OPERATING CONDITIONS OF AN IDEAL-DISPLACEMENT REACTOR WITH RECYCLE

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The effect of recirculation on the operating conditions of a chemical reactor, a model of which was proposed earlier in [1], is discussed. The feasibility and efficiency of carrying out many chemical processes in systems with recirculation was demonstrated in [2]. An investigation has also been made of the stability of operating conditions for one simple model of a reactor with a recycle [3]. In [1], a mathematical model was proposed for an ideal-displacement chemical reactor, taking integral account of heat evolution, in which diffusional transfer is negligibly small in comparison with convective transfer, and the thermal conductivity is so great that the temperature inside the reactor can be assumed to be identical. An investigation was made of the question of steady-state conditions and their stability. Below, this question is discussed for the case where, in such a reactor, part of the stream passing through the reactor is again fed to its inlet. As in [1, 4], account is taken of the dependence of the viscosity of the mixture of reagents and the reaction products on the temperature.

1. Equations. Boundary Condition. Steady-State Conditions

The equations of mass and heat transfer in an adiabatic reactor taking integral account of heat evolution in the presence of a recycle have the form

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

$$\rho \frac{dT}{dt} + \frac{c_1}{cl} m(1-r)(T-T_0) - \frac{h}{c} f(T)\left(\xi_m - \frac{1}{l}\int_0^l \xi dx\right) = 0 \tag{1.2}$$

Here x, t are the coordinate and the time; l is the length of the reactor ($0 \leq x \leq l$); ξ is the degree to which the reaction has taken place; ξ_m is the maximum value of the degree to which the reaction has taken place; m is the mass velocity of the mixture in the reactor; ρ is the density of the mixture; T is the temperature; $f(T)$ is the dependence of the rate of the chemical reaction on the temperature, a function of the Arrhenius type; h is the head of the reactions; c_1 is the heat capacity of the mixture; c is the total heat capacity of the mixture and the catalyst; T_0 is the temperature of the starting mixture; r is the recirculation coefficient.

Assuming that the filtrational motion of the mixture through the bed of catalyst obeys the Darcy law, the mass velocity of the flow can be expressed in terms of the pressure drop at the outlet and inlet of the reactor P,

$$m = kP / \nu l \tag{1.3}$$

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

We supplement Eq. (1.1) by a boundary condition taking account of the presence of a

$$\xi(0, t) = r\xi(l, t) + (1-r)\xi_0 \tag{1.4}$$

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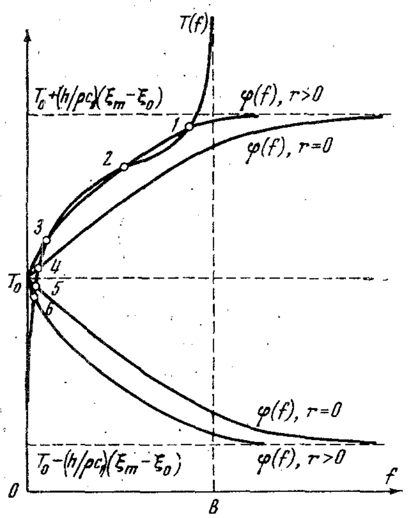

Fig. 1

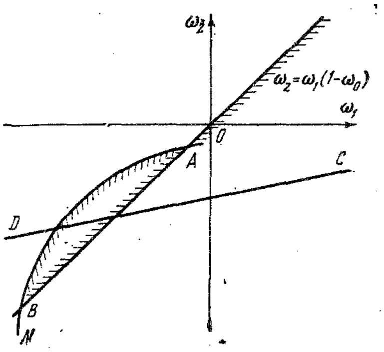

Fig. 2

The analysis of steady-state conditions reduces to determination of the function $\xi^\circ(x)$ and the value of T° from (1.2) with $\partial/\partial t = 0$; for $\xi^\circ(x)$ we can obtain

$$\xi^\circ(x) = \xi_m - \left[(\xi_m - \xi_0)(1-r)\exp\left(-\frac{\rho f(T^\circ)}{m^\circ}x\right)\right]\left[1 - r\exp\left(-\frac{\rho f(T^\circ)\,l}{m^\circ}\right)\right]^{-1} \tag{1.5}$$

The transcendental equation for T° has the form

$$T^\circ = T_0 + \frac{h}{\rho c_1}\left[(\xi_m - \xi_0)\left(1 - \exp\left(-\frac{\rho f(T^\circ)}{m^\circ}\,l\right)\right)\right]\left[1 - r\exp\left(-\frac{\rho l f(T^\circ)}{m^\circ}\right)\right]^{-1} \tag{1.6}$$

The number of sets of steady-state operating conditions with a recycle is equal to the number of solutions of Eq. (1.6).

