Chemical Engineering Journal 91 (2003) 159–166

Chemical Engineering Journal

www.elsevier.com/locate/cej

Parametric sensitivity of methanol oxidation process as solution of boundary-value problem with an unknown parameter

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Abstract

A new approach to parametric sensitivity studies of a catalytic fixed-bed operation is presented. This approach is based on the sensitivity functions of technological characteristics with respect to small variations of control parameters under the condition that the pressure drop over the catalyst bed is fixed. The problem of parametric sensitivity of the methanol oxidation process is formulated as an example serving to illustrate the computational technique discussed in the paper. The mathematical model can be written as a boundary-value problem for ordinary differential equations with the linear gas velocity as an unknown parameter. Our approach provides the possibility of estimating the influence of space-nonuniformities on the technological process characteristics in a real fixed-bed reactor using a relatively simple one-dimensional model.

Keywords: Parametric sensitivity; Catalytic fixed-bed; Nonuniformities; Mathematical modeling

1. Introduction

The behavior of chemical reactors depends on variations in the inlet conditions, as well as in other physical and chemical parameters of the system. Operation of a large-scale catalytic fixed-bed reactor may be complicated by high parametric sensitivity with respect to a small change of the process parameters. The general idea can be conveyed with an example of "wrong way behavior" [1]. Attempts to estimate the regions of steady-state multiplicity or stable operation, and to determine parametric sensitivity using conventional technique under the condition of given linear velocity of the gas flow [2,3] may provide essential errors especially for high-exothermic processes. Multidimensional mathematical description accounting for the aerodynamics of the reacting gas flow inside a particulate bed as well as the distribution of physical and chemical properties in the system "catalyst—reactive flow" may hardly be applied for every-day engineering purpose because the choice of an adequate model for a nonlinear chemical process and its parameters is rather complicated [2–5]. Therefore, the parametric sensitivity analysis for processes occurring in the catalytic fixed-bed reactors still attracts attention of researchers and engineers [5–8].

The present study concerns a new approach to analyze a steady-state operation of the catalytic fixed-bed and to determine its parametric sensitivity with respect to small variations of the main process parameters (inlet conditions, catalyst activity, particulate bed structure, etc.) [9–13]. We consider one-dimensional mathematical model under condition that pressure drop over the bed is a priori adjusted but not the gas flow velocity as it used to be done traditionally. As a result, analyzing the one-dimensional model we would be able to perform information about the influence of spatially distributed nonuniformities on the process operation parameters.

Let us consider some separate cylindrical regions differing for example, by porosity and located in the same adiabatic bed of a rather large diameter. Since the pressure is practically uniform over the cross-section both before and after the catalyst bed, the pressure drop (or hydraulic resistance) is the same over each region. At the same time, the local filtering velocities (or gas consumption) in individual cylindrical regions may be different under real process conditions depending on the bed structure, temperature, etc. Therefore, the one-dimensional models which are traditionally used for description of the processes occurring in the catalyst beds and based on the heat and mass balances at the a priori given gas filtering velocity, allow determine only some averaged process parameters that sometimes may give inaccurate conclusions about permitted variations of the control parameters. The assumption of fixed pressure

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PII: S1385-8947(02)00149-3

drop over the catalyst fixed-bed helps to estimate the process parameters, which can be realized in separate cylindrical regions with different inlet or inner bed conditions existed in the same adiabatic bed. Hence, we can observe the local responds to the perturbation of any control parameter. Such conclusions are of course approximate, because the one-dimensional model does not describe the detailed aerodynamics in particulate bed even if takes into account the heat and mass transfer through the outer surface of a separate cylindrical region in concern. Nevertheless, our approach focuses on the sources of potential danger for hot spots to occur in the course of highly exothermic reactions, and allows us more accurate estimating the maximum value for the permitted nonuniformities in the catalytic fixed-bed.

Note that earlier studies for the hydrodynamic problems [14,15], plug flow catalytic reactor [16], and polymerization reactors [17] had shown that there are parameter regions in the parameter space where different flow regimes correspond to the same pressure drop in the considered systems while the liquid phase properties, the viscosity in particular, are strongly dependent on the reaction mixture temperature and composition. This phenomenon is known as *thermomechanical* or *thermoflow multiplicity*. At the same time, for a catalytic system "gas–solid" this problem seemed to be of not high significance, and as a rule the momentum balance is not considered in mathematical models [9,18].

In this work we demonstrate how the effect of the inlet conditions or local structure nonuniformities over the bed cross-section on the temperature distribution at a steady-state operation can be estimated by means of the one-dimensional mathematical model consideration. The sensitivity functions of technological operation characteristics with respect to different control parameters are constructed and the comparative sensitivity analysis of solutions of the model with fixed pressure drop over the bed and the conventional plug flow model is carried out. We have considered an adiabatic fixed-bed and a large-scale unit with four adiabatic catalyst beds and heat exchangers between them.

