

Тема 3.10.6. МОДЕЛИРАНЕ И СИМУЛИРАНЕ НА ХИМИЧНИ И КАТАЛИТИЧНИ ПРОЦЕСИ В ИНДУСТРИАЛНИ КОЛОННИ АПАРАТИ

MODELING AND SIMULATION OF CHEMICAL AND CATALYTIC PROCESSES IN INDUSTRIAL COLUMN APPARATUSES

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Хорариум:

30 учебни часа

Анотация:

В курса се предлагат методите за моделиране и симулиране на химични и каталитични процеси в колонни промишлени апарати, развити в монографиите:

Chr. Boyadjiev, "Theoretical Chemical Engineering. Modeling and simulation", Springer-Verlag, Berlin Heidelberg, 2010, pp. 594.

Chr. Boyadjiev, M. Doichinova, B. Boyadjiev, P. Popova-Krumova, "Modeling of Column Apparatus Processes", Springer-Verlag, Berlin Heidelberg, 2016, pp. 313.

Ще бъдат разгледани конвективно-дифузионни и средно-концентрационни модели в приближенията на механиката на непрекъснатите среди в случаите на прости и сложни хомогенни химични реакции и на хетерогенни каталитични реакции в системи газ (течност)-твърдо, когато адсорбционният етап е физичен или химичен. Разглежданите модели дават възможност за качествен и количествен анализ на химични и каталитични процеси в колонни промишлени апарати. Ще бъдат разгледани и изчислителните проблеми при симулирането на разглежданите процеси.

Annotation:

In the course are presented the methods for modeling and simulation of chemical and catalytic processes in column industrial apparatuses, developed in the monographs:

Chr. Boyadjiev, "Theoretical Chemical Engineering. Modeling and simulation", Springer-Verlag, Berlin Heidelberg, 2010, pp. 594.

Chr. Boyadjiev, M. Doichinova, B. Boyadjiev, P. Popova-Krumova, "Modeling of Column Apparatus Processes", Springer-Verlag, Berlin Heidelberg, 2016, pp. 313.

Will be discussed the convective- diffusion and average-concentration models in approximations of Mechanics of Continua in cases of simple and complex homogeneous chemical reactions and heterogeneous catalytic reactions in the gas (liquid)-solid systems when the adsorption stage is physically or chemically. The models considered are suitable for qualitative and quantitative analysis of the chemical and catalytic processes in industrial column apparatuses. Will be discussed the calculation problems of the process simulations.

Литература:

Chr. Boyadjiev, M. Doichinova, B. Boyadjiev, P. Popova-Krumova, "Modeling of Column Apparatus Processes", Springer-Verlag, Berlin Heidelberg, 2016, pp. 313.

Страници 61-84, 123-133, 165-168, 169-178, 211-222, 233-246.

ПЪЛЕН ТЕКСТ

The fundamental problem of the one-phase processes modeling in the column apparatuses comes from the complicated hydrodynamic behavior of the flow and as a result the velocity distribution in the column is unknown. This problem can be avoided using a new approach on the basis of the physical approximations of the mechanics of continua [1–4].

One-phase fluid motion in cylindrical column apparatus [4] with radius r_0 [m] and active zone height l [m] will be considered. The convection-diffusion model is possible to be obtained from ((I.3)–(I.5)), where (in the case of one-phase fluid motion) the phase index $j=1,2,3$ is possible to be ignored. As a result $\varepsilon_1=1$ ($\varepsilon_2=\varepsilon_3=0$) or $\varepsilon_2=1$ ($\varepsilon_1=\varepsilon_3=0$),

$u_j(r,z)=u(r,z)$, $v_j(r,z)=v(r,z)$, $c_{ij}(t,r,z)=c_i(t,r,z)$, $Q_{ij}(c_{ij})=Q_i(c_1,c_2,\dots,c_{i_0})$, $i=1,2,\dots,i_0$;

$$u \frac{\partial c_i}{\partial z} + v \frac{\partial c_i}{\partial r} = D_i \left(\frac{\partial^2 c_i}{\partial z^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right) + Q_i(c_1, c_2, \dots, c_{i_0});$$

$$r=0, \quad \frac{\partial c_i}{\partial r} \equiv 0; \quad r=r_0, \quad \frac{\partial c_i}{\partial r} \equiv 0;$$

$$z=0, \quad c_i \equiv c_i^0, \quad u^0 c_i^0 \equiv u c_i^0 - D_i \frac{\partial c_i}{\partial z}; \quad i=1,2,\dots,i_0. \quad (0.0.1)$$

The axial and radial velocity components $u(r,z)$ and $v(r,z)$ satisfy the continuity equation (I.4).

1 Column Chemical Reactor

The main process in one-phase column apparatuses is mass transfer of a component of the moving fluid complicated with volume chemical reaction. The quantitative description of

this process in column chemical reactors is possible if the axial distribution of the average concentration $\bar{c}(z)$ over the cross-sectional area of the column is known:

$$\begin{aligned} \bar{c} &= \bar{c}(z), \quad 0 \leq z \leq l, \quad \bar{c}(0) = c^0, \quad \bar{c}(l) = c^l, \\ G &= \frac{c^0 - c^l}{c^0}, \quad c^0 > c^l, \end{aligned} \quad (0.1.1)$$

where $z=0$ ($z=l$) is the column inlet (outlet) and G is the conversion degree. Two main problems are possible to be solved on this basis:

- modeling (design) problem, i.e., to obtain l if G and c_0 are given;
- simulation (control) problem, i.e., to obtain G if l and c_0 are given.

The axial distribution of the average concentration $\bar{c}(z)$ is to be obtained as a solution of the mass transfer model equations. The modeling problems of the column chemical reactors are possible to be solved using a convection-diffusion type model.

1.1 Convection-diffusion type model

In the stationary case the convection-diffusion model of a two component chemical reaction in the column apparatuses [3] has the form:

$$u \frac{\partial c_i}{\partial z} + v \frac{\partial c_i}{\partial r} = D_i \left(\frac{\partial^2 c_i}{\partial z^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right) + Q_i(c_1, c_2), \quad i=1,2, \quad (0.1.2)$$

where $D_i, i=1,2$, are the diffusivities of the reagents in the fluid [$\text{m}^2 \cdot \text{s}^{-1}$].

The axial and radial velocity components $u(r, z)$ and $v(r, z)$ satisfy the continuity equation:

$$\frac{\partial u}{\partial z} + \frac{\partial v}{\partial r} + \frac{v}{r} = 0; \quad r = r_0, \quad v(r_0, z) \equiv 0, \quad z = 0, \quad u \equiv u(r, 0). \quad (0.1.3)$$

The model of the mass transfer processes in the column apparatuses (2.1.2) includes boundary conditions, which express a symmetric concentration distribution ($r=0$), impenetrability of the column wall ($r=r_0$), a constant inlet concentration $c_i^0, i=1,2$, [$\text{kg} \cdot \text{mol} \cdot \text{m}^{-3}$] and mass balance at the column input ($z=0$), i.e. the inlet mass flow ($u^0 c_i^0$) is divided into a convective mass flow ($u c_i^0$) and a diffusion mass flow ($-D_i \partial c_i / \partial z$):

$$\begin{aligned} r = 0, \quad \frac{\partial c_i}{\partial r} &\equiv 0; \quad r = r_0, \quad \frac{\partial c_i}{\partial r} \equiv 0; \\ z = 0, \quad c_i &\equiv c_i^0, \quad u^0 c_i^0 \equiv u c_i^0 - D_i \frac{\partial c_i}{\partial z}, \quad i=1,2, \end{aligned} \quad (0.1.4)$$

where u^0 [$\text{m} \cdot \text{s}^{-1}$] is the velocity at the column input. In (2.1.4) it is supposed that a symmetric radial velocity distribution will lead to a symmetric concentration distribution, too. The term $Q_i(c_1, c_2), i=1,2$ in (2.1.2) represents the volume chemical reaction rate (chemical kinetics model).

The mass transfer efficiency (g_i) in the column and conversion degree (G_i) are possible to be obtained using the inlet and outlet average convective mass flux at the cross-sectional area surface in the column:

$$g_i = u^0 c_i^0 - \frac{2}{r_0^2} \int_0^{r_0} r u(r, l) c_i(r, l) dr, \quad G_i = \frac{g_i}{u^0 c_i^0}, \quad i=1,2. \quad (0.1.5)$$

The average values of the velocity at the column cross-sectional area can be presented as

$$\bar{u}(z) = \frac{2}{r_0^2} \int_0^{r_0} ru(r, z) dr, \quad \bar{v}(z) = \frac{2}{r_0^2} \int_0^{r_0} rv(r, z) dr, \quad (0.1.6)$$

The velocity distributions assume to be presented by the average functions (2.1.6):

$$u(r, z) = \bar{u}(z)\tilde{u}(r, z), \quad v(r, z) = \bar{v}(z)\tilde{v}(r, z), \quad (0.1.7)$$

where $\tilde{u}(r, z), \tilde{v}(r, z)$ represent the radial non-uniformity of the velocity distributions satisfying the conditions:

$$\frac{2}{r_0^2} \int_0^{r_0} r\tilde{u}(r, z) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r\tilde{v}(r, z) dr = 1. \quad (0.1.8)$$

A differentiation of $u(r, z)$ in (2.1.7) with respect to z leads to:

$$\frac{\partial u}{\partial z} = \frac{d\bar{u}}{dz}\tilde{u} + \bar{u}\frac{\partial \tilde{u}}{\partial z}. \quad (0.1.9)$$

Practically, the cross-sectional area surface in the columns is a constant and the average velocity is a constant too ($d\bar{u}/dz = 0, \bar{u} = u^0$), i.e. $\partial u/\partial z \equiv 0$ if $\partial \tilde{u}/\partial z \equiv 0$ ($u = u(r), \tilde{u} = \tilde{u}(r)$).

In this case (practically $\partial \tilde{u}/\partial z \equiv 0$ in column apparatuses with big radius values, where the laminar boundary layer thickness at the column wall is negligible with respect to the column radius value) from (2.1.3) follows:

$$\frac{dv}{dr} + \frac{v}{r} = 0; \quad r = r_0, \quad v = 0 \quad (0.1.10)$$

and the solution is $v(r) \equiv 0$. This leads to a new form of the convection-diffusion type model [4]:

$$\begin{aligned} u \frac{\partial c_i}{\partial z} &= D_i \left(\frac{\partial^2 c_i}{\partial z^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right) + Q_i(c_1, c_2); \\ r = 0, \quad \frac{\partial c_i}{\partial r} &\equiv 0; \quad r = r_0, \quad \frac{\partial c_i}{\partial r} \equiv 0; \\ z = 0, \quad c_i &\equiv c_i^0, \quad u^0 c_i^0 \equiv u c_i^0 - D_i \frac{\partial c_i}{\partial z}; \quad i = 1, 2. \end{aligned} \quad (0.1.11)$$

The presented convection-diffusion type model (2.1.11) is possible to be used for the qualitative analysis of different chemical processes in the column apparatuses.

1.2 Complex chemical reaction kinetics

The complex chemical reaction rate is a function of the reagent concentrations. When the reaction rate is denoted by y and the reagent concentrations by x_1, \dots, x_m the next model equation will be used:

$$y = f(x_1, \dots, x_m). \quad (0.1.12)$$

The function f (like models of all physical processes) is invariant regarding the dimension transformations of the reagent concentration, i.e. this mathematical structure is invariant regarding similarity transformations [3]:

$$\bar{x}_i = k_i x_i, \quad i = 1, \dots, m, \quad (0.1.13)$$

i.e.

$$\begin{aligned} ky &= f(k_1 x_1, \dots, k_m x_m) = \varphi(k_1, \dots, k_m) \cdot f(x_1, \dots, x_m), \\ k &= \varphi(k_1, \dots, k_m). \end{aligned} \quad (0.1.14)$$

From (2.1.14) it follows that f is a homogenous function, i.e. the relation between the dependent and independent variables in the models is possible to be presented (approximated) by a homogenous function, when the model equations are invariant regarding similarity transformations.

A short recording of (2.1.14) is:

$$f[\bar{x}_i] = \phi[k_i] f[x_i]. \quad (0.1.15)$$

The problem consists in finding a function f that satisfies equation (2.1.15). A differentiation of equation (2.1.15) concerning k_1 leads to:

$$\frac{\partial f[\bar{x}_i]}{\partial k_1} = \frac{\partial \phi}{\partial k_1} f(x_i). \quad (0.1.16)$$

On the other hand

$$\frac{\partial f[\bar{x}_i]}{\partial k_1} = \frac{\partial f[\bar{x}_i]}{\partial \bar{x}_1} \frac{\partial \bar{x}_1}{\partial k_1} = \frac{\partial f[\bar{x}_i]}{\partial \bar{x}_1} x_1. \quad (0.1.17)$$

From (2.1.16) and (2.1.17) follows

$$\frac{\partial f[\bar{x}_i]}{\partial \bar{x}_1} x_1 = b_1 f[x_i], \quad (0.1.18)$$

where

$$b_1 = \left(\frac{\partial \phi}{\partial k_1} \right)_{k_i=1}. \quad (0.1.19)$$

The equation (2.1.18) is valid for different values of k_i including $k_i=1$ ($i=1, \dots, m$). As a result $\bar{x}_i = x_i$, $i=1, \dots, m$ and from (2.1.18) follows

$$\frac{1}{f} \frac{\partial f}{\partial x_1} = \frac{b_1}{x_1}, \quad (0.1.20)$$

i.e.

$$f = c_1 x_1^{b_1}. \quad (0.1.21)$$

When the above operations are repeated for x_2, \dots, x_m the homogenous function f assumes the form:

$$f = c x_1^{b_1}, \dots, x_m^{b_m}, \quad (0.1.22)$$

i.e. the function f is homogenous if it represents a power functions complex and as a result is invariant with respect to similarity (metric) transformations.

The result obtained shows that the chemical reaction rate in (2.1.11) is possible to be presented as

$$\frac{\partial c_i}{\partial t} = Q_i(c_1, c_2) = k_i c_1^m c_2^n, \quad i=1, 2. \quad (0.1.23)$$

1.3 Two components chemical reaction

Let's consider a complex chemical reaction in the column and $c_i(r, z)$ $i=1, 2$ are the concentrations [kg·mol·m⁻³] of the reagents. In this case the model (2.1.11) has the form:

$$\begin{aligned}
u \frac{\partial c_i}{\partial z} &= D_i \left(\frac{\partial^2 c_i}{\partial z^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right) - k_i c_1^m c_2^n; \\
r = 0, \quad \frac{\partial c_i}{\partial r} &\equiv 0; \quad r = r_0, \quad \frac{\partial c_i}{\partial r} \equiv 0; \\
z = 0, \quad c &\equiv c_i^0, \quad u^0 c_i^0 \equiv u c_i^0 - D_i \frac{\partial c_i}{\partial z}, \quad i = 1, 2.
\end{aligned} \tag{0.1.24}$$

The qualitative analysis of the model (2.1.24) will be made using generalized variables [3]:
 $r = r_0 R, \quad z = l Z, \quad u(r) = u(r_0 R) = u^0 U(R), \quad \tilde{u}(r) = \tilde{u}(r_0 R) = U(R),$

$$c_i(r, z) = c_i(r_0 R, l Z) = c_i^0 C_i(R, Z) \quad (i = 1, 2), \quad \varepsilon = \left(\frac{r_0}{l} \right)^2, \tag{0.1.25}$$

where r_0, l, u^0, c_i^0 ($i = 1, 2$) are the characteristic (inherent) scales (maximal or average values) of the variables. The introduction of the generalized variables (2.1.25) in (2.1.24) leads to:

$$\begin{aligned}
U \frac{\partial C_i}{\partial Z} &= \text{Fo}_i \left(\varepsilon \frac{\partial^2 C_i}{\partial Z^2} + \frac{1}{R} \frac{\partial C_i}{\partial R} + \frac{\partial^2 C_i}{\partial R^2} \right) - \text{Da}_i C_1^m C_2^n; \\
R = 0, \quad \frac{\partial C_i}{\partial R} &\equiv 0; \quad R = 1, \quad \frac{\partial C_i}{\partial R} \equiv 0; \\
Z = 0, \quad C_i &\equiv 1, \quad 1 \equiv U - \text{Pe}_i^{-1} \frac{\partial C_i}{\partial Z};
\end{aligned} \tag{0.1.26}$$

$$\begin{aligned}
\text{Fo}_i &= \frac{D_i l}{u_0 r_0^2}, \quad \text{Da}_i = \theta^{i-1} \text{Da}_i^0, \quad \text{Pe}_i = \frac{u_0 l}{D_i}, \\
\text{Da}_i^0 &= \frac{k_i l}{u_0} (c_1^0)^{m-1} (c_2^0)^n, \quad \theta = \frac{c_1^0}{c_2^0}; \quad i = 1, 2,
\end{aligned}$$

where Fo, Da and Pe are the Fourier, Damkohler and Peclet numbers, respectively.

1.4 Comparison qualitative analysis

As already noted [3, 4] when variable scales in (2.1.25) the maximal or average variable values are used. As a result the unity is the order of magnitude of all functions and their derivatives in (2.1.26), i.e. the effects of the physical and chemical phenomena (the contribution of the terms in (2.1.26)), are determined by the orders of magnitude of the dimensionless parameters in (2.1.26). If all equations in (2.1.26) are divided by the dimensionless parameter, which has the maximal order of magnitude, all terms in the model equations will be classified in three parts:

1. The parameter is unity or its order of magnitude is unity, i.e. this mathematical operator represents a main physical effect;
2. The parameter's order of magnitude is 10^{-1} , i.e. this mathematical operator represents a small physical effect;
3. The parameter's order of magnitude is $\leq 10^{-2}$, i.e. this mathematical operator represents a very small (negligible) physical effect and has to be neglected, because it is not possible to be measured experimentally.

Here and throughout the book it has to be borne in mind that the process (model) is composed of individual effects (mathematical operators) and if their relative role (influence) in the overall process (model) is less than 10^{-2} they have to be ignored, because the inaccuracy of the experimental measurements is above 1%.

1.5 Pseudo-first-order reactions

In the cases of big difference between inlet concentrations of the reagents ($c_1^0 \ll c_2^0$) in (2.1.24) the problem described by (2.1.26) is possible to be solved in zero approximation with respect to the very small parameter θ ($0 = \theta \leq 10^{-2}$) and as a result $Da_2 = 0, C_2 \equiv 1$. Very often $m = 1$ and from (2.1.26) follows:

$$U \frac{\partial C}{\partial Z} = Fo \left(\varepsilon \frac{\partial^2 C}{\partial Z^2} + \frac{1}{R} \frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial R^2} \right) - Da C; \quad \varepsilon = Fo^{-1} Pe^{-1};$$

$$R = 0, \quad \frac{\partial C}{\partial R} \equiv 0; \quad R = 1, \quad \frac{\partial C}{\partial R} \equiv 0; \quad Z = 0, \quad C \equiv 1, \quad 1 \equiv U - Pe^{-1} \frac{\partial C}{\partial Z}; \quad (0.1.27)$$

where $C = C_1, Da = Da_1^0$ and model (2.1.27) of column apparatuses with pseudo-first-order chemical reaction is obtained. The parameters ε and Fo are related with the column radius r_0 and as a result the convection-diffusion type of model (2.1.27) is possible to be used for solving the scale-up problem.

1.6 Similarity conditions

From (2.1.27) follows that two mass transfer processes in column apparatuses are similar if the parameters values of Fo, Da, Pe and ε are identical, i.e. these parameters are similarity criteria. In the real cases when the difference between two similar processes is in the parameter values $r_0^s, l^s, u_0^s, s = 1, 2$, from the similarity conditions follows:

$$Fo = \frac{D l^s}{u_0^{0s} r_0^{s2}}, \quad Da = \frac{k l^s}{u_0^{0s}}, \quad Pe = \frac{u_0^{0s} l^s}{D}, \quad \varepsilon = \left(\frac{r_0^s}{l^s} \right)^2, \quad s = 1, 2. \quad (0.1.28)$$

From (2.1.28) follow three expressions for the characteristic velocity:

$$u_0^{0s} = \frac{D}{\sqrt{\varepsilon} r_0^s Fo}, \quad u_0^{0s} = \frac{k r_0^s}{\sqrt{\varepsilon} Da}, \quad u_0^{0s} = \frac{D Pe \sqrt{\varepsilon}}{r_0^s}, \quad s = 1, 2, \quad (0.1.29)$$

i.e. the similarity criteria Fo, Da are incompatible, because from (2.1.29) follows, that (at constant values of Fo, Da and ε) the increase of the radius r_0 (from laboratory model to industrial apparatus) leads to decrease and increase of the velocity u_0^{0s} simultaneously. The increase of the radius r_0 is not possible to be compensated by the changes of velocity u_0^{0s} (practically the change of r_0^s is not possible to be compensated by the changes of D and k). These results show that the physical modeling is not possible to be used for a quantitative description of the mass transfer processes in column chemical reactors, i.e. the convection-diffusion model with radius r_0^1 is not physical model of the real process with radius r_0^2 if $r_0^1 \neq r_0^2$. The similar situation exists in two-phase processes with chemical reaction.

2 Model Approximations

The presentation of the models in generalized variables [3] permits to obtain different approximations of the models, i.e. the approximations of small ($\sim 10^{-1}$) and very small ($\leq 10^{-2}$, negligible) parameters.

2.1 Short columns model

For short columns $\varepsilon = (r_0/l)^2 = Fo^{-1} Pe^{-1}$ is a small parameter ($\varepsilon \sim 10^{-1}$), i.e. $Pe^{-1} \leq 10^{-1} Fo$ and for $Fo \leq 1$ the next small parameter is Pe^{-1} ($Pe^{-1} \leq 10^{-1}$). In these cases the problem (2.1.27) is possible to be solved using the perturbation method (see Chapter 7 and [6]):

$$C(R, Z) = C^{(0)}(R, Z) + \varepsilon C^{(1)}(R, Z) + \varepsilon^2 C^{(2)}(R, Z) + \dots, \quad (0.2.1)$$

where $C^{(0)}, C^{(1)}, C^{(2)}, \dots$ are solutions of the next problems:

$$U \frac{\partial C^{(0)}}{\partial Z} = \text{Fo} \left(\frac{1}{R} \frac{\partial C^{(0)}}{\partial R} + \frac{\partial^2 C^{(0)}}{\partial R^2} \right) - \text{Da} C^{(0)};$$

$$R = 0, \quad \frac{\partial C^{(0)}}{\partial R} \equiv 0; \quad R = 1, \quad \frac{\partial C^{(0)}}{\partial R} \equiv 0;$$

$$Z = 0, \quad C^{(0)} \equiv 1. \quad (0.2.2)$$

$$U \frac{\partial C^{(s)}}{\partial Z} = \text{Fo} \left(\frac{1}{R} \frac{\partial C^{(s)}}{\partial R} + \frac{\partial^2 C^{(s)}}{\partial R^2} \right) - \text{Da} C^{(s)} + \text{Fo} \frac{\partial^2 C^{(s-1)}}{\partial Z^2};$$

$$R = 0, \quad \frac{\partial C^{(s)}}{\partial R} \equiv 0; \quad R = 1, \quad \frac{\partial C^{(s)}}{\partial R} \equiv 0;$$

$$Z = 0, \quad C^{(s)} \equiv 0; \quad s = 1, 2, \dots \quad (0.2.3)$$

A multi-step procedure has to be used for solving (2.2.2) and (2.2.3):

1. Solving (2.2.2) and calculating $\frac{\partial^2 C^{(0)}}{\partial Z^2}$;
2. Solving of (2.2.3) and calculating $\frac{\partial^2 C^{(s-1)}}{\partial Z^2}, s = 1, 2, \dots$.

2.2 High-column model

For high columns ε is a very small parameter and the problem (2.1.27) is possible to be solved in zero approximation with respect to ε ($0 = \varepsilon \leq 10^{-2}$), i.e. $\text{Pe}^{-1} \leq 10^{-2} \text{Fo}$ and for $\text{Fo} \leq 1$ the next very small parameter is Pe^{-1} ($0 = \text{Pe}^{-1} \leq 10^{-2}$), i.e. $C = C^{(0)}$:

$$U \frac{\partial C}{\partial Z} = \text{Fo} \left(\frac{1}{R} \frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial R^2} \right) - \text{Da} C;$$

$$R = 0, \quad \frac{\partial C}{\partial R} \equiv 0; \quad R = 1, \quad \frac{\partial C}{\partial R} \equiv 0; \quad Z = 0, \quad C \equiv 1. \quad (0.2.4)$$

2.3 Effect of the chemical reaction rate

The effect of the chemical reaction rate is negligible if $0 = \text{Da} \leq 10^{-2}$ and from (2.2.4) follows $C \equiv 1$.

When fast chemical reactions take place ($\text{Da} \geq 10^2$), the terms in (2.2.4) must be divided by Da and the approximation $0 = \text{Da}^{-1} \leq 10^{-2}$ has to be applied. The result is:

$$0 = \frac{\text{Fo}}{\text{Da}} \left(\frac{1}{R} \frac{dC}{dR} + \frac{d^2 C}{dR^2} \right) - C; \quad R = 0, \quad \frac{dC}{dR} \equiv 0; \quad R = 1, \quad \frac{dC}{dR} \equiv 0, \quad (0.2.5)$$

i.e. the model (2.2.5) is diffusion type.

2.4 Convection types models

In the cases of big values of the average velocity ($0 = \text{Fo} \leq 10^{-2}$), from the convection-diffusion type model (2.1.27) is possible to obtain a convection type model when putting $\text{Fo} = 0$:

$$U(R) \frac{dC}{dZ} = -\text{Da} C; \quad Z = 0, \quad C \equiv 1. \quad (0.2.6)$$

3 Effect of the radial non-uniformity of the velocity distribution

The radial non-uniformity of the axial velocity distribution influences the conversion degree, concentration distribution and scale effect.

3.1 Conversion degree

As an example will be used the case [4] of parabolic velocity distribution (Poiseuille flow):

$$u(r) = \bar{u} \left(2 - 2 \frac{r^2}{r_o^2} \right). \quad (0.3.1)$$

From (2.1.25) and (2.3.1) follows

$$U(R) = 2 - 2R^2. \quad (0.3.2)$$

The solutions of the problem (2.2.4) for $Da = 1, 2$ and $Fo = 0, 0.1, 1.0$ permits to obtain $C(R, Z)$ and $\bar{C}(Z) = \bar{c}(z)/c_0$:

$$\bar{C}(Z) = 2 \int_0^1 RC(Z, R) dR. \quad (0.3.3)$$

As a result it is possible to obtain (Table 2.1) the conversion degree (2.1.5) in the cases of presence (G) and absence (G_0) of a radial non-uniformity of the axial velocity in the column:

$$G = 1 - 2 \int_0^1 RU(R)C(R, 1) dR, \quad G_0 = 1 - \bar{C}(1). \quad (0.3.4)$$

Table 2.1. Conversion degree

	G	G_0
Da	0.556	0.6734
Da	0.593	0.6452
Da	0.621	0.6281
Da	0.780	0.8516
Da	0.811	0.8502
Da	0.848	0.8538

Table 1.1 shows that the radial non-uniformity of the axial velocity component leads to substantial decrease of the conversion degree, but an increase of the diffusion transfer (Fo) leads to decrease of the convective transfer (all hydrodynamic effects) and as a result the effect of the radial non-uniformity of the axial velocity decreases.

3.2 Concentration distribution

Different expressions for the velocity distribution in the column apparatuses permit to analyze [4] the influence of the velocity distributions radial non-uniformities on the concentration distribution:

$$\begin{aligned} u^0 &= \bar{u}, \quad u^1(r) = \bar{u} \left(2 - 2 \frac{r^2}{r_o^2} \right); \\ u^s(r) &= \bar{u} \left(1 + a_s \frac{r^2}{r_o^2} + b_s \frac{r^4}{r_o^4} \right), \quad s = 2, 3, \quad a_2 = 2, \quad a_3 = -2, \quad b_2 = -3, \quad b_3 = 3; \\ u^s(r) &= \bar{u} \left(\frac{n+1}{n} - \frac{2}{n} \frac{r^2}{r_o^2} \right), \quad n = 2, \quad s = 4, \end{aligned} \quad (0.3.5)$$

where $n=1$ is the Poiseuille flow.

From (2.3.5) it is possible to obtain the following dimensionless velocity distributions $U^s(R) = u^s(r)/\bar{u}$:

$$\begin{aligned}
 U^0(R) &= 1, & U^1(R) &= 2 - 2R^2, & U^2(R) &= 1 + 2R^2 - 3R^4, \\
 U^3(R) &= 1 - 2R^2 + 3R^4, & U^4(R) &= \frac{3}{2} - R^2.
 \end{aligned}
 \tag{0.3.6}$$

The differences between maximal and minimal velocity values $\Delta U_s = U_s^{\max} - U_s^{\min}$ ($s = 1, \dots, 4$) are the velocity distribution radial non-uniformity parameters $\left(\Delta U_1 = 2, \Delta U_2 = \Delta U_3 = \frac{4}{3}, \Delta U_4 = 1 \right)$. The velocity distributions U^0, \dots, U^4 are presented on Fig. 2.1.

The numerical solutions of (2.2.4) using different velocity distributions (2.3.6) present the effect of the velocity radial non-uniformity on the conversion degree (G) and column height (H) in comparison with the plug flow.

