Low-dimensional Models for Real Time Simulations of Catalytic After-treatment Systems

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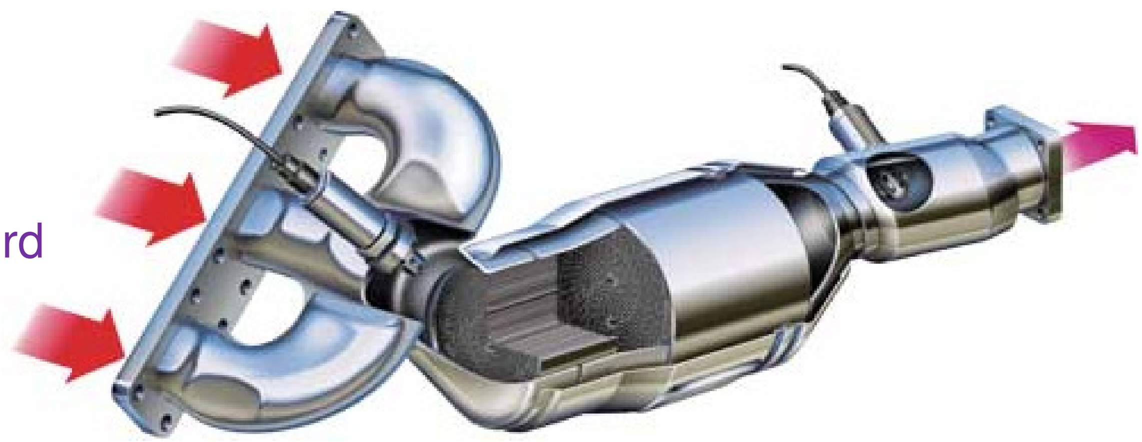


LNT/SCR, TWC/DOC & DPF Research at UH

Experiments

Modeling & Simulation

. Lean NOx Storage

. Steady-state lean NOx reduction

. NOx storage & reduction (cycling)

Transient kinetics studies (TAP)

Bench-scale reactor studies

Full-Scale Testing

Implementation / Optimization of LNTs

- *Software development*
- *Integration of engine & emission controls*

Engines & Controls (ME.)
Ford
BASF
City of Houston

Kinetic Modeling

- *Microkinetics (from TAP)*
- *Global kinetics*

Reactor Modeling

- *Isothermal / short monoliths*
- *Non-isothermal effects*

Analysis & Simulation

- *Bifurcation analysis*
- *Parametric studies*
- *Simulation and Comparison to Expts*

Low-dimensional Models for Control and Optimization

Overview

Part A: **Low-dimensional Models for Real Time Simulations of Catalytic After-treatment Systems (TWCs, DOCs, LNTs, SCRs and DPFs)**

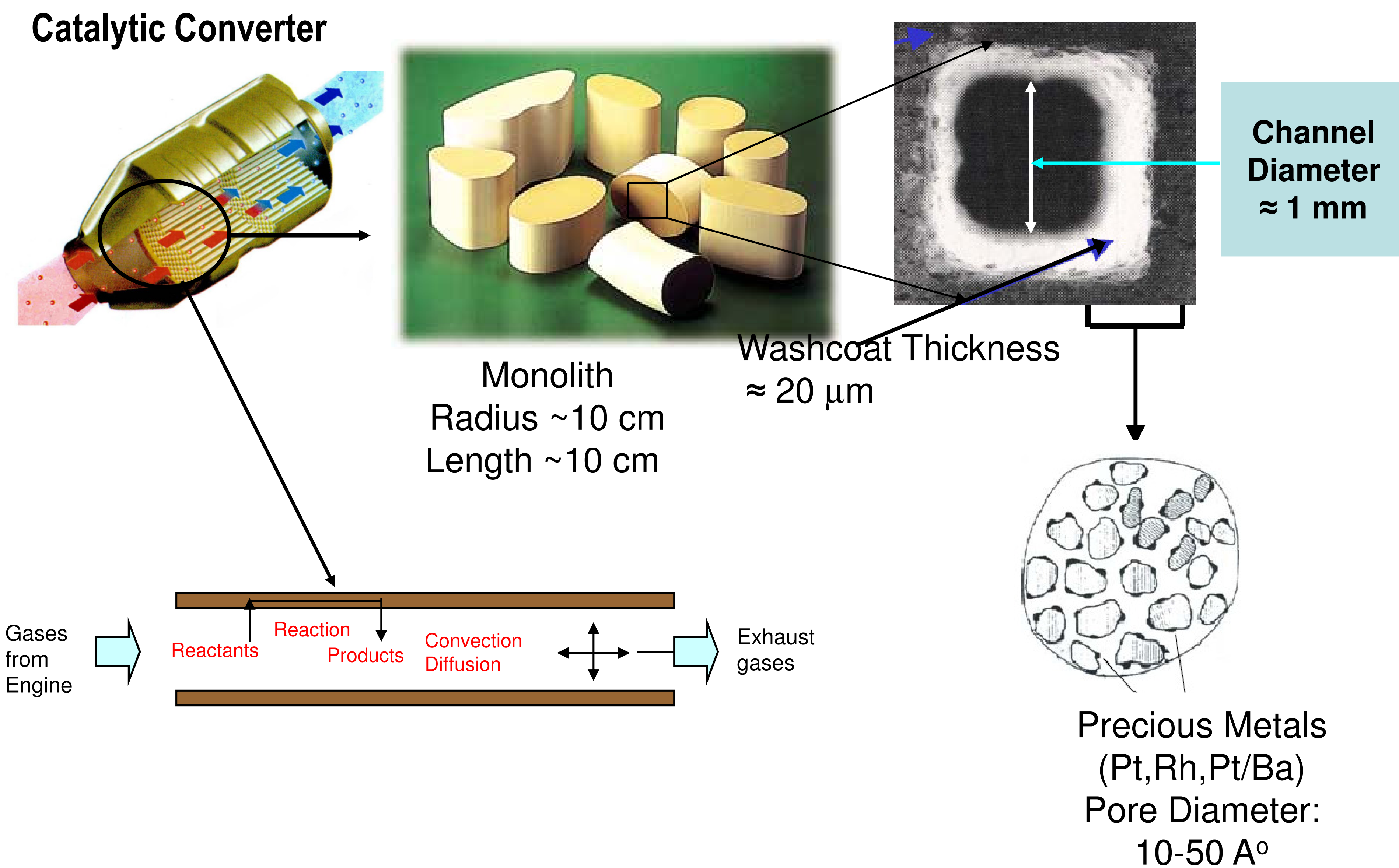
[Ref: Joshi, Harold and Balakotaiah, AIChE J., May 2009]

- low-d models for diffusion-convection-reaction
- simulation of TWC cold start behavior in real time
- extensions of low-d models

Part B: **Analysis of monolith reactors using low-d models**

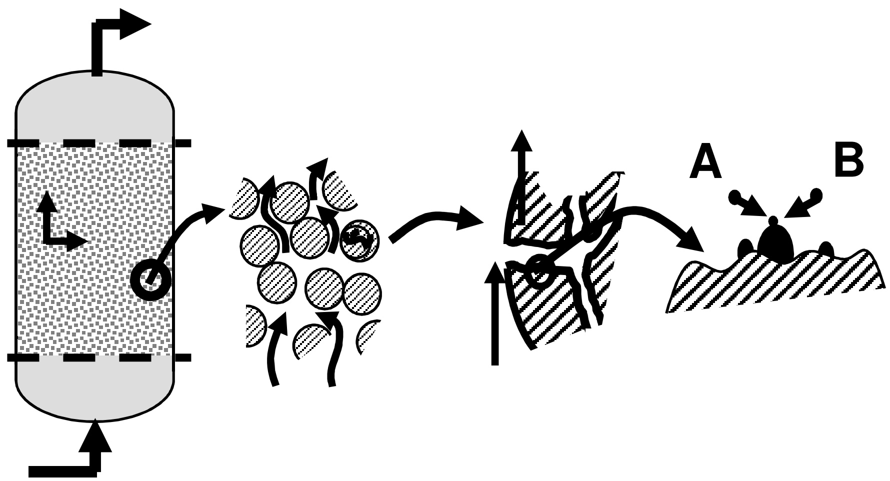
(i) Controlling regimes
(ii) External Mass transfer controlled regime
(iii) Light-off Behavior
(iv) Multiple steady-states and periodic states
(v) Fronts in monoliths
(vi) Bifurcation analysis
(vii) Microkinetic models vs. global kinetic models

Catalytic Monoliths- Multiple Length/ Time Scales



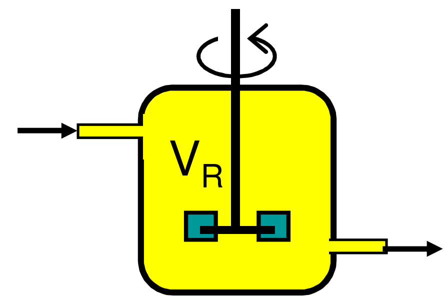
Models of Homogeneous & Catalytic Reactors

Packed-Bed Catalytic Reactor

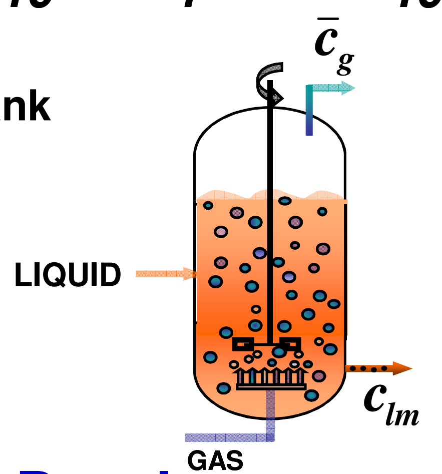


L(m)	*1*	10^{-3}	10^{-6}	10^{-9}
t(s)	$10\text{-}10^{3}$	*1*	10^{-5}	10^{-7}

Homogeneous Tank Reactor



Gas-Liquid Tank Reactor



Detailed Model:

$$C\frac{\partial \mathbf{u}}{\partial t} = \mathbf{F}(\mathbf{x},\mathbf{u},\nabla\mathbf{u},\nabla^2\mathbf{u},\mathbf{p}); \quad \mathbf{x} \text{ in } \Omega,\ t>0$$

$$\text{I.C.}: \Gamma(\mathbf{x},\mathbf{u},\nabla\mathbf{u},\mathbf{p}) = 0 \text{ in } \Omega,\ t=0$$

$$\text{B.C.}: \mathrm{B}(\mathbf{x},\mathbf{u},\nabla\mathbf{u},\mathbf{p}) = 0 \text{ in } \partial\Omega,\ t>0$$

