REDUCED ORDER MODELS WITH LOCAL PROPERTY DEPENDENT TRANSFER COEFFICIENTS FOR REAL TIME SIMULATION OF MONOLITH REACTORS

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Abstract

We present and evaluate the accuracy of reduced order models with local property dependent internal and external transfer coefficients for real time simulation of monolith reactors. We illustrate the application of the models to diesel oxidation catalysts (DOCs) and three-way catalytic converters (TWCs) with a single washcoat layer to determine the steady-state as well as transient behavior in real time. We also compare the solutions obtained using reduced order models with detailed model to assess the accuracy. We show that use of local property dependent transfer coefficients in terms of the Jacobian of reaction rate vector leads to the best match followed by its diagonal approximation followed by the asymptotic values, especially in the washcoat diffusion controlled regime.

Keywords

Multicomponent diffusion, Low-dimensional models, Transfer coefficients, Real time simulations; Transfer coefficients

Introduction

The monolith reactor is the most widely used reactor in catalytic after-treatment systems (e.g. TWC, DOC, LNT, etc). The detailed mathematical models of a monolith reactor consist of a system of coupled nonlinear partial differential equations (PDEs) in at least two spatial dimensions (axial and radial/transverse) and time along with highly nonlinear source/sink terms appearing in the solid (catalyst) phase species and energy balances. Although the numerical solution of such detailed models with complex catalytic chemistry is possible with the present day computers, it may be demanding in terms of time and memory requirements, especially for real time simulations that may be needed in the control and optimization schemes. Therefore, the development of low-dimensional (reduced order) models for these systems is important for various control and optimization algorithms related to fuel economy and real time implementation of emissions constraints. There are several simplified approaches proposed in the literature for the solution of diffusion-reaction equations in the washcoat to avoid the computational demand of the full numerical solution.

In many applications, the length (and corresponding time) scales in the transverse direction are small so that the gradients in the transverse direction are typically smaller compared to the same in the flow direction. Thus, it is preferable to eliminate the small transverse length scales and include these effects in the transverse averaged models through internal and external (heat and mass) transfer coefficients. Based on the approach proposed by Balakotaiah (2008), Joshi et al. (2009) developed and demonstrated the utility of low-dimensional models in the transient simulations of monolith reactors with a single washcoat layer. For the isothermal case, their model consists of two (phase averaged global) equations for each gas phase species, one for the fluid phase cup-mixing concentration and one for the average concentration in the washcoat. The interfacial concentration was eliminated in this model by use of an overall mass transfer coefficient that is defined in terms of the usual external transfer coefficient and an asymptotic internal mass transfer coefficient (which depends only on the thickness of the washcoat, effective diffusivity of the species in the washcoat and shape/geometry of the washcoat). While the use of asymptotic transfer coefficient was adequate for many applications, especially those involving cold-start transient simulations of various after-treatment systems, Kumar et al. (2012) showed that it was inadequate (or may have significant error) for describing ignited branches on which strong washcoat diffusional limitations may exist. They recommended to use a local property (Thiele matrix) dependent transfer coefficient with a diagonal approximation. More recently, Ratnakar et al. (2018)

developed multi-scale models for monoliths with dual and multiple-layers for multicomponent systems, where they demonstrated the utility of such diagonal approximation for the applications to DOC and hydrocarbon trapping..

Method

The detailed mathematical model describing diffusion-convection-reaction processes for a multi-component system in a catalytic monolith is given by Ratnakar et al. (2018):

$$\frac{\partial \mathbf{X}_f}{\partial t} + u\frac{\partial \mathbf{X}_f}{\partial x} = \frac{\mathbf{D}_{ew}}{a}\frac{\partial \mathbf{X}_w}{\partial y}\Big|_{y=0} \quad \text{in } \Omega_f$$

$$\boldsymbol{\epsilon}_w \frac{\partial \mathbf{X}_w}{\partial t} = \mathbf{D}_{ew}\frac{\partial^2 \mathbf{X}_w}{\partial y^2} + \frac{1}{C_{Total}}\boldsymbol{\nu}^T \mathbf{r}(\mathbf{X}_w, \mathbf{T}_s) \text{ in } \Omega_w$$

$$-\mathbf{D}_{ew}\frac{\partial \mathbf{X}_w}{\partial y}\Big|_{y=0} = \frac{\mathbf{Sh}_{ext}\mathbf{D}_m}{a}(\mathbf{X}_f - \mathbf{X}_w)\Big|_{y=0}$$

with continuity in mole fraction and interfacial fluxes. The reduced order model is derived from the above model by averaging in the transverse direction (y).