Analysis of Eq. (1.6) is most conveniently carried out graphically, assuming the left and right parts to be functions of f. Figure 1 shows the course of the dependences $T^\circ = T^\circ(f)$,

$$f(T^\circ) = B\exp(-E/RT^\circ) \tag{1.7}$$

The intersections of the curves determine the steady-state conditions. With an increase in the recirculation coefficient, the curves corresponding to the right-hand part will lie above (exothermic reaction) or below (endothermic reaction), as before passing through the point $T = T_0$, $f = 0$, and retaining the previous asymptotes,

$$\varphi = T_0 + \frac{h}{\rho c_1}(\xi_m - \xi_0)$$
$$\varphi = T_0 - \frac{h}{\rho c_1}(\xi_m - \xi_0)$$

It can be seen that a rise in the value of the parameter r in the case of an exothermic reaction can lead to a change in the number of sets of conditions (either to an increase or a decrease), while, at the same time, with an endothermic reaction, only one set of conditions is possible.

It can be seen also that both stable steady-state conditions (1) and unstable conditions (2) are possible.

2. Stability of Steady-State Conditions

We introduce the dimensionless variables

$$x' = x/l,\quad T' = T/T_0,\quad v' = v/v^\circ$$
$$m' = m/m_0,\quad P = P/P^\circ,\quad t' = t/(l\rho/m^\circ)$$
$$S = \frac{\rho f^\circ l}{m^\circ},\quad \Phi(T') = \frac{f(T)}{f^\circ},\quad \sigma = \frac{h}{c\rho}\,\frac{(\xi_m - \xi_0)}{T^\circ}$$
$$a = \frac{\xi_m - \xi}{\xi_m - \xi_0},\quad \gamma = T_0/T^\circ$$

Then relationships (1.1)-(1.6) (in what follows, we omit the primes on the newly introduced quantities) assume the form

$$\frac{\partial a}{\partial t} + m\frac{\partial a}{\partial x} + Sa\Phi(T) = 0 \tag{2.1}$$

$$\frac{\partial T}{\partial t} + \lambda m(T - \gamma) - \sigma S\Phi(T)\int_0^1 a\,dx = 0 \tag{2.2}$$

$$M = P / \nu \tag{2.3}$$

$$a(0, t) = ra(1, t) + 1 - r \tag{2.4}$$

$$a^\circ(x) = \frac{(1-r)}{(1-re^{-S})}e^{-Sx} \tag{2.5}$$

$$\lambda(1-\gamma) = \frac{\sigma(1-r)}{(1-re^{-S})}(1-e^{-S}) \tag{2.6}$$

In the analysis of the stability we use the method of small perturbations. We represent T(t), a(x, t), m(t), P(t) in the form

$$\begin{gathered} K = K^\circ + \delta K \\ T = 1 + \delta T, \quad a = a^\circ + \delta a, \quad m = 1 + \delta m \\ P = 1 + \delta p \end{gathered} \tag{2.7}$$

After linearization, in place of (2.1)-(2.4) we obtain

$$\frac{\partial(\delta a)}{\partial t} + \frac{\partial(\delta a)}{\partial x} + S\delta a + K_1e^{-Sx}\delta T - K_1e^{-Sx}\delta p = 0 \tag{2.8}$$

$$\frac{d}{dt}(\delta T) + K_3\delta T - K_4\int_0^1 \delta a\,dx + K_5\delta p = 0 \tag{2.9}$$

$$\begin{gathered} \delta a(0, t) = r\delta a(1, t) \\ \delta m = \left(\frac{\partial m}{\partial p}\right)^\circ \delta p + \left(\frac{\partial m}{\partial T}\right)^\circ \delta T = \delta p - \left(\frac{\partial \nu}{\partial T}\right)^\circ \delta T \\ K_1 = \frac{S(1-r)}{(1-re^{-S})}\left[\left(\frac{\partial\Phi}{\partial T}\right)^\circ + \left(\frac{\partial\nu}{\partial T}\right)^\circ\right] \\ K_2 = \frac{S(1-r)}{(1-re^{-S})}, \quad K_3 = \lambda - \frac{\sigma(1-r)}{(1-re^{-S})}\left[\left(\frac{\partial\Phi}{\partial T}\right)^\circ + \left(\frac{\partial\nu}{\partial T}\right)^\circ\right] \\ K_4 = \sigma S, \quad K_5 = \frac{\sigma(1-r)}{(1-re^{-S})}(1-e^{-S}), \quad \lambda = \frac{l_1}{l}(1-r) \end{gathered} \tag{2.10}$$

assuming λ = const, γ = const. We assume that perturbations of the steady-state conditions are brought about by a change in the pressure drop, the degree to which the reaction has taken place, and the temperature.

