OPERATIONAL STATES OF AN IDEAL-DISPLACEMENT CHEMICAL REACTOR WITH INTEGRAL HEAT RELEASE

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The mathematical representation of heat and mass transfer in continuous chemical reactors is usually based on an idealized one-dimensional model in which the controlling equations are those of heat conduction and diffusion [1, 2]. In some cases this model has to be supplemented with the equation of motion of the mixture of reagents and reaction products in the reactor [3].

Even in the case of such a simple model of processes in reactors, a full investigation of the existence, uniqueness, and stability of operational states involves considerable difficulties which have not yet been overcome. Hence, the usual approach is to simplify the mathematical model of the reactor further by making certain assumptions regarding the transport processes. In [1, 2] the authors considered ideal-displacement and complete-mixing models of reactors. These represent the two extreme cases of a continuous reactor. In one case convective mass and heat transfer greatly exceeds diffusive transfer (ideal displacement) and, in the other, diffusional transfer greatly exceeds convective transfer (complete mixing). In [4–8] the steady states of a continuous adiabatic reactor were investigated on the assumption that the diffusion coefficient and the thermal diffusivity were equal. With this assumption it was shown [8] that in the case of an endothermic reaction there is always a unique steady state. In the case of an exothermic reaction the problem of the steady-state regime always has a solution, which, however, may not be unique. It was shown that there could be several steady states, the number of which must be odd. These simplified models are applicable to a limited range of reactors, but they still provide further information regarding the existence, uniqueness, and stability of the operating regimes of continuous reactors and lead to some qualitative conclusions of a general nature.

Another important aspect of these investigations is that in several cases a real reactor can be represented by a combination of simple models.

Below we propose and analyze a simplified model of a chemical reactor which is applicable to cases in which diffusional mass transfer in the reactor can be neglected in comparison with convective transfer, while heat conduction is so great that the temperature can be regarded as equal throughout the interior of the reactor. Thus, the proposed model can be regarded as a combination of an ideal-displacement model for mass transfer and a complete-mixing model for heat transfer. In this model, as in [3], we take into account the variation of the viscosity of the mixture of reagents and reaction products with temperature.

This variation must be taken into consideration in view of the inverse relationship between the temperature and hydraulic resistance of the reactor. The effect of change in the concentration of reagents in the flow on the stability of the steady state of the reactor could probably be treated in a similar way.

A wide field of application of this model could be, for instance, the description of processes in chemical reactors with a fluidized catalyst. We know that the temperature at all the internal points of a fluidized-bed reactor is practically the same [9] owing to the intensive heat transfer by the catalyst particles, which move rapidly in longitudinal and transverse directions. The transfer of reagents and reaction products in a suspended bed can be represented in the general case by the equation of convective diffusion and often corresponds closely to the ideal-displacement case [10].

For the considered model, which we will call an ideal-displacement model with integral heat production, we determine the conditions of existence, number, and criteria of stability of the steady states. In this case, as distinct from the ideal-displacement model considered in [3], purely oscillatory regimes are possible when the reactor characteristics have particular values.

1. Reactor model. Steady states. The equations of heat and mass transfer in the considered reactor model can be put in the form

$$\rho \frac{\partial \xi}{\partial t} + m \frac{\partial \xi}{\partial x} - \rho f(T)(\xi_m - \xi) = 0 \qquad (1.1)$$

$$\rho\frac{dT}{dt}+\frac{\lambda_1}{l}m(T-T_0)-\frac{h}{c}f\ T)\left(\xi_m-\frac{1}{l}\int\limits_0^l\xi\,dx\right)=0 \qquad (1.2)$$

$$\left(\lambda_1=\frac{\alpha lS}{mcV}+\frac{c_1}{c},\quad T_0=\frac{\alpha lS}{mcV\lambda_1}T_0{}'+\frac{c_1}{c\lambda_1}T_0{}''\right)$$

