UNIQUENESS AND STABILITY OF STEADY STATES OF CONTINUOUS CHEMICAL REACTORS

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We examine the uniqueness and stability of the solutions to the problem of steady-state operation of a continuous chemical reactor in which longitudinal diffusion and heat conduction are taken into account. We investigate an adiabatic reactor in which the concentration and temperature distributions are similar (the thermal diffusivity and diffusion coeffecient are equal) and an isothermic reactor. These two cases are considered together because the mathematical formulations of the problem are equivalent.

The question of the existence and number of steady states was analyzed in [1, 2], where references were made to earlier investigations. The results obtained in [1, 2] are now extended. The stability of the steady states is investigated by the small-perturbation method.

1. **Statement of problem. Basic equations.** In the formulation of the problem we adopt the assumptions usually made in chemical reactor theory. The validity of these assumptions is discussed in [3, 4], for instance.

We assume that the continuous chemical reactor is a cylindrical volume filled with a porous catalyst and with impermeable side walls. A reacting mixture of initial and final reaction products filters through the catalyst. We assume that the processes in the reactor can be represented by assigning mean values to the physicochemical parameters (the catalyst granules are small in comparison with the volume of the reactor). In addition, the equations are formulated for quantities averaged over the reactor cross section, i.e., the one-dimensional approximation is considered.

Within the framework of these assumptions the mass and heat transfer processes in an adiabatic (nonconducting side walls) continuous reactor can be represented by the following system of diffusion and heat-conduction equations:

$$\frac{\partial \xi}{\partial t} = D\frac{\partial^2 \xi}{\partial x^2} - u\frac{\partial \xi}{\partial x} + r(\xi, T) \tag{1.1}$$

$$\frac{\partial T}{\partial t} = \frac{\varkappa}{\rho c}\frac{\partial^2 T}{\partial x^2} - u\frac{\partial T}{\partial x} + \frac{h}{\rho c} r(\xi, T) \tag{1.2}$$

Here ξ is the yield, or degree of advancement, of the reaction (moles/unit volume); T is the temperature; D and $\varkappa$ are the effective longitudinal diffusion coefficient and thermal conductivity (the diffusion coefficients for all the substances are assumed to be equal); ρ is the density of the mixture of reagents and reaction products; u is the filtration velocity; c is the total heat capacity of the reacting mixture and skeleton; the function $r(\xi, T)$ is the chemical reaction rate expressed as a function of yield and temperature (moles/unit volume × unit time); h is the heat of the reaction (for an exothermic reaction $h > 0$ and for an endothermic reaction $h < 0$). Let the length of the reactor be l, i.e., $0 \leq x \leq l$. For the boundary conditions at the entrance ($x = 0$) and outlet ($x = l$) of the reactor we take

$$-D\frac{\partial \xi}{\partial x} + u\xi = 0, \quad x = 0; \qquad \frac{\partial \xi}{\partial x} = 0, \quad x = l \tag{1.3}$$

$$-\frac{\varkappa}{\rho c}\frac{\partial T}{\partial x} + uT = uT_0, \quad x = 0; \qquad \frac{\partial T}{\partial x} = 0, \quad x = l \tag{1.4}$$

Here T_0 is the temperature of the initial mixture. The question of the validity of boundary conditions (1.3) and (1.4) was discussed in [5]. It was shown that these boundary conditions are valid in steady and unsteady conditions if certain restrictions are placed on the reactor model.

A complete mathematical description of unsteady heat and mass transfer processes in an adiabatic continuous reactor must include, in addition to relationships (1.1)–(1.4), initial conditions for the temperature and yield of the reaction. The specific form of these conditions is not used below.

We assume in what follows that the following equality is valid:

$$\frac{\varkappa}{\rho c} = D = \chi \tag{1.5}$$

For the description of processes in an isothermic continuous reactor, where the temperature has a specified constant value due, for instance, to rapid heat exchange with the reactor walls, Eq. (1.1), conditions (1.3), and the corresponding initial condition are sufficient.

2. **Steady states.** The investigation of the steady states of an adiabatic reactor reduces to an investigation of the solutions of Eqs. (1.1) and (1.2) with $\partial/\partial t = 0$ and conditions (1.3), (1.4). In view of assumption (1.5) these solutions entail similarity of the concentration and temperature distributions. This is expressed by a one-to-one correspondence between the yield of the reaction and the temperature at any section of the reactor:

$$T(x) - \frac{h}{\rho c}\xi(x) = T_0 \tag{2.1}$$

Using (2.1) we can put the expression for the rate of the chemical reaction in the form

$$r(\xi, T) = r\left(\rho c\,\frac{T - T_0}{h},\, T\right) \equiv \Phi(T) \tag{2.2}$$

In view of formula (2.2) the problem of the steady states of an adiabatic reactor reduces to an analysis of the solutions of the steady-state ($\partial/\partial t = 0$) equation (1.2) with conditions (1.4).

