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APPROXIMATE MODELS APPLICATION FOR MODELLING OF FIXED BED REACTORS

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The approximate linear driving-force model which is typical and commonly used for diffusion processes, fails in the case of diffusion with reaction processes (e.g. heterogeneous catalysis). This results from the rapidity of the mass transfer for processes with chemical reaction. A method based on a solution for a single catalyst pellet has been used to evaluate coefficients of the mentioned approximate formula. The application of this formula for modeling of an isothermal fixed-bed reactor with non-linear kinetic rate is presented. Accuracy of the proposed model is very good. The error does not exceed 0.02 for the steady state.

Introduction

Fixed bed reactors are commonly used in industrial practice for heterogeneous catalysis processes. There are two groups of models applied in modeling of such type of apparatus. (i) Pseudohomogeneous models, which assume the same temperature and component concentrations in the fluid bulk and catalyst particles. Due to this assumption the model is described by partial differential equations (PDE) only for fluid phase. Pseudohomogeneous models, despite of their low accuracy in most cases, are relatively easy to solve and they are willingly used for description of reactors. (ii) Heterogeneous models, in contrast to pseudo-homogeneous ones, give results with quite good accuracy. They are described by PDE both for fluid and for catalyst pellet but their solution is difficult to obtain. The widely reported way to avoid this drawback is to use an effectiveness factor concept. It reduces the equations set of the heterogeneous model and makes the solution much easier to obtain. Unfortunately, for most cases, finding the proper value of the mentioned factor is difficult and/or lengthy that limits its application.

There is another way for simplification of mathematical modeling, which is widely reported for diffusion and adsorption processes. In this approach PDE for mass balance in a pellet is replaced by a proper ordinary differential equation (ODE) - so-called „approximate model" - that simplifies greatly the model solution at the same or only slightly worse accuracy. For description of diffusion and reaction processes a small number of equations that approximate a mass balance in the porous particle has been found in literature. Kim [1] has proposed linear driving force approximation model that characterises good accuracy but also complexity of derived formula. Moreover the individual terms of the model - accumulation, rate of mass transfer and reaction rate - have no longer their physical meaning. Goto and Hirose [2], have presented a number of approximate models, but their accuracy for diffusion and reaction processes are unsatisfactory for a wide range of Thiele modulus and time. Szukiewicz [3] has presented the approximate formula free of the mentioned drawbacks. Reported models concern only first-order reactions.

The application of an approximate linear driving-force model of the catalyst pellet for modeling of a fixed bed reactor is presented. A method based on a solution for a single catalyst pellet has been used to evaluate coefficients in the approximate formula. The method can be used for any type of kinetic equations. Accuracy of the proposed model is very good. The error does not exceed 0.02 for the steady state.

Models

It is assumed that a single, isothermal and irreversible reaction is to be carried out on catalyst pellets in a

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heterogeneous fixed-bed reactor. Both models are presented in dimensionless form.

Heterogeneous (exact) model

Mass balance for fluid and for a pellet with initial and boundary conditions are described by eqs. (1) – (5)

$$\varepsilon_e \frac{\partial c_b}{\partial \tau} + \frac{\partial c_b}{\partial z} + (1-\varepsilon_e) St (c_b - c_s) = 0 \qquad (1)$$

$$\varepsilon_p \frac{\partial c}{\partial \tau} = \frac{St}{3Bi_m} \frac{1}{x^2} \frac{\partial}{\partial x}\left(x^2 \frac{\partial c}{\partial x} \right) - \Phi^2 R_A \qquad (2)$$

IC: $$c_b(0,z) = 0, \qquad c(0,x) = 0 \qquad (3)$$

BC: $$c_b(\tau,0) = 1 \qquad (4)$$

$$\left. \frac{\partial c}{\partial x} \right|_{x=0} = 0, \qquad \left. \frac{\partial c}{\partial x} \right|_{x=1} = Bi_m (c_b - c_s) \qquad (5)$$

In the above equations a pellet surface concentration is denoted by c_s, i.e. $c_s = c(\tau, x=1)$.

Approximate model

This model is based on the concept of approximate model for the pellet. Using it in heterogeneous model of the reactor leads to replacing all terms described mass transfer between a pellet and its surrounding by a single term describing overall mass transfer flux with an assumption that concentration profile inside the pellet is replaced by an average concentration c_{av}. See also derivation of the approximate model for the catalyst pellet [3] and presented there references concerned diffusion and adsorption processes.