Here x is the spatial coordinate ($0 \le x \le l$); l is the length of the reactor; t is the time; ξ is the degree of advancement of the reaction; ξ_m is the maximum degree of advancement of the reaction; m is the mass velocity of filtration of the mixture of reagents and reaction products; ρ is the density of the mixture; T is the temperature in the reactor, which depends only on the time; f(T) is the rate of the chemical reaction as a function of temperature, which can be described in many cases by the Arrhenius law; h is the heat of the reaction; c_1 is the heat capacity of the mixture; c is the total heat capacity of the mixture and solid catalyst; α is the coefficient of heat transfer to the side walls of the reactor; V and S are the volume and side surface of the reactor; T_0' is the temperature of the surroundings; T_0'' is the temperature of the entering mixture.

We consider continuous reactors in which diffusional transfer of the reagents can be neglected in comparison with convective transfer. In the reactor there is an irreversible first-order chemical reaction accompanied by the release (or absorption) of heat.

We assume that the heat transfer in the reactor is so rapid that temperature gradients inside the reactor can be neglected. This assumption is responsible for the form of the conservation of heat equation (1.2), which expresses the integral heat balance in the reactor. The second term in Eq. (1.2) takes into account the heat transfer between the reactor and the surroundings and the difference in temperatures of the mixture entering the reactor and the mixture present in the reactor. The third term takes into account the total heat release (absorption) in the reactor. The heat production was treated in a similar way in [11] in an examination of a chemical reaction inside a single catalyst granule with high thermal conductivity.

The proposed reactor model is intended for the representation of heat and mass transfer processes in continuous reactors with a fixed bed or reactors with a fluidized bed of catalyst.

It should be noted that the mechanism of equalization of the temperature in reactors with a fixed bed and reactors with a fluidized bed is different.

In reactors with a fixed bed rapid heat transfer is due to the high thermal conductivity of the solid catalyst. In reactors with a fluidized bed the temperature equalization is due primarily to heat transfer by solid particles moving randomly inside the bed. In almost every case this ensures practically complete equalization of the temperature throughout the reactor [9].

We assume that the filtration flow in the reactor is maintained by a pressure drop P and conforms to the Darcy law. The equation of motion of the mixture can then be written in the form

$$m=\frac{kP}{\nu l} \qquad (1.3)$$

Here $\nu = \nu$(T) is the kinematic viscosity of the mixture and k is the permeability.

We supplement Eqs. (1.1) and (1.2) with a boundary condition in the form

$$\xi(0,t)=0 \qquad (1.4)$$

To determine the steady states of operation of the reactor we first integrate Eq. (1.1) with $\partial/\partial t = 0$ and boundary condition (1.4). We then obtain the steady-state distribution of the degree of advancement of the reaction $\xi°(x)$ corresponding to a steady temperature T° in the reactor

$$\frac{\xi^\circ(x)}{\xi_m}=1-\exp\left(-\frac{\rho f(T^\circ)}{m^\circ}x\right) \qquad (1.5)$$

Substituting distribution (1.5) into Eq. (1.2) with $d/dt = 0$ we obtain an algebraic equation for determination of the steady temperature T°

$$\lambda_1(T^\circ-T_0)=\frac{h}{\rho c}\xi^\circ(l) \qquad (1.6)$$

The problem of the number of steady states for the considered reactor model reduces to an analysis of the number of solutions of Eq. (1.6). The steady values of the temperature correspond to the abscissas of the points of intersection of the curves of heat release (right-hand side of Eq. (1.6)) and heat removal (left-side of (1.6)).

Function $f(T)$ is a function of the Arrhenius type. It is a monotonically increasing function and has a horizontal asymptote and point of inflection. In addition, $f(0) = 0$. Function $\nu(T)$ is monotonically increasing in the case of gas-phase reactions and decreasing in the case of liquid-phase reactions. Proceeding from these general properties of function $f(T)$ and $\nu(T)$ and using formulas (1.3) and (1.5) we can conclude that the heat-release curves have the form of curves a and b in Fig. 1 (curve a is for an exothermic reaction; b is for an endothermic reaction). The heat-removal curves (curves 1–3 in Fig. 1) pass through points T_0, 0) and have at least one intersection with the heat release curves. Hence, steady states of the reactor always exist.

