It follows from the experimental results that the acoustic method of phase stabilization of a light beam makes it possible to reduce (prevent) significant phase distortions ($\gg \pi$) over times of the order of tens of milliseconds by acting on the nonuniform medium. The region and time of action are determined by the frequency and intensity of the acoustic pulse.

NOTATION

f, sound frequency; ρ_0, density of the medium; c_0, sound velocity; α, sound absorption coefficient; b, absorption constant; A, coefficient of proportionality; S, size of the region of stabilization; T_k, wavefront restoration time; Re_a, acoustic Reynolds number; Δv, amplitude of the particle velocity in the ultrasonic wave; I_0, intensity of the light; n, optical refractive index,; and, ε, nonlinear parameter of the medium.

LITERATURE CITED

1. D. K. Smith, TIIER, 65, No. 12, 59-64 (1977).
2. M. A. Vorontsov and V. I. Shmal'gauzen, Principles of Adaptive Optics [in Russian], Moscow (1985).
3. V. I. Zagorel'skii, D. O. Lapotko, O. G. Martynenko, and G. M. Pukhlov, Inzh.-Fiz. Zh., 55, No. 5, 751-754 (1988).
4. O. V. Rudenko and S. I. Soluyan, Theoretical Foundations of Nonlinear Acoustics [in Russian], Moscow (1975).
5. I. G. Mikhailov, V. A. Solov'ev, and Yu. P. Syrnikov, Principles of Molecular Optics [in Russian], Moscow (1964).

MULTIPLICITY OF HYDRODYNAMIC STATES OF THE FLOW OF A REACTING GAS THROUGH A LAYER OF CATALYST

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It is shown numerically for the example of a two-temperature quasistationary model of the processes occurring in a layer of catalyst that in a reactor operating with a fixed pressure differential a set of stationary states can in principle exist.

The pressure drop in a layer of catalyst through which a reacting gas flows is a quite important technological characteristic, determining the intensity of transport processes and the energy required to produce the layer. For most cases of practical interest there exists a single-valued relationship between the pressure drop and the flow rate; this relationship is most often expressed by the formula of Ergun [1].

A chemical reaction accompanied by intense heat release in the layer of catalyst can destroy the single-valued relationship between ΔP and G. This fact has already been investigated in [2, 3], where it was established that several stationary states exist for a fixed pressure drop over the layer of catalyst. In these works the single-temperature model of the ideal flow was employed and in the analysis of the model, in our opinion, quite strong assumptions that could affect the final quantitative results were made. Thus in the analysis of multiplicity in [2] the equation of state of the gas mixture was not taken into account, and in [3] the quadratic term in Ergun's equation [1] as well as the effect of heating of the layer of catalyst on the pressure drop were neglected.

In this work we analyze the multiplicity of hydrodynamic states based on a two-temperature model, usually employed to analyze the processes occurring in the layer, without making the assumptions described above.

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The mathematical model of the processes in the layer of catalyst consists of the equations of material balance and heat balance for the flow, the momentum equation and the equation of state, as well as the equation of heat balance for a solid catalyst:

$$\frac{d}{dx}(\rho_j u) = W_j \quad (j = 1, 2, \dots N), \tag{1}$$

$$G\frac{du}{dx} = -\frac{dP}{dx} - F_f, \tag{2}$$

$$GC_v\frac{dT}{dx} = \alpha S(\theta - T) - P\frac{du}{dx} + F_f u, \tag{3}$$

$$(1-\varepsilon)\rho_c c_c\frac{\partial\theta}{\partial t} = \lambda_{dc}\frac{\partial^2\theta}{\partial x^2} - \alpha S(\theta - T) + \sum_{i=1}^{m} R_i H_i, \tag{4}$$

$$P = \rho R_{mix} T, \quad \rho = \sum_{i=1}^{N} \rho_j, \quad G = \rho u. \tag{5}$$