Mass balance for fluid and for a pellet with initial and boundary conditions are described by eqs. (6) – (9)

$$\varepsilon_e \frac{\partial c_b}{\partial \tau} + \frac{\partial c_b}{\partial z} + (1-\varepsilon_e) St \cdot K (c_b - c_{av}) = 0 \qquad (6)$$

$$\varepsilon_p \frac{\partial c_{av}}{\partial \tau} = St \cdot K (c_b - c_{av}) - \frac{St}{3Bi_m} \Phi^2 R_A \qquad (7)$$

IC: $$c_b(0,z) = 0, \qquad c_{av}(0) = 0 \qquad (8)$$

BC: $$c_b(\tau,0) = 1 \qquad (9)$$

where

$$c_{av} = 3\int_0^1 c \cdot x^2 dx \qquad (10)$$

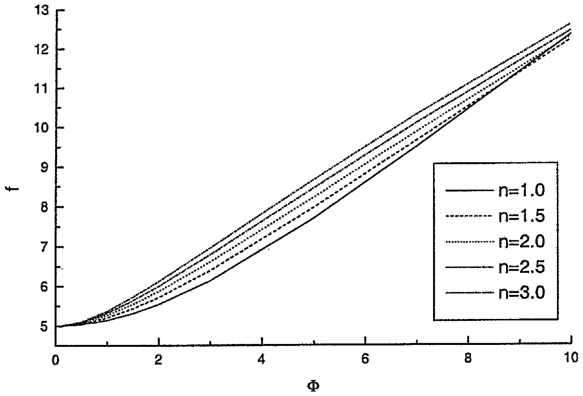

Fig.1 Coefficient f vs. Thiele modulus.

$$K = \frac{1}{1 + Bi_m / f} \qquad (11)$$

In the approximate model of the catalyst pellet an unknown coefficient f occurs, which is a reflection of the rapidity in the mass transfer rate resulting from chemical reaction. Passing over this coefficient leads to significant errors for larger values of Thiele modulus (cf. cited above Goto and Hirose [2]). The f value can be calculated as follows. Firstly a model of a single catalyst pellet (eq. (2) with accompanied IC and BC) for inlet reactor conditions should be solved that gives a concentration profile inside the pellet. Generally, it can be done numerically. Finding this solution is the basic difficulty of the presented method, however this task is relatively simple, well reported in literature (e.g. Finlayson [4], Davis [5]). Next, the found concentration profile enables calculation of both steady-state mass flux of a reactant (using e.g. the second of the boundary condition (5)) and steady-state average concentration in the pellet (using eq. (10)). Comparison of mentioned mass flux and overall mass flux gives a value of coefficient f. Although this coefficient is time-dependent the steady-state value of it is accepted for calculations [3].

For both models partial differential equations have been reduced to a set of ordinary differential equations by applying orthogonal collocation method. The set of ODEs has been solved using procedure LSODA.

Results and discussion

Calculations have been carried out for power-law type of kinetic rate:

$$R_A = c^n \qquad (12)$$

where

n=[1.0, 1.5, 2.0, 2.5, 3.0]

Firstly, for all values of n the coefficient f was computed assuming for the pellet the inlet reactor conditions. Results are presented in *Fig.1*. Value of f rises with Thiele modulus. It is, as mentioned above, a

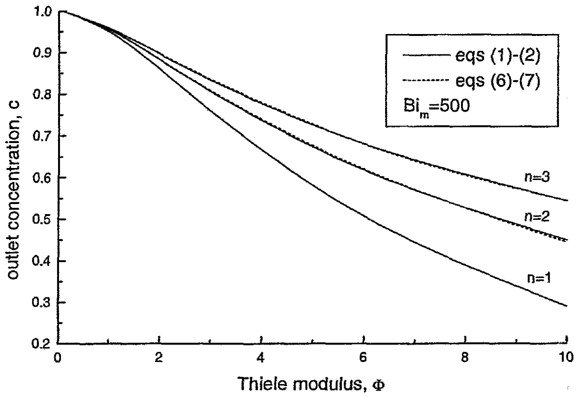

Fig.2 Steady state reactor outlet concentration vs. Thiele modulus for small external mass transfer resistance.