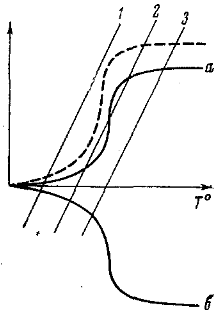

Fig. 1

In the case of an exothermic reaction at different temperatures T_0, there may be one (intersections of curves 1 and 3 with curve a) or several (intersections of curve 2 with curve a) steady states. In the case of an endothermic reaction there is always a unique steady state (intersections of curves 1–3 with curve b). It could also be shown that the presence of one or several steady states in the case of an exothermic reaction could be due to a change in the heat transfer coefficient, geometry of the reactor, flow rate of the reagents, etc. It is very important to note the effect of change in the viscosity of the mixture in the reactor with temperature. In particular, the usual assumption of constant viscosity leads to a shift of the heat-release curve (see dashed curve in Fig. 1) and this may lead to an erroneous estimate of the number of steady states.

2. Stability of steady state. To analyze the stability of the steady state of the reactor we use the small-perturbation method. Putting functions T(t), ξ(x, t), m(t), and P(t) in the form $q = q^\circ + \delta q$, linearizing the system of equations (1.1), (1.2), and using (1.5) and (1.6), we obtain the equations for small perturbations

$$\frac{\partial \delta\xi}{\partial t} + d_{11}\delta\xi + d_{12}\frac{\partial \delta\xi}{\partial x} + d_{13}(x)\,\delta T + d_{14}(x)\,\delta P = 0 \tag{2.1}$$

$$\frac{d\delta T}{dt} + d_{21}\delta T + d_{22}\int_0^l \delta\xi\,dx + d_{23}\delta P = 0 \tag{2.2}$$

$$\delta\xi\,(0,\,t) = 0 \tag{2.3}$$

Here

$$d_{11} = f(T^\circ),\quad d_{13}(x) = -(\xi_m - \xi^\circ)\,f(T^\circ)\frac{d}{dT^\circ}\ln[\nu(T^\circ)\,f(T^\circ)]$$

$$d_{12} = \frac{m^\circ}{\rho},\ d_{14}(x) = (\xi_m - \xi^\circ)\frac{f(T^\circ)}{P^\circ},\quad d_{22} = \frac{hf(T^\circ)}{\rho cl}$$

$$d_{21} = \lambda_1\frac{m^\circ}{\rho l}\{1 - (T^\circ - T_0)\frac{d}{dT_0}\ln[\nu(T^\circ)\,f(T^\circ)]\}$$

$$d_{23} = \lambda_1(T^\circ - T_0)\frac{m^\circ}{\rho l P^\circ}$$

The case of simultaneous consideration of the thermomechanical effects associated with the variation of viscosity with temperature and the nonadiabaticity of the reactor is excluded from the discussion here and henceforth. This shortens the calculations, since then λ_1 = const and T_0 = const. We note that the general case does not give rise to difficulties of a fundamental nature.

We assume that the perturbations of the steady state are due to a change in the pressure drop, the degree of advancement of the reaction, and the temperature:

$$\delta P = \begin{cases} 0 & (t < 0) \\ P_0 \exp(-\sigma_0 t) & (t > 0,\ \operatorname{Re}\sigma_0 > 0) \end{cases} \tag{2.4}$$

$$\delta\xi(x, 0) = \eta_1(x), \quad \delta T(0) = \eta_2$$

Here the function $\eta_1(x)$ and the constant η_2 are arbitrary.

