CERTAIN PROBLEMS WITH THE APPLICATION OF STOCHASTIC DIFFUSION PROCESSES FOR THE DESCRIPTION OF CHEMICAL ENGINEERING PHENOMENA. STOCHASTIC MODEL OF NON-ISOTHERMAL FLOW CHEMICAL REACTOR

Vladimir KUDRNA[a], Libor VEJMOLA[b] and Pavel HASAL[a]

[a] *Department of Chemical Engineering,*
Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic
[b] *OIS SPOLANA Inc., 277 11 Neratovice, Czech Republic*

Received December 22, 1994
Accepted June 4, 1995

Recently developed stochastic model of a one-dimensional flow-through chemical reactor is extended in this paper also to the non-isothermal case. The model enables the evaluation of concentration and temperature profiles along the reactor. The results are compared with the commonly used one-dimensional dispersion model with Danckwerts' boundary conditions. The stochastic model also enables to evaluate a value of the segregation index.

Key words: Non-isothermal flow reactor; Stochastic model; Segregation index.

A stochastic model of a one-dimensional flow-through mixer[1] and of an isothermal chemical reactor[2] has been developed recently using an idea of stochastic motion of molecules of an active (reacting) component transported by means of carrier (inert) fluid flow. The model was denoted[1,2] as a dynamic one as it considers also forces acting on the moving molecules. The term dynamic model will be therefore used also throughout this paper. Linear dependence of the forces on the molecule velocity was assumed. This assumption, together with certain considerations concerning molecule reverberation at system boundaries, yielded two-parameter model enabling description of all flow regimes in continuous mixers and chemical reactors commonly considered in chemical engineering. The model was compared with the one-dimensional dispersion model with Danckwerts' boundary conditions[3]. The dynamic stochastic model was recognized to be more correct from the theoretical point of view as it does not make use of ambiguous Danckwerts' assumption on zero value of concentration derivative at the reactor outlet. However, the comparison of the component conversion values predicted by the two models under isothermal conditions revealed negligible differences with respect to the common engineering accuracy requirements. In this paper, the dynamic model is extended to the case of non-isothermal reactor.

THEORETICAL

Let us consider (as in the case of the isothermal reactor model[2]) the one-dimensional continuous flow reactor of length L and cross-sectional area S (cf. Fig. 1 in ref.[2]). Cross-sectional areas of both inlet and outlet openings are of the same size S_0 which can be either equal to S (a so-called open system) or less than S (a closed system). We shall further make use of all the assumptions adopted in refs[1,2] except of the assumption of isothermal process. The assumptions imply the velocities of molecules in the system to be randomly distributed and determined both by the deterministic and stochastic forces[1]. The velocity v distribution is expressed by the probability density function $f_v(v)$ (cf. Eq. (*9*) in ref.[1])

$$f_v(v) = \frac{1}{e\Gamma(b)} \left(\frac{e}{v} \right)^{b+1} \exp\left(-e/v\right) \quad . \tag{1}$$

Parameters e and b characterize the deterministic and stochastic forces acting on the fluid molecules[1,2]. Another assumption was formulated (cf. Eqs (*4*) in ref.[2]) concerning the probability of molecule escape from the system at the outlet opening

$$p = \frac{w}{w+v} \quad , \tag{2}$$

where parameter w describes geometrical configuration of the system (for an open system, w grows to infinity, for an ideal mixer, w approaches zero).

Summing the equations describing the motion and the chemical reaction of the molecules positioned within reactor cross section at distance x measured from the reactor inlet yields the first-order ordinary differential equation (Eq. (*8*) in ref.[2])

$$v \frac{\mathrm{d}\rho_\mathrm{A}}{\mathrm{d}x} = \Phi \frac{[\rho_\mathrm{A}^2 - \rho_\mathrm{AK}^2 (1-g^2)]^{1/2}}{\rho_\mathrm{A}} \quad , \tag{3}$$

where $\rho_\mathrm{A} = \rho_\mathrm{A}(x,v)$ denotes the concentration of reacting component A at position with coordinate x and velocity v. Symbol $\Phi = \Phi(\rho_\mathrm{A},T)$ denotes the reaction rate which generally depends on the reacting component concentration and temperature T (in previous paper[2], the temperature dependence was not considered). The quantity g is defined by the relation following from Eqs (*3*) and (*4*) in ref.[2]

$$g \equiv g(v) = \frac{p}{2-p} = \frac{w}{w+2v} \quad . \tag{4}$$

Expression (1 – g^2) in the numerator of fraction on the right-hand side of Eq. (*3*) characterizes circulation of the fluid in the system. In case of an open system, Eq. (*3*) transforms to usual relation for a tube reactor with fluid plug-flow. When $g < 1$, the value of the reacting component concentration at reactor outlet occurs on the right-hand side of Eq. (*3*). Therefore an iterative procedure must be used to solve this equation. In the isothermal case[2], Eq. (*3*) can be simplified, and the solution may be found in an integral form. For simpler forms of the reaction rate term Φ, the integration can be performed analytically with subsequent iterations. In case of non-isothermal process, this approach is not applicable, and boundary conditions must be formulated in an explicit way (cf. Eq. (*A14*) in ref.[2])

$$\lim_{x\to 0+} \rho_A = \left[g^2\rho_{A0}^2 + (1-g^2)\rho_{AK}^2 \right]^{1/2} \quad . \tag{5}$$

