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CONTINUOUS-FLOW SYSTEM WITH FRACTIONAL ORDER CHEMICAL REACTION IN THE PRESENCE OF AXIAL DISPERSION*

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A detailed analysis of an irreversible single-stage chemical reaction of fractional order is carried out using a mathematical model of one-dimensional isothermal chemical reactor with axial dispersion.

Analysis of mathematical models of continuous-flow chemical reactors shows that a change from steady conditions of the reaction process in a continuous-flow system in which the initial concentration of reagent at reactor inlet is constant, to the dynamic mode with cyclic variation of initial reagent concentration about a mean value equal to that of the steady mode results, under certain conditions, in an increase of the degree of reagent transformation (see e.g., /1—7/). The relative effectiveness of the periodic mode compared to that of the steady mode can be defined by the magnitude of unsteady shift: the degree of transformation divergence, averaged over a period of time, from that of the steady mode. In a continuous-flow chemical reactor with axial dispersion the unsteady shift depends on dispersion intensity and chemical reaction kinetics.

An approximate analytic expression was obtained in /7/ for a model of one-dimensional continuous-flow chemical reactor with axial dispersion, in which a quasisteady irreversible single-stage chemical reaction takes place. The expression obtained there in the "weak" chemical reaction approximation for the unsteady shift, established the relation between the longitudinal diffusion coefficient, and properties of the function of chemical reaction rate. The formula indicates the presence of a singularity in the reactor unsteady behavior when the reaction is of an order close to 1/2. Because of the wide use of this type of reactions a more detailed investigation of this problem is presented here.

The unsteady equation for concentration, and for the boundary and initial conditions can be represented in dimensionless variables as follows:

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

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

$$t=0,\quad c(x,0)=c_{in}(x);\quad c_{in}=\frac{C_{in}}{C_0}$$

$$c=\frac{C}{C_0},\quad x=\frac{X}{L},\quad t=\frac{TU}{L},\quad P=\frac{UL}{D},\quad f(c)=\frac{LF(C)}{UC_0},\quad c_f=\frac{C_f}{C_0}$$

where X is a space coordinate $(0\leqslant X\leqslant L)$, L is the reactor length, T is the time, C is the reagent concentration in the reactor, C_{in} is the initial concentration distribution, C_f is the concentration of reagent at the reactor inlet, C_0 is the steady value of concentration C_f, U is the reagent feed rate, D is the coefficient of effective diffusion, $F(C)$ defines the dependence of chemical reaction rate on the reagent concentration, and P is the Péclet number. We also introduce the quantity $\xi=(C_0-C)/C_0$ which defines the degree of reagent transformation.

Let us assume the dimensionless rate of the chemical reaction to be low, i.e. that $f(c)=\varepsilon f_1(c)=O(\varepsilon)$, $\varepsilon\ll 1$ ("weak" chemical reaction), and restrict the analysis to quasi-periodic perturbations, assuming that function $c_f(t)$ varies only little in a time interval comparable to the characteristic time of /reagent/ passing through the reactor.

We seek a solution of problem (1) in the form of series in powers of ε, accurate to within terms of third order of smallness, and obtain for the quasisteady distribution of concentration in the reactor the following relations:

$$c(x,t)=c_f-\varepsilon f_1(c_f)\left[x+\frac{1-e^{-P(1-x)}}{P}\right]+\varepsilon^2 f_1(c_f)f_1'(c_f)\left[\frac{e^{-P}-3e^{-P(1-x)}+2}{P^2}+\frac{2x-2e^{-P(1-x)}+xe^{-P(1-x)}}{P}+\right. \tag{2}$$

