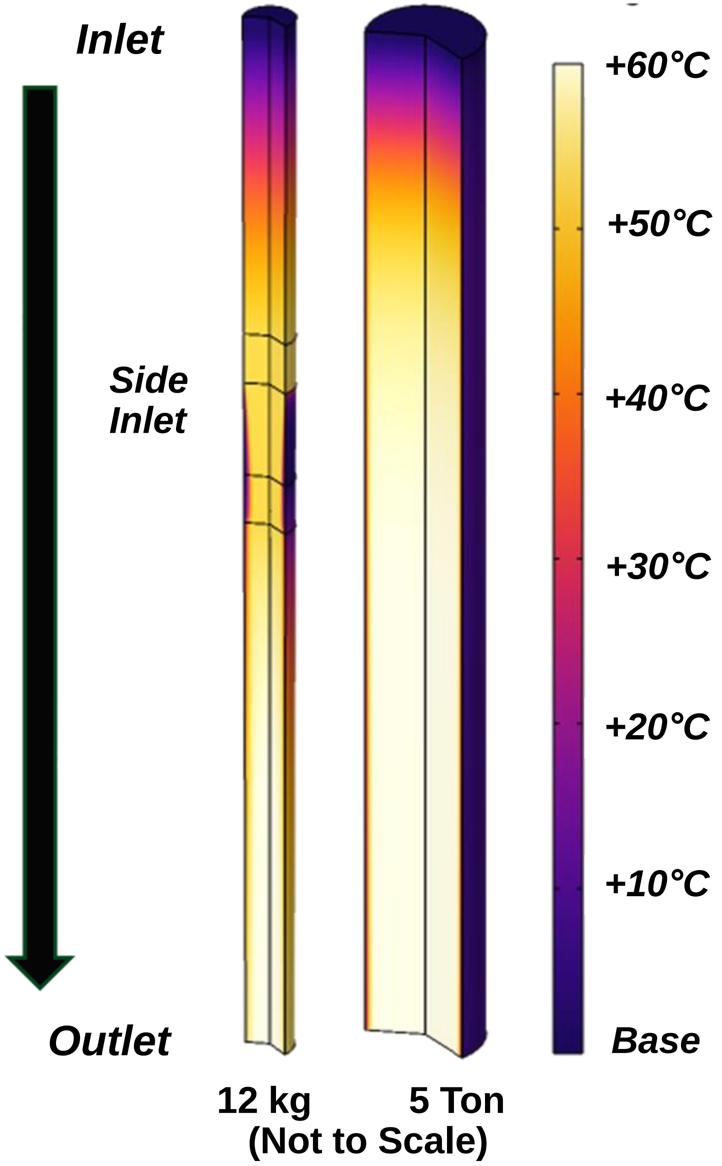


Repeat this comparison with LTN-PB <u>if possible</u>

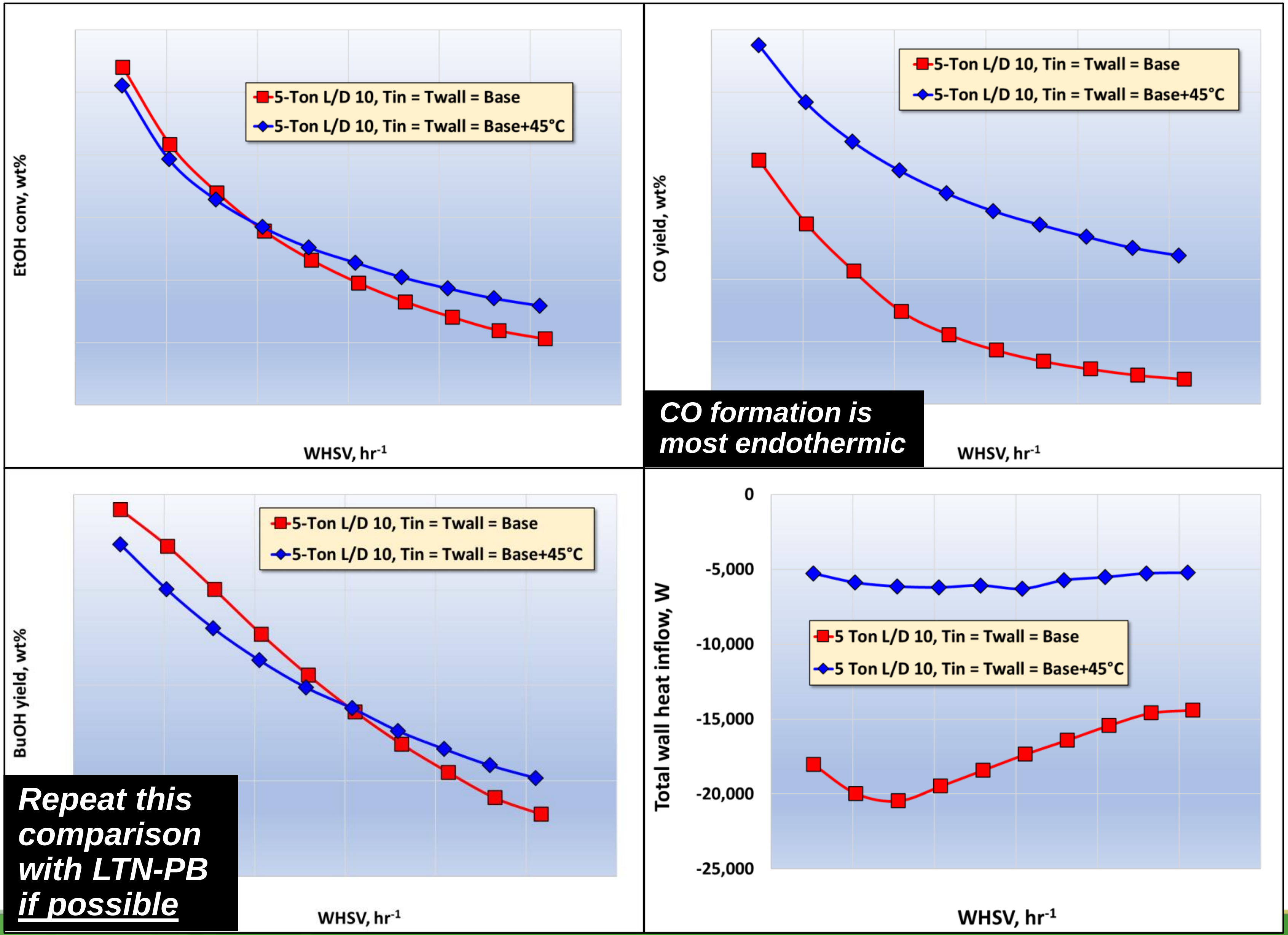




Note: P-plant reactor has a side inlet with 17% of flow

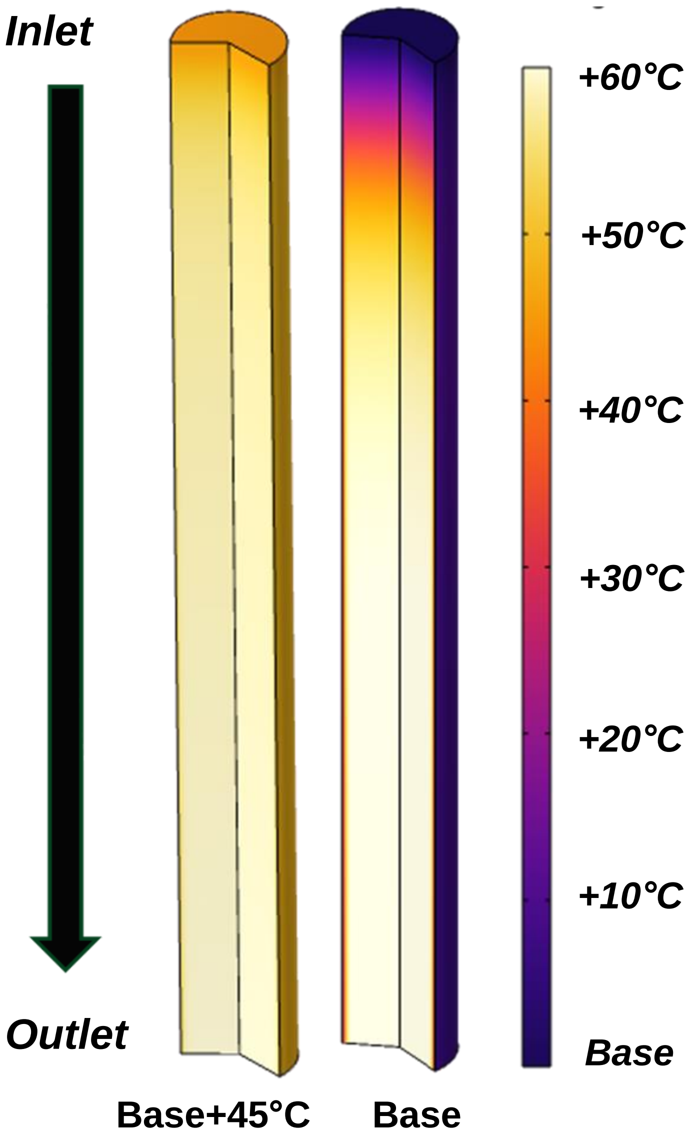


Yield Optimization Conditions at 5-ton Scale (Volume Average Model)



CO formation is most endothermic

Repeat this comparison with LTN-PB <u>if possible</u>



Conclusions

- **COMSOL *Reactive Pellet Bed* models have been developed for endothermic, exothermic and mixed chemical reaction systems in the bio-renewables space**
  - **Most complex to date: Guerbet chemistry with 26 species and 22 reactions, with complex LHHW-type kinetic expressions**
  - **Choice of heat transfer model and parameters is important for scaleup modeling**
    - **<u>In selecting a heat transfer model, quantity and quality of experimental data will probably be the limiting factor</u>**
    - **So … recommend a bracketing approach with the packed bed heat transfer model LTN-PB and the volume average porous medium model as extremes**
      - *Note: an LTN-PB bug fix is in the works. Contact us if you want to run model LTN-PB*