Available online at www.sciencedirect.com
SCIENCE DIRECT®
International Journal of Heat and Mass Transfer 49 (2006) 796–799
International Journal of HEAT and MASS TRANSFER
www.elsevier.com/locate/ijhmt

Diffusion models and scale-up

Christo B. Boyadjiev *

Institute of Chemical Engineering, Bulgarian Academy of Sciences, Acad. G. Bontchev Str. Bl. 103, 1113 Sofia, Bulgaria

Received 2 May 2005
Available online 10 November 2005

Abstract

A model for mass transfer processes in column apparatuses has been done. The model may be modified for different volume source (chemical reaction, interphase mass transfer). The using of the average velocities and concentration permits to solve the scale-up problem. A hierarchical approach for model parameter identification has been proposed.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Diffusion model; Scale-up; Average concentration; Scale effect

1. Introduction

Many mass transfer processes in column apparatuses may be described by the convection–diffusion equation with a volume reaction [1]. These are gas absorption in column with (or without) packet bed [2,3], chemical reactors for homogeneous or heterogeneous reactions [4], air-lift reactors for biochemical or photochemical reactions [5–8].

The convective transfer in column apparatuses is result of a laminar or turbulent (large-scale pulsation's) flows. The diffusive transfer is molecular or turbulent (small-scale pulsation's) The volume reaction is mass sours as a result of chemical reactions or interphase mass transfer [1,2].

The scale-up theory [1,2] show that the scale effect in mathematical modeling is result of the radial non-uniformity of the velocity distribution in the column. In many papers [2] are used diffusion models, where the scale effect is considered as an axial mixing increasing.

The creation of the models in these conditions and solving of the scale-up problem [4,7] require construction of a suitable diffusion models.

2. Diffusion model

Let's consider liquid motion in column apparatus with chemical reaction between two of the liquid components. If the difference between component concentrations is very big, the chemical reaction order will be one. In the case of liquid circulation the process will be non-stationary. If suppose for velocity and concentration distribution in the column:

$$u = u(r,z), \quad y = v(r,z), \quad c = c(t,r,z), \tag{1}$$

the mathematical description has the form:

$$\begin{aligned}
&\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial z} + v\frac{\partial c}{\partial r} = D\left(\frac{\partial^2 c}{\partial z^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2}\right) - kc,\\
&\frac{\partial u}{\partial z} + \frac{\partial v}{\partial r} + \frac{v}{r} = 0;\\
&t = 0; \quad c = c_0;\\
&r = 0, \quad \frac{\partial c}{\partial r} = 0; \quad r = R, \quad \frac{\partial c}{\partial r} = 0;\\
&z = 0, \quad c(t,r,0) = \bar{c}(t,l), \quad \bar{u}(0)\bar{c}(t,l) = uc - D\frac{\partial c}{\partial z},
\end{aligned} \tag{2}$$

where u and v are velocities components, c-concentration of the reagent (with small concentration), k-chemical reaction rate constant, t-the time, r and z-radial and axial coordinate, D-diffusivity, c_0-initial concentration, $\bar{c}(t,l)$ and

* Tel.: +359 2 70 41 54; fax: +359 2 73 49 36.
E-mail address: chboyadj@bas.bg

0017-9310/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijheatmasstransfer.2005.08.013

Nomenclature

c	concentration [kg/m^3]
D	diffusivity [m^2/s]
k	chemical reaction (interphase mass transfer) rate coefficient [s^{-1}]
r	radial coordinate [m]
R	column radius [m]
t	time [s]
u	axial velocity component [m/s]
v	radial velocity component [m/s]
z	axial coordinate [m]

Greek symbols

ε	hold-up
φ	angle coordinate [rad]
χ	Henry's number

$\bar{u}(0)$-average concentrations and the velocity at the inlet (outlet) of the column, R and l-column radius and height.

