MATHEMATICAL MODEL FOR THE DESCRIPTION OF HEAT AND MASS TRANSFER INSIDE A POROUS GRANULE IN THE PRESENCE OF PHASE TRANSITIONS

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1. Introduction

We consider the general case of a chemical reaction complicated by phase transition inside a porous catalyst granule; we represent the general scheme of the reaction in the form

$$\begin{tikzcd}
A_L \arrow[r] \arrow[d, leftrightarrow] & B_L \arrow[d, leftrightarrow] & \\
A_G \arrow[r] & B_G & + C_G
\end{tikzcd}$$

where A_L is a multicomponent liquid, which is converted into another multicomponent liquid B_L and a multicomponent gas C_G as a result of chemical reaction on the surface of the catalyst. Moreover, A_L and B_L evaporate with the formation of vapor-phase components A_G and B_G, where chemical conversion also takes place with the formation of B_G and C_G.

In the derivation of the mathematical description we consider the liquid phase to consist of m components, and the vapor—gas phase to consist of n components, where the fraction of the latter (k = n — m) formed by chemical reaction is insoluble in the liquid phase. We also assume that the temperatures of the granule matrix and the gas—liquid flow are equal, the liquid is incompressible, and the vapor—gas medium obeys the laws of ideal gases and mixtures. In addition to the foregoing, we also invoke the standard assumptions of multiphase hydrodynamics [1], viz.: Each of the phases is homogeneous and continuous, and averaging of the parameters over elementary volumes is allowed.

2. Mathematical Model

The transport of material (heat) inside the porous granule takes place in the general case by an effective diffusion (thermal conduction) process for each phase, and also by convective flow induced by a radial pressure gradient in the granule.

Phase transition takes place as a result of the liberation of a poorly soluble gas formed in chemical reaction and also as a result of evaporation (condensation) of the liquid components. The analysis of the latter phase transitions poses a rather difficult problem. The following approaches are possible in principle.

One approach is based on the notitions of molecular-kinetic theory [2]. In this case, however, it is necessary to introduce empirical coefficients, the numerical values of which are unknown for such a complicated process.

If the presence of concentration equilibrium is postulated, as is valid for low chemical reaction rates, the phase transition rates of the components can be calculated by numerical differentiation of the material balance equations for the vapor—gas phase [3].

The approach used in the present study is based on the notion that the main factor contributing to the formation of the vapor—gas mixture is chemical reaction, which takes place without equilibrium saturation of the porous structure, owing to the appreciable strength of the catalyst. In this formulation the problem differs considerably from the well-known models found in [4, 5] for the description of transport processes in porous media.

Here we give a mathematical model and some results of a numerical analysis. We write the material balance for the vapor—gas phase in the form

$$\frac{\partial}{\partial t}(\alpha_1\rho_1 y_{1i}) = \frac{\partial}{\partial l}\left(D_{1i}\alpha_1\frac{\partial}{\partial l}(\rho_1 y_{1i})\right) - \frac{\partial}{\partial l}(u_1\alpha_1\rho_1 y_{1i}) + \nu_i W_1 + \mu_i W_2 + \Phi y^*_{1i}, \qquad (2.1)$$

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where the term $\mu_i W_2$ is absent for $i = 1, \ldots, m$ and the term Φy_{1i}^* is absent for $i = m + 1, \ldots, n$.

The corresponding balance for the liquid phase is written in the form

$$\frac{\partial}{\partial t}(\alpha_2 \rho_2 c_{2i}) = \frac{\partial}{\partial l}\left(D_{2i}\alpha_2 \frac{\partial}{\partial l}(\rho_2 c_{2i})\right) - \frac{\partial}{\partial l}(u_2 \alpha_2 \rho_2 c_{2i}) - \Phi y_{1i}^* + \mu_i W_2, \qquad i = \overline{1, m}, \tag{2.2}$$

where α is the fraction of the phase, ρ is the density, D is the effective diffusion coefficient, y is the relative weight concentration of the component in the vapor–gas phase, c is the same in the liquid phase, u is the convective flow velocity inside the porous granule, W is the chemical reaction rate, ν and μ are the stoichiometric coefficients of the reactions, Φ is the total rate of transition from the liquid to the vapor–gas phase, t is the time, and l is the coordinate. The index 1 refers to the vapor–gas phase, the index 2 to the liquid, the index i to the particular component in the phase, and the asterisk * to the equilibrium value of a parameter at the phase interface.

