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EFFECT OF LONGITUDINAL DISPERSION ON THE DYNAMIC CHARACTERISTICS OF A CONTINUOUS-FLOW CHEMICAL REACTOR*

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An approximate solution is constructed for the two-point boundary value problem occurring in the simulation of a continuous-flow isothermic reactor with longitudinal mixing. The derived solution is used for analyzing the effect of transport processes on the efficiency of a reactor working unsteady conditions.

A number of theoretical and experimental investigations had shown that the use of periodic modes in continuous-flow chemical reactors may result in considerable change of time averaged values of the degree of transformation, of output and selectivity in comparison with steady operation values (e.g., /1—8/).

Deviation of mean dynamic characteristics of a reactor from their respective steady values is due to the nonlinearity of the considered systems, and depends on reactor characteristics, particularly on the intermixing intensity and chemical transformation kinetics.

A numerical analysis was carried out in /9/ of unsteady modes of an isothermic reactor with longitudinal intermixing with certain specific values of controlling parameters. It was established that longitudinal intermixing increases the unsteady shift (Editor's note: definition given at the very end of Sect.1) which for the selected numerical values of constants reaches its maximum in a reactor with perfect intermixing, and is minimum in a perfect displacement reactor. In the present paper the effect of kinetics and diffusion on the unsteady shift of transformation rate in the reactor is analyzed in greater detail. It is established that the fundamental conclusion reached in /9/ is not universal.

1. Statement of the problem.

Let us consider the one-dimensional model of a continuous-flow isothermic reactor with longitudinal intermixing in wich a single irreversible chemical reaction takes place. In dimensionless variables the unsteady equation for concentration and the boundary and initial conditions may in this case be written in the form

$$\frac{\partial c}{\partial t}=\frac{1}{P}\frac{\partial^2 c}{\partial x^2}-\frac{\partial c}{\partial x}-f(c), \quad x=0, \quad -\frac{1}{P}\frac{\partial c}{\partial x}+c=c_f(t), \quad x=1, \quad \frac{\partial c}{\partial x}=0, \quad t=0, \quad c(x,0)=c_{in}(x) \tag{1.1}$$

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

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

The object of this analysis is to compare the time averaged degree of reagent transformation when the reacting substance concentration at the reactor intake is periodically varied, with that in a reactor under steady operation conditions which corresponds to concentration at the reactor intake averaged over a period of work at various Péclet numbers and forms of function $f(c)$.

We define the relative effectiveness of the periodic operation mode to that of the steady mode by the magnitude of mean divergence of the degree of transformation in the periodic mode to that in the steady mode. This divergence is called below, the unsteady shift. Let us consider several particular cases.

2. Reactors with perfect mixing and perfect through-put.

The equations and boundary conditions (1.1) for models of perfect intermixing $(P=0)$ and perfect through-put $(P=\infty)$ are, respectively, of the form

$$dc/dt=c_f(t)-c-f(c), \quad P=0, \qquad \frac{\partial c}{\partial t}+\frac{\partial c}{\partial x}=-f(c), \quad c(0,t)=c_f(t), \quad P=\infty \tag{2.1}$$

Let us consider a second order reaction at small harmonic perturbations of concentration at the reactor intake, i.e.

$$c_f=1+\varepsilon g_1 \sin \omega t, \quad f(c)=kc^2 \tag{2.2}$$

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*Prikl.Matem.Mekhan,44,No.3, 470-476,1980 where ε is the small parameter, $0 < \varepsilon \ll 1$, the time averaged dimensionless concentration at the reactor intake is equal unity (steady value), and k is the dimensionless constant of the reaction rate.

Using the method of small perturbations /10/ for solving Eqs. (2.1) for the unsteady shift of the mean degree of reagent transformation with an accuracy to second order terms with respect to ε, in the quasisteady approximation $(\omega \ll 1)$ we obtain

$$\langle \Delta\xi \rangle = \langle \xi_p \rangle - \xi_s = \frac{\varepsilon^2 k g_1^2}{2(1+4k)^{3/2}}, \quad P = 0 \tag{2.3}$$

$$\langle \Delta\xi \rangle = \langle \xi_p \rangle - \xi_s = \frac{\varepsilon^2 k g_1^2}{2(1+k)^3}, \quad P = \infty \tag{2.4}$$

where $\langle \xi_p \rangle$ is the time averaged degree of reagent transformation in an unsteady periodic mode, and ξ_s is the degree of transformation in the steady mode.