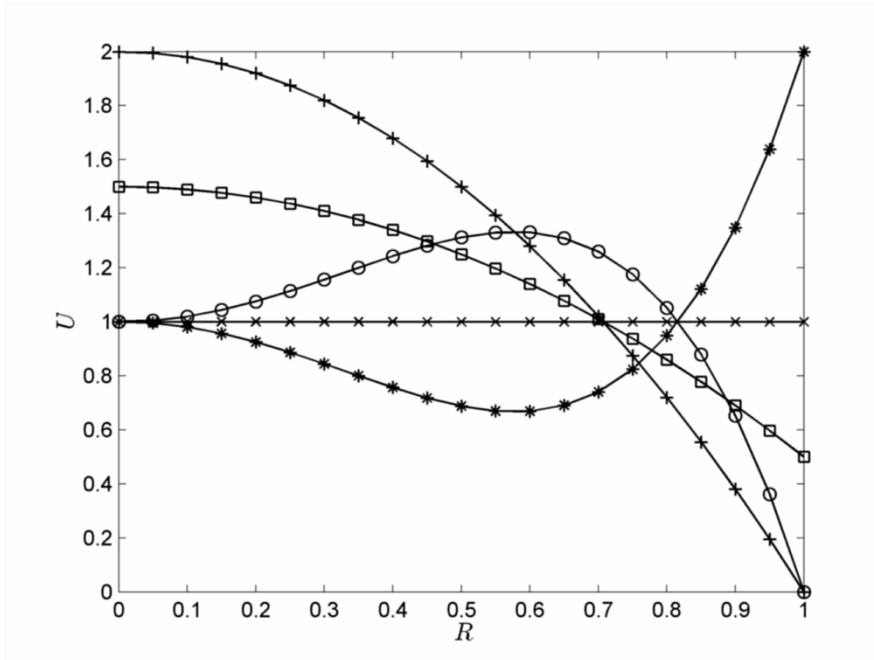


Fig. 2.1 Velocity distributions: \times - U^0 ; $+$ - U^1 ; \circ - U^2 ; $*$ - U^3 ; \square - U^4

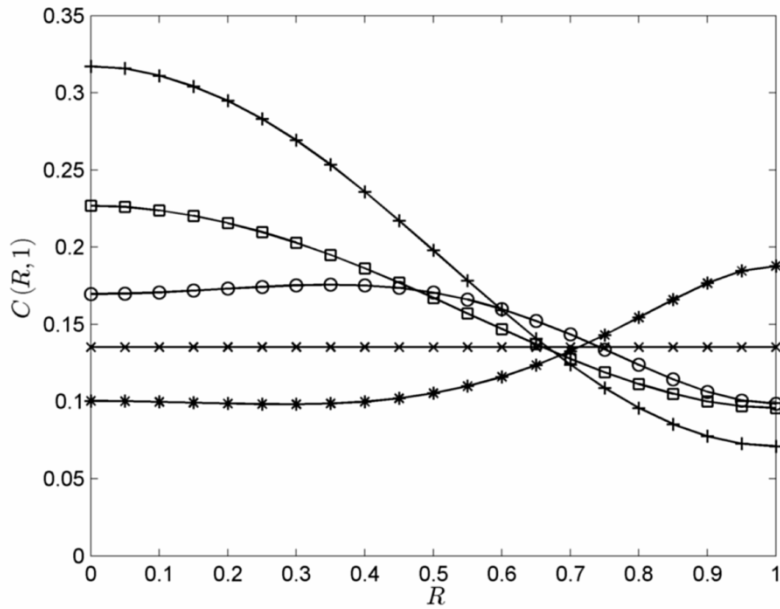


Fig. 2.2 Concentration distributions using the 5 velocity profiles: $\times-U^0$; $+-U^1$; $\circ-U^2$; $*-U^3$; $\square-U^4$

The concentration distributions obtained with the solution of (2.2.4) for $Fo = 0.1$ and $Da = 2$ are shown on Fig.2.2.

Table 2.2 presents the values of the conversion degree G_0, \dots, G_3 at $Da = 2$ and $Fo = 0.01, 0.1$. The column heights $Z = H_1, \dots, H_3$, for which the maximum conversion degree of the plug flow $G_0 = 0.8643$ (0.8645) is reached, were calculated.

Table 2.2 Process efficiency G at $Z = 1$ and column height $H = Z$ at $G_0 = 0.8643$

Table 2.3 presents the effect of the velocity radial non-uniformity on the relative conversion degree and column height at $G_0 = 0.8643$:

$$\Delta G_s = \frac{G_0 - G_s}{G_s} \cdot 100, \quad \Delta H_s = \frac{H_s - H_0}{H_0} \cdot 100, \quad s = 1, 2, 3, \quad (0.3.7)$$

where G_0 is the conversion degree in the case of plug flow.

Fo	U^0	U^1	U^2	U^3
0.1 laboratory	$G_0 =$ 0.8643	$G_1 =$ 0.8143	$G_2 =$ 0.8516	$G_3 =$ 0.8513
	$H_0 = 1$	$H_1 =$ 1.2	$H_2 =$ 1.05	$H_3 =$ 1.05
0.01 industrial	$G_0 =$ 0.8645	$G_1 =$ 0.7870	$G_2 =$ 0.8349	$G_3 =$ 0.8371
	$H_0 = 1$	$H_1 =$ 1.34	$H_2 =$ 1.12	$H_3 =$ 1.12

Fo	U^1	U^2	U^3
0.1 laboratory	ΔG_1	ΔG_2	ΔG_3
	=	=	=
	6%	1.4%	1.5%
	ΔH_1	ΔH_2	ΔH_3
	=	=	=

Table 2.3 Effect of the velocity radial non-uniformity on the process efficiency and column height

0.01 industrial	20%	5%	5%
	ΔG_1	ΔG_2	ΔG_3
	=	=	=
	9.8%	3.5%	3.3%
	ΔH_1	ΔH_2	ΔH_3
	=	=	=
	34%	12%	12%

The numerical results (Table 2.3) show the necessity of an essential augmentation of the column height in order to compensate the velocity distribution radial non-uniformity effect.

The comparison of the results in the Table 2.2 and Table 2.3 show that the effects of ΔU_2 and ΔU_3 are similar, i.e. the velocity distribution radial non-uniformity effects are caused by the velocity non-uniformity $\Delta U_s = U_s^{\max} - U_s^{\min}$ ($s=1, \dots, 4$), but not by the velocity distribution U_s , ($s=1, \dots, 4$).

3.3 Influence of the velocity radial non-uniformity shape

The influence of the shape of the velocity profile and the average velocity value in a column chemical reactor on the conversion degree has been presented in [8]. The effect of a simple velocity distribution (Poiseuille type)

$$0 \leq r \leq R_0, \quad u = \bar{u} \left(2 - 2 \frac{r^2}{R_0^2} \right), \quad (0.3.8)$$

is compared with three complicated velocity distributions, which shapes change at different values of $b = b_0, b_1, b_2, b_3$:

$$0 \leq r_1 \leq r_0, \quad u_1(r_1) = \bar{u} \left(2 - 2 \frac{r_1^2}{r_0^2} \right), \quad r_0 = \frac{R_0}{1+b};$$

$$r_0 \leq r_2 \leq R_0, \quad u_2(r_2) = \bar{u} \cdot F(b) \cdot \Phi(r_2);$$

$$\Phi(r_2) = \frac{r_2^2}{r_0^2} - 1 - \frac{2b+b^2}{\ln(1+b)} \ln(r_2/r_0),$$

$$\bar{\Phi}(b) = \frac{2}{R_0^2 - r_0^2} \int_{r_0}^{R_0} r_2 \Phi(r_2) dr_2, \quad F(b) = [\bar{\Phi}(b)]^{-1},$$

$$F(b) = \frac{2 \ln(1+b)}{b^2 + 2b - (b^2 + 2b + 2) \ln(1+b)}, \quad b = \frac{R_0 - r_0}{r_0}, \quad (0.3.9)$$

where $b_0 = 0$ (Poiseuille type flow), $b_1 = 1, b_2 = 0.42, b_3 = 0.11$. As a result two convection-diffusion equations are considered:

$$u_1 \frac{\partial c_1}{\partial z} = D \left(\frac{1}{r_1} \frac{\partial c_1}{\partial r_1} + \frac{\partial^2 c_1}{\partial r_1^2} \right) - kc_1,$$

$$u_2 \frac{\partial c_2}{\partial z} = D \left(\frac{1}{r_2} \frac{\partial c_2}{\partial r_2} + \frac{\partial^2 c_2}{\partial r_2^2} \right) - kc_2. \quad (0.3.10)$$

The boundary conditions of (2.3.10) are:

$$r_1 = 0, \quad \frac{\partial c_1}{\partial r_1} = 0; \quad r_2 = R_0, \quad \frac{\partial c_2}{\partial r_2} = 0;$$

$$r_1 = r_2 = r_0, \quad c_1 = c_2, \quad \frac{\partial c_1}{\partial r_1} = \frac{\partial c_2}{\partial r_2};$$

$$z = 0, \quad c_1 = c_2 = c_0. \quad (0.3.11)$$

The introduction of the dimensionless variables

$$\begin{aligned} Z &= \frac{z}{L}, \quad R_1 = \frac{r_1}{R_0}, \quad R_2 = \frac{r_2}{R_0}, \\ U_1(R_1) &= \frac{u_1(r_1)}{\bar{u}}, \quad U_2(R_2) = \frac{u_2(r_2)}{\bar{u}}, \\ C_1(R_1, Z) &= \frac{c_1}{c_0}, \quad C_2(R_2, Z) = \frac{c_2}{c_0} \end{aligned} \quad (0.3.12)$$

in (2.3.8)-(2.3.11) leads to

$$\begin{aligned} U_1 \frac{\partial C_1}{\partial Z} &= \text{Fo} \left(\frac{1}{R_1} \frac{\partial C_1}{\partial R_1} + \frac{\partial^2 C_1}{\partial R_1^2} \right) - \text{Da} C_1, \\ U_1(R_1) &= 2 - 2(1+b_i)^2 R_1^2, \quad 0 \leq R_1 \leq \frac{1}{1+b_i}; \\ U_2 \frac{\partial C_2}{\partial Z} &= \text{Fo} \left(\frac{1}{R_2} \frac{\partial C_2}{\partial R_2} + \frac{\partial^2 C_2}{\partial R_2^2} \right) - \text{Da} C_2, \\ U_2(R_2) &= F(b_i) \left[(1+b_i)^2 R_2^2 - 1 - \frac{2b_i + b_i^2}{\ln(1+b_i)} \ln(1+b_i) R_2 \right], \\ \frac{1}{1+b_i} &\leq R_2 \leq 1. \end{aligned} \quad (0.3.13)$$

$$\begin{aligned} R_1 = 0, \quad \frac{\partial C_1}{\partial R_1} &= 0; \quad R_2 = 1, \quad \frac{\partial C_2}{\partial R_2} = 0; \\ R_1 = R_2 &= \frac{1}{1+b_i}, \quad C_1 = C_2, \quad \frac{\partial C_1}{\partial R_1} = \frac{\partial C_2}{\partial R_2}, \quad i = 0, 1, 2, 3; \\ Z = 0, \quad C_1 &= C_2 = 1. \end{aligned} \quad (0.3.14)$$

The dimensionless velocity profiles in (2.3.13) are shown on Figs. 2.3 through 2.6.

At the boundary condition $R_1 = R_2$ given by (2.3.14), the concentrations have to be presented as a polynomial by three parameters:

$$\begin{aligned} R_1 = R_2 &= \frac{1}{1+b_i}, \quad i = 1, 2, 3, \\ C_1(R_1, Z) &= C_2(R_2, Z) = 1 + a_1^i Z + a_2^i Z^2 + a_3^i Z^3, \end{aligned} \quad (0.3.15)$$

where the parameters $a_1^i, a_2^i, a_3^i, i = 1, 2, 3$, have to be obtained by the minimization of the function:

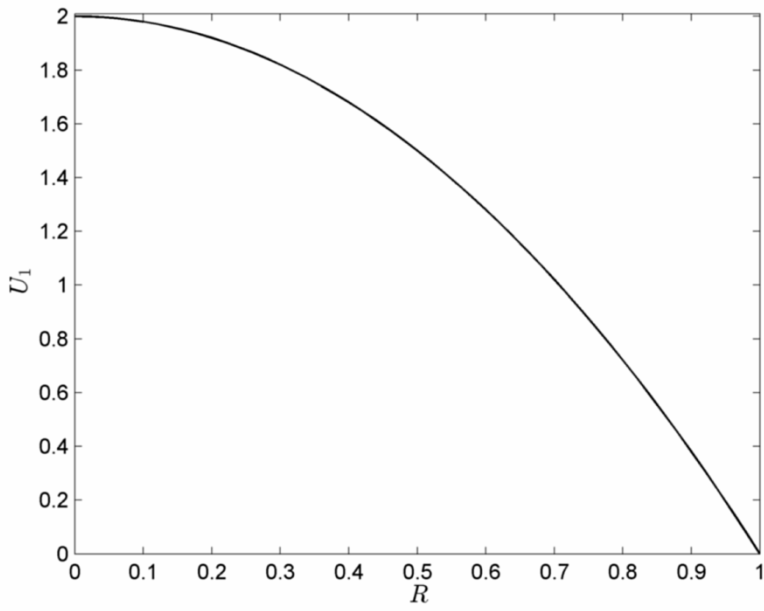


Fig. 2.3 Dimensionless velocities profiles (2.3.13) at $b = b_0 = 0$

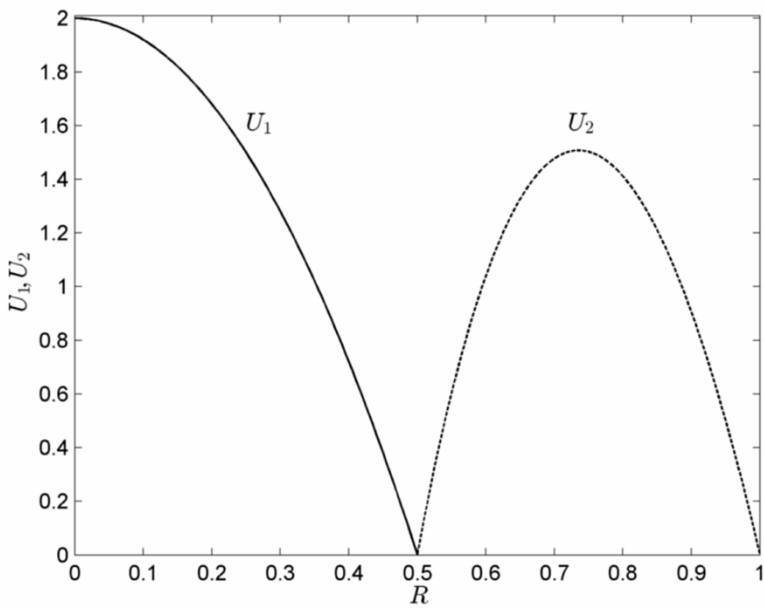


Fig. 2.4 Dimensionless velocities profiles (2.3.13) at $b = b_1 = 1$

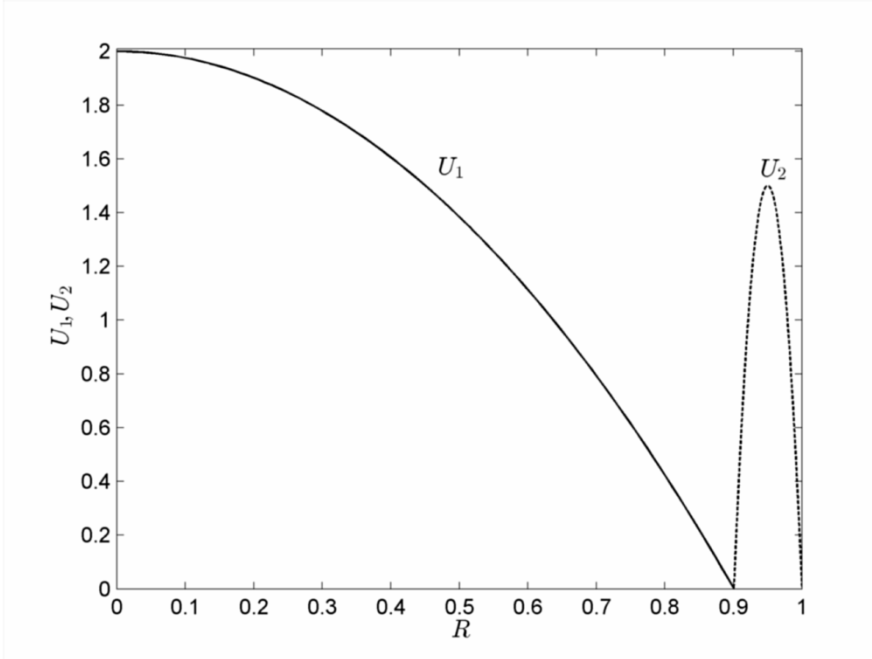


Fig. 2.5 Dimensionless velocities profiles (2.3.13) at $b = b_2 = 0.11$

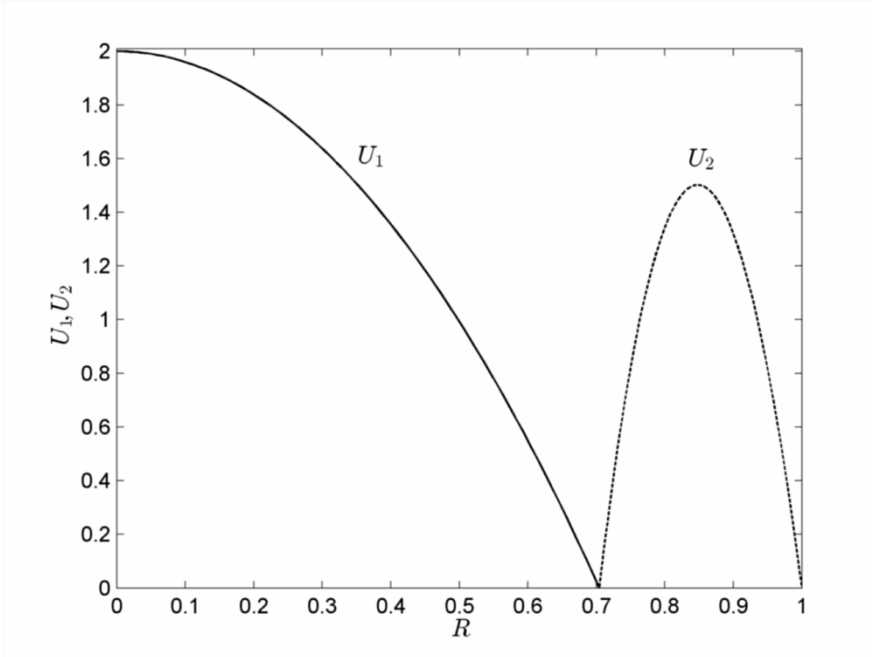


Fig. 2.6 Dimensionless velocities profiles (2.3.13) at $b = b_3 = 0.42$

$$F(a_1^i, a_2^i, a_3^i) = \int_0^1 f(a_1^i, a_2^i, a_3^i, Z) dZ,$$

$$f(a_1^i, a_2^i, a_3^i, Z) = [\alpha_1(a_1^i, a_2^i, a_3^i, Z) - \alpha_2(a_1^i, a_2^i, a_3^i, Z)]^2,$$

$$\alpha_1(a_1^i, a_2^i, a_3^i, Z) = \left(\frac{\partial C_1}{\partial R_1} \right)_{R_1=R_2}, \quad \alpha_2(a_1^i, a_2^i, a_3^i, Z) = \left(\frac{\partial C_2}{\partial R_2} \right)_{R_2=R_1}. \quad (0.3.16)$$

The obtained parameter values a_1^i, a_2^i, a_3^i , $i = 1, 2, 3$, are presented in Table 2.4.

Fo,	b	a_1, a_2, a_3	G	G_0
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Table 2.4 Parameters values and values of conversion degree

Fig. 2.7 presents three cases of the concentration gradient difference

$f(a_1^i, a_2^i, a_3^i, Z)$, $i=1,2,3$, which show that the conditions

$$R_1 = R_2 = \frac{1}{1+b_i}, \quad \frac{\partial C_1}{\partial R_1} = \frac{\partial C_2}{\partial R_2}, \quad \frac{i}{\Gamma} = 1, 2, 3, \quad (0.3.17)$$

are satisfied.

These solutions permit to obtain the conversion degree (2.3.4) and the results for different values of Da and Fo are presented in Table

Da					
	0		-0.2807, -0.1735, 0.04094	0.3722	0.3934
Fo = 0.05	0.11		-0.8000, 0.4553, -0.1502	0.3794	
Da = 0.5	0.42		-0.8035, 0.6453, -0.2888	0.3846	0.3866
	1		-0.8169, 0.7366, -0.3487	0.3867	
	0		-0.9902, 0.4558, -0.09779	0.5938	0.6321
Fo = 0.1	0.11		-1.4869, 1.2044, -0.4319	0.6072	
Da = 1, 2, 3,	0.42		-1.3512, 1.1535, -0.4741	0.6186	0.6320
	1		-1.3204, 1.1857, -0.5171	0.6229	
	0		-1.9348, 1.6008, -0.5326	0.8241	0.8650
Fo = 0.2	0.11		-2.6316, 3.0105, -1.2783	0.8386	
Da = 2	0.42		-2.3088, 2.4350, -1.0111	0.8518	0.8645
	1		-2.2008, 2.2693, -0.9443	0.8572	

2.4, where it is seen that the conversion degree increases if the average velocity increases. The impact of the different shapes of velocity profile ($b_0 = 0$, $b_1 = 1$, $b_2 = 0.42$, $b_3 = 0.11$) on the column apparatus efficiency is negligible compared with that of Damkohler number. The concentration profiles $C_1(R_1, Z)$, $C_2(R_2, Z)$, which are solution of (2.3.13) for $Fo = 0.1$, $Da = 1$, $b_1 = 1$ and column height $Z = 0.1; 0.3; 0.5; 0.7; 0.9$, are shown on Fig. 2.8.

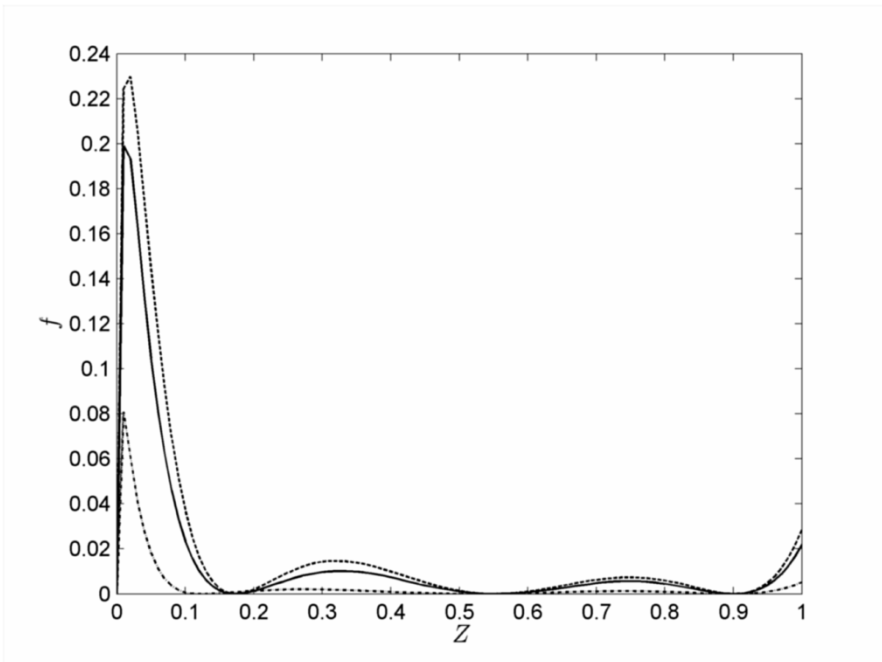


Fig. 2.7 Concentration gradient differences

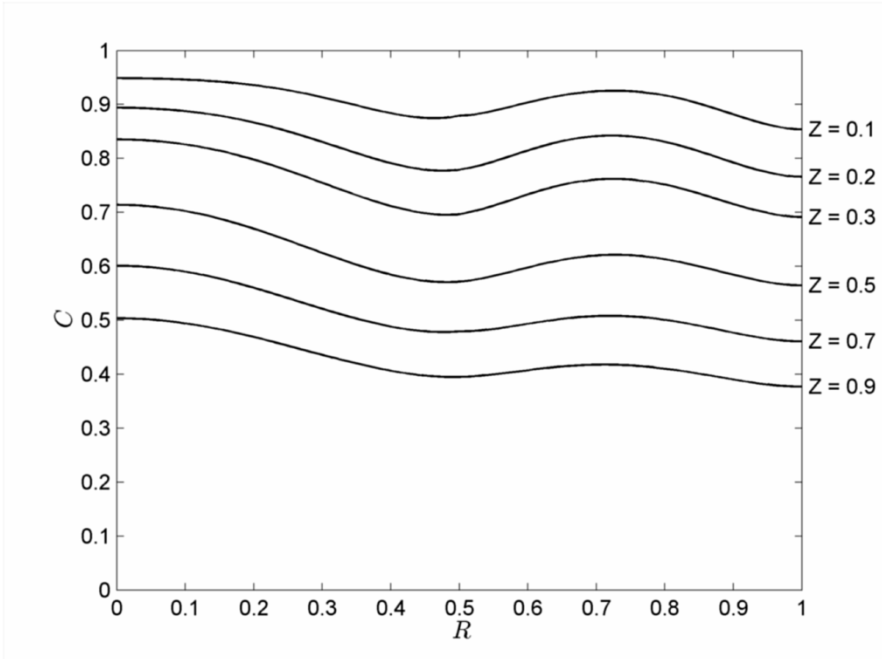


Fig. 2.8 Concentration distribution

3.4 Scale effect

The analyses [1, 3, 8, 9] of the influence of the column size on the mass transfer efficiency shows that the process efficiency in column apparatuses decreases with the column diameter increase. This scale-up effect is a result of the radial non-uniformity of the velocity distribution.

Let us consider “model” column ($r_0 = 0.2[\text{m}]$, $\text{Da} = 2$, $\text{Fo} = 0.1$) and “industrial” column ($r_0 = 0.5[\text{m}]$, $\text{Da} = 2$, $\text{Fo} = 0.01$) [7]. The scaling effects on the conversion degrees $\Delta G_{\text{scale}}^s$ and column heights $\Delta H_{\text{scale}}^s$:

$$\Delta G_{\text{scale}}^s = \frac{G_{\text{mod}}^s - G_{\text{ind}}^s}{G_{\text{ind}}^s} \cdot 100\%, \quad \Delta H_{\text{scale}}^s = \frac{H_{\text{ind}}^s - H_{\text{mod}}^s}{H_{\text{mod}}^s} \cdot 100\%, \quad s = 1, \dots, 3, \quad (0.3.18)$$

are possible to be obtained using Table 2.2. The results obtained are shown in Table 1.5. The comparison between the two columns on the basis of (2.3.7) (ΔQ_{mod} , ΔQ_{ind}) and (2.3.18) (ΔH_{mod} , ΔH_{ind}) shows that the scale-up leads to decrease of the conversion degree (for constant column height). If consider the columns with constant conversion degree, it leads to the column height increase as result of the column radius increase.

Table 2.5. Comparison of the scaling effect between different velocity profiles

	U^1	U^2	U^3
ΔG_{scale}	3.5%	1.9%	1.7%
ΔH_{scale}	11.6%	6.6%	6.6%

3.5 On the “back mixing” effect

The reduction of the conversion degree in the column chemical reactors, resulting from the radial non-uniformity in the velocity distribution in the cross sectional area of the column, is explained [9–12] by the mechanism of a back mass transfer (“back mixing” effect). The new approach for modeling of column apparatuses [1–5] permits a new explanation of this effect [27].

Let us consider a pseudo-first order chemical reaction in a high column (2.1.27). The concentration distributions in the column as solutions of (2.1.27) was obtained in the case of $\varepsilon = 0.05$ using the perturbations method [6]. As a radial non-uniformity in the velocity distribution in the cross sectional area of the column will be used

$$U = 2 - 2R^2. \quad (0.3.19)$$

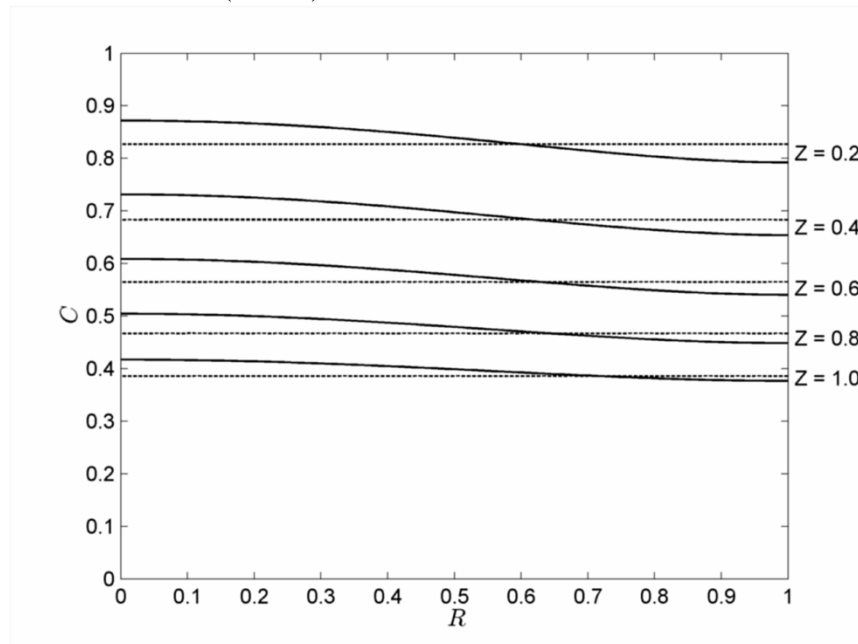


Fig. 2.9 Concentration distributions $C(R,Z)$ for $\varepsilon = 0.05$, $\text{Fo} = 1$, $\text{Da} = 1$ and different Z : $U = 2 - 2R^2$ (solid lines); $U = 1$ (dotted lines)

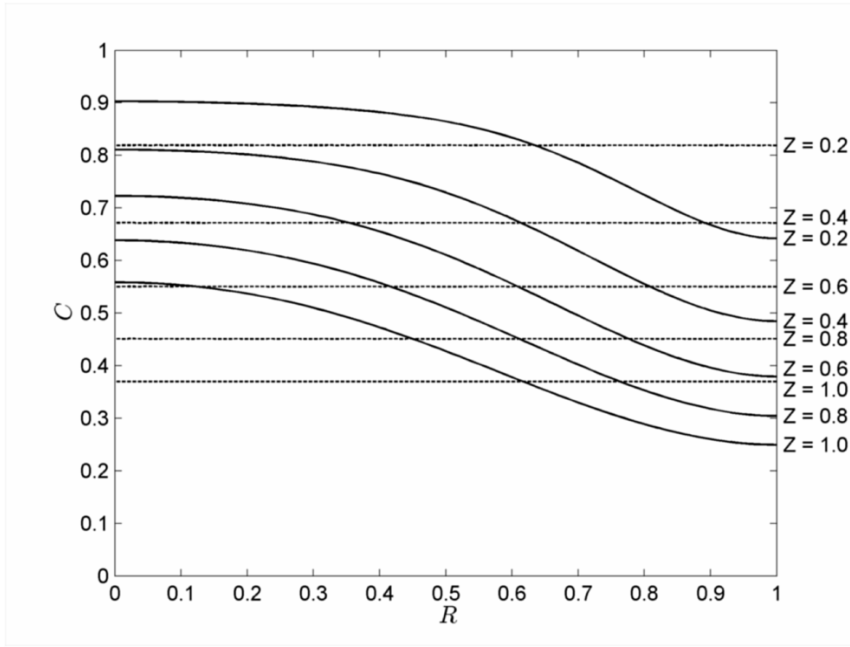


Fig. 2.10 Concentration distributions $C(R,Z)$ for $\varepsilon = 0.05$, $Fo = 0.1$, $Da = 1$ and different Z : $U = 2 - 2R^2$ (solid lines); $U = 1$ (dotted lines)

Figs. 2.9 and 2.10 present comparison of the results obtained in the cases $Fo = 1$, $Da = 1$ and $Fo = 0.1$, $Da = 1$ for different values of Z (solid lines) with the case of absence of the radial non-uniformity in the velocity distribution $U = 1$ (dotted lines).