Obviously, the concentration of the reacting component averaged over the reactor cross section just behind the reactor inlet equals to the inlet concentration ρ_{A0} only in an open mixer (reactor). The concentration averaged with respect to all possible molecule velocities (cf. Eq. (*10*) in ref.[2]) is

$$\overline{\rho}_A(x) = \int_0^\infty \rho_A(x,v)\, f_v(v)\, dv \quad . \tag{6}$$

Equations describing the heat transfer in the reactor can be formulated in a way formally identical to that used in refs[1,2]. However, less lucid idea of random motion of energy quanta is to be postulated in comparison with the more simple case of chemical reaction. This idea was adopted recently[4] in stochastic modelling of heat conduction.

Assuming that the density ρ and heat capacity c_p of the reaction mixture do not depend on temperature, the differential enthalpy balance of the reactor can be written in the form

$$v\,\frac{dT}{dx} = -\frac{1}{T}\left\{\frac{\Delta H}{\rho c_p}\,\Phi + \frac{kP}{\rho c_p S}\,(T - T_m)\right\}\left\{[T^2 - T_K^2(1-g^2)]^{1/2}\right\} \quad . \tag{7}$$

Boundary condition for temperature can be written in a similar way as in Eq. (*5*), namely

$$\lim_{x\to 0+} T = \left[g^2 T_0 + (1-g^2) T_K \right]^{1/2} \quad . \tag{8}$$

System of Eqs (*3*) and (*7*) along with boundary conditions (*5*) and (*8*) has to be solved by an iterative procedure due to the presence of outlet concentration and temperature values on right-hand sides of these equations. Averaged concentration at position x is evaluated according to Eq. (*6*), and averaged temperature at the same location is given by the relation

$$\overline{T}(x) = \int_0^\infty T(x,v) f_v(v)\, \mathrm{d}v \ . \tag{9}$$

RESULTS AND DISCUSSION

Model equations formulated in the previous section enable to evaluate the longitudinal concentration and temperature profiles in the reactor for given kinetic term Φ. Computations presented in this paper were performed for the case of the adiabatic reactor (i.e., for $k = 0$ in Eq. (*7*)) and the results were compared with data obtained from the one-dimensional dispersion model

$$D_\rho \frac{\mathrm{d}^2\overline{\rho}_\mathrm{A}}{\mathrm{d}x^2} - \overline{v}\frac{\mathrm{d}\overline{\rho}_\mathrm{A}}{\mathrm{d}x} + \Phi(\overline{\rho}_\mathrm{A},\overline{T}) = 0 \ ,$$

$$D_\mathrm{T} \frac{\mathrm{d}^2\overline{T}}{\mathrm{d}x^2} - \overline{v}\frac{\mathrm{d}\overline{T}}{\mathrm{d}x} + A\Phi(\overline{\rho}_\mathrm{A},\overline{T}) = 0 \ , \tag{10}$$

where $\overline{v}$ is the mean fluid velocity in the reactor, D_ρ and D_T are the dispersion coefficients for mass and temperature, and $A = \Delta H/(\rho c_p)$. Danckwerts' boundary conditions were used

$$\overline{v}\rho_{\mathrm{A}0} = \lim_{x\to 0+}\left(\overline{v}\,\overline{\rho}_\mathrm{A} - D_\rho \frac{\mathrm{d}\overline{\rho}_\mathrm{A}}{\mathrm{d}x}\right) ,$$

$$\lim_{x\to L-}\frac{\mathrm{d}\overline{\rho}_\mathrm{A}}{\mathrm{d}x} = 0 \ ,$$

$$\overline{v}T_0 = \lim_{x\to 0+}\left(\overline{v}\overline{T} - D_\mathrm{T}\frac{\mathrm{d}\overline{T}}{\mathrm{d}x}\right) ,$$

$$\lim_{x\to L-}\frac{\mathrm{d}\overline{T}}{\mathrm{d}x} = 0 \ . \tag{11}$$

Identical values of dispersion coefficients D_ρ and D_T were considered in computations, i.e., molecular diffusion and heat conduction were neglected with respect to the convective transport. In following we put $D_\rho = D_T = D$.