2. Mathematical model of processes in catalyst fixed-bed

A quasi-homogeneous plug flow model is used to model the steady-state processes in a catalyst fixed-bed reactor. Following [19], we consider the one-dimensional model of methanol to formaldehyde oxidation in the adiabatic fixed-bed of oxide-catalyst:

$$v\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}l} = \boldsymbol{F}(\boldsymbol{x}), \quad \boldsymbol{x}(0) = \boldsymbol{x}^0, \tag{1}$$

where v is the linear gas flow velocity (calculated at normal conditions), the vector $\boldsymbol{x} = (x_1, x_2, x_3, x_4, x_5)$ consists of the volume concentrations of methanol (x_1), formaldehyde (x_2), water (x_3) and oxygen (x_5) (mol/m^3) and the temperature (x_4) (K), $\boldsymbol{x}^0 = (x_{10}, x_{20}, x_{30}, x_{40}, x_{50})$ is the inlet conditions vector, $\boldsymbol{F} = (f_1, f_2, f_3, f_4, f_5)$, $f_1 = -W_1$, $f_2 = W_1 - W_2$, $f_3 = W_1 + W_2$, $f_4 = Q_1W_1 + Q_2W_2$ and $f_5 = -0.5(W_1 + W_2)$; $W_j = (1-\varepsilon)W_{3j}$ $(j = 1, 2)$; ε is the bed porosity, W_{31}, W_{32} are the reaction rates of methanol and formaldehyde oxidation stages referred to the catalyst volume unit [20], Q_1 and Q_2 are the heats of stages, l is the axial coordinate along the bed, $0 < l < L$.

Using balances which are valid for given form of the source function $\boldsymbol{F}(\boldsymbol{x})$

$$\begin{aligned} x_3 &= x_{30} + 2(x_{10} - x_1) + x_{20} - x_2, \\ x_4 &= x_{40} + (Q_1 + Q_2)(x_{10} - x_1) + Q_2(x_{20} - x_2), \\ x_5 &= x_{50} - (x_{10} - x_1) - 0.5(x_{20} - x_2), \end{aligned} \tag{2}$$

we come from the system (1) to a reduced system of only two equations for x_1 and x_2.

Now let us consider the pressure drop over the nonisothermal granular bed. At a given structure of the particulate bed the increase dP in the pressure drop over the length dl is determined by the local flow velocity $\tilde{v}$ through the bed, gas density ρ and dynamic viscosity μ. Regarding the accuracy of practical importance for a wide range of parameters we may use the Ergun equation [21]:

$$\frac{\mathrm{d}P}{\mathrm{d}l} = \alpha_0\mu\tilde{v} + \beta_0\rho\tilde{v}^2, \tag{3}$$

where $P(l)$ denotes the pressure drop over the length l (hence $P(0) = 0$), the constants α_0 and β_0 depend on the properties of the packing and the porosity ε, in particular. If a chemical reaction evolving or consuming heat occurs in the bed then μ, ρ, and $\tilde{v}$ in the contact zone will change along l according to the temperature distribution. We may neglect the effect of the gas composition on the thermal and physical flow properties, assuming that mixture in concern is low-concentrated that is typical for most catalytic processes. Let the reaction occur without volume change, and pressure drop over the bed be much less than the average pressure in the reactor. Then, according to the continuum equation and in assumption of the ideal gas, it follows that:

$$\rho = \rho_0\frac{T_0}{x_4}, \qquad \tilde{v} = v\frac{x_4}{T_0}. \tag{4}$$

Moreover, $\mu = \mu_0\varphi(x_4)$ where ρ_0, μ_0, and v are the density, dynamic viscosity and linear velocity of the gas mixture at STP (273 K and 0.1 MPa).

Integrating the Eq. (3) and using the ratios (4) we get the pressure drop over the nonisothermal particulate bed of the length L

$$\Delta P = \int_0^L A\rho\left(v\frac{x_4}{T_0}\right)^2\left(\frac{\alpha}{Re} + \beta\right)\mathrm{d}l, \tag{5}$$

where $\Delta P = P(L) - P(0)$, A is a coefficient determined by the bed structure and by the catalyst particle size and shape, $Re = Re(v, \varepsilon, x_4)$ is the Reynolds number, α and β are constants.

Therefore, if we introduce a dimensionless axial coordinate $\xi = l/L$, $0 \le \xi \le 1$, and take into consideration the balances (2), the mathematical model for the process in the catalyst bed can be rewritten in the following form:

$$\begin{aligned}\frac{dx_1}{d\xi} &= \frac{L}{v}(1-\varepsilon)W_{31},\\ \frac{dx_2}{d\xi} &= \frac{L}{v}(1-\varepsilon)(W_{31}-W_{32}),\\ \frac{dP}{d\xi} &= A\cdot L\cdot\rho\left(v\frac{x_4}{T_0}\right)^2\left(\frac{\alpha}{Re}+\beta\right),\end{aligned} \qquad (6)$$

with the conditions at the inlet

$$x_1(0)=x_{10},\qquad x_2(0)=x_{20},\qquad P(0)=0, \qquad (7)$$

and given pressure drop over the bed

$$P(1)=\Delta P. \qquad (8)$$

The model (6)–(8) contains the parameter v to be found. Physically, it means that the local gas velocity is determined by the local conditions and tunes after the general pressure drop over the catalyst bed. From the formal point of view, now the mathematical model is the boundary-value problem, and moreover contains one unknown parameter. This is its principal difference from the conventional approach as the initial-value problem (6) and (7). Note that if the thermal-physical parameters ρ and μ of the mixture do not change along the bed, then the gas flow velocity $\tilde{v}$ also does not change, and the relationship (5) between $\tilde{v}$ and ΔP is a quadratic equation. Moreover, both models have the same unique solution under real conditions for the methanol to formaldehyde oxidation process: regimes are completely determined by the inlet conditions $\boldsymbol{x}^0$ and by the gas supply v for the model (6) and (7) in traditional approach or by the pressure drop ΔP for the model (6)–(8).