It is convenient to put problem (1.2), (2.2), (1.4) in the following form:

$$\frac{d^2\theta}{dx^2} - U\frac{d\theta}{dx} + F(\theta) = 0, \qquad 0 \leqslant \theta \leqslant \theta_m \tag{2.3}$$

$$\frac{d\theta}{dx} - U\theta = 0, \quad x = 0; \qquad \frac{d\theta}{dx} = 0, \quad x = l \tag{2.4}$$

$$(U = u\rho c / \varkappa, \ \theta_m = |T_m - T_0|)$$

Here

$$\theta = |T - T_0| = \begin{cases} T - T_0 & \text{for an exothermic reaction,} \\ T_0 - T & \text{for an endothermic reaction;} \end{cases}$$

the temperature T_m corresponds to the maximum yield of the reaction; and

$$F(\theta) = \frac{|h|}{\varkappa}\Phi\left(T_0 + \frac{h}{|h|}\theta\right) \tag{2.5}$$

The problem of the steady states of an isothermic reactor, i.e., the problem of the steady-state solutions of Eq. (1.1) with conditions (1.3) and $\partial/\partial t = 0$, $T = \text{const}$, can also be put in the form (2.3), (2.4). This merely requires the introduction of the new symbols $\theta = \xi$ and $F(\theta) = r(\xi, T = \text{const})$ in relationships (1.1) and (1.3).

Thus, the general analysis of the solutions in the case of an adiabatic reactor is mathematically equivalent to an analysis of the solutions in the case of an isothermic reactor. The only difference lies in the specific form of function $F(\theta)$, which will always be assumed to be sufficiently smooth.

It was shown earlier in [1] that a solution of problem (2.3), (2.4) always exists and that if function $F(\theta)$ is monotonic, the solution will be unique. The conclusion of uniqueness of the solution can be extended to a larger class of functions $F(\theta)$. The sufficient condition for uniqueness depends on the condition for stability of the solution.

Let an assigned function $F(\theta)$ correspond to several solutions of the problem (2.3), (2.4). We consider the two solutions $\theta_1(x)$ and $\theta_2(x)$. The difference of these two solutions $\tau(x) = \theta_1(x) - \theta_2(x)$ will satisfy the equation

$$\frac{d^2\tau}{dx^2} - U\frac{d\tau}{dx} + F(\theta_1) - F(\theta_2) = 0 \tag{2.6}$$

with conditions

$$\frac{d\tau}{dx} - U\tau = 0, \quad x = 0; \quad \frac{d\tau}{dx} = 0, \quad x = l \tag{2.7}$$

We put the difference of functions $F(\theta)$ in the form

$$F(\theta_1) - F(\theta_2) = \frac{dF}{d\theta}\bigg|_{\theta=\theta_*}\tau \tag{2.8}$$

where θ_* lies between θ_1 and θ_2.

We introduce a new unknown function

$$\tau(x) = y(x)\exp({}^1/{}_2Ux)$$

Using formula (2.8) we obtain, in place of relationships (2.6) and (2.7),

$$\frac{d^2y}{dx^2} + \left(\frac{dF}{d\theta} - \frac{U^2}{4}\right)y = 0 \tag{2.9}$$

$$\frac{dy}{dx} - \frac{U}{2}y = 0, \quad x = 0; \quad \frac{dy}{dx} + \frac{U}{2}y = 0, \quad x = l \tag{2.10}$$

It can be shown that Eq. (2.9) with conditions (2.10) has no nontrivial solution when

$$dF / d\theta \leqslant {}^1/{}_4U^2 \tag{2.11}$$

This means that when inequality (2.11) is satisfied, problem (2.3), (2.4) has a unique solution. Thus, condition (2.11) will be a sufficient condition for uniqueness of the solution of (2.3), (2.4). It is clear that in comparison with the previous requirement of monotonicity of function $F(\theta)$, condition (2.11) greatly enlarges the class of functions for which the problem of the steady state of a chemical reactor has a unique solution (see also [6]).

3. Stability of steady state. We investigate in a linear approximation the stability of the steady states of adiabatic and isothermic reactors by examining the behavior of small unsteady deviations from the solutions of problem (2.3), (2.4).

The equations and boundary conditions for the perturbations can be obtained by linearizing relationships (1.1)–(1.4) by putting

$$\xi(x, t) = \xi^\circ(x) + \delta\xi(x, t), \qquad T(x, t) = T^\circ(x) + \delta T(x, t) \tag{3.1}$$

In an adiabatic reactor the functions $\xi^\circ(x)$ and $T^\circ(x)$—the steady-state solutions—are connected with one another by relationship (2.1) and can be expressed in terms of function $\theta(x)$, which is a solution of problem (2.3), (2.4); in an isothermic reactor

$$T^\circ(x) = \text{const}, \quad \delta T = 0, \quad \theta = \xi$$

It can be shown that it is sufficient in an analysis of the stability of an adiabatic reactor to consider only perturbations which satisfy the similarity condition, i.e., such that $\delta T = (h/\rho c)\delta\xi$. After linearization of (1.1)–(1.4) we obtain by subtraction, using (1.5),

$$\chi\frac{\partial^2 e}{\partial x^2} - \frac{\partial e}{\partial t} - u\frac{\partial e}{\partial x} = 0, \qquad e = \delta T - \frac{h}{\rho c}\delta\xi \tag{3.2}$$

$$-\chi\frac{\partial e}{\partial x} + ue = 0, \quad x = 0; \qquad \frac{\partial e}{\partial x} = 0, \quad x = l \tag{3.3}$$