Dependence of the unsteady shift in perfect intermixing and perfect through-put reactors, (2.3) and (2.4), respectively, are shown in terms of the dimensionless constant k of chemical reaction rate in Fig.1, where $g = \varepsilon g_1$. Both curves (*1* for $P=0$ and *2* for $P = \infty$) have their maxima for $k = 0.5$ and intersect at $k = 2$.

Thus, depending on the intensity of the second order chemical reaction, the longitudinal diffusion in a continuous chemical reactor may increase (for $k > 2$ as well as decrease (for $k < 2$) the magnitude of the nonlinear shift of the transformation degree in the unsteady mode.

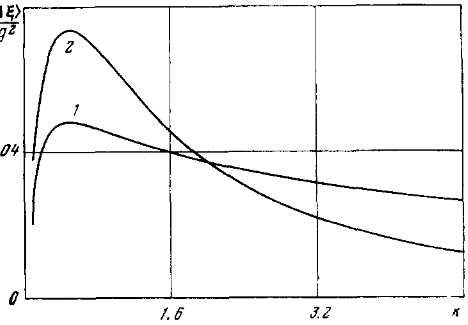

Fig.1

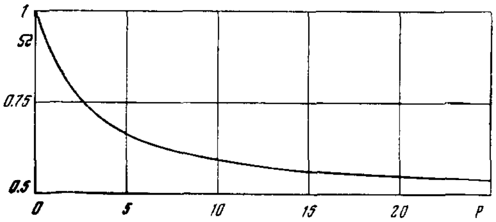

Fig.2

Note that the data in /9/ relate to $k = 12$, i.e. to the region of $k > 2$.

3. **Reactor with longitudinal dispersion.** Let us consider problem (1.1) at finite Péclet numbers. Unlike in Sect.1 where the approximate analytic solution is based on the assumption of small unsteady perturbation of input concentration, here we take the chemical intensity, i.e. $f(c) = \varepsilon f_1(c) = O(\varepsilon)$, $\varepsilon \ll 1$ as the small quantity. As previously, the analysis is restricted to quasisteady periodic perturbations, and function $c_f(t)$ is assumed to change little during the time comparable to the characteristic time of stay in the reactor. We shall consider the term in (1.1) which defines the chemical transformation, as the regular perturbation, and seek for problem (1.1) an approximate quasisteady solution of the form /10/

$$c(x,t) = c_0(x,t) + \varepsilon c_1(x,t) + \varepsilon^2 c_2(x,t) + \ldots \tag{3.1}$$

It is assumed here and in what follows that the dependence of solution on t is parametric.

Substituting (3.1) into (1.1) with $\partial / \partial t = 0$ and, then successively determining the terms of series (3.1) with an accuracy to terms of second order of smallness, for the quasi-steady concentration distribution in the reactor we obtain

$$c(x,t) = c_f - \varepsilon f_1(c_f)\left[x + \frac{1-e^{-P(1-x)}}{P}\right] + \varepsilon^2 f_1(c_f) f_1'(c_f)\left[\frac{e^{-P} - 3e^{-P(1-x)} + 2}{P^2} + \frac{2x - 2e^{-P(1-x)} + xe^{-P(1-x)}}{P} + \frac{x^2}{2}\right] \tag{3.2}$$

Passing to limit, from (3.2) we obtain for the concentration in perfect intermixing $(P = 0)$ and perfect through-put $(P = \infty)$ the expressions

$$c = c_f - \varepsilon f_1(c_f) + \varepsilon^2 f_1(c_f) f_1'(c_f), \quad P = 0 \tag{3.3}$$

$$c(x) = c_f - \varepsilon f_1(c_f) + \varepsilon^2 f_1(c_f) f_1'(c_f)\frac{x^2}{2}, \quad P = \infty \tag{3.4}$$

These expressions can also be obtained directly from solutions of respective problems for the indicated limit cases.