Results and Discussion

The transverse averaging of the above model leads to the global equations that are equivalent to the phase averaged models:

$$\frac{\partial \boldsymbol{X}_{fm}}{\partial t} = -\langle u\rangle\frac{\partial \boldsymbol{X}_{fm}}{\partial x} - \frac{\boldsymbol{k}_{mo}}{R_\Omega}\left(\boldsymbol{X}_{fm} - \langle \boldsymbol{X}_{wc}\rangle\right)$$

$$\epsilon_\omega \frac{\partial \langle \mathbf{X}_{wc}\rangle}{\partial t} = \frac{1}{C_{Total}}\boldsymbol{\nu}^T \mathbf{r}(\langle \mathbf{X}_{wc}\rangle, \mathbf{T}_s) + \frac{\mathbf{k}_{mo}}{\delta_c}\left(\mathbf{X}_{fm} - \langle \mathbf{X}_{wc}\rangle\right)$$

$$\mathbf{k}_{mo}^{-1} = \mathbf{k}_{me}^{-1} + \mathbf{k}_{mi}^{-1}; \quad \mathbf{k}_{mi} = \frac{\mathbf{D}_{ew}\mathbf{Sh}_i}{\delta_c}$$

$$\mathbf{Sh}_i = \mathrm{Sh}_{i,\infty}\mathbf{I} + (\mathbf{I} + \Lambda\boldsymbol{\phi})^{-1}\Lambda\boldsymbol{\phi}^2$$

The accuracy of the above reduced order model as well as other models proposed in the literature is demonstrated by comparing the exit conversions versus inlet temperature (light-off) curves for the TWC example.

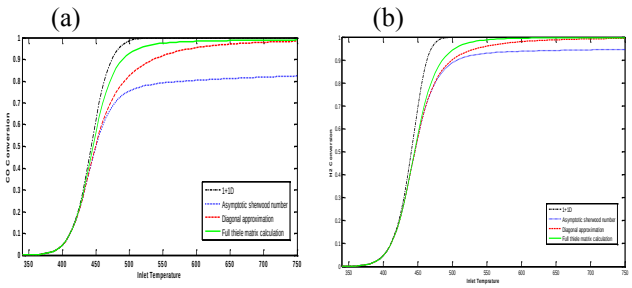

Figure 1. *Comparison of CO (a) and H_2 (b) conversion profiles predicted by various low-dimensional models and detailed model.*

Figure 1 shows a comparison of monolith exit conversions predicted by various reduced order models along with the detailed (1+1D) model using the same TWC kinetic model used by Joshi et al. (2009). The black curve is the result of the detailed 1+1D model, blue curve is the result of asymptotic Sherwood number, red curve is the result of diagonal approximation, while the green curve uses full Thiele matrix (which has never been used in prior literature studies). It is noted that the green curve, closest to the detailed solution compared to others is the most accurate followed by the diagonal approximation.

Summary and Conclusions

All the reduced order model approaches lead to accurate solution at low temperature (slow reactions). However, as the inlet temperature increases, washcoat diffusion becomes significant and hence the asymptotic model begins showing errors in the solution. As inlet temperature is further increased, the gradients in the washcoat become significant and the process goes into the washcoat diffusion (and external mass transfer) controlled regime. In such regime, the diagonal approximation may not be sufficient enough to capture the kinetic effect on mass-transfer and hence, the full Thiele matrix model must be used.

This work presents more accurate reduced order model for a catalytic monolith where the transfer coefficients are expressed in terms of local kinetic and transport parameters. It was shown that the use of asymptotic transfer coefficients leads to accurate solution only in case of slow reactions but breaks-down for fast reactions. When local property dependent transfer coefficients are used, the reduced order model leads to accurate solution even for fast reactions. In addition, the work presents the correct form of transfer coefficients for the multicomponent systems.

References

1. Balakotaiah, V. (2008). On the relationship between Aris and Sherwood numbers and friction and effectiveness factors, *Chem. Eng. Sci. 5802-5812*.
2. S.Y. Joshi, M.P. Harold, V. Balakotaiah, (2009). Low-dimensional models for real time simulation of catalytic monoliths, *AIChE J. 1771-1783*.
3. P. Kumar, I. Makki, J. Kerns, K. Grigoriadis, M. Franchek, V. Balakotaiah, (2012). A low-dimensional model for describing the oxygen storage capacity and transient behavior of a three-way catalytic converter, *Chem. Eng. Sci., 373-387*.
4. Ratnakar, R.R., Dadi, R.K. and Balakotaiah, V. (2018). Multi-scale reduced order models for transient simulation of multi-layered monolith reactors. *Chem. Eng. Sc., 352, 293*.
5. S. Y. Joshi, M.P. Harold, V. Balakotaiah, (2009). On the use of internal mass transfer coefficient in modeling of diffusion and reaction in catalytic monoliths, *Chem. Eng. Sci. 4976-4991*.