We sum (2.1) over all vapor–gas components and sum (2.2) over the components of the liquid phase. Taking into account the fact that

$$\sum_{i=1}^{n} y_{1i} = 1, \quad \sum_{i=1}^{m} c_{2i} = 1, \quad \sum_{i=1}^{n} \nu_i = 0, \quad \sum_{i=1}^{n} \mu_i = 0,$$

$$\sum_{i=1}^{m} \frac{\partial}{\partial l}\left(D_{2i}\alpha_2 \frac{\partial \rho_2 c_{2i}}{\partial l}\right) = 0, \quad \sum_{i=1}^{n} \frac{\partial}{\partial l}\left(D_{1i}\alpha_1 \frac{\partial \rho_1 y_{1i}}{\partial l}\right) = 0,$$

we obtain

$$\frac{\partial}{\partial t}(\alpha_1 \rho_1) = -\frac{\partial}{\partial l}(u_1 \alpha_1 \rho_1) + \Phi; \tag{2.3}$$

$$\frac{\partial}{\partial t}(\alpha_2 \rho_2) = -\frac{\partial}{\partial l}(u_2 \alpha_2 \rho_2) - \Phi \sum_{i=1}^{m} y_{1i}^* + W_2 \sum_{i=1}^{m} \mu_i. \tag{2.4}$$

The following relation must naturally be satisfied:

$$\Phi = \Phi \sum_{i=1}^{m} y_{1i}^* - W_2 \sum_{i=1}^{m} \mu_i,$$

whence we infer that the total phase-transition rate is

$$\Phi = -W_2 \sum_{i=1}^{m} \mu_i \Big/ \left(1 - \sum_{i=1}^{m} y_{1i}^*\right). \tag{2.5}$$

The heat balance equation, written in terms of the enthalpies of the components, goes over to the temperature equation after suitable transformations:

$$\left(c_c \frac{1-\varepsilon}{\varepsilon} + \alpha_2 \rho_2 \sum_{i=1}^{m} c_{2i} c_{p2i} + \alpha_1 \rho_1 \sum_{i=1}^{n} y_{1i} c_{p1i}\right) \frac{\partial T}{\partial t} = \frac{\partial}{\partial l}\left(\lambda_{ef} \frac{\partial T}{\partial l}\right) -$$

$$- \left(u_1 \alpha_1 \rho_1 \sum_{i=1}^{n} y_{1i} c_{p1i} + u_2 \alpha_2 \rho_2 \sum_{i=1}^{m} c_{2i} c_{p2i}\right) \frac{\partial T}{\partial l} + \sum_{j=1}^{2} W_j Q_j - \Phi \sum_{i=1}^{m} y_{1i}^* h_i,$$

where T is the temperature, λ_{ef} is the effective thermal conductivity of the porous granule, c_c is the specific heat of the catalyst, ε is the fraction of pores inside the granule, c_p is the specific heat of the phase, h is the heat of phase transition, and Q is the energy release. The remaining notation is analogous to that described for the material balance equation.

The system of equations (2.1)-(2.6) must be augmented with the equation of state of the vapor–gas phase

$$p = \rho_1 R T \sum_{i=1}^{n} \frac{y_{1i}}{M_i},$$

where p is the pressure, R is the gas constant, and M is the molecular weight of the component.

To close the system it is necessary to determine the values of the equilibrium concentrations y^*_{1i} at the phase interface and the velocities u_1 and u_2.

The value of y^*_{1i} depends on the concentration of the component in the liquid phase and the temperature of the medium. For its determination it is necessary to use Raoult's and Dalton's laws and the Clausius–Clapeyron equation:

$$y^{M}_{1i} = \frac{p_{1i}}{p} c^{M}_{2i},$$

where y^{M}_{1i} and c^{M}_{2i} are the mole concentration of the corresponding components and p_{1i} is the saturated vapor pressure of the component. The transition from mole concentrations to weight concentrations can be made on the basis of conventional relations.

In calculating the flow velocities u_1 and u_2 of the phases we assume that Darcy's law holds inside the porous structure:

$$u_j = -\gamma_j \partial p_j / \partial l, \quad j = 1, 2,$$

where γ is the permeability of the granule for the j-th phase. Making use of the fact that the pressures in the liquid and vapor–gas phases are connected through the capillary pressure, we deduce the expressions

$$u_2 = -\gamma_2 \partial p / \partial l - B \partial \alpha_2 / \partial l, \quad u_1 = -\gamma_1 \partial p / \partial l,$$

where p is the pressure in the system of gas-filled pores inside the granule and B is a coefficient characterizing the rate of capillary transport of the liquid. Analytical formulas for the estimation of this parameter according to the type of capillary porous structure of the medium are given in [6].