Using (3.2) we determine the time averaged degree of reagent transformation in the unsteady periodic mode and compare it with that in the steady mode. For the unsteady shift of the reagent transformation degree we can obtain

$$\langle\Delta\xi\rangle = \varepsilon\left[\langle f_1(c_f)\rangle - f_1(\langle c_f\rangle)\right] + \frac{\varepsilon^2}{2}\left\{\frac{df_1^2}{dc}(\langle c_f\rangle) - \left\langle\frac{df_1^3}{dc}(c_f)\right\rangle\right\}\Omega(P), \qquad \Omega(P) = \frac{e^{-P}-1}{P^2} + \frac{1}{P} + \frac{1}{2} \tag{3.5}$$

where, as previously, angle brackets denote averaging over the period of change of function $c_f(t)$. It follows from (3.5) that the unsteady shift of the mean transformation degree $\langle\Delta\xi\rangle$ is in the first approximation with respect to ε independent of the longitudinal diffusion intensity, i.e. it does not change with the change of the Péclet number $0 \leqslant P \leqslant \infty$. Dependence of the quantity $\langle\Delta\xi\rangle$ on the longitudinal intermixing intensity becomes apparent only in the second approximation with respect to ε, and is determined by function $\Omega(P)$ whose curve appears in Fig.2; it is monotonically decreasing and its limit points $\Omega(0) = 1$ and $\Omega(\infty) = {}^1/_2$ correspond to limit cases of the considered model. The type of dependence of the unsteady shift $\langle\Delta\xi\rangle$ on the Péclet number is determined by the sign of the derivative $d\langle\Delta\xi\rangle / dP$. Since the inequality $d\Omega / dP < 0$ is satisfied for all P, the sign of derivative $d\langle\Delta\xi\rangle / dP$ is determined by the sign of the expression in braces in (3.5) which, in turn depends on the form of function $f_1(c)$ and on the character of variation of the input concentration $c_f(t)$. On the basis of (3.5) it is possible to conclude that, when the inequality

$$\frac{d^3f_1^2}{dc^3}(c_f(t)) > 0 \tag{3.6}$$

is satisfied for all t, the derivative $d\langle\Delta\xi\rangle / dP$ is positive and the unsteady shift increases as the Péclet number is increased. When the inequality of opposite sign to (3.6) holds, the unsteady shift decreases as the Péclet number is increased.

The derivative in (3.6) may generally change its sign with time. It is then necessary to use formula (3.5) for determining the effect of longitudinal dispersion on the unsteady shift, taking into account the specific form of functions $f_1(c)$ and $c_f(t)$. The nature of the longitudinal dispersion effect on the magnitude of the unsteady shift is, thus, determined by the third derivative of the squared function that specifies the chemical reaction engineering.

Let us consider, as an example, a reaction of order γ, $f_1 = k_1c^\gamma$. The criterion (3.6) enables us to draw the following conclusions.

When $\gamma < 0$, the mean transformation degree under unsteady operation conditions is higher than under steady ones ($\langle\Delta\xi\rangle > 0$), and, as the longitudinal diffusion intensity increases (decreasing Péclet number), the unsteady shift increases.

If $0 < \gamma < 1$, the mean transformation degree is lower under unsteady conditions than under steady ones ($\langle\Delta\xi\rangle < 0$), and as the longitudinal diffusion intensity is increased, the absolute value of the unsteady shift ($|\langle\Delta\xi\rangle|$) increases when $0 < \gamma < 0.5$ and falls when $0.5 < \gamma < 1$.

If $\gamma > 1$, the mean transformation degree is higher under unsteady conditions than under steady operation conditions, and the unsteady shift decreases as the longitudinal diffusion intensity is increased.

This example shows that the interaction of the system nonlinearity with the longitudinal diffusion in a chemical reactor is fairly complex.