We find the solution of problem (2.1)–(2.4) by the Laplace transformation method, introducing for $\delta P(t)$, $\delta\xi(x, t)$, and $\delta T(t)$ the images from the formula

$$\delta q^*(\sigma) = \int_0^\infty \exp(-\sigma t)\,\delta q\,dt$$

From (2.1)–(2.4) after the Laplace transformation we obtain

$$(\sigma + d_{11})\,\delta\xi^* + d_{12}\frac{d\delta\xi^*}{dx} + d_{13}(x)\,\delta T^* + d_{14}(x)\frac{P_0}{\sigma + \sigma_0} - \eta_1(x) = 0 \tag{2.5}$$

$$(\sigma + d_{21})\,\delta T^* + d_{22}\int_0^l \delta\xi^* dx + d_{23}\frac{P_0}{\sigma + \sigma_0} - \eta_2 = 0 \tag{2.6}$$

$$\delta\xi^*(0, \sigma) = 0 \tag{2.7}$$

For the solution of problem (2.5)–(2.7) we first integrate Eq. (2.5) with condition (2.7), bearing in mind that δT^* is independent of x. We obtain

$$\delta\xi^* = J(\eta_1(x)) - \frac{P_0}{\sigma + \sigma_0}J(d_{14}(x)) - \delta T^* J(d_{13}(x))$$

$$J(q(x)) = \frac{1}{d_{12}}\exp\left(-\frac{\sigma + d_{11}}{d_{12}}\right)\int_0^x \exp\left(\frac{\sigma + d_{11}}{d_{12}}x\right) q(x)\,dx$$

Substituting into this result the expression for δT^* from (2.6) we obtain an equation for $\delta\xi^*$ in the form

$$\delta\xi^* = J(\eta_1) + \frac{d_{13}}{\sigma(\sigma + d_{21})}\left[1 - \exp\left(-\frac{\sigma x}{d_{12}}\right)\right]\left[d_{22}\int_0^l \delta\xi^* dx - \eta_2 + \left(d_{23} - \frac{d_{14}d_{21} + d_{14}\sigma}{d_{13}}\right)\frac{P_0}{\sigma + \sigma_0}\right] \tag{2.8}$$

Integrating both sides of this equation with respect to x from 0 to l, we find the value of the integral

$$\int_0^l \delta\xi^*\,dx$$

Then, using (2.6) and (2.8) we obtain

$$\delta T^* = \lambda_2\left(\frac{d}{dT^\circ}\ln \nu f\right)^{-1}\left[\frac{P_0}{fP^\circ}\frac{1}{s + s_0} - \frac{1}{\xi_m}I(s)\frac{s + \lambda_2}{(s + s_0)\,\psi(s)}\right]$$

$$\delta\xi^* = J(\eta_1) - \lambda_2^2 J(s)\exp\left(-\frac{\lambda_2 x}{l}\right)\left[1 - \exp\left(-\frac{sx}{l}\right)\right]\frac{s + \lambda_2}{s(s + s_0)\,\psi(s)} \tag{2.9}$$

Here

$$I(s) = (s + s_0)\,\lambda_3\frac{1}{l}\int_0^l J(\eta_1(x))\,dx -$$

$$-(s + s_0)\,\eta_2\frac{\xi_m}{f(T^0)}\frac{d}{dT^\circ}\ln \nu f + (s + \lambda_1)\frac{\xi_m P_0}{fP^\circ}, \quad s = \frac{\sigma\rho l}{m^\circ}$$

$$\psi(s) = s^2 + \omega_3 s - \omega_1 + \omega_2\frac{1 - e^{-s}}{s} \tag{2.10}$$

$$\omega_1 = -\lambda_1\lambda_2, \quad \omega_2 = -\lambda_2^2\lambda_3 e^{-\lambda_2}, \quad \omega_3 = \lambda_1 + \lambda_2 - \lambda_3(1 - e^{-\lambda_2}) \tag{2.11}$$

$$\lambda_1 = \frac{l\alpha S}{Vm^\circ c} + \frac{c_1}{c}, \quad \lambda_2 = \frac{\rho f(T^\circ)\,l}{m^\circ}, \quad \lambda_3 = \frac{h\xi_m}{\rho c}\frac{d}{dT^\circ}\ln \nu f \tag{2.12}$$

Conversion from the Laplace images (2.9) to the originals is easy, since all the singularities of functions (2.9) are poles. If all the poles of functions (2.9) lie to the left of the imaginary axis in the complex plane, the perturbations of the steady state will decay with time and the regime will be stable. Otherwise the regime will be unstable. The poles of functions (2.9) are situated at the point $s = -s_0$ and the zeros of the function $\Psi(s)$ given by formula (2.10) (point $s = 0$ is not a pole).

