Impact of Heat and Mass Dispersion and Thermal Effects on the Scale-up of Monolith Reactors Used in Catalytic After-treatment

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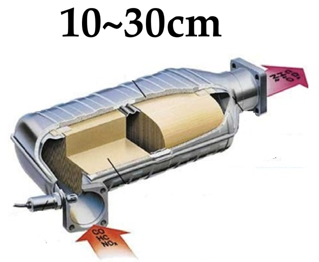
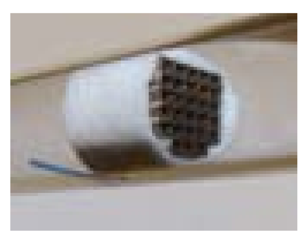
Motivation

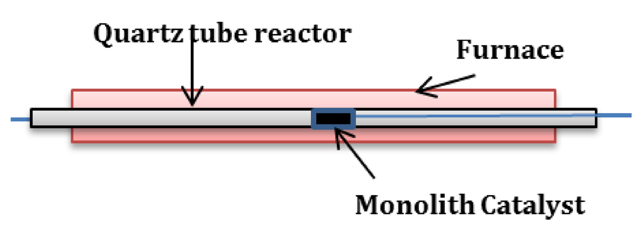
- Monolith reactors are used in many catalytic after-treatment systems (e.g. TWC, DOC, LNT and SCR). These systems are often studied using monolith samples of the same cell density, washcoat thickness and catalyst loading but of a smaller length compared to the full scale systems. The space time is maintained the same in different scales in order to obtain similar performances.
- However, similarity may not exist and the ignition/extinction behavior of the two systems can be qualitatively different when thermal effects are significant (or adiabatic temperature rise is large) and heat and mass transfer and dispersion effects are not negligible.

Full Scale Reactor/Catalyst
10~30cm



Lab Scale Reactor/Catalyst
0.5~2cm





Objectives

- Use modeling and dimensional analysis to quantify the impact of heat and mass dispersion and thermal effects on reactors with different scales.
- Develop criteria for similarity for experimental designs based on simulation and modeling results.

Model Equations

Species balance

$$\frac{\partial y_f}{\partial \hat{t}} = \frac{1}{Pe_{m,f}}\frac{\partial^2 y_f}{\partial z^2} - \frac{1}{P_m}(y_f - y_{wc}) - \frac{\partial y_f}{\partial z}$$

$$\epsilon\frac{\partial y_{wc}}{\partial \hat{t}} = \frac{1}{Pe_{m,s}}\frac{\partial^2 y_{wc}}{\partial z^2} + \frac{1}{P_m}(y_{fm} - y_{wc}) - Da_0 y_{wc} exp\left(\frac{-1/\beta}{\hat{T}_s + \theta^{in}}\right)$$

Energy balance

$$\frac{\partial \hat{T}_f}{\partial \hat{t}} = \frac{1}{Pe_{h,f}}\frac{\partial^2 \hat{T}_f}{\partial z^2} - \frac{1}{P_h}(\hat{T}_f - \hat{T}_s) - \frac{\partial \hat{T}_f}{\partial z}$$

$$\sigma\frac{\partial \hat{T}_s}{\partial \hat{t}} = \frac{1}{Pe_{h,s}}\frac{\partial^2 \hat{T}_s}{\partial z^2} + \frac{1}{P_h}(\hat{T}_f - \hat{T}_s) + Da_0 y_{wc} exp\left(\frac{-1/\beta}{\hat{T}_s + \theta^{in}}\right)$$