Hydrolysis of acetanhydride was used as a model chemical reaction:

$$(CH_3CO)_2O + H_2O = 2\ CH_3COOH \qquad (12)$$

which can be supposed to be an irreversible first-order reaction. The temperature dependence of the reaction rate was approximated by the Arrhenius equation

$$\Phi(\rho_A,T) = \rho_A k_\infty \exp{(-E/RT)}\ . \qquad (13)$$

The following set of model parameter values was used[5]: $k_\infty = 39.67 \,.\, 10^4\ s^{-1}$, $E = 46.7 \,.\, 10^3$ J mol^{-1}, $c_p = 3\ 800$ J kg^{-1} K^{-1}, $\rho = 1\ 050$ kg m^{-3}, $\Delta H = -2.13 \,.\, 10^4$ J kg^{-1}, $\rho_{A0} = 22.03$ kg m^{-3}, $T_0 = 288$ K. Mean residence time of the liquid in the reactor was 750 s. Dimensionless longitudinal coordinate x^* and dimensionless liquid velocity v^* were introduced (cf. Eqs (*14*) in ref.[2])

$$x^* = x/L\ ,$$
$$v^* = b(1 + 2\Omega)\frac{v}{e}\ . \qquad (14)$$

Earlier introduced[1] quantities b and Ω are model parameters also in the non-isothermal case. Parameter Ω quantifies intensity of liquid circulation within the reactor. Reciprocal value of parameter b can be interpreted as a measure of randomness of liquid molecule velocities. The only single dimensionless variable – Peclet number $Pe = \overline{v}L/D$ – is parameter of the dispersion model. Recently derived relation[2] $\Omega = 0.368/Pe$ at constant value of parameter $b = 8.99$ was used for comparison of both the models.

Conversion of the reacting component is defined by the relation

$$Y(x^*) = 1 - \frac{\overline{\rho}_A(x^*L)}{\rho_{A0}}\ , \qquad (15)$$

and dimensionless temperature of the reaction mixture by the relation

$$\Theta(x^*) = \frac{\overline{T}(x^*L)}{T_0} - 1\ . \qquad (16)$$

The set of differential equations (*3*) and (*7*) together with corresponding boundary conditions was solved numerically: Adams–Bashforth method[6] was used with spatial integration step size 0.001L. The Newton method was applied to the iterative evaluation of the outlet conversion and temperature. Integrals in Eqs (*6*) and (*9*) were, in general case, evaluated numerically using 2 000 equidistant values of velocity v. The probability density function, $f_v(v)$, approaches Dirac's δ-function for $b = 8.99$ (i.e., the value used for comparison of the proposed model to the dispersion model). Therefore, just a single value of the dimensionless velocity – the mean value – was used for the evaluation of conversion and dimensionless temperature. It can be proved easily (using Eq. (*16*) in ref.[2]) that in this case the following relation holds for the mean value of the dimensionless velocity

$$\bar{v}^* = \lim_{b\to\infty} \frac{(2\Omega + 1)b}{b - 1} = 2\Omega + 1 \quad . \tag{17}$$

Results of computations are depicted in Figs 1–4. Figures 1*a*, 2*a*, and 3*a* show spatial profiles of reacting component A conversion, Figs 1*b*, 2*b*, and 3*b* show profiles of dimensionless temperature. Figures 2 and 3 are plotted with high resolution to enhance differences between the models. Figure 2 shows also the conversion and temperature data obtained with the continuous stirred tank reactor (CSTR) model. Figure 3 shows also conversion and temperature profiles in the plug-flow reactor (PFR) model. First

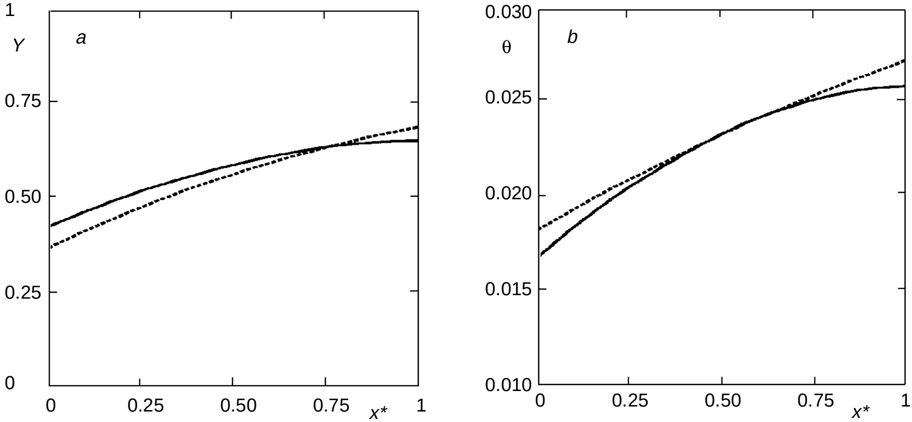

FIG. 1

Conversion (*a*) and dimensionless temperature (*b*) profiles in reactor. General flow regime (*Pe* = 1): ——— Disperison model with Danckwerts' boundary conditions (DM), — — — stochastic model (SM) spatial derivatives of the conversion and dimensionless temperature are plotted in Fig. 4 as functions of the reactor longitudinal coordinate and both models discussed in this paper are compared with the PFR model.

Figure 5 also shows results for the case close to macromixing regime. Full circles indicate the outlet conversion and dimensionless reaction temperature for the macro-

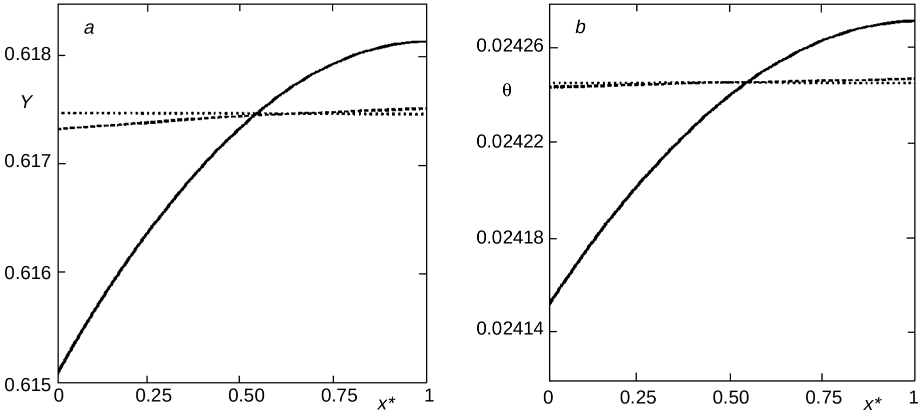

FIG. 2

Conversion (*a*) and dimensionless temperature (*b*) profiles in reactor. Flow regime close to ideal mixing with microflow (*Pe* = 0.01): ——— Dispersion model with Danckwerts' boundary conditions (DM), — — — stochastic model (SM), – – – – ideal mixer with microflow (CSTR)

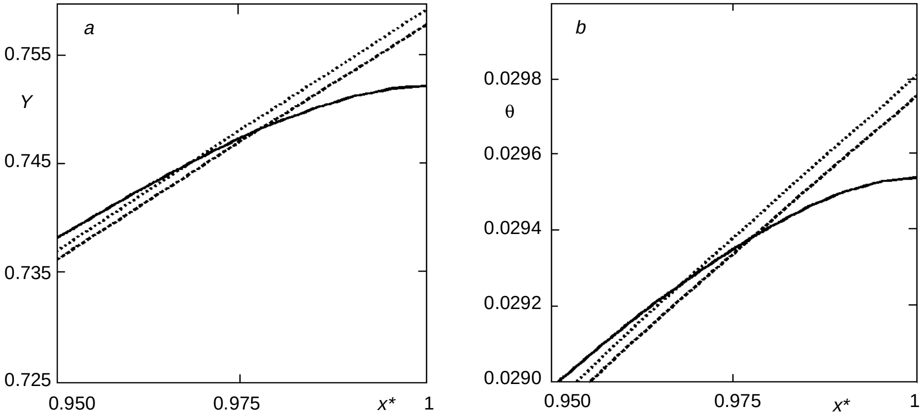

FIG. 3

Conversion (*a*) and dimensionless temperature (*b*) profiles in reactor. Flow regime close to plug flow (*Pe* = 50): ——— Dispersion model with Danckwerts' boundary conditions (DM), — — — stochastic model (SM), – – – – plug-flow reactor (PFR) mixing regime obtained by a common procedure, i.e., by evaluating the time course of conversion and temperature in a batch reactor with subsequent averaging according to the exponential residence time distribution function

$$\bar{\rho}_A = \frac{1}{\bar{t}} \int_0^\infty \rho_A(t) \exp(-t/\bar{t}) \quad . \qquad [Y = 1 - \frac{\bar{\rho}_A}{\rho_{A0}}] \tag{18}$$

Analogous equation holds for dimensionless reaction temperature.

Simulations with the adiabatic reactor model confirmed the earlier made conclusions for an isothermal reactor[2]. First of all, it is the conclusion that the differences between the compared models are negligible from the point of view of the usual engineering accuracy requirements. It is well documented in Fig. 5 in ref.[2] where the outlet conversion value is plotted against the Peclet number. This conclusion is valid not only for the outlet conversion values, but also for the global conversion and temperature profiles within the reactor as documented in Fig. 1 in this paper. For both low and large values of the Peclet number ($Pe \le 0.1$ or $Pe \ge 10$), the differences between the models are even smaller. Despite this fact, the conclusion (cf. ref.[2]) stating that the proposed dynamic model is much more correct in the sense, that it yields the conversion and temperature values which are in excellent agreement with the results of basic models (plug-flow model and ideal mixer with liquid micromixing), remains valid. This conclusion is confirmed in Figs 2 and 3 which are plotted with high resolution. The correctness of the dynamic model is also documented in Fig. 4 where profiles of the first derivatives of the conversion and temperature are plotted. The profiles from the dy-

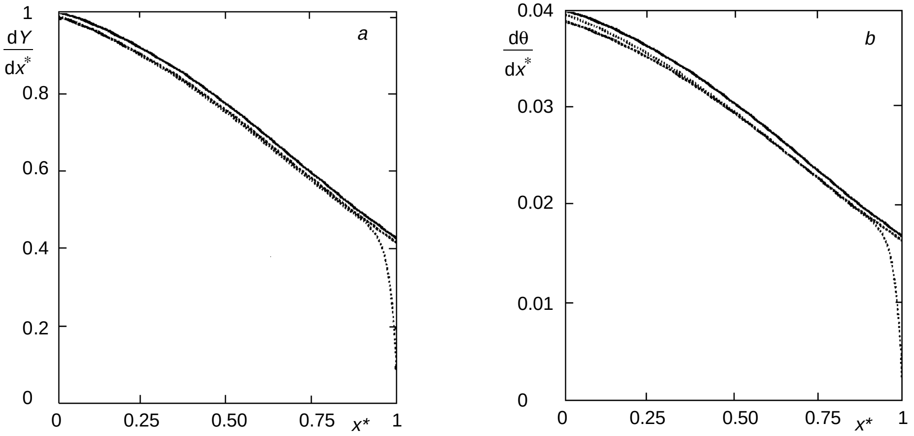

FIG. 4

Spatial profile of derivative of conversion (*a*) and of dimensionless temperature (*b*). Flow regime close to plug flow ($Pe = 50$): – – – – Dispersion model with Danckwerts' boundary conditions (DM), — — — stochastic model (SM), ——— plug-flow reactor (PFR) namic model are close to those generated by the plug-flow model; the profiles from the dispersion model, however, decline substantially at the outlet of the reactor as the controversary Danckwerts' boundary condition must be fulfilled. This remarkable declination of the conversion and temperature derivatives at the outlet does not influence markedly the conversion and temperature profiles within the reactor itself.

Range of applicability of Danckwerts' boundary condition is analogous to the applicability of the condition of an absorbing boundary used in theory of stochastic processes and analyzed, e.g., by Zeldovich and Myshkis[7] who stated that the zero concentration value usually supposed at the absorbing boundary (see, e.g. ref.[8]) cannot be correct at zero drift velocity (in our case, at zero mean velocity of the liquid in the reactor): If the velocity at the boundary was zero, no particles can be absorbed there. The authors concluded that the application of this boundary yields correct results in the whole system except of a close vicinity of the absorbing boundary. This fact must be kept in mind. Figure 4 documents that the stochastic model proposed here eliminates this problem.

We have already concluded[1,2] that the dynamic stochastic model enables, unlike the dispersion model, the description of flow pattern in the regime of fluid macroflow. This case is documented in Fig. 5 for parameter values $\Omega = 0$ and $b = 1.01$. The values of the outlet conversion and dimensionless temperature for the dynamic model almost do not differ from the values obtained by conventional procedure according to Eq. (*18*) (full circles in Fig. 5).

Flow regimes between complete microflow and macromixing are qualitatively characterized by segregation index J introduced by Danckwerts[9] and Zwietering[10] by the relation

$$J = \frac{Var(\alpha_p)}{Var(\alpha)} \quad , \qquad (19)$$

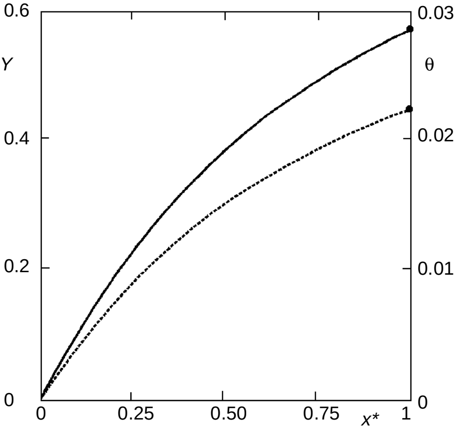

FIG. 5
Conversion and dimensionless temperature profiles in reactor. Flow regime close to ideal mixing with macroflow (Ω = 0.0, b = 1.01): ——— Conversion Y, — — — dimensionless temperature θ

i.e., as the ratio of particle age variance between points[10] to particle age variance for the whole system. The dynamic model enables the evaluation of the segregation index as a function of model parameters (see Appendix). Since the values of both parameter Ω and parameter *b* may grow to infinity, the modified parameters (taking finite values only) were defined

$$a \equiv \frac{1}{b} \ ,$$
$$z \equiv \frac{2\Omega}{2\Omega + 1} \ . \qquad (20)$$

The segregation index as a function of these parameters is depicted in Fig. 6. The value of segregation index is influenced mainly by the value of parameter *z* characterizing intensity of liquid circulation in the reactor. In agreement with expectations (cf., e.g., Rippin[11]) the value of segregation index decreases with increasing circulation intensity. The randomness of liquid molecule velocities (increases with increasing value of parameter *a*) has substantially less effect on the segregation index value; a more pronounced effect is detectable at medium circulation intensity. At boundary values of parameter *z*, the parameter *a* has negligible effects. This observation agrees well with the known fact[9,10] that the segregation index value cannot differentiate among flow regimes close to the plug-flow and the macroflow with the exponential residence time distribution. Therefore, the only single parameter (e.g., considered segregation index) is not sufficient for distinguishing among flow regimes. The two-parameter model proposed in this paper enables such a differentiation as the above-mentioned distinct flow regimes are characterized by distinct pairs of parameters *b* and Ω values.