Ideal CSTR Model:

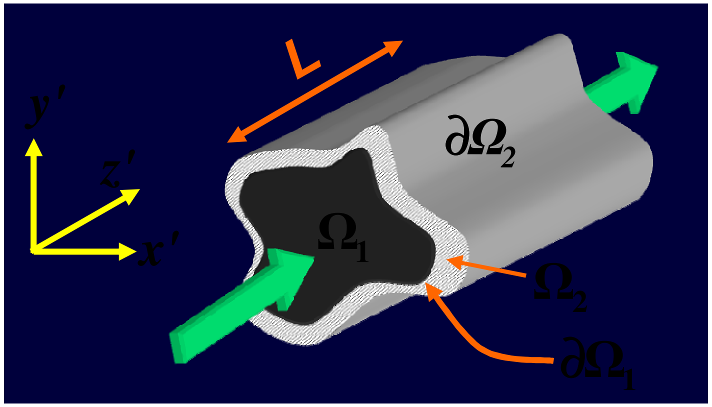
(Bodenstein & Wolgast, 1908)

$$\frac{d\bar{C}}{dt} = \frac{1}{\tau}(C_{in} - \bar{C}) - R(\bar{C}); \quad t>0$$

$$I.C.: \bar{C}(t=0) = \bar{C}_0$$

<u>Objective</u>: Develop accurate low-dimensional models (in terms of average/measurable quantities) ***without losing any important physics at small length/time scales.***

Detailed Diffusion-Convection-Reaction Models for Monoliths



Shape Normalized Diffusion Lengths

$$R_{\Omega} = \frac{A_{\Omega_1}}{P_{\Omega}}$$

fluid

$$\delta_w = \frac{A_{\Omega_2}}{P_{\Omega}}$$

washcoat

Steady State Balance Equations

$$\underbrace{\frac{\partial C_f}{\partial t} + u(x', y')\frac{\partial C_f}{\partial z'}}_{\text{convection}} = \underbrace{D_m\left(\nabla_*^2 C_f + \frac{\partial^2 C_f}{\partial z'^2}\right)}_{\text{diffusion}}, \quad (x', y') \in \Omega_1$$

$$\varepsilon_p \frac{\partial C_s}{\partial t} + \underbrace{R(C_s)}_{\text{reaction}} = \underbrace{D_e\left(\nabla_*^2 C_s + \frac{\partial^2 c_s}{\partial z'^2}\right)}_{\text{diffusion}}, \quad (x', y') \in \Omega_2$$

$$\textit{Coupled PDEs in } (x', y', z')$$

interfacial coupling

Boundary Conditions

$$\left.\begin{aligned} n.D_m \nabla_* C_f &= n.D_e \nabla_* C_s \\ C_f &= C_s \end{aligned}\right\}, \quad (x', y') \in \partial\Omega_1$$

$$n.D_e \nabla_* C_s = 0, \quad (x', y') \in \partial\Omega_2$$

$$D_m \frac{\partial C_f}{\partial z'} = u(x', y')\left(C_f - C_{in}(t)\right) \;\&\; \frac{\partial C_s}{\partial z'} = 0, \quad @\, z' = 0$$

$$\frac{\partial C_f}{\partial z'} = \frac{\partial C_s}{\partial z'} = 0, \quad @\, z' = L$$

Traditional Low-dimensional Models for Catalytic Reactor Models

Pseudo-homogeneous PFR model

$$\frac{\partial c}{\partial t}+\bar{u}\frac{\partial c}{\partial x}+R(c)=0;\ 0<x<L,\ \ t>0 \quad B.C.\ c(0,t)=c_{in}(t),\quad I.C.\ \ c(x,0)=c_o(x)$$

Two-phase model for a packed-bed reactor

(Wicke, 1960; Liu & Amundson, 1963)

$$\varepsilon_f\frac{\partial c_f}{\partial t}+\bar{u}\frac{\partial c_f}{\partial x}=-k_c a_v\left(c_f-c_s\right);\ <0<x<L,t>0$$

$$\left(1-\varepsilon_f\right)\frac{\partial c_s}{\partial t}=k_c a_v\left(c_f-c_s\right)\text{-}\ R(c_s);\ t>0$$

$$B.C.\quad c_f(0,t)=c_{f,in}(t)$$

$$I.C.\quad c_f(x,0)=c_{fo}(x)$$

$$c_s(x,0)=c_{so}(x)$$

Catalytic Reactor Model with Dispersion and Mass Transfer Coefficients

$$\varepsilon_f\frac{\partial c_f}{\partial t}+\bar{u}\frac{\partial c_f}{\partial x}=D_{ef}\frac{\partial^2 c_f}{\partial x^2}-k_c a_v\left(c_f-c_s\right);\ <0<x<L,t>0 \quad B.C\ 1\quad D_{ef}\frac{\partial c_f}{\partial x}=\bar{u}[c_f(0,t)-c_{f,in}(t)]$$

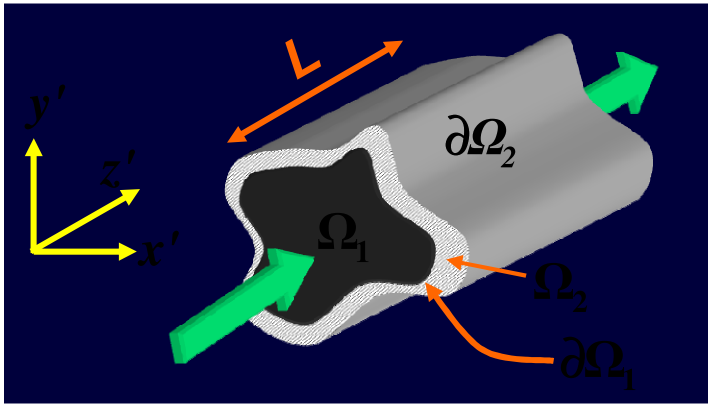
$$\left(1-\varepsilon_f\right)\frac{\partial c_s}{\partial t}=k_c a_v\left(c_f-c_s\right)\text{-}\ R(c_s);\ t>0 \qquad B.C\ 2\quad \frac{\partial c_f}{\partial x}=0$$

Catalytic Reactor Model with Dispersion, Mass Transfer Coefficients & Intra-particle diffusion

$$\left(1-\varepsilon_f\right)\frac{\partial c_s}{\partial t}=k_c a_v\left(c_f-c_s\right)\text{-}\ R(c_s)\eta;\ t>0$$

$$\nabla.\left(D_e\nabla c\right)=R(c)\ \text{ in }\Omega;\ c=c_s\ \text{ on }\partial\Omega;\ \ \eta=\frac{1}{V_\Omega}\int_\Omega R(c)d\Omega/R(c_s)$$

Detailed Diffusion-Convection-Reaction Models for Monoliths



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$$\varepsilon_p \frac{\partial C_s}{\partial t} + \underbrace{R(C_s)}_{\text{reaction}} = \underbrace{D_e\left(\nabla_*^2 C_s + \frac{\partial^2 c_s}{\partial z'^2}\right)}_{\text{diffusion}}, \quad (x',y')\in \Omega_2$$

Coupled PDEs in (x',y',z')

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$$D_m\frac{\partial C_f}{\partial z'} = u(x',y')\left(C_f - C_{in}(t)\right) \;\&\; \frac{\partial C_s}{\partial z'} = 0, \quad @\, z' = 0$$

$$\frac{\partial C_f}{\partial z'} = \frac{\partial C_s}{\partial z'} = 0, \quad @\, z' = L$$

Spatial Averaging of Convection-Diffusion-Reaction (CDR) Models

Balakotaiah & Chang; SIAM J. Appl. Math., 63,1231-1258 (2003)
Balakotaiah, Chem. Engng. Sci., 63, 5802-5812,2008
Joshi, S. Y. , Harold, M. P. , V. Balakotaiah, AIChE J., May 2009

Observations:

- Diffusion is dominant at small length scales
- Local Diffusion operator of the CDR equation (with a periodic/ Neumann & Robin BCs has a zero eigenvalue with a constant eigenfunction.
- Spatial degrees of freedom (small length scales) can be eliminated near the zero eigenvalue (small parameter).

