# CERTAIN PROBLEMS WITH THE APPLICATION OF STOCHASTIC DIFFUSION PROCESSES FOR THE DESCRIPTION OF CHEMICAL ENGINEERING PHENOMENA. DYNAMIC STOCHASTIC MODEL OF FLOW MIXER

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The one-dimensional stochastic diffusion model of a continuous flow mixer is proposed incorporating (contrary to commonly used diffusion models) a distribution of velocities of diffusing particles. Simplifying assumptions enabled us to derive an analytical expression for the liquid residence time distribution and concentration profile inside the mixer. For extreme values of parameters, the model becomes identical with the common idealized models usually adopted in chemical engineering.

In our previous paper[1], certain problems related to the description of a flow-through equipment by means of the classical diffusion model were discussed. The problem of proper formulation of boundary conditions was analyzed. Danckwerts' well-known one-dimensional axial dispersion model of a flow reactor was reported[2]. It was emphasized that the general diffusion model (without a source term) describing temporal changes of a component concentration in a three-dimensional space by means of a parabolic partial differential equation (PPDE, cf. Eq. (*6*) in ref.[1]) can be reformulated in the form of a stochastic differential equation (SDE, cf. Eq. (*17*) in ref.[1]). Random trajectory of single liquid particle motion generated by this SDE is characterized by transitive probability density function, this being a solution of diffusion model. By the term liquid particle, either single molecule or a small volume of liquid negligible with respect to the total volume of system is denoted. The value of transitive probability density is directly proportional to the local component concentration.

Owing to the presence of Wiener process in the SDE, serious problems in physical interpretation of results appear. Problems stem particularly from the fact that time derivative of the Wiener process approaches infinity at each time instant, therefore, the liquid particle velocity also takes permanently an infinite value. Physically unrealistic solution of the PPDE, supposing unlimited rate of diffusion, arises as a consequence of this drawback of common diffusion models.

Further problems arise from the fact that, according to diffusion model, particles of a component can move with the non-zero probability in the direction opposite to the direction of the carrier liquid stream flow (consequence of the Gaussian distribution of the Wiener process). The possibility of this counter-motion is frequently in contradiction to the real situation at the inlet and/or outlet of a flow mixer. The liquid residence time in the system can then be defined only with a certain degree of ambiguity.

The first drawback of diffusion models (i.e., the step change of concentration at the beginning of the process) can be solved by formulating the SDE in a so-called dynamic form involving also forces acting on the moving particles[3]. By a proper definition of coefficients in these equations, the second drawback (significant counter-motion of component particles at the inlet and outlet of the mixer) can be solved. This approach will be used in this paper for the description of a one-dimensional flow mixer.

Two types of continuous flow systems are commonly considered in chemical engineering literature: an open system and a closed one (cf. Figs 3.1 and 3.3 in monograph[4]). This classification reflects application of different types of boundary conditions.

## THEORETICAL

An incompressible liquid flowing through systems with one inlet and one outlet is considered (Fig. 1). A detectable component A is injected into the liquid stream uniformly over the system cross-section at the inlet. Only one-dimensional motion of both carrier liquid and component A particles is supposed (in other words: a projection of the motion on the longitudinal system axis is considered).

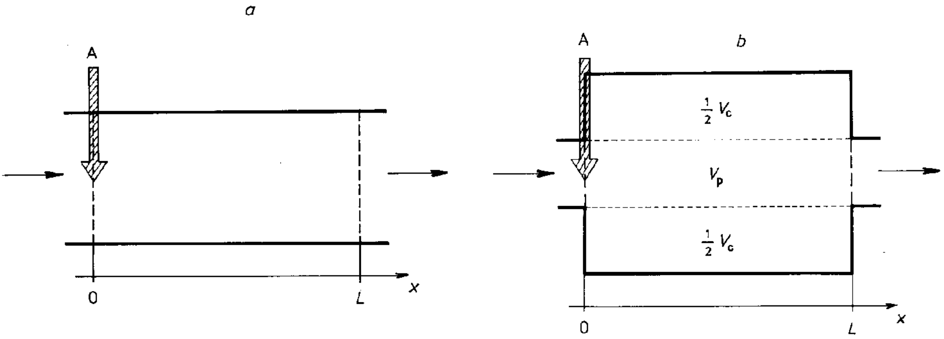

FIG. 1
Two basic types of continuous flow mixers: *a* An open mixer, *b* a closed mixer