The boundary and initial conditions are:

$$\text{at } x = 0: \quad GC_v(T - T_{in}) = \lambda_{dc}\frac{\partial\theta}{\partial x}, \quad \rho_j = \rho_j^0 \ (j = 1, \dots, N), \tag{6}$$

$$u = u^0 = G/\rho^0,$$

$$\text{at } x = L: \frac{\partial\theta}{\partial x} = 0; \tag{7}$$

$$\text{at } t = 0: \theta(0, x) = \theta_0(x). \tag{8}$$

Here R_i is the rate of the i-th chemical reaction, which is determined by the reaction constant k_i, the mass transfer coefficient β_i between the i-th component of the gas mixture and the surface of the catalyst, as well as the corresponding concentration y_i. Thus for a first-order reaction we can write

$$R_i = k_i\beta_i S y_i \rho/(k_i + \beta_i).$$

The coefficients α_i and β_i were calculated with the help of the following dependences:

$$\alpha = \frac{Z(Gd_3)^n \mathrm{Pr}^{0,33}}{d_3\mu^n}\lambda, \quad \beta_i = \frac{Z(Gd_3)^n \mathrm{Sc}^{0,33}}{d_3\mu^n} D_i,$$

where Pr and Sc are the dimensionless Prandtl and Shmidt numbers, respectively. The constants Z and n were determined from the results of [4]: Z = 0.395 and n = 0.64 in the region $Gd_3/\mu = 30 - 8\cdot10^4$; Z = 0.725 and n = 0.47 in the region $Gd_3/\mu = 2 - 30$; and, Z = 0.515 and n = 0.85 in the region $Gd_3/\mu = 0.01 - 2$.

The viscosity and thermal conductivity of both separate components and the mixture as well as the diffusion coefficients were assumed to depend on the temperature T, and the formulas for calculating them were taken from the handbook [5]. Thus, for example,

$$\mu_j(T) = \mu_{j0}\frac{273 + C_1}{T + C_1}\left(\frac{T}{273}\right)^{1,5},$$

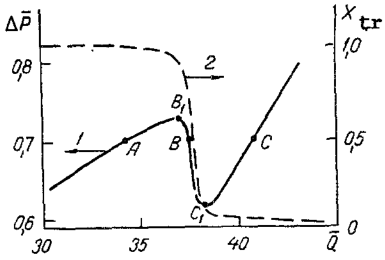

Fig. 1

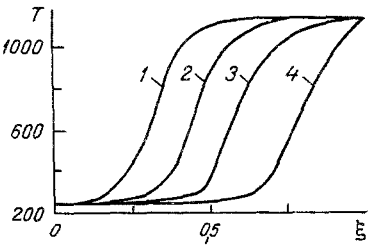

Fig. 2

Fig. 1. The pressure drop $\Delta\bar{P}$ (1) and the degree of transformation X_{tr} (2) as a function of the quantity of the mixture $\bar{Q}$ fed into the reaction: $\Delta\bar{P}=\Delta P/P_0$, $Q=Q/Q_0$; P_0 and Q_0 are, respectively, the reference pressure and the standard flow rate.

Fig. 2. The behavior of the temperature profiles as a function of the flow rate $\bar{Q}$ of the mixture fed into the reactor: 1) $\bar{Q}$ = 20; 2) 25; 3) 30; 4) 37.5. T, °C.

where $\mu_j(T)$ is the viscosity of the j-th component of the mixture; μ_{j0} is its corresponding value at a temperature of 273 K; and, C_1 is Sutherland's constant, determined from tables.

The formulation presented above has the characteristic feature that in the model under study the pressure drop in the layer is not given in an explicit form, as is done in [2, 3]. For this reason the method used to study the multiplicity of hydrodynamics states with ΔP = const consisted of the following. The flow variables at the inlet into the layer (see (6)), including also the pressure P_{in}, are given and the values of all variables at the outlet from the reactor and therefore the pressure drop ΔP are determined based on the solution of Eqs. (1)-(8). If now the input parameters are fixed, with the exception of the value of the rate of inflow (which is equivalent to changing the input velocity u^0), and the procedure described above is repeated, then we can obtain the dependence $\Delta P(G)$. This dependence can be either monotonic or of an S-shaped character. In the first case we shall say that in the layer of catalyst (with fixed parameters) there exists a unique stationary state, while in the second case there is a set of hydrodynamic states. The set in this case is understood in the sense that to one and the same pressure drop ΔP in the layer there can correspond several input velocities $u^0{}_i$ and therefore stationary distributions of the basic variables along the apparatus.