Procedure:

- Write the detailed (microscopic) model
- Identify the smallest length/time scale (expressed in terms of a small parameter, say p)
- Express all other parameters (λ_i) as $\lambda_i = \alpha_i p^n$, where α_i is O(1) & $n = 1, 0, -1, \ldots$
- Apply the L-S reduction (eliminate spatial degrees of freedom)

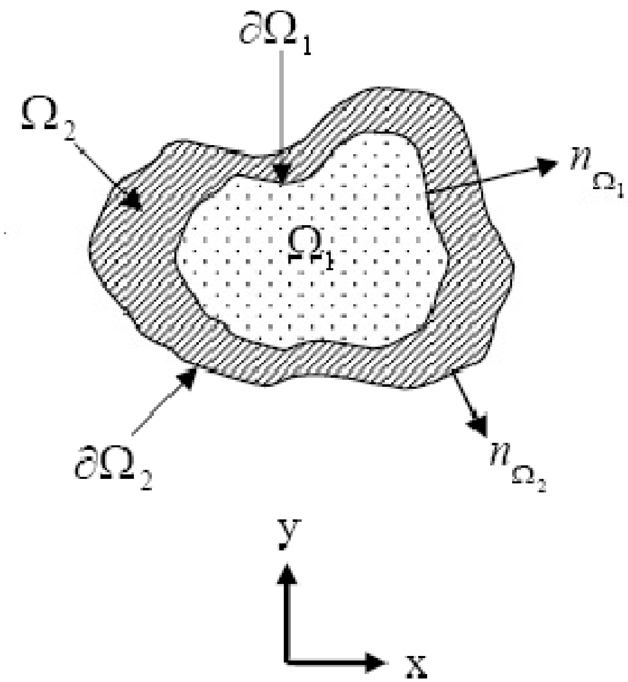
Concentration Modes

$$C_{fm} = \frac{\int_{\Omega_1} u(x,y)\, C_f(x,y)\, d\Omega}{\int_{\Omega_1} u(x,y)\, d\Omega} = \text{cup - mixing concentration}$$

$$< C_f >= \frac{\int_{\Omega_1} C_f(x,y)\, d\Omega}{\int_{\Omega_1} d\Omega} = \text{average concentration in fluid}$$

$$C_s = \frac{\int_{\partial\Omega_1} C_1(x,y)\, d\Gamma}{\int_{\partial\Omega_1} d\Gamma} = \frac{\int_{\partial\Omega_1} C_2(x,y)\, d\Gamma}{\int_{\partial\Omega_1} d\Gamma}$$

$$\langle C_{wc} \rangle = \frac{\int_{\Omega_2} C_2(x,y)\, d\Omega}{\int_{\Omega_2} d\Omega} = \frac{1}{A_{\Omega_2}} \int_{\Omega_2} C_2(x,y)\, d\Omega$$



On the Relationship Between Aris and Sherwood Numbers and Friction and Effectiveness Factors

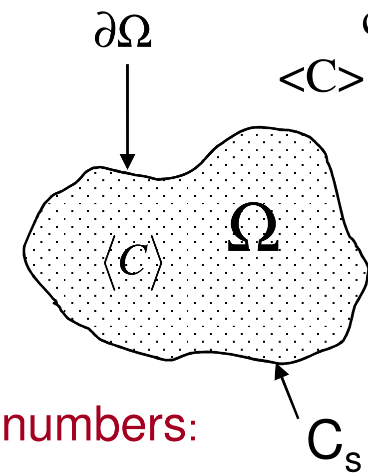
V. Balakotaiah, Chem. Engng. Sci., 2008

(i) Concept of an internal mass transfer coefficient:

$$k_{ci} = \frac{\frac{1}{A_{\Omega'}}\int_{A_{\Omega'}} D_e \nabla C.n\, dS}{(\overline{C_s} - \langle C \rangle)},$$

C_s = solid-fluid interfacial concentration

<C> = volume averaged concentration.



Flux, $j = k_{ci}(C_s - \langle C \rangle)$

Sherwood number, $Sh_\Omega = \dfrac{k_{ci} R_\Omega}{D_e}$

$$R_\Omega = \frac{V_\Omega}{A_\Omega}$$

$$\Phi^2 = \frac{R_\Omega^2 k}{D_e}$$

(ii) Effectiveness factor:

$$\eta = \frac{\langle r(C) \rangle}{r(C_s)} = \frac{\langle C \rangle}{C_s} \text{ (for linear kinetics)}$$

(iii) Aris numbers:

$$\eta = 1 - Ar_1\Phi^2 + Ar_2\Phi^4 - \ldots$$

$$\eta = \frac{1}{1 + \dfrac{\Phi^2}{Sh_\Omega}}$$

(iv) Friction factors for viscous flow in a duct (2-D):

$$\frac{f\,\mathrm{Re}}{8} = Sh_{\Omega\infty} = \frac{1}{Ar_1}; \quad \mathrm{Re} = \frac{4R_\Omega \langle u \rangle}{\nu}$$

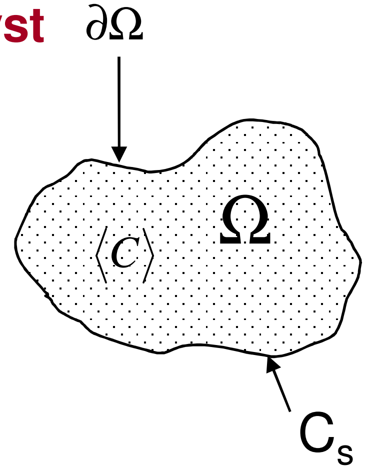
(i) Low-dimensional Model for Multicomponent Nonlinear Diffusion-Reaction Problems

(ii) Low-dimensional Models for Diffusion-Convection-Reaction Problems

Joshi, S.Y., Harold, M. P. and Balakotaiah, V. AIChE J., May 2009

Low-Dimensional Models for Diffusion-Reaction Problems

The Internal Diffusion-Reaction Problem in a Porous Catalyst



$$\varepsilon_p \frac{\partial C}{\partial t'} = \nabla.(D_e \nabla C) - R(C); \quad (x', y', z') \in \Omega', t' > 0$$

$$C = C_s(t'); \quad \text{on } \partial\Omega'.$$

$$C = C_i(x', y', z') \quad \text{at} \quad t' = 0$$

Volume averaged concentration in particle

$$\langle C \rangle (t') = \frac{1}{V_{\Omega'}} \int_{\Omega'} C(x', y', z', t') d\Omega'$$

$$C = \langle C \rangle + C'$$

$$\langle C' \rangle = 0$$

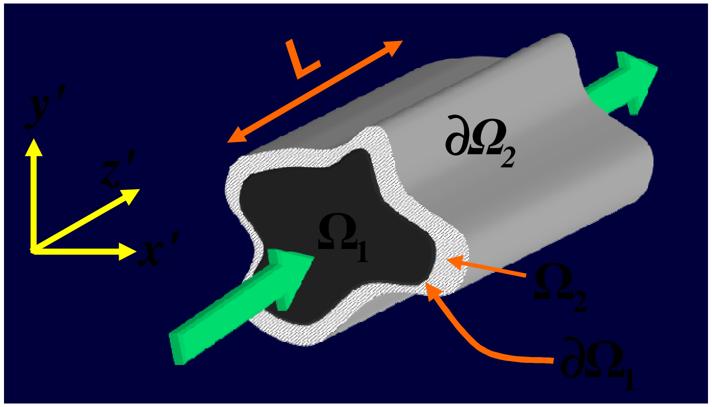
$$\langle R(\langle C \rangle + C') \rangle = R(\langle C \rangle) + O(C')^2$$

Low-Dimensional Model

$$\varepsilon_p V_{\Omega'} \frac{d\langle C \rangle}{dt'} = A_{\Omega'}\, k_{ci}\, (\overline{C_s(t')} - \langle C \rangle) - V_{\Omega'} R(\langle C \rangle)$$

$$\langle C \rangle = \langle C_i \rangle \quad \text{at} \quad t' = 0,$$

Three-mode Model for an Isothermal Monolith ($L/d_h >>1$)



$$\frac{\partial C_{fm}}{\partial t} + \langle u \rangle \frac{\partial C_{fm}}{\partial x} = -\frac{k_{ce}}{R_\Omega}\left(C_{fm} - C_s\right)$$

$$\varepsilon_p \delta_w \frac{\partial \langle C_w \rangle}{\partial t} = k_{ci}\left(C_s - \langle C_w \rangle\right) + \delta_w R\left(\langle C_w \rangle\right)$$

$$k_{ce}\left(C_{fm} - C_s\right) = k_{ci}\left(C_s - \langle C_w \rangle\right)$$

$$k_{ci} = \frac{Sh_{i\Omega} D_e}{\delta_w} \qquad k_{ce} = \frac{Sh_{e\Omega} D_m}{R_\Omega}$$

Two-Mode form:

$$\frac{\partial C_{fm}}{\partial t} + \langle u \rangle \frac{\partial C_{fm}}{\partial x} = -\frac{k_{mo}}{R_\Omega}(C_{fm} - \langle C_w \rangle)$$

$$\varepsilon_p \delta_w \frac{\partial \langle C_w \rangle}{\partial t} = k_{mo}(C_{fm} - \langle C_w \rangle) - \delta_w R(\langle C_w \rangle)$$