Dimension Analysis

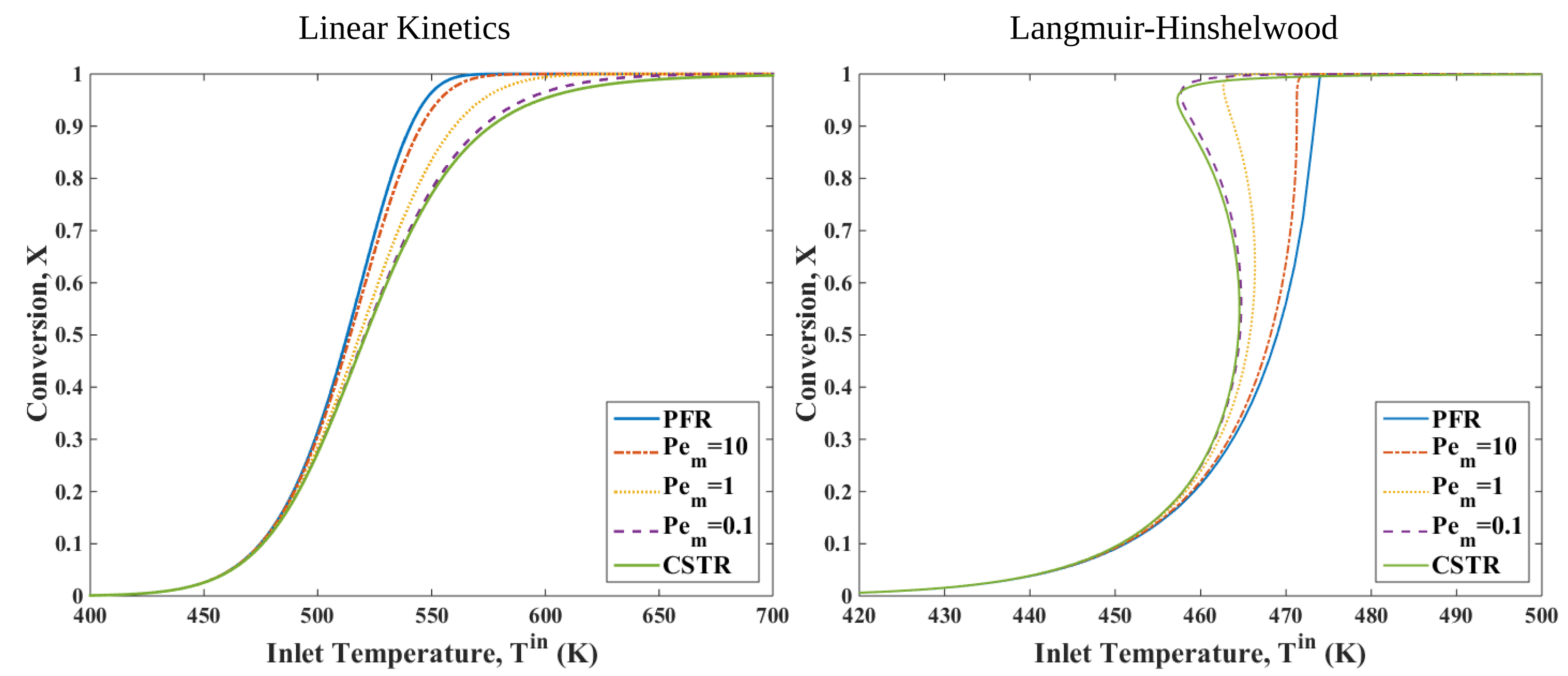
$$\hat{t} = \frac{t}{L/\langle u\rangle} \qquad z = \frac{x}{L} \qquad y = \frac{C}{C^{in}} \qquad \hat{T} = \frac{T - T^{in}}{\Delta T_{ad}} \qquad \theta^{in} = \frac{T^{in}}{\Delta T_{ad}}$$

Adiabatic T Rise (K)	Damköhler Number	Dimensionless T Rise	Volume Fraction	Cp Ratio
$\Delta T_{ad} = \frac{(-\Delta H)C^{in}}{\rho_f Cp_f}$	$Da_0 = \frac{A\tau\delta_{wc}}{R_\Omega}$	$\beta = \frac{\Delta T_{ad}}{E_a/R}$	$\epsilon = \epsilon_{wc}\frac{\delta_{wc}}{R_\Omega}$	$\sigma = \frac{\delta_s}{R_\Omega}\frac{\rho_s Cp_s}{\rho_f Cp_f}$

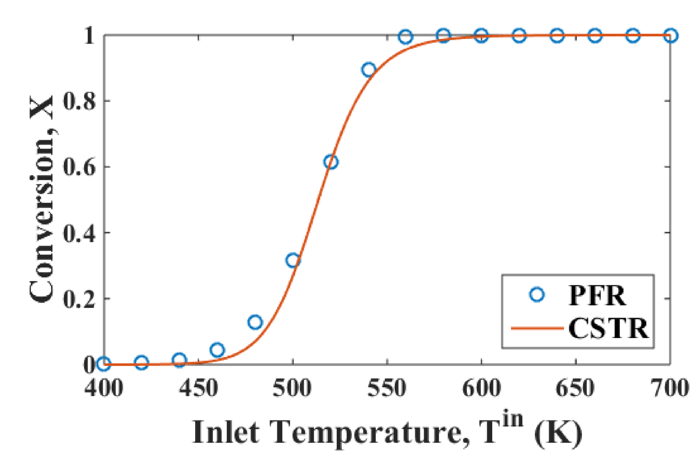
Péclet Num.	Transverse	Axial		
		Fluid		Solid
Mass	$P_m = \frac{R_\Omega\langle u\rangle}{L}\frac{1}{k_{mo}}$	$Pe_{m,f} = \frac{\langle u\rangle L}{D_f}$	$\ll$	$Pe_{m,s} = \frac{\langle u\rangle L}{D_{wc}}\frac{R_\Omega}{\delta_{wc}}$
Heat	$P_h = \frac{R_\Omega\langle u\rangle}{L}\frac{\rho_f Cp_f}{h}$	$Pe_{h,f} = \frac{\langle u\rangle L\rho_f Cp_f}{k_f}$	$\gg$	$Pe_{h,s} = \frac{\langle u\rangle L\rho_f Cp_f}{k_s}\frac{R_\Omega}{\delta_s}$
	Matched	Not Matched		Negligible