The algorithm for solving the system (1)-(8) and its partial analysis are presented in [6], so that these questions will not be examined here. We merely note that the change in the pressure in the apparatus, as shown in [6], is determined primarily by the friction between the phases. This makes it possible to simplify somewhat the momentum equation for qualitative analysis.

Qualitative Analysis of the Momentum Equation. We shall rewrite Eq. (2) in the form

$$\frac{dP}{dx} = -(A_1\mu + A_2G)\,u \tag{9}$$

and we shall integrate it from 0 to L

$$\frac{\Delta P}{L} = \frac{1}{L}\int_0^L (A_1\mu + A_2G)\,u\,dx, \tag{10}$$

where A_1 and A_2 are constants which are determined in accordance with the dependences presented in [4] and can be taken in the form

$$A_1 = 18.15S/(\varepsilon d_3),\quad A_2 = 0{,}2S/\varepsilon.$$

Since A_1, A_2, and G are constant along the layer of catalyst, Eq. (10) can be put in the form

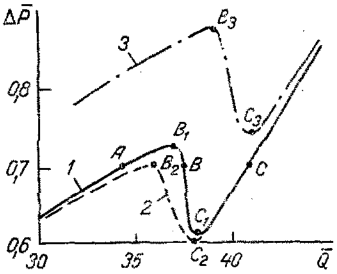

Fig. 3

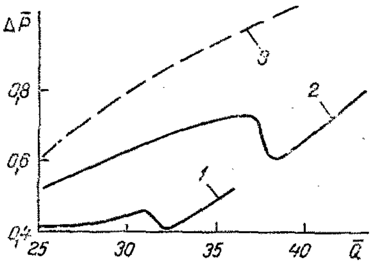

Fig. 4

Fig. 3. The effect of the viscosity of the mixture μ on the multiplicity of stationary states: 1) $\mu = \mu(T)$; 2) $\mu = \mu(T_{in})$; 3) $\mu = \mu(T_{max})$ (T_{in} is the temperature of the reagent fed into the reactor, T_{max} is the maximum temperature in the layer).

Fig. 4. The effect of the initial activity of the catalyst θ_0 and the temperature of the reagent fed into the system T_{in} on the multiplicity of stationary solutions: 1) $\theta_0 = T_{in} = 503$ K; 2) 513 K; 3) 523 K.

$$\frac{\Delta P}{L} = \frac{1}{L}\left[A_1 \int_0^L \mu u dx + A_2 G \int_0^L u dx\right].$$

We differentiate the expression obtained with respect to G and group together the terms on the right side:

$$\frac{1}{L}\,\frac{d(\Delta P)}{dG} = A_1\left(\nu + G\,\frac{d\bar{\nu}}{dG}\right) + A_2\left(\bar{u} + G\,\frac{d\bar{u}}{dG}\right). \tag{11}$$

Here we have introduced the following notation: $\bar{u} = \frac{1}{L}\int_0^L u dx,\ \bar{\nu} = \frac{1}{L}\int_0^L \frac{\mu}{\rho}\,dx$. A necessary condition for multiplicity is that the condition $\left(\frac{d(\Delta P)}{dG}\right)_{G=G^*} = 0$ must be satisfied for some G = G*; this corresponds to

$$(A_1\bar{\nu} + A_2\bar{u}) + G\left(A_1\frac{d\bar{\nu}}{dG} + A_2\frac{d\bar{u}}{dG}\right) = 0. \tag{12}$$