In order to compare the parametric sensitivity for solutions of two models in a correct way, it is necessary to take ΔP-value in the boundary-value problem (6)–(8) as one corresponded to the gas flow velocity in the initial-value problem (6) and (7). That means the identity of the technological modes in both reactor models considered.

Note, that in case of a more complex reaction scheme we obtain a similar one-dimensional mathematical model consisted of N equations:

$$\frac{dX}{d\xi}=F(x,v,\theta),\qquad X=(x_1,\ldots,x_N)^{\mathrm{T}}, \qquad (9)$$

where the last equation defines the pressure drop again. For such system the approach suggested leads also to a similar boundary conditions with N conditions at the inlet and one condition at the outlet of the catalyst fixed-bed:

$$X(0)=X_0(\theta), \qquad (10)$$

$$x_N(1)=\Delta P(\theta). \qquad (11)$$

where, θ denotes a selected parameter of the model, sensitivity analysis with respect to which is of practical interest.

To solve the boundary-value problem (9)–(11) with the parameter v we used Newton's method, at each iteration step of which the arising linearized boundary-value problem with a parameter was solved numerically by means of the orthogonal factorization method [22]. That allows the solution to be found more accurate in regions of high gradients. Some further details of the numerical technique are presented in the Appendix A.

3. Parametric sensitivity functions

First results on the parametric sensitivity of steady-state processes in catalytic fixed-bed reactors under condition of the given pressure drop over the bed were presented in [10–13]. Now to analyze the sensitivity of the solution X and v of the problem (9)–(11) with respect to a certain parameter θ, we introduce parametric sensitivity functions:

$$Z=\frac{\partial X}{\partial\theta},\qquad u=\frac{\partial v}{\partial\theta}.$$

Differentiation of the problem (9)–(11) with respect to θ gives the corresponding linear boundary-value problem for the vector-function Z and parameter u:

$$\frac{dZ}{d\xi}=F_X(X,v,\theta)\cdot Z+F_\theta(X,v,\theta)+F_v(X,v,\theta)\cdot u, \qquad (12)$$

$$Z(0)=\frac{\partial X_0}{\partial\theta},\qquad z_N(1)=\frac{\partial(\Delta P)}{\partial\theta}, \qquad (13)$$

where X and v represent the solution of the original problem. We solve this problem numerically using the orthogonal factorization method as well (see Appendix A).

In order to make a quantitative comparison of the sensitivities of different x_i-components with respect to various parameters we consider some dimensionless values like in [7]. Thus, we introduce the normalized sensitivity function of the function x_i with respect to a parameter θ:

$$S(x_i,\theta)=\frac{\partial x_i}{\partial\theta}\frac{\theta^*}{x_i^*} \qquad (14)$$

where x_i^* and θ^* stand for some basic values of the x_i-function and parameter θ.

4. Results

In Fig. 1 the temperature and methanol conversion profiles along the reactor with four catalyst beds and heat removal between them are shown. The porosity is 0.45 and gas flow velocity is $v_0 = 1.112$ m/s in each bed. The beds lengths were chosen to provide the methanol conversion to be about 25% in each bed. It allows achieving an almost complete methanol conversion avoiding high temperatures [19,23].

Process robustness is a key operation factor, which is determined first of all by the parametric sensitivity of the operation mode with respect to the control parameters variations. Now let us consider the process in the first catalyst bed. The

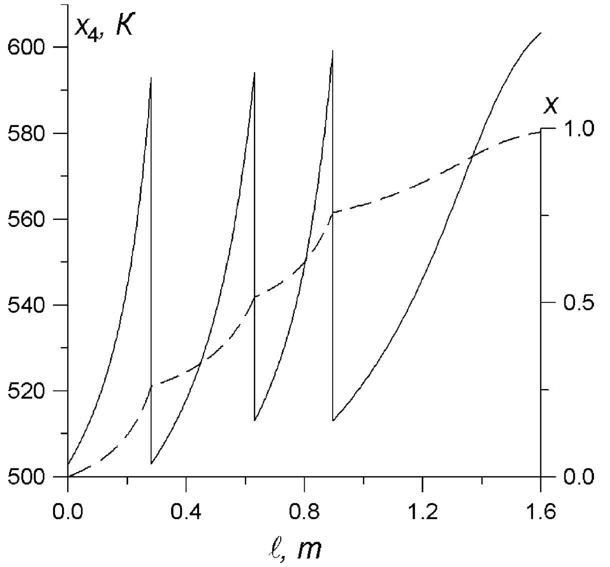

Fig. 1. Profiles of temperature x_4 (solid lines) and methanol conversion x (dash lines) in four adiabatic catalyst beds. The inlet conditions are $x_{10} = 2.93$, $x_{20} = 0$, $x_{30} = 1.34$ and $x_{50} = 4.014\,\mathrm{mol/m^3}$ for the first bed, the inlet temperature is $x_{40} = 503\,\mathrm{K}$ for the first and second beds and $x_{40} = 513\,\mathrm{K}$ for the third and fourth beds.