Impact of Mass Dispersion on Light-off

Isothermal Reactor Steady-state Conversion



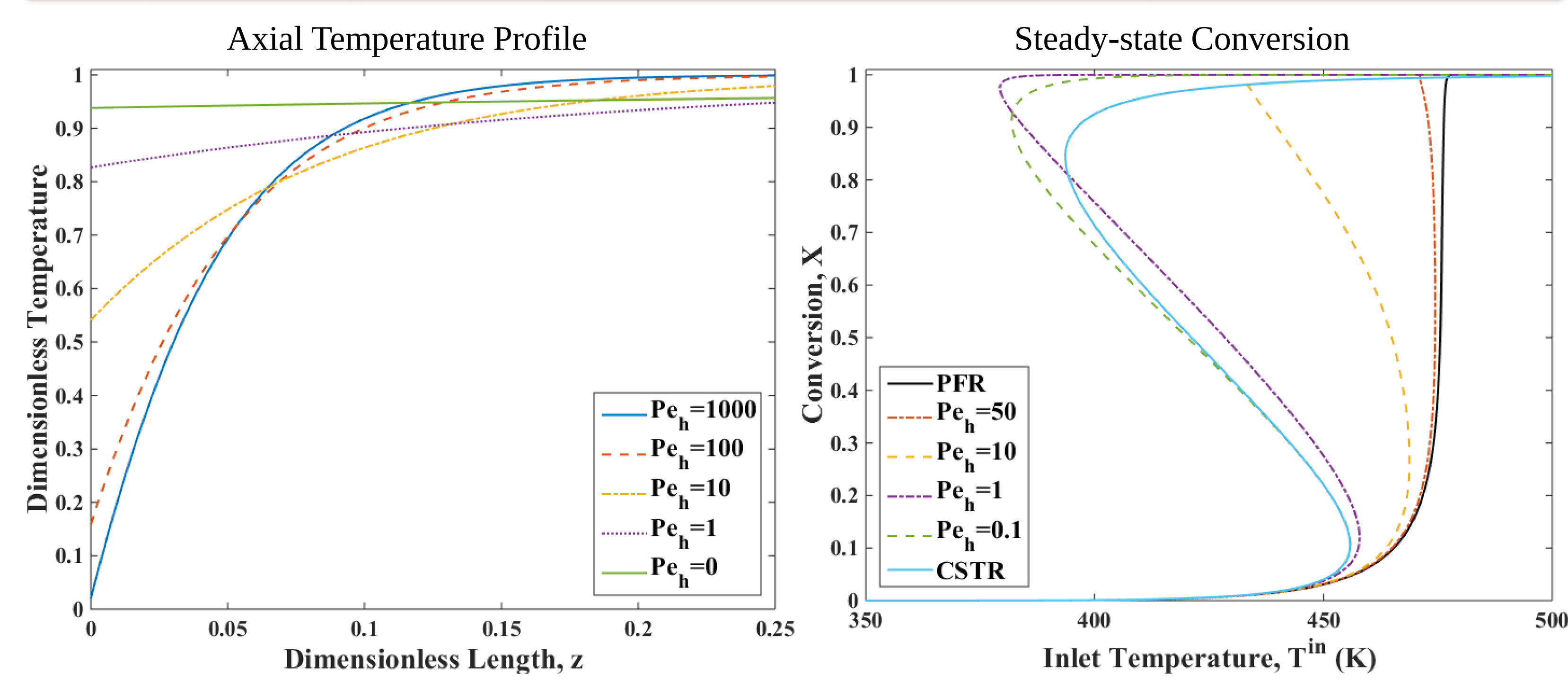
- For linear kinetics, mass dispersion only cause quantitative differences, thus there can be similarity provided that the Pe_m are large enough in both scales.
- For Langmuir-Hinshelwood kinetics (negative order), mass dispersion can cause qualitative differences (multiple solutions).

