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STABILITY AND DYNAMICS ANALYSIS OF A COOLED CO-CURRENT FIXED-BED REACTOR

Bifurcation theory and numerical computations are used to investigate the steady states and dynamic behavior of a cooled co-current fixed-bed reactor simulated by a one-dimensional pseudo-homogeneous model of heat and mass transfer including first order exothermic reaction.

Introduction. The subject investigation in this paper is a fixed-bed tubular reactor where single exothermic reaction occurs. In previous works the steady-states and dynamic behavior of a fixed-bed reactor was studied using both pseudo-homogeneous and heterogeneous models of heat and mass transfer [1-3]. Deactivation and regeneration of catalyst, non-uniform flow velocity distribution and changing heat-physical properties of catalyst and reactant with temperature were taken into account in these models to provide clarifying their influence on reactor stability and dynamics. All those models assume constant wall temperature. This study is concerned with mathematical modeling of a cooled fixed-bed reactor with taking into consideration wall temperature, which is not constant but varies along reactor length. Such is the case when the cooling tubes and reactor tubes form an integral part of a composite heat exchanger. Co-current flow of coolant and reaction mixture is considered. The process is simulated by one dimensional pseudo-homogeneous model of heat and mass transfer including first order exothermic reaction. The stability analysis is carried out on simplified model by applying methods of bifurcation theory and the 1st Lyapunov method. The dynamics of fixed-bed reactor is examined on one-dimensional model with by using finite-difference method. Numerically obtained solutions are compared with those predicted by linear theory.

Formulation of the problem. Heat and mass transfer phenomena in a cooled co-current fixed bed reactor are modeled by a system of partial differential equations formulated with various simplifying assumptions [4]. It is well known that radial tempera-ture profiles in packed beds are parabolic with most of the resistance to heat transfer near the tube wall. So it is fair approach to the preliminary investigation is to assume that all resistance to heat transfer is in a thin layer near the tube wall. With this assumption a one-dimensional model, which becomes quite accurate for small diameter tubes is used. Neglecting diffusion and conduction in the direction of flow, the heat and mass balances equations in dimensionless form are:

$$\frac{\partial \vartheta}{\partial \tau} + Pe\ \frac{\partial \vartheta}{\partial x} = Da \cdot q \cdot C \cdot \Gamma(\vartheta) - Bi_T\ (\vartheta - \vartheta_c); \tag{1}$$

$$\frac{\partial \vartheta_c}{\partial \tau} + Pe_c\ \frac{\partial \vartheta_c}{\partial x} - Bi_{T_C}\ (\vartheta - \vartheta_c) = 0; \tag{2}$$

$$\frac{\partial C}{\partial \tau} + Pe \frac{\partial C}{\partial x} = - Da \cdot C \cdot \Gamma(\vartheta). \tag{3}$$

The initial and boundary conditions are:

$$\begin{aligned} &\tau = 0: \quad \vartheta = \vartheta_1;\ \vartheta_c = \vartheta_{c_1};\ C = C_1; \\ &x = 0: \quad \vartheta = \vartheta_0;\ \vartheta_c = \vartheta_{c_0};\ C = C_0; \\ &x = 1: \quad \frac{d\vartheta}{dx} = 0; \quad \frac{d\vartheta_c}{dx} = 0; \quad \frac{dC}{dx} = 0. \end{aligned} \tag{4}$$

The various dimensionless groups appearing in the above equations are defined below:

$$x = \frac{\tilde{x}}{L}; \quad \tau = \frac{a\,t}{L^2}; \quad \vartheta = \frac{R\,T}{E}; \quad \vartheta_c = \frac{R\,T_c}{E}; \quad C = \frac{Y}{\tilde{c}_1}; \quad Pe = \frac{G\,L}{\rho\,a}; \quad Pe_c = \frac{G_C\,L}{\rho_c\,a_c};$$

$$Da = \frac{k_0\,L^2}{a}; \quad Bi_T = \frac{\alpha\,L^2}{n\,\lambda}; \quad Bi_{T_c} = \frac{\alpha\,L^2}{n\,\lambda_c}; \quad q = \frac{Q\,R\,\tilde{c}_1}{\tilde{c}_p\,E}; \quad \Gamma(\vartheta) \quad f(\vartheta)\cdot\exp(-\frac{1}{\vartheta}).$$

Dimensionless variables and parameters: ϑ and C are the temperature and the concentration of reactant mixture; τ is the time; x is the axial coordinate; Pe, Da, Bi_T are the parameters Peclet, Damkohler and Biot, respectively; q is the reaction heat; $\Gamma(\vartheta)$ is the reaction rate.

