Introduction in the chemical engineering processes modeling

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In the paper is presented a theoretical analysis of the methods for chemical engineering processes modeling. The methods for modeling specific processes may be different, but in all cases they must bring the mathematical description closer to the real process by using appropriate experimental data. These methods are presented in the cases of co-current absorption column without packings, counter-current absorption column with random packings and modeling of processes with unknown mechanism.

PRELUDE

The main problems in the chemical industry (biotechnology, heat energy) are the optimal design of new devices and the optimal control of active processes, i.e. minimization of the investment and operating costs. These problems are solved by chemical engineering with modeling methods [1].

The creation of the mathematical model begins with the formulation of the physical model of the complex process, i.e. the definition of the simple processes that make it up and the interactions between them. The second step is to define simple processes that have mathematical descriptions (equivalent mathematical operators). The other simple processes are introduced into the mathematical model through quantitative information obtained from experimental data, which brings the mathematical model as close as possible to the real process. The experiment brings mathematics closer to physics (reality).

The optimal design and control in the chemical industry is uniquely related to processes rates, so all mathematical descriptions of processes are linked to algorithms to determine these rates, i.e. processes kinetics.

Industrial Processes Kinetics

The industrial systems consist of separate phases (gas, liquid, solid) in the industrial apparatuses volumes. They are in thermodynamic equilibrium when the velocities, temperatures and concentrations of substances in the individual parts or points of the phases are equal.

The processes in the chemical industry (biotechnology, heat energy) are a result of the deviation of the systems from their thermodynamic equilibrium [2]. One system is not in a thermodynamic equilibrium when the velocities, concentrations of the components (substances) and the temperatures at the individual points in the phase volumes are different. These differences are the result of reactions, i.e. of processes that create or consume substance and (or) heat. As a result, the industrial processes kinetics is equivalent to the reactions kinetics [3].

The presented analysis shows that processes in the chemical industry are result of reactions that occur in the phase volume (homogeneous) or on the boundary between two phases (heterogeneous). Homogeneous reactions are generally chemical, while heterogeneous reactions are chemical, catalytic, physical and chemical adsorption, interphase mass transfer in gas-liquid and liquid-liquid systems (on the interphase surface the substance disappears from one phase and occurs in the other phase). The rates of these processes are determined by the reaction kinetics [3], which lies at the basis of modeling in chemical engineering, and solving the basic problems in the chemical industry (biotechnology, heat energy).

Modeling

The basics of modeling in chemical engineering, as part of human knowledge and science, are related to the combination of intuition and logic that has different forms in individual sciences [4]. In mathematics the intuition is the axiom (unconditional statements that cannot be proven), while the logic is the theorem (the logical consequences of the axiom), but logic prevails over intuition. In the natural sciences (physics, chemistry, biology), the "axioms" (principles, postulates, laws) are not always unconditional, but logic prevails over intuition too.

The processes in chemical engineering take place in the industrial apparatuses, where gas, liquid and solid phases move together or alone.

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They are described by variables which are extensive or intensive. In the case of merging of two identical systems, the extensive variables are doubled, but the intensive variables are retained.

In the chemical industry (biotechnology, heat energy), processes take place in moving phases (gas, liquid, solid). Reactions (reaction processes) lead to different concentrations (and temperatures) in the phase volumes and the phase boundaries. As a result, hydrodynamic processes, diffusion mass transfer and heat conduction are joined to the reaction processes. Under these conditions there are various forms of mass transfer (heat transfer) that are convective (as a result of phase movements) and diffusion (as a result of concentration (temperature) gradients in the phases).

Convective mass transfer (heat transfer) can be laminar or turbulent (as a result of large-scale turbulent pulsations). Diffusion mass transfer (heat transfer) can be molecular or turbulent (as a result of small-scale turbulent pulsations).

Mathematical models of industrial apparatuses aim at determining the concentration of substances (flow temperatures) in the phases. They have different degrees of approximation – thermodynamic, hydrodynamic and Boltzmann's approximations.

Thermodynamic Approximation

The processes in chemical engineering are the result of a deviation from the thermodynamic equilibrium between two-phase volumes or the volume and phase boundaries of one phase and represent the pursuit of systems to achieve thermodynamic equilibrium [2]. They are irreversible processes and their kinetics use mathematical structures derived from Onsager's principle of linearity. According to him, the average values of the derivatives at the time of the extensive variables depend linearly on the mean deviations of the conjugated intensive variables from their equilibrium states. The principle is valid close to equilibrium, and the Onsager's linearity coefficients are kinetic constants. When the process is done away from equilibrium (high-intensity processes) kinetic constants become kinetic complexes, depending on the corresponding intensive variables. The thermodynamic approximation models cover the entire volume of the phase or part of it.

Hydrodynamic Approximations

The hydrodynamic level uses the 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. In this level the molecules are not visible, as is done in the next level of detail of Boltzmann.

The models of the hydrodynamic approximations can be created on the basis of the mass (heat) transfer theory, whose models are created by the models of the hydrodynamics, diffusion, thermal diffusion and reaction kinetics, using the logical structures of three main "axioms", related with the impulse, mass and heat transfer:

1. The postulate of Stokes for the linear relationship between the stress and deformation rate, which is the basis of the Newtonian fluid dynamics models;
2. The first law of Fick for the linear relationship between the mass flow and the concentration gradient, which is the basis of the linear theory of the mass transfer;
3. The first law of Fourier for the linear relationship between the heat flux and the temperature gradient, which is the basis of the linear theories of the heat transfer.

These are the laws of the impulse, mass and energy transfer.

Boltzmann's Approximation

In Boltzmann's kinetic theory of the ideal gas, the hydrodynamic "axioms" are three "theorems" that derive from the axiom of the "elastic shock" (in a shock between two molecules the direction and the velocity of the movement change, but the sum of their kinetic energies is retained, i.e. there is no loss of kinetic energy) and the rate coefficients are theoretically determined by the average velocity and the average free run of the molecules.

Mechanism of Influence of Reaction Kinetics

The mathematical model of an engineering chemical process is a mass (heat) balance in the phase's volumes, where the mathematical operators are mathematical descriptions of the composite processes, and the relationship between them (differential equations) corresponds to the mechanism of the complex process. The boundary conditions of the differential equations are formulated at the interphase boundaries. For this purpose, the knowledge of the mathematical descriptions of the velocity distribution in the phases and the interphase boundaries is necessary.

Industrial processes are a set of physical and chemical reactions, hydrodynamic, diffusion and thermal processes that take place in the industrial

apparatus volume. The problems in compiling the models of the kinetics of industrial apparatuses arise from the need for information about the interaction between the individual processes in the complex process (its mechanism) and a mathematical description of the geometry of the industrial apparatus volume.

For the most part, industrial cases do not have the above information, which requires simplification of the models and introduction of some effects through experimentally determined parameters. As examples will be considered a co-current absorption column without packings and a counter-current absorption column with random packings.

Co-current Absorption Column without Packings

In the absorption columns without packings, the velocity distributions in the gas and liquid phases and the interfacial limits are unknown, i.e. the differential equations (mass balances in the phases) and their boundary conditions at the interphase boundaries (velocity of the interphase mass transfer) cannot be formulated. These problems are overcome by creating of convection-diffusion and average-concentration models [5, 6]. In the convection-diffusion model the velocity of the interphase mass transfer is replaced by volume physical reaction and experimentally determinable parameter. In this model, the velocities are unknown, so it can only be used for qualitative analysis. From it the average-concentration models are obtained, by model averaging along the cross section of the column. The obtained average-concentration model involves average velocities and concentrations, and the velocity distributions in the phase volumes are introduced with experimentally determined parameters.

Convection-diffusion model

In the stationary case, the convection-diffusion model [3, 4] of the co-current chemical absorption process, with a pseudo-first-order chemical reaction in the liquid phase, in cylindrical coordinate system (r, z) [m], has the form:

$$u_j \frac{\partial c_j}{\partial z} + v_j \frac{\partial c_j}{\partial r} = D_j \left(\frac{\partial^2 c_j}{\partial z^2} + \frac{1}{r} \frac{\partial c_j}{\partial r} + \frac{\partial^2 c_j}{\partial r^2} \right) + (-1)^{(2-j)} k \left(c_1 - \chi c_2 \right) - (j-1) k_0 c_2;$$

$$r = 0, \quad \frac{\partial c_j}{\partial r} \equiv 0; \quad r = r_0, \quad c_j = (j-1) c_1^0 \chi^{-1}; \quad j = 1, 2; \tag{1}$$

$$z = 0, \quad c_1 \equiv c_1^0, \quad c_2 \equiv 0, \quad u_1^0 c_1^0 \equiv u_1 c_1^0 - D_1 \left(\frac{\partial c_1}{\partial z} \right)_{z=0}, \quad \left(\frac{\partial c_2}{\partial z} \right)_{z=0} = 0.$$

$$\frac{\partial u_j}{\partial z} + \frac{\partial v_j}{\partial r} + \frac{v_j}{r} = 0; \tag{2}$$

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

In (1, 2) $u_j = u_j(r, z), v_j = v_j(r, z)$ and $c_j = c_j(r, z)$ are the axial and radial velocity components and transferred substance concentrations in the gas ($j=1$) and liquid ($j=2$) phases, D_j are the diffusivities in the phases, u_j^0 and c_j^0 are the inlet velocities and the concentrations in the phases, k is the interphase mass transfer rate coefficient, χ - the Henry's number, k_0 - the chemical reaction rate constant. The concentrations of the transferred substance in the phases are presented as kg-mol of the transferred substance in 1 m³ of the phase volume. The inlet velocities u_j^0 ($j=1, 2$) of the gas and liquid phases are equal to the average velocities $\bar{u}_j$ ($j=1,2$) of the phases in the column.

On the column wall the velocity components are zero $(r = r_0, u_j = v_j \equiv 0, j = 1, 2)$, i.e. there is no convective mass transfer. At the surface of the column, the motionless gas phase substance is absorbed into the motionless liquid phase. As a result, the concentration of the absorbent substance in the gas on the wall decreases to zero and its concentration in the liquid increases maximally (until thermodynamic equilibrium is reached), i.e. $r = r_0, c_1 = 0, c_2 = c_1^0 \chi^{-1}$.

In the physical absorption, the interphase mass transfer between gas and liquid phases is a surface physical reaction. In (1) this reaction is presented as a volume reaction and its rate

$Q = (-1)^{(2-j)} k (c_1 - \chi c_2)$, $j = 1, 2$ participates in the mass balances in the gas and liquid phases.

Average-concentration model

The averaging of the convection-diffusion model [5, 6] along the cross section of the column leads to the average-concentration model:

$$\alpha_j(z)\bar{u}_j \frac{d\bar{c}_j}{dz} + \left[\beta_j(z) + \varepsilon\gamma_j(z)\right]\bar{u}_j \bar{c}_j =$$
$$= D_j \frac{d^2\bar{c}_j}{dz^2} + (-1)^{(2-j)} k(\bar{c}_1 - \chi\bar{c}_2) - (j-1)k_0\bar{c}_2; \qquad (3)$$

$$z = 0, \quad \bar{c}_j(0) \equiv (2-j)c_j^0, \quad \frac{d\bar{c}_j}{dz} \equiv 0; \quad j = 1, 2,$$

where

$$\alpha_j(z) = 1 + a_{j1}z + a_{j2}z^2, \quad \beta_j(z) = 1 + b_{j1}z + b_{j2}z^2, \quad \gamma_j(z) = 1 + g_{j1}z + g_{j2}z^2, \quad j = 1, 2, \qquad (5)$$

where the values of $a_{j1}, a_{j2}, b_{j1}, b_{j2}, g_{j1}, g_{j2}, j = 1, 2$ can be obtained using experimental data for the average concentration at the column end:

$$\bar{c}_{jm}(l), \quad j = 1, 2, \quad m = 1, ..., 10. \qquad (6)$$

Introducing (5) into (3) leads to

$$(1 + a_{j1}z + a_{j2}z^2)\bar{u}_j \frac{d\bar{c}_j}{dz} + \left[(1 + b_{j1}z + b_{j2}z^2) + \varepsilon(1 + g_{j1}z + g_{j2}z^2)\right]\bar{u}_j \bar{c}_j =$$
$$= D_j \frac{d^2\bar{c}_j}{dz^2} + (-1)^{(2-j)} k(\bar{c}_1 - \chi\bar{c}_2) - (j-1)k_0\bar{c}_2; \qquad (7)$$

$$z = 0, \quad \bar{c}_j(0) \equiv (2-j)c_j^0, \quad \frac{d\bar{c}_j}{dz} \equiv 0; \quad j = 1, 2,$$

where the unknown parameters values $P(k, a_{j1}, a_{j2}, b_{j1}, b_{j2}, g_{j1}, g_{j2}, j = 1, 2)$ must be obtained, using experimental data, by the minimization of the of the least-squares function Q with respect to P:

$$Q(P) = \sum_{m=1}^{10}\left[\bar{c}_1(l, P) - \bar{c}_{1m}(l)\right]^2 + \sum_{m=1}^{10}\left[\bar{c}_2(l, P) - \bar{c}_{2m}(l)\right]^2, \qquad (8)$$

where $\bar{c}_1(l, P)$, $\bar{c}_2(l, P)$ are solutions of the average-concentration model (7).

The presented approach is used for modeling of chemical, absorption, adsorption and catalytic processes in column apparatuses without packings [5, 6].

Counter-current Absorption Column with Random Packings

Counter-current absorption columns with random packings are characterized by the presence of a layer of liquid that flows along the wall of the column and practically does not participate in the absorption process and reduces the working volume of the column. The created hydrodynamic situation does not allow the approach to be used in the modeling of columns without packings.

Fluid flow along the column wall

The liquid flow on the surface of the random packings and when it reaches the column wall most

$$\alpha_j(z) = \frac{2}{r_0^2}\int_0^{r_0} r \frac{u_j}{\bar{u}_j} \frac{c_j}{\bar{c}_j} dr, \quad \beta_j(z) = \frac{2}{r_0^2}\int_0^{r_0} r \frac{u_j}{\bar{u}_j\bar{c}_j} \frac{\partial c_j}{\partial z} dr, \qquad (4)$$

$$\gamma_j(z) = \frac{2}{r_0^2}\int_0^{r_0} r \frac{v_j}{\varepsilon\bar{u}_j\bar{c}_j} \frac{\partial c_j}{\partial r} dr, \quad \varepsilon = \frac{r_0}{l}.$$

The functions $\alpha_j(z), \beta_j(z), \gamma_j(z), j = 1, 2$ can to be presented as the following approximations:

of it flows on this surface and cannot return to the column volume due to the small contact surface between the wall surface and the random packings. The thickness of the flowing layer of liquid increases and conditions are created for the return of liquid from the layer to the packings and further the two effects are equalized. In this way, the layer of liquid reaches a constant maximum thickness, with which it moves to the end of the column. The amount of liquid entering the flowing layer leads to a reduction in the amount of liquid in the volume of the column, i.e. to the radial non-uniformity of the axial component of the liquid velocity in the column and to the reduction of the mass transfer rate in the liquid phase. In addition, this layer is not involved in the absorption process.

The effect of liquid flowing on the column wall is the result only of the geometric shape of the random packings and thus determines the rate of absorption of slightly soluble gases, which reaches a maximum value at maximum packings surface

per unit volume of the column and minimum thickness of the flowing layer of liquid.

Problems with random packings in the columns

In the case of modeling the hydrodynamics in the gas and liquid phases in columns with random packings, the following problems arise:

1. The flow rate of the liquid flowing on the surface of the random packings [m³.s⁻¹] and the retention of the liquid on this surface are unknown;
2. The flow rate of the liquid flowing on the column wall [m³.s⁻¹] and the retention of the liquid on this surface are unknown;
3. The hydrodynamic resistance of the random packings on the gas phase is unknown.

Theoretical analysis [7] shows that this problem can be overcome in the presence of experimental data on the flow rate of the liquid flowing along the column wall, at different packings heights and on the packing pressure drop, during the movement of the gas phase. This requires the creation of a hydrodynamic model in which the liquid and the gas move in separate channels and interact on the surface of the flowing layer. The introduction of experimentally determined quantities into the model brings it as close as possible to the real process.

Experimental data

The wall flow thickness in columns with random packing changes smoothly from 0 to a constant maximal value δ_{max} and can be expressed by an approximation function $\delta(z)$:

$$\delta(z) = \frac{z}{a+bz}, \quad \delta(0) = 0, \quad \delta(\infty) = \frac{1}{b} = \delta_{max}, \quad (9)$$

where z is the axial coordinate. The parameters (a, b) is possible to be determined from experimental data for the flow rate of the wall flow Q_{WF} at various packing heights l in the column - $Q_{WF}(z), z = l_i, i = 1,...,n$. The available experimental data can be described by the following approximation:

$$Q_{WF}(z) = \frac{z}{k_1 + k_2 z}. \quad (10)$$

From (10) is possible to determine the flow rate $Q(z)$ of the wall flow per unit periphery of the column ($2\pi r_0$).

$$Q(z) = \frac{Q_{WF}(z)}{2\pi r_0} = \frac{z}{m_1 + m_2 z}, \quad m_1 = 2\pi r_0 k_1, \quad m_2 = 2\pi r_0 k_2, \quad (11)$$

where r_0 is the column radius.

Phase volume parts in the column volume

The volumes of the solid, gas, and liquid phases per unit volume of the column can be represented as:

$$\varepsilon_j, \quad j = 0,1,2, \quad \varepsilon_0 + \varepsilon_1 + \varepsilon_2 = 1, \quad (12)$$

where the indices $j = 0,1,2$ corresponds to solid, gas, and liquid phases.

As a result of the liquid flow on the column wall, the liquid phase is divided into two parts:

$$\varepsilon_2 = \varepsilon_{21}(z) + \varepsilon_{22}(z), \quad (13)$$

where $\varepsilon_{22}(z)$ is the fraction of the liquid flowing along the wall.

The gas and liquid flow rates Q_G, Q_L, Q_{WF} [m³.s⁻¹] permit to obtain the gas-liquid and liquid-liquid ratios in the column volume:

$$\bar{\varepsilon}_1 = \frac{Q_G}{Q_G + Q_L}, \quad \bar{\varepsilon}_2 = \frac{Q_L}{Q_G + Q_L}, \quad \bar{\varepsilon}_{21} = \frac{Q_L - Q_{WF}}{Q_L}, \quad \bar{\varepsilon}_{22} = \frac{Q_{WF}}{Q_L} \quad (14)$$

and gas and liquid hold-up in the packing:

$$\varepsilon_1 = \frac{\bar{\varepsilon}_1}{1-\varepsilon_0}, \quad \varepsilon_2 = \frac{\bar{\varepsilon}_2}{1-\varepsilon_0}, \quad \varepsilon_{21} = \frac{\bar{\varepsilon}_{21}}{\varepsilon_2}, \quad \varepsilon_{22} = \frac{\bar{\varepsilon}_{22}}{\varepsilon_2}. \quad (15)$$

The parameters ε_1, ε_2 denote the volume fraction, as well as the cross-section fraction of the gas and liquid in the packing and are used to determine their inlet average velocities:

$$u_z^0 = \frac{Q_G}{\varepsilon_1 \pi r_0^2}, \quad v_z^0 = \frac{Q_L}{\varepsilon_2 \pi r_0^2}, \quad (16)$$

where u_z^0, v_z^0 are the average velocities in the void cross-section of the gas and liquid phase at the inlet of the packing bed, Q_G, Q_L - gas and liquid inlet flow rates.

Pressure drop of random packings columns

The hydraulic resistance of the fillings H, i.e. the pressure drop through a layer of random packings with a thickness of 1 meter, at a given gas velocity:

$$H = \frac{p^0 - p(0, z_0)}{z_0}, \quad (17)$$

is determined from experimental data on the pressure difference at both ends $p^0 - p(0, z_0)$ of the random packings height z_0.

The obtained results permit a physical model to be used, where the gas and the liquid move in parts of the column volume and through parts of the column cross section ($\varepsilon_1, \varepsilon_{21}, \varepsilon_{22}$) and contact on a

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cylindrical surface with variable radius $R_0(z) = r_0 - \delta(z)$.

Hydrodynamics of the liquid phase in the column volume

The flows in the column are axially symmetrical and the model of the hydrodynamics of the liquid phase in the volume of the column will be presented in a cylindrical coordinate system (r, z), where r and z are the radial and axial coordinates. In the packings columns the pressure is constant during the movement of liquid under the action of weight. In this case the axial and radial components of the velocity v_z and v_r satisfy the Navier and Stokes equations:

$$v_z \frac{\partial v_z}{\partial z} + v_r \frac{\partial v_z}{\partial r} = \nu\left(\frac{\partial^2 v_z}{\partial z^2} + \frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r}\frac{\partial v_z}{\partial r}\right) + g,$$

$$v_z \frac{\partial v_r}{\partial z} + v_r \frac{\partial v_r}{\partial r} = \nu\left(\frac{\partial^2 v_r}{\partial z^2} + \frac{\partial^2 v_r}{\partial r^2} + \frac{1}{r}\frac{\partial v_r}{\partial r} - \frac{v_r}{r^2}\right). \tag{18}$$

The inlet boundary conditions are:

$$z = 0, \quad v_z = v_z^0, \quad \frac{\partial v_z}{\partial z} = 0, \quad v_r = 0, \quad \frac{\partial v_r}{\partial z} = 0. \tag{19}$$

The boundary conditions along the axis of the column are:

$$r = 0, \quad \frac{\partial v_z}{\partial r} = 0, \quad \frac{\partial v_r}{\partial r} = 0. \tag{20}$$

The effect of the flow of liquid on the wall of the column must be taken into account when $r = R_0(z) = r_0 - \delta(z)$, where the amount of liquid which enters the wall of the column through the surface $2\pi R_0 dz$ by the radial velocity component v_r, i.e. $2\pi R_0 v_r dz$ must be equal to the volume of the liquid layer obtained on the wall of the column $2\pi r_0 v_0 d\delta$, where $v_0 = v_0(z)$ is the surface velocity of the liquid layer:

$$2\pi R_0 v_r(R_0, z) dz = 2\pi r_0 v_0(z) d\delta. \tag{21}$$

As a result

$$r = R_0 = r_0 - \delta(z), \quad v_r(R_0, z) = \frac{r_0 v_0(z)}{r_0 - \delta(z)} \frac{d\delta}{dz}, \quad \frac{d\delta}{dz} = \frac{a}{(a+bz)^2}. \tag{22}$$

The axial component of the liquid velocity v_z at the boundary $r = r_0 - \delta(z)$ must be equal to the surface velocity of the film flowing down the column wall $v_0(z)$:

$$r = r_0 - \delta(z) = r_0 - \frac{z}{a+bz}, \quad v_z = v_0(z), \tag{23}$$

where the surface velocity changes smoothly from 0 to a constant maximal value and can be expressed by an approximation function:

$$v_0(z) = \frac{z}{\alpha + \beta z}. \tag{24}$$

The parameters (a, b, a, β) in the approximation functions (9, 24) must be obtained using experimental data.

Finally, the hydrodynamic model of the liquid phase in column volume can be written as:

$$v_z \frac{\partial v_z}{\partial z} + v_r \frac{\partial v_z}{\partial r} = \nu\left(\frac{\partial^2 v_z}{\partial z^2} + \frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r}\frac{\partial v_z}{\partial r}\right) + g,$$

$$v_z \frac{\partial v_r}{\partial z} + v_r \frac{\partial v_r}{\partial r} = \nu\left(\frac{\partial^2 v_r}{\partial z^2} + \frac{\partial^2 v_r}{\partial r^2} + \frac{1}{r}\frac{\partial v_r}{\partial r} - \frac{v_r}{r^2}\right);$$

$$z = 0, \quad v_z = v_z^0, \quad \frac{\partial v_z}{\partial z} = 0, \quad v_r = 0, \quad \frac{\partial v_r}{\partial z} = 0;$$

$$r = 0, \quad \frac{\partial v_z}{\partial r} = 0, \quad \frac{\partial v_r}{\partial r} = 0; \quad r = r_0 - \delta(z), \quad v_z = v_0(z), \quad v_r = \frac{r_0 v_0(z)}{r_0 - \delta(z)} \frac{d\delta}{dz};$$

$$\delta(z) = \frac{z}{a+bz}, \quad \frac{d\delta}{dz} = \frac{a}{(a+bz)^2}, \quad v_0(z) = \frac{z}{\alpha + \beta z}. \tag{25}$$

Liquid layer hydrodynamics

The wall flow in the column is described by the equations:

$$w_z \frac{\partial w_z}{\partial z} + w_r \frac{\partial w_z}{\partial r} = \nu \left(\frac{\partial^2 w_z}{\partial z^2} + \frac{\partial^2 w_z}{\partial r^2} + \frac{1}{r} \frac{\partial w_z}{\partial r} \right) + g,$$

$$w_z \frac{\partial w_r}{\partial z} + w_r \frac{\partial w_r}{\partial r} = \nu \left(\frac{\partial^2 w_r}{\partial z^2} + \frac{\partial^2 w_r}{\partial r^2} + \frac{1}{r} \frac{\partial w_r}{\partial r} - \frac{w_r}{r^2} \right);$$

$$z = 0, \quad w_z = 0, \quad \frac{\partial w_z}{\partial z} = 0, \quad w_r = 0, \quad \frac{\partial w_r}{\partial z} = 0;$$

$$r = r_0, \quad w_z = 0, \quad w_r = 0; \quad r = r_0 - \delta(z), \quad w_z = v_0(z), \quad w_r = v_r = \frac{r_0 v_0(z)}{r_0 - \delta(z)} \frac{d\delta}{dz};$$

$$\delta(z) = \frac{z}{a + bz}, \quad \frac{d\delta}{dz} = \frac{a}{(a + bz)^2}, \quad v_0(z) = \frac{z}{\alpha + \beta z}.$$

$$(26)$$

Parameters identification

The comparison of (25) and (26) shows that there is a common boundary condition at an unknown boundary $\delta(z)$:

$$r = r_0 - \delta(z), \quad w_z = v_z = v_0(z), \qquad (27)$$

where the surface velocity of the wall flow $v_0(z)$ is unknown too.

The flow rate of the liquid flowing on the wall, per unit of column circumference $Q(z)$ in (11), which has passed from the bulk of the liquid in the column, depends on the functions $\delta(z), v_0(z)$ and must be determined by the equations:

$$Q(z) = \frac{z}{m_1 + m_2 z} = \int_{r_0 - \delta(z)}^{r_0} w_z dr = \int_0^{r_0 - \delta(z)} \left[v_z^0 - v_z \right] dr, \quad v_z^0 = \frac{Q_L}{\varepsilon_2 \pi r_0^2},$$

$$(28)$$

i.e. the flow rate of the wall flow is equal to the difference in the flow rates of the liquid in the bulk of the column in presence and absence of a wall flow. The conditions (28) and the solution of the system of equations (25, 26) permit to obtain the parameters (a, b, α, β), using a suitable algorithm [7].

Gas phase hydrodynamics

The hydrodynamics of the gas phase will be represented in a cylindrical coordinate system $(r, z_0), z_0 = l - z$, where the axial coordinate is directed back to the axial coordinate of the liquid phase. The movement of the gas is the result of the pressure gradient along the height of the column (hydraulic resistance), which depends on the packings and is determined experimentally. The axial u_z and radial u_r components of velocity in the gas phase and pressure (per unit volume) p satisfy the Navier-Stokes equations:

$$u_z \frac{\partial u_z}{\partial z_0} + u_r \frac{\partial u_z}{\partial r} = -\frac{1}{\rho} \frac{\partial p}{\partial z_0} + \nu \left(\frac{\partial^2 u_z}{\partial z_0^2} + \frac{\partial^2 u_z}{\partial r^2} + \frac{1}{r} \frac{\partial u_z}{\partial r} \right),$$

$$u_z \frac{\partial u_r}{\partial z_0} + u_r \frac{\partial u_r}{\partial r} = -\frac{1}{\rho} \frac{\partial p}{\partial r} + \nu \left(\frac{\partial^2 u_r}{\partial z_0^2} + \frac{\partial^2 u_r}{\partial r^2} + \frac{1}{r} \frac{\partial u_r}{\partial r} - \frac{u_r}{r^2} \right),$$

$$\frac{\partial u_z}{\partial z_0} + \frac{\partial u_r}{\partial r} + \frac{u_r}{r} = 0;$$

$$z_0 = 0, \quad u_z = u_z^0, \quad \frac{\partial u_z}{\partial z_0} = 0, \quad u_r = 0, \quad \frac{\partial u_r}{\partial z_0} = 0, \quad p = p^0;$$

$$r = 0, \quad \frac{\partial u_z}{\partial r} = 0, \quad \frac{\partial u_r}{\partial r} = 0, \quad p = p(0, z);$$

$$r = r_0 - \frac{l - z_0}{a + b(l - z_0)}, \quad u_z = -v_0(l - z_0), \quad u_r = 0.$$

$$(29)$$

The pressure in the gas phase $p(r, z_0)$ can be presented in (29) as

$$\frac{\partial p}{\partial r} \equiv 0, \quad \frac{\partial p}{\partial z_0} = H = \frac{p^0 - p(0, z_0)}{z_0}, \qquad (30)$$

where H is the packing pressure drop, i.e. the pressure drop through a packing layer of a thickness of 1 meter at a given gas velocity.

Modeling of Processes with Unknown Mechanism

There are complex processes whose mechanism is unknown. A typical example of this are the complex chemical reactions, the rate of which depends on the concentrations of several substances, but the simple chemical reactions and the relationships between them are unknown.

The kinetics of processes with an unknown mechanism can be modeled on the basis of the axiom, according to which "The mathematical structure of the quantitative description of real processes does not depend on the measuring system of the quantities involved in them". On the basis of this axiom, Guchmann's theorem can be proved [8] – "If the mathematical structure is invariant with respect to similar transformations, it can be presented as power functions complex", i.e. „Mathematical structure of the quantitative

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description of real systems can be presented as power functions complex", because the mathematical structure which is invariant with respect to similar transformations is a mathematical structure of real processes which does not depend on the measuring system.

The kinetics of the chemical engineering processes depends on a set of variables. If the velocity of these processes is denoted by y and the values of these variables are $x_1, ..., x_n$, the equation of the kinetic model will have the form:

$$y = f(x_1, ..., x_n). \tag{31}$$

This function is a mathematical structure that is retained when changed the measurement system of the variable, i.e. this mathematical structure is invariant with respect to similar transformations [7]:

$$\bar{x}_i = k_i x_i, \quad i = 1, ..., n, \tag{32}$$

i.e. f is a homogeneous function:

$$ky = f(k_1 x_1, ..., k_n x_n) = \phi(k_1, ..., k_n).f(x_1, ..., x_n), \quad k = \phi(k_1, ..., k_n). \tag{33}$$

A short recording of (33) is:

$$f[\bar{x}_i] = \phi[k_i] f[x_i]. \tag{34}$$

The problem consists in finding a function f that satisfies equation (34). A differentiation of equation (34) concerning k_1 leads to:

$$\frac{\partial f[\bar{x}_i]}{\partial k_1} = \frac{\partial \phi}{\partial k_1} f(x_i). \tag{35}$$

On the other hand

$$\frac{\partial f[\bar{x}_i]}{\partial k_1} = \frac{\partial f[\bar{x}_i]}{\partial \bar{x}_1} \frac{\partial \bar{x}_1}{\partial k_1} = \frac{\partial f[\bar{x}_i]}{\partial \bar{x}_1} x_1. \tag{36}$$

From (35, 36) follows

$$\frac{\partial f[\bar{x}_i]}{\partial \bar{x}_1} x_1 = \alpha_1 f[x_i], \tag{37}$$

where

$$\alpha_1 = \left(\frac{\partial \phi}{\partial k_1}\right)_{k_i=1}. \tag{38}$$

The equation (37) is valid for different values of k_i including $k_i = 1 \ (i = 1, ..., n)$. As a result $\bar{x}_i = x_i, i = 1, ..., n$ and from (37) follows

$$\frac{1}{f} \frac{\partial f}{\partial x_1} = \frac{\alpha_1}{x_1}, \tag{39}$$

i.e.

$$f = c_1 x_1^{\alpha_1}. \tag{40}$$

When the above operations are repeated for $x_2, ..., x_n$, the homogenous function f assumes the form:

$$f = k x_1^{\alpha_1}, ..., x_n^{\alpha_n}, \tag{41}$$

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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 parameters $k, a_1, ...a_n$ are determined by experimental data of the industrial process velocity.

The power functions complex (41) is used in the similarity criterion models equation in the similarity theory [7], where $x_i, i = 1, ..., n$ are similarity criteria. The information about the process mechanism permits to obtain dimensionless combinations of the model parameters (similarity criteria) which represent the ratio of the efficiency of two processes, for example [1]:

$$\text{Fo} = \frac{Dl}{u^0 r_0^2}, \quad \text{Da} = \frac{kl}{u^0}, \tag{42}$$

are the Fourier and Damkohler numbers and represent the ratio of the efficiency of the convective and diffusion mass transfer (Fo) and convective mass transfer and chemical reaction rate (Da). In (42) D is diffusivity, r_0, l - linear characteristic scales, u^0 - velocity characteristic scale.

The power functions complex (41) is used by the dimension analysis [1], but the dimension criteria do not represent the ratio of the efficiency of two processes, because the method is used in absence of the processes mechanism information.

CONCLUSIONS

In the paper is presented a theoretical analysis of the methods for chemical engineering processes modeling. The methods for modeling specific processes may be different, but in all cases they must bring the mathematical description closer to the real process by using appropriate experimental data.

The role of the kinetics of industrial apparatuses for solving the problems of optimal design and control is analyzed. The thermodynamic, hydrodynamic and Boltzmann approximations for the mathematical description of the kinetics of industrial apparatuses are described.

They are presented for the cases of co-current absorption column without packings, counter-current absorption column with random packings and modeling of processes with unknown mechanism.

mass transfer and separation in distillation, absorption, adsorption and catalytic processes in industrial column apparatuses".

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