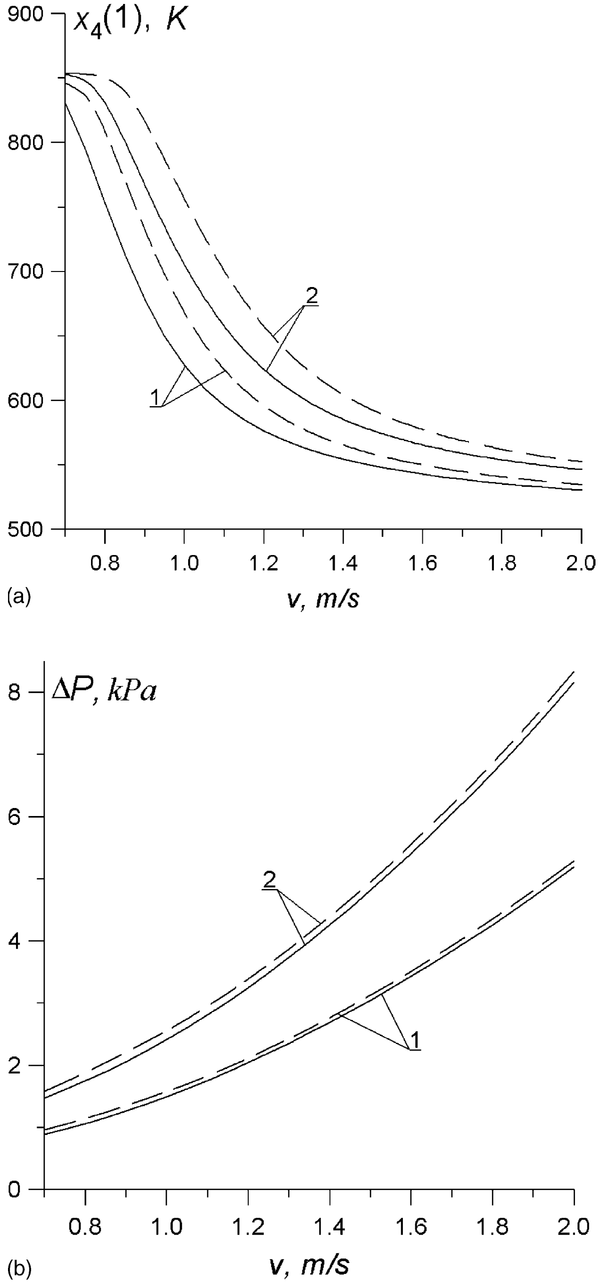

Fig. 2. Temperature at the adiabatic catalyst bed outlet (a) and pressure drop over the bed (b) versus gas flow velocity at various porosities: $\varepsilon = 0.45$ (solid lines), 0.4 (dash lines). Inlet conditions: $x_{10} = 2.93$; $x_{20} = 0$; $x_{30} = 1.34$; $x_{50} = 4.014\,\mathrm{mol/m^3}$; and $x_{40} = 503$ (1), 509 K (2).

outlet temperature $x_4^{\mathrm{out}} = x_4(1)$ is the more important parameter of the state in our case. Fig. 2a shows how the inlet gas mixture temperature affects x_4^{out} at various bed packing. We see that in the bed with the porosity $\varepsilon = 0.4$, at the gas flow velocity $v = v_0$ and temperature $x_{40} = 503\,\mathrm{K}$, the outlet temperature respond to x_{40} change by 1 K equals 12 K, and methanol conversion changes by 2.9%. If the packing is more rough and $\varepsilon = 0.45$, then the parametric sensitivity of x_4^{out} with respect to x_{40} is 7–9 K/K at the same other conditions.

In case we fix the pressure drop over the bed, ΔP, any perturbation of inlet conditions will affect the local gas flow velocity (see Fig. 2b). Since $\Delta P(v)$ is a growing function while $x_4^{\mathrm{out}}(v)$ is a decreasing function, then the parametric sensitivity determined at some definite ΔP_0 is higher than that calculated at constant velocity v_0. Certainly, one should make comparison at the equal values $\Delta P_0 = \Delta P(v_0)$. In fact, for $v = v_0$, $\boldsymbol{x}^0 = (2.93, 0, 1.34, 503, 4.014)$, and $\varepsilon = 0.45$ we obtain $\Delta P_0 = 1.813\,\mathrm{kPa}$. The parametric sensitivity with respect to x_{40} perturbation is by 20–25% higher than that determined by conventional procedure at the given gas velocity $v = v_0$.