$$\begin{gathered} \delta p = \begin{cases} 0, & t < 0 \\ \exp(-\sigma_0 t)(t > 0), & \operatorname{Re}\sigma_0 > 0 \end{cases} \\ \delta a(x, 0) = \eta_1(x), \quad \delta T(0) = \eta_2 \end{gathered} \tag{2.11}$$

Here the values of η_1(x) and η_2 are arbitrary. We find the solution of the problem (2.8)-(2.10) by the method of Laplace transformation; for δp(t), δa(x, t), and δT(t) we introduce transforms using the formula

$$\delta K^*(z, x) = \int_0^\infty \exp(-zt)\,\delta K\,dt$$

After application of a Laplace transform, we obtain

$$(S + z)\delta a^* + \frac{d}{dx}(\delta a^*) + K_1e^{-Sx}\delta T^* - \frac{K_2e^{-Sx}}{\sigma_0 + z} - \eta(x) = 0 \tag{2.12}$$

$$\delta T^*(z + K_3) - K_4\int_0^1 \delta a^* dx + \frac{K_5}{\sigma_0 + z} - \eta_2 = 0 \tag{2.13}$$

$$\delta a^*(0, z) = r\delta a^*(1, z) \tag{2.14}$$

To solve (2.12)-(2.14), we first integrate Eq. (2.12),

$$\delta a^* = ce^{-(S+z)x} + \frac{K_2e^{-Sx}}{(\sigma_0 + z)z} - \frac{K_1}{z}\delta T^*e^{-Sx} + J(x)$$

$$c = c(z), \quad J(x) = e^{-(S+z)x} \int_0^x e^{(S+z)y} \eta_1(y)\, dy$$

where c is found from Eq. (2.14),

$$c = \frac{K_z}{(\sigma_0 + z) z} \frac{(re^{-S} - 1)}{(1 - re^{-(S+z)})} + \frac{K_1 (1 - re^{-S})}{z (1 - re^{-(S+z)})} \delta T^* + \frac{J(1)}{[1 - re^{-(S+z)}]} \tag{2.15}$$

Calculating $\int_0^1 \delta a^* dx$ and substituting into (2.13), we obtain

$$\delta T^* = \left[\eta_2 + K_4 (N_1 + N_2) - \frac{K_5}{\sigma_0 + z}\right] \psi^{-1} \tag{2.16}$$

Here

$$N_1 = \frac{K_2}{z(\sigma_0 + z)} \left[\frac{(1 - e^{-S})}{S} + \frac{(re^{-S} - 1)}{(1 - re^{-(S+z)})} \frac{(1 - e^{-(S+z)})}{(z + S)}\right]$$

$$N_2 = \int_0^1 J(x)\, dx + \frac{J(1)\,[1 - e^{-(S+z)}]}{[1 - re^{-(S+z)}]\,(S + z)}$$

$$\psi = \frac{f_1}{z(z + S)(e^z - re^{-S})}$$

$$f_1 = e^z [z^3 + \omega_3 z^2 - \omega_1 z + \omega_2] - \omega_0 [z^3 + \omega_3 z^2 - \omega_1] - \omega_2 \tag{2.17}$$

$$\omega_0 = re^{-S}, \quad \omega_1 = -S\lambda$$

$$\omega_2 = -\sigma S^2 \frac{(1 - r)}{(1 - e^{-S} r)} \left[\left(\frac{\partial \Phi}{\partial T}\right)^\circ + \left(\frac{\partial \nu}{\partial T}\right)^\circ\right] \tag{2.18}$$

$$\omega_3 = S + \lambda - \frac{\sigma (1 - r)}{(1 - e^{-S} r)} \left[\left(\frac{\partial \Phi}{\partial T}\right)^\circ + \left(\frac{\partial \nu}{\partial T}\right)^\circ\right]$$

Here the degree sign denotes quantities related to steady-state conditions. A transition from the Laplace transform to the inverse transform raises no difficulty, since all the singularities of the function are poles; the point z = 0 is not a pole, therefore, the numerator also has this value as a single root. The quantities $J(x)$, $\int_0^1 J(x)\, dx$ have poles only in the plane z with the real part Re z = —S.