Dimensional variables and parameters: T is the temperature of reactant mixture (K); Y is the concentration of reactant mixture (kmol/kg); $\tilde{c}_1$ is the inlet concentration of reactant mixture (kmol/kg); t is the time (s); $\tilde{x}$ is the axial coordinate (m); L is the reactor length (m); G is the mass flow rate of reactant mixture per unit area to the reactor (kg/m^2 s); ρ and $\tilde{c}_p$ are the bulk density (kg/m^3) and the heat capacity (kJ/kg K) of reactant mixture, respectively; λ is the heat conductivity factor (W/m K); a is the thermal diffusivity (m^2/s); α is the overall heat transfer coefficient for the transfer of heat between the fluid streams (W/m^{2}K); Q is the reaction heat (kJ/kmol); k_0 is the reaction rate coefficient (s^{-1}); E and R are the activation energy (kJ/kmol) and universal gas constant (kJ/kmol K), respectively; n is the surface area for heat transfer per unit hydraulic radius (m). Index "c" refers to coolant, "1" to initial conditions, "0" to reactor inlet.

Stability analysis. One of the main problems in theoretical analysis of chemical reactors is the problem of steady states of a given system. Due to the non-linearity, instability and numerous number of varied parameters it is difficult to obtain solutions (numerically or analytically) of steady-states problem. To investigate the nonlinear system behavior, it is necessary to simplify the above equations by replacement the partial derivatives on finite-differences with account the boundary conditions [5]. Obtained zero-dimensional model is the dynamic system of the 3rd order:

$$\frac{d\hat{\vartheta}}{d\tau} = -Pe\,(\hat{\vartheta} - \vartheta_0) - Bi_T\,(\hat{\vartheta} - \vartheta_c) + Da\cdot q\cdot\hat{C}\cdot\Gamma(\hat{\vartheta}) \equiv P_1(\hat{\vartheta}, \hat{\vartheta}_c, \hat{C}); \tag{5}$$

$$\frac{d\hat{\vartheta}_c}{d\tau} = -Pe_c\,(\hat{\vartheta}_c - \vartheta_{c_0}) + Bi_{T_c}\,(\hat{\vartheta} - \vartheta_c) \equiv P_2(\hat{\vartheta}, \hat{\vartheta}_c); \tag{6}$$

$$\frac{d\hat{C}}{d\tau} = -Pe\,\left(\hat{C} - C_0\right) - Da\cdot\hat{C}\cdot\Gamma(\hat{\vartheta}) \equiv P_3(\hat{\vartheta}, \hat{C}). \tag{7}$$

$$\tau = 0: \quad \hat{\vartheta} = \vartheta_1; \quad \hat{\vartheta}_c = \vartheta_{c_1}; \quad \hat{C} = C_1. \tag{8}$$

Where $\hat{\vartheta}$, $\hat{\vartheta}_c$, $\hat{C}$ are the reactant mixture tempe-rature, coolant temperature and reactant mixture concentration, respectively at point x=0,5.

The static equilibrium positions can be found from:

$$P_i(\hat{\vartheta}_s, \hat{\vartheta}_{c_s}, \hat{C}_s) = 0, \qquad (i = 1,2,3), \tag{9}$$

where subscript "s" indicates the steady-state conditions.