Our model (6)–(8) can be used to study the effect of nonuniform structure (the local porosity fluctuations) on the operation mode. Assume that there are cylindrical domains in the bed whose structures are different. With the cylindrical particles of equal height and diameter (that is valid for the process in concern) the typical bed porosity is 0.35–0.45 [21]. At smaller ε the linear gas flow velocity is lower. So, we deal with a longer contact time, higher temperature, and more intensive methanol oxidation going to higher conversions, though formaldehyde produced will be partially oxidized. At larger ε, on the contrary, the gas flow velocity v is higher, and the temperature is lower. Curves shown in Fig. 3 correspond to the gas flow velocities 1.112 m/s (1), 0.814 m/s (2) and 0.541 m/s (3), respectively. Thus curve 1 reveal small gradients along the bed, temperature does not exceed 600 K, and the formaldehyde generation rate dominates over its oxidation rate. The temperature profile 2 has a larger gradient. At last, at $\varepsilon = 0.35$ the mixture filtration through the bed is more slow, and process parameters continue to grow worse (curve 3): almost complete methanol

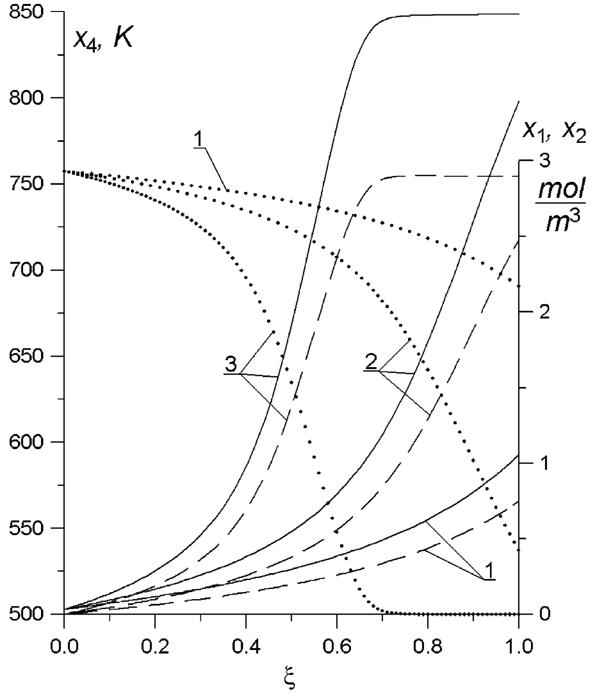

Fig. 3. Temperature and concentration profiles in the adiabatic catalyst bed at x^0=(2.93, 0, 1.34, 503, 4.014), $\Delta P = 1.813\,\text{kPa}$, $\varepsilon = 0.45$ (1), 0.4 (2), 0.35 (3). Dots: x_1, dashes: x_2, solid line: x_4.

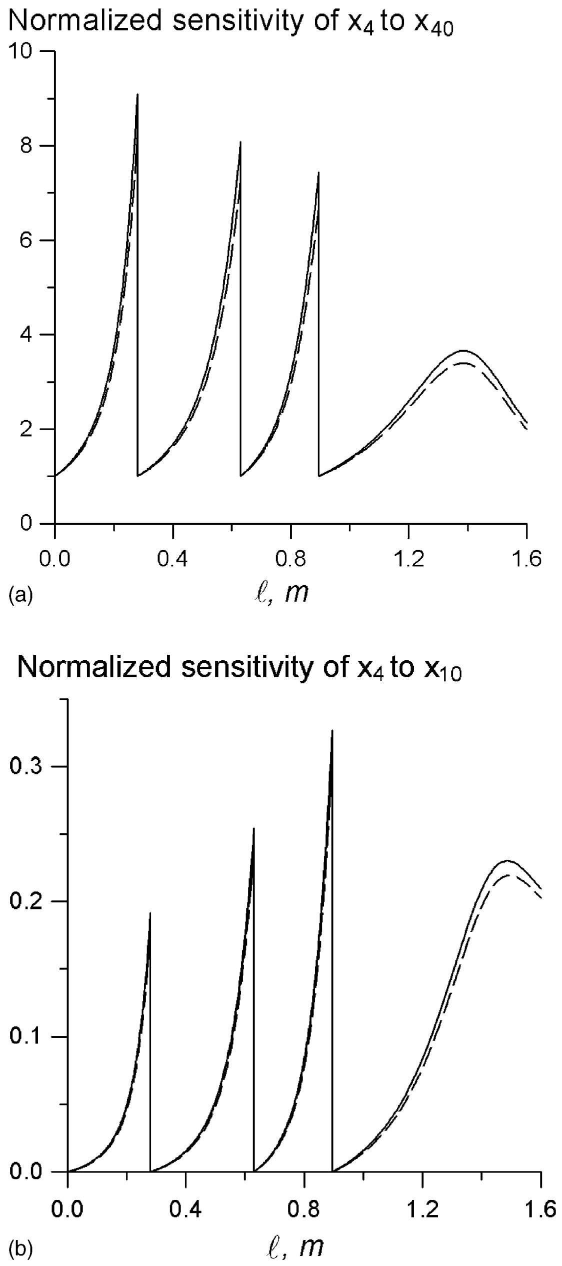

Fig. 4. Normalized sensitivity functions of the temperature x_4 with respect to the inlet temperature (a) and the inlet methanol concentration (b) at the fixed pressure drop (solid lines) and at the given gas flow velocity (dash lines) on each catalyst bed. Conditions correspond to Fig. 1. The inlet temperatures and methanol concentrations at each bed were used as normalizing factors.

conversion occurs at $\xi = 0.7$, and the process selectivity decreases. If we fix the gas flow velocity v and consider the model (6) and (7), then at each velocity corresponding to curves 1–3 in Fig. 3 the same fluctuations of ε lead to the far less changes in temperature and selectivity.