Since the expression in the first set of parentheses in Eq. (12) is always positive, when the condition

$$A_1\frac{d\bar{\nu}}{dG} + A_2\frac{d\bar{u}}{dG} > 0 \tag{13}$$

holds, the inequality $\frac{d(\Delta P)}{dG} > 0$ is always satisfied, i.e., there exists a unique relation between the pressure drop and the flow rate. For this reason several hydrodynamic states can arise if the condition Eq. (13) is not satisfied and $\left|G\left(A_1\frac{d\bar{\nu}}{dG} + A_2\frac{d\bar{u}}{dG}\right)\right| > |A_1\bar{\nu} + A_2\bar{u}|$. This can happen if when the flow rate is increased the average flow velocity in the layer $\bar{u}$ or the average kinematic viscosity $\bar{\nu}$ or both of these quantities together will decrease. To evaluate the effect of each component of the inequality opposite to that of (13) we shall rewrite it in the form

$$\frac{d}{dG}\left[\frac{A_2}{L}\int_0^L u\left(1+\frac{A_1}{A_2}\frac{\mu}{G}\right)dx\right]<0,$$

where $1+\frac{A_1}{A_2}\frac{\mu}{G}\approx 1+\frac{90}{\mathrm{Re}}$. From here it follows that the effect of viscosity on the multiplicity is bounded by the condition

$$1 \gg \frac{90}{\mathrm{Re}}. \tag{14}$$

Computational Results. The purpose of numerical analysis was to refine the qualitative results obtained in finding the region of multiplicity of hydrodynamic sets as well as to study the effect of technological parameters on this region. All calculations were performed on a computer for catalytic oxidation of vapors of acetic acid. The necessary kinetic data as well as the characteristics of the layer of catalyst were taken from [7]. Thus, for example, the prosity of the layer of catalyst ε was set equal to 0.92, the length of the apparatus L_a = 0.25-1 m, the pressure in the reactor P = 0.25-1 MPa, the equivalent diameter of the porous channel d_3 = 0.003 m, the cross-sectional area of the apparatus S_{ap} = 0.48 m^2, and the standard flow rate Q_0 = 0.36 kg/sec.

The basic results are presented in Figs. 1-4. Thus Fig. 1 shows for one set of boundary conditions the change in the pressure drop $\overline{\Delta P}$ in the layer as a function of the amount of matter $\bar{Q}$ fed into the reactor (curve 1). This curve is S-shaped, and it was constructed by the method described above. The figure also shows the change in the degree of transformation $X_{tr} = X_{tr}(\bar{Q})$ of the reagent (curve 2). For this reason, examining together the results given by the curves 1 and 2 it may be concluded that the point A corresponds to the high-temperature regime with a degree of transformation close to 1, while the point C corresponds to the low-temperature regime with $X_{tr} \cong 0.1$. In the case of the third "intermediate" state (it corresponds to the point B) a degree of transformation $\cong$ 0.93 is achieved at the outlet from the reactor with a quite low average temperature in the layer (curve 4 in Fig. 2). The indicated regime is apparently unstable.

Thus one and the same pressure drop, for example, $\overline{\Delta P}$ = 0.7, can be achieved with three different values of the flow rate: Q_A, Q_B and Q_C. This result agrees with the results obtained with the qualitative analysis of Eq. (2), and is connected with the decrease in the average linear velocity in the fluidized bed (owing to the decrease in the average temperature, see Fig. 2) with an increase in the flow rate of the mixture fed into the reactor. The decrease in the average temperature is associated with the decrease in the average degree of transformation of the reacting mixture.

According to the results of [3] such a multiplicity could be due to the temperature dependence of the viscosity of the gas mixture. For this reason it seemed interesting to find out whether or not there is a multiplicity of hydrodynamic states when the viscosity of the mixture is constant. The answer is affirmative, as indicated by the data in Fig. 3. Figure 3 shows the pressure drop in the layer for different values of the viscosity of the gas mixture: variable $\mu(T)$ (curve 1), μ determined at the input temperature (curve 2) and the temperature corresponding to the maximum temperature in the layer (curve 3). It is obvious that transferring to constant viscosity (curves 2 and 3) does not eliminate the multiplicity of stationary states. As the average values $\bar{\mu}$ in the layer is increased (transfer from curve 2 to curve 3) the region of $\overline{\Delta P}$ where multiplicity can exist increases.