From Figs. 2.9 and 2.10 it is possible to obtain the average concentrations $\bar{C}(Z)$:

$$\bar{C}(Z) = 2 \int_0^1 RC(R,Z) dR. \quad (0.3.20)$$

The results are presented on Fig. 2.11.

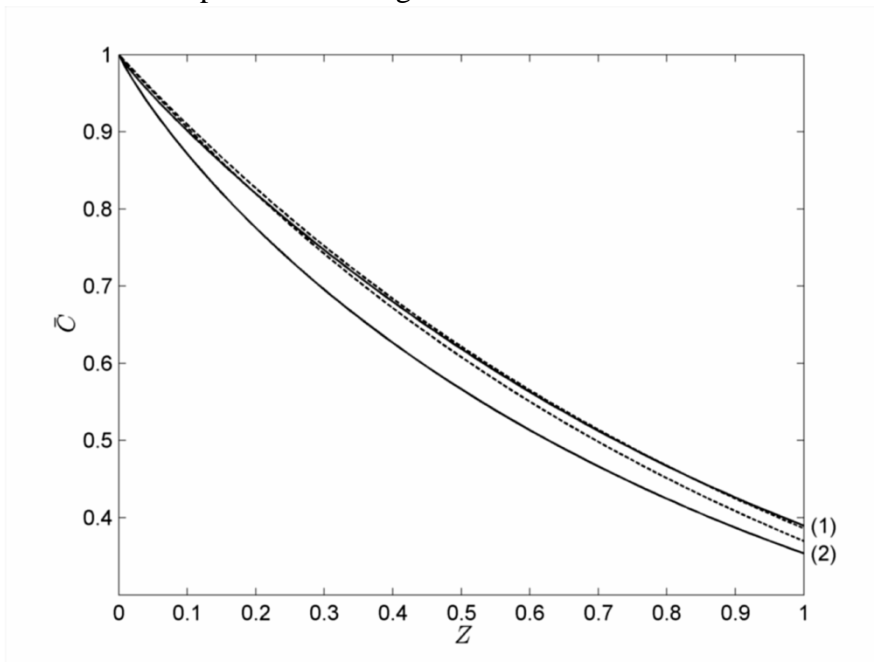


Fig. 2.11 Average concentration $\bar{c}(Z)$:

- (1) $\varepsilon = 0.05$, $Fo = 1$, $Da = 1$; $U = 2 - 2R^2$ (solid lines); $U = 1$ (dotted lines).
 (2) $\varepsilon = 0.05$, $Fo = 0.1$, $Da = 1$; $U = 2 - 2R^2$ (solid lines); $U = 1$ (dotted lines).

The convection-diffusion mass flux in the column \mathbf{j} [kg-mol.m⁻².s⁻¹] is possible to be presented as

$$\mathbf{j}(r, z) = \mathbf{u}c - D \mathbf{grad} c = \left[u(r)c(r, z) - D \frac{\partial c}{\partial z} \right] \hat{\mathbf{z}} - D \frac{\partial c}{\partial r} \hat{\mathbf{r}}, \quad (0.3.21)$$

or in generalized variables (2.1.25) as:

$$\mathbf{J}(R, Z) = \frac{\mathbf{j}(r, z)}{u^0 c^0} = \left[U(R)C(R, Z) - Pe^{-1} \frac{\partial C}{\partial Z} \right] \hat{\mathbf{z}} - \varepsilon^{-0.5} Pe^{-1} \frac{\partial C}{\partial R} \hat{\mathbf{r}}, \quad (0.3.22)$$

where $\hat{\mathbf{r}}$ and $\hat{\mathbf{z}}$ are the unit vectors, $U = 2 - 2R^2$, C – the solution of the problem (2.1.27). From the solution it is seen (Figs. 1.9 and 1.10) that in (2.3.22)

$$U(R)C(R, Z) \geq 0, \quad \frac{\partial C}{\partial Z} \leq 0, \quad \frac{\partial C}{\partial R} \leq 0, \quad (0.3.23)$$

i.e. the vector components of $\mathbf{J}(R, Z)$ are positive and there are no conditions for a backward mass transfer (“back mixing” effect).

The mass flux in every point (r, z) in the column (see the lines on Figs. 2.12 and 2.13) is possible to be obtained from (2.3.21):

$$j(r, z) = \left\{ \left[u(r)c(r, z) - D \frac{\partial c}{\partial z} \right]^2 + \left[D \frac{\partial c}{\partial r} \right]^2 \right\}^{0.5} \quad (0.3.24)$$

or in generalized variables (2.1.25):

$$J(R, Z) = \frac{j(r, z)}{u^0 c^0} = \left\{ \left[U(R)C(R, Z) - Pe^{-1} \frac{\partial C}{\partial Z} \right]^2 + \left[\varepsilon^{-0.5} Pe^{-1} \frac{\partial C}{\partial R} \right]^2 \right\}^{0.5}, \quad (0.3.25)$$

where $Pe^{-1} = \varepsilon Fo$.

The average mass flux in the cross sectional area of the column in generalized variables (2.1.25)

$$\bar{J}(Z) = 2 \int_0^1 R J(R, Z) dR \quad (0.3.26)$$

is presented on Fig. 2.14.

The conversion degree is possible to be obtained using the difference between the average mass fluxes in the cross sectional area at the column's ends:

$$G = \frac{\bar{J}(0) - \bar{J}(1)}{\bar{J}(0)} \quad (0.3.27)$$

and the results are presented in Table 2.6.

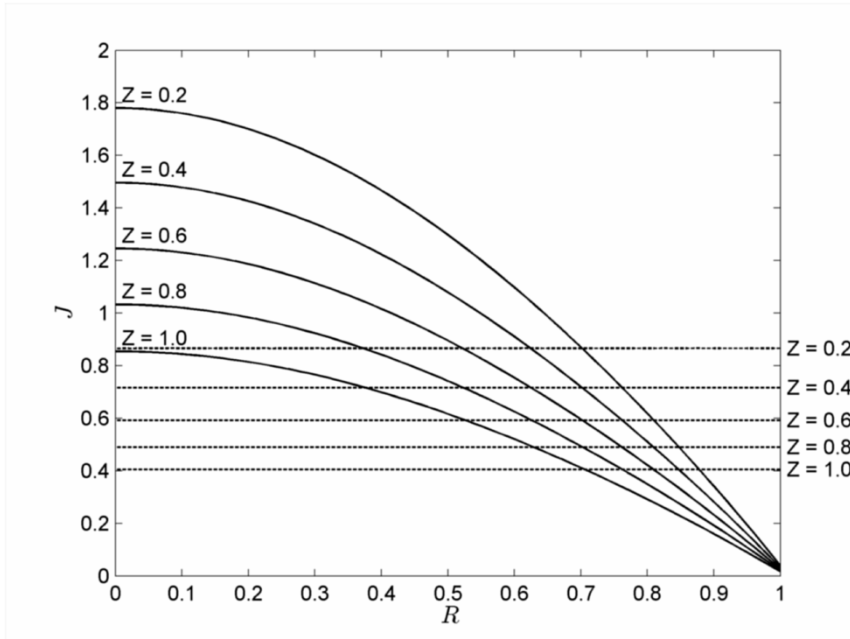


Fig. 2.12 Mass flux $J(R,Z)$ for different Z : $U = 2 - 2R^2$, $\varepsilon = 0.05$, $Fo = 1$, $Da = 1$ (solid lines);
 $U = 1$, $\varepsilon = 0.05$, $Fo = 1$, $Da =$ (dotted lines)

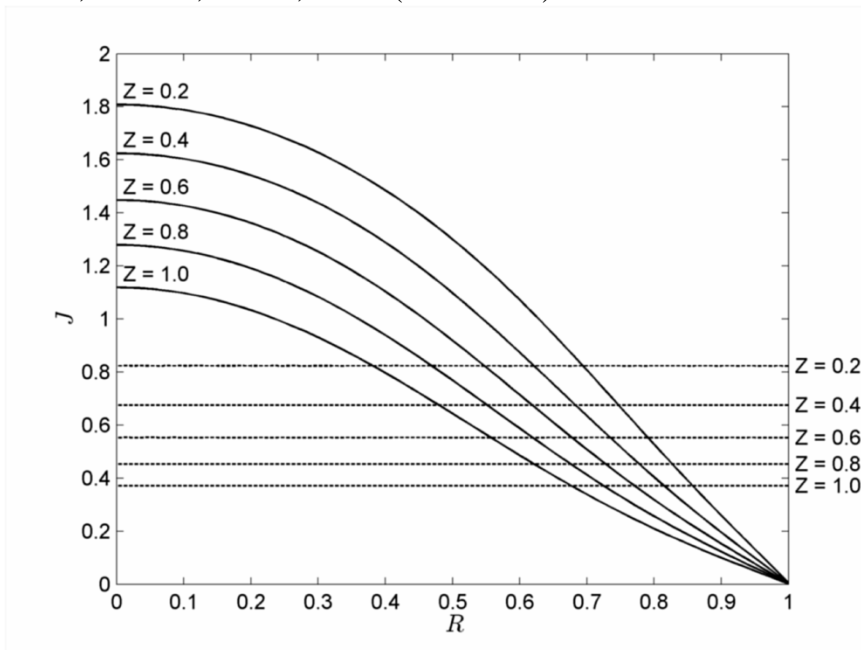


Fig. 2.13 Mass flux $J(R,Z)$ for different Z : $U = 2 - 2R^2$, $\varepsilon = 0.05$, $Fo = 0.1$, $Da = 1$ (solid lines);
 $U = 1$, $\varepsilon = 0.05$, $Fo = 0.1$, $Da =$ (dotted lines)

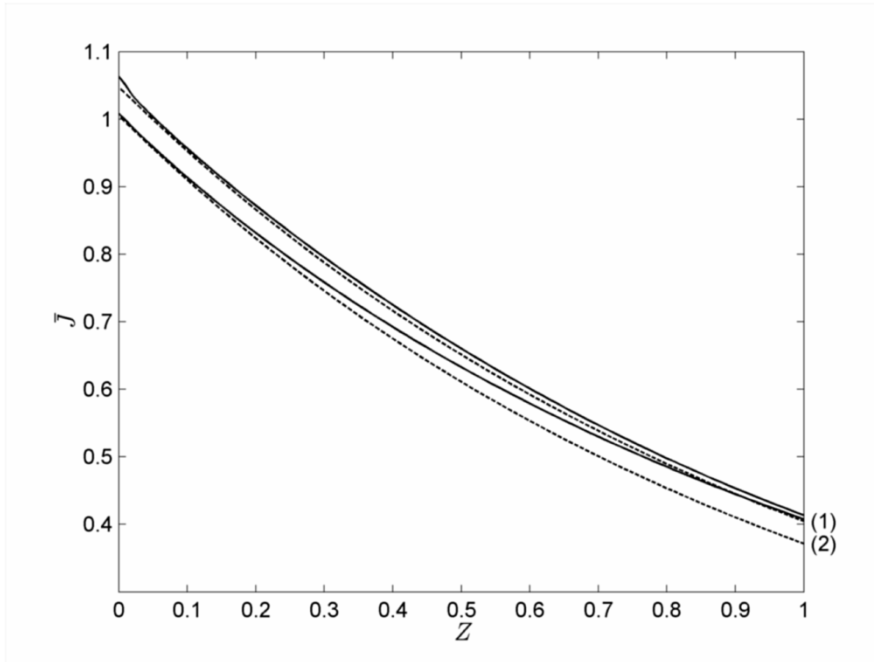


Fig. 2.14 Average $\bar{J}(z)$:

- mass flux
- (1) $\varepsilon = 0.05$, $Fo = 1$, $Da = 1$; $U = 2 - 2R^2$ (solid lines); $U = 1$ (dotted lines).
 (2) $\varepsilon = 0.05$, $Fo = 0.1$, $Da = 1$; $U = 2 - 2R^2$ (solid lines); $U = 1$ (dotted lines).

Table 2.6
 Conversion degree

It is seen from Table 2.6 that the conversion degree decreases as a result of the radial non-uniformity in the velocity distribution in the cross sectional area of the column. As was shown, this effect cannot be explained by “back mixing” effect, but may be explained by the residence times of the flows in the column.

The radial non-uniformity in the velocity distribution in the cross sectional area of the column leads to flows with different axial velocities, different residence times and chemical reaction times of these flows, which results in non-uniformity of the concentration distribution in the cross sectional area of the column. The conversion degree is related to the average residence time and the average reaction times in these flows in the column.

Let us consider the cases of presence ($u = u(r)$) and absence ($u = u^0$) of radial non-uniformity in the velocity distribution in the cross sectional area of the column. The residence times of the flows in the column in these cases are:

$$\theta(r) = \frac{l}{u(r)}, \quad \theta_0 = \frac{l}{u^0}. \quad (0.3.28)$$

The average residence times at the cross sectional area of the column are

$$\bar{\theta} = \frac{2}{r_0^2} \int_0^{r_0} r \frac{l}{u(r)} dr, \quad \bar{\theta}_0 = \frac{l}{u^0}. \quad (0.3.29)$$

	Fo = 1, U = 2 - 2R ²	Fo = 1, U = 1	Fo = 0.1, U = 2 - 2R ²	Fo = 0.1, U = 1
$\bar{J}(0)$	1.0634	1.0473	1.0085	1.0049
$\bar{J}(1)$	0.4137	0.4048	0.4080	0.3716
G	0.6110	0.6135	0.5954	0.6302

The using of generalized variables (2.1.25) and θ_0 as a scale leads to

$$\theta(r) = \theta_0 \Theta(R), \quad \theta_0 = \theta_0 \Theta_0, \quad \Theta = \frac{1}{U(R)}, \quad \Theta_0 = 1 \quad (0.3.30)$$

and the dimensionless average residence times are:

$$\bar{\Theta} = 2 \int_0^1 R \frac{1}{U(R)} dR, \quad \bar{\Theta}_0 = 1. \quad (0.3.31)$$

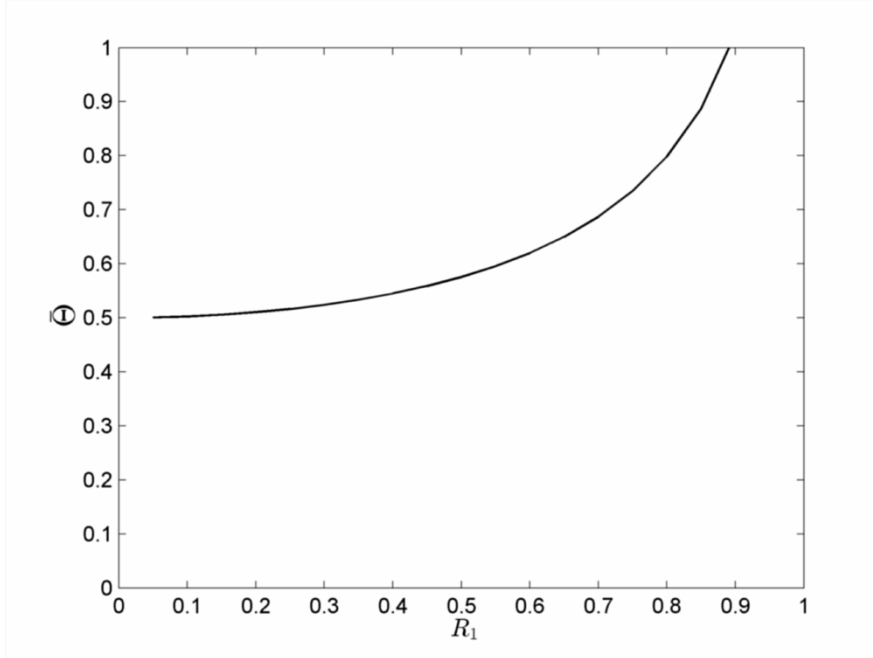


Fig. 2.15 Average residence time $\bar{\Theta}(R_1)$ in the interval $(0, R_1)$

Fig. 2.15 presents the average residence time for different values of R_1 in the interval $(0, 1)$:

$$\bar{\Theta}(R_1) = \frac{1}{R_1^2} \int_0^{R_1} \frac{R}{1-R^2} dR. \quad (0.3.32)$$

It can be seen, that in the interval $0 \leq R_1 < 0.9$ $\bar{\Theta}(R_1) < \bar{\Theta}_0 = 1$, which explains the low conversion degree in this interval.

A comparison of the average mass fluxes in the intervals $(0, R_1)$ and $(R_1, 1)$:

$$\bar{J}_1(R_1, Z) = \frac{2}{R_1^2} \int_0^{R_1} R J(R, Z) dR, \quad \bar{J}_2(R_1, Z) = \frac{2}{1-R_1^2} \int_{R_1}^1 R J(R, Z) dR \quad (0.3.33)$$

and the average mass flux (2.3.26) in the interval $(0, 1)$ for $Fo = 1, 0.1; Z = 1, R_1 = 0.9$ (see Table 2.7, where $\bar{J}_0(1)$ is the average mass flux (2.3.26) in the interval $(0, 1)$ in the case $U = 1$) reveals that in the interval $(0, R_1)$ the residence time $\bar{\Theta}(R_1)$ is less, the average mass flux $\bar{J}_1(R_1, Z)$ is larger and the conversion degree is less than in the case $U = 1$. The average mass flux $\bar{J}_2(R_1, Z)$ is much smaller than the average mass flux $\bar{J}_1(R_1, Z)$ and, as a result, the average mass flux (2.3.26) in the interval $(0, 1)$ is larger than the average mass flux $\bar{J}_0(1)$, i.e. the conversion degree is less than in the case $U = 1$.

Table 2.7

	$Fo = 1$	$\bar{J}(1) = 0.4137$	$\bar{J}_0(1) = 0.4048$	$\bar{J}_1(0.9,1) = 0.4902$	$\bar{J}_2(0.9,1) = 0.0875$
The pres	$Fo = 0.1$	$\bar{J}(1) = 0.4080$	$\bar{J}_0(1) = 0.3716$	$\bar{J}_1(0.9,1) = 0.4920$	$\bar{J}_2(0.9,1) = 0.0496$

ented theoretical analysis shows that the reduction of the conversion degree in the column chemical reactors, which results from the radial non-uniformity in the velocity distribution in the cross sectional area of the column, is not possible to be explained by the mechanism of a back mass transfer (“back mixing” effect). The new approach for modeling of column apparatuses permits to provide a new explanation of this effect. The radial non-uniformity in the velocity distribution in the cross sectional area of the column leads to decrease of the average residence time of the flow in the column (chemical reaction time), increase of the average mass flux at the column outlet and thus to decrease of the conversion degree in the column. This effect increases if the convection part of the convection-diffusion flow in the column increases due to the average velocity increase or the flow viscosity reduction.

Average Concentration Type Models

In the Part I it was shown that the column apparatuses are possible to be modeled using a new approach [1–4] on the basis of the physical approximations of the mechanics of continua, where the mathematical point is equivalent to a small (elementary) physical volume, which is sufficiently small with respect to the apparatus volume, but at the same time sufficiently large with respect to the intermolecular volumes in the medium. These convection-diffusion models are possible to be used for qualitative analysis only, because the velocity distribution functions are unknown and cannot be obtained. The problem can be solved by using average values of the velocity and concentration over the cross-sectional area of the column, i.e. the medium elementary volume (in the physical approximations of the mechanics of continua) will be equivalent to a small cylinder with column radius r_0 and a height, which is sufficiently small with respect to the column height and t the same time sufficiently large with respect to the intermolecular distances in the medium. All models in this part will be created on this basis.

Let us consider a cylinder with radius $R = R(\phi)$ in a cylindrical coordinate system (r, z, ϕ) , where r, z, ϕ are the radial, axial and angular coordinates, respectively. The average value of a function $f(r, z, \phi)$ at the cross sectional area of the cylinder is:

$$\bar{f}(z) = \frac{\iint_{(S)} f(r, z, \phi) dS}{S}, \quad (.34)$$

where

$$S = \int_0^{2\pi} \frac{[R(\phi)]^2}{2} d\phi, \quad \iint_{(S)} f(r, z, \phi) dS = \int_0^{2\pi} \left[\int_0^{R(\phi)} r f(r, z, \phi) dr \right] d\phi. \quad (.35)$$

$$\frac{\partial f}{\partial \phi} = 0$$

In the practical cases and the cylinder is circular ($R = const$), i.e. from (II.1) and (II.2) follows:

$$S = \pi R^2, \quad \iint_{(S)} f(r, z) dS = 2\pi \int_0^R r f(r, z) dr, \quad \bar{f}(z) = \frac{2}{R^2} \int_0^R r f(r, z) dr. \quad (.36)$$

Let us consider a column reactor with radius r_0 and height of the active volume l . The average concentration model will be presented on the base of a convection-diffusion model in the case of pseudo-first order chemical reaction. Further, if the fluid circulation takes place, the process is non-stationary and the velocity and concentration distributions in the column must be defined as:

$$u = u(r, z), \quad v = v(r, z), \quad c = c(t, r, z), \quad (.37)$$

i.e. the convection-diffusion model can be expressed as

$$\begin{aligned} \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial z} + v \frac{\partial c}{\partial r} &= D \left(\frac{\partial^2 c}{\partial z^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right) - kc; \quad \frac{\partial u}{\partial z} + \frac{\partial v}{\partial r} + \frac{v}{r} = 0; \\ t = 0 \quad c &\equiv c^0 \quad r = 0, \quad \frac{\partial c}{\partial r} \equiv 0; \quad r = r_0, \quad \frac{\partial c}{\partial r} \equiv 0, \quad v \equiv 0; \\ z = 0 \quad c(t, r, 0) &\equiv \bar{c}(t, l), \quad u \equiv u^0, \quad u^0 \bar{c}(t, l) \equiv u \bar{c}(t, l) - D \frac{\partial c}{\partial z}. \end{aligned} \quad (.38)$$

In (II.5) c^0 is the initial concentration, $\bar{c}(t, l)$ is the average concentration at the column outlet ($z=l$) and inlet ($z=0$) (as a result of the fluid circulation in the column), u^0 is the average velocity at the column inlet.

From (II.3) follow the average values of the velocity and concentration at the column cross-sectional area:

$$\bar{u}(z) = \frac{2}{r_0^2} \int_0^{r_0} ru(r, z) dr, \quad \bar{v}(z) = \frac{2}{r_0^2} \int_0^{r_0} rv(r, z) dr, \quad \bar{c}(t, z) = \frac{2}{r_0^2} \int_0^{r_0} rc(t, r, z) dr. \quad (.39)$$

The functions $u(r, z), v(r, z), c(t, r, z)$ in (II.5) can be presented with the help of the average functions (II.6):

$$\begin{aligned} u(r, z) &= \bar{u}(z) \tilde{u}(r, z), \quad v(r, z) = \bar{v}(z) \tilde{v}(r, z), \\ c(t, r, z) &= \bar{c}(t, z) \tilde{c}(t, r, z), \end{aligned} \quad (.40)$$

where $\tilde{u}(r, z), \tilde{v}(r, z)$ and $\tilde{c}(t, r, z)$ present the radial non-uniformity of the velocity and concentration and satisfy the following conditions:

$$\frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}(r, z) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{v}(r, z) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}(t, r, z) dr = 1. \quad (.41)$$

The average concentration model may be obtained when putting (II.7) into (II.5), multiplying by r and integrating over r in the interval $[0, r_0]$. As a result, the following is obtained:

$$\begin{aligned} \frac{\partial \bar{c}}{\partial t} + \alpha(t, z) \bar{u} \frac{\partial \bar{c}}{\partial z} + \beta(t, z) \bar{u} \bar{c} + \gamma(t, z) \bar{v} \bar{c} &= D \frac{\partial^2 \bar{c}}{\partial z^2} - k \bar{c}; \\ t = 0, \quad \bar{c}(0, z) &\equiv c^0; \quad z = 0, \quad \bar{c}(t, 0) \equiv \bar{c}(t, l), \quad \frac{\partial \bar{c}}{\partial z} \equiv 0, \end{aligned} \quad (.42)$$

where

$$\alpha(t, z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{u} \tilde{c} dr, \quad \beta(t, z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{u} \frac{\partial \tilde{c}}{\partial z} dr, \quad \gamma(t, z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{v} \frac{\partial \tilde{c}}{\partial r} dr. \quad (.43)$$

The average radial velocity component \bar{v} can be obtained from the continuity equation in (II.5) if it is multiplied by r^2 and then integrated with respect to r over the interval $[0, r_0]$:

$$\bar{v} = \delta \frac{d\bar{u}}{dz} + \frac{d\delta}{dz} \bar{u}, \quad \delta(z) = \frac{2}{r_0^2} \int_0^{r_0} r^2 \tilde{u} dr. \quad (.44)$$

If (II.11) is put into (II.9), the average concentration model assume the form:

$$\frac{\partial \bar{c}}{\partial t} + \alpha \bar{u} \frac{\partial \bar{c}}{\partial z} + \left(\beta + \frac{d\delta}{dz} \right) \bar{u} \bar{c} + \gamma \delta \bar{c} \frac{d\bar{u}}{dz} = D \frac{\partial^2 \bar{c}}{\partial z^2} - k \bar{c};$$

$$t = 0, \quad \bar{c}(0, z) \equiv c^0; \quad z = 0, \quad \bar{c}(t, 0) \equiv \bar{c}(t, l), \quad \frac{\partial \bar{c}}{\partial z} \equiv 0. \quad (.45)$$

Practically the cross-sectional area surface in the columns is a constant ($r_0 = const$), i.e.

$$\frac{d\bar{u}}{dz} = 0, \quad u = u(r). \quad (.46)$$

In many practical cases $\frac{\partial \tilde{u}}{\partial z} = 0$ and from (II.7), (II.10) and (II.13) follows:

$$\bar{v} = \tilde{v} = \gamma = \frac{d\delta}{dz} = 0, \quad \beta = \frac{\partial \alpha}{\partial z}. \quad (.47)$$

As a result from (II.12) is obtained:

$$\frac{\partial \bar{c}}{\partial t} + \alpha \bar{u} \frac{\partial \bar{c}}{\partial z} + \frac{\partial \alpha}{\partial z} \bar{u} \bar{c} = D \frac{\partial^2 \bar{c}}{\partial z^2} - k \bar{c};$$

$$t = 0, \quad \bar{c}(0, z) \equiv c^0; \quad z = 0, \quad \bar{c}(t, 0) \equiv \bar{c}(t, l), \quad \frac{\partial \bar{c}}{\partial z} \equiv 0. \quad (.48)$$

In the model (II.15) \bar{u} is the average velocity of the laminar or turbulent flow in the column, D is the diffusivity or the turbulent diffusivity (as a result of the small scale pulsations). The model parameter α is related with the radial non-uniformity of the velocity distribution and shows the influence of the column radius on the mass transfer kinetics. The parameter k may be obtained beforehand as a result of the chemical kinetics modeling.

The parameters in the model (II.15) show the influence of the scale-up (column radius increase) on the mass transfer kinetics if there exists a radial non-uniformity of the velocity distribution.

The presented theoretical analysis shows, that in the convection-diffusion and average concentration models, the velocity components and average velocity are:

$$u = u(r), \quad v = 0, \quad \bar{u} = const. \quad (.49)$$

The theoretical procedure (II.5–II.15) presented in the Part II will be used for creation of average concentration models of simple and complex chemical processes in one-phase column apparatuses. On this basis the effect of the velocity radial non-uniformity will be analyzed and methods for model parameters identification [1–3] proposed.

The convection-diffusion model of the one-phase systems has the form (2.1.11):

$$\begin{aligned}
u \frac{\partial c_i}{\partial z} &= D_i \left(\frac{\partial^2 c_i}{\partial z^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right) + Q_i(c_1, c_2); \\
r=0, \quad \frac{\partial c_i}{\partial r} &\equiv 0; \quad r=r_0, \quad \frac{\partial c_i}{\partial r} \equiv 0; \\
z=0, \quad c_i &\equiv c_i^0, \quad u^0 c_i^0 \equiv u c_i^0 - D_i \frac{\partial c_i}{\partial z}; \quad i=1,2.
\end{aligned} \tag{0.3.50}$$

The average values of the velocity and concentration at the column cross-sectional area in one-phase systems follow from (II.3):

$$\bar{u} = \frac{2}{r_0^2} \int_0^{r_0} r u(r) dr, \quad \bar{c}_i(z) = \frac{2}{r_0^2} \int_0^{r_0} r c_i(r, z) dr \quad i=1,2. \tag{0.3.51}$$

The functions $u(r), c_i(r, z)$ can be presented with the help of the average functions (5.0.2):

$$u(r) = \bar{u} \tilde{u}(r), \quad c_i(r, z) = \bar{c}_i(z) \tilde{c}_i(r, z), \quad i=1,2, \tag{0.3.52}$$

where $\tilde{u}(r)$ and $\tilde{c}_i(r, z)$ represent the radial non-uniformity of the velocity and concentration and satisfy the following conditions:

$$\frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}(r) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_i(r, z) dr = 1, \quad i=1,2. \tag{0.3.53}$$

The average concentration model may be obtained if (5.0.3) is put into (5.0.1), multiplied by r and integrated over r in the interval $[0, r_0]$. As a result, the average concentration model has the form:

$$\begin{aligned}
\alpha_i \bar{u} \frac{d \bar{c}_i}{dz} + \frac{d \alpha_i}{dz} \bar{u} \bar{c}_i &= D_i \frac{d^2 \bar{c}_i}{dz^2} + \frac{2}{r_0^2} \int_0^{r_0} r Q_i(c_1, c_2) dr; \\
z=0, \quad \bar{c}_i &= c_i^0, \quad \left(\frac{d \bar{c}_i}{dz} \right)_{z=0} = 0; \quad i=1,2.
\end{aligned} \tag{0.3.54}$$

where

$$\alpha_i(z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}(r) \tilde{c}_i(r, z) dr, \quad i=1,2. \tag{0.3.55}$$

1 Simple chemical reactions

Let us consider the stationary simple chemical reaction case

$$\begin{aligned}
u \frac{\partial c}{\partial z} &= D \left(\frac{\partial^2 c}{\partial z^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right) - kc; \\
r=0, \quad \frac{\partial c}{\partial r} &\equiv 0; \quad r=r_0, \quad \frac{\partial c}{\partial r} \equiv 0; \\
z=0, \quad c &\equiv c^0, \quad u^0 c^0 \equiv u c^0 - D \frac{\partial c}{\partial z}.
\end{aligned} \tag{0.4.1}$$

1.1 Average concentration model

From (II.3) follow the average values of the velocity and concentration at the column cross-sectional area:

$$\bar{u} = \frac{2}{r_0^2} \int_0^{r_0} r u(r) dr, \quad \bar{c}(z) = \frac{2}{r_0^2} \int_0^{r_0} r c(r, z) dr. \tag{0.4.2}$$

The functions $u(r), c(r, z)$ in (5.1.1) can be presented with the average functions (5.1.2):

$$u(r) = \bar{u} \tilde{u}(r), \quad c(r, z) = \bar{c}(z) \tilde{c}(r, z), \quad (0.4.3)$$

where $\tilde{u}(r)$ and $\tilde{c}(r, z)$ represent the radial non-uniformity of the velocity and concentration and satisfy the following conditions:

$$\frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}(r) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}(r, z) dr = 1. \quad (0.4.4)$$

The average concentration model may be obtained if (5.1.3) is put into (5.1.1), multiplied by r and integrated over r in the interval $[0, r_0]$. As a result, the average concentration model has the form:

$$\begin{aligned} \alpha \bar{u} \frac{d\bar{c}}{dz} + \frac{d\alpha}{dz} \bar{u} \bar{c} &= D \frac{d^2 \bar{c}}{dz^2} - k \bar{c}; \\ z = 0, \quad \bar{c}(0) &= c^0, \quad \frac{d\bar{c}}{dz} = 0, \end{aligned} \quad (0.4.5)$$

where

$$\alpha(z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}(r) \tilde{c}(r, z) dr \quad (0.4.6)$$

represents effect of the radial non-uniformity of the velocity.