3. Boundary Conditions and Difference Scheme

Equality of the heat and material fluxes are taken as the natural boundary conditions on the sidewall of the granule:

$$\begin{gathered} D_{1i}\alpha_1 \frac{\partial}{\partial l}(\rho_1 y_{1i}) = D^*_{1i}\alpha^*_1 \frac{\partial}{\partial l}(\rho^*_1 y^*_{1i}) = \beta_1 \alpha^*_1 (y^*_{1i} - y_{1i}), \\ D_{2i}\alpha_2 \frac{\partial}{\partial l}(\rho_2 c_{2i}) = D^*_{2i}\alpha^*_2 \frac{\partial}{\partial l}(\rho^*_2 c^*_{2i}) = \beta_2 \alpha^*_2 (c^*_{2i} - c_{2i}), \\ \lambda_{\text{ef}} \frac{\partial T}{\partial l} = \lambda_{\text{ef}} \frac{\partial T^*}{\partial l} = \alpha (T^* - T), \end{gathered} \tag{3.1}$$

where β_j is the coefficient of mass transfer of the j-th phase from the surface of the granule (j = 1 for the vapor–gas phase, and j = 2 for the liquid) and α is the coefficient of heat transfer between the granule and the gas–liquid medium. The asterisk * refers to quantities outside the porous granule. However, an inherent difficulty in the application of relations (3.1) is the determination of the heat and mass fluxes to the outside surface of the granule.

We consider two cases.

1. The temperature of the granule surface is lower than the boiling point of any component of the liquid phase at the ambient pressure.

We assume that the granule is surrounded by a two-phase zone, the thickness δ of which is numerically equal to the capillary constant calculated from the Taylor instability [7]:

$$\delta = \sqrt{\sigma / g(\rho_2 - \rho_1)},$$

where σ is the coefficient of surface tension of the liquid and g is the free-fall acceleration.

On the other hand, the thickness of the two-phase zone can be determined from the balance of the quantities of substance formed as a result of chemical reaction and phase transition and entrained by continuously ascending bubbles:

$$\frac{4}{3}\pi \frac{d}{dt}(R_g + R^*)^3 = -u_1^{(*)}\alpha_1^{(*)}\varepsilon 4\pi (R_g + R^*)^2 - u^*\pi (R_g + R^*)^2,$$

where $u_1^{(*)}$ and $\alpha_1^{(*)}$ are the velocity of the vapor–gas phase and its fraction at $l = L$, R_g is the radius of the granule, R* is the thickness of the gas cavity around the granule, and u* is the rate of ascension of the bubbles.

Now, if the thickness of the gas cavity is smaller than the detached bubble radius, $R^* < \delta$, then

$$\delta_0 = \delta, \quad \alpha_1^* = \frac{R^*}{\delta}, \quad T^* = T_g - \frac{T_g - T_\infty}{L_\infty}\delta, \tag{3.2}$$

and if $R^* > \delta$,

$$\delta_0 = R^*, \quad \alpha_1^* = 1, \quad T^* = T_g - \frac{T_g - T_\infty}{L_\infty} R^*,$$

where T_g is the temperature of the surface the granule, T_∞ is the bulk temperature at a distance L_∞ from the surface of the granule, δ_0 is the thickness of the two-phase zone, and T^* is the temperature of the vapor–liquid medium in the zone δ_0 around the granule. Here the heat- and mass-transfer coefficients are calculated according to formulas given in [8].

2. The temperature of the surface of the granule is higher than the temperature of the surrounding liquid (T_{bo}). Then the thickness of the vapor bubble can be calculated:

$$R^* = \frac{T_g - T_{bo}}{T_g - T_\infty} L_\infty.$$

Once again, if the thickness of the vapor bubble is smaller than the detached bubble radius ($R^* < \delta$),

$$\delta_0 = \delta, \quad \alpha_1^* = \frac{R^*}{\delta}, \quad T^* = T_g - \frac{T_g - T_\infty}{L_\infty}\delta, \tag{3.3}$$

and if $R^* > \delta$,

$$\delta_0 = R^*, \quad \alpha_1^* = 1, \quad T^* = T_{bo},$$

where the heat- and mass-transfer coefficients are calculated according to the film-boiling formulas [8].