The radial non-uniformity of the velocity is the cause for the scale effect (decreasing of the process efficiency with increasing of the column diameter) in the column scale-up. That is why average velocity and concentration for the cross-section's area must be used. It leads to big priority beside experimental data obtaining for the parameters identification, because the measurement of the average concentration is very simple in comparison with the local concentration measurement.

3. Average function values

Let consider cylinder with $R = R(\varphi)$ where φ is an angle in cylindrical coordinates (z, r, φ). The average values of a function $f(z, r, \varphi)$ for the cross section's area is:

$$\bar{f}(z) = \frac{\int\int_{(s)} f(z,r,\varphi)\,\mathrm{d}S}{S}, \tag{3}$$

where

$$S = \int_0^{2\pi} \frac{[R(\varphi)]^2}{2}\,\mathrm{d}\varphi,$$
$$\int\int_{(S)} f(z,r,\varphi)\,\mathrm{d}S = \int_0^{2\pi}\left[\int_0^{R(\varphi)} rf(z,r,\varphi)\,\mathrm{d}r\right]\mathrm{d}\varphi. \tag{4}$$

For a circular cylinder $R = \text{const}$ and from (3, 4) follow:

$$S = \pi R^2, \quad \int\int_{(S)} f(z,r)\,\mathrm{d}S = 2\pi\int_0^R rf(z,r)\,\mathrm{d}r,$$
$$\bar{f}(z) = \frac{2}{R^2}\int_0^R rf(z,r)\,\mathrm{d}r. \tag{5}$$

For the average values of the velocity and concentration for the cross-section's area from (5) follow:

$$\bar{u}(z) = \frac{2}{R^2}\int_0^R ru(r,z)\,\mathrm{d}r, \quad \bar{v}(z) = \frac{2}{R^2}\int_0^R rv(r,z)\,\mathrm{d}r,$$
$$\bar{c}(t,z) = \frac{2}{R^2}\int_0^R rc(t,r,z)\,\mathrm{d}r. \tag{6}$$

The functions (1) may be presented by the help of the average function (6):

$$u(r,z) = \bar{u}(z)\tilde{u}(r,z), \quad v(r,z) = \bar{v}(z)\tilde{v}(r,z),$$
$$c(t,r,z) = \bar{c}(t,z)\tilde{c}(r,z), \tag{7}$$

where

$$\frac{2}{R^2}\int_0^R r\bar{u}(r,z)\,\mathrm{d}r = 1, \quad \frac{2}{R^2}\int_0^R r\tilde{v}(r,z)\,\mathrm{d}r = 1,$$
$$\frac{2}{R^2}\int_0^R r\tilde{c}(r,z)\,\mathrm{d}r = 1. \tag{8}$$

4. Average concentration model

The average concentration model may be obtained if put (7) in (2), multiply with r and to integrate over r in the interval $[0, R]$ the equations in (2). As a result is obtained:

$$\frac{\partial\bar{c}}{\partial t} + \alpha(R,z)\bar{u}\frac{\partial\bar{c}}{\partial z} + \frac{\partial\alpha}{\partial z}\overline{uc} + a\overline{vc} = D\frac{\partial^2\bar{c}}{\partial z^2} - k\bar{c};$$
$$t = 0; \quad \bar{c}(0,z) = c_0; \quad z = 0, \quad \bar{c}(t,0) = \bar{c}(t,l),$$
$$\bar{u}(0)\bar{c}(t,l) = \alpha(R,z)\bar{u}\bar{c} - D\frac{\partial\bar{c}}{\partial z}, \tag{9}$$

where

$$\alpha(R,z) = \frac{2}{R^2}\int_0^R r\tilde{u}\tilde{c}\,\mathrm{d}r, \quad a(R,z) = \frac{2}{R^2}\int_0^R r\tilde{v}\frac{\partial\tilde{c}}{\partial z}\,\mathrm{d}r. \tag{10}$$