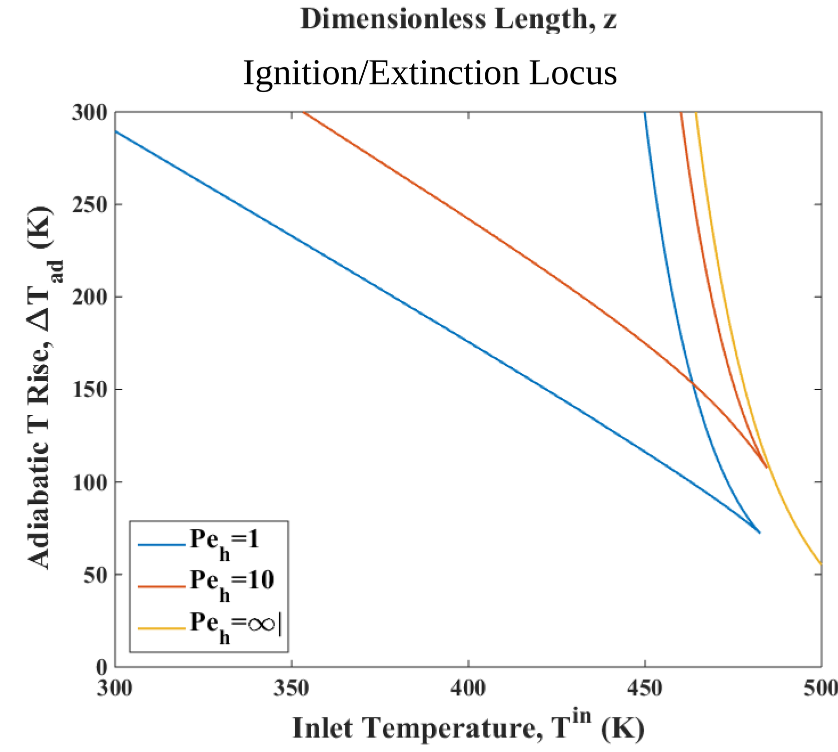


- Fitting data using inappropriate model can lead to false kinetic parameters.
- For example, using CSTR model to fit data from a reactor with high Pe_m, (close to PFR) will result in