*Open Mixer*

An equality of the cross-sectional area of the mixer itself and of the inlet and outlet mixer openings is a characteristic feature of this system (Fig. 1*a*). An attempt to formulate a one-dimensional dynamic SDE describing particle motion inside this system was made in one of our previous papers[5] assuming that both deterministic and stochastic forces act on particles. These forces were considered to be linear functions of particle velocity $V(t)$ which can take only finite values

$$\mathrm{d}V(t) = [\alpha - \beta V(t)]\,\mathrm{d}t + \sqrt{2}\,[\gamma + \delta V(t)]\,\mathrm{d}W(t) \;, \tag{1}$$

$$\mathrm{d}X(t) = V(t)\,\mathrm{d}t \;, \qquad\qquad \beta > 0 \;. \tag{2}$$

The corresponding Kolmogorov equation reads as follows[6]

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} + \frac{\partial}{\partial v}[(\alpha - \beta v)\, f] - \frac{\partial^2}{\partial v^2}[(\gamma + \delta v)^2 f] = 0 \;, \tag{3}$$

where $f(x,v;t)$ is the simultaneous transitive probability density function for the particle position and velocity. This function can be interpreted as a product of the component A concentration and conditional probability density function for the particle velocity at a fixed position

$$kf(x,v;t) = \rho_{\mathrm{A}}(x;t)\, f_v(v;t|x) \;, \tag{4}$$

where $k$ denotes the proportionality constant given by the total amount of component A inside the system (cf. e.g. ref.[7])

$$\rho_{\mathrm{A}}(x;t) = k\int_{-\infty}^{\infty} f(x,v;t)\,\mathrm{d}v \;. \tag{5}$$

Equation (*3*) is more complex than Eq. (*6*) in ref.[1] for spatially one-dimensional system. However, the initial and boundary conditions for Eq. (*3*) are more natural: The initial condition is given by an initial distribution of particle velocities and positions at the mixer inlet, the boundary conditions with respect to the velocity must fulfil the requirement of convergence of $f(x,v;t)$ to zero with the velocity absolute value increasing to infinity. Equation (*3*) involves, contrary to common diffusion equation (Eq. (*6*) in ref.[1]), only the first derivative with respect to the spatial coordinate. Therefore, only one boundary condition is to be specified (usually at the mixer inlet ($x$ = 0))

$$\lim_{x \to 0+} f(x,v;t) = \frac{1}{k} \rho_A(0,t)\, f_v(v;t|0) \quad , \tag{6}$$

i.e., the component A concentration and particle velocity distribution are prescribed. It may be supposed that particle velocities do not differ significantly from the mean liquid velocity at the inlet.

The formulation of Eq. (*1*) does not eliminate the second drawback of the common diffusion models, i.e., the possibility of particle counter-motion at the mixer outlet. The ordinates of the Wiener process are Gaussian distributed with zero mean[6], hence, the solution of Eq. (*1*) can take, in general, both positive and negative values.

In order to eliminate this possibility, Eq. (*1*) can be simplified by putting $\gamma = 0$. Then the random force is directly proportional to the particle velocity. Therefore, supposing simultaneously $\alpha > 0$ and initial particle velocity to be positive, the particle velocity can take only positive values at each time instant $t > 0$. The effect of the Wiener process is attenuated by decreasing velocity and, eventually at zero velocity, this effect vanishes completely. Therefore, the velocity cannot change the sign (direction), cf. e.g. ref.[8]. The same holds in case of negative velocity, i.e., supposing $\alpha < 0$ and negative initial velocities. In this way the simplification $\gamma = 0$ enables us to formulate the stochastic diffusion equation ensuring only unidirectional particle motion. The particle, once leaving the system (at $x = L$), will never return into the system with probability one.

The Kolmogorov diffusion equation, corresponding to SDEs (*1*) and (*2*), has then the form

$$\frac{\partial f}{\partial t} + v\,\frac{\partial f}{\partial x} + \frac{\partial}{\partial v}[(\alpha - \beta v)\, f] - \delta^2 \frac{\partial^2}{\partial v^2}(v^2 f) = 0 \quad . \tag{7}$$

The solution of this equation does not suffer from the physically unrealistic features of the common one-dimensional diffusion model, i.e., the step change of concentrations at the inlet and the counter-motion of particles at the outlet.

However, the form of Eq. (*7*) is too complex, and its analytical solution was not found. Previously[5] a simplification was adopted enabling us to solve Eq. (*7*) in case of very short mixer. Here this simplification is extended to one-dimensional systems of arbitrary length: It is assumed that both deterministic and stochastic forces act on the particles over only a very short distance from the mixer inlet. The stationary velocity distribution is attained during liquid passage over this interval. The forces have negligible effects along the remaining part of the mixer. The Kolmogorov diffusion equation for the stationary velocity distribution then reads, considering Eq. (*1*) and $\gamma = 0$, as follows

$$\frac{\mathrm{d}}{\mathrm{d}v}[(\alpha - \beta v)\, f_v] - \delta^2 \frac{\mathrm{d}^2}{\mathrm{d}v^2}(v^2 f_v) = 0 \ . \tag{8}$$

The solution of Eq. (*8*) has a form of the gamma-distribution with the reciprocal argument $1/v$

$$f_v(v) = \frac{(e/v)^{b+1}}{e\Gamma(b)} \exp(-e/v) \ , \quad e = \frac{\alpha}{\delta^2} \ ; \quad b = 1 + \frac{\beta}{\delta^2} \ , \tag{9}$$

where $\Gamma(b)$ denotes the complete gamma-function (see e.g. ref.[9]). According to the last assumption, coefficients $\alpha$, $\beta$ and $\delta$ in Eq. (*7*) acquire negligible values at a larger distance from the mixer inlet. Therefore, in this mixer region,

$$\frac{\partial f^f}{\partial t} + v \frac{\partial f^f}{\partial x} = 0 \ . \tag{10}$$

The fundamental solution of Eq. (*10*) is

$$f^f(x,v;t) = \tilde{f}(x - vt) \ ; \tag{11}$$

the actual form of function $f^f(x,v;t)$ depends on the initial and boundary conditions. The component A concentration at any position inside the mixer at any time can be evaluated by a so-called randomization of a parameter[9] using Eq. (*5*)

$$\rho_A(x;t) = k f_x(x;t) = k \int_{-\infty}^{\infty} \tilde{f}(x - vt)\, f_v(v)\, \mathrm{d}v \ . \tag{12}$$

The function $f^f(x,v;t)$ is identical with the Dirac $\delta$-function, i.e., $f^f(x,v;t) = \delta(x)$ if $\delta$-impulse of component A is introduced at the system inlet. The component A concentration is then given by the relation

$$\rho_A(x;t) = k f_v(x/t) \left| \frac{\mathrm{d}v}{\mathrm{d}x} \right| = \frac{k}{t} f_v(x/t) \ . \tag{13}$$

The probability density function $f_t(t)$ of residence time of liquid particles inside the mixer can be derived by means of the following operation (see e.g. ref.[10])

$$f_t(t) = -\frac{\partial}{\partial t}\int_0^L f_x(x;t)\,\mathrm{d}x \ , \tag{14}$$

resulting in this case in the gamma-distribution

$$f_t(t) = L f_v(L/t)/t^2 = \frac{\kappa b}{\Gamma(b)}(\kappa bt)^{b-1}\exp(-\kappa bt) \ , \qquad \kappa = e/(Lb) \ . \tag{15}$$

The hitherto described approach allowed us to find a solution of Eq. (*7*) in the analytical form. The gamma-distribution (*15*) is frequently used for the description of residence time distribution in flow systems[11].

It will be shown that relations derived in this section describe the limiting case behavior of the closed mixer analyzed below.

### *Closed Mixer*

The closed mixer[4,11] is a flow system with cross-sectional areas of the inlet and outlet openings smaller than the cross-sectional area of the mixer itself (in a plane perpendicular to the system axis). Therefore, the mixer is closed, excepting for the inlet and the outlet opening area, with impermeable walls at mixer inlet and outlet (points $x = 0$ and $x = L$), Fig. 1*b*. The particles of component A and of the carrier liquid reverberate on these walls. Liquid circulation arises in a real mixer in this way; in a one-dimensional model, the liquid circulation is replaced with the swinging motion of liquid particles from the one end of the mixer to the other one. This motion terminates when the particle leaves the system (after reaching the outlet opening). Let $p$ denotes the probability that a particle will leave the system when reaching the position $x = L$. Then the probability of particle reverberation back into the mixer is, supposing that the particle does not adhere to the wall,

$$q = 1 - p \ . \tag{16}$$

For a quantitative description of the particle motion, the assumptions adopted in previous section are used together with the following ones:

The probability of particle reverberation at the mixer inlet ($x = 0$) is equal to one. At the mixer outlet ($x = L$), the ratio of the probability of particle reverberation to the probability of particle escape is directly proportional to the instantaneous particle velocity. This assumption is based on the idea that the probability of the particle attraction into the outlet stream of the carrier liquid increases with decreasing particle velocity. Therefore, the following relations

$$\begin{aligned} q &= 1 \ , \quad (X(t) = 0) \\ \frac{q}{p} &= \frac{V(t)}{w} \ , \quad (X(t) = L) \end{aligned} \qquad (17)$$

hold where $w$ is a constant.

The particle velocity sign (direction of motion) changes in the course of the reverberation. The forces acting on the particles as well as the range of their action after reverberations are supposed to be analogous to the forces acting on the particle after its first entry into the mixer. The forces acting at the mixer outlet are supposed to be identical with the forces acting at the inlet, except for the active force (characterized by coefficient $\alpha$) which changes its direction (sign). The effects of these forces are, therefore, localized to the only close vicinity of the outlet wall, i.e., to the mixer subregion where significant change of the liquid flow direction occurs. The steady particle motion is considered outside the close vicinity of the mixer inlet and outlet.