We take the initial condition for function e in the form

$$t = 0, \qquad e(x) = \delta T_0(x) - \frac{h}{\rho c}\delta\xi_0(x) \tag{3.4}$$

where $\delta\xi_0(x)$ and $\delta T_0(x)$ are the perturbations at the initial instant. Condition (3.4) becomes the zero condition when the initial perturbations are similar.

The solution of the boundary-value problem (3.2), (3.3) can be written in the form

$$e(x, t) = \sum C_n \Psi_n (x)\, e^{-\lambda_n t} \tag{3.5}$$

where λ_n are eigenvalues. It is obvious that $\lambda_n > 0$. If the initial perturbations are similar the solution of problem (3.2), (3.4) is identically equal to zero, so that the property of similarity is not lost with time. In the case of dissimilar initial perturbations it follows from the form of solution (3.5) and the properties of the eigenvalues λ_n that the perturbations will become similar with time.

For similar perturbations from (1.1)–(1.4) after linearization we find

$$-\frac{1}{D}\frac{\partial \delta\theta}{\partial t} + \frac{\partial^2 \delta\theta}{\partial x^2} - U\frac{\partial \delta\theta}{\partial x} - \frac{dF(\theta)}{d\theta}\delta\theta = 0 \tag{3.6}$$

$$(\delta\theta = |\delta T|)$$

$$\frac{\partial \delta\theta}{\partial x} - U\delta\theta = 0, \quad x = 0; \ \frac{\partial \delta\theta}{\partial x} = 0, \quad x = l \tag{3.7}$$

$$\delta\theta = \eta(x), \qquad t = 0 \tag{3.8}$$

Here $\eta(x)$ is an arbitrary initial perturbation.

Let us solve problem (3.6)–(3.8) by separation of the variables. We set

$$\delta\theta\,(x, \ t) = \exp\,(-\lambda Dt + {}^1/_2 Ux) y\,(x) \tag{3.9}$$

Substituting (3.9) into (3.6) and (3.7) we arrive at the following self-adjoint problem of eigenvalues with boundary conditions of the Sturm type:

$$\begin{gathered}\frac{d^2y}{dx^2} + \left[\frac{dF(\theta)}{d\theta} - \frac{U^2}{4} + \lambda\right] y = 0 \\ \frac{dy}{dx} - \frac{U}{2}y = 0, \quad x = 0; \qquad \frac{dy}{dx} + \frac{U}{2}y = 0, \quad x = l\end{gathered} \tag{3.10}$$

If in the spectrum of eigenvalues of (3.10) all $\lambda_n > 0$, the considered steady state is stable. If even one $\lambda_n < 0$ can be found, the state is unstable.

The number of negative eigenvalues is always finite. If the condition

$$\frac{dF}{d\theta} \leqslant \frac{U^2}{4} \tag{3.11}$$

is satisfied, all the eigenvalues are positive.

Thus, inequality (3.11) is a sufficient condition for stability of the steady state.

Condition (3.11) is fulfilled, in particular, in all cases where function $F(\theta)$ is decreasing or where the parameter U is sufficiently large. It was shown above that in this case there is a unique steady state. It is now clear that this state is stable.

We give examples where there is a unique stable steady state.

1. An isothermic reactor in which a unique reversible or irreversible reaction takes place in the absence of autocatalysis.

2. An adiabatic reactor in which the concentration and temperature distributions are similar and a unique endothermic reaction takes place.

3. The same as 2, but the reaction is exothermic and the condition

$$U \geqslant 2\sqrt{dF / d\theta}$$

is fulfilled.

REFERENCES

1. Yu. P. Gupalo and Yu. S. Ryazantsev, "Steady states of a continuous adiabatic chemical reactor," PMTF [Journal of Applied Mechanics and Technical Physics], no. 5, 1967.

2. Yu. P. Gupalo and Yu. S. Ryazantsev, "Steady states of a continuous isothermic chemical reactor," PMTF [Journal of Applied Mechanics and Technical Physics], no. 3, 1969.

3. R. Aris, Introduction to the Analysis of Chemical Reactors, Prentice Hall, New Jersey, 1965.

4. D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics [in Russian], 2nd edition, Nauka, Moscow, 1967.

5. A. R. van Cauwenberghe, "Further note on Danckwerts' boundary conditions for flow reactors," Chem. Engng. Sci., vol. 21, no. 2, 1966.

6. D. Luss and N. R. Amundson, "Uniqueness of the steady-state solutions for chemical reaction occurring in a catalyst particle or in a tubular reactor with axial diffusion," Chem. Engng. Sci., vol. 22, no. 3, 1967.

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