Natural symmetry conditions are specified at the center of the granule:

$$\frac{\partial \alpha_1}{\partial l} = \frac{\partial y_{1i}}{\partial l} = \frac{\partial c_{2i}}{\partial l} = \frac{\partial p}{\partial l} = 0. \tag{3.4}$$

We fix the following sequence of solution of the system of equations (2.1)-(2.6) with the boundary conditions (3.2)-(3.4). Substituting the expression (2.7) for u_2 in (2.4), we determine α_2 from the equation

$$\frac{\partial}{\partial t}(\alpha_2\rho_2) = \frac{\partial}{\partial l}\left(B\alpha_2\rho_2\frac{\partial \alpha_2}{\partial l}\right) + \frac{\partial}{\partial l}\left(\alpha_2\rho_2\gamma_2\frac{\partial p}{\partial l}\right) - \Phi\sum_{i=1}^{m} y_{1i}^* + W_2\sum_{i=1}^{m}\mu_i. \tag{3.5}$$

Then from Eqs. (2.1) and (2.2) we determine the n concentrations y_{1i} and the $m - 1$ concentrations c_{2i}, and from Eq. (2.6) we determine T. We can now calculate ρ_1, p, u_1, and u_2.

In formulating the difference schemes for Eqs. (3.5), (2.1), and (2.2) we use a so-called scheme with donor cells [9], which has the conservative property, i.e., it transfers any disturbance by convection only in the direction of the velocity. For an equation of the form

$$\frac{\partial}{\partial t}(\alpha u) = \frac{\partial}{\partial l}\left(D\frac{\partial u}{\partial l}\right) - \frac{\partial}{\partial l}(vu) + f$$

this scheme is written as follows:

$$\frac{\alpha_i u_i^{n+1} - \alpha_i u_i^n}{\tau} = \frac{1}{h}\left(D_{i+1/2}\frac{u_{i+1}^{n+1} - u_i^{n+1}}{h} - D_{i-1/2}\frac{u_i^{n+1} - u_{i-1}^{n+1}}{h}\right)$$

$$+ f - \frac{1}{h}\left(\frac{v_{i+1/2} + |v_{i+1/2}|}{2}u_i^{n+1} + \frac{v_{i+1/2} - |v_{i+1/2}|}{2}u_{i+1}^{n+1} - \frac{v_{i-1/2} + |v_{i-1/2}|}{2}u_{i-1}^{n+1} - \frac{v_{i-1/2} - |v_{i-1/2}|}{2}u_i^{n+1}\right).$$

For Eq. (2.6) we use an ordinary upwind differencing scheme [9].

Owing to the nonlinearity of the resulting system of difference equations, it is integrated in each time step. It can be shown in this connection that for sufficiently small times steps τ the iterations converge, and the solution of the finite-difference problem approximates the solution of the differential problem with order $O(\tau, h)$.

The computational process is therefore formulated as follows. If the number of iterations in the time step exceeds $k_{max} = 6$, the time step is decreased by 1/4, and if the number of iterations is smaller than $k_{min} = 2$, the time step is doubled.

4. Numerical Analysis and Its Results

It is convenient to carry out the numerical analysis of the model equations after expressions (2.1)-(2.6) have been reduced to dimensionless form. We choose the dimensionless variables

$$\xi = l/L, \quad \tau = at/L^2, \quad \tilde{p} = p/p_0, \quad \tilde{\rho} = \rho_1/\rho_2, \quad \theta = \frac{T - T_0}{RT_0^2} E,$$

where T_0 is a reference temperature, E is the activation energy of the chemical reaction, and a is the thermal diffusivity of the granule. We analyze the process as a function of the dimensionless parameters

$$\tilde{\gamma}_1 = \frac{\gamma_1 p_0}{D_1}, \quad \tilde{\gamma}_2 = \frac{\gamma_2 p_0}{D_2}, \quad \tilde{B} = \frac{B}{D_2}, \quad \psi_i^2 = \frac{k_i L^2}{D_i},$$

where k_i is the reaction rate constant (i = 1, 2) and p_0 is the pressure outside the granule. Ths significance of these parameters is clear from an analysis of the dimensioned quantities entering into them.

At the present time the authors are unaware of any experimental data on the temperature, pressure, and concentration fields inside a porous granule. It is therefore difficult to estimate the reliability of the mathematical model.

Accordingly, here we give the numerical analysis results that provide a qualitatively correct description of the ongoing process and quantitative agreement with experimentally observed characteristics such as, e.g., the period of the mean-temperature fluctuations.

As a result of the calculations we have discerned several of the most typical regimes of the process.