Taking inlet reactant mixture temperature ϑ_0 as bifurcation parameter, the bifurcation equation can be obtained:

$$\vartheta_0 = \hat{\vartheta}_s + \frac{Bi_T}{Pe}\left(\hat{\vartheta}_s - \hat{\vartheta}_{c_s}\right) - \frac{Da\cdot q\cdot\hat{C}_s\cdot\Gamma(\hat{\vartheta}_s)}{Pe}, \tag{10}$$

where $\hat{\vartheta}_{c_s}, \hat{C}_s$ are determined from (9).

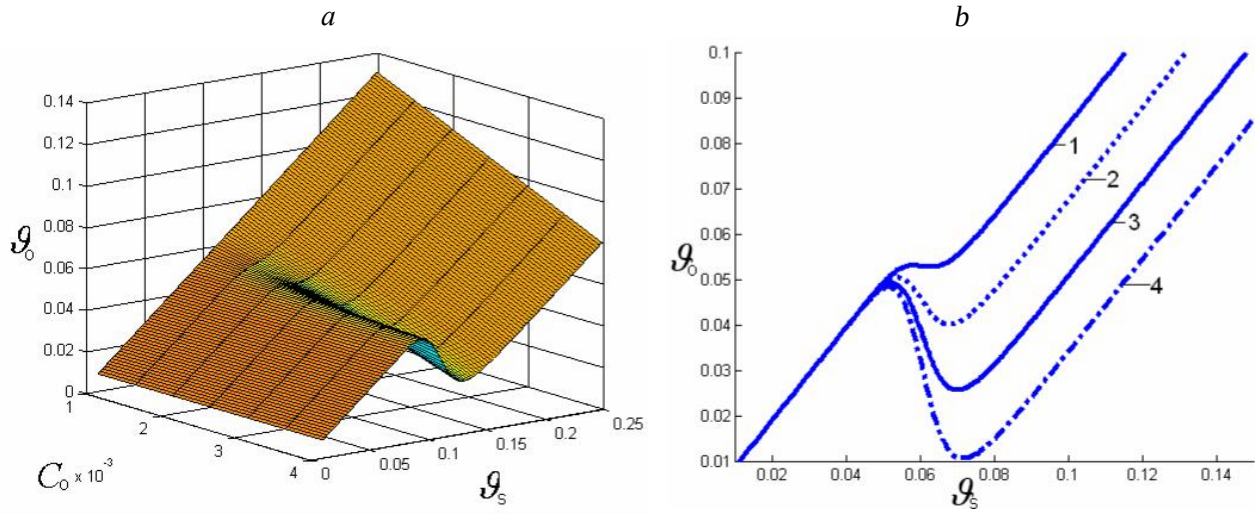

Fig. 1. Bifurcation set (*a*) and bifurcation diagram (*b*): *a* – $\vartheta_{c_0} = 0,025$; *Pe* = 130; Pe_c = 130; *Da* = 1,7 10^9; Bi_T = 2; $Bi_{T_c} = 2$; *q* = 16,7; *b* – C_0 = 0,001 (1); 0,002 (2); 0,003 (3); 0,004 (4)

In Fig.1,a the bifurcation set obtained in $\hat{\vartheta}_s, \vartheta_0, C_0$ space is depicted. Typical cross sections for a fixed C_0 are shown in Fig.1,b. Bifurcation diagram as that in Fig.1,b provides information about the range of parameters where multiple and unique regimes exist. The S-shape of the curves indicates that the ϑ_s may correspond to any one or three values for a given values of ϑ_0 and C_0.

By applying the methods of bifurcation theory [6] the parametric equations of non-unique boundary in the plane "inlet gas temperature" (ϑ_0) -"reaction heat" (q) were obtained:

$$q = \frac{\left[Pe\left(Pe_c + Bi_{T_C}\right) + Pe_c \cdot Bi_T\right] \cdot \left[Pe + Da \cdot \Gamma(\hat{\vartheta}_s)\right]}{Pe \cdot Da \cdot \hat{C}_s \cdot \Gamma'(\hat{\vartheta}_s) \cdot (Pe_c + Bi_{T_C})}, \tag{11}$$

with (10).

