Reduced order model for real-time simulation of packed-bed reactors with pore diffusional effects.

Bhaskar Sarkar[1], Ram R. Ratnakar[1], Vemuri Balakotaiah[2]*

1 Shell International Explorations and Production Inc., USA; 2 University of Houston, TX, USA

Corresponding author: vbalakot@central.uh.edu

Highlights

- Multi-scale coarse grained model is presented for real-time simulation of catalytic packed beds.
- Intra particle diffusional resistance is considered by Thiele Modulus matrix calculation.
- The usefulness of the method is illustrated through global and microkinetic reaction mechanisms.

1. Introduction

Packed-beds reactors are widely used in the production of various chemicals as well as in energy transition technologies. The length scales in these reactors vary from the bed scale (0.1 to 1 m) to particle scale (10^{-3} to 10^{-2} m) to pore scale (10^{-6} to 10^{-8} m) to the active center or crystallite scale (~10^{-9} m). The corresponding transport and reaction time scales also vary by several orders of magnitude. The real time simulation of these reactors with detailed kinetic models and in the presence of external and internal concentration and temperature gradients can be challenging. In this work, we present multi-scale coarse-grained models that can speed-up the simulation of catalytic packed-bed reactors by several orders of magnitude in comparison to detailed CFD based models without compromising accuracy. The reduced order model is expressed in terms of internal and external mass transfer coefficients that are dependent on local transport, kinetic and bed properties (such as particle shape). The efficacy of our model is illustrated with three examples: a four-step reaction model of CO & HC oxidation with global kinetics, steam methane reforming with global kinetics and CO oxidation with microkinetic mechanism. The model results are validated against detailed pore-diffusion model as well as with literature-derived experimental results.

2. Methods

A two-phase reduced order model with local property dependent external and internal mass transfer coefficients is developed in this work. A detailed description on the derivation of the model can be found in Ratnakar et al. [1]. Assuming negligible radial gradients, the species conservation equation in the fluid phase is expressed as,

$$\epsilon_f \frac{\partial \mathbf{c}_f}{\partial t} + u_f \frac{\partial \mathbf{c}_f}{\partial x} = \mathbf{D}_{ef} \frac{\partial^2 \mathbf{c}_f}{\partial x^2} - a_v \mathbf{j}_{fc} \tag{1}$$

where $\mathbf{c}_f$ is the average concentration in fluid phase and $\mathbf{j}_{fc}$ describes the interfacial flux from the fluid phase to the catalyst particle. The species balance equation in the catalyst particle in terms of the average concentration $\mathbf{c}_c$ is given by,

$$\varepsilon_c \frac{\partial \mathbf{c}_c}{\partial t} = a_p \mathbf{j}_{fc} + \mathbf{v}_c^T \mathbf{r}_c(c_c, T_s) \tag{2}$$

The interfacial flux vector, $\mathbf{j}_{fc}$, is related to the overall mass transfer coefficient matrix $\mathbf{K}_o$ and the concentration difference as follows,

$$\mathbf{j}_{fc} = \mathbf{K}_o(\mathbf{c}_f - \mathbf{c}_c) \tag{3}$$

where, $\mathbf{K}_o$ is calculated from the external ($\mathbf{K}_e$) and internal mass transfer coefficient matrices ($\mathbf{K}_i$) as $\mathbf{K}_o^{-1} = \mathbf{K}_e^{-1} + \mathbf{K}_i^{-1}$. These transfer coefficients are derived from their respective Sherwood numbers. While the external Sherwood number is a diagonal matrix and can be easily derived using correlations

available in literature [2], the internal Sherwood number is dependent on Thiele modulus matrix which could be non-diagonal. As a result, it requires computation of function of matrices using Caley Hamilton Theorem [3]. The generalized expression of internal Sherwood number applicable to different catalyst shapes is given by,

$$\mathbf{Sh}_i = \mathbf{D}_{ec}^{-1}\mathbf{K}_i\delta_c = Sh_{i,\infty}\mathbf{I} + \boldsymbol{\phi}_c tanh\,(\Lambda\boldsymbol{\phi}_c) \tag{4}$$

where, $\boldsymbol{\phi}_c^2$ is the Thiele modulus matrix expressed as a Jacobian of the reaction rate vector. The asymptotic Sherwood number, $Sh_{i,\infty}$ and the shape factor Λ depend on the catalyst shapes. Values of these parameters are calculated for some commonly used catalyst particles such as spherical, cylinders, trilobes and eggshells.