Let us assume for definiteness that the reagent concentration at the reactor intake varies in conformity with the law $c_f(t) = 1 + g\sin\omega t$ and $f_1(c) = k_1c^\gamma$. From (3.5) we then have

$$\langle\Delta\xi\rangle = \varepsilon k_1\left[\langle(1+g\sin\omega t)^\gamma\rangle - 1\right] + \varepsilon^2k_1^2\gamma\left[1 - \langle(1+g\sin\omega t)^{2\gamma-1}\rangle\right]\Omega(P) \tag{3.7}$$

The averaged expressions in (3.7) may in some particular cases be represented in terms of known functions /11/. Let $\gamma = n$, where n is an integer, then

$$\langle(1+g\sin\omega t)^n\rangle = (1-g^2)^{n/2}P_n\left(\frac{1}{\sqrt{1-g^2}}\right) = \frac{1}{2^n}\sum_{m=0}^{E(n/2)}\frac{(-1)^m(2n-2m)!}{m!\,(n-m)!\,(n-2m)!}(1-g^2)^m$$

where ($E(x)$ is the integral part of x and P_n is a Jacobi' polynomial.

When $\gamma = 1/(n+1)$, we have

$$\langle(1+g\sin\omega t)^{1/(n+1)}\rangle = \frac{1}{(1-g^2)^{(n+1)/2}}P_n\left(\frac{1}{\sqrt{1-g^2}}\right) = \frac{1}{2^n(1+g)\sqrt[n]{1-g^2}}\sum_{m=0}^{n}\frac{(2n-2m-1)!!\,(2m-1)!!}{(n-m)!\,m!}\left(\frac{1+g}{1-g}\right)^m$$

The obtained formulas enable us to directly determine the unsteady shift of the transformation degree for certain classes of kinetic dependence.

If the perturbations of input concentration are small, i.e. when $c_f(t) = 1 + \delta g_1\sin\omega t$, where $\delta \ll 1$, then from (3.5) we obtain

$$\langle\Delta\xi\rangle = \varepsilon\left[\delta^2g_1^2D_1 + O(\delta^4)\right] + \varepsilon^2\left[\delta^2g_1^2D_2 + O(\delta^4)\right], \qquad D_1 = \frac{1}{4}\frac{d^2f_1}{dc^2}(1), \quad D_2 = -\frac{1}{8}\frac{d^3f_1^2}{dc^3}(1)\,\Omega(P) \tag{3.8}$$

from which for $\varepsilon = \delta$ we have

$$\langle \Delta\xi \rangle = \varepsilon^3 g_1{}^2 D_1 + \varepsilon^4 g_1{}^2 D_2 + O(\varepsilon^5)$$

To illustrate the above conclusions we shall consider a reaction of order γ for which we have

$$D_1 = \frac{k_1}{4} d_1(\gamma), \quad D_2 = \frac{k_1{}^2}{4} d_2(\gamma, P), \quad d_1(\gamma) = \gamma(\gamma - 1), \quad d_2(\gamma, P) = -4\gamma \cdot (\gamma - {}^1/_2)(\gamma - 1)\,\Omega(P)$$

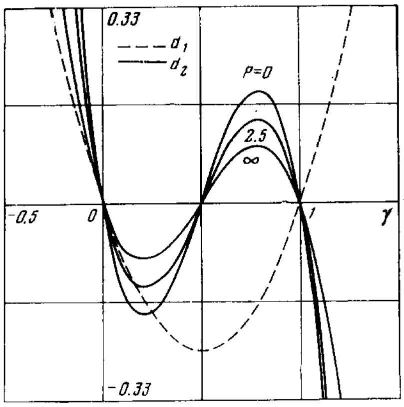

Fig.3

Curves $d_1(\gamma)$ and $d_2(\gamma, P)$ appearing in Fig.3 for several Péclet numbers show the effect of longitudinal diffusion effect on the magnitude of the unsteady shift. It will be seen that in conformity with the conclusions reached above, the unsteady shift may increase, as well as decrease, depending on the reaction order, when the longitudinal diffusion intensity is increased.

This analysis shows the complexity of the longitudinal diffusion effect of a chemical reactor operating under unsteady conditions, and that the nature of that effect is essentially determined by the kinetics and the rate of the chemical reaction.

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