The stability of steady states is investigated using the first Lyapunov method. From Routh-Hurwitz stability criterion the stability boundaries can be obtained:

$$\sigma = -sp\mathbf{A};\ \theta = \text{-det}\mathbf{A};$$

$$\Delta = \sum_{i=1}^{3}\sum_{j=2}^{3}\left(a_{ii} \cdot a_{jj} - a_{ij} \cdot a_{ji}\right),$$

here **A** – matrix of coefficient of linear transform [6].

Stability boundary $\sigma = 0$ in ϑ_0, q plane is determined by:

$$q = \frac{2Pe + Pe_c + Bi_T + Bi_{T_C} + Da \cdot \Gamma(\hat{\vartheta}_s)}{Da \cdot \hat{C}_s \cdot \Gamma'(\hat{\vartheta}_s)} \tag{12}$$

with (10).

Stability boundary $\Delta = 0$ in ϑ_0, q plane is determined by:

$$q = \frac{\left(Pe + Da \cdot \Gamma(\hat{\vartheta}_s)\right)\left(Pe + Pe_c + Bi_T + Bi_{T_C}\right) + Pe\left(Pe_c + Bi_{T_C}\right) + Bi_T Pe_c}{Da \cdot \hat{C}_s \cdot \Gamma'(\hat{\vartheta}_s)\left(Pe + Pe_c + Bi_{T_C}\right)} \tag{13}$$

with (10).

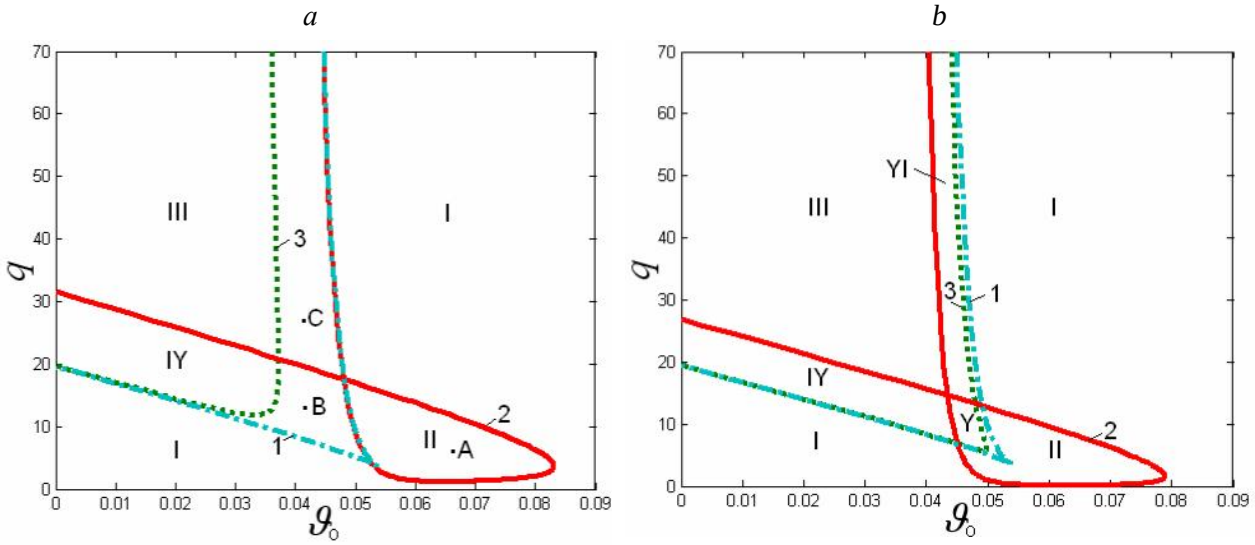

Fig. 2. Stability regions for different values inlet coolant flow velocity.
C_0 = 0,004; ϑ_{c_0} = 0,025; *Pe* = 130; *Da* = 1,7 10^9; Bi_T = 2: Pe_c = 130 (*a*); 0 (*b*)

The parametric equations of stability boundary θ=0 agree with parametric equations of non-unique boundary (10), (11). It was obtained that $\sigma = 0$ is an oscillation boundary and for given parameters is located inside non-unique boundary; $\Delta = 0$ is a neutral stability boundary.