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$$\left.\frac{x^2}{2}\right] + \varepsilon^3 \{A(x) - A(0) + [B(x) - B(1)]\, e^{Px}\} + O(\varepsilon^4)$$

$$A(x) = -f_1(c_f)\,[f_1'(c_f)]^2 \left[\frac{e^{-P}+2}{P^2}\, x - \left(\frac{4e^{-P}}{P^3} + \frac{2e^{-P}}{P^2}\right) e^{Px} + \frac{e^{-P}}{P^2}\, x e^{Px} + \frac{x^2}{P} + \frac{x^3}{6}\right] - \frac{f_1''(c_f)}{2}\,[f_1(c_f)]^2 \left[\frac{x}{P^2} + \frac{e^{-2P}}{2P^3}\, e^{2Px} - \frac{2e^{-P}}{P^2}\, x e^{Px} + \frac{x^2}{P} + \frac{x^3}{3}\right]$$

$$B(x) = f_1(c_f)\,[f_1'(c_f)]^2 \left[-\frac{e^{-P}+5}{P^3}\, e^{-Px} - \left(\frac{3e^{-P}}{P^2} + \frac{2e^{-P}}{P}\right) x - \frac{3}{P^2}\, x e^{-Px} - \frac{1}{2P}\, x^2 e^{-Px} + \frac{e^{-P}}{2P}\, x^2\right] + \frac{f_1''(c_f)}{2}\,[f_1(c_f)]^2 \left[-\frac{5}{P^3}\, e^{-Px} - \frac{2e^{-P}}{P^2}\, x - \frac{4}{P^2}\, x e^{-Px} - \frac{1}{P}\, x^2 e^{-Px} - \frac{e^{-P}}{P}\, x^2 + \frac{e^{-2P}}{P^3}\, e^{Px}\right]$$

Using formula (2) for the reagent concentration at the reactor exit we obtain

$$c(1, t) = c_f - \varepsilon f_1 + \varepsilon^2 f_1 f_1' \Omega(P) - \varepsilon^3 [f_1 (f_1')^2 \Omega_1(P) + {}^1\!/_2\, f_1^2 f_1'' \Omega_2(P)] + O(\varepsilon^4) \qquad (3)$$

$$\Omega(P) = \frac{e^{-P}-1}{P^2} + \frac{1}{P} + \frac{1}{2}, \quad \Omega_1(P) = \frac{4(e^{-P}-1)}{P^3} + \frac{3e^{-P}+1}{P^2} + \frac{1}{P} + \frac{1}{6}, \quad \Omega_2(P) = \frac{1-e^{-2P}}{2P^3} - \frac{1}{P^2} + \frac{1}{P} + \frac{1}{3}$$

where $c_f(t)$ is the argument of function f_1 and its derivatives.

Using (3), for the unsteady shift in quasisteady approximation it is possible to obtain

$$\langle \Delta\xi \rangle = \varepsilon G_0 - \varepsilon^2 G\Omega(P) + \varepsilon^3 [G_1\Omega_1(P) + G_2\Omega_2(P)] + O(\varepsilon^4) \qquad (4)$$

$$G_0 = \langle f_1(c_f)\rangle - f_1(\langle c_f\rangle), \quad G = \langle f_1(c_f)\, f_1'(c_f)\rangle - f_1(\langle c_f\rangle) f_1'(\langle c_f\rangle)$$

$$G_1 = \langle f_1(c_f)(f_1'(c_f))^2\rangle - f_1(\langle c_f\rangle)\,(f_1'(\langle c_f\rangle))^2$$

$$G_2 = \left\langle \frac{f_1''(c_f)}{2}\,(f_1(c_f))^2 \right\rangle - \frac{f_1''(\langle c_f\rangle)}{2}\,(f_1(\langle c_f\rangle))^2$$

where the angled brackets denote averaging over the period of variation of function $c_f(t)$.

The term of first order with respect to ε is obviously independent of the Péclet number, and the effect of longitudinal diffusion on the unsteady shift makes itself felt only in the second approximation. Formula (4) was analyzed in /7/ to within terms of order ε^2, and the obtained there results are applicable to a wide class of kinetic functions $f_1(c)$.