Thus, the analysis of the stability of the steady state reduces to an investigation of the position of the zeros of function $\Psi(s)$ on the complex plane. To solve the problem of the roots of equation $\Psi(s) = 0$ which have a positive real part we use the argument principle, according to which the number of zeros of the function $\Psi(s)$ within the region bounded by the closed contour Γ on which $\Psi(s) \neq 0$ is equal to the increment of the argument of function $\Psi(s)$ on completion of the contour Γ, divided by 2π.

As the contour Γ we take the contour $\Gamma_1 + \Gamma_2$, composed of the right semicircle of radius R with center at the origin of coordinates (Γ_1) and the segment of the ordinate axis between the points (0, R) and (0, −R). If the zeros of function $\Psi(s)$ are on the imaginary axis the contour Γ_2 will be composed of segments of the ordinate axis and the right semicircles of small radius r with centers situated at the purely imaginary zeros of function $\Psi(s)$. We then proceed to the limit where $R \to \infty$, $r \to 0$.

The analysis shows that the increment of the argument of function $\Psi(s)$ on Γ_1 when $R \to \infty$ is independent of ω and is equal to 2π.

To calculate the increment of the argument of $\Psi(s)$ on the contour Γ_2 we first determine the values of ω at which function $\Psi(s)$ has purely imaginary zeros. It follows from (2.10) that function $\Psi(s)$ has purely imaginary zeros when the values of parameters ω_1, ω_2, and ω_3 lie on a surface, ω_1, ω_2, ω_3 given by the equations

$$\omega_1 = -y^2 + \omega_3 \frac{y \sin y}{1 - \cos y}, \quad \omega_2 = \omega_3 \frac{y^2}{1 - \cos y}$$

$$(0 \leqslant y < \infty) \tag{2.13}$$

The surface (2.13) consists of an infinite number of sheets corresponding to the following regions of y:

$$2\pi n \leqslant y < 2\pi (n+1) \quad (n = 0, 1, 2, \ldots)$$

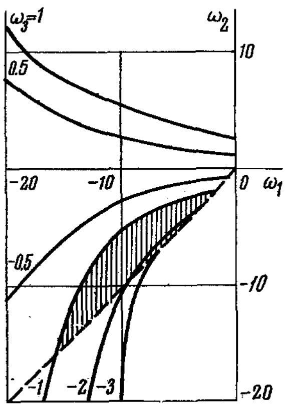

Fig. 2

As will be seen from what follows, only the sheet of the surface closest to the plane $\omega_2 = 0$ and corresponding to the interval $0 \leq y < 2\pi$ is of interest. Henceforth for brevity we will call it the "first sheet." When $\omega_3 > 0$ it lies in the region $\omega_2 > 0$, and when $\omega_3 < 0$ it lies in the region $\omega_2 < 0$. The curves of intersection of the first sheet with the planes ω_3 = const are shown in Fig. 2 for the region $\omega_1 < 0$ (the region $\omega_1 > 0$, as formulas (2.11) and (2.12) show, has no physical sense).

It can be shown by a method similar to that described in [3] that in the region $\omega_1 > \omega_2$ the increment of the argument of $\Psi(s)$ on the contour Γ_2 when $R \to \infty$ is 2π. Hence, in the region $\omega_1 > \omega_2$ function $\Psi(s)$ has two roots in the right half-plane and the corresponding steady state is unstable. It can also be shown that in the region enclosed between the first sheet of surface (2.13) and the plane $\omega_1 = \omega_2$ the increment $\Delta_2 \arg\Psi(s) = -2\pi$ and the steady state is stable. In the rest of the space ω_1, ω_2, ω_3 the steady state is again unstable.