Fig. 2, a illustrates the non-unique (curve 1), neutral stability (curve 2) and oscillation (curve 3) boundaries for Pe_c =130. Here, the obtained boundaries divide ϑ_0, q plane into 4 regions, corresponding to a different type of stability and number of steady states. In region I and II here is one equilibrium state: stable (I) or auto-oscillating (II). In region III and IY the reactor possesses three different equilibrium states. One equilibrium state represents a meta-stable and the remaining two states correspond to high- or low-temperature regime, depending on initial conditions. The both high- and low-temperature equilibrium states in region III are stable. In region IY the high temperature equilibrium state is unstable, and low temperature equilibrium state is stable.

The stability boundaries obtained for case when coolant flow velocity Pe_c =0 are shown in Fig. 2, b. It is seen that there are two additional regions are appeared in this case. Inside region Y the both high- and low temperature equilibrium states are unstable. In region YI the high-temperature regime is stable and low temperature one is unstable.

The overall bifurcation structure becomes clearer when influence of different parameters is studied. Fig.3 demonstrates the influence of inlet reactant mixture concentration C_0 on stability boundaries. It is seen that a decrease in the value of C_0 enlarges the auto-oscillation region (curve 2' in Fig.3,b), but shrinks the region of multiplicity (curve 2 in Fig.3,a). Non-unique boundary is displaced so that extinction is taken place at higher values of reaction heat q.

It was found that decreasing in system parameter Da, which characterized the time of residence of reaction mixture in reactor leads to displacing the non-unique boundary so that extinction and ignition are occurred at higher values inlet reactant mixture temperature ϑ_0 and reaction heat q. Auto-oscillating region is considerably enlarged in this case.

Increase in the value of inlet coolant temperature ϑ_{c_0} negligible influences on the size of stability regions, but effects on critical conditions of ignition, which is occurred at the lower values of inlet reactant mixture temperature.

Decrease in the value of inlet reactant flow velocity Pe leads to displacing the non-unique boundary, so that ignition is occurred at the lower values inlet reactant mixture temperature. Moreover auto-oscillating region is considerably shrunk.