The use of the generalized variables

$$\begin{aligned} r = r_0 R, \quad z = lZ, \quad u(r) &= \bar{u} U(R), \quad \tilde{u}(r) = \frac{u(r)}{\bar{u}} = U(R), \\ c(r, z) &= c^0 C(R, Z), \quad \bar{c}(z) = c^0 \bar{C}(Z), \quad \tilde{c}(r, z) = \frac{c(r, z)}{\bar{c}(z)} = \frac{C(R, Z)}{\bar{C}(Z)}, \\ \bar{C}(Z) &= 2 \int_0^1 R C(R, Z) dR, \quad \alpha(z) = \alpha(lZ) = A(Z) = 2 \int_0^1 R U(R) \frac{C(R, Z)}{\bar{C}(Z)} dR, \end{aligned} \quad (0.4.7)$$

leads to:

$$\begin{aligned} A(Z) \frac{d\bar{C}}{dZ} + \frac{dA}{dZ} \bar{C} &= \text{Pe}^{-1} \frac{d^2 \bar{C}}{dZ^2} - \text{Da} \bar{C} \\ Z = 0, \quad \bar{C} &= 1, \quad \frac{d\bar{C}}{dZ} = 0, \end{aligned} \quad (0.4.8)$$

where Pe and Da are the Peclet and Damkohler numbers, respectively:

$$\text{Pe} = \frac{\bar{u} l}{D}, \quad \text{Da} = \frac{kl}{\bar{u}}. \quad (0.4.9)$$

The case of parabolic velocity distribution (Poiseuille flow) will be presented as an example:

$$u = \bar{u} \left(2 - 2 \frac{r^2}{r_0^2} \right), \quad \bar{u} = u^0, \quad U(R) = 2 - 2R^2. \quad (0.4.10)$$

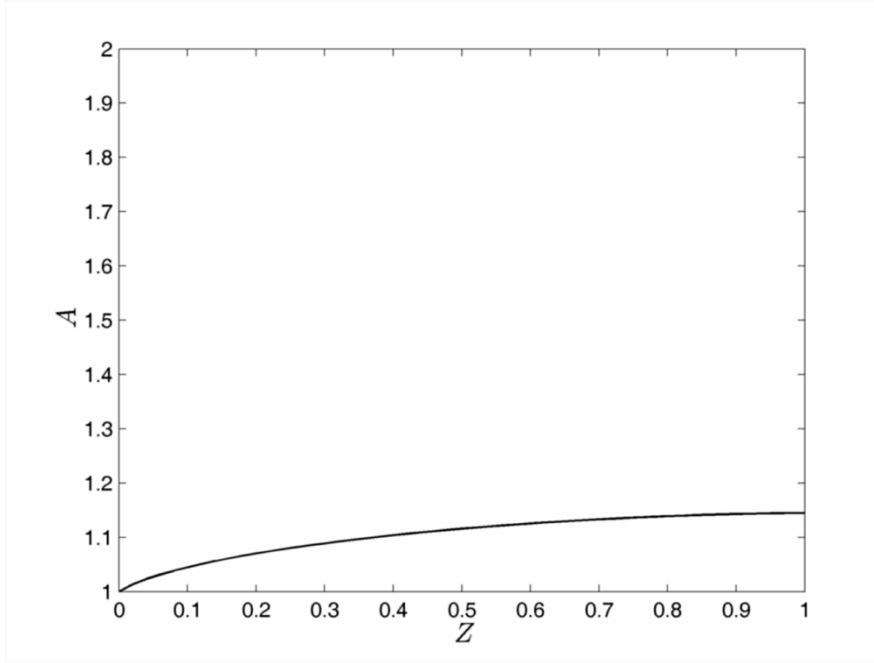


Fig. 5.1 Function $A(Z)$ for $Da = 1$, $Fo = 0.1$, $\varepsilon = 0.1$.

The use of the velocity distribution (5.1.10) permits to obtain the function $A(Z)$ in (5.1.7), where $C(R,Z)$ is the solution of the model (1.1.15) for short ($\varepsilon = 10^{-1}$) columns [4]. Fig. 5.1 displays the function $A(Z)$ for $Fo = 0.1$, $Da = 1$ showing that the function can be presented [3, 4] as linear approximation $A = a_0 + a_1 Z$ ($a_0 = 1, a_1 = 0.254$). As a result, the model (5.1.8) assumes the form:

$$(a_0 + a_1 Z) \frac{d\bar{C}}{dZ} + a_1 \bar{C} = Pe^{-1} \frac{d^2 \bar{C}}{dZ^2} - Da \bar{C};$$

$$Z = 0, \quad \bar{C} = 1, \quad \frac{d\bar{C}}{dZ} = 0. \quad (0.4.11)$$

1.2 Effect of the velocity radial non-uniformity

In the cases of absence of radial non-uniformity of the velocity distribution at the column cross-sectional area (plug flow cases) $u = \bar{u}, U(R) \equiv 1$ and from (5.1.7) follows that $A(Z) \equiv 1$, i.e. the radial non-uniformity of the velocity distribution leads to $A(Z) > 1$.

The equation in (5.1.8) can be modified as

$$\frac{d\bar{C}}{dZ} = [A(Z)]^{-1} \left[Pe^{-1} \frac{d^2 \bar{C}}{dZ^2} - \left(Da + \frac{dA}{dZ} \right) \bar{C} \right], \quad (0.4.12)$$

i.e. the radial non-uniformity of the velocity distribution leads ($A(Z) > 1$) to a decrease of the axial gradient of the average concentration ($d\bar{C}/dZ$) and the conversion degree, because the conversion degree is possible to be presented as $G = \bar{C}(0) - \bar{C}(1)$.

1.3 Model parameters identification

Here (until the end) methods for the model parameters identification will use "artificial experimental data".

The solution of the model (1.1.27) for short ($\varepsilon = 10^{-1}$) columns [5], in the case $Fo = 0.1$, $Da = 1$, $Pe^{-1} = \varepsilon Fo = 0.05$, permits to $C(Z_n, R)$ be obtained for different $Z_n = 0.1n$, $n = 1, 2, \dots, 10$ and average concentrations:

$$\bar{C}(Z_n) = 2 \int_0^1 RC(Z_n, R) dR, \quad n = 1, \dots, 10. \quad (0.4.13)$$

As a result it is possible to obtain “artificial experimental data” for different values of Z :

$$\bar{C}_{\text{exp}}^m(Z_n) = (0.95 + 0.1B_m) \bar{C}(Z_n), \quad m = 1, \dots, 10, \quad Z_n = 0.1n, \quad n = 1, 2, \dots, 10, \quad (0.4.14)$$

where $0 \leq B_m \leq 1$, $m = 1, \dots, 10$ are obtained with a generator of random numbers. The obtained artificial experimental data (5.1.14) are used for illustration of the parameters’ (a_0, a_1) identification in the average concentrations models (5.1.11) by minimization of the least-squares functions for different values of Z :

$$Q_n(a_{0n}, a_{1n}) = \sum_{m=1}^{10} [\bar{C}(Z_n, a_{0n}, a_{1n}) - \bar{C}_{\text{exp}}^m(Z_n)]^2, \quad Z_n = 0.1n, \quad n = 1, 3, 5, \quad (0.4.15)$$

where the values of $\bar{C}(Z_n, a_{0n}, a_{1n})$ are obtained as solutions of (5.1.11) for different $Z_n = 0.1n$, $n = 1, 3, 5$. For the solution of (5.1.11) in the cases of short columns ($Fo = 0.1$, $Da = 1$, $\varepsilon = 10^{-1}$, $Pe^{-1} = \varepsilon Fo = 0.01$) the perturbation method is to be used (see Chap. 7 and [5])

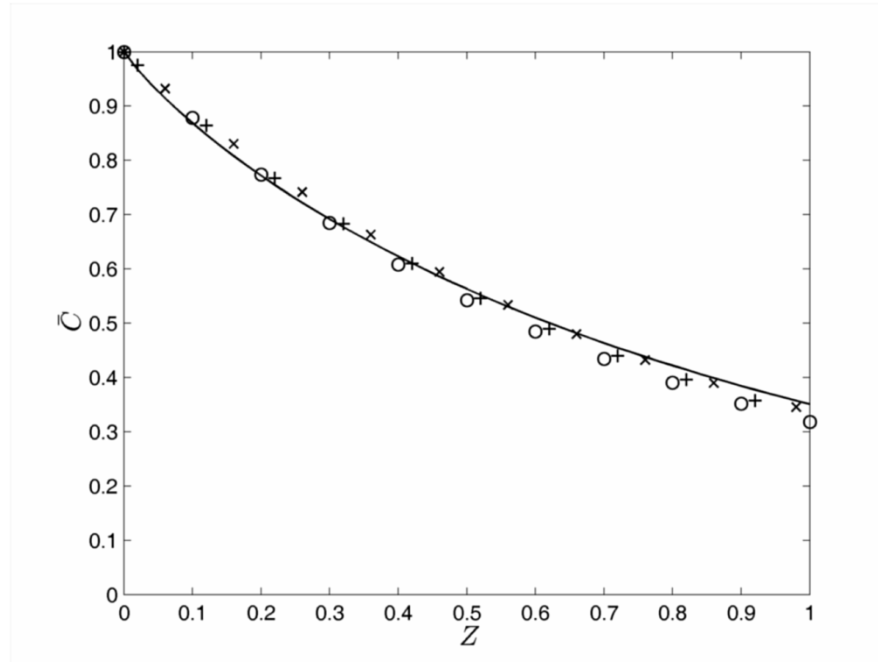


Fig. 5.2 Average concentration $\bar{C}(Z)$ for $Fo = 0.1$, $Da = 1$, $\varepsilon = 10^{-1}$, $Pe^{-1} = 0.01$:
line — $\bar{C}(Z)$ — (1.1.27), (5.1.7)
○ — $Z = 0.1$, $a_{01} = 1$, $a_{11} = 0.3519$, $\bar{C}(Z, a_{01}, a_{11})$ — (5.1.11)
+ — $Z = 0.3$, $a_{03} = 1$, $a_{13} = 0.2707$, $\bar{C}(Z, a_{03}, a_{13})$ — (5.1.11)
× — $Z = 0.5$, $a_{05} = 1$, $a_{15} = 0.2162$, $\bar{C}(Z, a_{05}, a_{15})$ — (5.1.11)

The solutions (a_{0n}, a_{1n}) , $n=1,3,5$, of the inverse problem for the parameter identification in the two-parameter average concentrations model (5.1.11) for different values of Z_n , $n=1,3,5$, after the minimization of (5.1.15), are obtained in [4]. These parameter values are used for the calculations of the average concentration in the model (5.1.11). The obtained values $\bar{C}(Z_n, a_{0n}, a_{1n})$, $Z_n = 0.1n$, $n=1,3,5$ (the points) are compared (see Fig.5.2) with the “exact” function (5.1.7) of the average concentration $\bar{C}(Z)$ (the line) obtained after solution of the model equation (2.1.27).

From Fig.5.2 it is evident that the experimental data, obtained in a short column ($Z=0.1$) with real diameter, are useful for the model parameters identification.

2 Complex chemical reaction

The theoretical procedure (II.5–II.15) is possible to be used for the creation of an average concentration model of the complex chemical processes in one-phase column apparatuses. The base is the convection-diffusion model:

$$\begin{aligned} u \frac{\partial c_i}{\partial z} &= D_i \left(\frac{\partial^2 c_i}{\partial z^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right) - k c_1^m c_2^n; \\ r=0, \quad \frac{\partial c_i}{\partial r} &\equiv 0; \quad r=r_0, \quad \frac{\partial c_i}{\partial r} \equiv 0; \\ z=0, \quad c &= c_i^0, \quad u^0 c_i^0 \equiv u c_i^0 - D_i \frac{\partial c_i}{\partial z}, \quad i=1,2. \end{aligned} \quad (0.5.1)$$

From (II.3) follow the average values of the velocity and concentration functions in (5.2.1) at the column cross-sectional area:

$$\bar{u} = \frac{2}{r_0^2} \int_0^{r_0} r u(r) dr, \quad \bar{c}_1(z) = \frac{2}{r_0^2} \int_0^{r_0} r c_1(r, z) dr, \quad \bar{c}_2(z) = \frac{2}{r_0^2} \int_0^{r_0} r c_2(r, z) dr. \quad (0.5.2)$$

The functions $u(r), c_1(r, z), c_2(r, z)$ in (4.1.2) can be presented with the help of the average functions (5.2.2):

$$u(r) = \bar{u} \tilde{u}(r), \quad c_1(r, z) = \bar{c}_1(z) \tilde{c}_1(r, z), \quad c_2(r, z) = \bar{c}_2(z) \tilde{c}_2(r, z) \quad (0.5.3)$$

where

$$\frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}(r) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_1(r, z) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_2(r, z) dr = 1. \quad (0.5.4)$$

The average concentration model may be obtained when (5.2.3) is put into (5.2.1), multiplied by r and integrated over r in the interval $[0, r_0]$. As a result, the average concentration model has the form:

$$\begin{aligned} \alpha_i \bar{u} \frac{d \bar{c}_i}{d z} + \frac{d \alpha_i}{d z} \bar{u} \bar{c}_i &= D_i \frac{d^2 \bar{c}_i}{d z^2} - \delta k \bar{c}_1^m \bar{c}_2^n; \\ z=0, \quad \bar{c}_i(0) &= c_i^0, \quad \frac{d \bar{c}_i}{d z} = 0, \quad i=1,2, \end{aligned} \quad (0.5.5)$$

where

$$\alpha_i(z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}(r) \tilde{c}_i(r, z) dr, \quad i=1,2; \quad \delta(z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_1^m(r, z) \tilde{c}_2^n(r, z) dr. \quad (0.5.6)$$

The using of the generalized variables

$$\begin{aligned}
r &= r_0 R, \quad z = lZ, \quad u(r) = \bar{u}U(R), \quad \tilde{u}(r) = \frac{u(r)}{\bar{u}} = U(R), \\
c_i(r, z) &= c_i^0 C_i(R, Z), \quad \bar{c}_i(z) = c_i^0 \bar{C}_i(Z), \quad \bar{C}_i(Z) = 2 \int_0^1 R C_i(R, Z) dR, \\
\tilde{c}_i(r, z) &= \frac{c_i(r, z)}{\bar{c}_i(z)} = \frac{C_i(R, Z)}{\bar{C}_i(Z)}, \\
\alpha_i(z) &= \alpha_i(lZ) = A_i(Z) = 2 \int_0^1 R U(R) \frac{C_i(R, Z)}{\bar{C}_i(Z)} dR, \quad i = 1, 2, \\
\delta(z) &= \delta(lZ) = \Delta = 2 \int_0^1 R \left[\frac{C_1(R, Z)}{\bar{C}_1(Z)} \right]^m \left[\frac{C_2(R, Z)}{\bar{C}_2(Z)} \right]^n dR,
\end{aligned} \tag{0.5.7}$$

leads to:

$$\begin{aligned}
A_i(Z) \frac{d\bar{C}_i}{dZ} + \frac{dA_i}{dZ} \bar{C}_i &= \text{Pe}_i^{-1} \frac{d^2 \bar{C}_i}{dZ^2} - \Delta(Z) \text{Da}_i \bar{C}_1^m \bar{C}_2^n; \\
Z = 0, \quad \bar{C}_i &= 1, \quad \frac{d\bar{C}_i}{dZ} = 0; \quad i = 1, 2,
\end{aligned} \tag{0.5.8}$$

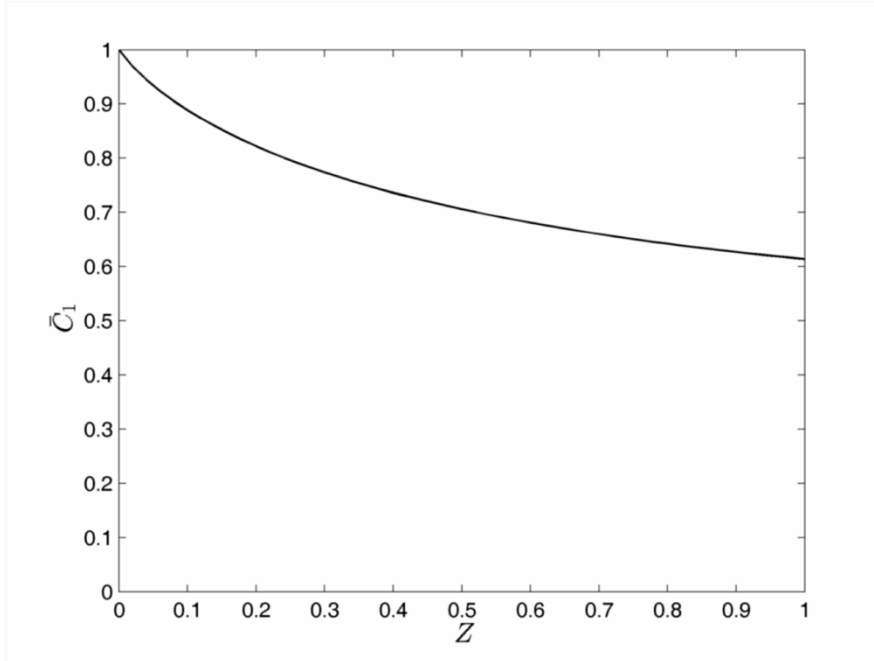


Fig. 5.3 Average concentration $\bar{C}_1(z)$

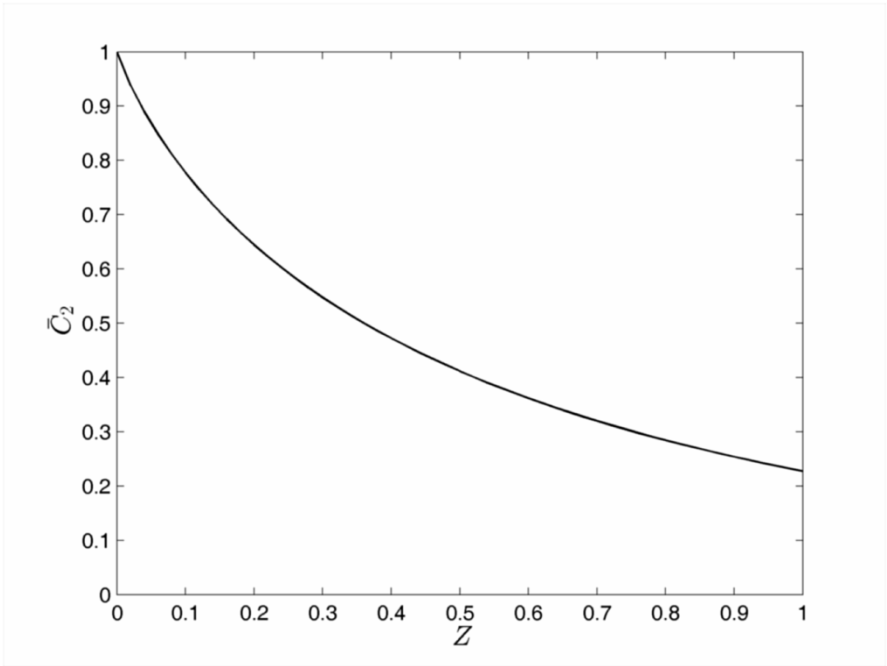


Fig. 5.4 Average concentration $\bar{c}_2(Z)$

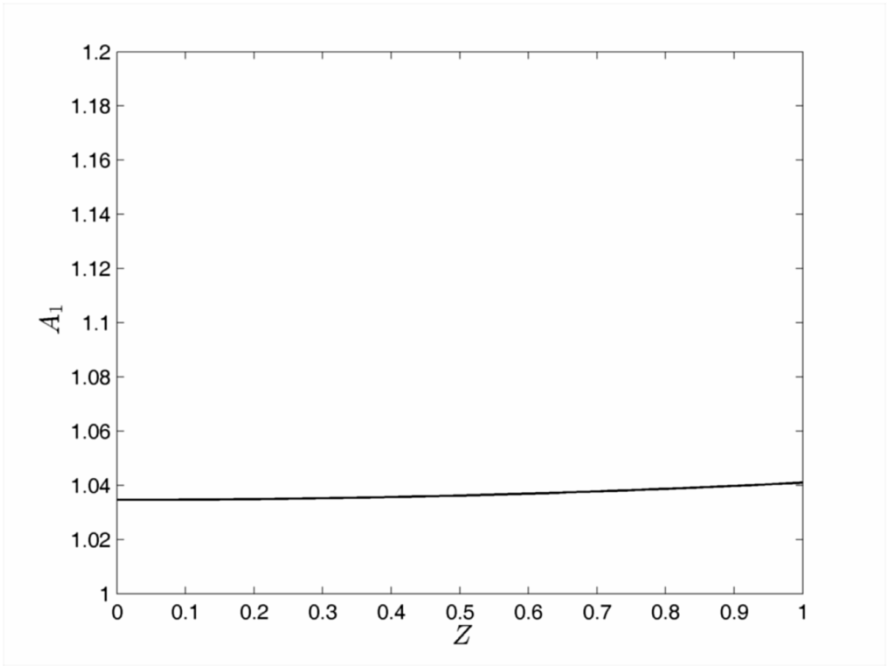


Fig. 5.5 Function $A_1(Z)$

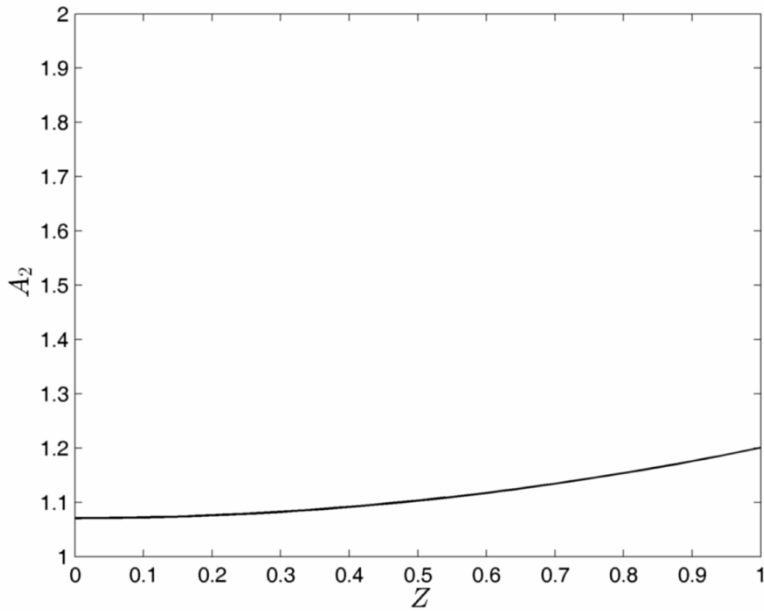


Fig. 5.6 Function $A_2(Z)$

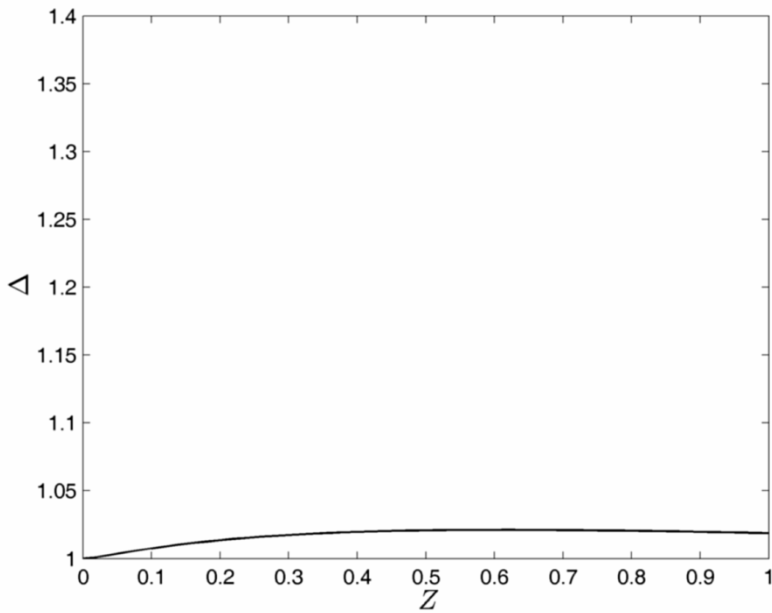


Fig. 5.7 Function $A(Z)$

where Pe and Da are the Peclet and Damkohler numbers, respectively:

$$Pe_i = \frac{\bar{u}l}{D_i}, \quad Da_i = \theta^{i-1} Da, \quad Da = \frac{kl}{\bar{u}} (c_1^0)^{m-1} (c_2^0)^n, \quad \theta = \frac{c_1^0}{c_2^0}; \quad i = 1, 2. \quad (0.5.9)$$

The model (2.1.26) for the high column ($\varepsilon = 0$) has the form:

$$U \frac{\partial C_i}{\partial Z} = Fo_i \left(\frac{1}{R} \frac{\partial C_i}{\partial R} + \frac{\partial^2 C_i}{\partial R^2} \right) - Da_i C_1^m C_2^n;$$

$$R = 0, \quad \frac{\partial C_i}{\partial R} \equiv 0; \quad R = 1, \quad \frac{\partial C_i}{\partial R} \equiv 0; \quad Z = 0, \quad C_i \equiv 1. \quad (0.5.10)$$

The solution of (5.2.10) for $m=n=1$, $Fo_i=0.1$, $Da_i=1$, $i=1,2$, permits to calculate the functions $\bar{C}_i(Z)$, $A_i(Z)$, $i=1,2$, $\Delta(Z)$ in (5.2.7). The functions $\bar{C}_i(Z)$, $i=1,2$, are presented on the Figs. 5.3 and 5.4. The functions $A_i(Z)$, $i=1,2$, $\Delta(Z)$ are presented on Figs. 5.5, 5.6 and 5.7, where it is seen that linear approximations are possible to be used:

$$A_i = a_{0i} + a_{1i}Z, \quad i=1,2, \quad \Delta = \Delta_0 + \Delta_1Z \quad (0.5.11)$$

and the values of the parameters are:

$$\begin{aligned} a_{01} &= 1.0346, & a_{11} &= 0.0063, & a_{02} &= 1.0708, \\ a_{12} &= 0.1297, & \Delta_0 &= 1.0095, & \Delta_1 &= 0.0148. \end{aligned} \quad (0.5.12)$$

3. Catalytic processes

The catalytic process is a chemical reaction between three reagents ($i_0=3$) in gas ($j=1$), liquid ($j=2$) or solid ($j=3$) phase [11]. For definiteness catalytic processes in gas or gas-solid systems will be discussed.

The catalytic processes are of heterogeneous or homogeneous type. In the first case the chemical reaction is implemented on a solid catalytic surface, where the first reagent is connected (adsorbed) physically or chemically with the third reagent (catalyst). The adsorption leads to a decrease of the activate energy E of the chemical reaction between the first and second reagents and the chemical reaction rate increases. Analogous effects are possible in the cases of homogeneous chemical reactions, but they are result of the dissolved catalytic substances (third reagent), which change the chemical reaction route and as a result the general activate energy decreases, too.

The modeling of the homogeneous catalytic processes is possible to be realized using the model (2.1.12) for three component chemical reaction ($i_0=3$) and one-phase ($j=1$) column, where the concentration (c_{31}) of the third reagent (catalyst) is a constant and the catalytic effect is focused in the chemical kinetics term $kc_{11}^m c_{21}^n$, where the chemical reaction rate constant k is a function of the catalyst concentration (c_{31}).

The heterogeneous catalytic processes are a result of the chemical reaction between two reagents on the catalytic interface, wherein one of them is adsorbed physically or chemically on the free active sites (AS) of the solid catalytic surface. After the chemical reaction the physical (Van der Vaals's) or chemical (valence) force between the obtained new substance and AS decreases and the new substance (reaction product) is desorbed from the solid surface. As a result the convection-diffusion models of the heterogeneous catalytic processes are possible to be created in the cases of physical adsorption mechanism (2.2.6) and chemical adsorption mechanism (2.2.18).

3.1 Physical adsorption mechanism

Let us consider a heterogeneous chemical reaction between two reagents (AC) in gas-solid system, where the first reagent is adsorbed physically on the free active sites (AS) of the solid catalytic surface. The reagents concentrations in the gas phase elementary volume are c_{11}, c_{21} [kg-mol.m⁻³], while in the void elementary volume of the solid phase (catalyst) the concentrations are c_{13}, c_{23} . The concentration of the free AS in the solid (catalytic) phase elementary volume is c_{33} [kg-eq.m⁻³]. The maximal concentrations of AC and AS are

$c_{11}^0, c_{21}^0, c_{33}^0$, where c_{11}^0, c_{21}^0 are input AC concentrations in the gas phase. The volume concentration of the adsorbed AC in the solid phase elementary volume is $c_{33}^0 - c_{33}$.

Accordinging the physical adsorption mechanism the gas-solid interphase, the mass transfer rate of the first reagent is $k_{01}(c_{11} - c_{13})$, while that of the physical adsorption rate in the solid

phase is $bk_1c_{13}\frac{c_{33}}{c_{33}^0} - k_2c_{33}^0\left(1 - \frac{c_{33}}{c_{33}^0}\right)$. The gas-solid interphase mass transfer rate of the second

reagent is $k_{02}(c_{21} - c_{23})$, while the catalytic reaction rate is $kc_{23}(c_{33}^0 - c_{33})$. The difference between the interphase mass transfer coefficients k_{01}, k_{02} [s^{-1}] is a result of the difference between the diffusivities of the reagents in the gas phase. The concentration of AS decreases as a result of the physical adsorption and increases as a result of the catalytic reaction, because the reaction product does not have adsorption properties.

