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ON UNSTEADY MODES OF OPERATION OF AN ISOTHERMAL REACTOR WITH LONGITUDINAL MIXING

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V. A. NOVIKOV
(Moscow)

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Methods of the perturbation theory are used to investigate the unsteady mode of operation of an isothermal reactor with longitudinal dispersion. An approximate expression for the performance of the reactor working in dynamic mode is obtained. The results obtained are compared with the corresponding data obtained for a reactor with perfect mixing.

Mathematical analysis of the distinctive features of the chemical flow reactors with perfect mixing in the unsteady mode was carried out in a number of works e.g. [1—10]. It was shown that use of the unsteady modes of operation may lead to improvement in the performance of a chemical reactor not only in the case of a straightforward single stage chemical reaction with nonlinear kinetics [7—9], but also in the case of reactors in which complex multistep chemical reactions take place [1—6, 10]. The significant influence of the unsteady character on the selectivity and other characteristics of the chemical process [1—6] is noted.

1. Formulation of the problem. Consider a one-dimensional model of a tubular, isothermal reactor in which a single, irreversible chemical reaction takes place. The unsteady equation for the concentration written in dimensionless variables has the form

$$\frac{\partial c}{\partial t} = \frac{1}{P}\frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\partial x} - f(c) \qquad (1.1)$$

$$c = \frac{C}{C_0}, \quad x = \frac{X}{L}, \quad t = \frac{TU}{L}, \quad P = \frac{UL}{D}, \quad f(c) = \frac{UF(C)}{LC_0}$$

Here X denotes the spatial coordinate $(0 \leqslant X \leqslant L)$; L is the reactor length; T is time; C is the concentration of the reacting species; C_0 is the steady state concentration of the reacting species in the input flow; U is the rate of supply of the reagent; D is the diffusion coefficient and $F(C)$ describes the dependence of the chemical reaction rate on the reagent concentration.

We assume that the concentration of the reacting species at the reactor input can be expressed as a sum of a constant term C_0 and an unsteady perturbation $\Phi(t)\, C_0$. Then the boundary conditions at the reactor input for (1.1), which are also valid for the unsteady state, have the following dimensionless form [4, 12]:

$$x = 0, \quad c - \frac{1}{P}\frac{\partial c}{\partial x} = 1 + \Phi(t); \quad x = 1, \quad \frac{\partial c}{\partial x} = 0 \qquad (1.2)$$

We specify, as the initial condition, the following distribution of concentration corresponding to the stable, steady state solution of the problem (1.1), (1.2) for

$\Phi(t) \equiv 0$:

$$t = 0, \quad c(x, 0) = c_s(x) \tag{1.3}$$

The problem (1.1)–(1.3) of unsteady distribution of concentration in the reactor in the presence of a perturbation at the input, does not have an exact analytic solution. We construct an approximate solution for this problem, using the perturbation theory under the assumption that the parameter P is small [13]. We shall assume that the perturbation of the initial concentration is small and of order P, i.e. $\Phi(t) = P\varphi(t) = O(P)$. Thus we assume that the perturbation of the initial concentration is of the same order of smallness as the Peclet number. When their order of magnitude is not the same, then the solution can be obtained in the manner analogous to that used below.

We note that when $P = 0$, then the problem formulated for a reactor with axial dispersion is transformed into the problem for a reactor with complete mixing in which the reagent concentration at the input is equal to its unperturbed, steady state value. The solution of this problem corresponds to the zero approximation in the asymptotic expansion of the solution of the problem (1.1)–(1.3) in P.

2. **Solution of the problem.** We shall seek a solution of the problem (1.1)–(1.3) in the form of an expansion in powers of P, and write the initial condition (1.3) also in the form of a series

$$c(x, t) = \sum_{n=0}^{\infty} P^n c_n(x, t) \tag{2.1}$$

$$t = 0, \quad c(x, 0) = c_s(x) = \sum_{n=0}^{\infty} P^n c_{ns}(x) \tag{2.2}$$

We note that the choice of the initial condition in the form of the steady distribution of concentration, eliminates the need for considering the time-dependent boundary layer near $t = 0$ and for matching the outer and inner asymptotic expansion [14]. The above condition does not affect the unsteady behavior of the solution provided that the time interval is sufficiently long.

Let us substitute the expansion (2.1) into (1.1), (1.2) and write the function $f(c)$ in the form of a series in powers of P. Equating the coefficients of like powers of P, we obtain the equations as well as the boundary and initial conditions for the functions $c_n(x, t)$. The boundary value problems for $n = 0, 1, 2$ and 3 are, respectively,

$$\partial^2 c_0 / \partial x^2 = 0$$

$$x = 0, \quad \frac{\partial c_0}{\partial x} = 0; \quad x = 1, \quad \frac{\partial c_0}{\partial x} = 0$$

$$t = 0, \quad c_0(x, 0) = c_{0s}$$

$$\frac{\partial^2 c_1}{\partial x^2} = \frac{\partial c_0}{\partial t} + \frac{\partial c_0}{\partial x} + f(c_0)$$