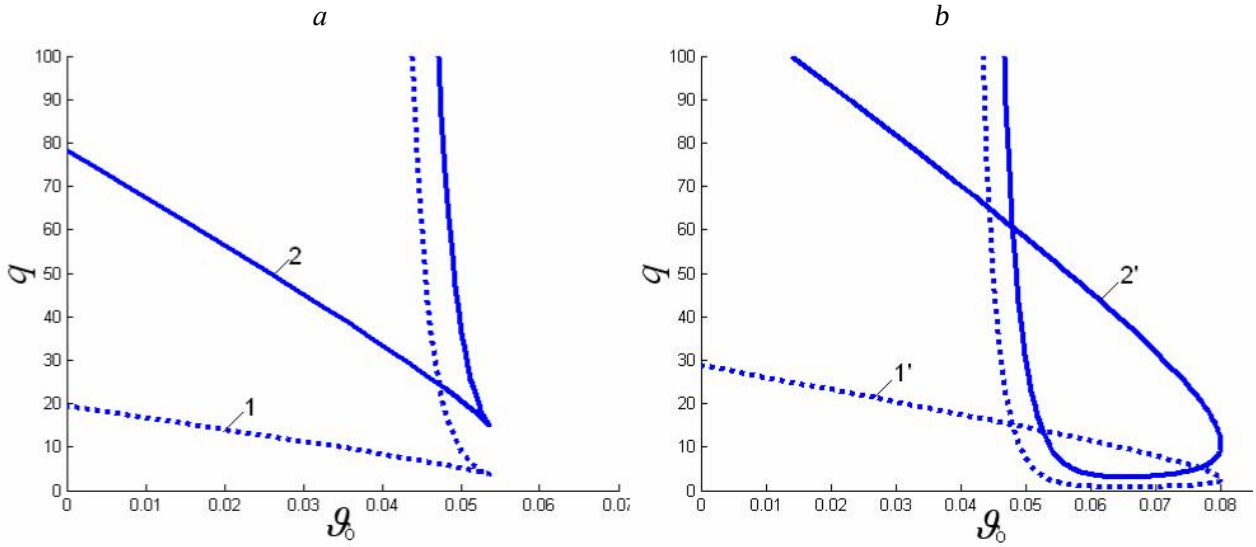

Fig. 3. Influence of inlet reactant mixture concentration C_0 on non-unique (*a*) and neutral stability (*b*) boundaries: C_0 = 0,004 (1,1'); 0,001 (2,2'); other parameters corresponding Fig. 2, a

Increasing the value of Bi_T, which characterized the heat exchange with coolant, results in a larger auto-oscillating region but a narrower non-unique region.

Thus bifurcation analysis can provide a qualitative prediction for the behavior of non-linear system.

Numerical solution. The stability analysis on simplified model allows obtain a preview of possible dynamics and initial guesses for numerical computations. To examine the qualitative prediction by the bifurcation theory, the predicted by linear theory regimes are compared with those computed numerically on model (1)-(4). The numerical solutions were obtained by using an explicit finite difference approximation [7]. Time step is "automatically" decreased with increasing reaction rate that provides stability of calculations on each time layer.

According to the prediction by the bifurcation theory in the point A (Fig.2,a) a unique, stable limit cycle occurs. The corresponding limit cycle simulated on model (1)-(4) is displayed in Fig.4. As an illustration of the dynamics of predicted unstable high-temperature and stable low-temperature regimes, corresponding point B from multiplicity region IY in Fig. 2,a the numerically computed high-temperature auto-oscillating (curve 2) and low-temperature stable (curve 1) regimes are shown in Fig.4,b. Numerical simulation of predicted multiple low- and high-temperature stable regimes corresponding point C from region III are presented in Fig. 5 (curves 1, 2). It can be seen that numerically computed regimes (curves 1 and 2) are located close to equilibrium states predicted by the bifurcation diagram (dotted lines in Fig. 4,b and Fig. 5). The medium equilibrium state is unstable and numerically is not realized.

Results of comparison show, although some negligible discrepancies between predicted approximately-analytically and obtained numerically regimes are happened, in total the strongly nonlinear simulation supports the existence of auto-oscillating, stable, unique and multiple regimes as established by linear theory.

Thus it can be concluded that zero-dimensional model (5)-(8) describes all qualitative features of the one-dimensional model (1)-(4) and therefore obtained regions of possible regimes (Fig.2,a) may be used for prediction the dynamics in the reactor and for choice of the parameters of required regime for numerical solution of complete model.

As well known when an exothermic catalytic reaction occurs in non-isothermal reactor, a small change in coolant temperature may cause thermal instability in the sense that the reaction may either become extinguished or continue at a higher temperature. Fig.5 illustrates the influence of coolant temperature on low temperature regime (curve 1). It is seen increasing in coolant temperature results in a higher temperature in reactor (curve 3). Exceeding certain value of coolant temperature causes the temperature in reactor to increase sharply to higher temperature and reactor operates in high temperature regime (curve 4, Fig.5).