The average radial velocity component $\bar{v}$ may be obtained from the continuity equation in (2), if multiply with r^2 and to integrate over r in the interval $[0, R]$:

$$\bar{v} = b\frac{\partial\bar{u}}{\partial z} + \frac{\partial b}{\partial z}\bar{u}, \tag{11}$$

where

$$b = \frac{2}{R^2}\int_0^R r^2\tilde{u}\,\mathrm{d}r. \tag{12}$$

If put (11) in (9), the diffusion model has the form:

$$\frac{\partial\bar{c}}{\partial t} + \alpha(R,z)\bar{u}\frac{\partial\bar{c}}{\partial z} + \beta\overline{uc} + \gamma\bar{c}\frac{\partial\bar{u}}{\partial z} = D\frac{\partial^2\bar{c}}{\partial z^2} - k\bar{c}, \tag{13}$$

where

$$\beta = \frac{\partial\alpha}{\partial z} + a\frac{\partial b}{\partial z}, \quad \gamma = ab. \tag{14}$$

In the model (13) $\bar{u}$ is average velocity of the laminar or turbulent flow in the column, D is diffusivity or turbulent diffusivity (as a result of the small scale pulsations). The model parameters α, β and γ are related with the radial non-uniformity and show the influence of the column radius on the mass transfer kinetics.

The parameter k in the model (13) may be obtained beforehand as a result of the chemical kinetics modeling. If the velocity and concentration radial non-uniformities are independent from the axial coordinate z, the parameters α and γ are related with the column radius only, $\beta = 0$. A constant average velocity in these conditions leads to very simple model ($\frac{\partial \bar{u}}{\partial z} = 0$).

The parameters in the diffusion model (13) show the influence of the scale-up (column radius increase) of the mass transfer kinetics.

The identification of the parameters α, β, γ and D may be made by using experimental data for average velocity and concentration, obtained on the laboratory model. In the cases of scale-up must be obtained $\alpha(R,z)$, $\beta(R,z)$ and $\gamma(R,z)$ only (using real column), because the values of D and k are the same.

5. Interphase mass transfer model

In the cases of interphase mass transfer in gas–liquid or liquid–liquid systems, in the model Eq. (2) must be to introduce convection–diffusion equations for the two phases and the chemical reaction rate must be replaced with interphase mass transfer rate:

$$k(c_1 - \chi c_2), \tag{15}$$

where k is interphase mass transfer coefficient, c_1-concentration of the transferred substance in the gas (liquid) phase, c_2-the concentration of the transferred substance in the liquid phase, χ-Henry's number (liquid–liquid distribution coefficient).

As a result the diffusion model for interphase mass transfer in the column apparatuses has the form:

$$\varepsilon_i u_i \frac{\partial c_i}{\partial z} = \varepsilon_i D_i \left(\frac{\partial^2 c_i}{\partial z^2} + \frac{1}{r}\frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right) - (-1)^{i+1} k(c_i - \chi \cdot c_2), \tag{16}$$

where D_i and $\varepsilon_i (i = 1,2)$ are diffusivities and hold-up coefficients ($\varepsilon_1 + \varepsilon_2 = 1$). The boundary conditions for (16) are similar to the boundary conditions in (2), but a difference is possible depending on the conditions for contact between two phases.

Let consider counter-current gas–liquid bubble column with column height l, where $c_1(z_1, r)$ and $c_2(z_2, r)$ are concentrations of the absorbed substance in the gas and liquid phases ($z_1 = l - z_2$). The boundary conditions of (16) have the form:

$$z_1 = 0, \quad c_1(0,r) = c_1^0,$$
$$\bar{u}_1(0)c_1^0 = u_1(0,r)c_1(0,r) - D_1 \left(\frac{\partial c_1}{\partial z_1} \right)_{z_1=0};$$
$$z_2 = 0, c_2(0,r) = c_2^0,$$
$$\bar{u}_2(0)c_2^0 = u_2(0,r)c_2(0,r) - D_2 \left(\frac{\partial c_2}{\partial z_2} \right)_{z_2=0};$$
$$r = 0, \quad \frac{\partial c_1}{\partial r} = \frac{\partial c_2}{\partial r} = 0; \quad r = R, \quad \frac{\partial c_1}{\partial r} = \frac{\partial c_2}{\partial r} = 0, \tag{17}$$

where $\bar{u}_i(0), i = 1, 2$, are inlet average velocities in gas and liquid phases.

