Multiscale Modeling and Solution Multiplicity in Catalytic Pellet Reactors

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Transport and reaction phenomena in catalytic pellet reactors are often difficult to analyze because of coupling between heat and mass transport occurring at different space and time scales. To calculate the reactor concentrations and temperatures, it is necessary to account for the species reaction and transport occurring in the reactor bulk at the macroscopic level as well as the catalyst pellets at the microscopic level. The resulting approach yields a large system of nonlinear partial differential equations with multiple scales and solutions that are difficult to find numerically. In addition, the catalyst pellets may operate in multiple steady states for identical conditions. Conventional computational methods may entirely miss the multiplicity phenomenon at the catalyst pellet level and, as a result, may not correctly predict overall reactor yields. In this paper, we introduce two numerical techniques to address multiple scales and multiplicity in heterogeneous reaction models. The first method expands existing bisection with “shooting”; the second global method deploys orthogonal collocation over finite elements with niche evolutionary algorithms. We also propose a new multiscale method entitled effectiveness factor maps to expedite and simplify the numerical effort to solve transport and reaction phenomena at different length scales.

1. Introduction

Many industrial reactors involve heterogeneous reaction kinetics of packed catalytic pellets in fixed-bed reactors. To predict the concentration and temperature profiles in a fixed-bed catalytic pellet reactor, mass and energy conservation equations for the reactor bulk need to be solved simultaneously with heat and mass transport inside the catalytic pellets. The robust numerical solution of this multiscale problem of reactions in the bulk and inside the pellets is still challenging.

One more issue further compounding the difficult multiscale reactor problem is the possibility of multiple steady states in the catalyst pellets. Catalyst pellets are capable of operating in multiple steady states for identical reaction conditions; each steady state corresponds to different concentration and temperature profiles in the catalyst pellet leading to different overall realized conversions.1 Thus, multiple reactor concentrations and temperature profiles are possible. It is thus extremely important to quantify all possible steady states and study their impact on the resulting reactor performance.

In this paper, we consider the case of a simplified fixed bed catalytic pellet reactor with coupled reaction and transport. In a catalytic pellet reactor, the reactant is converted into the product as it traverses the reactor length. It is a distributed system because the system states, such as the concentrations and temperatures, vary spatially. In addition, the reactor is packed with a catalyst bed to enhance overall yield and selectivity. The reactant may diffuse deeply into the catalyst pellets, while simultaneously being consumed within the porous microstructure. The reaction and transport phenomena in the reactor thus occur at multiple length scales in the reactor bulk at the macroscopic level, as well as in the catalyst pellets at the microscopic level.

Discretization of the distributed mass and energy balances for the reactor bulk, as well as the catalyst pellets, yields a large system of nonlinear algebraic equations. There are numerical solution techniques to solve these coupled boundary value problems. However, ill-conditioning caused by the multiple length scales and solution multiplicity make many algorithms unsuitable. This article proposes numerical techniques to overcome the challenges posed by multiple scales and solution multiplicity. The paper is organized as follows. Section 2 briefly introduces the general transport and reaction equations. Section 3 introduces two novel methods to handle steady state multiplicity. Section 4 discusses problems in direct simulation of the reactor bulk with full consideration of the pellet kinetics and mass transfer limitation. A novel interpolation approach entitled effectiveness factor maps will be presented as a robust and efficient approximation technique. Section 5 closes the paper with conclusions and future work.

2. Reactions and Species Transport in a Packed Bed Reactor

This section develops general reaction and transport equations in the packed bed reactor as well as in the catalyst pellets. A simplified packed bed catalytic pellet reactor with a spherical catalyst pellet packing is shown in Figure 1.

2.1. Macroscopic Level. We consider the heterogeneous overall stoichiometry of the reaction in the fixed bed reactor, as shown in eq. (1).

$\text{A} \xrightarrow{\Delta t} \text{B}$

The species and heat balance in the axial and radial directions for a cylindrical control volume of the catalytic packed bed reactor are given in eqs 2 and 3, respectively.2 The momentum transfer in the packed bed of the reactor can be approximated by Darcy’s law as in eq 4.

$\nabla (\rho C_p \nabla T) = \nabla \cdot (K_c \nabla T) + r_A \Delta H$

$\nabla (\rho \nabla H) = \nabla \cdot (D_C \nabla C_A) + r_A$

$\rho D_C \nabla C_A = \nabla (D_C \nabla C_A) + r_A$

$-\nabla P = \frac{\mu}{\kappa_m} u$

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or slab pellet geometry models are similar in mathematical structure as described elsewhere.\textsuperscript{4}

Assuming that the pellet properties $D_c$ and $K_c$ are constants and that the reaction constant $k$ is a function of the temperature only, the system in eqs 8–10 can be written in terms of the dimensionless concentration, $y = C_A/C_{A0}$, as well as the dimensionless activation energy, $\gamma$, the heat of reaction, $\beta$, and the Thiele modulus, $\phi$, as follows:

$$
\frac{d^2y}{dx^2} + \frac{2dy}{dx} - \gamma^2y \exp\left(\frac{\gamma y(1-y)}{1+\beta(y^2-1)}\right) = 0
$$ (11)

$$
\frac{dy}{dx} = 0
$$ (12)

$$
y^{\gamma-1} = 1
$$ (13)