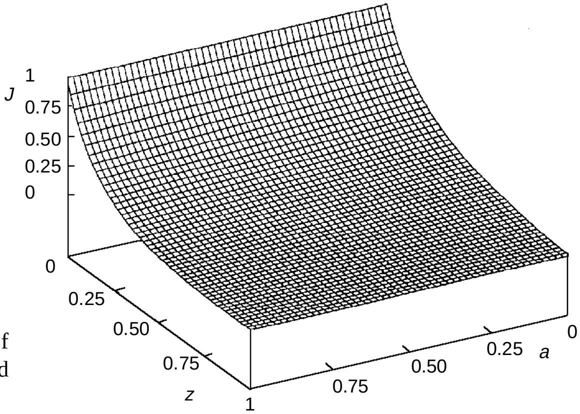

FIG. 6
Segregation index *J* as function of modified intensity of circulation *z* and parameter *a* (cf. Eq. (*20*))

CONCLUSIONS

Theoretical considerations and numerical simulations presented in this paper can be summarized into the following conclusions:

The earlier proposed stochastic model of continuous flow mixer and chemical reactor was extended to the non-isothermal case. Analysis of the model confirmed that also in this case the model is capable of describing the whole range of liquid flow regimes usually considered in chemical engineering. At limiting values of parameters, the predictions of the stochastic model practically do not differ from the predictions of basic models used in chemical engineering, i.e., the model of plug-flow and the model of an ideal continuous flow mixer both fluid micro- and macromixing.

It was shown that results of the dynamic model of an adiabatic reactor do not nearly differ from results of the dispersion model with Danckwerts' boundary conditions. The applicability of Danckwerts' condition at reactor outlet was discussed and the proposed stochastic model was proved to be more correct with respect to the boundary condition formulation. The proposed model also enables the evaluation of the segregation index of liquid within reactor.

APPENDIX

Relation of Segregation Index to Parameters of Stochastic Model

Segregation index J is defined by Eq. (*19*) as the ratio of particle age variance between points[9,10] and in the whole flow system. Denominator of this fraction

$$Var(\alpha) = \langle \alpha^2 \rangle - \langle \alpha \rangle^2 \tag{A1}$$

can easily be evaluated as the difference of the second moment of particle age probability density function $I(\alpha)$ for whole system and square of the first moment

$$\langle \alpha^i \rangle = \int_0^\infty \alpha^i I(\alpha)\, \mathrm{d}\alpha \ . \tag{A2}$$

Zwietering[10] derived the simple relation between function $I(\alpha)$ and probability density function $f_t(t)$ of residence time in the system

$$I(\alpha) = \frac{1}{\langle t \rangle} \int_\alpha^\infty f_t(t)\, \mathrm{d}t \ , \tag{A3}$$

where $\langle t\rangle$ is the mean residence time of particles in system.

We shall demonstrate that for the one-dimensional model with random distribution of particle velocities proposed in this paper, both the numerator and the denominator of the fraction in Eq. (*19*) can be evaluated after a minor alteration of the quantity α_p definition compared with original Danckwerts' definition[9]: we shall consider α_p to be particle age at given position x and at given velocity v.

First, we shall write a relation for the probability density function of residence time $f_t(t)$ for the presented model (cf. Eqs (*23*) and (*14*) in ref.[1]):

$$f_t(t) = -\frac{\partial}{\partial t}\int_0^L\int_0^\infty f_v(v) f_c(x|v;t)\,\mathrm{d}v\,\mathrm{d}x \quad , \tag{A4}$$

where the integrated function is a product of solutions of differential equations (*8*) and (*10*) in ref.[1] with boundary conditions given by Eq. (*17*) in the same reference. After inserting into Eq. (*A3*) we obtain the relation

$$I(\alpha) = \int_0^L\int_0^\infty \left[\frac{1}{\langle t\rangle} f_v(v) f_c(x|v;\alpha)\right]\mathrm{d}v\,\mathrm{d}x \tag{A5}$$

assuming that for increasing values of age α, function $f_c()$ converges to zero. For the sake of brevity we shall denote

$$f_\alpha(r,\alpha) \equiv \frac{1}{\langle t\rangle} f_v(v) f_c(x|v;\alpha) \quad . \tag{A6}$$

Further we shall formally denote, with symbol $\boldsymbol{r} \equiv (x,v)$, a vector of the one-dimensional position and velocity in configuration space of these quantities. Simplification of notation of double integral is further introduced as

$$\int_0^L\int_0^\infty \mathrm{d}v\,\mathrm{d}x \equiv \int_{(\Delta)} \mathrm{d}\boldsymbol{r} \quad . \tag{A7}$$

Function $f_a(\boldsymbol{r},\alpha)$ is a simultaneous probability density for particle age α, particle position x, and particle velocity v. Integration of this function with respect to particle age α yields the marginal probability density function for particle velocity and position which characterizes flow in the system

$$\Psi(\boldsymbol{r}) = \int_0^\infty f_a(\boldsymbol{r},\alpha)\,\mathrm{d}\alpha \quad . \tag{A8}$$

Further we define the conditional probability density function for age of particle being at position x and moving with velocity v, i.e., particle being at point $\boldsymbol{r}$ of the configuration space

$$f_{a\boldsymbol{r}}(\alpha|\boldsymbol{r}) = \frac{f_a(\boldsymbol{r},\alpha)}{\Psi(\boldsymbol{r})} \quad . \tag{A9}$$