The average concentration model may be obtained on the analogy of (13):

$$\alpha_i(R,z)\bar{u}_i \frac{\partial \bar{c}_i}{\partial z_i} + \beta_i(R,z_i)\bar{u}_i \cdot \bar{c}_i + \gamma_i(R,z_i)\bar{c}_i \frac{\partial \bar{u}_i}{\partial z_i} = D_i \frac{\partial^2 \bar{c}_i}{\partial z_1^2} - (-1)^{i+1} \frac{k}{\varepsilon_i}(\bar{c}_1 - \chi \bar{c}_2), \tag{18}$$

where α_i, β_i and $\gamma_i (i = 1,2)$ are similar to α, β and γ in (10, 14).

The boundary conditions are

$$z_1 = 0, \ \bar{c}_1(0) = c_1^0, \ \bar{u}_1(0)c_1^0 = \alpha_1(R,z_1)\bar{u}_1(0)\bar{c}_1(0) - D_1 \left(\frac{\partial \bar{c}_1}{\partial z_1} \right)_{z_1=0};$$
$$z_2 = 0, \ \bar{c}_2(0) = c_2^0, \ \bar{u}_2(0)c_2^0 = \alpha_2(R,z_2)\bar{u}_2(0)\bar{c}_2(0) - D_2 \left(\frac{\partial \bar{c}_2}{\partial z_2} \right)_{z_2=0}. \tag{19}$$

6. Conclusion

The results obtained show that the diffusion models in column apparatuses permit to change the velocity and concentration radial distributions with the averages velocities and concentration's for the cross-section's area of the column.

These new models permit to identify the model parameters using a hierarchical approach. As a first step must be obtained chemical reaction (or mass transfer) rate constant. The next step is identification of the parameters α, β, γ and D, using experimental data, obtained with real liquids. The scale-up is a specification of the parameter values α, β and γ for the real apparatus. As a result the mathematical model may be used for the simulation of real column apparatus processes.

Acknowledgements

This work was completed with the financial support of the National Science Fund, Ministry of Education and Science, Republic of Bulgaria, under Contract No. TH-1506/2005.

References

[1] Chr. Boyadjiev, Fundamentals of Modeling and Simulation in Chemical Engineering and Technology, Bulg. Acad. Sci., Sofia, (1993).
[2] L. Boyadjiev, Chr. Boyadjiev, Etude de la Dispersion Longitudinal dans les Colonnes d'Extraction Liquid–Liquid, Chem. Eng. J. 6 (1973) 107–110.

[3] W.O. Deckwer, A. Schumpe, Improved tools for bubble column reactor design and scale-up, Chem. Eng. Sci. 48 (1993) 889.
[4] B.T. Frohlich, T.A. Webster, M.M. Ataai, M.L. Sculer, Fhotobioreactors, models for interaction of light intensity, reactor design and algae physiology, Biotechnol. Bioeng. Symp. 13 (1983) 331–350.
[5] J.H.J. Kluytmans, B.G.M. van Wachem, B.F.M. Kuster, J.C. Schowten, Design of an Industrial size airlift loop redox cycle (ALRC) reactor for catalytic alcohol oxidation and catalyst reactivation, Ind. Eng. Chem. Res. 42 (2003) 4174–4185.
[6] Al.W.A. Masry, A.E. Abasaeed, On the scale-up of external loop airlift reactors. Newtonian systems, Chem. Eng. Sci. 53 (1998) 4085.
[7] R.S. Oey, R.F. Mudde, L.M. Portela, H.E.A. van den Akker, Simulation of a slurry airlift using two-fluid model, Chem. Eng. Sci. 56 (2001) 673.
[8] Scale-up in Chemical Technology, ed. A.M. Rozen, Chemistry, Moscow,1980.