The independent variable $x$ is the dimensionless catalyst pellet radius, $x = r/R$. The parameters $\gamma$, $\beta$, and $\phi$ can be expressed in terms of the bulk transport and reaction properties, as well as the pellet surface concentration, $C_{A0}$, and temperature, $T_s$, as follows:

$$
\gamma = \frac{E}{R_k T_s}
$$ (14)

$$
\beta = \frac{-\Delta H_c C_{A0}}{K_c T_s}
$$ (15)

$$
\phi = R\sqrt{\frac{k_{ref}^2}{D_c}} \exp\left[\frac{E}{R_k T_{ref}} \left( \frac{T_{ref}}{T_s} - 1 \right) \right]
$$ (16)

Finally, the desired effectiveness factor, $\eta$, accounting for the overall consumption of the reactant can be obtained by solving eq 11 and taking the flux at the surface as shown in eq 17.

$$
\eta = \frac{3}{\gamma} \frac{dy}{dx}
$$ (17)

3. Multiplicity in Catalytic Pellets

The solution to the nonlinear system in eqs 11–13 gives the steady state concentration profile of reactant A as a function of the dimensionless pellet radius. For the same reactor or pellet conditions, multiple reaction rates corresponding to different conversions are physically possible. Steady state multiplicity in the catalytic pellet means that for identical conditions given by the dimensionless parameters $\gamma$, $\beta$, and $\phi$, the effectiveness factor can assume several distinct, yet physically meaningful solutions. Figure 2 displays $\eta$–$\phi$ relations over various ranges of $\gamma$, $\beta$, and $\phi$.\textsuperscript{1} In some ranges of $\gamma$, $\beta$, and $\phi$, multiple concentration profiles satisfy the same species transport and energy balances. The precise value of the effectiveness factors thus depends on which branch of the multiple concentration profiles is selected. For the values $\gamma = 30$, $\beta = 0.6$, and $\phi = 0.2$, there are three distinct solutions with three different effectiveness factors, whose values differ by several orders of magnitude ($\eta_1 = 1.0639$, $\eta_2 = 9.8791$, $\eta_3 = 513.928$). Given the dimensionless reaction and transport coefficients, $\gamma$, $\beta$, and $\phi$, it is desirable to identify all steady state catalytic pellet profiles possible for the boundary value problem in eqs 11–13. While a number of methods, such as finite difference, shooting, collocation, and spectral methods, apply to boundary value problems, few specifically address multiplicity of pellet profile. One example is a recent contribution from Stadtherr’s group that addressed boundary value problem with interval method.\textsuperscript{10} Most iterative methods depend strongly on initial
guesses. Only the solution “nearest” to the initial guess is typically found; there is no systematic process to ascertain the existence and values of different solutions.

3.1. Complete Solutions to the Pellet Problem. This section discusses two methods that can identify all solutions to the pellet problem in practice. It is more concise to state that our method is “highly likely” to identify all solutions because kinetic problems are non-polynomial hard and because floating point precision on a digital computer is used. The first method is an interval-based global bisection method modeled on shooting. The second method uses global hybrid niche evolutionary algorithms combined with orthogonal collocation over finite elements (OCFE). A third method based on global terrain methods has been presented elsewhere. The method based on global terrain methods has been presented elsewhere. The section closes with a comparison of the methods’ performance and robustness.

3.2. Shooting-Based Global Bisection Method over Intervals. This subsection introduces a global shooting bisection method to determine all possible effectiveness factors and corresponding concentration profiles. Shooting methods solve the boundary value problem by accurate forward integration. However, the earlier methods did not address multiplicity. These methods start with an initial guess for the center concentration.

In our adapted method, we “shoot” for the Thiele modulus, \( \phi \), as a function of the center concentration, \( y_0 \), with eq 18.

\[
\phi_{\text{model}}(y_0) - \phi = 0 \tag{18}
\]

Here, \( \phi_{\text{model}}(y_0) \) is the value of the calculated Thiele modulus as a function of a center concentration, \( y_0 \). In our global bisection method, the entire domain of possible center concentrations, \( y_0 \), is divided into a fixed number of intervals. We then search each of the brackets successively using global bisection.

This method uses only function evaluations without requiring gradients. Gradient-based methods that are potentially faster were tried but often failed because of the steepness of concentration profiles in the reaction regimes with multiplicity.

3.3. Global Hybrid Niche Evolutionary Methods with OCFE Discretization. A different strategy adopts orthogonal collocation over finite elements (OCFE) to solve the equation system (eqs 11–13). The following two subsections introduce OCFE with stochastic niche evolutionary methods to identify all solutions to the pellet problem. Deterministic approaches are described elsewhere.

![Figure 1. Schematic depicting the multiscale nature of the simulation problem in the catalytic pellet reactor. The multiscale model accounts for transport and reaction occurring in the reactor bulk (macroscopic level), as well as in the catalyst pellets (microscopic level).](image)

**Figure 1.** Schematic depicting the multiscale nature of the simulation problem in the catalytic pellet reactor. The multiscale model accounts for transport and reaction occurring in the reactor bulk (macroscopic level), as well as in the catalyst pellets (microscopic level). The section closes with a comparison of the methods’ performance and robustness.

**Figure 2.** \( \eta-\phi \) curves from Weisz and Hicks depicting the existence of multiple steady states leading to multiple effectiveness factor values. For a specific Thiele modulus, \( \phi \), more than one overall reaction rate is possible.