Note that we suppose here that the domains of various porosities do not interact with each other. Therefore, the obtained regimes may realize in the central parts of relatively large domains, being each uniform by structure. However, the mathematical modeling confirms that under consideration of the regarding radial heat and mass transfer on the boundaries of these domains, the temperature difference between them remains quite large though it decreases [13]. This conclusion is also valid for the model describing transfer processes at the fixed gas flow velocity.

If we choose the inlet temperature x_{40} or methanol concentration x_{10} as a selected parameter θ, the normalized sensitivity functions of the temperature x_4 with respect to these parameters do not much distinguish for the model (6)–(8) (solid lines in Fig. 4a and b) and (6) and (7) (dash lines). In this case, the difference in sensitivity is 5–10%. Note also that the sensitivity with respect to the inlet temperature variations decreases from the first to the fourth bed, but the sensitivity with respect to the inlet methanol concentration increases in general.

Another situation is observed with the temperature sensitivity with respect to the structure nonuniformities (see Fig. 5). The sensitivity functions appear to be much bigger in magnitude for the model (6)–(8), what is more compatible with practical surveys. Thus, at the given gas velocity $v_0 = 1.112\,\text{m/s}$ and $\varepsilon = 0.45$, the normalized sensitivity function value equals −0.415 at the first bed outlet, that corresponds to the outlet temperature sensitivity to the porosity as −463.5 K. Then the porosity ε decrease from 0.45 to 0.4 leads to the outlet temperature increase by 23 K and allowed bed structure nonuniformity may be as high as 0.15. If we impose condition (8), then at the same change of

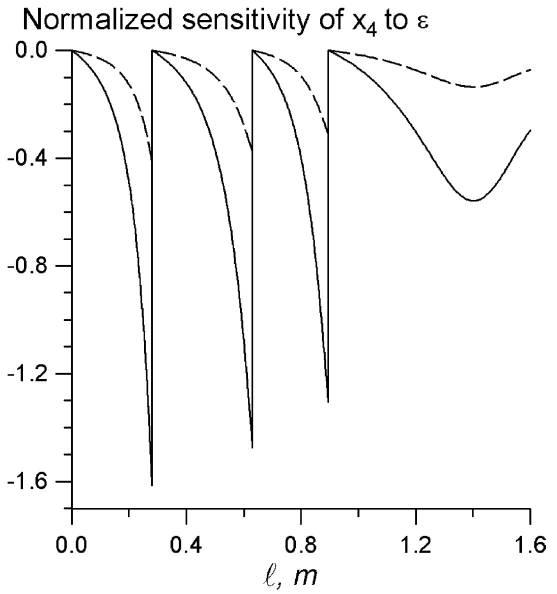

Fig. 5. Normalized sensitivity functions of the temperature x_4 with respect to the local porosity at fixed pressure drop over each catalyst bed (solid lines) and at given gas flow velocity (dash lines). The inlet temperatures at each bed and the porosity value were used as normalizing factors.

ε the outlet temperature increase is by several folds larger. In this case, for the value $\Delta P = 1.813$ kPa (the pressure drop over the catalyst bed at $v_0 = 1.112$ m/s and $\varepsilon = 0.45$) the allowed porosity variations can be not more than 0.04. That means that the catalyst packing should be more uniform than the initial-value problem (6) and (7) estimates.

Fig. 6 shows the sensitivity functions of methanol and formaldehyde concentrations with respect to small variations of the porosity (solid lines) and pressure drop (dash lines) in the first catalyst bed. We can see that the sensitivity to ΔP is not high if compared with sensitivity to ε.

Note that the sensitivity functions estimate the reactor behavior just for the small fluctuations of control parameters considered, i.e. specify the local sensitivity in the parametric space. For appreciable parameter variations the reactor respond can be much different from the predicted by means of sensitivity functions (see Fig. 7). The tangents to the outlet temperature versus porosity curves are determined by the sensitivity functions, and they are close to each other only in a small region near the point of contact. At 0.05 changes in porosity, the sensitivity function in the model (6)–(8) can underestimate the temperature respond for over 100 K.

Experience of catalytic fixed-bed operation shows that some significant nonuniformities of the outlet temperature, so called "hot spots", can appear in the large diameter adiabatic beds. This phenomenon might be caused by the nonuniform bed structure, in particular. In this case it is reasonable to take into account that different regions of the particulate fixed-bed work at the same pressure drop while the local gas flow velocities can be different.