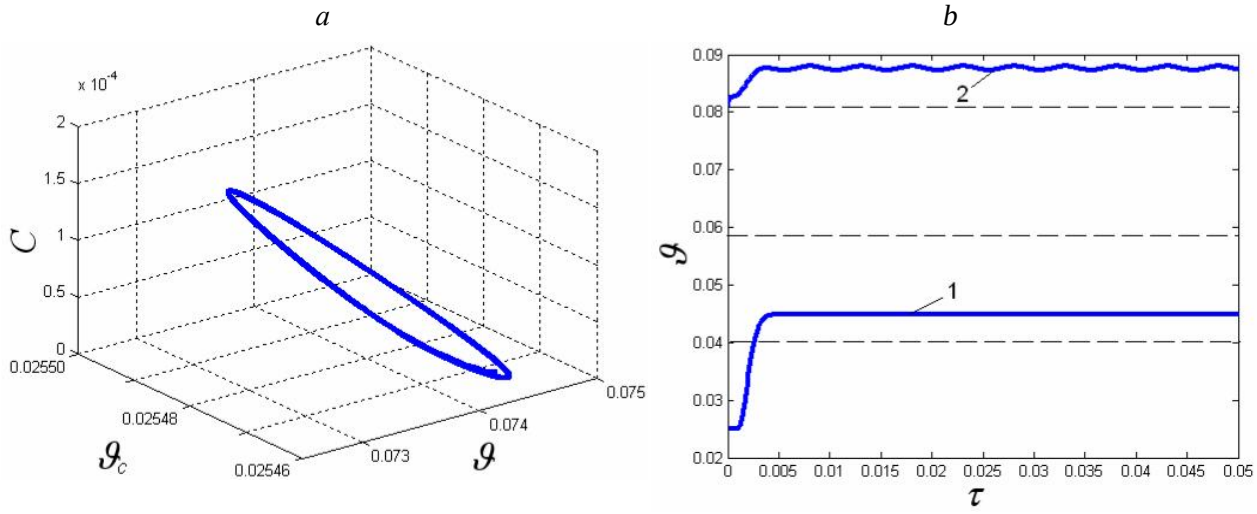

Fig. 4. Phase portrait of auto-oscillating regime, corresponding point A (*a*) and multiple regimes, corresponding point B in Fig. 2,a (*b*). *a*) q = 7; ϑ_0 = 0,067; x = 0,6; *b*) q = 14; ϑ_0 = 0,042

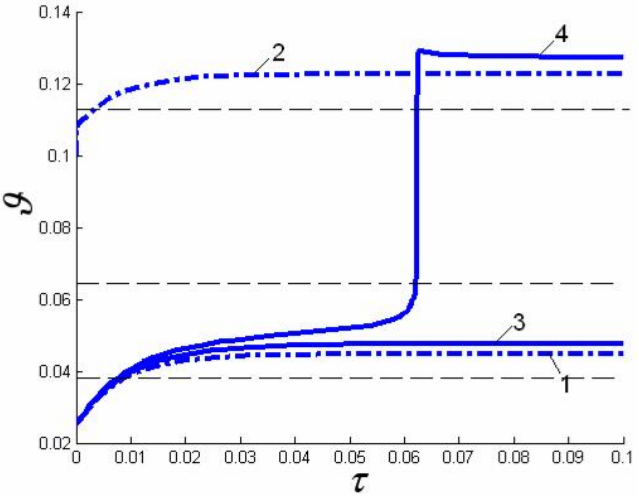

Fig. 5. Sensitivity of reactor to change of coolant temperature: 1, 2 – high- and low temperature stable regimes corresponding point *C* in Fig.2,a: x=0,6; ϑ_{c_0} = 0,025 (1,2); 0,04 (3); 0,055 (4)

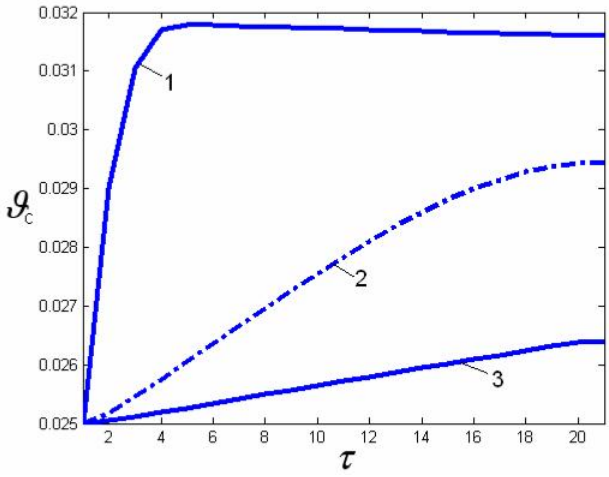

Fig. 6. Influence of inlet coolant flow velocity on coolant temperature: x=0,6; Pe_c=0 (1); 30 (2); 130(3). Other parameters corresponding point *C* in Fig. 2, a

Fig.6 shows the influence of inlet coolant flow velocity on coolant temperature. Due to decreasing rate of heat removal, the coolant temperature higher when coolant velocity is slower (Fig.6, curves 1-3). It was obtained that temperature in reactor increases with decrease in coolant velocity. So it can be concluded that taking into consideration changing coolant temperature along reactor length in the model allows more accurate estimate the effect of wall temperature on reactor behavior.