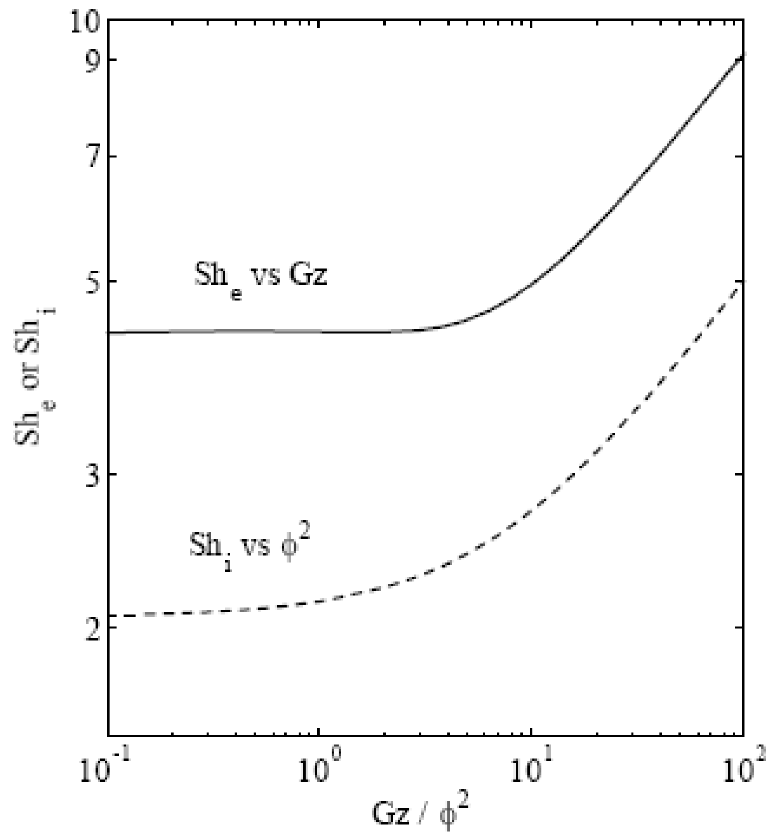
$$IC1:\ C_{fm}(x, t=0) = C_{m0}(x)$$

$$IC2:\ \langle C_w \rangle(x, t=0) = \langle C_{w0} \rangle(x)$$

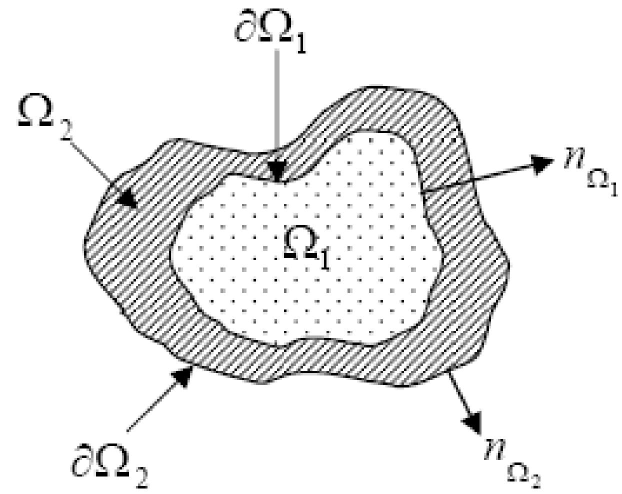
$$BC:\ C_{fm} = C_{in}(t)\ @\ x = 0$$

$$\frac{1}{k_{mo}} = \frac{1}{k_{ci}} + \frac{1}{k_{ce}} = \frac{\delta_w}{Sh_{i\Omega} D_e} + \frac{R_\Omega}{Sh_{e\Omega} D_m} \approx \frac{\delta_w}{Sh_{i\Omega\infty} D_e} + \frac{R_\Omega}{Sh_{e\Omega\infty} D_m}$$

Analogy between internal and external mass transfer coefficients



Theory and Computation of Internal Mass Transfer Coefficients



$$\nabla^2 c = g(x', y')\phi^2 c \qquad (x', y') \in \Omega_2' \quad n_{\Omega_2}.\nabla c = 0 \ \text{ on } \partial\Omega_2' \quad c = 1 \ \ on \ \ \partial\Omega_1'$$

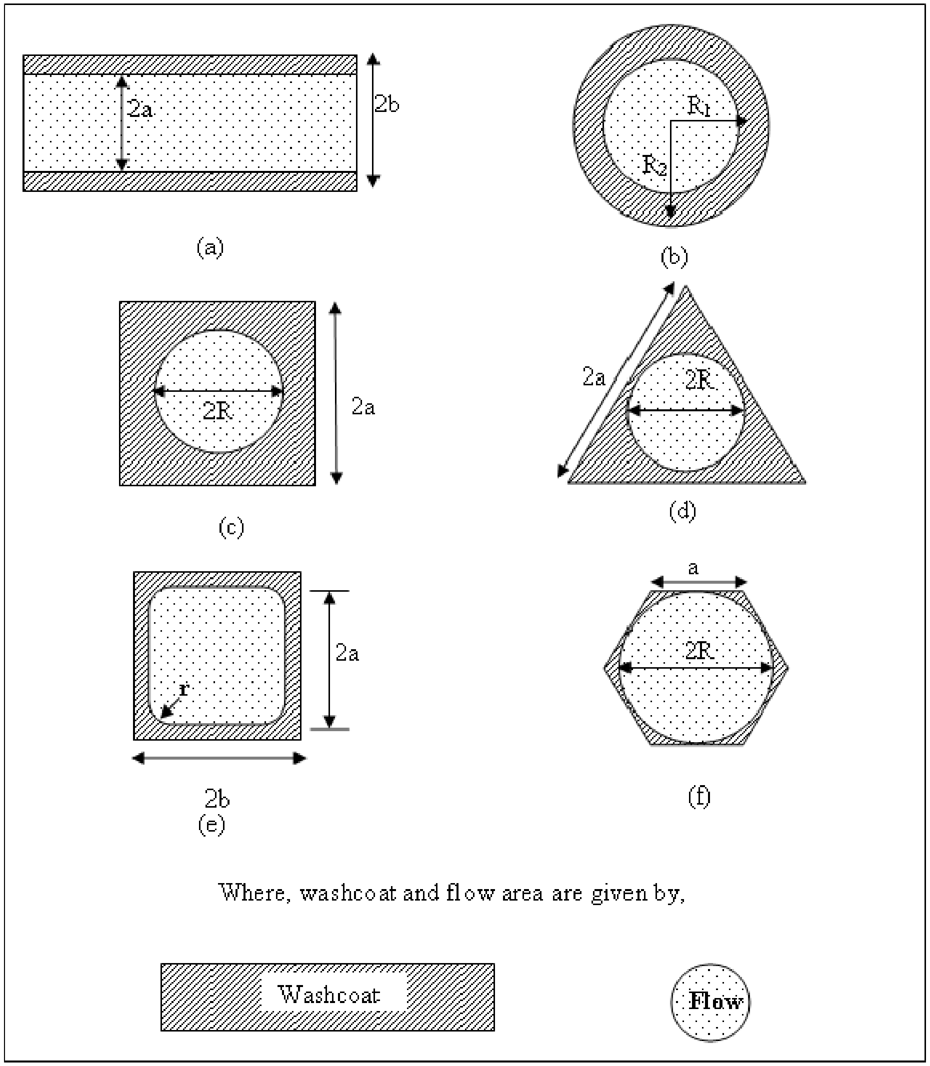
$$k_{mi} = \frac{\int_{A_{\Omega_2}} R(C)\, dA}{P_\Omega \left(C_s - \langle C \rangle\right)} \qquad Sh_i = \frac{k_{mi} R_\Omega}{D_e} \qquad Sh_i = Sh_{i\infty} + \frac{\Lambda \phi^2}{1 + \Lambda \phi}$$

Approximation

Balakotaiah V. "On the relationship between Aris and Sherwood numbers and friction factor and effectiveness factors", Chemical Engineering Science. 2008;63,5802-5812.

Joshi, S. Y., Harold, M. P. and V. Balakotaiah, Chem. Engng. Sci., 2009, in review

Sh_i for some common geometries



Channel Shape	$Sh_{i\infty}$ and Λ			
Figure a	$Sh_{i\infty} = 3$ and $\Lambda = 0.32$			
Figure b	R_2/R_1	$Sh_{i\infty}$	Λ	
	1.01	3.0125	0.38	
	1.1	3.153	0.36	
	1.2	3.311	0.34	
Figure c	a/R	$Sh_{i\infty}$	Λ	
	1	0.826	0.67	
	1.1	1.836	1.2	
	1.2	2.533	0.73	
Figure d	a/R	$Sh_{i\infty}$	Λ	
	1.7321	0.84	0.62	
	1.9245	1.45	1.25	
	2.4744	2.92	0.85	
Figure e	b/a	b/r	$Sh_{i\infty}$	Λ
	1.11	5	2.645	0.58
	1.25	10	3.088	0.39
Figure f	a/R	$Sh_{i\infty}$	Λ	
	1.155	0.814	0.77	
	1.17	1.16	2.08	
	1.2	1.74	1.6	

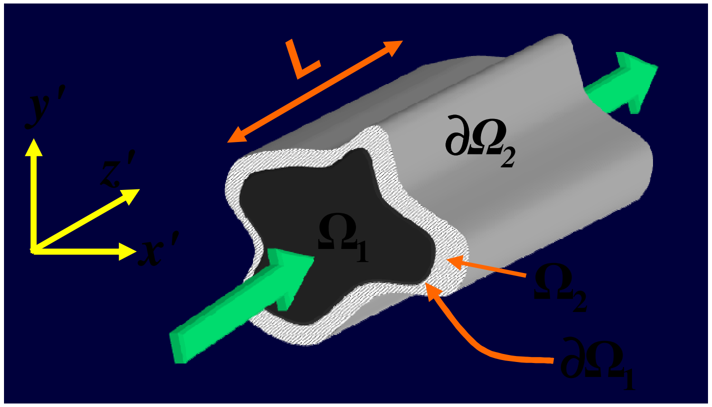
Joshi SY, Harold MP and Balakotaiah V. On the use of internal mass transfer coefficients in modeling of diffusion and reaction in catalytic monoliths. Chemical Engineering Science (in review)

Three-mode Model for an Isothermal Monolith ($L/d_h >>1$)

$$\frac{\partial C_{fm}}{\partial t} + \langle u \rangle \frac{\partial C_{fm}}{\partial x} = -\frac{k_{ce}}{R_\Omega}\left(C_{fm} - C_s\right)$$

$$\varepsilon_p \delta_w \frac{\partial \langle C_w \rangle}{\partial t} = k_{ci}\left(C_s - \langle C_w \rangle\right) + \delta_w R\left(\langle C_w \rangle\right)$$

$$k_{ce}\left(C_{fm} - C_s\right) = k_{ci}\left(C_s - \langle C_w \rangle\right)$$



$$k_{ci} = \frac{Sh_{i\Omega} D_e}{\delta_w} \qquad k_{ce} = \frac{Sh_{e\Omega} D_m}{R_\Omega}$$