In the cases of a non-stationary catalytic process the mass balance of AC and AS in the gas and solid phases leads to the convection-diffusion model of a heterogeneous catalytic chemical reaction in a column apparatus:

$$\begin{aligned}\frac{\partial c_{11}}{\partial t} + u_1 \frac{\partial c_{11}}{\partial z} &= D_{11} \left(\frac{\partial^2 c_{11}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{11}}{\partial r} + \frac{\partial^2 c_{11}}{\partial r^2} \right) - k_{01}(c_{11} - c_{13}); \\ \frac{\partial c_{21}}{\partial t} + u_1 \frac{\partial c_{21}}{\partial z} &= D_{21} \left(\frac{\partial^2 c_{21}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{21}}{\partial r} + \frac{\partial^2 c_{21}}{\partial r^2} \right) - k_{02}(c_{21} - c_{23}); \\ \frac{dc_{13}}{dt} &= k_{01}(c_{11} - c_{13}) - bk_1c_{13}\frac{c_{33}}{c_{33}^0} + k_2c_{33}^0\left(1 - \frac{c_{33}}{c_{33}^0}\right); \\ \frac{dc_{23}}{dt} &= k_{02}(c_{21} - c_{23}) - kc_{23}(c_{33}^0 - c_{33}); \\ \frac{dc_{33}}{dt} &= -bk_1c_{13}\frac{c_{33}}{c_{33}^0} + k_2c_{33}^0\left(1 - \frac{c_{33}}{c_{33}^0}\right) + kc_{23}(c_{33}^0 - c_{33}),\end{aligned}\tag{0.6.1}$$

where $u_1 = u_1(r)$ is the velocity distribution in the gas phase, $\varepsilon_1, \varepsilon_3$ ($\varepsilon_1 + \varepsilon_3 = 1$) are the parts of the gas and solid phases in the column volume.

The initial and boundary conditions of (2.3.1) are:

$$\begin{aligned}t = 0, \quad c_{11} &\equiv c_{11}^0, \quad c_{21} \equiv c_{21}^0, \quad c_{13} \equiv 0, \quad c_{23} \equiv 0, \quad c_{33} \equiv c_{33}^0; \\ r = 0, \quad \frac{\partial c_{11}}{\partial r} &= \frac{\partial c_{21}}{\partial r} \equiv 0; \quad r = r_0, \quad \frac{\partial c_{11}}{\partial r} = \frac{\partial c_{21}}{\partial r} \equiv 0; \\ z = 0, \quad c_{11} &\equiv c_{11}^0, \quad u_1^0 c_{11}^0 \equiv u_1(r)c_{11}^0 - D_{11} \left(\frac{\partial c_{11}}{\partial z} \right)_{z=0}, \\ c_{21} &\equiv c_{21}^0, \quad u_1^0 c_{21}^0 \equiv u_1(r)c_{21}^0 - D_{21} \left(\frac{\partial c_{21}}{\partial z} \right)_{z=0},\end{aligned}\tag{0.6.2}$$

where u_1^0 is the inlet velocity of the gas phase.

For a long duration process the concentration of AS is a constant with respect to the time (as a result of the desorption of the reaction product) and the model (2.3.1) and (2.3.2) is stationary form:

$$\begin{aligned}
u_1 \frac{\partial c_{11}}{\partial z} &= D_{11} \left(\frac{\partial^2 c_{11}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{11}}{\partial r} + \frac{\partial^2 c_{11}}{\partial r^2} \right) - k_{01} (c_{11} - c_{13}); \\
u_1 \frac{\partial c_{21}}{\partial z} &= D_{21} \left(\frac{\partial^2 c_{21}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{21}}{\partial r} + \frac{\partial^2 c_{21}}{\partial r^2} \right) - k_{02} (c_{21} - c_{23}); \\
k_{01} (c_{11} - c_{13}) - b_0 k_1 c_{13} \frac{c_{33}}{c_{33}^0} + k_2 c_{33}^0 \left(1 - \frac{c_{33}}{c_{33}^0} \right) &= 0; \\
k_{02} (c_{21} - c_{23}) - k c_{23} (c_{33}^0 - c_{33}) &= 0; \\
-b_0 k_1 c_{13} \frac{c_{33}}{c_{33}^0} + k_2 c_{33}^0 \left(1 - \frac{c_{33}}{c_{33}^0} \right) + k c_{23} (c_{33}^0 - c_{33}) &= 0; \\
r = 0, \quad \frac{\partial c_{11}}{\partial r} = \frac{\partial c_{21}}{\partial r} &\equiv 0; \quad r = r_0, \quad \frac{\partial c_{11}}{\partial r} = \frac{\partial c_{21}}{\partial r} \equiv 0; \\
z = 0, \quad c_{11} \equiv c_{11}^0, \quad u_1^0 c_{11}^0 \equiv u_1(r) c_{11}^0 - D_{11} \left(\frac{\partial c_{11}}{\partial z} \right)_{z=0}, \\
c_{21} \equiv c_{21}^0, \quad u_1^0 c_{21}^0 \equiv u_1(r) c_{21}^0 - D_{21} \left(\frac{\partial c_{21}}{\partial z} \right)_{z=0}.
\end{aligned} \tag{0.6.3}$$

The use of dimensionless (generalized) variables [1] permits to make a qualitative analysis of the model (2.3.3), where the inlet velocity and concentrations and the column parameters (r_0, l) are used as characteristic scales:

$$\begin{aligned}
R = \frac{r}{r_0}, \quad Z = \frac{z}{l}, \quad U = \frac{u_1}{u_1^0}, \quad C_{11} = \frac{c_{11}}{c_{11}^0}, \\
C_{21} = \frac{c_{21}}{c_{21}^0}, \quad C_{33} = \frac{c_{33}}{c_{33}^0}, \quad C_{13} = \frac{c_{13}}{c_{11}^0}, \quad C_{23} = \frac{c_{23}}{c_{21}^0}.
\end{aligned} \tag{0.6.4}$$

If (2.3.4) is put in (2.3.3) the model in generalized variables takes the form:

$$\begin{aligned}
U(R) \frac{\partial C_{11}}{\partial Z} &= \text{Fo}_{11} \left(\varepsilon \frac{\partial^2 C_{11}}{\partial Z^2} + \frac{1}{R} \frac{\partial C_{11}}{\partial R} + \frac{\partial^2 C_{11}}{\partial R^2} \right) - K_{01} (C_{11} - C_{13}); \\
U(R) \frac{\partial C_{21}}{\partial Z} &= \text{Fo}_{21} \left(\varepsilon \frac{\partial^2 C_{21}}{\partial Z^2} + \frac{1}{R} \frac{\partial C_{21}}{\partial R} + \frac{\partial^2 C_{21}}{\partial R^2} \right) - K_{02} (C_{21} - C_{23}); \\
R = 0, \quad \frac{\partial C_{i1}}{\partial R} &\equiv 0; \quad R = 1, \quad \frac{\partial C_{i1}}{\partial R} \equiv 0;
\end{aligned} \tag{0.6.5}$$

$$Z = 0, \quad C_{i1} \equiv 1, \quad 1 \equiv U(R) - \text{Pe}_{i1}^{-1} \left(\frac{\partial C_{i1}}{\partial Z} \right)_{Z=0}; \quad i = 1, 2.$$

$$C_{13} = \frac{C_{11} + K_1(1 - C_{33})}{1 + K_2 C_{33}}, \quad C_{23} = \frac{C_{21}}{1 + K_3(1 - C_{33})}, \quad C_{33} = \frac{K_5 + C_{23}}{K_4 C_{13} + K_5 + C_{23}}. \tag{0.6.6}$$

In (2.3.5), (2.3.6) the following parameters are used:

$$\begin{aligned}
K_{0i} = \frac{k_{0i} l}{u_1^0}, \quad \text{Fo}_{i1} = \frac{D_{i0} l}{u_1^0 r_0^2}, \quad \text{Pe}_{i1} = \frac{u_1^0 l}{D_{i0}}, \quad i = 1, 2, \quad \varepsilon = \frac{r_0^2}{l^2} = \text{Fo}_{i1}^{-1} \text{Pe}_{i1}^{-1}, \\
K_1 = \frac{k_2 c_{33}^0}{k_{01} c_{11}^0}, \quad K_2 = \frac{b_0 k_1}{k_{01}}, \quad K_3 = \frac{k_{23} c_{33}^0}{k_{02}}, \quad K_4 = \frac{b_0 k_1 c_{11}^0}{k_{23} c_{21}^0 c_{33}^0}, \quad K_5 = \frac{k_2}{k_{23} c_{21}^0}.
\end{aligned} \tag{0.6.7}$$

For high columns the parameter ε is very small ($0 = \varepsilon \leq 10^{-2}$) and the problem (2.3.5) is possible to be solved in zero approximation with respect to ε :

$$\begin{aligned}
U(R) \frac{\partial C_{11}}{\partial Z} &= \text{Fo}_{11} \left(\frac{1}{R} \frac{\partial C_{11}}{\partial R} + \frac{\partial^2 C_{11}}{\partial R^2} \right) - K_{01} (C_{11} - C_{13}); \\
U(R) \frac{\partial C_{21}}{\partial Z} &= \text{Fo}_{21} \left(\frac{1}{R} \frac{\partial C_{21}}{\partial R} + \frac{\partial^2 C_{21}}{\partial R^2} \right) - K_{02} (C_{21} - C_{23}); \\
R=0, \quad \frac{\partial C_{i0}}{\partial R} &\equiv 0; \quad R=1, \quad \frac{\partial C_{i0}}{\partial R} \equiv 0; \quad Z=0, \quad C_{i0} \equiv 1; \quad i=1,2.
\end{aligned} \tag{0.6.8}$$

For big values of the average velocities $0 = \text{Fo}_{11} \leq 10^{-2}$, $0 = \text{Fo}_{21} \leq 10^{-2}$ and from (2.3.8) follows the convective type of model

$$\begin{aligned}
U(R) \frac{dC_{11}}{dZ} &= -K_{01} (C_{11} - C_{13}); \\
U(R) \frac{dC_{21}}{dZ} &= -K_{02} (C_{21} - C_{23}); \quad Z=0, \quad C_{i0} \equiv 1; \quad i=1,2.
\end{aligned} \tag{0.6.9}$$

For small values of the average velocities $0 = K_{0i}^{-1} \leq 10^{-2}$, $i=1,2$, from (2.3.5) follows the diffusion type of model:

$$\begin{aligned}
0 &= K_{01}^{-1} \text{Fo}_{11} \left(\varepsilon \frac{\partial^2 C_{11}}{\partial Z^2} + \frac{1}{R} \frac{\partial C_{11}}{\partial R} + \frac{\partial^2 C_{11}}{\partial R^2} \right) - (C_{11} - C_{13}); \\
0 &= K_{02}^{-1} \text{Fo}_{21} \left(\varepsilon \frac{\partial^2 C_{21}}{\partial Z^2} + \frac{1}{R} \frac{\partial C_{21}}{\partial R} + \frac{\partial^2 C_{21}}{\partial R^2} \right) - (C_{21} - C_{23}); \\
R=0, \quad \frac{\partial C_{i0}}{\partial R} &\equiv 0; \quad R=1, \quad \frac{\partial C_{i0}}{\partial R} \equiv 0;
\end{aligned} \tag{0.6.10}$$

$$Z=0, \quad C_{i0} \equiv 1, \quad 1 \equiv U(R) - \text{Pe}_{i0}^{-1} \left(\frac{\partial C_{i0}}{\partial Z} \right)_{Z=0}; \quad i=1,2.$$

The solution of the model equations (2.3.6), (2.3.8) requires a velocity distribution in the column. As an example the case of parabolic velocity distribution (Poiseuille flow) in the gas phase will be presented [11]:

$$u_1 = \bar{u}_1 \left(2 - 2 \frac{r^2}{r_0^2} \right), \quad U(R) = 2 - 2R^2. \tag{0.6.11}$$

The solution of (2.3.8) depends on the two functions:

$$C_{13} = \frac{C_{11} + K_1(1 - C_{33})}{1 + K_2 C_{33}}, \quad C_{23} = \frac{C_{21}}{1 + K_3(1 - C_{33})}, \tag{0.6.12}$$

where C_{33} is the solution of the cubic equation:

$$\begin{aligned}
\omega_3 (C_{33})^3 + \omega_2 (C_{33})^2 + \omega_1 C_{33} + \omega_0 &= 0, \\
\omega_3 &= K_3 (K_1 K_4 - K_2 K_5), \\
\omega_2 &= K_5 (K_2 + 2K_2 K_3 - K_3) - K_4 (K_1 + 2K_1 K_3 + K_3 C_{11}) + K_2 C_{21}, \\
\omega_1 &= K_4 (C_{11} + K_1)(1 + K_3) + K_5 (1 + 2K_3 - K_2 - K_2 K_3) + (1 - K_2) C_{21}, \\
\omega_0 &= -C_{21} - K_3 K_5 - K_5.
\end{aligned} \tag{0.6.13}$$

As a solution of (2.3.13) $0 \leq C_{33} \leq 1$ is to be used.

A solution of the problem (2.3.8), (2.3.12), (2.3.13) has been obtained for the case $K_{0i} = 1$, $\text{Fo}_{i0} = 0.1$, $i=1,2$, $K_1 = 2.5$, $K_2 = 1$, $K_3 = 1$, $K_4 = 0.5$, $K_5 = 1$ (0.6.14)

as five-matrix forms:

$$\begin{aligned}
C_{11}(R, Z) &= \|C_{11(\rho\zeta)}\|, & C_{21}(R, Z) &= \|C_{21(\rho\zeta)}\|, & C_{13}(R, Z) &= \|C_{13(\rho\zeta)}\|, \\
C_{23}(R, Z) &= \|C_{23(\rho\zeta)}\|, & C_{33}(R, Z) &= \|C_{33(\rho\zeta)}\|; \\
R &= \frac{\rho-1}{\rho^0-1}, & \rho &= 1, 2, \dots, \rho^0; & Z &= \frac{\zeta-1}{\zeta^0-1}, & \zeta &= 1, 2, \dots, \zeta^0, & \rho^0 &= \zeta^0.
\end{aligned}
\tag{0.6.15}$$

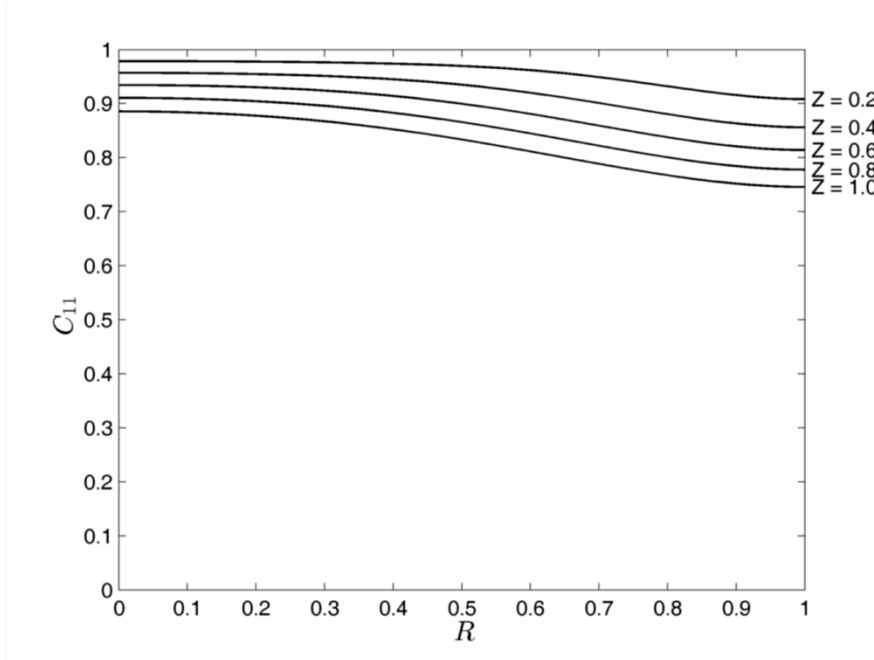


Fig. 3.5 Radial distribution of the concentration $C_{11}(R, Z)$.

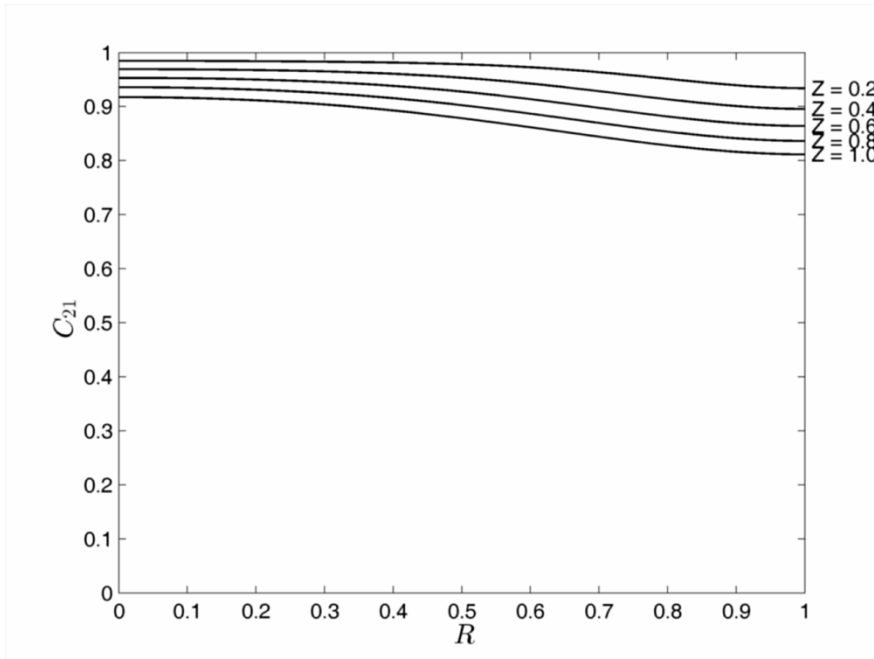


Fig. 3.6 Radial distribution of the concentration $C_{21}(R, Z)$.

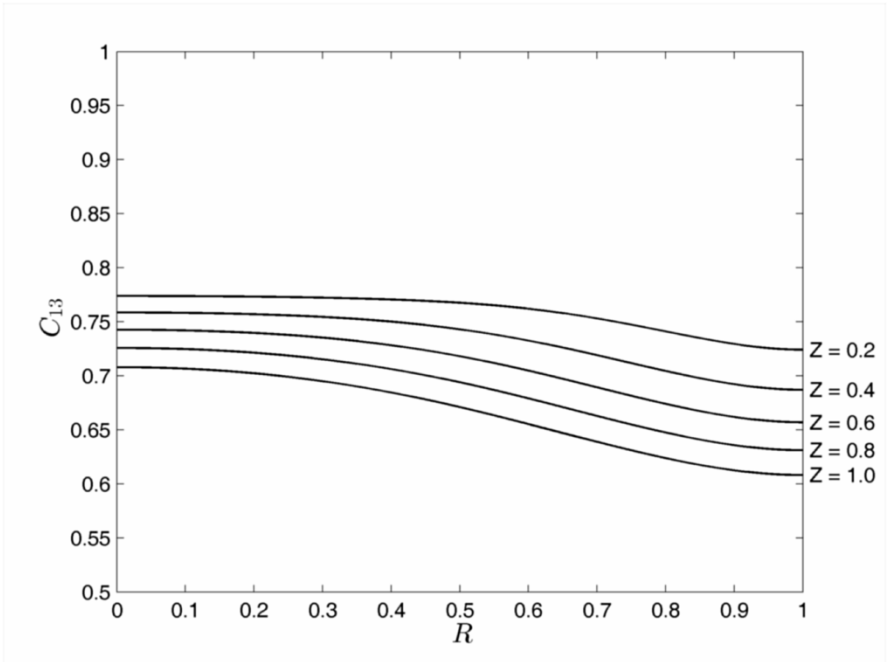


Fig. 3.7 Radial distribution of the concentration $C_{13}(R,Z)$.

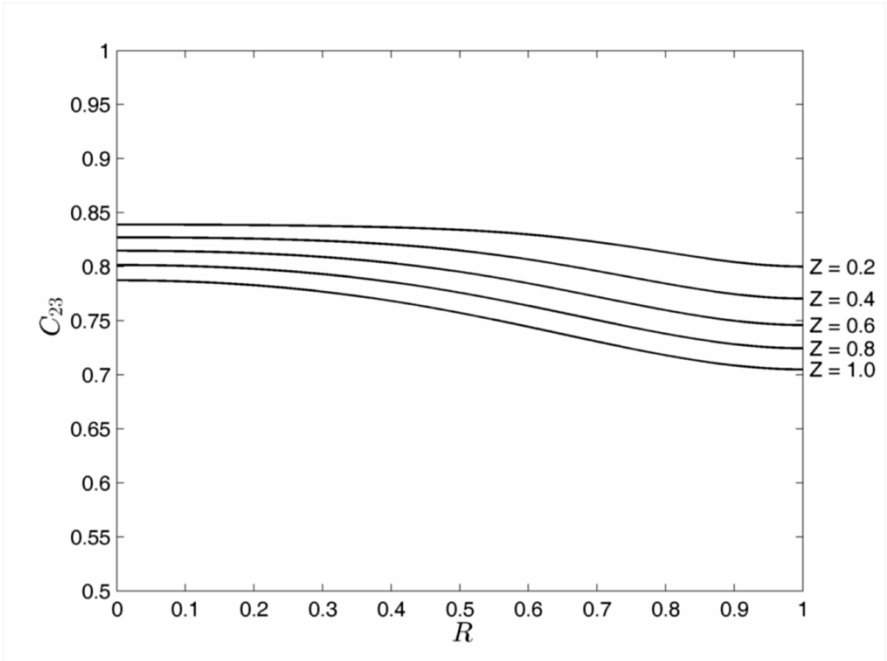


Fig. 3.8 Radial distribution of the concentration $C_{23}(R,Z)$.

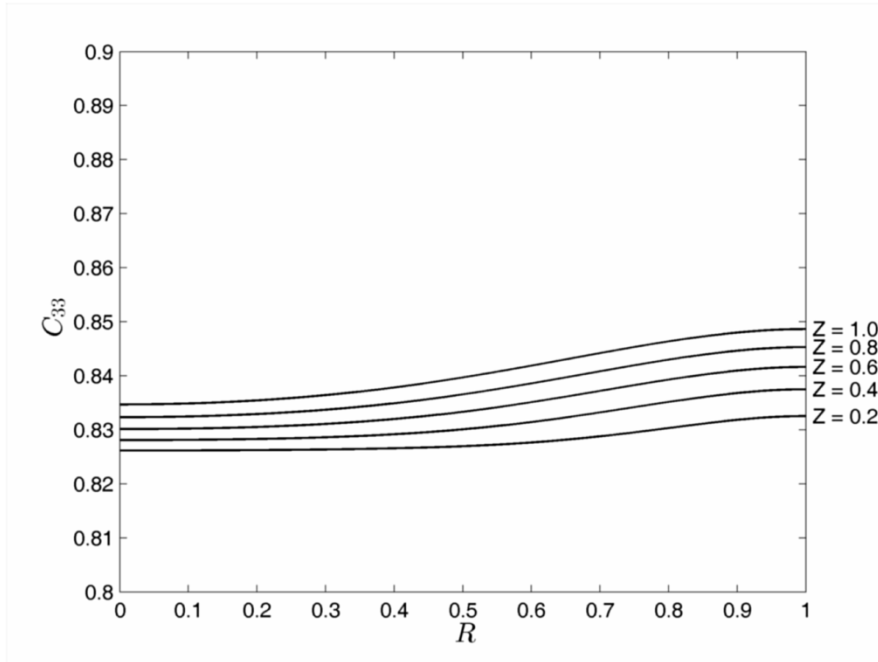


Fig. 3.9 Radial distribution of the concentration $c_{33}(R, Z)$.

The concentration distributions for different Z are presented on Figs. 3.5–3.9.

3.2 Chemical adsorption mechanism

The difference between the physical and chemical adsorption mechanisms (in the stationary

case) is that in (2.3.3) the physical adsorption rate $-bk_1c_{13}\frac{c_{33}}{c_{33}^0} + k_2c_{33}^0\left(1 - \frac{c_{33}}{c_{33}^0}\right)$ has to be replaced by the chemical adsorption rate $-k_{13}c_{13}c_{33}$. As a result:

1. The gas-solid interphase mass transfer rate of the first reagent $k_{01}(c_{11} - c_{13})$ is equal to the chemical reaction between this reagent and AS in the solid phase (catalyst) capillaries $k_{13}c_{13}c_{33}$.
2. The gas-solid interphase mass transfer rate of the second reagent $k_{02}(c_{21} - c_{23})$ is equal to the chemical reaction between this reagent and adsorbed reagent in the solid phase (catalyst) $kc_{23}(c_{33}^0 - c_{33})$.
3. The adsorption rate of the first reagent $k_{13}c_{13}c_{33}$ must be equal to the desorption rate of the catalytic reaction product, i.e. to the catalytic reaction rate $kc_{23}(c_{33}^0 - c_{33})$.

In these conditions the convection-diffusion model of a stationary heterogeneous catalytic chemical reaction in a column apparatuses between two AC in the cases of chemical adsorption of one AC has the form:

$$\begin{aligned}
u_1 \frac{\partial c_{11}}{\partial z} &= D_{11} \left(\frac{\partial^2 c_{11}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{11}}{\partial r} + \frac{\partial^2 c_{11}}{\partial r^2} \right) - k_{01} (c_{11} - c_{13}); \\
u_1 \frac{\partial c_{21}}{\partial z} &= D_{21} \left(\frac{\partial^2 c_{21}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{21}}{\partial r} + \frac{\partial^2 c_{21}}{\partial r^2} \right) - k_{02} (c_{21} - c_{23}); \\
r = 0, \quad \frac{\partial c_{11}}{\partial r} = \frac{\partial c_{21}}{\partial r} &\equiv 0; \quad r = r_0, \quad \frac{\partial c_{11}}{\partial r} = \frac{\partial c_{21}}{\partial r} \equiv 0; \\
z = 0, \quad c_{11} &\equiv c_{11}^0, \quad u_1^0 c_{11}^0 \equiv u_1(r) c_{11}^0 - D_{11} \left(\frac{\partial c_{11}}{\partial z} \right)_{z=0}, \\
c_{21} &\equiv c_{21}^0, \quad u_1^0 c_{21}^0 \equiv u_1(r) c_{21}^0 - D_{21} \left(\frac{\partial c_{21}}{\partial z} \right)_{z=0}.
\end{aligned} \tag{0.6.16}$$

$$\begin{aligned}
k_{01} (c_{11} - c_{13}) &= k_{13} c_{13} c_{33}; \quad k_{02} (c_{21} - c_{23}) = k c_{23} (c_{33}^0 - c_{33}); \\
k_{13} c_{13} c_{33} &= k c_{23} (c_{33}^0 - c_{33}).
\end{aligned} \tag{0.6.17}$$

The introduction of the dimensionless variables (2.3.4) in (2.3.16), (2.3.17) leads to:

$$\begin{aligned}
U(R) \frac{\partial C_{11}}{\partial Z} &= \text{Fo}_{11} \left(\varepsilon \frac{\partial^2 C_{11}}{\partial Z^2} + \frac{1}{R} \frac{\partial C_{11}}{\partial R} + \frac{\partial^2 C_{11}}{\partial R^2} \right) - K_{01} (C_{11} - C_{13}); \\
U(R) \frac{\partial C_{21}}{\partial Z} &= \text{Fo}_{21} \left(\varepsilon \frac{\partial^2 C_{21}}{\partial Z^2} + \frac{1}{R} \frac{\partial C_{21}}{\partial R} + \frac{\partial^2 C_{21}}{\partial R^2} \right) - K_{02} (C_{21} - C_{23}); \\
R = 0, \quad \frac{\partial C_{i1}}{\partial R} &\equiv 0; \quad R = 1, \quad \frac{\partial C_{i1}}{\partial R} \equiv 0; \\
Z = 0, \quad C_{i1} &\equiv 1, \quad 1 \equiv U(R) - \text{Pe}_i^{-1} \left(\frac{\partial C_{i1}}{\partial Z} \right)_{Z=0}; \quad i = 1, 2. \\
C_{13} &= \frac{C_{11}}{1 + K_1 C_{33}}, \quad C_{23} = \frac{C_{21}}{1 + K_2 (1 - C_{33})}, \quad C_{33} = \frac{C_{23}}{C_{23} + K_3 C_{13}},
\end{aligned} \tag{0.6.18}$$

where

$$K_1 = \frac{k_{13} c_{33}^0}{k_{01}}, \quad K_2 = \frac{k_{23} c_{33}^0}{k_{02}}, \quad K_3 = \frac{k_{13} c_{11}^0}{k_{23} c_{21}^0}. \tag{0.6.20}$$

The models (2.3.5) and (2.3.18) are equivalent and the theoretical analysis of the physical adsorption mechanism of the catalytic reactions in column chemical reactors (2.3.8), (2.3.9), (2.3.10) is valid in the chemical adsorption case. The difference is in the expressions (2.3.6), (2.3.19) of the volume concentrations in the solid phase (catalyst), only.

The solution of the model equations (2.3.18), (2.3.19) needs a velocity distribution in the column. The case of parabolic velocity distribution (2.3.11) will be presented [11] as an example.

The solution of (2.3.18) depends on the two functions (C_{13}, C_{23}) in (2.3.19), where C_{33} is the solution of the quadratic equation

$$(C_{21} K_1 - C_{11} K_2 K_3) (C_{33})^2 + (C_{21} + C_{11} K_3 + C_{11} K_2 K_3 - C_{21} K_1) C_{33} - C_{21} = 0. \tag{0.6.21}$$

As a solution of (2.3.21) $0 \leq C_{33} \leq 1$ is to be used.

A solution of the problem (2.3.18), (2.3.19), (2.3.21) is obtained for the case

$$K_{0i} = 1, \quad \text{Fo}_{i0} = 0.1, \quad \varepsilon = 0, \quad i = 1, 2, \quad K_1 = 1, \quad K_2 = 0.5, \quad K_3 = 1, \tag{0.6.22}$$

as five-matrix forms (2.3.15). The concentration distributions for different Z are presented in Figs. 3.10–3.14.

The presented new approach for modeling of two-phase processes in column apparatuses is a basis for qualitative analysis of particular processes and for the creation of the average concentration models and quantitative analysis of the processes.