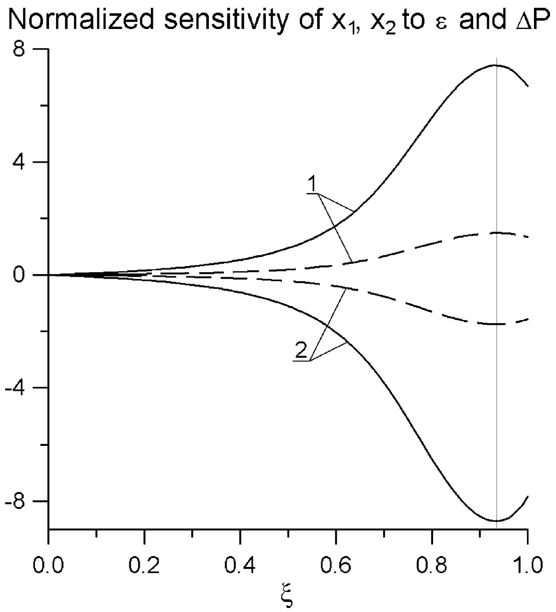

Fig. 6. Normalized sensitivity functions of methanol (1) and formaldehyde (2) concentration in the first bed with respect to the local porosity (solid lines) and pressure drop (dash lines) for $\varepsilon = 0.4$ and $\Delta P = 1.813$ kPa. The inlet conditions correspond to Fig. 1. The inlet methanol and outlet formaldehyde concentrations, the pressure drop over the bed and the porosity values were used as normalizing factors.

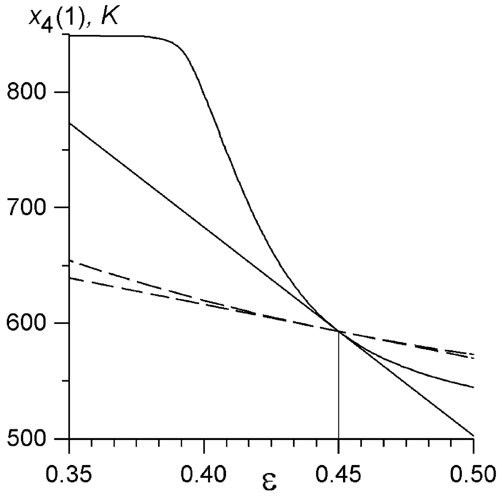

Fig. 7. The outlet temperature of the first bed versus the porosity in boundary-value problem (6)–(8) at $\Delta P = 1.813$ kPa (solid lines) and initial-value problem (6) and (7) at $v = 1.112$ m/s (dash lines). Straight lines are defined with sensitivity functions at $\varepsilon = 0.45$.

5. Conclusion

For efficient and accurate theoretical analysis of the processes in catalytic fixed-bed reactors, a new approach has been described. In the approach the sensitivity functions technique has been adopted for treatment of possible nonuniform temperature spots appearing in real catalyst beds due to fluctuations of the inlet conditions or bed structure parameters.It has been demonstrated that the permitted parameter variations, so-called practical operation stability of steady-state regimes, can be more precise determined by a relatively simple one-dimensional mathematical model under condition that the pressure drop over the bed is given while the local gas flow velocity is to be found. The approach has been successfully applied to the sensitivity analysis of methanol oxidation process on oxide catalyst.

We believe it will be possible to use this technique for various exothermic processes performed in the catalytic fixed-bed reactors. The numerical algorithm applied to solve the boundary-value problem for the system of ordinary differential equations with an unknown parameter appears to be an important tool to determine the parameters region of the efficient and safe catalytic fixed-bed reactors operation.

Acknowledgements

We are grateful to the European Community Program Copernicus-2 for partly funding this work under ICA2-CT-2000-10035.

Appendix A

Here we shall describe the numerical technique for solving the nonlinear boundary-value problem (9)–(11) with the unknown parameter v in detail. This technique is based on the construction of a sequence of approximations of a solution of the problem (9)–(11). We apply the Newton method and the orthogonal factorization method for solving the linear boundary-value problems in the course of iterations [22]. Note that the orthogonal factorization method was used also for solving the linear boundary-value problem (12) and (13) with the parameter u for sensitivity functions.

When the values X^0, v^0 (previous approximation) of the vector X and parameter v are known, after linearization within a neighborhood of X^0, v^0 the boundary-value problem for the functions $\tilde{X}(\xi) = X(1-\xi)$ can be written in the following form

$$\frac{d\tilde{X}}{d\xi} = A(\tilde{X}^0, v^0)\tilde{X} + f(\tilde{X}^0, v^0) + g(\tilde{X}^0, v^0)\,(v - v^0), \tag{A.1}$$

$$\tilde{x}_N(1) = \Delta P, \qquad \tilde{X}(0) = X_0,$$

where

$$A(\tilde{X}^0, v^0) = -F_X(\tilde{X}^0, v^0),$$
$$f(\tilde{X}^0, v^0) = F_X(\tilde{X}^0, v^0)\tilde{X}^0 - F(\tilde{X}^0, v^0),$$
$$g(\tilde{X}^0, v^0) = -F_v(\tilde{X}^0, v^0).$$

Its solution $\tilde{X}$, v is used as the next approximation of X and v. For a proper choice of the initial approximation the described iteration procedure converges to the solution of the original nonlinear problem (9)–(11).