Two-Mode form:

$$\frac{\partial C_{fm}}{\partial t} + \langle u \rangle \frac{\partial C_{fm}}{\partial x} = -\frac{k_{mo}}{R_\Omega}(C_{fm} - \langle C_w \rangle)$$

$$\varepsilon_p \delta_w \frac{\partial \langle C_w \rangle}{\partial t} = k_{mo}(C_{fm} - \langle C_w \rangle) - \delta_w R(\langle C_w \rangle)$$

$$IC1: \ C_{fm}(x, t=0) = C_{m0}(x)$$

$$IC2: \ \langle C_w \rangle (x, t=0) = \langle C_{w0} \rangle (x)$$

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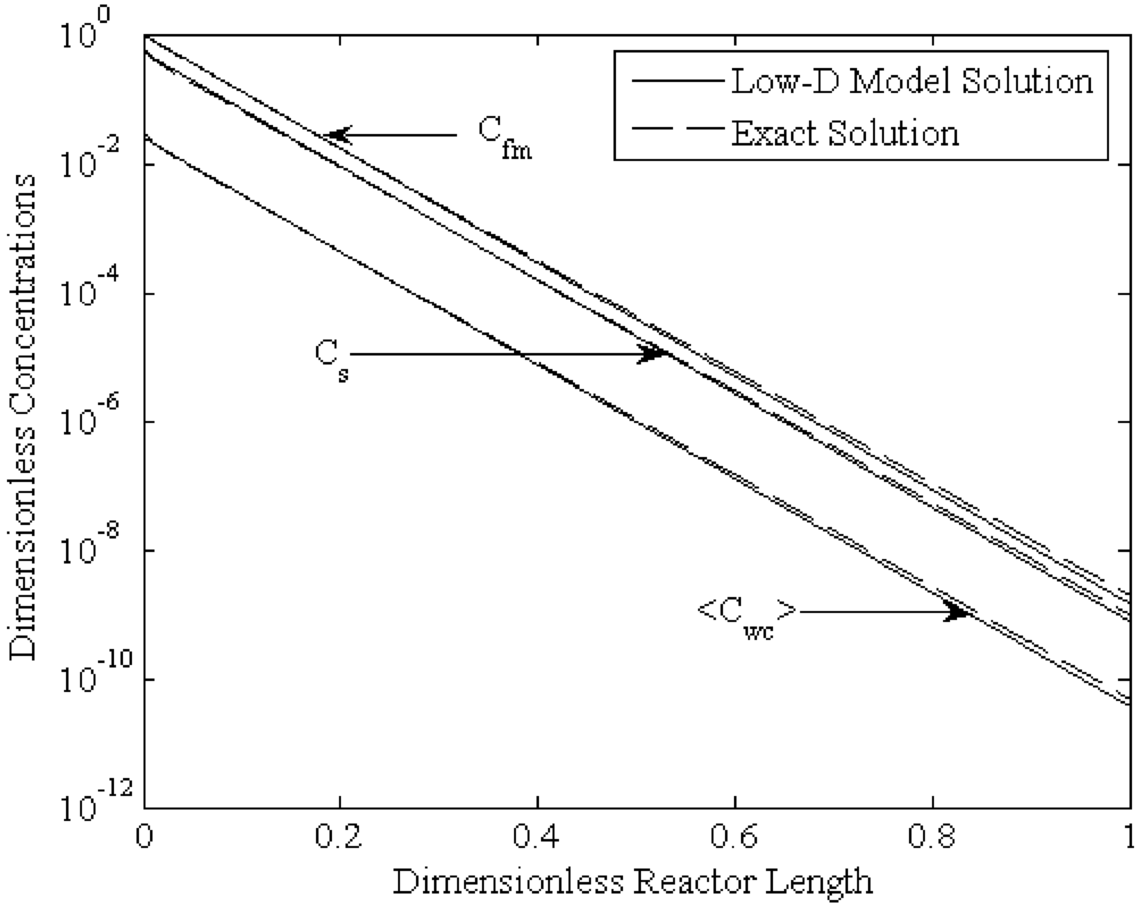
$$\frac{1}{k_{mo}} = \frac{1}{k_{ci}} + \frac{1}{k_{ce}} = \frac{\delta_w}{Sh_{i\Omega} D_e} + \frac{R_\Omega}{Sh_{e\Omega} D_m} \approx \frac{\delta_w}{Sh_{i\Omega\infty} D_e} + \frac{R_\Omega}{Sh_{e\Omega\infty} D_m}$$

Comparison of Accuracy of Low-D Model for Linear Kinetics, Single Reaction and Isothermal Case:

Circular channle with uniform washcoat thickness



Joshi , Harold & Balakotaiah, AIChE J., May 2009.

Low-Dimensional Model for Multi-component DCR Problem:

Balakotaiah, Chem. Engng. Sci., 63, 5802-5812,2008
Joshi , Harold & Balakotaiah,, AIChE J., May 2009

Species conservation:

$$\frac{\partial C_{fm_j}}{\partial t}+\langle u\rangle\frac{\partial C_{fm\,j}}{\partial x}=-\frac{k_{ce,j}}{R_\Omega}\left(C_{fm_j}-C_{s\,j}\right)$$

$$\varepsilon_p\delta_w\frac{\partial\langle C_w\rangle_j}{\partial t}=\sum_{m=1}^{S} k_{ci,jm}\left(C_{ms}-\langle C_w\rangle_m\right)+\delta_w\sum_{i=1}^{N}\nu_{ij}R_i\left(\langle C_w\rangle_1,\langle C_w\rangle_2\ldots\langle C_w\rangle_S,T_s\right)$$

$$k_{ce,j}\left(C_{fm\,j}-C_{s\,j}\right)=k_{ci,j}\left(C_{s\,j}-\langle C_{wc}\rangle_j\right)\qquad k_{ce,j}=\frac{Sh_{e\Omega\infty}D_{m,j}}{R_\Omega}\qquad k_{ci,j}=\frac{Sh_{i\Omega\infty}D_{ej}}{\delta_w}$$

j=1,2 …. S (species); N reactions

+ IC + BCs

Energy balance:

$$\rho_f c_{pf}\frac{\partial T_f}{\partial t}+\langle u\rangle\rho_f c_{pf}\frac{\partial T_f}{\partial x}=-\frac{h}{R_\Omega}\left(T_f-T_s\right)$$

$$\delta_s\rho_s c_{ps}\frac{\partial T_s}{\partial t}=\delta_s k_s\frac{\partial^2 T_s}{\partial x^2}+h\left(T_f-T_s\right)+\delta_w\sum_{j=1}^{M} R_j\left(\langle C_w\rangle_1,\langle C_w\rangle_2,\ldots\langle C_w\rangle_N,T_s\right)\times\left(-\Delta H_j\right)$$

$$\boldsymbol{T_f=T_{fin}(t)\ @\ \mathrm{x}=0;\ T_s(x,t=0)=T_{s0}(x);\ T_f(x,t=0)=T_{f0}(x);\ \frac{\partial T_s}{\partial x}=0\ @\ \mathrm{x}=0,L}$$

Simulation of Transient Behavior of a TWC with Global Kinetics

1. $CO + \frac{1}{2}O_2 \rightarrow CO_2$

2. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

3. $CH_y + \frac{4+y}{4}O_2 \rightarrow CO_2 + \frac{y}{2}H_2O$

4. $NO + CO \rightarrow CO_2 + N_2$

$$R_{CO} = \frac{k_1 \hat{X}_{CO} \hat{X}_{O_2}}{F(\underline{\hat{X}}, T_s)}$$

$$R_{H_2} = \frac{k_1 \hat{X}_{H_2} \hat{X}_{O_2}}{F(\underline{\hat{X}}, T_s)}$$

$$R_{HC} = \frac{k_3 \hat{X}_{HC} \hat{X}_{O_2}}{F(\underline{\hat{X}}, T_s)}$$

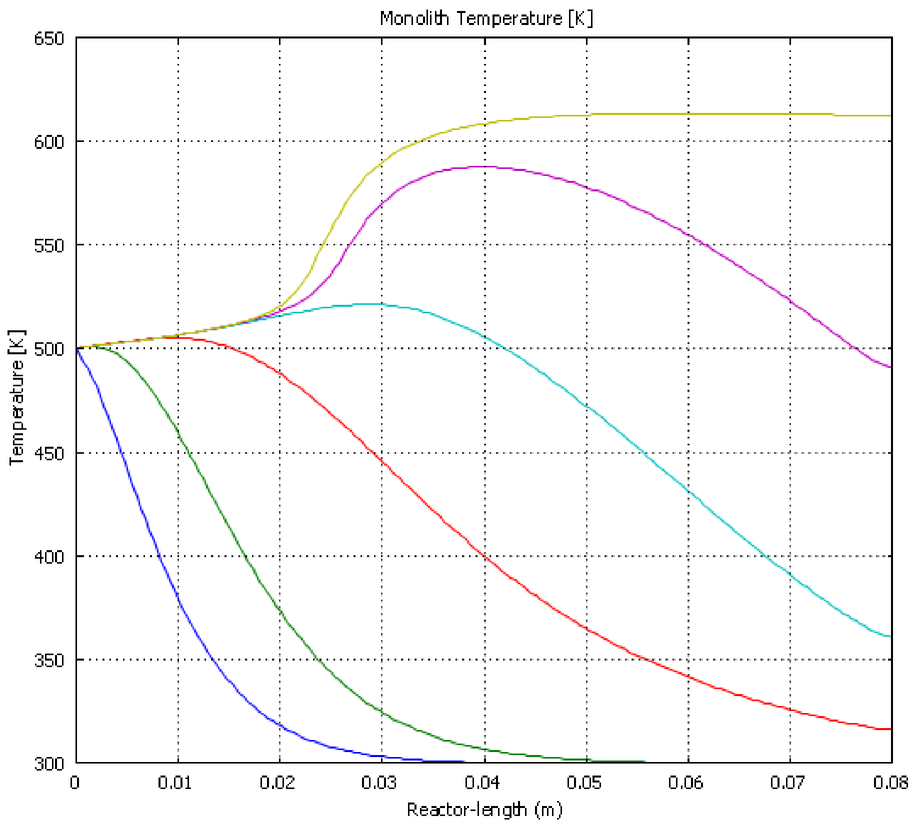
$$R_{NO} = \frac{k_4 \hat{X}_{CO}^{1.4} \hat{X}_{O_2}^{0.3} \hat{X}_{NO}^{0.13}}{T_s^{-0.17}(T_s + ka_5 \hat{X}_{CO})^2}$$