Catalytic processes modeling

3.1 Physical adsorption mechanism

The convection-diffusion model of the catalytic processes in the column apparatuses [8] in the cases of physical adsorption mechanism has the form (3.3.3):

$$\begin{aligned}
u_1 \frac{\partial c_{11}}{\partial z} &= D_{11} \left(\frac{\partial^2 c_{11}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{11}}{\partial r} + \frac{\partial^2 c_{11}}{\partial r^2} \right) - k_{01} (c_{11} - c_{13}); \\
u_1 \frac{\partial c_{21}}{\partial z} &= D_{21} \left(\frac{\partial^2 c_{21}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{21}}{\partial r} + \frac{\partial^2 c_{21}}{\partial r^2} \right) - k_{02} (c_{21} - c_{23}); \\
k_{01} (c_{11} - c_{13}) - b_0 k_1 c_{13} \frac{c_{33}}{c_{33}^0} + k_2 c_{33}^0 \left(1 - \frac{c_{33}}{c_{33}^0} \right) &= 0; \\
k_{02} (c_{21} - c_{23}) - k c_{23} (c_{33}^0 - c_{33}) &= 0; \\
-b_0 k_1 c_{13} \frac{c_{33}}{c_{33}^0} + k_2 c_{33}^0 \left(1 - \frac{c_{33}}{c_{33}^0} \right) + k c_{23} (c_{33}^0 - c_{33}) &= 0; \\
r = 0, \quad \frac{\partial c_{11}}{\partial r} = \frac{\partial c_{21}}{\partial r} &\equiv 0; \quad r = r_0, \quad \frac{\partial c_{11}}{\partial r} = \frac{\partial c_{21}}{\partial r} \equiv 0; \\
z = 0, \quad c_{11} &\equiv c_{11}^0, \quad u_1^0 c_{11}^0 \equiv u_1(r) c_{11}^0 - D_{11} \left(\frac{\partial c_{11}}{\partial z} \right)_{z=0}, \\
c_{21} &\equiv c_{21}^0, \quad u_1^0 c_{21}^0 \equiv u_1(r) c_{21}^0 - D_{21} \left(\frac{\partial c_{21}}{\partial z} \right)_{z=0}.
\end{aligned} \tag{0.7.1}$$

From (II.3) follow the average values of the velocity and the concentration functions in (6.3.1) at the column cross-sectional area:

$$\begin{aligned}
\bar{u}_1 &= \frac{2}{r_0^2} \int_0^{r_0} r u_1(r) dr, \quad \bar{c}_{11}(z) = \frac{2}{r_0^2} \int_0^{r_0} r c_{11}(r, z) dr, \\
\bar{c}_{21}(z) &= \frac{2}{r_0^2} \int_0^{r_0} r c_{21}(r, z) dr, \quad \bar{c}_{13}(z) = \frac{2}{r_0^2} \int_0^{r_0} r c_{13}(r, z) dr, \\
\bar{c}_{23}(z) &= \frac{2}{r_0^2} \int_0^{r_0} r c_{23}(r, z) dr, \quad \bar{c}_{33}(z) = \frac{2}{r_0^2} \int_0^{r_0} r c_{33}(r, z) dr.
\end{aligned} \tag{0.7.2}$$

The functions in (6.3.1) can be presented by the average functions (6.3.2):

$$\begin{aligned}
u_1(r) &= \bar{u}_1 \tilde{u}_1(r), \quad c_{11}(r, z) = \bar{c}_{11}(z) \tilde{c}_{11}(r, z), \\
c_{21}(r, z) &= \bar{c}_{21}(z) \tilde{c}_{21}(r, z), \quad c_{13}(r, z) = \bar{c}_{13}(z) \tilde{c}_{13}(r, z), \\
c_{23}(r, z) &= \bar{c}_{23}(z) \tilde{c}_{23}(r, z), \quad c_{33}(r, z) = \bar{c}_{33}(z) \tilde{c}_{33}(r, z).
\end{aligned} \tag{0.7.3}$$

where

$$\begin{aligned}
\frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}_1(r) dr &= 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_{11}(r, z) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_{21}(r, z) dr = 1, \\
\frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_{13}(r, z) dr &= 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_{23}(r, z) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_{33}(r, z) dr = 1.
\end{aligned} \tag{0.7.4}$$

The use of (6.3.2), (6.3.3), (6.3.4) and the averaging procedure (6.0.1)–(6.0.5) leads to the average concentration model of the catalytic processes in the column apparatuses in the cases of physical adsorption mechanism:

$$\begin{aligned}
\alpha_1 \bar{u}_1 \frac{d\bar{c}_{11}}{dz} + \frac{d\alpha_1}{dz} \bar{u}_1 \bar{c}_{11} &= D_{11} \frac{d^2 \bar{c}_{11}}{dz^2} - k_{01} (\bar{c}_{11} - \bar{c}_{13}); \\
\alpha_2 \bar{u}_1 \frac{d\bar{c}_{21}}{dz} + \frac{d\alpha_2}{dz} \bar{u}_1 \bar{c}_{21} &= D_{21} \frac{d^2 \bar{c}_{21}}{dz^2} - k_{02} (\bar{c}_{21} - \bar{c}_{23}); \\
k_{01} (\bar{c}_{11} - \bar{c}_{13}) - \beta b_0 k_1 \bar{c}_{13} \frac{\bar{c}_{33}}{c_{33}^0} + k_2 c_{33}^0 \left(1 - \frac{\bar{c}_{33}}{c_{33}^0}\right) &= 0; \\
k_{02} (\bar{c}_{21} - \bar{c}_{23}) - k \bar{c}_{23} c_{33}^0 + \gamma k \bar{c}_{23} \bar{c}_{33} &= 0; \\
-\beta b_0 k_1 \bar{c}_{13} \frac{\bar{c}_{33}}{c_{33}^0} + k_2 c_{33}^0 \left(1 - \frac{\bar{c}_{33}}{c_{33}^0}\right) + k \bar{c}_{23} c_{33}^0 - \gamma k \bar{c}_{23} \bar{c}_{33} &= 0; \\
z = 0, \quad \bar{c}_{11} = c_{11}^0, \quad \left(\frac{d\bar{c}_{11}}{dz}\right)_{z=0} = 0, \quad \bar{c}_{21} = c_{21}^0, \quad \left(\frac{d\bar{c}_{21}}{dz}\right)_{z=0} &= 0.
\end{aligned} \tag{0.7.5}$$

where

$$\begin{aligned}
\alpha_1 = \alpha_1(z) &= \frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}_1(r) \tilde{c}_{11}(r, z) dr, \\
\alpha_2 = \alpha_2(z) &= \frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}_1(r) \tilde{c}_{21}(r, z) dr, \\
\beta = \beta(z) &= \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_{13}(r, z) \tilde{c}_{33}(r, z) dr, \\
\gamma = \gamma(z) &= \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_{23}(r, z) \tilde{c}_{33}(r, z) dr.
\end{aligned} \tag{0.7.6}$$

The use of the generalized variables

$$\begin{aligned}
Z = \frac{z}{l}, \quad \bar{C}_{11} = \frac{\bar{c}_{11}}{c_{11}^0}, \quad \bar{C}_{21} = \frac{\bar{c}_{21}}{c_{21}^0}, \quad \bar{C}_{13} = \frac{\bar{c}_{13}}{c_{11}^0}, \quad \bar{C}_{23} = \frac{\bar{c}_{23}}{c_{21}^0}, \quad \bar{C}_{33} = \frac{\bar{c}_{33}}{c_{33}^0}, \\
\tilde{C}_{11} = \frac{\tilde{c}_{11}}{c_{11}^0}, \quad \tilde{C}_{21} = \frac{\tilde{c}_{21}}{c_{21}^0}, \quad \tilde{C}_{13} = \frac{\tilde{c}_{13}}{c_{11}^0}, \quad \tilde{C}_{23} = \frac{\tilde{c}_{23}}{c_{21}^0}, \quad \tilde{C}_{33} = \frac{\tilde{c}_{33}}{c_{33}^0},
\end{aligned} \tag{0.7.7}$$

leads to:

$$\begin{aligned}
A_1 \frac{d\bar{C}_{11}}{dZ} + \frac{dA_1}{dZ} \bar{C}_{11} &= \text{Pe}_1^{-1} \frac{d^2 \bar{C}_{11}}{dZ^2} - K_{01} (\bar{C}_{11} - \bar{C}_{13}); \\
A_2 \frac{d\bar{C}_{21}}{dZ} + \frac{dA_2}{dZ} \bar{C}_{21} &= \text{Pe}_2^{-1} \frac{d^2 \bar{C}_{21}}{dZ^2} - K_{02} (\bar{C}_{21} - \bar{C}_{23}); \\
Z = 0, \quad \bar{C}_{11} = 1, \quad \left(\frac{d\bar{C}_{11}}{dZ}\right)_{Z=0} = 0, \quad \bar{C}_{21} = 1, \quad \left(\frac{d\bar{C}_{21}}{dZ}\right)_{Z=0} &= 0.
\end{aligned} \tag{0.7.8}$$

$$\begin{aligned}
\bar{C}_{13} &= \frac{\bar{C}_{11} + K_1 (1 - \bar{C}_{33})}{1 + BK_2 \bar{C}_{33}}, \quad \bar{C}_{23} = \frac{\bar{C}_{21}}{1 + K_3 (1 - G\bar{C}_{33})}, \\
\bar{C}_{33} &= \frac{K_5 + \bar{C}_{23}}{BK_4 \bar{C}_{13} + K_5 + G\bar{C}_{23}}.
\end{aligned} \tag{0.7.9}$$

The parameters in (6.3.8), (6.3.9) and the new functions have the forms:

$$\begin{aligned}
K_{0i} &= \frac{k_{0i}l}{u_1^0}, \quad Pe_{i1} = \frac{u_1^0 l}{D_{i0}}, \quad i = 1, 2; \quad K_1 = \frac{k_2}{k_{01}} \frac{c_{33}^0}{c_{11}^0}, \\
K_2 &= \frac{b_0 k_1}{k_{01}}, \quad K_3 = \frac{k_{23} c_{33}^0}{k_{02}}, \quad K_4 = \frac{b_0 k_1}{k_{23} c_{21}^0} \frac{c_{11}^0}{c_{33}^0}, \quad K_5 = \frac{k_2}{k_{23} c_{21}^0}.
\end{aligned} \tag{0.7.10}$$

$$\begin{aligned}
A_i(Z) &= \alpha_i(lZ) = \alpha_i(z) = 2 \int_0^1 RU(R) \frac{C_{i1}(R, Z)}{\bar{C}_{i1}(Z)} dR, \quad i = 1, 2, \\
B(Z) &= \beta(lZ) = \beta(z) = 2 \int_0^1 R \frac{C_{13}(R, Z)}{\bar{C}_{13}(Z)} \frac{C_{33}(R, Z)}{\bar{C}_{33}(Z)} dR, \\
G(Z) &= \gamma(lZ) = \gamma(z) = 2 \int_0^1 R \frac{C_{23}(R, Z)}{\bar{C}_{23}(Z)} \frac{C_{33}(R, Z)}{\bar{C}_{33}(Z)} dR, \\
\bar{C}_{11}(Z) &= 2 \int_0^1 RC_{11}(R, Z) dR, \quad \bar{C}_{21}(Z) = 2 \int_0^1 RC_{21}(R, Z) dR, \\
\bar{C}_{13}(Z) &= 2 \int_0^1 RC_{13}(R, Z) dR, \quad \bar{C}_{23}(Z) = 2 \int_0^1 RC_{23}(R, Z) dR, \\
\bar{C}_{33}(Z) &= 2 \int_0^1 RC_{33}(R, Z) dR.
\end{aligned} \tag{0.7.11}$$

The use of (5.3.11) and $C_{11}(R, Z), C_{21}(R, Z), C_{13}(R, Z), C_{23}(R, Z), C_{33}(R, Z)$ as a solution of the problem (3.3.8, 3.3.12, 3.3.13) for the case (3.3.14) permits to obtain the average concentrations $\bar{C}_{11}(Z), \bar{C}_{21}(Z), \bar{C}_{13}(Z), \bar{C}_{23}(Z), \bar{C}_{33}(Z)$ and the functions $A_i(Z), i = 1, 2, B(Z), G(Z)$. They are presented on Figs. 6.17 and 6.18, where it is seen that the functions $A_i(Z), i = 1, 2, B(Z), G(Z)$ can be presented as linear approximations:

$$A_i(Z) = a_{0i} + a_{1i}Z, \quad i = 1, 2, \quad B(Z) = b_{0i} + b_{1i}Z, \quad G(Z) = g_{0i} + g_{1i}Z. \tag{0.7.12}$$

The approximations ("theoretical") parameters values are presented in Table 6.3, where it is seen that $B \approx 1, G \approx 1$, practically.

Table 6.3 Parameters values

For high columns ($0 = \varepsilon \leq 10^{-2}$,
 $0 = Pe_i^{-1} = \varepsilon.Fo_{i1} \leq 10^{-2}, Fo_{i1} \leq 1, i = 1, 2$)

and the problem (5.3.8) takes the form:

	A_1	A_2	B	G
	$a_{01} =$	$a_{02} =$	$b_0 =$	$g_0 =$
	1.0090	1.0063	1.0000	1.0000
	$a_{11} =$	$a_{12} =$	$b_1 =$	$g_1 =$
	0.0257	0.0183	-0.0003	-0.0002

$$\begin{aligned}
A_1 \frac{d\bar{C}_{11}}{dZ} + \frac{dA_1}{dZ} \bar{C}_{11} &= -K_{01} (\bar{C}_{11} - \bar{C}_{13}); \\
A_2 \frac{d\bar{C}_{21}}{dZ} + \frac{dA_2}{dZ} \bar{C}_{21} &= -K_{02} (\bar{C}_{21} - \bar{C}_{23}); \quad Z = 0, \quad \bar{C}_{11} \equiv 1, \quad \bar{C}_{21} \equiv 1.
\end{aligned} \tag{0.7.13}$$

The solution of (5.3.13) depends on the two functions:

$$\bar{C}_{13} = \frac{\bar{C}_{11} + K_1(1 - \bar{C}_{33})}{1 + BK_2\bar{C}_{33}}, \quad \bar{C}_{23} = \frac{\bar{C}_{21}}{1 + K_3(1 - G\bar{C}_{33})}, \tag{0.7.14}$$

where \bar{C}_{33} is the solution of the cubic equation:

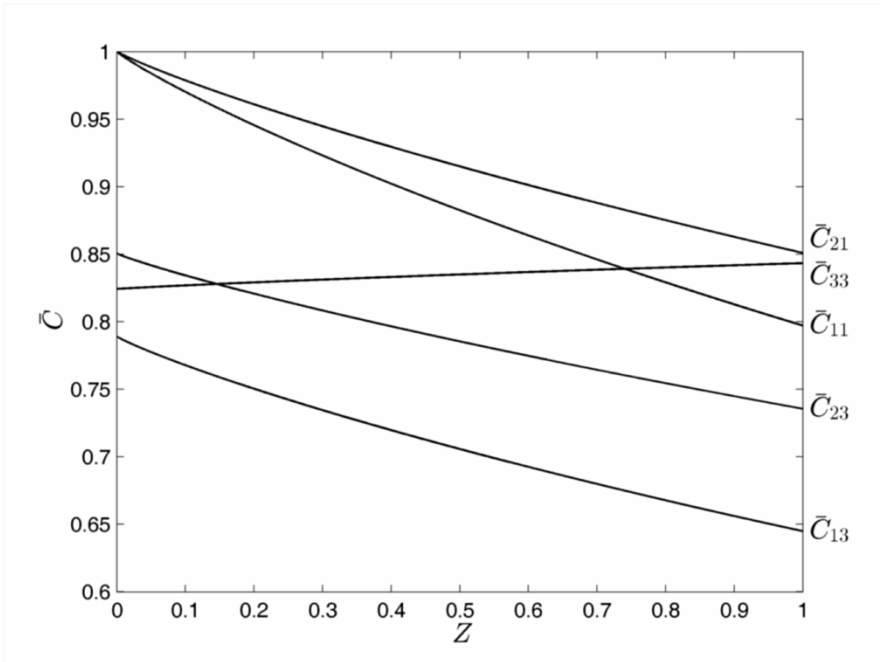


Fig. 6.17 Average functions $\bar{c}(z)$

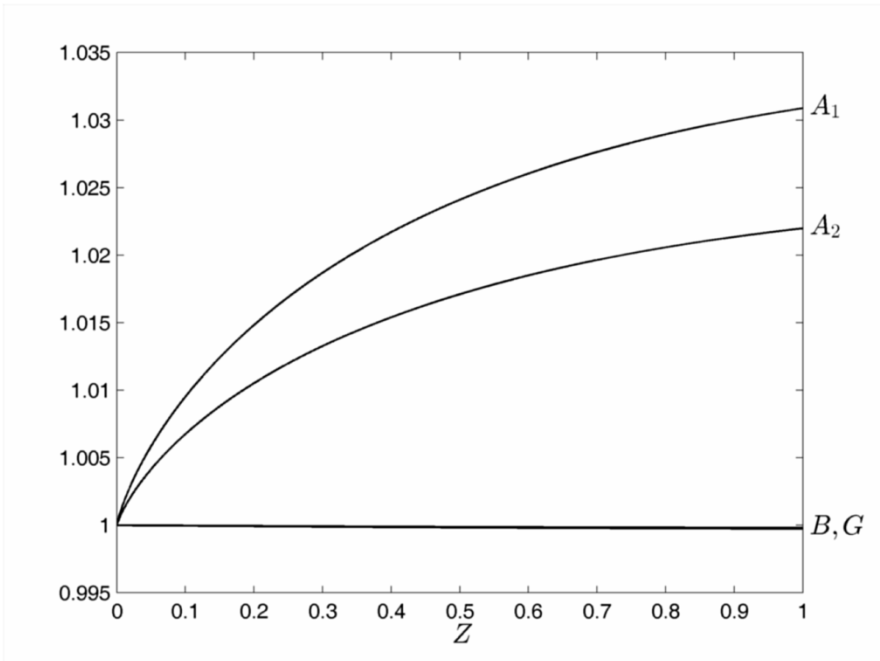


Fig. 6.18 Functions $A_i(z)$, $i=1,2$, $B(z)$, $G(z)$

$$\begin{aligned}
\omega_3 (\bar{C}_{33})^3 + \omega_2 (\bar{C}_{33})^2 + \omega_1 \bar{C}_{33} + \omega_0 &= 0, \\
\omega_3 &= BGK_3 (K_1 K_4 - K_2 K_5), \\
\omega_2 &= K_5 (BK_2 + 2BK_2 K_3 - GK_3) - \\
&- K_4 (BK_1 + BK_1 K_3 + BGK_1 K_3 + BGK_3 C_{11}) + BGK_2 C_{21}, \\
\omega_1 &= BK_4 (C_{11} + K_1) (1 + K_3) + \\
&+ K_5 (1 + K_3 + GK_3 - BK_2 - BK_2 K_3) + (G - BK_2) C_{21}, \\
\omega_0 &= -C_{21} - K_3 K_5 - K_5.
\end{aligned} \tag{0.7.15}$$

For solving (6.3.15) $0 \leq \bar{C}_{33} \leq 1$ has to be used.

The solution of (6.3.13)–(6.3.15) is obtained [8] as five vector forms:

$$\begin{aligned}
\bar{C}_{11}(Z) &= \left| \bar{C}_{11(\zeta)} \right|, \quad \bar{C}_{21}(Z) = \left| \bar{C}_{21(\zeta)} \right|, \quad \bar{C}_{13}(Z) = \left| \bar{C}_{13(\zeta)} \right|, \\
\bar{C}_{23}(Z) &= \left| \bar{C}_{23(\zeta)} \right|, \quad \bar{C}_{33}(Z) = \left| \bar{C}_{33(\zeta)} \right|, \quad Z = \frac{\zeta - 1}{\zeta^0 - 1}, \quad \zeta = 1, 2, \dots, \zeta^0.
\end{aligned} \tag{0.7.16}$$

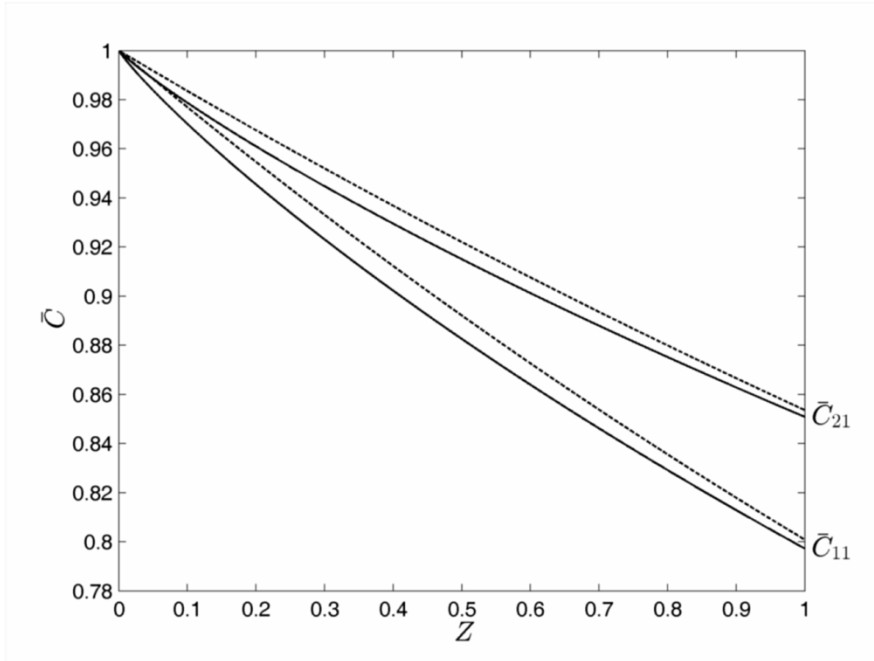


Fig. 6.19 Functions $\bar{C}_{11}(Z), \bar{C}_{21}(Z)$: dotted lines - solution of (6.3.13)–(6.3.15) using Table. 6.3; lines - solution of (3.3.8), (3.3.12), (3.3.13) using (6.3.11)

For the case (3.3.14) Fig. 6.19 provides comparison of the functions $\bar{C}_{11}(Z), \bar{C}_{21}(Z)$ obtained as solutions of (6.3.13)–(6.3.15) using Table 6.3 (the dotted lines) with the solution of (3.3.8), (3.3.12), (3.3.13), using (6.3.11) (the lines).

The obtained concentrations $\bar{C}_{11}(Z), \bar{C}_{21}(Z)$ for the case (3.3.14) after solution of (3.3.8, 3.3.12, 3.3.13) using (6.3.11) allows to obtain “artificial experimental data” for different values of Z :

$$\begin{aligned}
\bar{C}_{11\text{exp}}^m(Z_n) &= (0.95 + 0.1S_m) \bar{C}_{11}(Z_n), \\
\bar{C}_{21\text{exp}}^m(Z_n) &= (0.95 + 0.1S_m) \bar{C}_{21}(Z_n), \\
m &= 1, \dots, 10, \quad Z_n = 0.1n, \quad n = 1, 2, \dots, 10,
\end{aligned} \tag{0.7.17}$$

where $0 \leq S_m \leq 1, m=1, \dots, 10$ are obtained by means of a generator of random numbers. The obtained “artificial experimental data” (6.3.17) are used for illustration of the parameter identification in the average concentrations model (6.3.13)–(6.3.15) by minimization of the least-squares functions Q_n and Q :

$$Q_n(Z_n, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n) = \sum_{m=1}^{10} [\bar{C}_{11}(Z_n, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n) - \bar{C}_{11\text{exp}}^m(Z_n)]^2 +$$

$$+ \sum_{m=1}^{10} [\bar{C}_{21}(Z_n, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n) - \bar{C}_{21\text{exp}}^m(Z_n)]^2, \quad Z_n = 0.1n, \quad n = 1, 2, \dots, 10;$$

$$Q(a_{01}^0, a_{11}^0, a_{02}^0, a_{12}^0) = \sum_{n=1}^{10} Q_n(Z_n, a_{01}^0, a_{11}^0, a_{02}^0, a_{12}^0), \quad (0.7.18)$$

where the values of $\bar{C}_{11}(Z_n, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n)$ and $\bar{C}_{21}(Z_n, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n)$ are obtained as solutions of (5.3.13–5.3.15) for different values of Z : $Z_n = 0.1n, n = 1, 2, \dots, 10$.

The obtained (“experimental”) parameter values of $a_{01}^0, a_{11}^0, a_{02}^0, a_{12}^0, a_{01}^1, a_{11}^1, a_{02}^1, a_{12}^1, a_{01}^2, a_{11}^2, a_{02}^2, a_{12}^2$ are presented in Table 6.4. They are used for calculation of the functions $\bar{C}_{11}(Z, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n), \bar{C}_{21}(Z, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n), n = 0, 1, 2$ in the case (3.3.14) as solutions of (6.3.13)–(6.3.15) (the lines in Fig. 6.20), where the points are the “artificial experimental data” (6.3.17) (average values for every Z).

The comparison of the functions (lines) with the “artificial experimental data” (points) in Figs. 6.20 and 6.21 shows that the experimental data obtained from a column with real radius and small height ($Z = 0.1$) are useful for parameters identifications.

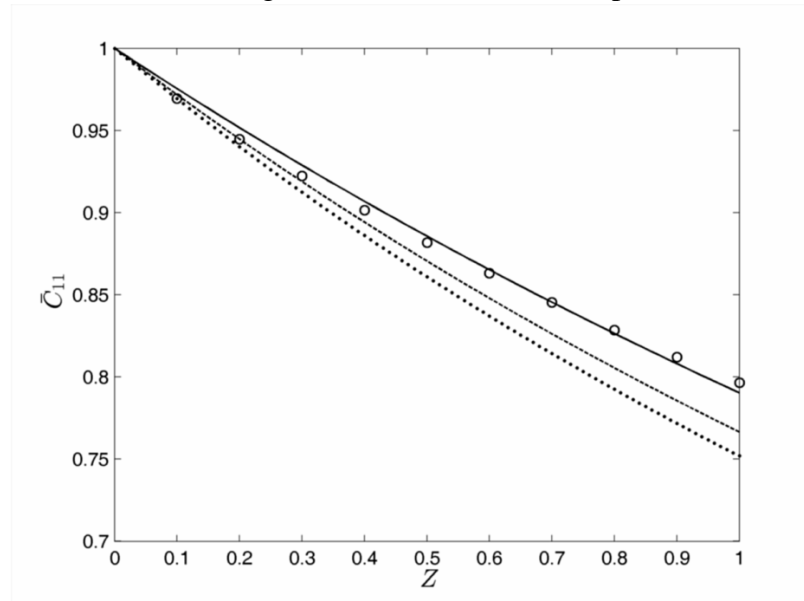


Fig. 6.20 Concentration distributions $\bar{C}_{11}(Z, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n), n = 0, 1, 2$: lines - solutions of (6.3.13)–(6.3.15) in the case (3.3.14); points - the “artificial experimental data” (6.3.17) (average values for every Z).

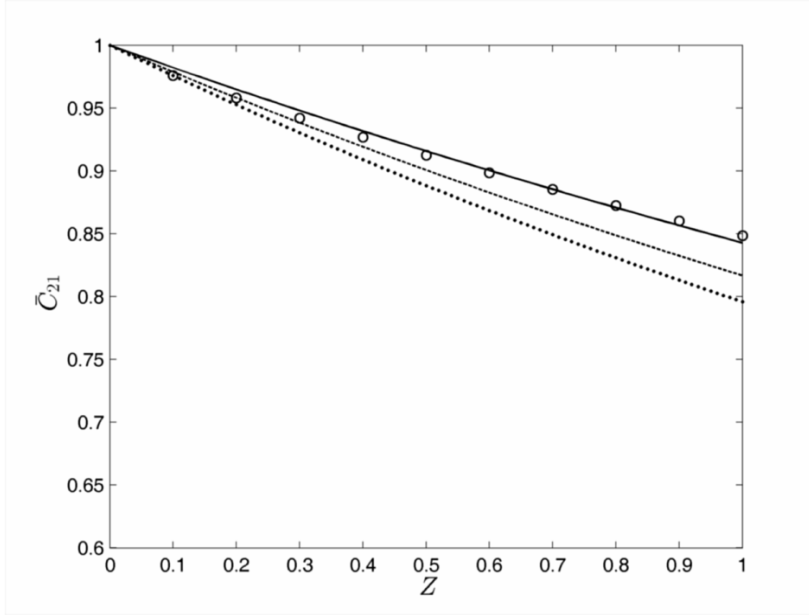


Fig. 5.21 Concentration distributions $\bar{c}_{21}(Z, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n)$, $n = 0, 1, 2$:
 lines - solutions of (6.3.13)–(6.3.15) in the case (3.3.14);
 points - the “artificial experimental data” (6.3.17) (average values for every Z).