$$\tilde{E}_a \approx 1.582E_a, \qquad \tilde{A} \approx 1.718A^{1.582}$$

Impact of Heat Conduction on Light-off



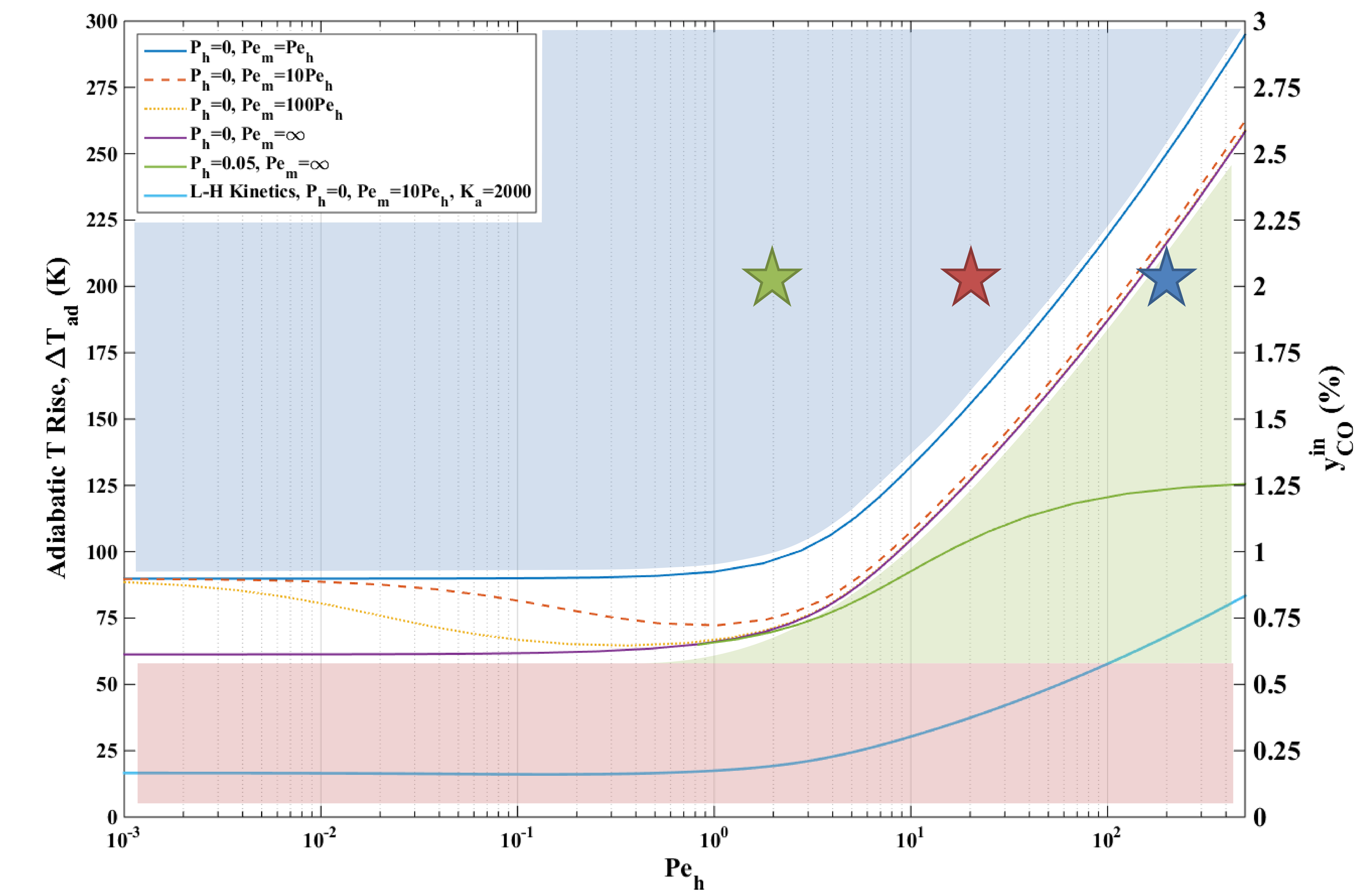


- Similarity exists only when both lab and full scale systems have large Pe_h.
- Unmatched Pe_h in the two scales can lead to different widths of temperature front, different steady-state conversions and different ignition/extinction behaviors.
- Existence and width of the hysteresis region is determined by the adiabatic temperature rise.

References

[1] Balakotaiah, V., *Chemical Engineering Education* 30 (1996): 234-239..
[2] Subramanian, S., and Balakotaiah, V., *Chemical Engineering Science* 51.3 (1996): 401-421.
[3] Gu, T. and Balakotaiah, V., CLEERS Telecon Presentation, Jan. 21, 2015

Impact of Thermal Effects / Adiabatic T Rise



Multiple solution region	Single solution region
Conditionally single solution region (depending on P_h and P_m)	
Conditionally multiple solution region (depending on Pe_m/Pe_h) Pe_m/Pe_h~10 for ceramic monolith, Pe_m/Pe_h~100 for metallic monolith	

★ Typical full scale ceramic monolith ★ Lab scale with 1/10 length
★ Lab scale with 1/3 length / Typical full scale metallic monolith

Simulation Conditions

- Since reactors in different scales have the same catalyst loading and space time, a constant typical value of $Da_0 = 10^{10}$ and E_a/R=12000 are used for all simulations. Similarly, $P_m = P_h = 0$ except for the hysteresis locus calculations, since they're matched in different scales and are usually very small.
- $\Delta T_{ad} = 200K$ is used for steady-state conversions (bifurcation diagrams), this can also be interpreted as 2% CO since $\Delta T_{ad} \approx 10^4 y^{in}_{CO}$

Summary

- **Similarity between different scales generally doesn't exist, thus a direct scale-up from lab scale is not possible.**
- **One should use the lab scale for kinetic studies only and make predictions of full scale system performances using modelling approach.**
- **For qualitative similarity, experiments should be designed such that lab scale reactors fall in the same multiplicity region as the full scale system.**
- **Mass and heat dispersion should be considered while estimating kinetic parameters to avoid false predictions.**

Current Work

- In this work we only considered isothermal and adiabatic reactors, where the external heat transfer coefficient are considered to be either infinity or zero.
- Since one can not match the external heat transfer conditions in different scales, this can lead to more scale-up issues to consider.

Acknowledgement: NSF Grant (CMMI-0727999) and Ford Motor Company