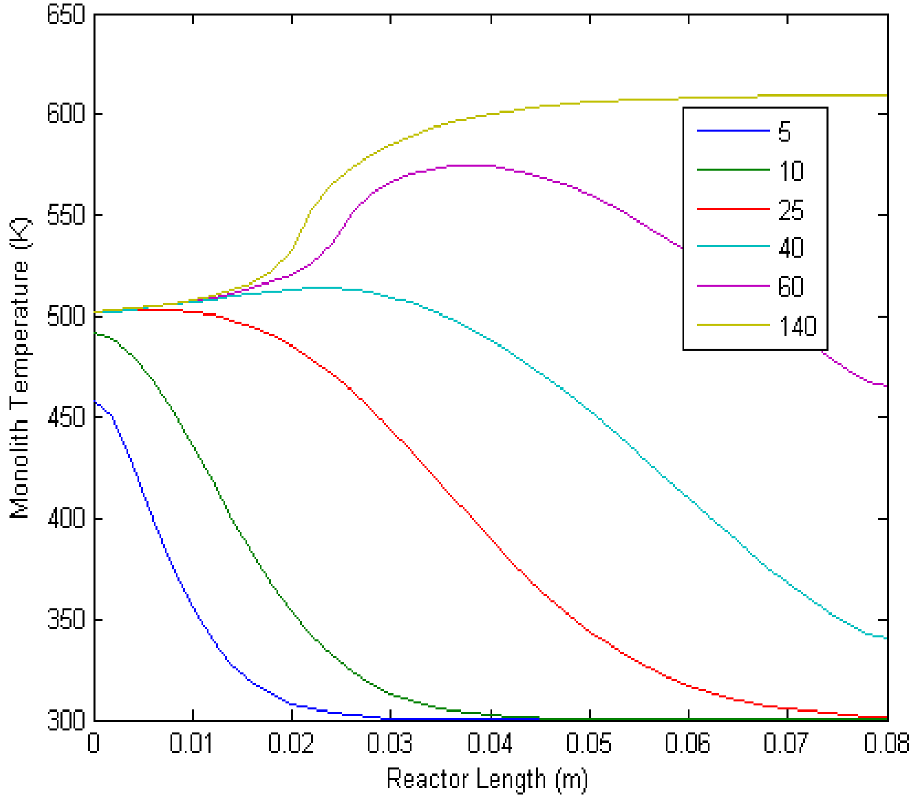
$$F(\underline{\hat{X}}, T_s) = T_s(1 + ka_1 \hat{X}_{CO} + ka_2 \hat{X}_{HC})^2 (1 + ka_3 \hat{X}_{CO}^2 \hat{X}_{HC}^2)(1 + ka_4 \hat{X}_{NO}^{0.7})$$

$$k_i = A_i e^{-\frac{E_i}{T_s}} \qquad i = 1, 3, 4$$

$$ka_i = A_{ii} e^{-\frac{E_{ii}}{T_s}} \qquad i = 1 - 5$$

Monolith Temperature

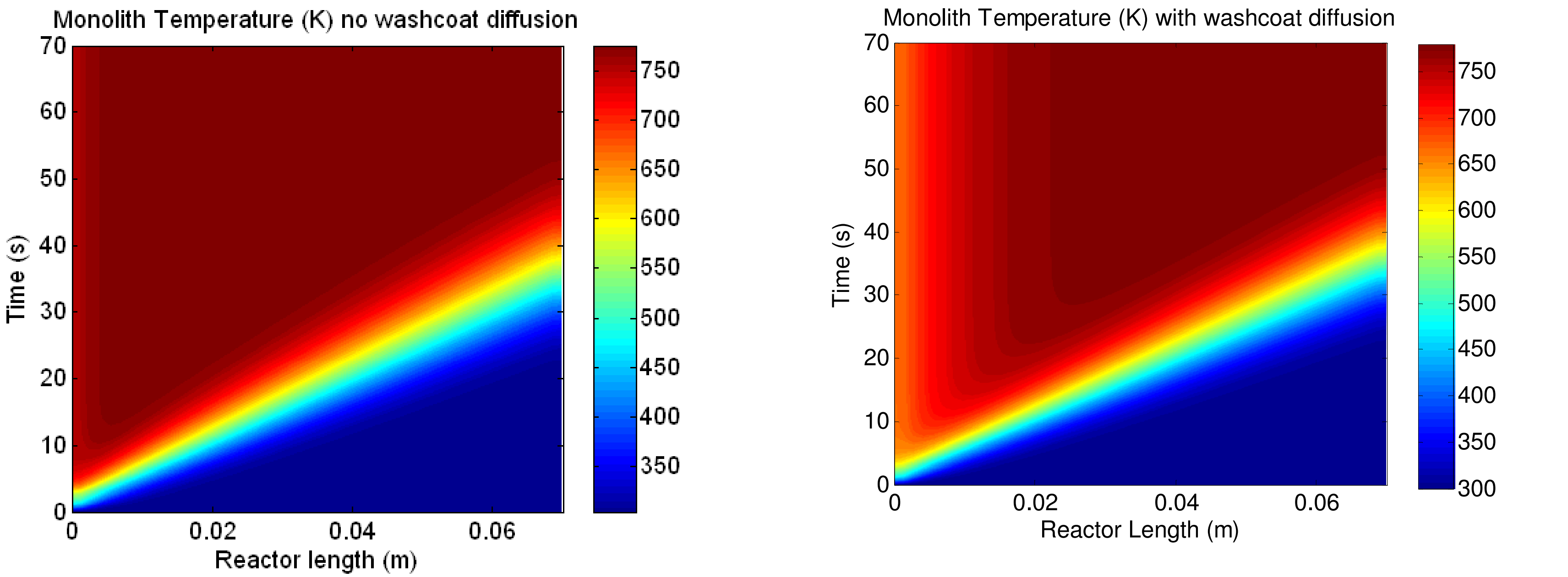




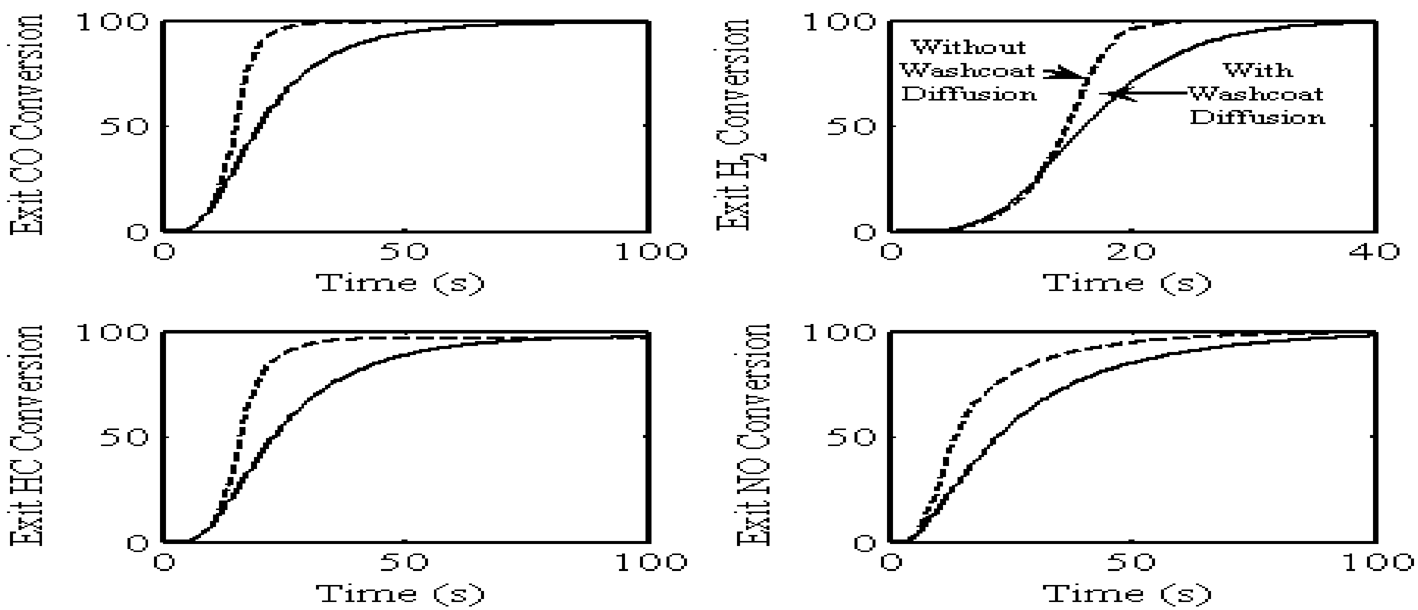
COMSOL SOLUTION

LOW-D MODEL SOLUTION

Joshi , Harold & Balakotaiah,
AIChE J., May 2009



Transient simulation showing front end ignition (a) monolith temperature without washcoat diffusion (b) monolith temperature with washcoat diffusion



Demonstration of Real Time Simulation of the Cold-start Behavior of a TWC

Extensions to the low-D models

- **Developing flows**
- **Microkinetics** (2 equations for each gas phase species, one eqn. for each surface species)
- **Estimation of kinetic parameters from bench scale expts.**
- **Axial variations of PGM loading**
- **Transverse variations in temperature (heat losses)**
- **Other types of catalytic and multi-phase reactors**

Overview

Models:

Low-dimensional Models for Real Time Simulations of Catalytic After-treatment Systems (TWCs, DOCs, LNTs, SCRs and DPFs)

- **low-d models for diffusion-convection-reaction**
- **simulation of TWC cold start behavior in real time**
- **extensions of low-d models**

Analysis:

Generic features of monoliths using low-d models

(i) Controlling regimes

(ii) External Mass transfer controlled regime

(iii) Fronts in monoliths

(iv) Multiple steady-states and periodic states

(v) Light-off behavior

(vi) Bifurcation analysis

(vii) Microkinetic models vs. global kinetic models

(i) Controlling Regimes

Comparison of various resistances

$$\underbrace{\frac{1}{k_{m_{app}}}}_{\substack{\text{Total} \\ \text{Resistance } (R_t)}} = \underbrace{\frac{1}{k_{me}}}_{\substack{\text{External} \\ \text{Resistance } (R_e)}} + \underbrace{\frac{1}{k_{mi}}}_{\substack{\text{Internal (Washcoat)} \\ \text{Resistance } (R_w)}} + \underbrace{\frac{1}{kR_{\Omega_2}}}_{\substack{\text{Reaction} \\ \text{Resistance } (R_r)}}$$