This is easily demonstrated. We represent $\eta_1(x)$ in the form of a Fourier series; then

$$\eta_1(x) = \sum_{K=0}^{\infty} [a_K \sin(K\pi x) + b_K \cos(K\pi x)]$$

$$J(x) = e^{-(S+z)} \sum_{k=0}^{\infty} \frac{e^{(S+z)x}}{(S + z)^2 + (K\cdot\pi)^2} \{[(z + S)\sin(K\pi x) - K\pi\cos(K\pi x)] - [(z + S)\cos(K\pi x) + K\pi \sin(K\pi x)]\}$$

consequently, $z_K = -S \pm iK\pi$.

Therefore, the source of the instability [i.e., of the poles (2.16), lying to the right of the straight line Re z = 0] can only be the function f_1. In investigation of the position of the roots of this function, we shall use the idea of the method of a D-partition, developed by Neimark [5, 6]. Since ω_i depend on more than four parameters, we can consider the case where all ω_i (except, perhaps, for one or two) are fixed, while the remaining ones can vary.

Let ω_0 and ω_3 be fixed; we consider the plane $\omega_1\omega_2$ in the four-dimensional space (ω_0, ω_1, ω_2, ω_3). Let us find the curve for which (2.17) has a purely imaginary root z = iy. It consists of a curve in the parametric statement

$$N: \begin{cases} \omega_1 = -y^2 + \dfrac{\omega_3 y \sin y\,(1 - \omega_0)}{(1 - \omega_0 y)(1 + \omega_0)} \\ \omega_2 = \omega_3 \dfrac{(1 - 2\omega_0 \cos y + \omega_0^2)}{(1 - \cos y)(1 + \omega_0)} y^2 \end{cases} \tag{2.19}$$

as well as of the straight line

$$\left.\begin{aligned}\omega_1 &= 2\frac{\omega_3(1-\omega_0)}{(1+\omega_0)}\\ \omega_2 &= 2\frac{\omega_3(1-\omega_0)^2}{(1+\omega_0)}\end{aligned}\right\}\quad \omega_2 = \varphi_1(1-\omega_0) \tag{2.20}$$

which is obtained for the case y = 0, since, under these circumstances, the equations

$$\operatorname{Im} f_1(iy) = 0, \quad \operatorname{Re} f_1(iy) = 0$$

coincide.

With a change in ω_i, the root can go over from the region where Re z > 0 to the region Re z < 0, intersecting the curve N(Re z = 0). We hatch the curve of N with a positive rotation of y from $-\infty$ to ∞ from the right, if the root goes over from the right-hand half-plane z to the left-hand half-plane, and from the left, in the contrary plane. The region of stability must be sought in the region [4]

$$1 - |\omega_0| \geqslant 0 \tag{2.21}$$

i.e.,

$$0 \leqslant \omega_0 \leqslant 1$$

The region of stability is illustrated in Fig. 2. Depending on the values of ω_0 and ω_3, the region of stability varies from the region lying (with a fixed value of ω_0) between the axis $\omega_2 = 0$; $\omega_1 < 0$ and the straight line $\omega_2 = \omega_1(1 - \omega_0)$ with the value $\omega_3 = 0$, to the point

$$\left(2\omega_3^*\frac{(1-\omega_0)}{(1+\omega_0)},\ 2\omega_3^*\frac{(1-\omega_0)^2}{(1+\omega_0)}\right) \tag{2.22}$$

with

$$\omega_3^* = -\frac{3(1-\omega_0)}{\sigma\omega_0 + (1+\omega_0)^2}$$

We return now to the parameters of (2.18). From (2.21) it follows that the recycle parameter can vary from 0 to 1. It follows from (2.18) that, with ω_3 = const,

$$\omega_2 = \omega_1 S + S^2(\omega_3 - S) \tag{2.23}$$

Following the values of S, we can determine the intervals in which the operating conditions of the reactor are stable; the limiting value S* is found from (2.23) taking account of (2.22). Thus, with $\omega_0 = 0$, i.e., r = 0,

$$S^* \cong 0.7 \tag{2.24}$$

It follows from (2.24) that there is stability if $S \in [S_A, S_B]$, where S_A and S_B are, respectively, the values of the parameter S with the intersection between the straight line DC, determined by (2.23), and the straight line $\omega_2 = \omega_1(1 - \omega_0)$ at points A and B (see Fig. 2).

It can be shown further that, at the boundary of the region of stability, the conditions are stable in a neutral manner; at the part of the boundary which is formed by the surface N, the perturbation of the steady-state conditions has the character of neutral fluctuations with a frequency differing from zero.

Clarification of the region of stability in the physical variables S, r, λ, σ, ... reduces to a transition to the parameters ω_i and to an investigation of the position of the corresponding point with respect to the stability limits found.

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