Conclusions. In this work a one-dimensional model of a co-current fixed-bed reactor with a first-order exothermic reaction was analyzed. The stability investigation was carried out on zero-dimensional model. Using first Lyapunov method and Routh-Hurwitz stability criterion the analytical expressions for stability boundaries were obtained. It was shown that cooled co-current reactor can exhibit unique, multiple, stable and auto-oscillating regimes. Numerically computed regimes are agreed with those predicted approximately-analytically by its character, number of equilibrium states and its range. Thus it can be concluded that zero-dimensional analysis provides a detailed insight into various dynamical modes occurring in the system and gives information about the range of parameters where unique, multiple, stable or unstable regimes exist and therefore to what values the adjustable parameters of the process should be set at numerical computation of complete model.

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Резюме

Исследуется устойчивость и динамика режимов работы трубчатого реактора с неподвижным слоем катализатора, описываемого одномерной моделью тепло-и массопереноса с учетом экзотермической химической реакции 1-го порядка и изменением температуры хладагента по длине реактора. На упрощенной модели с помощью 1-го метода Ляпунова получены параметрические уравнения границ устойчивости и на плоскости параметров системы выделены области с различным типом устойчивости и числом стационарных состояний. Показано, что в реакторе могут иметь место множественные и единственные, автоколебательные и устойчивые режимы окисления. Сравнение предсказанных линейной теорией режимов работы реактора и полученных численно на одномерной модели показало их согласование.

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СХОДИМОСТЬ ИТЕРАЦИОННОГО МЕТОДА ДЛЯ ЛИНЕЙНОЙ МОДЕЛИ ОКЕАНА

Исследована сходимость одного класса итерационного метода для модели океана. Доказано, что решение итерационного метода сходится со скоростью геометрической прогрессии.

Рассмотрим систему уравнений

$$\mathrm{B}v_{\bar{t}}^{n+1} = \mu_0 v_{x_3\bar{x}_3}^{n+1} + \mu\Delta_h v^{n+1} - \hat{\nabla}_h \xi^{n+1} + f_h - \left(\alpha l \times v^{n+1} + \beta l \times v^n\right),\ \alpha + \beta = 1,\ \alpha > 0,\ \beta > 0_h, \quad (1)$$

$$\aleph\, \tau \xi_{\bar{t}}^{n+1} + \sum_{k=1}^{N-1} d\hat{i}v_h v^{n+1} h = 0,\ (\xi,1)_{\Omega_h} = 0. \quad (2)$$

Здесь $\aleph$, τ – итерационные параметры, B – некоторый положительный оператор v.

$$v^0 = v_0,\quad \xi^0 = \xi_0,\quad x \in \overline{\Omega}_h,\quad v^n\big|_{S_h} = 0. \quad (3)$$

В некотором смысле (по аналогам устойчивости двухслойных разностных схем для эллиптического уравнения) этот итерационный метод найлучший. Действительно, если положим $\aleph = 0,\ \mathrm{B} = 0$, то метод сойдется за одну итерацию (хотя в этом случае метод будет неконструктивным). Непосредственно применение теории двухслойных итерационных методов [4] для модели океана затруднительно, потому что запись итерационного метода (5.1), (5.2) отличается от формы классических двухслойных итерационных методов

$$\mathrm{B}y_t + \mathrm{A}y = \varphi.$$

Исследуем сходимость итерационных методов (1)–(3). Переходя к погрешности $\omega^{n+1} = v^{n+1} - v$, $\pi^{n+1} = \xi^{n+1} - \xi$, из (1)–(3) получим сеточную краевую задачу для $\omega^{n+1},\ \pi^{n+1}$: