

TRANSFER PROCESSES IN INDUSTRIAL COLUMN APPARATUSES

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Abstract: The paper is a presentation of the monography "Chr. Boyadjiev, M. Doichinova, B. Boyadjiev, P. Popova-Krumova, Modeling of Column Apparatus Processes, Springer-Verlag, Berlin Heidelberg, 2016, pp. 313. A new approach to modeling the mass transfer processes in industrial column apparatuses, in the physical approximations of the mechanics of continua, is used for the creation of convection-diffusion and average-concentration models. The models of chemical, absorption, adsorption and catalytic processes are presented.

Keywords: COLUMN APPARATUSES, NEW MODELS, CHEMICAL PROCESSES, ABSORPTION, ADSORPTION, CATALYTIC PROCESSES

1. Introduction

The modeling and simulation are the main approach for the quantitative description of the mass transfer processes in the chemical, power, biotechnological and other industries [1]. The models of the mass transfer processes are possible to be created on the basis of the physical approximations of the mechanics of continua, where the mathematical point is equivalent to an 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.

The big part of the industrial mass transfer processes are realized in one, two or three phase systems as a result of volume (homogeneous) and surface (heterogeneous) reactions, i.e. mass appearance (disappearance) of the reagents (phase components) in the elementary volumes in the phases or on the its interphase surfaces. As a result, the reactions are mass sources (sinks) in the volume (homogeneous chemical reactions) and on the surface (interphase mass transfer in the cases of absorption, adsorption, catalytic reactions) of the elementary phase volumes.

The volume reactions lead to different concentrations of the reagents in the phase volumes and as a result two mass transfer processes are realized – convective transfer (caused by the movement of the phases) and diffusion transfer (caused by the concentration gradients in the phases). The mass transfer models are a mass balance in the phases, where components are convective transfer, diffusion transfer and volume reactions (volume mass sources or sinks). The surface reactions participate as mass sources or sinks in the boundary conditions of the model equations.

A fundamental prerequisite for the use of the interphase mass transfer theory is the existence of a theoretical possibility to determine the velocity distribution in the phases and the interphase boundaries (surfaces). In the cases of modeling of the interphase mass transfer processes (absorption, adsorption and catalytic reactions) in column apparatuses, the velocity and the interphase boundaries are unknown and as a result this theory is useful.

The use of the physical approximations of the mechanics of continua for the interphase mass transfer process modeling in industrial column apparatuses [2] is possible if the mass appearance (disappearance) of the reagents on the interphase surfaces of the elementary physical volumes (as a result of the heterogeneous reactions) are replaced by the mass appearance (disappearance) of the reagents in the same elementary physical volumes (as a result of the equivalent homogenous reactions), i.e. the surface mass sources (sinks), caused by absorption, adsorption or catalytic reactions must be replaced with equivalent volume mass sources (sinks).

The new approach to modeling the mass transfer processes in industrial column apparatuses is the creation of the convection-diffusion and average-concentration models.

The convection-diffusion models permit the qualitative analysis of the processes only, because the velocity distribution in the

column is unknown. On this base is possible to be obtained the role of the different physical effect in the process and to reject those processes, whose relative influence is less than 1%, i.e. to be made process mechanism identification.

The average-concentration models are obtained from the convection-diffusion models, where average velocities and concentrations are introduced. The velocity distribution effects are introduced by the parameters in the model, which must to be determined experimentally.

2. Convection-diffusion type models

In the general case a multicomponent ($i=1,2,\dots,i_0$) and multiphase ($j=1,2,3$ for gas, liquid and solid phases) flow in a cylindrical column with radius r_0 [m] and active zone height l [m] will be considered. If F_0 is the fluid flow rate in the column and F_j , $j=1,2,3$ are the phase flow rates [$\text{m}^3\cdot\text{s}^{-1}$], the parts of the column volume occupied by the gas, liquid and solid phase, respectively, i.e. the phase volumes [m^3] in 1 m^3 of the column volume (hold-up coefficients of the phases), are:

$$\varepsilon_j = \frac{F_j}{F_0}, \quad j=1,2,3, \quad \sum_j \varepsilon_j = 1, \quad (1)$$

The input velocities of the phases in the column u_j^0 [$\text{m}\cdot\text{s}^{-1}$], $j=1,2,3$ are possible to be defined as:

$$u_j^0 = \frac{F_j}{\varepsilon_j \pi r_0^2}, \quad j=1,2,3; \quad F_0 = \sum_{j=1}^3 F_j. \quad (2)$$

The physical elementary column volumes contain the elementary phase volumes ε_j , $j=1,2,3$ and will be presented as mathematical points $M(r,z)$ in a cylindrical coordinate system (r,z) , where r and z [m] are radial and axial coordinates. As a result, the mathematical point $M(r,z)$ is equivalent to the elementary phase volumes, too.

The concentrations [$\text{kg}\cdot\text{mol}\cdot\text{m}^{-3}$] of the reagents (components of the phases) are c_{ij} , $i=1,2,\dots,i_0$, $j=1,2,3$, i.e. the quantities of the reagents (kg-mol) in 1 m^3 of the phase volumes in the column.

In the cases of a stationary motion of fluids in cylindrical column apparatus, $u_j(r,z)$, $v_j(r,z)$, $j=1,2,3$ [$\text{m}\cdot\text{s}^{-1}$] are the axial and radial velocity components of the phases in the elementary phase volumes.

The volume reactions [$\text{kg}\cdot\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$] in the phases (homogeneous chemical reactions and heterogeneous reactions, as a volume mass source or sink in the phase volumes in the column) are $Q_{ij}(c_{ij})$, $j=1,2,3$, $i=1,2,\dots,i_0$. The reagent concentrations in the

elementary phase volumes increase ($Q_{ij} > 0$) or decrease ($Q_{ij} < 0$) and the reaction rates Q_{ij} are determined by these concentrations $c_{ij}(r, z)$ [kg·mol·m⁻³].

The volume reactions lead to different values of the reagent concentrations in the elementary phase volumes and as a result, two mass transfer effects exist – convective transfer (caused by the fluid motion) and diffusion transfer (caused by the concentration gradient).

The convective transfer in column apparatus is caused by a laminar or turbulent (as a result of large-scale turbulent pulsations) flow. In the elementary phase volume around the point $M(r, z)$ in the column, the mass transfer in this volume, as a result of the convection, is $u_j \frac{\partial c_{ij}}{\partial z} + v_j \frac{\partial c_{ij}}{\partial r}$ [kg·mol·m⁻³·s⁻¹], $j=1,2,3$, $i=1,2,\dots,i_0$, i.e. convective transfer rate (kg·mol·s⁻¹) in 1 m³ of the phase volume.

The molecular or turbulent (caused by small-scale turbulent pulsations) diffusive transfer is $D_{ij} \left(\frac{\partial^2 c_{ij}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{ij}}{\partial r} + \frac{\partial^2 c_{ij}}{\partial r^2} \right)$ [kg·mol·m⁻³·s⁻¹], i.e., diffusive transfer rate (kg·mol·s⁻¹) in 1 m³ of the phase volume and D_{ij} [m²·s⁻¹] are the diffusivities of the reagents ($i=1,2,\dots,i_0$) in the phases ($j=1,2,3$).

The mathematical model of the processes in the column apparatuses, in the physical approximations of the mechanics of continua, represents the mass balances in the phase volumes (phase parts in the elementary column volume) between the convective transfer, the diffusive transfer and the volume mass sources (sinks). The sum total of these three effects (in the cases of stationary processes) is equal to zero:

$$u_j \frac{\partial c_{ij}}{\partial z} + v_j \frac{\partial c_{ij}}{\partial r} = D_{ij} \left(\frac{\partial^2 c_{ij}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{ij}}{\partial r} + \frac{\partial^2 c_{ij}}{\partial r^2} \right) + Q_{ij}(c_{ij}), \quad (3)$$

$$j=1,2,3, \quad i=1,2,\dots,i_0.$$

The axial and radial velocity components $u_j(r, z)$ and $v_j(r, z)$, $j=1,2,3$ satisfy the continuity equations

$$\frac{\partial u_j}{\partial z} + \frac{\partial v_j}{\partial r} + \frac{v_j}{r} = 0; \quad z=0, \quad u_j \equiv u_j(r, 0);$$

$$r=r_0, \quad v_j(r_0, z) \equiv 0; \quad j=1,2,3. \quad (4)$$

The model of the mass transfer processes in the column apparatuses (3) includes boundary conditions, which express a symmetric concentrations distributions ($r=0$), impenetrability of the column wall ($r=r_0$), constant input concentrations c_{ij}^0 and mass balances at the column input ($z=0$):

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

$$z=0, \quad c_{ij} \equiv c_{ij}^0, \quad u_j^0 c_{ij}^0 \equiv u_j c_{ij}^0 - D_{ij} \left(\frac{\partial c_{ij}}{\partial z} \right)_{z=0}, \quad (5)$$

$$j=1,2,3, \quad i=1,2,\dots,i_0.$$

2.1. Column chemical reactor

In the case of one-phase fluid motion [6,7] in the column chemical reactors, the phase index $j=1,2,3$ is possible to be ignored.

For a two component chemical reaction in the column, the convection-diffusion model (3) has the form:

$$u \frac{\partial c_i}{\partial z} + v \frac{\partial c_i}{\partial r} = D_i \left(\frac{\partial^2 c_i}{\partial z^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right) - Q_i(c_1, c_2), \quad i=1,2, \quad (6)$$

where $Q_i(c_1, c_2) = k_i c_1^m c_2^n$, $i=1,2$.

2.2. Column physical (chemical) absorber

The convection-diffusion type models of the absorption processes in the gas-liquid systems is possible to be obtained if $j=1,2$ ($1 = \varepsilon_1 + \varepsilon_2$), $i=1,2$. The kinetic terms Q_{ij} , $i=1,2$, $j=1,2$ [kg·mol·m⁻³·s⁻¹] are the interphase mass transfer rates $Q_{1j} = (-1)^j k_0 (c_{11} - \chi c_{12})$, $j=1,2$ in the gas and liquid phases and the chemical reaction rate ($Q_{i2} = -k c_{12} c_{22}$, $i=1,2$) in the liquid phase, as volume sources or sinks of the reagents in the phase parts of the elementary (column) volume. As a result:

$$u_1 \frac{\partial c_{11}}{\partial z} = D_{11} \left(\frac{\partial^2 c_{11}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{11}}{\partial r} + \frac{\partial^2 c_{11}}{\partial r^2} \right) - k_0 (c_{11} - \chi c_{12}),$$

$$u_2 \frac{\partial c_{12}}{\partial z} = D_{12} \left(\frac{\partial^2 c_{12}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{12}}{\partial r} + \frac{\partial^2 c_{12}}{\partial r^2} \right) + k_0 (c_{11} - \chi c_{12}) - k c_{12} c_{22}, \quad (7)$$

$$u_2 \frac{\partial c_{22}}{\partial z} = D_{22} \left(\frac{\partial^2 c_{22}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{22}}{\partial r} + \frac{\partial^2 c_{22}}{\partial r^2} \right) - k c_{12} c_{22},$$

where k_0 [s⁻¹] is the volume interphase mass transfer coefficient, χ - the Henry's number, k - the chemical reaction rate constant. The same models is possible to be used for modeling of the extraction processes if χ is the redistribution factor. In the counter-current absorber $z = z_j$, $j=1,2$ ($z_1 + z_2 = l$).

2.3. Column physical (chemical) adsorber

In the adsorption process participate two reagents ($i_0 = 2$), where the first (active component) is in the gas or liquid phase ($i=1$, $j=1,2$) and the second (active site) is in the solid phase ($i=2$, $j=3$). The adsorption is a process of interphase mass transfer of an active component (AC) from the gas (liquid) volume to the solid interface and a heterogeneous reaction with an active site (AS), due to a physical (Van der Waals's) or chemical (valence) force.

The convection-diffusion type models of the adsorption processes in the gas (liquid)-solid systems are possible to be obtained if $j=1,3=2,3$ ($1 = \varepsilon_1 + \varepsilon_3 = \varepsilon_2 + \varepsilon_3$), $i_0 = 2$, where $i=1$ is for (AC) in the gas (liquid) phase, $i=2$ is for (AS) in the adsorbent (solid phase). The volume adsorption rate in the case of a solid adsorbent is $Q_3 = b_0 Q_{03}$ [kg·mol·m⁻³·s⁻¹], where b_0 [m²·m⁻³] is m² of the inner surface in the solid phase (the surface of the capillaries in the solid phase) in 1 m³ of the solid phase (adsorbent), Q_{03} [kg·mol·m⁻²·s⁻¹] – the surface adsorption rate.

A gas adsorption will be considered for convenience, where c_{11} [kg·mol·m⁻³] is the volume concentration of the AC in the gas phase (elementary) volume, c_{13} [kg·mol·m⁻³] – the volume concentration of the AC in the void volume of the solid phase (adsorbent), c_{23} [kg·eq·m⁻³] – the volume concentration of the AS in the solid phase (elementary) volume (1 kg·eq AS in the adsorbent combine 1 kg·mol AC), $1 = \varepsilon_1 + \varepsilon_3$, $u_1 = u_1(r)$ – velocity of the gas phase [m·s⁻¹], $u_3 = 0$ (solid phase is immobile). All concentrations are in kg·mol (kg·eq) in 1 m³ of the phase (elementary) volume.

2.3.1 Physical adsorption

In the cases of physical adsorption the surface adsorption rate is:

$$Q_{03} = k_1 c_{13} C_{23} - k_2 \frac{c_{23}^0}{b_0} (1 - C_{23}), \quad C_{23} = \frac{c_{23}}{c_{23}^0}. \quad (8)$$

Let us consider a non-stationary gas adsorption in a column apparatus, where the solid phase (adsorbent) is immobile. The convection-diffusion model of this process is possible to be obtained, where the diffusivity of the free AS in the solid phase (adsorbent) volume is equal to zero. If the rate of the interphase mass transfer of the AC from the gas phase to the solid phase is $k_0(c_{11} - c_{13})$ and the process is non-stationary as a result of the free AS concentration decrease, the convection-diffusion model has the form:

$$\begin{aligned} \frac{\partial c_{11}}{\partial t} + u_1 \frac{\partial c_{11}}{\partial z} &= D_{11} \left(\frac{\partial^2 c_{11}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{11}}{\partial r} + \frac{\partial^2 c_{11}}{\partial r^2} \right) - k_0 (c_{11} - c_{13}); \\ \frac{dc_{13}}{dt} &= k_0 (c_{11} - c_{13}) - b_0 k_1 c_{13} \frac{c_{23}}{c_{23}^0} + k_2 c_{23}^0 \left(1 - \frac{c_{23}}{c_{23}^0} \right); \\ \frac{dc_{23}}{dt} &= -b_0 k_1 c_{13} \frac{c_{23}}{c_{23}^0} + k_2 c_{23}^0 \left(1 - \frac{c_{23}}{c_{23}^0} \right), \end{aligned} \quad (9)$$

where t [s] is the time.

2.3.2 Chemical adsorption

In the cases of chemical adsorption the model is

$$\begin{aligned} \frac{\partial c_{11}}{\partial t} + u_1 \frac{\partial c_{11}}{\partial z} &= D_{11} \left(\frac{\partial^2 c_{11}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{11}}{\partial r} + \frac{\partial^2 c_{11}}{\partial r^2} \right) - k_0 (c_{11} - c_{13}), \\ \frac{dc_{13}}{dt} &= k_0 (c_{11} - c_{13}) - k c_{13} c_{23} = 0, \quad \frac{dc_{23}}{dt} = -k c_{13} c_{23}, \end{aligned} \quad (10)$$

where k is the chemical reaction rate constant.

2.4. Heterogeneous catalytic reactor

In a heterogeneous catalytic process participate two reagents, where the first reagent is adsorbed physically (chemically) 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 $c_{33}^0 - c_{33}$ and the catalytic reaction rate is $k c_{23} (c_{33}^0 - c_{33})$. The concentration of AS decreases as a result of the adsorption and increases as a result of the catalytic reaction, because the reaction product does not have adsorption properties.

2.4.1 Physical adsorption mechanism

For a long duration process in the case of physical adsorption mechanism the model has the form:

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

$$\begin{aligned} k_{01} (c_{11} - c_{13}) - b_0 k_1 c_{13} \frac{c_{33}}{c_{33}^0} + k_2 c_{33}^0 \left(1 - \frac{c_{33}}{c_{33}^0} \right) &= 0; \\ k_{02} (c_{21} - c_{23}) - k c_{23} (c_{33}^0 - c_{33}) &= 0; \\ -b_0 k_1 c_{13} \frac{c_{33}}{c_{33}^0} + k_2 c_{33}^0 \left(1 - \frac{c_{33}}{c_{33}^0} \right) + k c_{23} (c_{33}^0 - c_{33}) &= 0; \end{aligned} \quad (12)$$

2.4.2 Chemical adsorption mechanism

In the cases of chemical adsorption mechanism the last model has the form:

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

2.5. Qualitative analysis of the models

The qualitative analysis of the convective-diffusion models will be illustrated with the case of a complex chemical reaction:

$$\begin{aligned} u \frac{\partial c_i}{\partial z} &= D_i \left(\frac{\partial^2 c_i}{\partial z^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right) - k_i c_1^m c_2^n; \\ r = 0, \quad \frac{\partial c_i}{\partial r} &\equiv 0; \quad r = r_0, \quad \frac{\partial c_i}{\partial r} \equiv 0; \\ z = 0, \quad c &\equiv c_i^0, \quad u^0 c_i^0 \equiv u c_i^0 - D_i \frac{\partial c_i}{\partial z}, \quad i = 1, 2, \end{aligned} \quad (14)$$

using generalized variables:

$$\begin{aligned} r &= r_0 R, \quad z = l Z, \quad u(r) = u(r_0 R) = u^0 U(R), \\ \tilde{u}(r) &= \tilde{u}(r_0 R) = U(R), \\ c_i(r, z) &= c_i(r_0 R, l Z) = c_i^0 C_i(R, Z) \quad (i = 1, 2), \quad \varepsilon = \left(\frac{r_0}{l} \right)^2, \end{aligned} \quad (15)$$

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 (15) leads to:

$$\begin{aligned} U \frac{\partial C_i}{\partial Z} &= \text{Fo}_i \left(\varepsilon \frac{\partial^2 C_i}{\partial Z^2} + \frac{1}{R} \frac{\partial C_i}{\partial R} + \frac{\partial^2 C_i}{\partial R^2} \right) - \text{Da}_i C_1^m C_2^n; \\ R = 0, \quad \frac{\partial C_i}{\partial R} &\equiv 0; \quad R = 1, \quad \frac{\partial C_i}{\partial R} \equiv 0; \\ Z = 0, \quad C_i &\equiv 1, \quad 1 \equiv U - \text{Pe}_i^{-1} \frac{\partial C_i}{\partial Z}; \\ \text{Fo}_i &= \frac{D_i l}{u_0 r_0^2}, \quad \text{Da}_i = \theta^{i-1} \text{Da}_i^0, \quad \text{Pe}_i = \frac{u_0 l}{D_i}, \\ \text{Da}_i^0 &= \frac{k_i l}{u_0} (c_1^0)^{m-1} (c_2^0)^n, \quad \theta = \frac{c_1^0}{c_2^0}; \quad i = 1, 2, \end{aligned} \quad (16)$$

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

2.5.1. Comparison qualitative analysis

If all equations in a model 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.

2.5.2. Pseudo-first-order reactions

In the cases of big difference between inlet concentrations of the reagents ($c_1^0 \square c_2^0$) in the chemical reactor model, the problem 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 (1.16) follows:

$$\begin{aligned} U \frac{\partial C}{\partial Z} &= Fo \left(\varepsilon \frac{\partial^2 C}{\partial Z^2} + \frac{1}{R} \frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial R^2} \right) - Da C; \quad \varepsilon = Fo^{-1} Pe^{-1}; \\ R = 0, \quad \frac{\partial C}{\partial R} &\equiv 0; \quad R = 1, \quad \frac{\partial C}{\partial R} \equiv 0; \\ Z = 0, \quad C &\equiv 1, \quad 1 \equiv U - Pe^{-1} \frac{\partial C}{\partial Z}; \end{aligned} \quad (17)$$

where $C = C_1, Da = Da_1^0$ and model of column apparatuses with pseudo-first-order chemical reaction is obtained.

2.5.3. High-column model

For high columns ε is a very small parameter and the problem (1.18) is possible to be solved in zero approximation with respect to ε ($0 = \varepsilon \leq 10^{-2}$), i.e. $Pe^{-1} \leq 10^{-2} Fo$ and for $Fo \leq 1$ the next very small parameter is Pe^{-1} ($0 = Pe^{-1} \leq 10^{-2}$).

2.5.4. Effect of the chemical reaction rate

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

2.5.5. Effect of the average velocity

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

2.6. Calculation problems

The solutions of the model equations lead to different calculation problems as solution of set of equations in two systems of coordinates and the presence of small parameters at the highest derivatives.

2.7. Models applications

The convection-diffusion models are applied for theoretical analysis of the "back mixing effect" and the modeling of the scale effect, circulation zones, and airlift apparatuses.

3. Average-concentration type models

The average-concentration model will be presented on the bases of the convection-diffusion model of the one-phase system in the case of pseudo-first-order chemical reaction:

$$\begin{aligned} u \frac{\partial c}{\partial z} &= D \left(\frac{\partial^2 c}{\partial z^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right) - kc; \\ r = 0, \quad \frac{\partial c}{\partial r} &\equiv 0; \quad r = r_0, \quad \frac{\partial c}{\partial r} \equiv 0; \\ z = 0, \quad c &\equiv c^0, \quad u^0 c^0 \equiv u c^0 - D \frac{\partial c}{\partial z}. \end{aligned} \quad (18)$$

The average values of the velocity and concentration at the column cross-sectional area in one-phase systems are:

$$\bar{u} = \frac{2}{r_0^2} \int_0^{r_0} r u(r) dr, \quad \bar{c}(z) = \frac{2}{r_0^2} \int_0^{r_0} r c(r, z) dr. \quad (19)$$

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

$$u(r) = \bar{u} \tilde{u}(r), \quad c(r, z) = \bar{c}(z) \tilde{c}(r, z), \quad (20)$$

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

$$\frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}(r) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}(r, z) dr = 1. \quad (21)$$

The introduction of the average values of the velocity and concentration in the convection-diffusion model leads to the average concentration model:

$$\begin{aligned} \alpha \bar{u} \frac{d\bar{c}}{dz} + \frac{d\alpha}{dz} \bar{u} \bar{c} &= D \frac{d^2 \bar{c}}{dz^2} - k \bar{c}; \\ z = 0, \quad \bar{c}(0) &= c^0, \quad \frac{d\bar{c}}{dz} = 0, \end{aligned} \quad (22)$$

where

$$\alpha(z) = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}(r) \tilde{c}(r, z) dr \quad (23)$$

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

The use of the generalized variables

$$\begin{aligned} r = r_0 R, \quad z = lZ, \quad u(r) &= \bar{u} U(R), \quad \tilde{u}(r) = \frac{u(r)}{\bar{u}} = U(R), \\ c(r, z) &= c^0 C(R, Z), \quad \bar{c}(z) = c^0 \bar{C}(Z), \\ \tilde{c}(r, z) &= \frac{c(r, z)}{\bar{c}(z)} = \frac{C(R, Z)}{\bar{C}(Z)}, \quad \bar{C}(Z) = 2 \int_0^1 R C(R, Z) dR, \\ \alpha(z) = \alpha(lZ) &= A(Z) = 2 \int_0^1 R U(R) \frac{C(R, Z)}{\bar{C}(Z)} dR, \end{aligned} \quad (24)$$

leads to:

$$\begin{aligned} A(Z) \frac{d\bar{C}}{dZ} + \frac{dA}{dZ} \bar{C} &= Pe^{-1} \frac{d^2 \bar{C}}{dZ^2} - Da \bar{C}; \\ Z = 0, \quad \bar{C} &= 1, \quad \frac{d\bar{C}}{dZ} = 0, \end{aligned} \quad (25)$$

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

$$Pe = \frac{\bar{u} l}{D}, \quad Da = \frac{kl}{\bar{u}}. \quad (26)$$

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

$$u = \bar{u} \left(2 - 2 \frac{r^2}{r_0^2} \right), \quad \bar{u} = u^0, \quad U(R) = 2 - 2R^2. \quad (27)$$

The use of the velocity distribution permits to obtain the function $A(Z)$. The result obtained shows, that the function $A(Z)$ for $Fo = 0.1, Da = 1$ can be presented as linear approximation $A = a_0 + a_1 Z$ ($a_0 = 1, a_1 = 0.254$). As a result, the model assumes the form:

$$\begin{aligned} (a_0 + a_1 Z) \frac{d\bar{C}}{dZ} + a_1 \bar{C} &= Pe^{-1} \frac{d^2 \bar{C}}{dZ^2} - Da \bar{C}; \\ Z = 0, \quad \bar{C} &= 1, \quad \frac{d\bar{C}}{dZ} = 0. \end{aligned} \quad (28)$$

3.1. 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 $A(Z) \equiv 1$, i.e. the radial non-uniformity of the velocity distribution leads to $A(Z) > 1$.

The equation can be modified as

$$\frac{d\bar{C}}{dZ} = [A(Z)]^{-1} \left[Pe^{-1} \frac{d^2\bar{C}}{dZ^2} - (Da + \frac{dA}{dZ})\bar{C} \right], \quad (29)$$

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 $G = \bar{C}(0) - \bar{C}(1)$.

3.2. Model parameters identification

The solution of the convection-diffusion model permits to $C(Z_n, R)$ be obtained for different $Z_n = 0.1n, n = 1, 2, \dots, 10$ and the average concentrations:

$$\bar{C}(Z_n) = 2 \int_0^1 RC(Z_n, R) dR, \quad n = 1, \dots, 10. \quad (30)$$

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

$$\bar{C}_{\text{exp}}^m(Z_n) = (0.95 + 0.1B_m)\bar{C}(Z_n), \quad (31)$$

$$m = 1, \dots, 10, \quad Z_n = 0.1n, \quad n = 1, 2, \dots, 10,$$

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

$$Q_n(a_{0n}, a_{1n}) = \sum_{m=1}^{10} [\bar{C}(Z_n, a_{0n}, a_{1n}) - \bar{C}_{\text{exp}}^m(Z_n)]^2, \quad (32)$$

$$Z_n = 0.1n, \quad n = 1, 3, 5.$$

These parameter values are used for the calculations of the average concentration in the model. The obtained values $\bar{C}(Z_n, a_{0n}, a_{1n}), Z_n = 0.1n, n = 1, 3, 5$ (the points) are compared (Fig. 1) with the "exact" function of the average concentration $\bar{C}(Z)$ (the line). From Fig. 1 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.

Similar results are obtained in the cases of the co-current and counter-current physical (chemical) absorption, non-stationary physical (chemical) adsorption, gas (liquid) – solid catalytic reactions in the cases of physical (chemical) adsorption mechanism.

4. Conclusions

The convection-diffusion and average-concentration models are used for the qualitative and quantitative analysis of the homogeneous chemical reactions, co-current and counter-current physical (chemical) absorption, non-stationary physical (chemical) adsorption, gas (liquid) – solid catalytic reactions in the cases of physical (chemical) adsorption mechanism. In all these cases it is used an approximation, according to which the radial non-uniformity of the axial velocity component does not change along the column height, i.e. the radial velocity component is equal to zero. This approach is not effective for very high columns, where the axial velocity component decreases along the column height. In

these cases ($u_j = u_j(r, z), v_j = v_j(r, z), j = 1, 2, 3$) will be proposed new type models.

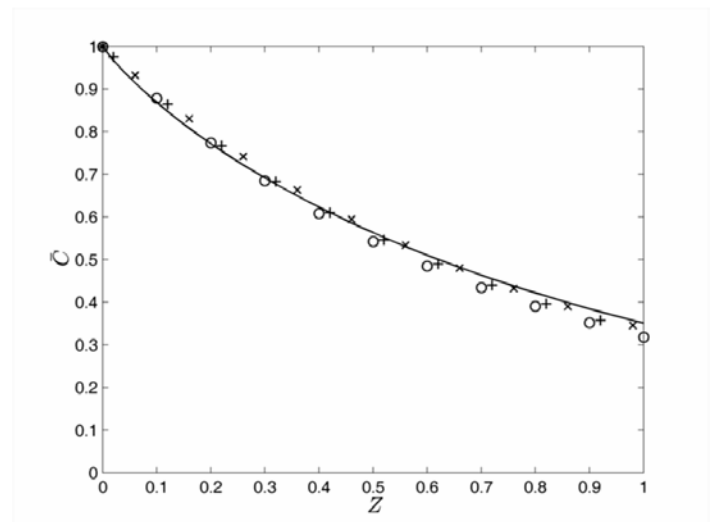


Fig. 1 Average concentration $\bar{C}(Z)$ for $Fo = 0.1, Da = 1, \varepsilon = 10^{-1}, Pe^{-1} = 0.01$:
line – average concentration (24) after solution of (17);

○ – solution of (28) $\bar{C}(Z, a_{01}, a_{11}), Z = 0.1, a_{01} = 1, a_{11} = 0.3519$;

+ – solution of (28) $\bar{C}(Z, a_{03}, a_{13}), Z = 0.3, a_{03} = 1, a_{13} = 0.2707$;

× – solution of (28) $\bar{C}(Z, a_{05}, a_{15}), Z = 0.5, a_{05} = 1, a_{15} = 0.2162$.

5. References

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