Function $f_{a\boldsymbol{r}}(\alpha|\boldsymbol{r})$ enables to find the relation for particle age at location x and velocity v

$$\alpha_{\mathrm{p}}(\boldsymbol{r}) = \int_0^\infty \alpha f_{a\boldsymbol{r}}(\alpha|\boldsymbol{r})\, \mathrm{d}\alpha \tag{A10}$$

and further all i-th moments of the age over the whole configuration space

$$\langle\alpha_{\mathrm{p}}\rangle^i = \int_{(\Delta)} \alpha_{\mathrm{p}}^i(\boldsymbol{r})\Psi(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} \quad . \tag{A11}$$

From comparison of Eq. (*A2*) with Eq. (*A10*), considering also Eq. (*A6*), it is obvious that the above-defined first moments of particle age at points and in the whole system are identical unlike the second moments. We shall use Eqs (*A2*) and (*A11*) for evaluating the segregation index. Similarly as in the preceding paper[1], we shall use the Laplace transformation of pertinent functions $f()$, and their Laplace transforms will be denoted by symbols $g()$, i.e., $g(s) = \hat{L}[f(\alpha)]$, where $\hat{L}$ is the Laplace transformation operator. The moments of pertaining functions can then be easily evaluated using the well-known relation (see, e.g., Appendix in ref.[12])

$$\langle\alpha^i\rangle = (-1)^i \frac{\mathrm{d}^i g(s)}{\mathrm{d}s^i}\Big|_{s=0} \equiv (-1)^i g^{(i)}(0) \quad . \tag{A12}$$

Required moments are given by the equations

$$\langle\alpha\rangle = \langle\alpha_{\mathrm{p}}\rangle = -\int_{(\Delta)} g_a^{(1)}(\boldsymbol{r},0)\, \mathrm{d}\boldsymbol{r} \quad , \tag{A13}$$

$$\langle\alpha^2\rangle = \int_{(\Delta)} g_a^{(2)}(\boldsymbol{r},0)\, \mathrm{d}\boldsymbol{r} \quad , \tag{A14}$$

$$\langle\alpha_{\mathrm{p}}^2\rangle = \int_{(\Delta)} [g_{a\boldsymbol{r}}^{(1)}(\boldsymbol{r},0)]^2\, \Psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \int_{(\Delta)} \frac{1}{\Psi(\boldsymbol{r})}\, [g_a^{(1)}(\boldsymbol{r},0)]^2\, \mathrm{d}\boldsymbol{r} \quad . \tag{A15}$$

Laplace transform of Eq. (*A10*) and of its first derivative (*A13*) was used in Eq. (*A15*). Laplace transform of Eq. (*A6*) can then be written as

$$g_a(\mathbf{r},s) = \frac{1}{\langle t\rangle} f_v(v) g_c(x,v,s) \ , \tag{A16}$$

where function $f_v(v)$ is defined by Eq. (*1*) in this paper and function $g_c()$ by relation (*A2*) in ref.[1]

$$g_c(x,v,s) = \frac{1}{v}\left[\exp(-sx/v) + \frac{2\cosh(sx/v)Q}{1-Q}\right] \ , \tag{A17}$$

where $Q = v/[(v + w)\exp(-2sL/v)]$. Mean residence time according to the proposed model is (see Eqs (*30*, (*29*) and (*15*) in ref.[1])

$$\langle t\rangle = L\left(\frac{b}{e} + 2w\right) . \tag{A18}$$

After performing the operations in integrals of Eqs (*A13*)–(*A15*) and subsequent integration within limits $[0,L]$, the relations for required moments result:

$$\langle\alpha\rangle = \langle\alpha_\mathrm{p}\rangle = \frac{1}{\langle t\rangle}\int_0^\infty f_v(v)(L/v)^2(\frac{1}{2} + h^2 - 1)\,\mathrm{d}v \tag{A19}$$

$$\langle\alpha^2\rangle = \frac{1}{\langle t\rangle}\int_0^\infty f_v(v)(L/v)^3\left[\frac{h}{3} + 2h(h^2-1)\right]\mathrm{d}v \tag{A20}$$

$$\langle\alpha_\mathrm{p}^2\rangle = \frac{1}{\langle t\rangle}\int_0^\infty f_v(v)(L/v)^3\left[\frac{1}{3h} + h(h^2-1)\right]\mathrm{d}v \ , \tag{A21}$$

where $h \equiv 2v/w + 1$.