Thus, the region of stability is enclosed between the first sheet of the surface (2.13) and the plane $\omega_2 = \omega_1$. The sections of the region of stability by the planes $\omega_3 = \text{const}$ are unbounded when $\omega_3 \geq 0$ and bounded when $\omega_3 < 0$ (see Fig. 2). To illustrate this, the section of the stability region by the plane $\omega_3 = -1$ is hatched in Fig. 2. These sections decrease with reduction of ω_3, and when $\omega_3 = -3$ the section contracts to a point with coordinates $(-6, -6, -3)$.

We can also show that on the border of the stability region the state is neutrally stable and on the part of the boundary which is formed by the first sheet of surface (2.13) the perturbations of the steady state have the nature of neutral oscillations with nonzero frequency. It should be noted that not all the points $(\omega_1, \omega_2, \omega_3)$ have physical sense, i.e., correspond to values of λ_1, λ_2, λ_3. Hence, we consider the stability conditions for the parameters λ. Using formulas (2.11) we can show that the steady state is unstable in the region

$$\lambda_3 > \inf\,[\lambda_3^{(1)}(\lambda_2, \lambda_1), \lambda_3^{(2)}(\lambda_2, \lambda_1)] \tag{2.14}$$

and stable in the region

$$\lambda_3 < \inf\,[\lambda_3^{(1)}(\lambda_2, \lambda_1), \lambda_3^{(3)}(\lambda_2, \lambda_1)] \tag{2.15}$$

Here

$$\lambda_3^{(1)} = \frac{\lambda_1}{\lambda_2}\exp\lambda_2, \quad \lambda_3^{(2)} = \frac{\lambda_1 + \lambda_2 + 3}{1 - \exp(-\lambda_2)}, \quad \lambda_3^{(3)} = \frac{\lambda_1 + \lambda_2}{1 - \exp(-\lambda_2)}$$

The positions of the stability and instability regions in the plane λ_2, λ_3 for different values of λ_1 are shown in Fig. 3. Here the instability regions lie above the solid curves (condition (2.14)), and the stability regions lie below the dashed curves (condition (2.15)). It can be shown by means of formulas (1.6) and (2.12) that the instability condition $\lambda_3 > \lambda_3$ (1) resulting from condition (2.14) corresponds to the case in which the angle of inclination of the heat removal curve to the horizontal axis at the point of intersection of this curve with the heat-release curve (see Fig. 1) is greater than the angle of inclination of the heat-release curve at this point. It follows from this that if there are three steady states the middle one will always be unstable. The same conclusion can be reached from purely physical considerations; it corresponds to the similar conclusion for the case of a complete-mixing reactor.

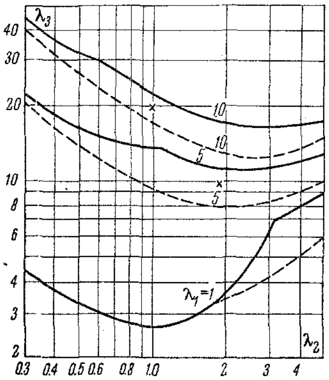

Fig. 3

Figure 3 shows that between the instability and stability regions there is a region which satisfies neither of conditions (2.14) and (2.15). The question of the stability of the steady state for values of λ belonging to this region can be solved most easily by calculating the values of ω from formulas (2.11) and then using the stability conditions for the parameters ω.

We note that purely oscillatory perturbations of the steady state of the reactor correspond to certain values of λ. As an example we cite the values $\lambda_1 = 1$, $\lambda_2 = 9.87$, $\lambda_3 = 10.9$, $\{5, 1.97, 9.35\}$, and $\{10, 0.987, 19.8\}$ denoted by crosses in Fig. 3.

Thus, we have shown that the steady states of operation of a chemical reactor which is mathematically represented by Eqs. (1.1) and (1.2) and of the reactor model examined in [3] include stable, unstable, and neutral regimes. Some of the neutral regimes in the reactor model with integral heat release are oscillatory. It seems likely that an examination of a more general reactor model in which longitudinal mixing, reactions with complex kinetics, and so on, are considered will reveal steady states of all the types described above.

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