However for some of functions $f_1(c)$ parameter G may be small or zero (for instance, $G = 0$ when $f_1(c) = k_1 c^{1/2}$). To estimate the effect of longitudinal diffusion on the unstable shift it is necessary to analyze (4) with an accuracy to terms of higher of ε. In the analysis we assume that the reagent concentration at the reactor inlet varies in conformity with a harmonic law and at small amplitude, i.e. $c_f(t) = 1 + \delta g_1 \sin \omega t,\ \delta \ll 1$. Then from (4) we can obtain

$$\langle \Delta\xi \rangle = \varepsilon \left[\delta^2 g_1^2 \frac{f_1''(1)}{4} + \delta^4 g_1^4 \frac{f_1''''(1)}{32} + O(\delta^6)\right] - \varepsilon^2 \left[\delta^2 g_1^2 \frac{R''(1)}{4} + O(\delta^4)\right] \Omega(P) + \varepsilon^3 \left[\left(\delta^2 g_1^2 \frac{R_1''(1)}{4} + O(\delta^4)\right) \Omega_1(P) + \left(\delta^2 g_1^2 \frac{R_2''(1)}{4} + O(\delta^4)\right) \Omega_2(P)\right] + O(\varepsilon^4\delta^2) \qquad (5)$$

$$R(c) = f_1(c)\, f_1'(c), \quad R_1(c) = f_1(c)\,[f_1'(c)]^2, \quad R_2(c) = {}^1\!/_2 f_1^{\,2}(c)\, f_1''(c)$$

Let the reaction rate dependence on concentration conform to the law $f_1(c) = k_1 c^{1/2+\varepsilon b}$, $b = O(1)$. Then, setting $\delta = \varepsilon$ and using formula (5), we obtain

$$\langle \Delta\xi \rangle = -\varepsilon^3 \frac{g_1^2 k_1}{16} + \varepsilon^5 \left[-\frac{15 g_1^4 k_1}{16\cdot 32} + \frac{g_1^2 b^2 k_1}{4} - \frac{3 g_1^2 k_1^3}{64} W(P)\right] + O(\varepsilon^6) \qquad (6)$$

$$W(P) = -\left[\Omega_1(P) - \frac{1}{2}\Omega_2(P)\right] - \alpha\Omega(P), \quad \alpha = \frac{16b}{3k_1}$$

Equality (6) implies that in the considered here kinetic dependence $\langle \Delta\xi \rangle < 0$, i.e. the transformation rate in the unsteady mode is slower than in the steady mode. The effect of longitudinal mixing on the unsteady shift is determined by function $W(P)$ whose curves are shown in Fig.1 for several values of parameter α. The pattern of the $W(P)$ curve substantially depends on parameter α which is determined by the order of the reaction and by the rate constant.

Depending on α the $W(P)$ curve can be monotonic (increasing or decreasing), as well as nonmonotonic, in particular, to have a maximum ($\alpha = -1$) and a minimum ($\alpha = -1.09$), whose positions also depend on α.

When $\alpha \geqslant -0.5$, curve $W(P)$ monotonically increases, attaining its maximum at $P_{\max} = \infty$. The decrease of parameter α leads to function $W(P)$ attaining maximum already at finite Péclet numbers. The quantity $P_{\max}$ decreases with decreasing α, i.e. the maximum shifts to the left. For α close to -0.5 we have

$$P_{\max}\,(\alpha \to -0.5-0) \approx [2\,(\alpha - 1.5)]/(\alpha + 0.5)$$

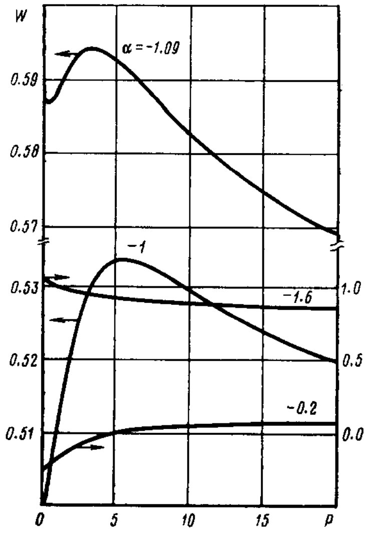

Fig.1

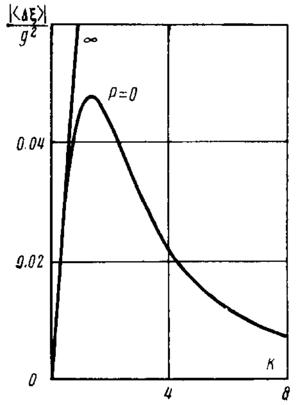

Fig.2

When parameter α passes through the value $\alpha = -1$, curve $W(P)$ has a minimum at point $P_{\min} = 0$ and $P_{\min}$ increases as α decreases. When α is close to -1 we have