The linear boundary-value problem (A.1) is solved numerically by means of the orthogonal factorization method [22]. Being applied to the problem (A.1) with the parameter v this algorithm has the following scheme. The interval [0, 1] is divided into several subintervals $0 = \xi_0 < \xi_1 < \cdots < \xi_l = 1$ by a proper way. On each subinterval the solution is found as the following linear combination:

$$\tilde{X}(\xi) = U_N(\xi) + (v - v^0)U_{N+1}(\xi) + \sum_{j=1}^{N-1}\beta_j^s U_j(\xi),$$
$$\xi_s \le \xi < \xi_{s+1}, \tag{A.2}$$

where the coefficients β_j^s and $\gamma = v - v^0$ are determined from conditions at the point $\xi = 1$, and the vector functions $U_j(\xi)$ for $j = 1, \dots, N+1$ are determined at the "straight-run stage" consecutively on each subinterval $[\xi_s, \xi_{s+1}]$ for $s = 0, \dots, l-1$ as solutions of the following initial-value problems, respectively:

$$\frac{dU_j}{d\xi} = A(\tilde{X}^0, v^0)U_j(\xi), \qquad U_j(\xi_s) = Z_j(\xi_s),$$
$$j = 1, \dots, N-1,$$

$$\frac{dU_N}{d\xi} = A(\tilde{X}^0, v^0)U_N(\xi) + f(\tilde{X}^0, v^0),$$
$$U_N(\xi_s) = Z_N(\xi_s),$$

$$\frac{dU_{N+1}}{d\xi} = A(\tilde{X}^0, v^0)U_{N+1}(\xi) + g(\tilde{X}^0, v^0),$$
$$U_{N+1}(\xi_s) = Z_{N+1}(\xi_s).$$

The corresponding initial conditions for these problems are determined as follows.

For $s = 0$ the initial conditions are chosen at $\xi = 0$:

$$Z_1(0) = \boldsymbol{e}_1, \ \dots, \ Z_{N-1}(0) = \boldsymbol{e}_{N-1},$$
$$Z_N(0) = \Delta P \cdot \boldsymbol{e}_N, \qquad Z_{N+1}(0) = \boldsymbol{0},$$

where $\boldsymbol{e}_j$ is the N-dimensional vector with jth component equals 1 and other components equal to 0. Thus the vectors $\{Z_j(0)\}_{j=1}^{N-1}$ form an orthonormal basis in the subspace satisfied to the uniform condition at the point $\xi = 0$, while the vector $Z_N(0)$ is orthogonal to each $Z_j(0)$ for $j = 1, \dots, N-1$, and satisfies the nonuniform condition at $\xi = 0$. Thus we have a complete set of initial conditions. Now, we can integrate the above system from $\xi_0 = 0$ to $\xi = \xi_1$ and obtain the values $\{U_j(\xi_1)\}_{j=1}^{N+1}$ at the end-point of the first subinterval.

At the point ξ_s for $s = 1, \dots, l$ the vectors $\{Z_j(\xi_s)\}_{j=1}^{N-1}$ are defined from the system $\{U_j(\xi_s)\}_{j=1}^{N-1}$ by the orthogonalization by use the reflection method, thus the initial conditions at ξ_s are an orthonormal system. The vectors $Z_N(\xi_s)$ and $Z_{N+1}(\xi_s)$ are obtained as projections of $U_N(\xi_s)$ and $U_{N+1}(\xi_s)$ on the orthogonal supplement to the linear span of $\{U_j(\xi_s)\}_{j=1}^{N-1}$. We can write this transformation in a matrix form:

$$[U_1(\xi_s), \dots, U_{N+1}(\xi_s)] = [Z_1(\xi_s), \dots, Z_{N+1}(\xi_s)] \times \begin{pmatrix} R_s & r_N^s & r_{N+1}^s \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

where R_s is a square upper-triangular matrix, and vector r_{N+i}^s for $i = 0$ or 1 consists of the resolution coefficients of $U_{N+i}(\xi_s)$ by the basis $\{Z_j(\xi_s)\}_{j=1}^{N-1}$.

Further, substituting expression (A2) to the conditions at $\xi = 0$ we obtain the parameter value $v = v^0 + \gamma$ and vector $\beta^l = (\beta_1^l, \dots, \beta_{N-1}^l)^{\mathrm{T}}$ by solving the following linear algebraic system:

$$\sum_{j=1}^{N-1} \beta_j^l Z_j(1) + \gamma Z_{N+1}(1) = X_0 - Z_N(1).$$

Finally at the “backward stage” using conditions of the solution continuity at the points ξ_s we consecutively obtain vectors $\boldsymbol{\beta}^l = (\beta_1^l, \dots, \beta_{N-1}^l)^T$ for $s = l-1, \dots, 0$ from the relationship

$$R_{s+1}\beta^s = \beta^{s+1} - r_N^{s+1} - \gamma r_{N+1}^{s+1}.$$

Thus, we can build the solution of the linearized boundary-value problem (A.1) in the form (A.2) in each subinterval.

The algorithm described allows avoiding the effect of basis “squashing”, i.e. situations when during integration of initial-value problems from the orthogonal initial conditions some of the angles between the vectors $\{U_j(\xi_s)\}_{j=1}^{N}$ vanish and the solution of the linearized boundary-value problem (A.1) cannot be computed as a linear combination of these vectors. The partition of integration interval and the vectors orthogonalization at the end-point of each subinterval provide more accurate construction of the linearized boundary-value problem (A.1) solution over the whole interval.

A general computer code for these procedures has been developed.

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