Integrations with respect to velocity v in foregoing equations are somewhat difficult as Euler gamma-functions (both complete and incomplete ones, see, e.g., ref.[13]). After pertinent rearrangements and with use of the dimensionless parameters b and Ω (cf. Eq. (*14*)), the segregation index can be evaluated. Parameters b and Ω were transformed according to Eq. (*20*). Required moments in dimensionless form are

$$\frac{\langle\alpha\rangle}{\langle t\rangle} = \frac{1}{2}(2z_{20} + 4z_{11} + z_{02}a_1) \tag{A22}$$

$$\frac{\langle \alpha^2 \rangle}{\langle t \rangle^2} = \frac{1}{3}(6z_{30} + 18z_{21} + 13z_{12}a_1 + z_{03}a_1a_2) \qquad (A23)$$

$$\frac{\langle \alpha_p^2 \rangle}{\langle t \rangle^2} = \frac{1}{3}[z_{30}(2 + I) + 10z_{21} + 5z_{12}a_1 + z_{03}a_1a_2] \ , \qquad (A24)$$

where

$$I \equiv c^{1/a} \exp{(c)}\Gamma(1 - 1/a;c)$$

$$c \equiv \frac{z}{a(1 - z)}$$

$$z_{ij} \equiv z^i(1 - z)^j$$

$$a_i \equiv a + i \qquad (A25)$$

and $\Gamma(x;y)$ denotes the incomplete gamma-function. By inserting Eqs (*A22*)–(*A25*) into Eq. (*A1*) and then into Eq. (*19*), the required segregation index value is obtained. The values of segregation index for limiting values of parameters a and z can be found after applying l'Hospital's rule

$$\lim_{z\to0} I = \lim_{z\to1} I = \lim_{a\to0} I = z; \quad \lim_{a\to1} I = c \exp{(c)}\, Ei(c) \ , \qquad (A26)$$

where $Ei(x)$ is the integral exponential function[13] and after inserting into Eq. (*19*), the limit values of segregation index are obtained

$$\lim_{z\to0} J = 1; \quad \lim_{z\to1} J = 0 \ . \qquad (A27)$$

SYMBOLS

a	modified model parameter defined by Eq. (*20*)
b	dimensionless model parameter
c_p	specific heat capacity, J kg^{-1} K^{-1}
D	dispersion coefficient, m^2 s^{-1}
E	activation energy, J mol^{-1}
e	parameter in Eq. (*1*), m s^{-1}
f_v	probability density function for particle velocity, s m^{-1}

g	parameter defined by Eq. (*4*)
ΔH	reaction enthalpy, J kg^{-1}
J	segregation index
k	heat transfer coefficient, W m^{-2} K^{-1}
k_∞	frequency factor, s^{-1}
L	length of reactor, m
P	reactor perimeter, m
$Pe = \bar{v}L/D$	Peclet number
p	probability of particle escape
R	universal gas constant, J mol^{-1} K^{-1}
S	cross-sectional area of reactor, m^2
T	temperature, K
T_m	temperature of environment, K
t	time, s
v	particle (molecule) velocity, m s^{-1}
v^*	dimensionless velocity defined by Eq. (*14*)
w	constant characterizing geometry of system, m s^{-1}
x	longitudinal coordinate, m
x^*	dimensionless coordinate defined by Eq. (*14*)
Y	conversion of component A defined by Eq. (*15*)
z	modified model parameter defined by Eq. (*20*)
α	particle age in system, s
α_p	particle age at point, s
Θ	dimensionless temperature defined by Eq. (*16*)
ρ_A	concentration of reacting component, kg m^{-3}
ρ	density, kg m^{-3}
Φ	reaction rate, kg m^{-3} s^{-1}
Γ	gamma-function
Ω	liquid circulation intensity (model parameter)

Other symbols

u_K	related to outlet value of quantity u
u_0	related to inlet value of quantity u
$\bar{u}$	mean value of quantity u

REFERENCES

1. Kudrna V., Vejmola L., Hasal P.: Collect. Czech. Chem. Commun. *59*, 1551 (1994).
2. Kudrna V., Vejmola L., Hasal P.: Collect. Czech. Chem. Commun. *59*, 1772 (1994).
3. Danckwerts P. V.: Chem. Eng. Sci. *2*, 1 (1953).
4. Laso M.: AIChE J. *40*, 1297 (1994).
5. Ilavsky J., Valtyni J., Brunovska A., Surovy J.: *Aplikovana chemicka kinetika a teoria reaktorov*. Alfa, Bratislava 1990.
6. Kubicek M.: *Numericke algoritmy reseni chemicko-inzenyrskych uloh*. SNTL, Praha 1983.
7. Zeldovich Ya. B., Myshkis A. D.: *Elementy matematicheskoi fiziki*. Nauka, Moskva 1973.
8. Gardiner C. W.: *Handbook of Stochastic Methods for Physics, Chemistry and Natural Sciences*. Springer, Berlin 1985.
9. Danckwerts P. V.: Chem. Eng. Sci. *8*, 93 (1958).

10. Zwietering T. N.: Chem. Eng. Sci. *11*, 1 (1959).
11. Rippin D. W. T.: Ind. Eng. Chem., Fundam. *6*, 488 (1967).
12. Wen C. Y., Fan L. T.: *Models for Flow Systems and Chemical Reactors*. Dekker, New York 1975.
13. Prudnikov A. P., Brytchkov Yu. A., Maritchev O. I.: *Integraly i ryady. Spetsialnye funktsii*. Nauka, Moskva 1983.