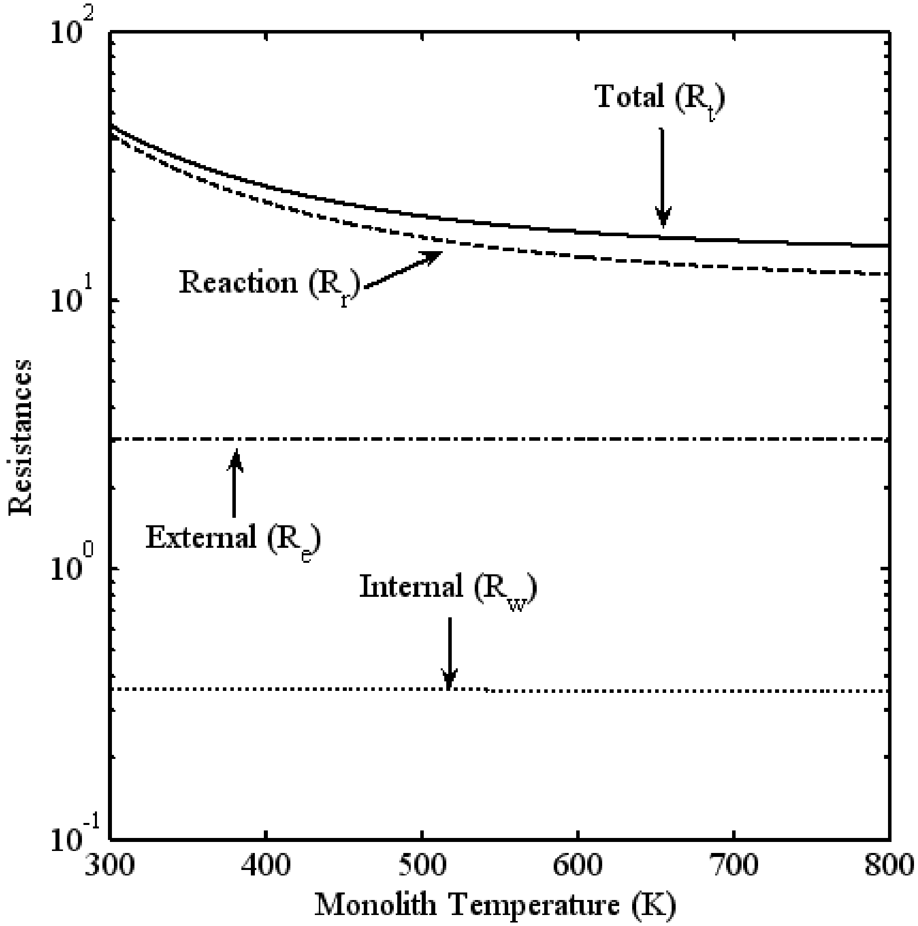
Criterion for controlling regimes

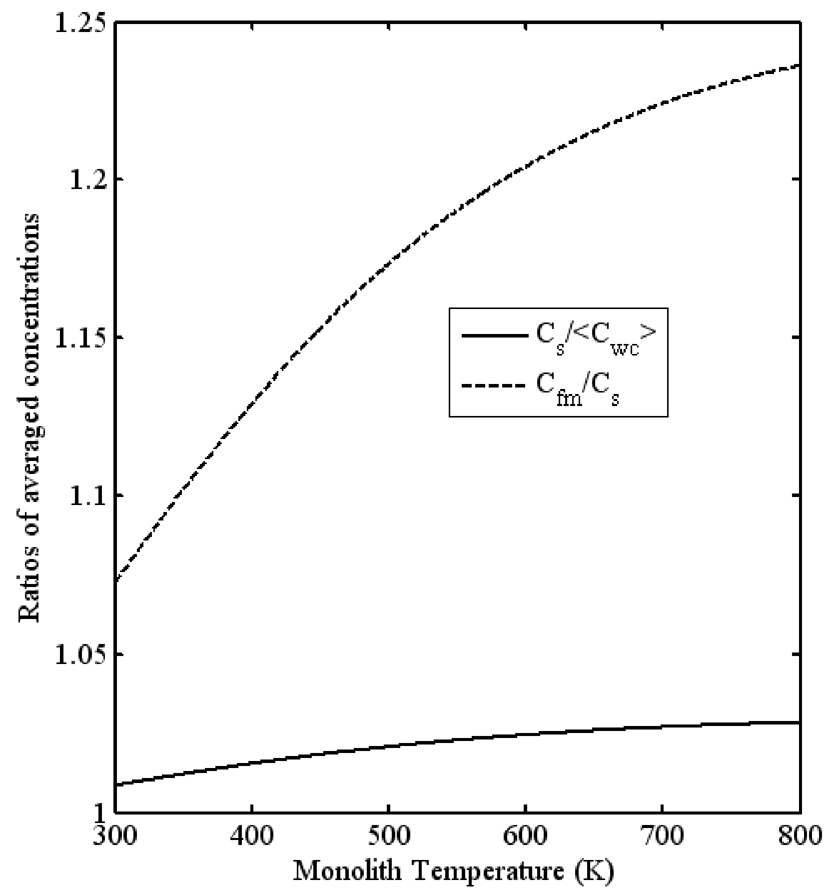
$R_r \geqslant 0.9R_t$ for kinetic regime or reaction controlling

$R_e \geqslant 0.9R_t$ for external mass transfer controlling

$R_w \geqslant 0.9R_t$ for washcoat diffusion controlling

Kinetic Regime-H_2 Oxidation





Kinetics and Parameters

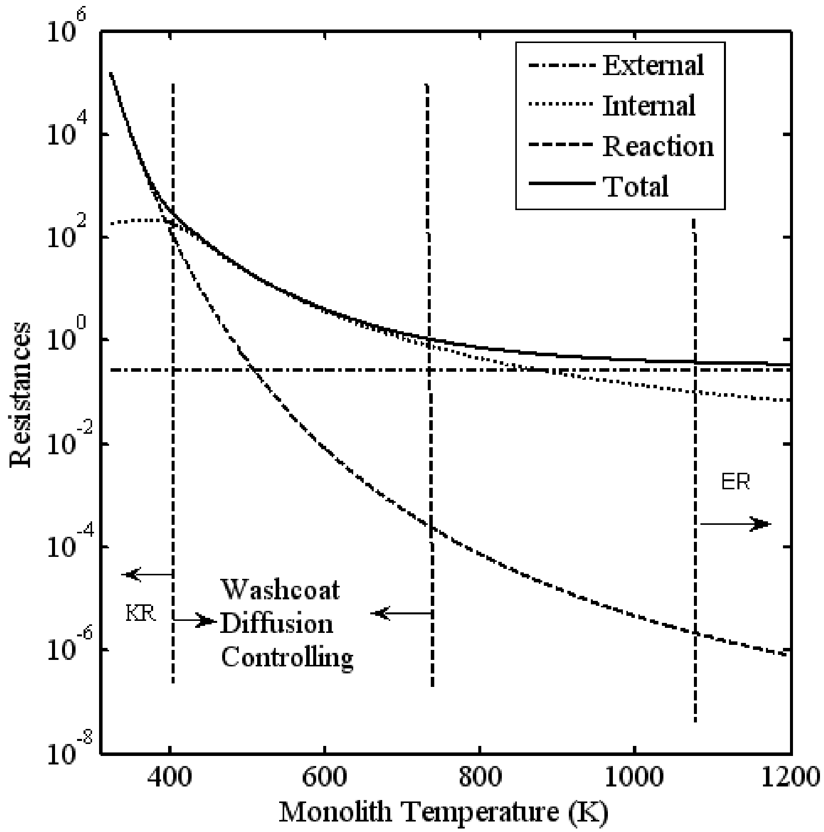
$$R_{\Omega_1} = 0.5\,mm,\ R_{\Omega 2} = 20\,\mu m,\ L = 7\,cm, \langle u \rangle = 1\,m/s \qquad R = \frac{1.1835\times10^7}{T_s}\exp\left(-\frac{1046.4}{T_s}\right)C_{H_2}$$

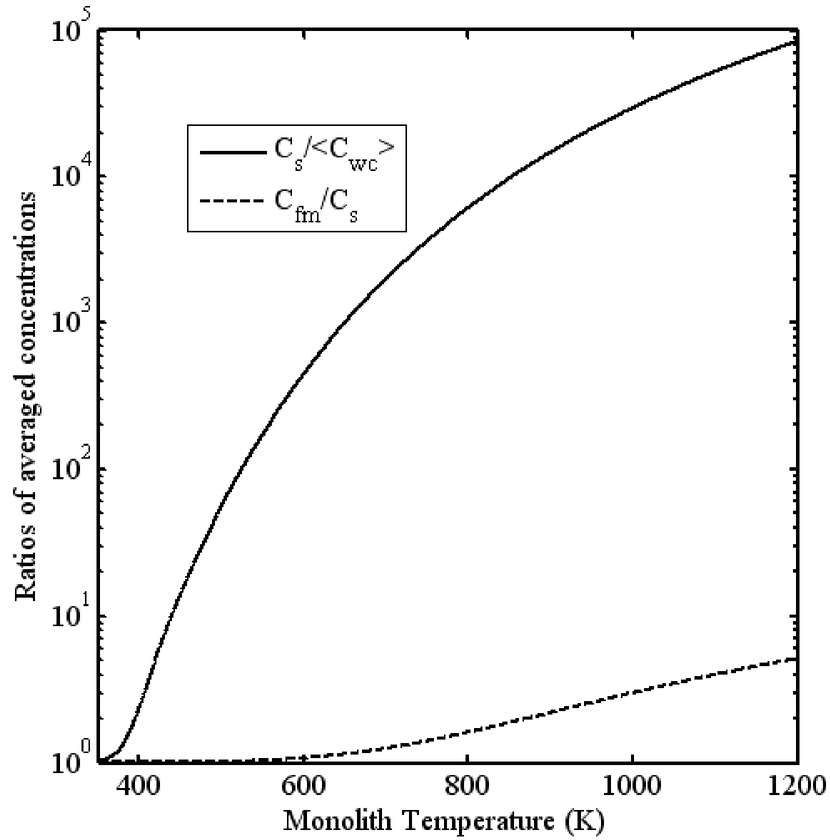
Kinetics Reference: Bhatia D, Harold MP and Balakotaiah V. Kinetics and bifurcation analysis of cooxidation of CO and H2 in catalytic monolith reactors. Chemical Engineering Science. 2009;64,1544-1558.