3. Results and discussion

The usefulness of the model is demonstrated using two examples with global kinetics and one with microkinetics. One such case with global kinetic model is a three-reaction model of steam methane reforming. Figure 1 depicts the CH_4 conversion at varying feed temperatures for two particle diameters, d_p = 5 mm (left) and d_p = 25.4 mm (right), computed using three different pore-diffusion models. As the name implies, the infinite diffusivity model assumes negligible diffusional resistance within the catalyst particle. Naturally, this model tends to overpredict the CH_4 conversion, particularly when the particle size is large and pore diffusional resistance is notable, as observed in the right figure. The 'Asymptotic Sh' approach considers only the asymptotic value of Sherwood number, i.e., $\mathbf{Sh}_i = Sh_{i,\infty}\mathbf{I}$, whereas the Thiele Matrix Sherwood number considers the complete expression of the internal Sherwood number as given by eqn. (4). As shown, at a lower particle diameter where the internal diffusional resistance is insignificant (or $\phi_c^2 \sim 1$), both the asymptotic and Thiele matrix approach yields the same results. However, as the particle diameter is increased, making the internal diffusional resistance higher (or $\phi_c^2 \gg 1$), the asymptotic approach underpredicts the CH_4 conversion. The Thiele matrix approach gives exactly same results as the detailed pore-diffusion model while achieving two orders of magnitude faster computational speeds.
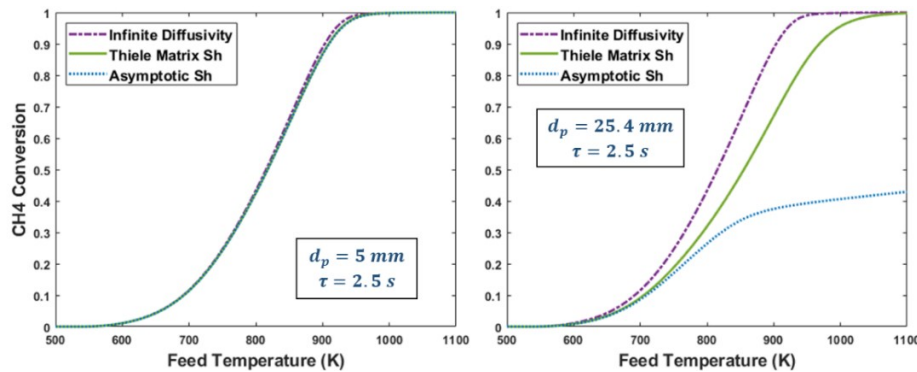
Figure 1. Computed CH_4 conversion vs feed temperature using different pore diffusion models at particle diameters, d_p = 5 mm (left) and d_p = 25.4 mm (right).

4. Conclusions

A novel and accurate reduced order model for real time simulation of catalytic packed bed reactors is presented. The proposed method is generalizable to different reaction systems and is demonstrated to significantly speed up calculations compared to detailed models.

References

[1] R. R. Ratnakar, R. K. Dadi, V. Balakotaiah, Chem. Eng. J. 352 (2018) 293–305
[2] B. V. R. Kuncharam, A. G. Dixon, Fuel Process. Technol. 200 (2020) 106314
[3] M. Tu, R. Ratnakar, V. Balakotaiah, Chem. Eng. J. 383 (2020) 123074

Keywords