Figure 4 shows the effect of the initial activity of the catalyst θ_0 and the temperature T_{in} of the mixture fed into the system on the multiplicity in the layer. One can see that if the S-shaped dependence occurs (this corresponds to multiplicity) with $\theta_0 = T_{in}$ = 503 K, $\theta_0 = T_{in}$ = 513 K, then it vanishes with $\theta_0 = T_{in}$ = 523 K. These results indicate that the initial activity of the catalyst strongly affects the behavior of the curve $\overline{\Delta P} = \overline{\Delta P}(Q)$. It should also be noted that with $\theta_0 = T_{in}$ = 523 K (curve 3) the initial activity and the energy of the mixture fed into the system make it possible to realize a smooth transition from the upper temperature regime to the lower temperature regime.

Thus in this work we have shown numerically that based on the model (1)-(8) it is in principle possible for multiple stationary states to exist with a fixed pressure drop. An important point here is that the density of the mixture and the flow velocity are variables, i.e., they depend on the temperature and composition of the mixture. As regards the viscosity of the mixture, we have shown that multiplicity occurs even when μ = const.

The realization of different stationary states in different pipes of a multiple reactor is an extremely undesirable phenomenon, since this could result in thermal stresses which affect the mechanical properties of the reactor. The method proposed in this paper makes it possible to determine each specific case the region of parameters where several stationary states can exist.

NOTATION

C, heat capacity, J/(kg·K); d_g, diameter of a grain of catalyst; D, diffusion coefficient, m^2/sec; F_f, interphase friction force, N/m^3; G, flow rate, kg/(m^2·sec); H_i, heat effect of the i-th reaction, J/kg; m, number of reactions; N, number of components of the gas mixture; P, pressure in the apparatus, N/m^2; Q, volume flow rate of the gas mixture, m^3/sec; R_i, rate of the i-th reaction, J/kg; $R_{mix} = C_p - C_v$, gas constant of the mixtures, J/(kg·deg); S, specific surface area of the layer, m^{-1}; t, time, sec; T, temperature of the flow, K; u, velocity of the flow, m/sec; W_j, velocity of the reaction for the j-th component, kg/(m^3·sec); x, coordinate along the space, m; y, concentration by weight; a, heat transfer coefficient, W/(m^2·K); β, mass transfer coefficient, m/sec; θ, temperature of the catalyst, K; λ, thermal conductivity, W/(m·K); μ, coefficient of dynamic viscosity, N/(sec·m^2); $\xi = x/L$, dimensionless length of the apparatus; ρ, density, kg/m^3. Indices: j, components of the gas mixture; c, catalyst; p, constant pressure; and v, constant volume.

LITERATURE CITED

1. S. Ergun, J. Chem. Eng. Progr., 48, No. 2, 227 (1952).
2. Yu. Sh. Matros and N. A. Chumakova, Dokl. Akad. Nauk SSSR, 250, No. 6, 1421-1425 (1980).
3. J. P. Lee, V. Balakotaiah, and D. Luss, Chem. Eng. Sci., 41, No. 4, 749-755 (1986).
4. M. É. Aérov, O. M. Todes, and D. A. Narinskii, Apparatus with Stationary and a Fluidized Bed [in Russian], Leningrad (1968).
5. S. Bretshnaider, Properties of Gases and Liquids [in Russian], Moscow (1966).
6. A. N. Stegasov and V. A. Kirillov, Inzh.-Fiz. Zh., 52, No. 1, 135-140 (1987).
7. Yu. I. Goglyuvatyi, A. N. Stegasov, V. N. Orlik, et al., Khim. Promyshlennost', No. 3, 22-23 (1985).