$$P_{\min}\,(\alpha \to -1 + 0) \approx (\alpha + 1)/(0.5\alpha + 0.3)$$

Further decrease of parameter α results in the merging of maxi and minimum, and the $W(P)$ curve becomes monotonically decreasing.

At the limit points $P = 0$ and $P = \infty$ the dependence of $W(P)$ on parameter α is of the form $W(0) = -\alpha - 0.5$, $W(\infty) = -0.5\,\alpha$. It will be seen that for $\alpha = -1$ we have $W(0) = W(\infty)$.

The above investigation of function $W(P)$ enables us to formulate the following conclusions about the effect of longitudinal mixing on the magnitude of unsteady shift.

When $\alpha > -0.5$, longitudinal mixing reduces the absolute value of the unsteady shift ($|\langle\Delta\xi\rangle|$) which is maximum in a reactor of perfect displacement ($P = \infty$).

When $-0.5 < \alpha < -1$, the longitudinal mixing may (depending on the Péclet number) either decrease or increase the absolute value of the unsteady shift which is maximum in a reactor with intermediate longitudinal diffusion intensity. The maximum value of unsteady shift in a reactor of perfect displacement exceeds the respective quantity in a reactor with perfect mixing.

When $\alpha < -1$, the effect of longitudinal mixing on the absolute value of the unsteady shift may become even more complex (Fig.1, $\alpha = -1.09$). Depending on the range of variation of the Péclet number, the longitudinal mixing may either decrease or increase the absolute value of the unsteady shift.

Further decrease of parameter α results in a monotonic dependence of the unsteady shift on the degree of mixing (Fig.1, $\alpha = -1.6$), and the longitudinal diffusion increases the absolute value of unsteady shift which is maximum in a reactor with perfect mixing.

When $\alpha = -1$, the magnitude of unsteady shift in a reactor of perfect displacement is equal to that of the reactor of perfect mixing. Note that it is at point $\alpha = -1$ and its neighborhood that the depencence of the unsteady shift on longitudinal dispersion becomes non-monotonic. At that characteristic point ($\alpha = -1$) the rate constant is $k_1 = -16b/3$. The disclosed singularity can be expected to appear also in the case of finite chemical reaction rates.

Let us now consider the expressions for the unsteady shift in the limit cases of kinetic dependence $f(c) = kc^{1/2}$ $(b = 0)$, viz. in that of the reactor of perfect mixing and of that of perfect displacement, without assuming the reaction to be weak, but considering the harmonic perturbations of concentration at the reactor inlet to be small. Using the method of small perturbations in the quasisteady state approximation, we obtain

$$\langle\Delta\xi\rangle = -\frac{\varepsilon^2 k g_1^2}{16(1+k^2/4)^{3/2}}, \quad P = 0 \tag{7}$$

$$\langle\Delta\xi\rangle = -\frac{\varepsilon^2 k g_1^2}{16}, \quad P = \infty \tag{8}$$

The dependence of absolute values of unsteady shift in reactors of perfect mixing and perfect displacement (7) and (8) is shown in Fig.2 as functions of the dimensionless constant k of the chemical reaction rate, with $g = \varepsilon g_1$. It will be seen that the unsteady shift in a reactor of perfect displacement is higher than that in one of perfect mixing; the curves intersect only at point $k = 0$, which is in agreement with the results obtained above in the analysis of a "weak" reaction.

Thus the unsteady shift interacts in a complex way with the longitudinal mixing, which results in the different situations described above. The above investigation shows the substantial effect of the presence of longitudinal dispersion on the dynamic characteristics of a continuous-flow chemical reactor. This must be taken into account in the selection of the optimal type of chemical reactor for operation under unsteady conditions.

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