$$x = 0, \quad \frac{\partial c_1}{\partial x} = c_0 - 1; \quad x = 1, \quad \frac{\partial c_1}{\partial x} = 0 \cdot$$

$$t = 0, \quad c_1(x, 0) = c_{1s}(x)$$

$$\frac{\partial^2 c_2}{\partial x^2} = \frac{\partial c_1}{\partial t} + \frac{\partial c_1}{\partial x} + f'(c_0)\, c_1$$

$$x = 0, \quad \frac{\partial c_2}{\partial x} = c_1 - \varphi; \quad x = 1, \quad \frac{\partial c_2}{\partial x} = 0$$

$$t = 0, \quad c_2(x, 0) = c_{2s}(x)$$

$$\frac{\partial^2 c_3}{\partial x^2} = \frac{\partial c_2}{\partial t} + \frac{\partial c_2}{\partial x} + f'(c_0)\, c_2 + \frac{f''(c_0)}{2} c_1^2$$

$$x = 0, \quad \frac{\partial c_3}{\partial x} = c_2; \quad x = 1, \quad \frac{\partial c_3}{\partial x} = 0$$

$$t = 0, \quad c_3(x, 0) = c_{3s}(x)$$

Using these boundary value problems to determine the functions $c_n(x, t)$ $(n = 0, 1, 2, 3)$ we obtain, for $c(x, t)$, the following expression with the accuracy of up to and including terms of second order of smallness:

$$c(x, t) = c_{0s} + P\left[\left(\frac{x^2}{2} - x\right) f + a_1\right] + P^2\left[\frac{x^4}{24} ff' + \frac{x^3}{6} f(1 - f') + \frac{x^2}{2}(a_1' + a_1 f' - f) + x(a_1 - \varphi) + \frac{D_s}{A} + e^{-At}\int_0^t D_1(\tau)\, e^{A\tau}\, d\tau\right] \tag{2.3}$$

$$A = 1 + f', \quad B = \left(\frac{1}{2} + \frac{1}{3} f'\right) f, \quad a(t) = e^{-At}\int_0^t \varphi(\tau)\, e^{A\tau}\, d\tau$$

$$D_s = f\left[\frac{1}{3} + f'\left(\frac{1}{4} + \frac{1}{30} f'\right) + f''\left(\frac{1}{3}\frac{B}{A} - \frac{1}{15} f\right)\right] - \frac{f''}{2}\frac{B^2}{A^2} - \frac{B}{A}\left[A + \frac{1}{6}(f')^2\right], \quad a_1(t) = \frac{B}{A} + a(t)$$

$$D_1(t) = \frac{1}{2}\varphi' + \varphi\left(1 + \frac{1}{2} f'\right) - \frac{1}{6} a'' - a'\left(1 + \frac{1}{3} f'\right) - a\left[1 + f'\left(1 + \frac{1}{6} f'\right) + f''\left(\frac{B}{A} - \frac{1}{3} f\right)\right] - \frac{1}{2} f'' a^2$$

The approximate analytic expression (2.3) obtained makes it possible to investigate the influence which the unsteady perturbations of concentration in the input flow have on the time-averaged degree of conversion of the reagent within the reactor, and compare it with the steady state degree of conversion.

Let us assume, for definiteness, that the time-dependence of the perturbations of the input concentration has the form

$$\varphi(t) = g \sin \omega t \tag{2.4}$$

where the time-averaged value of the reagent concentration in the input flow retains its steady state value.

By definition, the mean degree of conversion in the unsteady periodic mode of frequency ω is equal to:

$$\bar{\xi} = 1 - \frac{\omega}{2\pi}\int_{\tau}^{\tau + 2\pi/\omega} c(1, t)\, dt \tag{2.5}$$

Using (2.3)—(2.5), we can obtain the following expression for the variation in the reactor performance caused by the fluctuation in the input concentration, for the case when the perturbation is harmonic in character:

$$\Delta\xi = \bar{\xi}_p - \xi_s = \frac{g^2 f'' P^2}{4(1+f')\left[(1+f')^2+\omega^2\right]} \qquad (2.6)$$

where $\bar{\xi}_p$ denotes the mean degree of conversion of the reagent in the unsteady periodic mode, and ξ_s is the degree of conversion in the steady state process.

The expression (2.6) provides the means of estimating the influence of various factors on the performance efficiency of an isothermal reactor with longitudinal mixing, in the dynamic mode. It is clear that the increase (decrease) in the degree of reagent conversion on passing from the steady state to the unsteady mode depends in the type of reactor in question, to a large degree, on the chemical kinetics. The absolute value of the change in the degree of conversion attains its maximum in the quasisteady case, and the degree of conversion approaches its steady state value with increasing frequency of perturbation in the input reagent concentration.

Comparing (2.3) and (2.6) with the corresponding results for the reactor with complete mixing, we can see that although the concentration profiles can be appreciably different in the unsteady modes, the time-averaged values of the degree of conversion agree for both cases with the accuracy of up to the terms of second order in P inclusive. It follows that the unsteady effects appearing in the reactors with complete mixing will also be characteristic for the systems with distributed parameters. In the case of a weak dispersion, similar formulas can be used for the quantitative estimates of these effects.

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