Table 6.4 Parameters	“Theoretical values”	“Experimental” values - Q min.	“Experimental” values - Q_1 min.	“Experimental” values - Q_2 min.
	$a_{01} = 1.0090$	$a_{01}^0 = 1.0000$	$a_{01}^1 = 0.9984$	$a_{01}^2 = 0.9988$
	$a_{11} = 0.0257$	$a_{11}^0 = 0.0397$	$a_{11}^1 = 0.1032$	$a_{11}^2 = 0.0779$
3.3 Chemical	$a_{02} = 1.0063$	$a_{02}^0 = 1.0000$	$a_{02}^1 = 0.8865$	$a_{02}^2 = 0.9206$
adsorption mechanism	$a_{12} = 0.0183$	$a_{12}^0 = 0.0316$	$a_{12}^1 = 0.0688$	$a_{12}^2 = 0.0499$

The convection-diffusion model of the heterogeneous catalytic chemical reaction, in the case of chemical adsorption mechanism [8], has the form (3.3.11), (3.3.12), where the average values of the velocity and concentration functions at the column cross-sectional area have the forms (6.3.2)–(6.3.4). The use of (3.3.11), (3.3.12) and the averaging procedure (6.0.1)–(6.0.5) leads to the average concentration model of the catalytic processes in the column apparatuses in the cases of chemical adsorption mechanism:

$$\begin{aligned} \alpha_1 \bar{u}_1 \frac{d\bar{c}_{11}}{dz} + \frac{d\alpha_1}{dz} \bar{u}_1 \bar{c}_{11} &= D_{11} \frac{d^2 \bar{c}_{11}}{dz^2} - k_{01} (\bar{c}_{11} - \bar{c}_{13}); \\ \alpha_2 \bar{u}_1 \frac{d\bar{c}_{21}}{dz} + \frac{d\alpha_2}{dz} \bar{u}_1 \bar{c}_{21} &= D_{21} \frac{d^2 \bar{c}_{21}}{dz^2} - k_{02} (\bar{c}_{21} - \bar{c}_{23}); \\ z = 0, \quad \bar{c}_{11} &= c_{11}^0, \quad \left(\frac{d\bar{c}_{11}}{dz} \right)_{z=0} = 0, \quad \bar{c}_{21} = c_{21}^0, \quad \left(\frac{d\bar{c}_{21}}{dz} \right)_{z=0} = 0. \end{aligned} \quad (0.7.19)$$

$$\begin{aligned} k_{01} (\bar{c}_{11} - \bar{c}_{13}) - \beta k_{13} \bar{c}_{13} \bar{c}_{33} &= 0, \quad k_{02} (\bar{c}_{21} - \bar{c}_{23}) - k_{23} \bar{c}_{23} (c_{33}^0 - \gamma \bar{c}_{33}) = 0, \\ -\beta k_{13} \bar{c}_{13} \bar{c}_{33} + k_{23} \bar{c}_{23} (c_{33}^0 - \gamma \bar{c}_{33}) &= 0. \end{aligned} \quad (0.7.20)$$

The new functions in (6.3.19), (6.3.20) are

$$\begin{aligned}\alpha_i &= \alpha_i(z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}_1(r) \tilde{c}_{i1}(r, z) dr, \quad i=1,2, \\ \beta &= \beta(z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_{13}(r, z) \tilde{c}_{33}(r, z) dr, \\ \gamma &= \gamma(z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_{23}(r, z) \tilde{c}_{33}(r, z) dr.\end{aligned}\tag{0.7.21}$$

The use of the generalized variables

$$\begin{aligned}Z &= \frac{z}{l}, \quad \bar{C}_{11} = \frac{\bar{c}_{11}}{c_{11}^0}, \quad \bar{C}_{21} = \frac{\bar{c}_{21}}{c_{21}^0}, \quad \bar{C}_{13} = \frac{\bar{c}_{13}}{c_{11}^0}, \quad \bar{C}_{23} = \frac{\bar{c}_{23}}{c_{21}^0}, \quad \bar{C}_{33} = \frac{\bar{c}_{33}}{c_{33}^0}, \\ \tilde{C}_{11} &= \frac{\tilde{c}_{11}}{c_{11}^0}, \quad \tilde{C}_{21} = \frac{\tilde{c}_{21}}{c_{21}^0}, \quad \tilde{C}_{13} = \frac{\tilde{c}_{13}}{c_{11}^0}, \quad \tilde{C}_{23} = \frac{\tilde{c}_{23}}{c_{21}^0}, \quad \tilde{C}_{33} = \frac{\tilde{c}_{33}}{c_{33}^0},\end{aligned}\tag{0.7.22}$$

leads to:

$$\begin{aligned}A_1 \frac{d\bar{C}_{11}}{dZ} + \frac{dA_1}{dZ} \bar{C}_{11} &= \text{Pe}_{11}^{-1} \frac{d^2 \bar{C}_{11}}{dZ^2} - K_{01} (\bar{C}_{11} - \bar{C}_{13}); \\ A_2 \frac{d\bar{C}_{21}}{dZ} + \frac{dA_2}{dZ} \bar{C}_{21} &= \text{Pe}_{21}^{-1} \frac{d^2 \bar{C}_{21}}{dZ^2} - K_{02} (\bar{C}_{21} - \bar{C}_{23}); \\ Z=0, \quad \bar{C}_{11} &= 1, \quad \left(\frac{d\bar{C}_{11}}{dZ} \right)_{Z=0} = 0, \quad \bar{C}_{21} = 1, \quad \left(\frac{d\bar{C}_{21}}{dZ} \right)_{Z=0} = 0.\end{aligned}\tag{0.7.23}$$

$$\bar{C}_{13} = \frac{\bar{C}_{11}}{1 + BK_1 \bar{C}_{33}}, \quad \bar{C}_{23} = \frac{\bar{C}_{21}}{1 + K_2 (1 - G \bar{C}_{33})}, \quad \bar{C}_{33} = \frac{\bar{C}_{23}}{G \bar{C}_{23} + BK_3 \bar{C}_{13}},\tag{0.7.24}$$

where $K_1, K_2, K_3, A_i, i=1,2, B, G$ are presented in (3.3.20), (6.3.11).

The use of (6.3.11) and $C_{11}(R, Z), C_{21}(R, Z), C_{13}(R, Z), C_{23}(R, Z), C_{33}(R, Z)$, as a solution of (3.3.18, 3.3.19, 3.3.21) for the case (3.3.22), permits to obtain the average concentrations $\bar{C}_{11}(Z), \bar{C}_{21}(Z), \bar{C}_{13}(Z), \bar{C}_{23}(Z), \bar{C}_{33}(Z)$ and the functions $A_i(Z), i=1,2, B(Z), G(Z)$. They are presented on Figs. 6.22 and 6.23, where it is seen that the functions $A_i(Z), i=1,2, B(Z), G(Z)$ are possible to be presented as linear approximations (6.3.12). The approximation ("theoretical") values of the parameters are presented in Table 6.5, where it is seen that $B \approx 1, G \approx 1$, practically.

Table 6.5 Parameter's values

	A_1	A_2	B	G
For high columns	$a_{01} =$	$a_{02} =$	$b_0 =$	$g_0 =$
$(0 = \varepsilon \leq 10^{-2}, 0 = \text{Pe}_i^{-1} = \varepsilon \text{Fo}_{i1} \leq 10^{-2}, \text{Fo}_{i1} \leq 1, i=1,2)$	0,143	1,0078	1,0001	1,0000
the problem (6.3.23) has the form (6.3.13).	$a_{11} =$	$a_{12} =$	$b_1 =$	$g_1 =$
	0,0544	0,0204	-0,0041	-0,0012

The solution of (6.3.13) depends on the two functions $(\bar{C}_{13}, \bar{C}_{23})$:

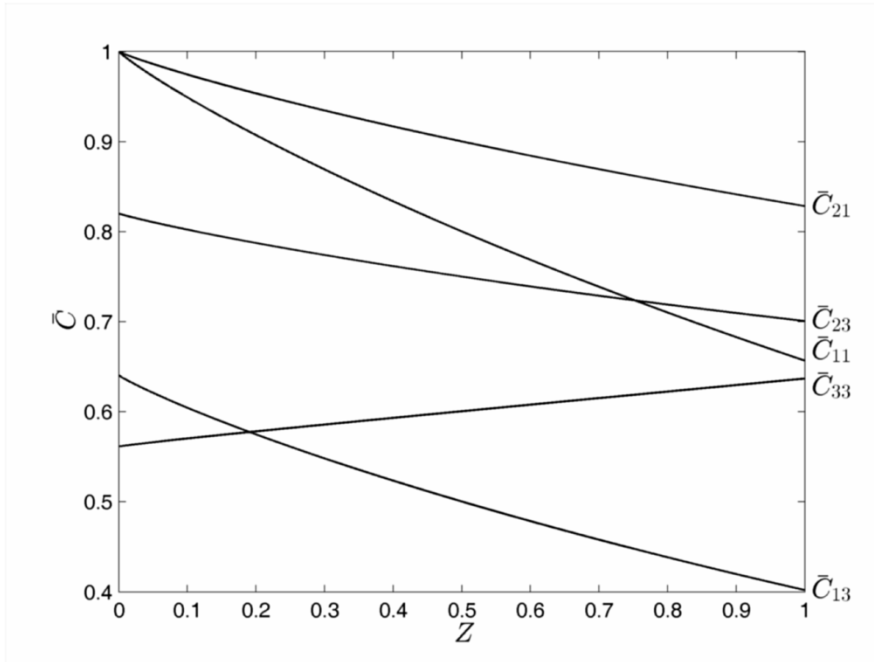


Fig. 6.22 Average functions $\bar{C}(Z)$

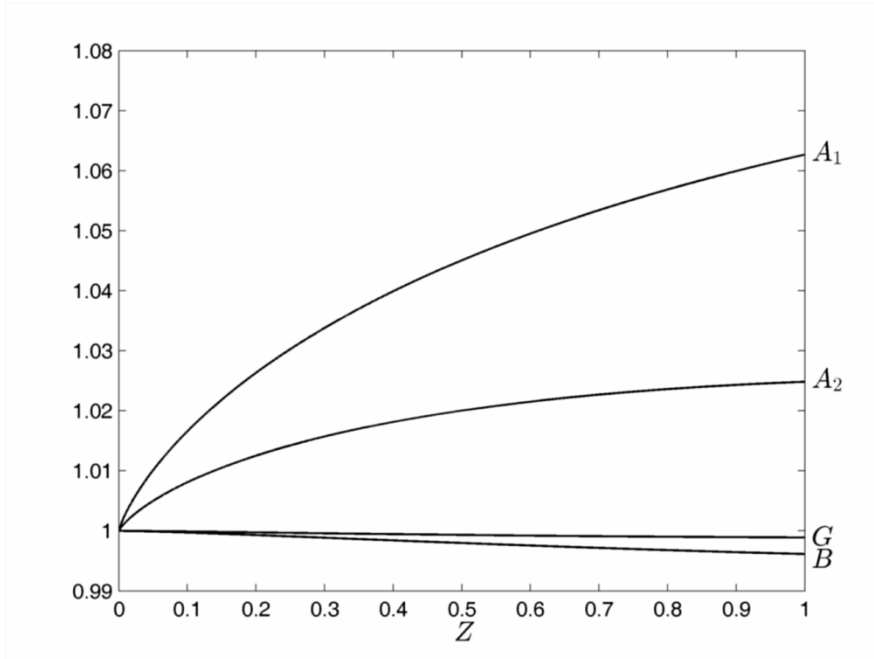


Fig. 6.23 Functions $A_i(Z), i=1,2, B(Z), G(Z)$

$$\bar{C}_{13} = \frac{\bar{C}_{11} + K_1(1 - \bar{C}_{33})}{1 + BK_2\bar{C}_{33}}, \quad \bar{C}_{23} = \frac{\bar{C}_{21}}{1 + K_3(1 - G\bar{C}_{33})}, \quad (0.7.25)$$

where \bar{C}_{33} is the solution of the quadratic equation

$$BG(\bar{C}_{21}K_1 - \bar{C}_{11}K_2K_3)(\bar{C}_{33})^2 + (G\bar{C}_{21} + B\bar{C}_{11}K_3 + B\bar{C}_{11}K_2K_3 - B\bar{C}_{21}K_1)\bar{C}_{33} - \bar{C}_{21} = 0. \quad (0.7.26)$$

In order to solve (6.3.26) $0 \leq \bar{C}_{33} \leq 1$ has to be used.

The solution of (6.3.13), (6.3.25), (6.3.26) is obtained [8] as five vector forms (6.3.16). For the case (3.3.22) Fig. 6.24 compares the functions $\bar{C}_{11}(Z)$, $\bar{C}_{21}(Z)$ as solutions of (6.3.13), (6.3.25), (6.3.26) using Table 6.5 (the dotted lines) with the results of the solution of (3.3.18), (3.3.19), (3.3.21) using (6.3.11) (the lines).

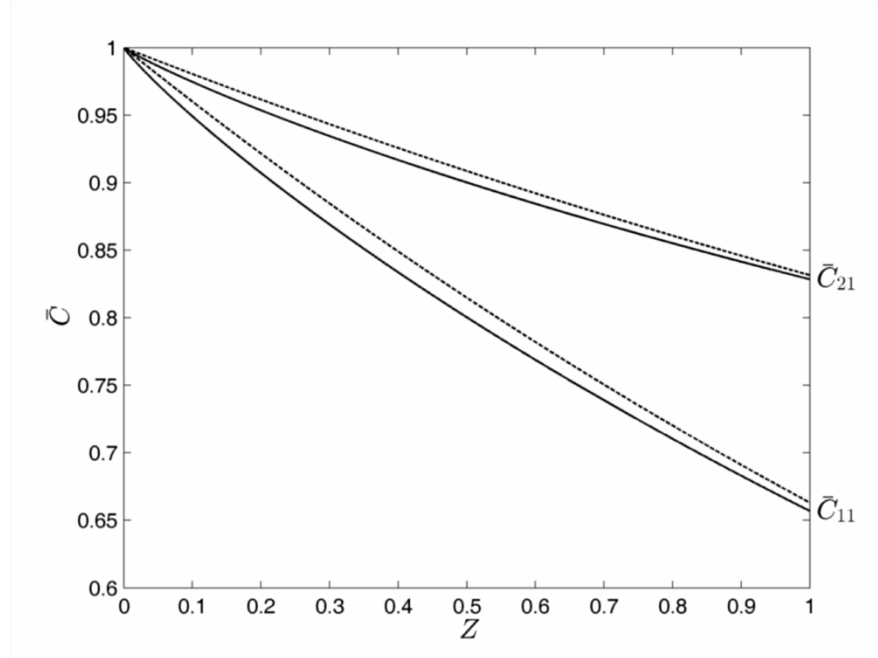


Fig. 6.24 Functions $\bar{C}_{11}(Z)$, $\bar{C}_{21}(Z)$: dotted lines - solution of (6.3.13), (6.3.25), (6.3.26) using Table 6.5; solid lines - solution of (3.3.18), (3.3.19), (3.3.21) using (6.3.11).

The obtained concentrations $\bar{C}_{11}(Z)$, $\bar{C}_{21}(Z)$ for the case (3.3.22) after solving (3.3.18), (3.3.19), (3.3.21) using (6.3.11) permits to obtain the “artificial experimental data” (6.3.17) for different values of Z . The obtained “artificial experimental data” (6.3.17) are used as illustration of the parameter identification in the average concentrations model (6.3.13), (6.3.25), (6.3.26) by minimization of the least-squares functions (6.3.18). The values of $\bar{C}_{11}(Z_n, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n)$ and $\bar{C}_{21}(Z_n, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n)$ are obtained for the case (3.3.22) as solutions of (6.3.13), (6.3.25), (6.3.26) for different $Z_n = 0.1n$, $n = 1, 2, \dots, 10$. The obtained (“experimental”) values of $a_{01}^0, a_{11}^0, a_{02}^0, a_{12}^0, a_{01}^1, a_{11}^1, a_{02}^1, a_{12}^1, a_{01}^2, a_{11}^2, a_{02}^2, a_{12}^2$ are presented in Table 6.6 They are used for calculation of the functions $\bar{C}_{11}(Z, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n)$, $\bar{C}_{21}(Z, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n)$, $n = 0, 1, 2$ in the case (3.3.22) as solutions of (6.3.13), (6.3.25), (6.3.26) (the lines in Fig. 6.25), where the points are the “artificial experimental data” (6.3.17) (average values for every value of Z).

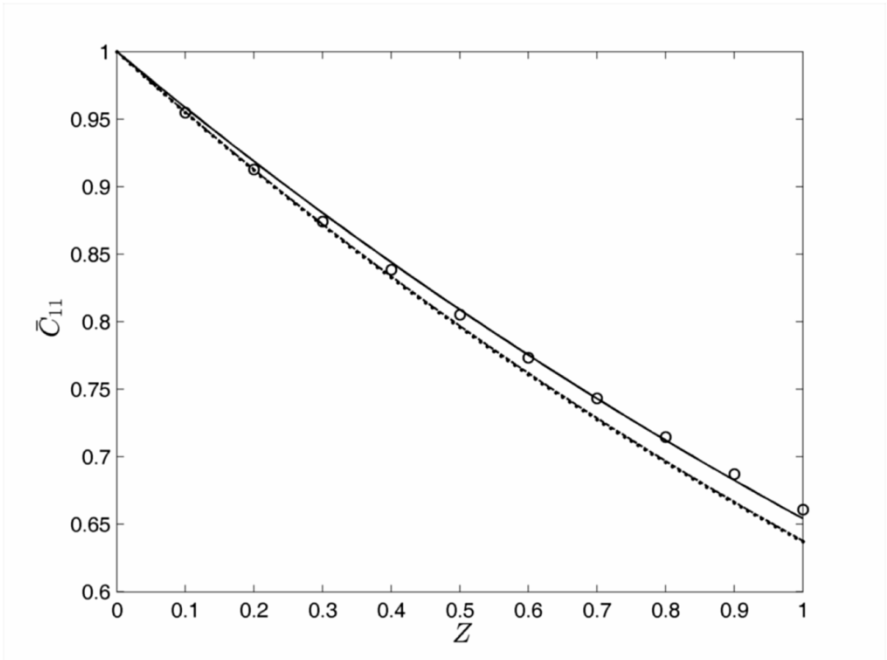


Fig. 6.25 Concentration distributions $\bar{C}_{11}(Z, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n)$, $n = 0, 1, 2$:
 lines - solutions of (6.3.13), (6.3.25), (6.3.26) in the case (3.3.22);
 points - the “artificial experimental data” (6.3.17) (average values for every Z).
 The comparison of the functions (lines) and experimental data (points) in Figs. 6.25 and 6.26 shows that the experimental data obtained from a column with a real radius and a small height ($Z = 0.1$) are useful for the parameter’s identifications.

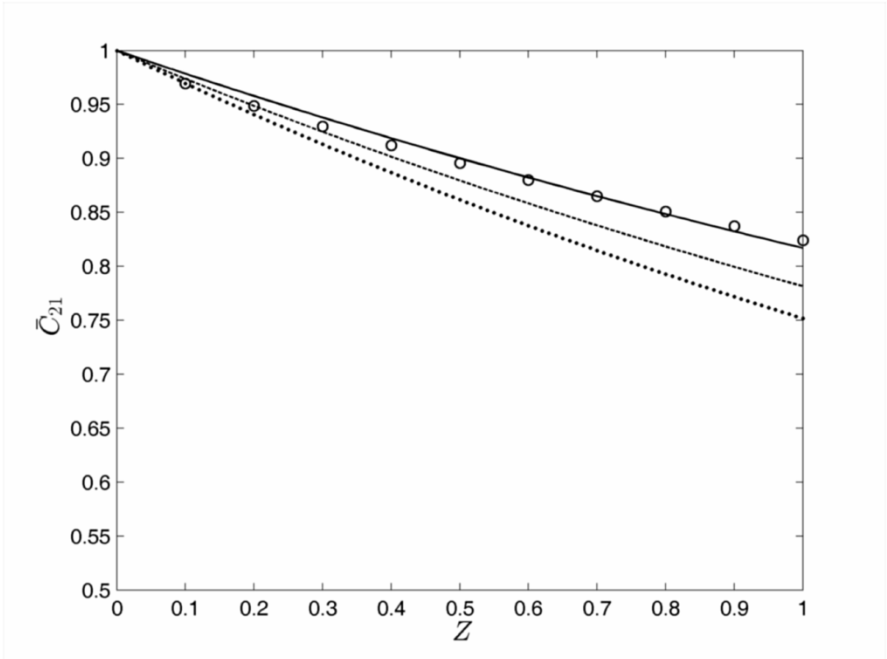


Fig. 6.26 Concentration distributions $\bar{C}_{21}(Z, a_{01}^n, a_{11}^n, a_{02}^n, a_{12}^n)$, $n = 0, 1, 2$:
 lines - solutions of (6.3.13), (6.3.25), (6.3.26) in the case (3.3.22);
 points - the “artificial experimental data” (6.3.17) (average values for every Z).
 “Theoretical” “Experimental” “Experimental” “Experimental”

Table 6.6 Parameter's value	values	values - Q min	values - Q_1 min	values - Q_2 min
	$a_{01} = 1.0143$	$a_{01}^0 = 1.0000$	$a_{01}^1 = 0.9946$	$a_{01}^2 = 0.9978$
	$a_{11} = 0.0544$	$a_{11}^0 = 0.0643$	$a_{11}^1 = 0.1007$	$a_{11}^2 = 0.0981$
	$a_{02} = 1.0078$	$a_{02}^0 = 1.0000$	$a_{02}^1 = 0.9081$	$a_{02}^2 = 0.9159$
	$a_{12} = 0.0204$	$a_{12}^0 = 0.0383$	$a_{12}^1 = 0.1024$	$a_{12}^2 = 0.0648$

s

A new approach for the column apparatuses modeling uses convection-diffusion type models and average-concentration models. All these new types of models [1–3] are characterized by the presence of small parameters at the highest derivatives. As a result the model equations have no exact solutions and approximate (asymptotic) solutions have to be obtained [4–6]. In these cases the use of the conventional software (MATLAB) for solving the model differential equations is difficult and this difficulty may be eliminated by an appropriate combination with the perturbations method.

1. Perturbations method

Let ε is a small parameter and $y = \varphi(t, \varepsilon)$ is the solution of the ordinary differential equation [4, 5]

$$y' = F(y, \varepsilon) \quad (0.7.27)$$

in the finite interval

$$t_0 \leq t \leq T, \quad 0 \leq \varepsilon \leq \varepsilon_0, \quad (0.7.28)$$

where ε_0 is a small numeral. The exact solution of **Error! Reference source not found.** is possible to be presented (like Taylor series expansion) as a power series expansion with respect to the small parameter ε :

$$\varphi(t, \varepsilon) = \sum_{s=0}^{\infty} \varepsilon^s \varphi_s(t), \quad (0.7.29)$$

where $\varphi_0(t)$ is the solution of the ordinary differential equation

$$y' = F(y, 0). \quad (0.7.30)$$

The exact solution (7.1.3) is valid [3, 4] in the finite interval (7.1.2), only.

In the case of existence of small parameters at the highest derivate

$$\varepsilon y' = f(y, z), \quad z' = g(y, z), \quad (0.7.31)$$

a new variable $\theta = t/\varepsilon$ has to be used:

$$y' = \frac{dy}{d\theta} \frac{1}{\varepsilon}, \quad z' = \frac{dz}{d\theta} \frac{1}{\varepsilon}, \quad \frac{dy}{d\theta} = f(y, z, \varepsilon), \quad \frac{dz}{d\theta} = \varepsilon g(y, z, \varepsilon), \quad (0.7.32)$$

but these equations set has no exact solution

$$\varphi(\theta, \varepsilon) = \sum_{s=0}^{\infty} \varepsilon^s \varphi_s(\theta), \quad \gamma(\theta, \varepsilon) = \sum_{s=0}^{\infty} \varepsilon^s \gamma_s(\theta), \quad (0.7.33)$$

because

$$\frac{t_0}{\varepsilon} \leq \theta \leq \frac{T}{\varepsilon} \rightarrow \infty, \quad \varepsilon \rightarrow 0, \quad (0.7.34)$$

i.e. the interval (7.1.8) is not finite [3, 4].

In the case of (7.1.5) an approximate solution $y = \bar{\varphi}(t, \varepsilon)$ has to be sought if

$$|\varphi(t, \varepsilon) - \bar{\varphi}(t, \varepsilon)| \leq \delta, \quad (0.7.35)$$

where practically $\delta \sim 10^{-2}$ because the relative error in the experimental measurements are typically more than 1% (all mathematical operators which represent very small $\leq 10^{-2}$ physical effects must be neglected, because they are not possible to be measured experimentally). This asymptotic solution is possible to be presented (like Taylor series expansion) as a power series expansion with respect to the small parameter ε :

$$\bar{\varphi}(t, \varepsilon) = \sum_{s=0}^{s_0} \varepsilon^s \varphi_s(t), \quad s_0 = s_0(\varepsilon, \delta). \quad (0.7.36)$$

Let us consider the function $y = \varphi(t, \varepsilon)$ in the interval $0 \leq t \leq 1$ as a solution of the differential equation

$$\varepsilon y'' = y' + y, \quad y(0) = 1, \quad y'(0) = 0. \quad (0.7.37)$$

An approximate (asymptotic) solution $y = \bar{\varphi}(t, \varepsilon)$ of (7.1.11) is possible to be presented as

$$\bar{\varphi}(t, \varepsilon) = \bar{\varphi}_0(t) + \varepsilon \bar{\varphi}_1(t) + \varepsilon^2 \bar{\varphi}_2(t). \quad (0.7.38)$$

The introduction of (7.1.12) in (7.1.11) and grouping of members with the same power of ε and their equalization to zero leads to individual differential equations for the functions in (7.1.12):

$$\begin{aligned} \bar{\varphi}_0' + \bar{\varphi}_0 &= 0, & \bar{\varphi}_0 &= 1; \\ \bar{\varphi}_1' + \bar{\varphi}_1 &= \bar{\varphi}_0, & \bar{\varphi}_1 &= 0; \\ \bar{\varphi}_2' + \bar{\varphi}_2 &= \bar{\varphi}_1, & \bar{\varphi}_2 &= 0. \end{aligned} \quad (0.7.39)$$

2. Convection-diffusion type models

Let us consider a model of the column apparatuses with pseudo-first-order chemical reaction (2.1.27), where the fluid flow is of Poiseuille type:

$$\begin{aligned} (2 - 2R^2) \frac{\partial C}{\partial Z} &= \text{Fo} \left(\varepsilon \frac{\partial^2 C}{\partial Z^2} + \frac{1}{R} \frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial R^2} \right) - \text{Da}C; \\ R = 0, \quad \frac{\partial C}{\partial R} &= 0; \quad R = 1, \quad \frac{\partial C}{\partial R} = 0; \\ Z = 0, \quad C = 1, \quad 1 = U - \text{Pe}^{-1} \frac{\partial C}{\partial Z}. \end{aligned} \quad (0.8.1)$$

The convection-diffusion type model (7.2.1) is of elliptical type. In the case of a short column ε is a small parameter and the perturbations method [4–6] can be used, i.e. the substitution of an elliptical equation by a set of parabolic equations. A computer realization of this method will be presented as an example of the chemical reactor column modeling [2, 7].

2.1. Short columns model

For short columns ε is a small parameter and if $\varepsilon < 0.3$ the problem (7.2.1) is possible to be solved using the following approximation of the perturbation method [6]

$$C(R, Z) = C^{(0)}(R, Z) + \varepsilon C^{(1)}(R, Z) + \varepsilon^2 C^{(2)}(R, Z) + \varepsilon^3 C^{(3)}(R, Z) \quad (0.8.2)$$

where $C^{(0)}$, $C^{(1)}$ and $C^{(2)}$ are solutions of the next problems:

$$(2-2R^2)\frac{\partial C^{(0)}}{\partial Z} = \text{Fo}\left(\frac{1}{R}\frac{\partial C^{(0)}}{\partial R} + \frac{\partial^2 C^{(0)}}{\partial R^2}\right) - \text{Da}C^{(0)};$$

$$R=0, \quad \frac{\partial C^{(0)}}{\partial R} = 0; \quad R=1, \quad \frac{\partial C^{(0)}}{\partial R} = 0; \quad Z=0, \quad C^{(0)} = 1. \quad (0.8.3)$$

$$(2-2R^2)\frac{\partial C^{(s)}}{\partial Z} = \text{Fo}\left(\frac{1}{R}\frac{\partial C^{(s)}}{\partial R} + \frac{\partial^2 C^{(s)}}{\partial R^2}\right) - \text{Da}C^{(s)} + \text{Fo}\frac{\partial^2 C^{(s-1)}}{\partial Z^2};$$

$$R=0, \quad \frac{\partial C^{(s)}}{\partial R} = 0; \quad R=1, \quad \frac{\partial C^{(s)}}{\partial R} = 0; \quad Z=0, \quad C^{(s)} = 0, \quad s=1, \dots, 3. \quad (0.8.4)$$

In (7.2.2) the individual effects (mathematical operators) and their relative role (influence) in the overall process (model) must be greater than 10^{-2} ($\varepsilon^4 < 10^{-2}$), because the accuracy of the experimental measurements is greater than 1%.

2.2. Calculation problem

The numerical solution of the equations set (7.2.3), (7.2.4) is possible if MATLAB and a four-step procedure are used, the functions $C^{(s)}(R, Z)$, $s=0,1,2,3$ being obtained in four matrix forms:

$$C^{(s)}(R, Z) = \|a_{\rho\zeta}^s\|, \quad s=0,1,2,3, \quad \rho=1,2,\dots,\rho^0, \quad \zeta=1,2,\dots,\zeta^0,$$

$$0 \leq R \leq 1, \quad 0 \leq Z \leq 1, \quad R = \frac{\rho-1}{\rho^0-1}, \quad Z = \frac{\zeta-1}{\zeta^0-1}, \quad \rho^0 = \zeta^0. \quad (0.8.5)$$

The first step is the solution of (7.2.3), i.e. element calculations of the matrix:

$$C^{(0)}(R, Z) = \|a_{\rho\zeta}^0\|, \quad \rho=1,2,\dots,\rho^0, \quad \zeta=1,2,\dots,\zeta^0,$$

$$0 \leq R \leq 1, \quad 0 \leq Z \leq 1, \quad R = \frac{\rho-1}{\rho^0-1}, \quad Z = \frac{\zeta-1}{\zeta^0-1}, \quad \rho^0 = \zeta^0. \quad (0.8.6)$$

The next step is a polynomial approximation of the function $C^{(0)}(R, Z)$:

$$C^{(0)}(R, Z) = \|a_{\rho\zeta}^0\| = |\alpha_{0\rho}^0| + |\alpha_{1\rho}^0|Z + |\alpha_{2\rho}^0|Z^2 + |\alpha_{3\rho}^0|Z^3 + |\alpha_{4\rho}^0|Z^4,$$

$$\rho=1,2,\dots,\rho^0, \quad 0 \leq R \leq 1, \quad R = \frac{\rho-1}{\rho^0-1} \quad (0.8.7)$$

and the determination of the second derivative

$$\frac{\partial^2 C^{(0)}}{\partial Z^2} = \|g_{\rho\zeta}^0\| = 2|\alpha_{2\rho}^0| + 6|\alpha_{3\rho}^0|Z + 12|\alpha_{4\rho}^0|Z^2,$$

$$\rho=1,2,\dots,\rho^0, \quad 0 \leq R \leq 1, \quad R = \frac{\rho-1}{\rho^0-1}. \quad (0.8.8)$$

The next step is the solution of (7.2.4) for $s=1$ using (7.2.8), i.e. elements calculations of the matrix:

$$C^{(1)}(R, Z) = \|a_{\rho\zeta}^1\|, \quad \rho=1,2,\dots,\rho^0, \quad \zeta=1,2,\dots,\zeta^0,$$

$$0 \leq R \leq 1, \quad 0 \leq Z \leq 1, \quad R = \frac{\rho-1}{\rho^0-1}, \quad Z = \frac{\zeta-1}{\zeta^0-1}, \quad \rho^0 = \zeta^0. \quad (0.8.9)$$

Then follows the polynomial approximation of the function $C^{(1)}(R, Z)$

$$C^{(1)}(R, Z) = \|a_{\rho}^1\| = |\alpha_{0\rho}^1| + |\alpha_{1\rho}^1|Z + |\alpha_{2\rho}^1|Z^2 + |\alpha_{3\rho}^1|Z^3 + |\alpha_{4\rho}^1|Z^4,$$

$$\rho = 1, 2, \dots, \rho^0, \quad 0 \leq R \leq 1, \quad R = \frac{\rho-1}{\rho^0-1} \quad (0.8.10)$$

and the determination of the second derivative

$$\frac{\partial^2 C^{(1)}}{\partial Z^2} = \|g_{\rho\zeta}^1\| = 2|\alpha_{2\rho}^1| + 6|\alpha_{3\rho}^1|Z + 12|\alpha_{4\rho}^1|Z^2,$$

$$\rho = 1, 2, \dots, \rho^0, \quad 0 \leq R \leq 1, \quad R = \frac{\rho-1}{\rho^0-1}. \quad (0.8.11)$$

The next step is the solution of (7.2.4) for $s=2$ using (7.2.8), i.e. elements calculations of the matrix:

$$C^{(2)}(R, Z) = \|a_{\rho\zeta}^2\|, \quad \rho = 1, 2, \dots, \rho^0, \quad \zeta = 1, 2, \dots, \zeta^0,$$

$$0 \leq R \leq 1, \quad 0 \leq Z \leq 1, \quad R = \frac{\rho-1}{\rho^0-1}, \quad Z = \frac{\zeta-1}{\zeta^0-1}, \quad \rho^0 = \zeta^0. \quad (0.8.12)$$

The next step is the polynomial approximation of the function $C^{(2)}(R, Z)$:

$$C^{(2)}(R, Z) = \|a_{\rho\zeta}^2\| = |\alpha_{0\rho}^2| + |\alpha_{1\rho}^2|Z + |\alpha_{2\rho}^2|Z^2 + |\alpha_{3\rho}^2|Z^3 + |\alpha_{4\rho}^2|Z^4,$$

$$\rho = 1, 2, \dots, \rho^0, \quad 0 \leq R \leq 1, \quad R = \frac{\rho-1}{\rho^0-1} \quad (0.8.13)$$

and the determination of the second derivative

$$\frac{\partial^2 C^{(2)}}{\partial Z^2} = \|g_{\rho\zeta}^2\| = 2|\alpha_{2\rho}^2| + 6|\alpha_{3\rho}^2|Z + 12|\alpha_{4\rho}^2|Z^2,$$

$$\rho = 1, 2, \dots, \rho^0, \quad 0 \leq R \leq 1, \quad R = \frac{\rho-1}{\rho^0-1}. \quad (0.8.14)$$

The last step is the solution of (7.2.4) for $s=3$ using (6.2.14).

