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New models of industrial column chemical reactors

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A new approach to modeling the industrial column chemical reactors is presented. A theoretical analysis of the effect of the radial non-uniformity of the axial velocity component in the industrial column chemical reactors is presented. A numerical analysis shows, that average concentration model, where the radial velocity component is equal to zero (in the cases of a constant velocity radial non-uniformity along the column height), is possible to be used in the cases of an axial modification of the radial non-uniformity of the axial velocity component. The use of experimental data, for the average concentration at the column end, for a concrete process and column, permits to be obtained the model parameters, related with the radial non-uniformity of the velocity. These parameter values permit to be used the average concentration model for modeling of different processes.

Keywords: Column apparatus, chemical reaction, convection-diffusion model, average concentration model, velocity radial non-uniformity.

INTRODUCTION

The fundamental problem in the column apparatuses modeling is result of the complicated hydrodynamic behavior of the flows in the columns and as a result the velocity distributions in the columns are unknown.

The industrial column chemical reactors is possible to be modeled, using a new approach [1-4] on the base 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. As a result, a convection-diffusion type model (for qualitative analysis) and an average concentration type model (for quantitative analysis) are possible to be used in the cases of isothermal chemical reactions [1-4].

CONVECTION-DIFFUSION MODEL

The physical elementary volumes will be presented as mathematical points in a cylindrical coordinate system (r,z), where r and z [m] are radial and axial coordinates. The concentrations [kg-mol.m^{-3}] of the reagents are $c_i(r,z)$, $i=1,2,...,i_0$, i.e. the quantities of the reagents (kg-mol) in 1 m^3 of the column volume.

In the cases of a stationary fluids motion in cylindrical column apparatus, when the radial non-uniformity of the axial velocity component $u(r)$ [m.s^{-1}] is permanent along the column height, the radial velocity component is equal to zero.

The homogeneous chemical reaction, as a volume source or sink in the column volume is $Q_i(c_i)$ [kg-mol.m^{-3}.s^{-1}], $i=1,2,...,i_0$ (i_0 - reagent number). They lead to different values of the reagent (substance) concentrations in the elementary volumes $c_i(r,z)$, $i=1,2,...,i_0$ 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 mathematical model of the processes in the column apparatuses, in the physical approximations of the mechanics of continua, is mass balances in the elementary volumes between the convective transfer, the diffusive transfer and the volume mass sources (sinks) (as a result of the chemical reaction). In the stationary case, the convection-diffusion equations (as a mathematical structures of the mass transfer process models in the industrial column chemical reactors) [1-4] are:

$$\begin{aligned} & u\frac{\partial c_i}{\partial z}=D_i\left(\frac{\partial^2 c_i}{\partial z^2}+\frac{1}{r}\frac{\partial c_i}{\partial r}+\frac{\partial^2 c_i}{\partial r^2}\right)+Q_i(c_i); \\ & r=0,\quad \frac{\partial c_i}{\partial r}\equiv 0;\quad r=r_0,\quad \frac{\partial c_i}{\partial r}\equiv 0; \\ & z=0,\quad c_i\equiv c_i^0,\quad u^0c_i^0\equiv u\,c_i^0-D_i\left(\frac{\partial c_i}{\partial z}\right)_{z=0}; \\ & i=1,2,\ldots,i_0, \end{aligned} \tag{1}$$

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where u^0, c_i^0 are the inlet velocity and concentrations, D_i [m^2.s^{-1}] - diffusivities, r_0 [m] - column radius.

In the cases of a two components complex chemical reactions $i=1,2$, $Q_i=-kc_1^m c_2^n$, where m, n are the reaction orders. For big difference between inlet concentrations of the reagents $\left(c_1^0 \gg c_2^0\right)$ and $m=1$, from (1) follows the pseudo-first-order reactions case $\left(i_0=1,\ c_1=c,\ c_2\equiv c_2^0\right)$:

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

AVERAGE CONCENTRATION MODEL

The average values of the velocity and concentration, at the column cross-sectional area is possible to be presented [1-4] as:

$$
\bar{u}=u^0=\frac{2}{r_0^{\,2}}\int_0^{r_0} r u(r)\,dr,\quad \bar{c}(z)=\frac{2}{r_0^{\,2}}\int_0^{r_0} r c(r,z)\,dr. \tag{3}
$$

The functions $u(r)$, $c(r,z)$ in (2) can be presented by the help of the average functions (3):

$$
u(r)=\bar{u}\,\tilde{u}(r),\quad c(r,z)=\bar{c}(z)\,\tilde{c}(r,z), \tag{4}
$$

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

$$
\frac{2}{r_0^{\,2}}\int_0^{r_0} r\,\tilde{u}(r)\,dr=1,\quad \frac{2}{r_0^{\,2}}\int_0^{r_0} r\,\tilde{c}(r,z)\,dr=1. \tag{5}
$$

The average concentration model may be obtained if put (4) into (2), multiply by r and integrate over r in the interval $[0,r_0]$. As a result, the following is obtained:

$$
\begin{aligned}
&\alpha\bar{u}\frac{d\bar{c}}{dz}+\frac{d\alpha}{dz}\bar{u}\,\bar{c}=D\frac{d^2\bar{c}}{dz^2}-k\bar{c};\\
&z=0,\quad \bar{c}(0)=c^0,\quad \frac{d\bar{c}}{dz}=0,
\end{aligned}
\tag{6}
$$

where

$$
\alpha(z)=\frac{2}{r_0^{\,2}}\int_0^{r_0} r\tilde{u}\tilde{c}\,dr. \tag{7}
$$

GENERALIZED VARIABLES

In (2) and (6) is possible to be introduced the generalized variables [2]:

$$
\begin{aligned}
&r=r_0R,\quad z=lZ,\quad u(r)=\bar{u}U(R),\\
&\tilde{u}(r)=\frac{u(r)}{\bar{u}}=U(R),\quad c(r,z)=c^0C(R,Z),\\
&\bar{c}(z)=c^0\bar{C}(Z),\quad \bar{C}(Z)=2\int_0^1 RC(R,Z)\,dR,\\
&\tilde{c}(r,z)=\frac{c(r,z)}{\bar{c}(z)}=\frac{C(R,Z)}{\bar{C}(Z)},\\
&\alpha(z)=\alpha(lZ)=A(Z)=2\int_0^1 RU(R)\frac{C(R,Z)}{\bar{C}(Z)}\,dR
\end{aligned}
\tag{8}
$$

and as a result is obtained:

$$
\begin{aligned}
&U\frac{\partial C}{\partial Z}=\mathrm{Fo}\left(\varepsilon\frac{\partial^2 C}{\partial Z^2}+\frac{1}{R}\frac{\partial C}{\partial R}+\frac{\partial^2 C}{\partial R^2}\right)-\mathrm{Da}\,C;\\
&\varepsilon=\mathrm{Fo}^{-1}\,\mathrm{Pe}^{-1};\\
&R=0,\quad \frac{\partial C}{\partial R}\equiv 0;\quad R=1,\quad \frac{\partial C}{\partial R}\equiv 0;\\
&Z=0,\quad \mathrm{C}\equiv 1,\quad 1\equiv U-\mathrm{Pe}^{-1}\frac{\partial C}{\partial Z}.
\end{aligned}
\tag{9}
$$

$$
\begin{aligned}
&A(Z)\frac{d\bar{C}}{dZ}+\frac{dA}{dZ}\bar{C}=\mathrm{Pe}^{-1}\frac{d^2\bar{C}}{dZ^2}-\mathrm{Da}\,\bar{C};\\
&Z=0,\quad \bar{C}=1,\quad \frac{d\bar{C}}{dZ}=0,
\end{aligned}
\tag{10}
$$

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

$$
\mathrm{Fo}=\frac{Dl}{\bar{u}r_0^2},\quad \mathrm{Pe}=\frac{\bar{u}l}{D},\quad \mathrm{Da}=\frac{kl}{\bar{u}}. \tag{11}
$$

The convection-diffusion model (9) permits to be made [1-4] a qualitative analysis of the process (model) for to be obtained the main, small and slight physical effects (mathematical operators), and to be rejected the slight effect (operators). As a result the process mechanism identification is possible to be made. On this base are possible different approximations for high column $\left(0=\varepsilon\le 10^{-2}\right)$, big average velocity $\left(0=\mathrm{Fo}\le 10^{-2}\right)$, small $\left(0=\mathrm{Da}\le 10^{-2}\right)$ or big $\left(0=\mathrm{Da}^{-1}\le 10^{-2}\right)$ chemical reaction rate.

In an industrial column ($l>1$ [m]), the average velocity is $\bar{u}>1$ [m.s^{-1}] and the diffusivity is $D_1<10^{-4}$ [m^2.s^{-1}]. In these conditions is possible to

be obtained the order of magnitude of the parameters values:

$$\mathrm{Pe}^{-1} < 10^{-4}, \quad \frac{h_0}{l} > 10^{-1}, \quad \mathrm{Fo} < 10^{-2}, \qquad (12)$$

and the models (9), (10) have convective forms:

$$U\frac{\partial C}{\partial Z} = -\mathrm{Da}\, C; \quad Z = 0, \quad \mathrm{C} \equiv 1. \qquad (13)$$

$$A(Z)\frac{d\bar{C}}{dZ} + \frac{dA}{dZ}\bar{C} = -\mathrm{Da}\,\bar{C}; \quad Z = 0, \quad \bar{C} = 1. \qquad (14)$$

The average concentration models allow a quantitative analysis of the processes in column apparatuses. The theoretical analysis of the models (13), (14) shows [1-4], that the function $A(Z)$ is possible to be presented as a linear approximation:

$$A = a_0 + a_1 Z, \qquad (15)$$

where the model parameters a_0, a_1 is possible to be obtained, using experimental data for a short column ($Z = 0.1$).

The presented theoretical analysis shows that the basic approximation of the convection-diffusion model (13) and average concentration model (14) is $\frac{\partial \tilde{u}}{\partial z} \equiv 0$.

MODELING OF THE INDUSTRIAL COLUMN CHEMICAL REACTORS

Very often in industrial conditions, an axial modification of the radial non-uniformity of the velocity, is realized. The radial non-uniformity of the axial velocity component in the column apparatuses is caused by the fluid hydrodynamics at the column inlet, where it has as maximum and decreases along the column height as a result of the fluid viscosity. The theoretical determination of the change in the radial non-uniformity of the axial velocity component in a column is difficult in one-phase processes and practical impossible in two-phase and three-phase processes. For a theoretical analysis of the effect of the axial modification of the radial non-uniformity of the velocity, this difficulty can be circumvented by appropriate hydrodynamic model, where the average velocity at the cross section of the column is a constant, while the maximal velocity (and as a result the radial non-uniformity of the axial velocity component too) decreases along the column height.

Let's considers the velocity distribution

$$u_n(r, z_n) = \bar{u}\ \tilde{u}_n(r, z_n) \qquad (16)$$

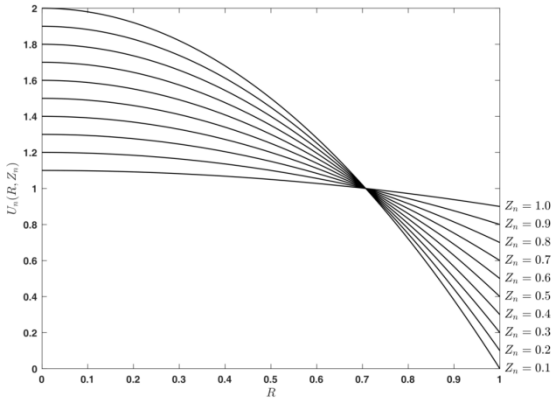

Fig.1. Velocity distributions $U_n(R, Z_n)$, $Z_n = 0.1(n+1),\ n = 0,1,...,9.$

and an axial step change of the radial non-uniformity of the axial velocity component in a column (Fig. 1):

$$\begin{aligned} &\tilde{u}_n(r, z_n) = \tilde{u}_n(r_0 R, lZ_n) = \\ &= U_n(R, Z_n) = a_n - b_n R^2, \\ &a_n = 2 - 0.1n, \quad b_n = 2(1 - 0.1n), \\ &0.1n \le Z_n \le 0.1(n+1) \quad n = 0,1,...,9, \end{aligned} \qquad (17)$$

where $\tilde{u}_n(r, z_n)$ satisfy the equation:

$$\frac{2}{r_0^2}\int_0^{r_0} r\ \tilde{u}_n(r, z_n)\ dr = 1, \qquad (18)$$

i.e. $\bar{u} = const$.

If put (16), (17) in (13), the convection-diffusion model has the form:

$$\begin{aligned} &U_n \frac{\partial C_n}{\partial Z_n} = -\mathrm{Da}\, C_n; \quad 0.1n \le Z_n \le 0.1(n+1); \\ &Z_n = 0.1n, \quad \mathrm{C}_n(R, Z_n) = C_{n-1}(R, Z_n); \\ &n = 0,1,...,9; \\ &Z_0 = 0, \quad \mathrm{C}_0(R, Z_0) \equiv 1. \end{aligned} \qquad (19)$$

MODEL EQUATIONS SOLUTION

The solution of (19) $C(R, Z) = C_n(R, Z_n),\ Z_n = 0.1(n+1),\ n = 0,1,...,9$ in the case $\mathrm{Da} = 1$ is presented on the Fig. 2. This solution $C(R, Z)$ permits to be obtained in (8) the average ("theoretical") concentration distribution $\bar{C}(Z) = \bar{C}_n(Z_n),\ Z_n = 0.1(n+1), \quad n = 0,1,...,9$ in the column (the points on the Fig. 3) and function $A(Z)$ (the points on the Fig. 4) on every step:

$$\bar{C}(Z)=\bar{C}_n(Z_n)=2\int_0^1 RC_n(R,Z_n)\,dR,$$

$$A(Z)=A_n(Z_n)=2\int_0^1 RU_n(R)\frac{C_n(R,Z_n)}{\bar{C}_n(Z_n)}\,dR, \qquad (20)$$

$$Z_n=0.1(n+1),\quad n=0,1,...,9,$$

which are presented on the Figs. 3, 4. From Fig. 4 is seen, that the function $A(Z)$ is possible to be presented as a quadratic approximation:

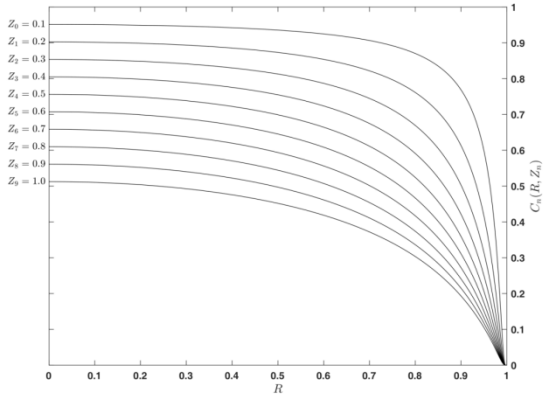

Fig. 2. Concentration distributions $C_n(R,Z_n)$, $Z_n=0.1(n+1)$, $n=0,1,...,9$.

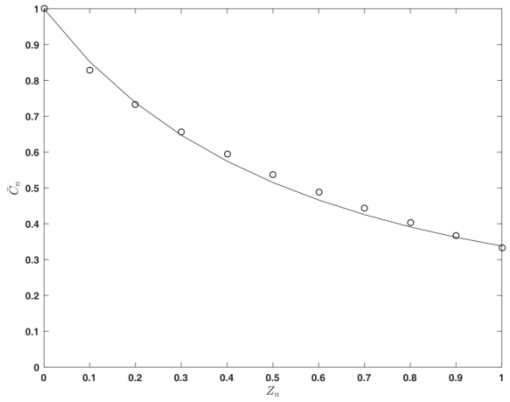

Fig. 3. Average concentration distribution: "theoretical" values (as solution of (19) and (20) $\bar{C}_n(Z_n)$, $Z_n=0.1(n+1)$, $n=0,1,...,9$ (points); $\bar{C}(Z)$ as a solution of (22)(22) for "experimental" values of a_0, a_1, a_2 (line).

$$A(Z)=a_0+a_1Z+a_2Z^2, \qquad (21)$$

where the ("theoretical") values of a_0, a_1, a_2 are presented in the Table 1. As a result, in the case of axial modification of the radial non-uniformity of the velocity, the model (14) has the form:

$$\left(a_0+a_1Z+a_2Z^2\right)\frac{d\bar{C}}{dZ}+\left(a_1+2a_2Z\right)\bar{C}= \qquad (22)$$
$$=-\mathrm{Da}\,\bar{C};\quad Z=0,\quad \bar{C}=1,$$

where the parameters a_0, a_1, a_2 must be obtained, using experimental data.

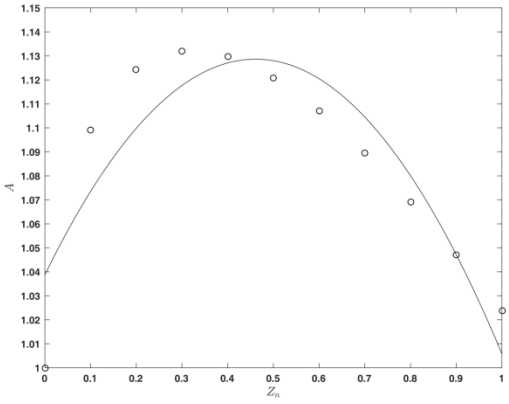

Fig. 4. Function $A(Z)$: $A(Z_n)$, $Z_n=0.1(n+1)$, $n=0,1,...,9$;as a quadratic approximation (21) (line).

PARAMETERS IDENTIFICATION

The obtained value of the function $\bar{C}_9(1)$ (Fig. 3) permit to be obtained the artificial experimental data $\bar{C}^m_{\exp}(1)$ for the column end ($Z_9=1$):

$$\bar{C}^m_{\exp}(1)=(0.95+0.1B_m)\bar{C}_9(1), \qquad (23)$$
$$m=1,...,10,$$

where $0\le B_m\le 1$, $m=0,1,...,10$ are obtained by a generator of random numbers.

The obtained artificial experimental data (23) are used for the illustration of the parameters (a_0, a_1, a_2) identification in the average concentrations model (22) by the minimization of the least-squares function:

$$Q(a_0,a_1,a_2)= \qquad (24)$$
$$=\sum_{m=1}^{10}\left[\bar{C}(1,a_0,a_1,a_2)-\bar{C}^m_{\exp}(1)\right]^2,$$

where the value of $\bar{C}(1,a_0,a_1,a_2)$ is obtained after the solution of (22) for $Z=1$. The obtained "experimental" parameter values are presented on the Table 1.

The obtained ("experimental") parameter values are used for the solution of (22) and the result (the line) is compared with the average ("theoretical") concentration values $\bar{C}(Z)=\bar{C}_n(Z_n)$, $Z_n=0.1(n+1)$, $n=0,1,...,9$. (points) (as solution of (19) and (20)) on the Fig. 3.

INFLUENCE OF THE MODEL PARAMETER

The model (22), with "experimental" parameters values of a_0, a_1, a_2 in the Table 1, is used for the calculation the average concentrations in the case $\mathrm{Da} = 2$ and the result (line) is compared (Fig. 5) with the average ("theoretical") concentration

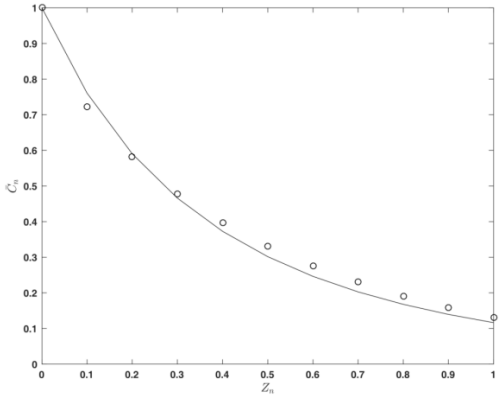

Fig. 5. Effect of the chemical reaction rate $(\mathrm{Da} = 2)$: average ("theoretical") concentration values $\bar{C}_n(Z_n), Z_n = 0.1(n+1), n = 0,1,...,9.$ (as solutions of (19) and (20) (points)); solution of (22) (line) values $\bar{C}_n(Z_n), Z_n = 0.1(n+1), n = 0,1,...,9.$ (as solutions of (19) and (20) (points)) for this case.

Table 1. Parameters a_0, a_1, a_2.

Parameters	"Theoretical" values	"Experimental" values
a_0	1.0387	0.8582
a_1	0.3901	0.4505
a_2	−0.4230	−0.4343

CONCLUSIONS

The presented numerical analysis of the industrial column chemical reactors shows, that average concentration model, where the radial velocity component is equal to zero (in the cases of a constant velocity radial non-uniformity along the column height), is possible to be used in the cases of an axial modification of the radial non-uniformity of the axial velocity component. The use of experimental data, for the average concentration at the column end, for a concrete process, permits to be obtained the model parameters (a_0, a_1, a_2), related with the radial non-uniformity of the velocity. These parameter values permit to be used the average concentration model for modeling of different processes (different values of the parameter Da, i.e. different values of the column height, average velocity, reagent diffusivity and chemical reaction rate constant).

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НОВИ МОДЕЛИ НА ИНДУСТРИАЛНИ КОЛОННИ ХИМИЧНИ РЕАКТОРИ

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(Резюме)

Представен е нов подход за моделиране на промишлени колонни химични реактори. Предложен е теоретичен анализ на ефекта на радиалната неравномерност на аксиалната компонента на скоростта в промишлени колонни химични реактори. Численият анализ показва, че моделът на средните концентрации, когато радиалната компонента на скоростта е равна на нула (в случаите на постоянна радиална неравномерност на скоростта по височината на колоната), е възможно да бъде използвана в случаите на аксиално изменение на радиалната неравномерност на аксиалната компонента на скоростта. Използването на експериментални данни за средната концентрация на изхода на колоната, за конкретен процес и колона, позволява да бъдат намерени моделните параметри, свързани с радиалната неравномерност на скоростта. Тези стойности на параметрите позволяват използването на модела на средните цонцентрации за моделиране на различни процеси.