One of those regimes corresponds to filling of the porous structure with a reacting liquid. It is interpreted as the time interval from the start of filling of the granule with the liquid until the establishment of a pressure profile therein that grows monotonically toward the center. This regime is characterized by a successive increase in the fraction of the liquid phase inside the porous granule and a considerable elevation of the pressure and temperature. Typical examples of such solutions are shown in Figs. 1-3.

The curves in Fig. 1 are numbered as follows: 1) $\tau = 0.632 \cdot 10^{-3}$; 2) $1.27 \cdot 10^{-3}$; 3) $2 \cdot 10^{-3}$; 4) $8.5 \cdot 10^{-3}$; 5) steady state; it is inferred from the figure that for small values of τ a local pressure increase is observed near the sidewall in connection with the chemical conversion of the liquid entering the granule. The value of this maximum and the rate of increase of the pressure fall between wide limits and depend on γ_1 and on the rate of phase transition.

As the process evolves, the coordinate of the maximum pressure shifts toward the center of the granule, in which case the fraction of the liquid phase decreases; see Fig. 2; 1) $\tau = 0.632 \cdot 10^{-3}$; 2) $1.27 \cdot 10^{-3}$; 3) $2 \cdot 10^{-3}$. After reaching the center, the liquid begins to move rapidly away, so that either the granule is completely dried out if the capillary absorption forces are not sufficiently large, or it is partially filled. The value of the pressure at the center of the granule can greatly exceed its value at the outer surface for a brief moment; this is obviously one of the causes of the destruction of catalyst granules when they become impregnated.

The temperature of the phases during filling varies between wide limits and can have a nonmonotonic behavior, particularly for large values of $\tilde{B}$ and ψ_2; see Fig. 3: 1) $\tau = 0.61 \cdot 10^{-3}$; 2) $0.611 \cdot 10^{-3}$; 3) $0.612 \cdot 10^{-3}$; 4) $11.6 \cdot 10^{-3}$; 5) steady state.

In addition to transient processes, we have also carried out a numerical analysis of the steady-state behavior of chemical reaction inside the granule. Three distinct steady states are obtained here, depending on the relationship of the dimensionless parameters.

The first state corresponds to a low-temperature liquid-filled granule and the second state to the high-temperature domain of the process. In this case the porous granule is

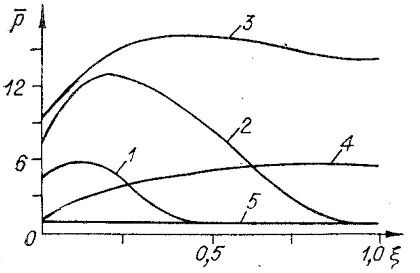

Fig. 1

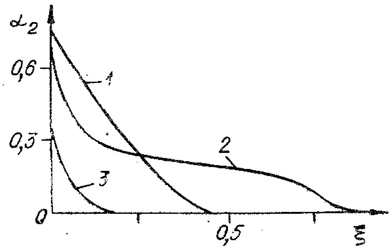

Fig. 2

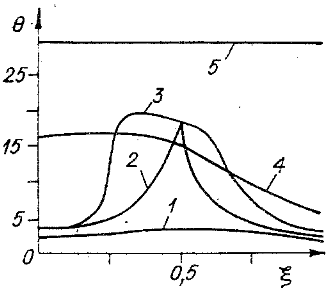

Fig. 3

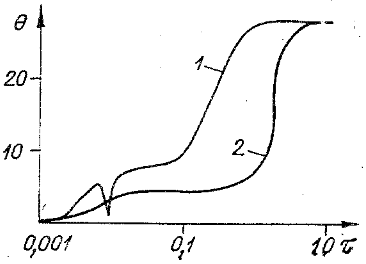

Fig. 4

surrounded by a vapor sheath, and the chemical reaction takes place only in the vapor phase. The dynamics of the evolution of this state is shown in Fig. 4: 1) $\gamma_1 = 2 \cdot 10^2$; 2) $2 \cdot 10^5$.

We have also obtained numerically a third, fluctuation steady-state regime, which is characterized by periodic fluctuations of the granule temperature and of the pressure and fraction of the liquid phase in it. This state is established when the heat of chemical reaction is inadequate for evaporation of the liquid and the creation of a stable vapor film. Here the fluctuation period depends not only on the relationship of the dimensionless parameters, but also on the temperature of the liquid surrounding the granule. It is important to note that all these steady states are observed experimentally.

The numerical calculations thus show that our proposed model provides a qualitatively correct description of the behavior of a multiphase process in and around a porous catalyst granule and can be used to analyze a number of industrially important processes.

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