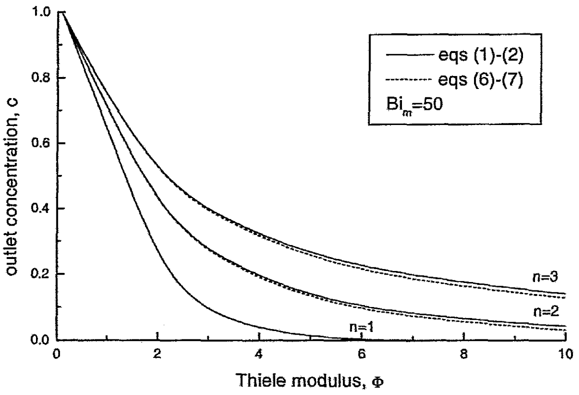

Fig.3 Steady state reactor outlet concentration vs. Thiele modulus for large external mass transfer resistance.

reflection of the rapidity in the mass transfer rate resulting from chemical reaction. It is significant that values of coefficient f for linear type kinetic are exactly the same as calculated analytically (see [3]).

Secondly both presented models have been compared in wide range of Thiele modulus ($\Phi \in [0..10]$) and Biot number ($Bi_m \in [10 .. \infty]$). Furthermore, it was assumed St=100, $\varepsilon_e=0.3$ and $\varepsilon_p=0.5$. All tests have shown good compatibility of the results obtained for heterogeneous and approximate models at steady state. The maximum absolute error has not exceeded 0.02. For linear type of kinetic rate the outlet concentrations were the same for entire range of Thiele modulus, for non-linear one the error grew with the value of mentioned parameter. It should be emphasized that for small and intermediate values of Thiele modulus (that is for most cases in practice) the error is very small. Examples of these observations are presented in *Fig.2* and in *Fig.3*.

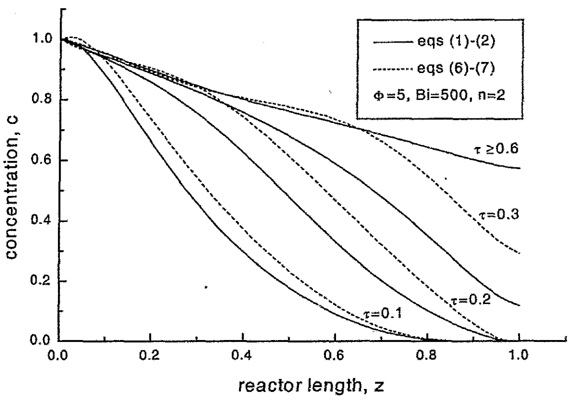

Fig.4 Time-dependence of concentration profiles for approximate and exact models.

It could be expected that the dynamic behaviors of the considered models are not the same. Taking into account the time dependence of a concentration a slightly worse compatibility for approximate and exact models was observed - see *Fig.4*. It is qualitative only but not bad. The models start from the same initial conditions so that differences grow firstly for $\tau<0.3$ (near this time the maximal deviation between results is observed), next drop and for a sufficiently long time vanish (here for $\tau\geq0.6$ appropriate curves for both models are the same). Some problems cause the defining of the time after which both considered models give the same results. This time depends on the model parameters values and it is difficult to find a simple relationship to define it. For practical purposes the inequality derived for the model of single catalyst pellet with linear reaction rate (given by Szukiewicz [3]) can be used (in modified form). For tested values of the model parameters considered time was shorter than τ_a (eq. 13).

$$\tau_a = \frac{25}{3f+\Phi^2} \qquad (13)$$

Summarizing, the approximate model evaluates the exact solution well for sufficiently long times, which results from the way of calculating the coefficient f.

The presented method of the heterogeneous fixed-bed reactor simulation can be recommended because the approximate model is much more tractable for solution than the exact one. We can get great simplification of the analysis of the heterogeneous fixed-bed reactor operation condition at the expense of solving a catalyst pellet model. The method is especially convenient with regard to steady-state conditions which task is of great importance in practice.

Conclusions

The approximation of the catalyst pellet by the lumped parameter model yields an essential simplification of analysis and computation for fixed-bed reactors. The accuracy of calculations is very good with respect to steady state and good with respect to time-dependence of concentration profiles. For short times compatibility of results is qualitative only but error quickly vanish as time passes. The presented method has a shortcoming. It is needed to solve the model of single catalyst pellet (to determine the coefficient f value). However this problem is relatively simple, well reported in literature.

SYMBOLS

Bi_m	mass Biot number
c	concentration of a reagent
c_{av}	average concentration of a reagent in a pellet
c_b	bulk concentration of a reagent
c_s	surface concentration of a reagent
f	coefficient
R_A	dimensionless reaction rate
St	Stanton number
x	spatial variable in a pellet
z	spatial variable in a reactor
ε_e	bed porosity
ε_p	pellet porosity
Φ	Thiele modulus
τ	time
τ_a	time after which both considered models give the same results

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