Washcoat Diffusion controlling

Parameters

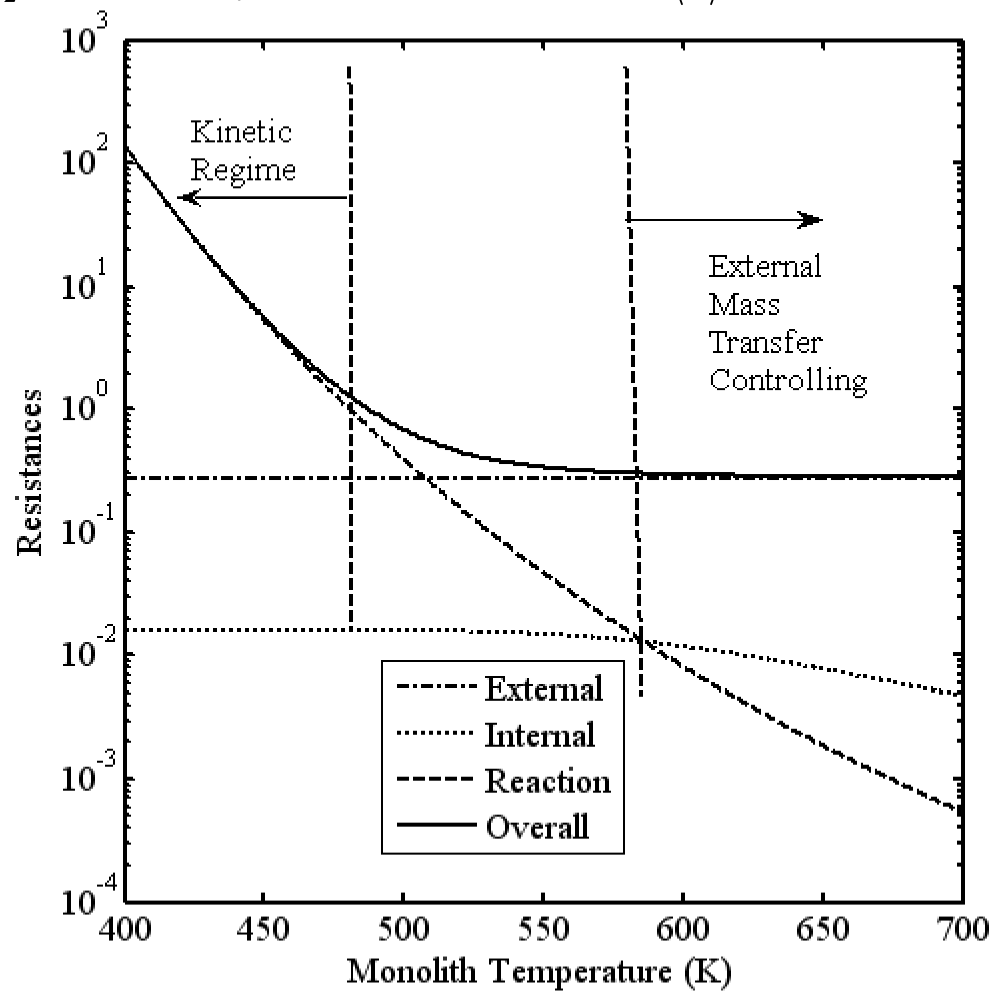
$$R_{\Omega_1} = 0.5\ mm,\ R_{\Omega 2} = 50\ \mu m,\ D_e = 10^{-9}\ m^2/s,\ L = 7cm,\ \langle u \rangle = 1\ m/s,\ PGM\ \ Loading = 10\ g/ft^3$$



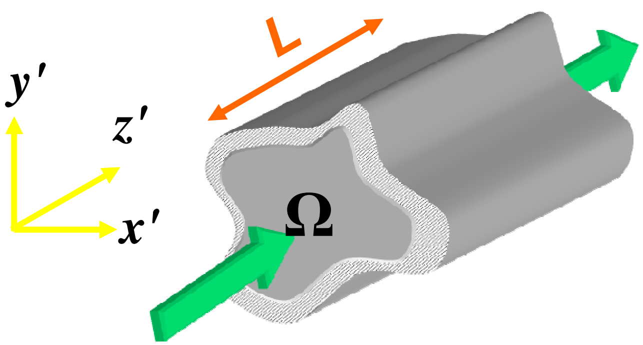


Washcoat diffusion NOT important

$$R_{\Omega_1} = 0.5\ mm,\ R_{\Omega 2} = 10\ \mu m,\ D_e = 10^{-6}\ m^2/s,\ L = 7 cm,\ \langle u \rangle = 1\ m/s, PGM\ \ Loading = 50\ g/ft^3$$



(ii) External Mass Transfer Controlled Regime in Monoliths



$$R_\Omega = \frac{A_\Omega}{P_\Omega}$$

$$\frac{C_{Af}}{C_{A0}} = \alpha_1 Exp\left[-\frac{\mu_1}{P}\right]$$

$$\mu_1 = \frac{Sh_T}{4} \qquad P = \frac{R_\Omega^2 \langle u \rangle}{L D_m}$$

$$L_{min} = 4\frac{R_\Omega^2 \langle u \rangle}{D_m}$$

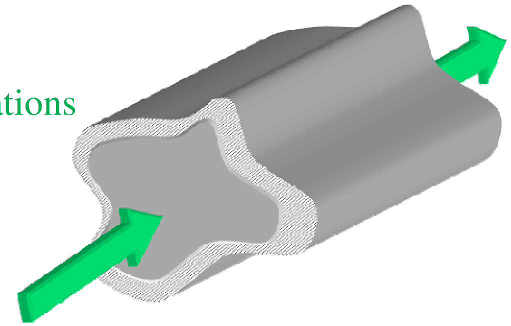
Minimum lengths/front widths
At 300 C with R_Ω=0.5mm

Species	H2	NO	NH3
<u> = 1 m/s	1.5 mm	6.0 mm	4.5 mm
<u> = 10 m/s	15 mm	60 mm	45 mm

(iii) Analysis of fronts in after-treatment systems

Observations: (i) Front speeds are independent of kinetics

(ii) front concentrations must satisfy stoichiometric relations



Adsorption/storage/Regeneration:

$$u_f = \langle u \rangle \frac{R_\Omega}{\delta_w} \left(\frac{C_{A,in}}{\nu N_{so}} \right)$$

Traveling wave

$$z = x - u_f t$$

Thermal (front end ignition):

$$u_f = \langle u \rangle \frac{R_\Omega}{\delta_s} \left(\frac{\rho_g c_{pg}}{\rho_s c_{ps}} \right)$$

NOx Storage on Pt/Ba catalyst

$$NO + \frac{1}{2} O_2 \longleftrightarrow NO_2$$

$$BaO + 3NO_2 \longleftrightarrow Ba(NO_3)_2 + NO$$

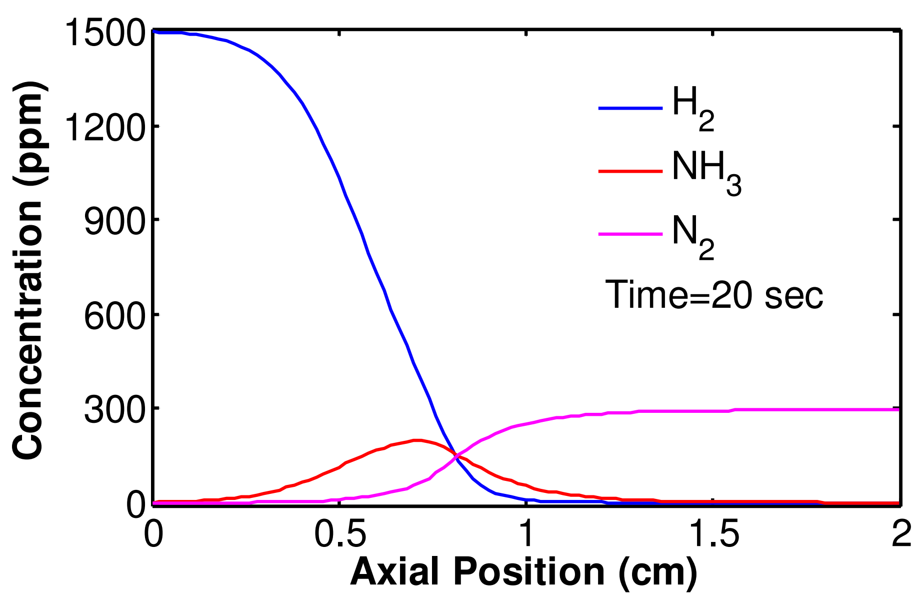
NOx Reduction on Pt/Ba catalyst

$$Ba(NO_3)_2 + 8H_2 \rightarrow BaO + 5H_2O + 2NH_3$$

$$Ba(NO_3)_2 + \frac{10}{3} NH_3 \rightarrow BaO + 5H_2O + \frac{8}{3} N_2$$

Reduction with H2:

$$C_{H2} + 4C_{NH3} + 5C_{N2} = C_{H2,f}$$



Summary/Conclusions

Part A: Fundamentals based
Low-dimensional Models for Real Time Simulations of Catalytic After-treatment Systems
(TWCs, DOCs, LNTs, SCRs and DPFs)

Part B: Analysis of monolith features using low-d models

(i) Controlling regimes
(ii) External Mass transfer controlled regime
(iii) Fronts in monoliths
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(v) Light-off behavior
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