The solution of the problem (7.2.3), (7.2.4) was obtained using MATLAB program. It solves the equations (7.2.3) and (7.2.4) using the built-in MATLAB function `pdepe`, which solves initial-boundary value problems for parabolic partial differential equations. The

second derivatives $\frac{\partial^2 C^{(s)}}{\partial Z^2}$, $s=0,1,2$ are obtained with a polynomial approximation using the functions `polyfit` and `polyder` of MATLAB, and then are introduced in the partial differential equations (7.2.3) and (7.2.4) using the built-in MATLAB function `interp2`.

2.3. Concentration distributions

The solutions of the problem (7.2.1) obtained for the cases $Fo=0.5$, $Da=1$, $\varepsilon=0.1, 0.3$ and concentration distributions $C(R, Z)$ in (7.2.2) for $Pe^{-1} = \varepsilon Fo = 0.05, 0.15$ and $Z = 0.2, 0.5, 0.8, 1.0$ are presented in Figs. 7.1 and 7.2.

3. Average-concentration models

In the cases where the velocity distribution in the column is unknown an average-concentration model (5.1.7) is possible to be used for the chemical reaction modeling:

$$A(Z) \frac{d\bar{C}}{dZ} + \frac{dA}{dZ} \bar{C} = Pe^{-1} \frac{d^2 \bar{C}}{dZ^2} - Da \bar{C}; \quad Z=0, \quad \bar{C}=1, \quad \frac{d\bar{C}}{dZ}=0; \quad (0.9.1)$$

where

$$A(Z) = 2 \int_0^1 R U(R) \frac{C(R,Z)}{\bar{C}(Z)} dR, \quad U(R) = 2 - 2R^2, \quad \bar{C}(Z) = 2 \int_0^1 R C(R,Z) dR. \quad (0.9.2)$$

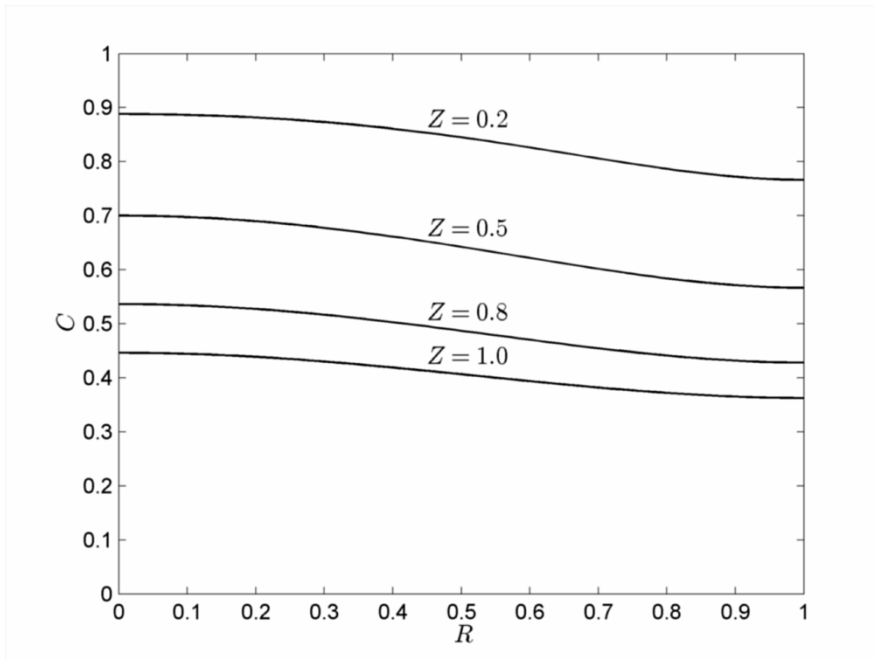


Fig. 7.1 Solution of (7.2.1) for $\varepsilon = 0.1$

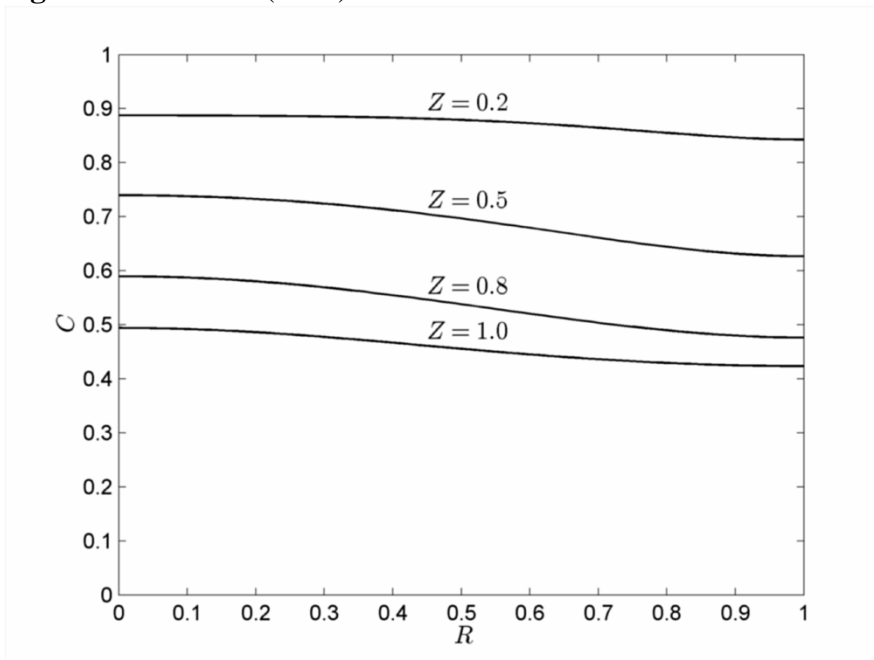


Fig. 7.2 Solution of (7.2.1) for $\varepsilon = 0.3$

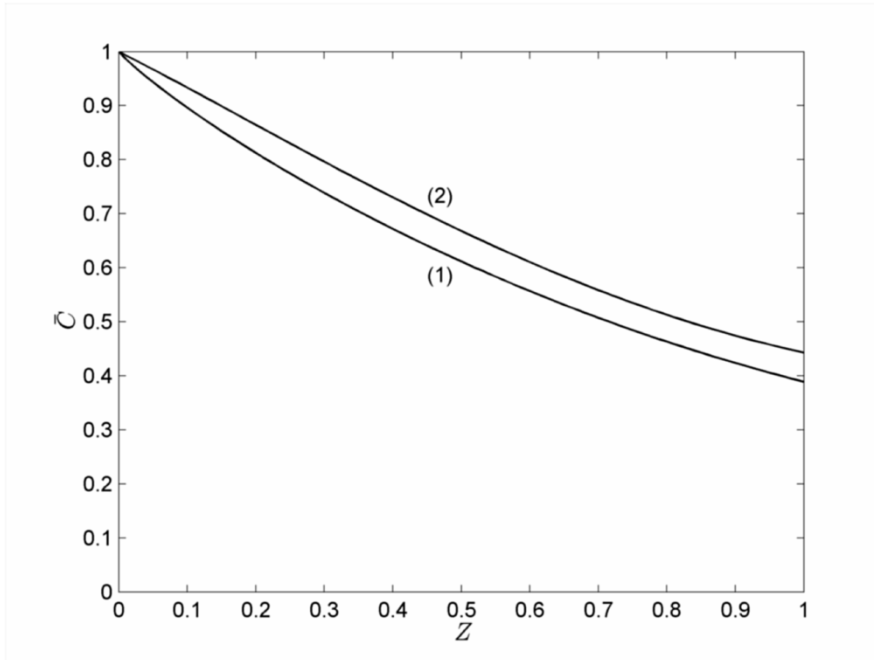


Fig. 7.3 Average concentration $\bar{C}(Z)$ (7.3.2): 1- $\varepsilon = 0.1$, 2- $\varepsilon = 0.3$.

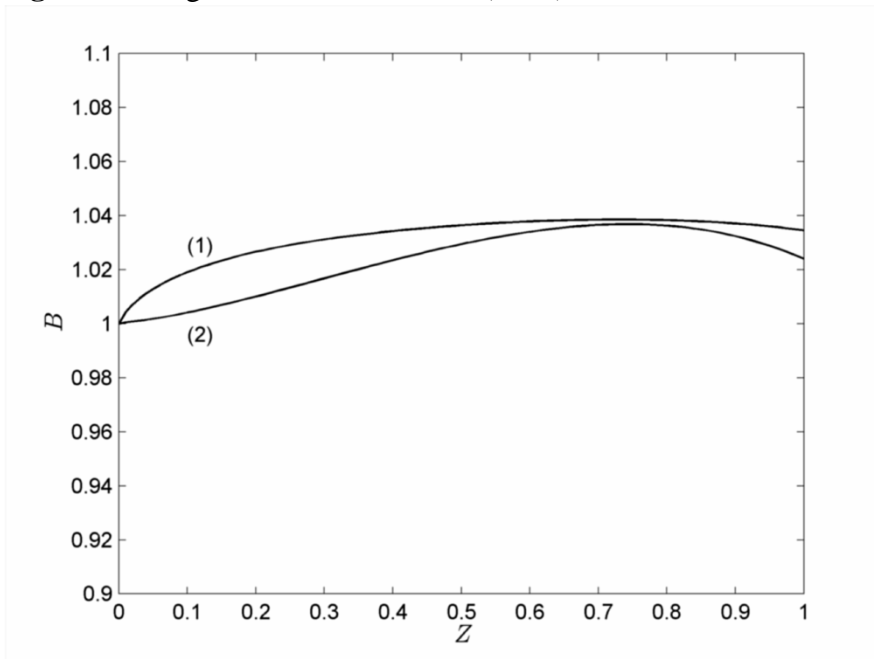


Fig. 7.4 Function $A(Z)$ (7.3.2): 1- $\varepsilon = 0.1$, 2- $\varepsilon = 0.3$.

The solution of (2.1.27) and (7.3.2) in the case $Fo = 0.5, Da = 1, Pe^{-1} = \varepsilon Fo, \varepsilon = 0.1, 0.3$ permits to obtain the functions $\bar{C}(Z), A(Z)$: they are presented on Figs. 7.3 and 7.4.

It is seen from Fig 7.4 that the function $A(Z)$ can be presented [2] as a linear approximation $A = a_0 + a_1 Z$ and the (theoretical) values of the parameters a_0, a_1 are presented in Table 7.1. As a result the model (7.3.1) has the form:

$$(a_0 + a_1 Z) \frac{d\bar{C}}{dZ} + a_1 \bar{C} = \text{Pe}^{-1} \frac{d^2 \bar{C}}{dZ^2} - \text{Da} \bar{C};$$

$$Z = 0, \quad \bar{C}(0) = 1, \quad \left(\frac{d\bar{C}}{dZ} \right)_{Z=0} = 0. \quad (0.9.3)$$

ε	a_0	a_1	a_0^0	a_1^0	a_0^1	a_1^1	a_0^2	a_1^2
0.	1,01	0,00	1.05	0.08	0.95	0.000	0.93	0.00
1	26	75	89	63	79	3	30	05
0.	0,99	0,02	1.07	0.16	1.20	-0.00	0.92	0.00
3	37	88	43	63	18	10	99	05

Table 7.1 Model parameters values

In (7.3.3) for $\text{Fo} = 0.5$, $\text{Da} = 1$, $\varepsilon = 0.3$, the small parameter is $\text{Pe}^{-1} = \varepsilon \text{Fo} = \theta = 0.15$, $\theta^3 < 10^{-2}$, i.e. the perturbation method is possible to be used:

$$\bar{C}(Z) = \bar{C}^{(0)}(Z) + \theta \bar{C}^{(1)}(Z) + \theta^2 \bar{C}^{(2)}(Z) \quad (0.9.4)$$

and from (7.3.3) and (7.3.4) follows:

$$(a_0 + a_1 Z) \frac{d\bar{C}^{(0)}}{dZ} + a_1 \bar{C}^{(0)} = -\text{Da} \bar{C}^{(0)}; \quad Z = 0, \quad \bar{C}^{(0)} = 1. \quad (0.9.5)$$

$$(a_0 + a_1 Z) \frac{d\bar{C}^{(s)}}{dZ} + a_1 \bar{C}^{(s)} = \frac{d^2 \bar{C}^{(s-1)}}{dZ^2} - \text{Da} \bar{C}^{(s)}; \quad Z = 0, \quad \bar{C}^{(s)}(0) = 0, \quad s = 1, 2. \quad (0.9.6)$$

3.1. Calculation problem

The numerical solution of the equations set (7.3.5), (7.3.6) is possible if MATLAB and a three-step procedure are used, where the functions $\bar{C}^{(s)}(Z)$, $s = 0, 1, 2$ will be obtained in four vectors forms:

$$\bar{C}^{(s)}(Z) = |\bar{a}_\zeta^s|, \quad s = 0, 1, 2,$$

$$0 \leq Z \leq 1, \quad Z = \frac{\zeta - 1}{\zeta^0 - 1}, \quad \zeta = 1, 2, \dots, \zeta^0. \quad (0.9.7)$$

The main problem in solving the equations set (7.3.5), (7.3.6) is the calculation of the second derivatives $\frac{d^2 \bar{C}^{(s)}}{dZ^2}(Z)$, $s = 0, 1, 2$. A circumvention of this problem may be the application of one of following two algorithms.

Algorithm 1

The equations set (7.3.5), (7.3.6) permits to obtain the expression for the derivatives ($k = 1, \dots, (4-s)$) of the functions $\bar{C}^{(s)}(Z)$ ($s = 0, 1, \dots, 4$):

$$\frac{d^k \bar{C}^{(s)}}{dZ^k} = \frac{\frac{d^{(k+1)} \bar{C}^{(s-1)}}{dZ^{(k+1)}} - (\text{Da} + kb_1) \frac{d^{(k-1)} \bar{C}^{(s)}}{dZ^{(k-1)}}}{(b_0 + b_1 Z)}, \quad s = 0, 1, \dots, 4,$$

$$k = 1, \dots, (4-s), \quad \bar{C}^{(-1)} = 0, \quad \frac{d^0 \bar{C}^{(s)}}{dZ^0} = \bar{C}^{(s)}. \quad (0.9.8)$$

The first step is the solution of (7.3.5)

$$\bar{C}^{(0)}(Z) = |\bar{a}_\zeta^0|, \quad 0 \leq Z \leq 1, \quad Z = \frac{\zeta - 1}{\zeta^0 - 1}, \quad \zeta = 1, 2, \dots, \zeta^0 \quad (0.9.9)$$

applying (7.3.8) ($s=0, k=1,2$) for calculating the elements of the vectors

$$\begin{aligned} \frac{d\bar{C}^{(0)}}{dZ} &= |\bar{a}_\zeta^0|, \quad \frac{d^2\bar{C}^{(0)}}{dZ^2} = |\bar{a}_\zeta^{00}|, \\ 0 \leq Z \leq 1, \quad Z &= \frac{\zeta-1}{\zeta^0-1}, \quad \zeta = 1, 2, \dots, \zeta^0. \end{aligned} \quad (0.9.10)$$

The next step is the solution of (7.3.6) using (7.3.10) for $s=1$

$$\bar{C}^{(1)}(Z) = |\bar{a}_\zeta^1|, \quad 0 \leq Z \leq 1, \quad Z = \frac{\zeta-1}{\zeta^0-1}, \quad \zeta = 1, 2, \dots, \zeta^0 \quad (0.9.11)$$

and (7.3.8) ($s=1, k=1,2$) for calculating the elements of the vectors

$$\begin{aligned} \frac{d\bar{C}^{(1)}}{dZ} &= |\bar{a}_\zeta^1|, \quad \frac{d^2\bar{C}^{(1)}}{dZ^2} = |\bar{a}_\zeta^{11}|, \\ 0 \leq Z \leq 1, \quad Z &= \frac{\zeta-1}{\zeta^0-1}, \quad \zeta = 1, 2, \dots, \zeta^0. \end{aligned} \quad (0.9.12)$$

The last step is the solving of (7.3.6) using (7.3.12) for $s=2$:

$$\bar{C}^{(2)}(Z) = |\bar{a}_\zeta^2|, \quad 0 \leq Z \leq 1, \quad Z = \frac{\zeta-1}{\zeta^0-1}, \quad \zeta = 1, 2, \dots, \zeta^0. \quad (0.9.13)$$

Algorithm 2

The first step is the solution of (7.3.5), i.e. element calculations of the vector:

$$\bar{C}^{(0)}(Z) = |\bar{a}_\zeta^0|, \quad 0 \leq Z \leq 1, \quad Z = \frac{\zeta-1}{\zeta^0-1}, \quad \zeta = 1, 2, \dots, \zeta^0. \quad (0.9.14)$$

The next step is a polynomial approximation of the function $\bar{C}^{(0)}(Z)$

$$\bar{C}^{(0)}(Z) = |\bar{a}_\zeta^0| = \bar{\alpha}_0^0 + \bar{\alpha}_1^0 Z + \bar{\alpha}_2^0 Z^2 + \bar{\alpha}_3^0 Z^3 + \bar{\alpha}_4^0 Z^4 \quad (0.9.15)$$

and the determination of the second derivative

$$\frac{d^2\bar{C}^{(0)}}{dZ^2}(Z) = |\bar{g}_\zeta^0| = 2\bar{\alpha}_2^0 + 6\bar{\alpha}_3^0 Z + 12\bar{\alpha}_4^0 Z^2. \quad (0.9.16)$$

The next steps is the solution of (7.3.6) using (7.3.16) for $s=1$, i.e. elements calculations of the vector:

$$\bar{C}^{(1)}(Z) = |\bar{a}_\zeta^1|, \quad 0 \leq Z \leq 1, \quad Z = \frac{\zeta-1}{\zeta^0-1}, \quad \zeta = 1, 2, \dots, \zeta^0. \quad (0.9.17)$$

The next steps is the polynomial approximation of the function $\bar{C}^{(1)}(Z)$:

$$\bar{C}^{(1)}(Z) = |\bar{a}_\zeta^1| = \bar{\alpha}_0^1 + \bar{\alpha}_1^1 Z + \bar{\alpha}_2^1 Z^2 + \bar{\alpha}_3^1 Z^3 + \bar{\alpha}_4^1 Z^4 \quad (0.9.18)$$

and the determination of the second derivative

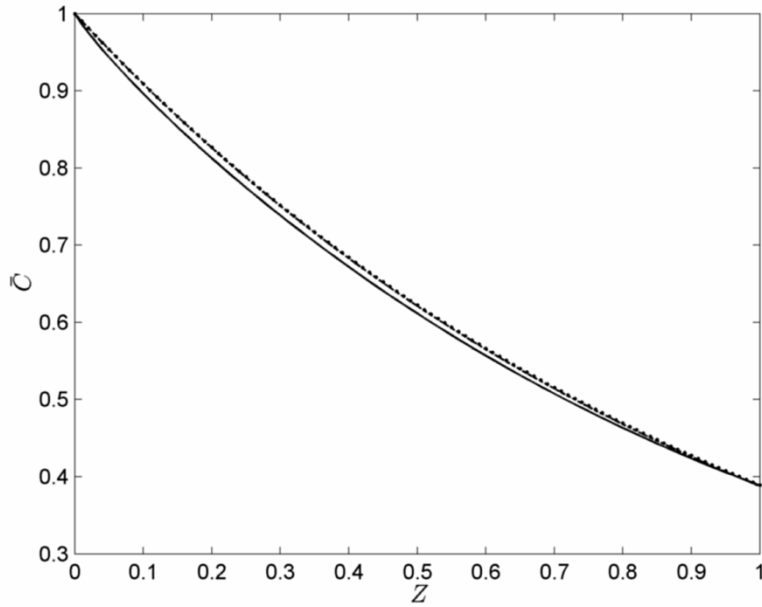


Fig. 7.5 Average concentrations for $\theta=0.05$: solid line - calculated by (7.3.2), dotted line - solution of (7.3.3) (algorithm 1), dashed line - solution of (7.3.3) (algorithm 2).

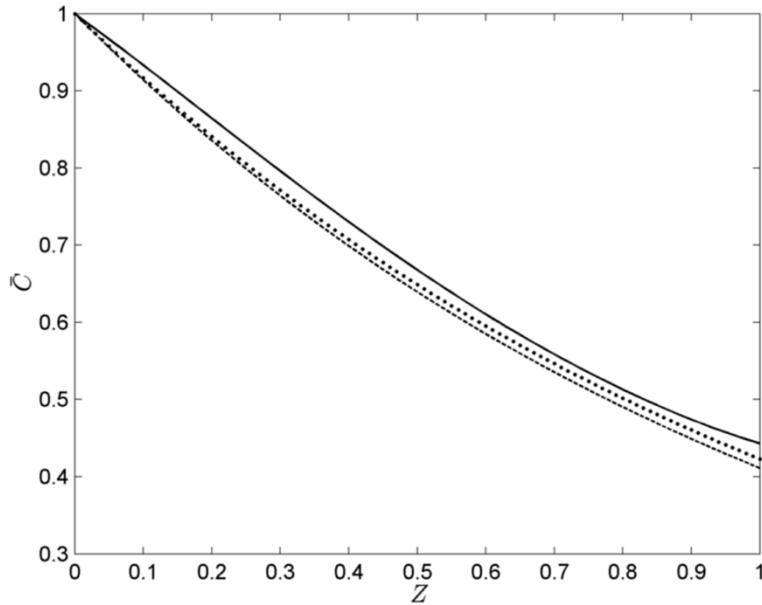


Fig. 7.6 Average concentrations for $\theta=0.15$: solid line - calculated by (7.3.2), dotted line - solution of (7.3.3) (algorithm 1), dashed line - solution of (7.3.3) (algorithm 2).

$$\frac{d^2\bar{C}^{(1)}}{dZ^2}(Z) = |\bar{g}_\zeta^1| = 2\bar{\alpha}_2^1 + 6\bar{\alpha}_3^1 Z + 12\bar{\alpha}_4^1 Z^2. \quad (0.9.19)$$

The last step is the solution of (7.3.6) using (7.3.19) for $s=2$.

The solution of the problem (7.3.3) was obtained using MATLAB program. It solves the equations (7.3.5) and (7.3.6) applying its the built-in MATLAB function `ode45`, which solves non-stiff differential equations. Two different algorithms are used to obtain the

second derivatives, which are introduced in the differential equations (7.3.5) and (7.3.6), by using the built-in MATLAB function `interp1`.

3.2. Average concentration distributions

The solutions of (7.3.3) for theoretical values of a_0, a_1 (see Table 7.1) and $\theta = 0.05, 0.15, Da = 1$, obtained applying the algorithms 1 and 2: they are presented (dotted lines) on Figs. 7.5 and 7.6, where they are juxtaposed with the calculated average concentrations (7.3.2) (lines).

3.3 Parameter identification

The concentration $C(R, Z)$ in (7.2.1) obtained for the cases $Fo = 0.5, Da = 1, \varepsilon = 0.1, 0.3, Pe^{-1} = \varepsilon Fo = 0.05, 0.15$ allows to obtain the average concentrations $\bar{C}(Z)$ in (7.3.2) and “artificial experimental data” for different values of Z :

$$\begin{aligned} \bar{C}_{\text{exp}}^m(Z_n) &= (0.95 + 0.1S_m) \bar{C}(Z_n), \quad m = 1, \dots, 10, \\ Z_n &= 0.1n, \quad n = 1, 2, \dots, 10, \end{aligned} \quad (0.9.20)$$

where $0 \leq S_m \leq 1, m = 1, \dots, 10$ are obtained by a generator of random numbers. The obtained “artificial experimental data” (7.3.20) are used for illustration of the parameter identification in the average-concentrations model (7.3.3) by minimization of the least-squares functions $Q_n, n = 1, 2$ and Q :

$$\begin{aligned} Q_n(Z_n, b_0^n, b_1^n) &= \sum_{m=1}^{10} [\bar{C}(Z_n, b_0^n, b_1^n) - \bar{C}_{\text{exp}}^m(Z_n)]^2, \\ Q(b_0^0, b_1^0) &= \sum_{n=1}^{10} Q_n(Z_n, b_0^0, b_1^0), \quad Z_n = 0.1n, \quad n = 1, 2, \dots, 10, \end{aligned} \quad (0.9.21)$$

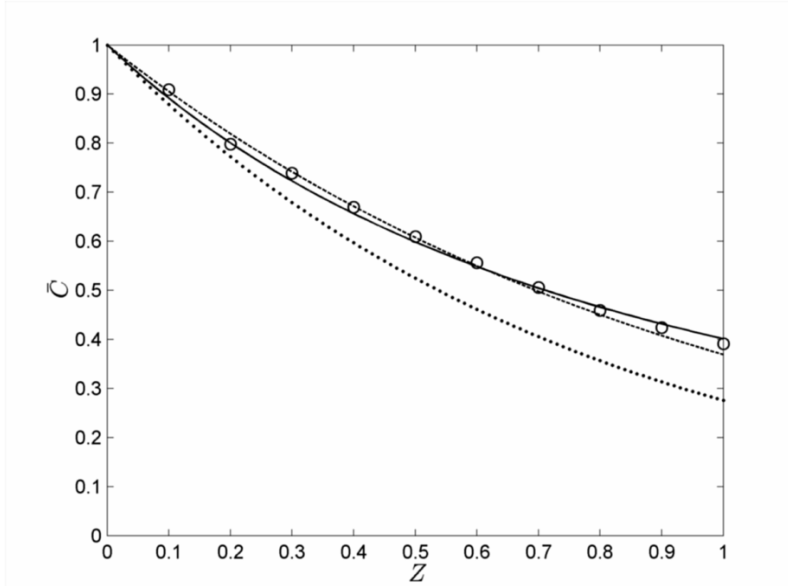


Fig. 7.7 Comparison of the concentration distributions (7.3.3) and “artificial experimental data” (7.3.20) for $\theta = 0.05$: dashed line – $\bar{C}(Z, a_0^1, a_1^1)$; dotted line – $\bar{C}(Z, b_0^2, b_1^2)$; solid line – $\bar{C}(Z, a_0^0, a_1^0)$; circles – “artificial experimental data” (7.3.20).

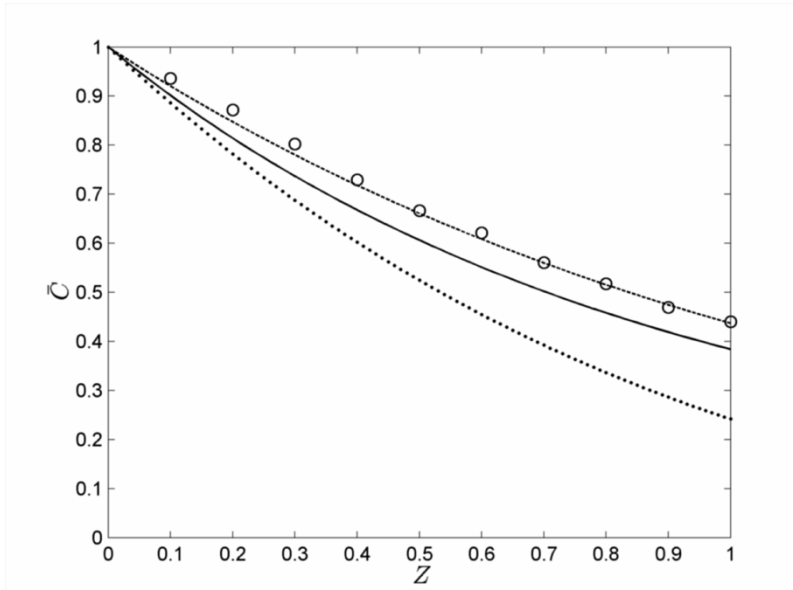


Fig. 7.8 Comparison of the concentration distributions (7.3.3) and “artificial experimental data” (7.3.20) for $\theta = 0.15$: dashed line – $\bar{C}(Z, a_0^1, a_1^1)$; dotted line – $\bar{C}(Z, a_0^2, a_1^2)$; solid line – $\bar{C}(Z, a_0^0, a_1^0)$; circles – “artificial experimental data” (7.3.20).

where the values of $\bar{C}(Z_n, b_0^n, b_1^n)$ are obtained as solutions of (7.3.3) for different $Z_n = 0.1n, n = 1, 2, \dots, 10$. The obtained values $(a_0^0, a_1^0; a_0^1, a_1^1; a_0^2, a_1^2)$ are presented in Table 7.1.

They are used for calculation of the functions $\bar{C}(Z, a_0^0, a_1^0), \bar{C}(Z, a_0^1, a_1^1), \bar{C}(Z, a_0^2, a_1^2)$ as solutions of (7.3.3) (the lines in Fig. 7.7), where the points are the “artificial experimental data” (7.3.20).

The comparison of the functions (lines) and experimental data (points) in Figs. 6.7 and 7.8 shows that the experimental data obtained from a column with real radius and small height ($Z = 0.1$) are useful for parameters identifications.

The computer modeling of the mass transfer processes in column apparatuses on the base of a new approach using a convection–diffusion type model and an average-concentration type model leads to calculation problems in the cases of presence of small parameters in the highest derivatives. This problem is solved by means of MATLAB and three algorithms applying the perturbations method.