Equation (*8*) is invariant with respect to the change of signs of $v$ and $\alpha$ even when particle moves in negative direction of the $x$-axis, therefore, its solution (*9*) remains unchanged. Equation (*10*) remains identical for the motion in positive direction of the $x$-axis, but the sign of the velocity changes in case of the motion in negative direction of the $x$-axis. Hence, set of two equations arises

$$\frac{\partial f^f}{\partial t} \pm v \frac{\partial f^f}{\partial x} = 0 \ , \quad (v > 0) \ . \qquad (18)$$

Let symbol $f_n^-$ denotes the particular solution of Eq. (*18*) during the particle motion against the positive direction of $x$-axis after the $n$-th particle reverberation at the mixer outlet but before reaching the mixer inlet ($x$ = 0). In an analogous way, symbol $f_n^+$ denotes the particular solution of Eq. (*18*) during the particle motion in positive direction of $x$-axis after the consecutive reverberation at the inlet. Thus, the set of particular solutions is obtained

$$\begin{aligned} f_n^+ &= f_n^+(x - vt) \ , \quad (n = 0,1,2,...) \ , \\ f_n^- &= f_n^-(x + vt) \ , \quad (n = 1,2,3,...) \ . \end{aligned} \qquad (19)$$

The actual form of functions $f_n^+$ and $f_n^-$ depends again on the initial and boundary conditions

$$\lim_{x\to L-} f_n^-(x+vt) = q \lim_{x\to L-} f_{n-1}^+(x-vt) + p \lim_{x\to L-} f_{n-1}^+(x-vt) \ ,$$
$$\lim_{x\to 0+} f_n^+(x-vt) = \lim_{x\to 0+} f_n^-(x+vt) \ , \qquad (20)$$

where $n$ = 1,2,3,.... The last term on the right-hand side of the first of Eqs (*20*) expresses the probability that the particle leaves the mixer before the $n$-th reverberation. With respect to Eq. (*16*) and the second of Eqs (*17*), the following relation holds

$$q = \frac{v}{v+w} \ . \qquad (21)$$

The sum of the particular solutions forms the general solution

$$f_c(x|v;t) = f_0^+ + \sum_{n=1}^{\infty} (f_n^- + f_n^+) \ . \qquad (22)$$

The integral $\int_x^{x+\Delta x} f_c(x|\, v;t)\, \mathrm{d}x$ equals to the probability that the position $X(t)$ of particle moving just with the velocity $v$ lies within the interval $<x, x + \Delta x)$. In a way similar to Eq. (*12*), the component A concentration at position $x$ can be evaluated by means of the velocity randomization

$$\rho_A(x,t) = kf_x(x;t) = k \int_0^{\infty} f_c(x|v;t)\, f_v(v)\, \mathrm{d}v \ . \qquad (23)$$

The function $\rho_A(x;t)$ defined by Eq. (*23*) is to be considered as the component A concentration averaged over the mixer cross-section.

Supposing the concentration signal in the form of the Dirac δ-function is introduced at the mixer inlet at time $t = 0$, the particular solutions are

$$f_n^+ = \delta(x + 2nL - vt)\, q^n \ ,$$
$$f_n^- = \delta(x - 2nL + vt)\, q^n \ , \qquad (24)$$

where the term $q^n$ expresses the probability of particle being still inside the mixer after $n$-th reverberation. The component A concentration profile inside the mixer is given by the relation (see Appendix)

$$\rho_{\mathrm{A}}(x;t) = \frac{k}{t}\left\{\sum_{n=0}^{\infty} f_v(v_n^+)\,\Psi_n(v_n^+) + \sum_{n=1}^{\infty} f_v(v_n^-)\,\Psi_n(v_n^-)\right\}\ , \qquad (25)$$

$$(0 \le x \le L)\ ,$$

where

$$\Psi_n(v) = \left(\frac{v}{v+w}\right)^n = q^n\ , \qquad (26)$$

and

$$v_n^{\pm} = (2nL \pm x)/t\ . \qquad (27)$$

By means of the operation used in Eq. (*14*), the probability density function of residence time in the closed mixer is obtained

$$f_t(t) = \frac{w}{t}\sum_{n=0}^{\infty} f_v[(2n+1)\,L/t]\;\Psi_{n+1}[(2n+1)\,L/t]\ , \qquad (28)$$

where parameter $w$ is defined by

$$w = 2\varepsilon L\ . \qquad (29)$$

The mean residence time is (see Appendix)

$$\bar{t} = \frac{1}{\kappa} + \frac{1}{\varepsilon}\ . \qquad (30)$$

Equations (*25*) and (*28*) can be transformed to a dimensionless form by introducing the dimensionless variables

$$t^* \equiv t/\bar{t} = \frac{t}{1/\kappa + 1/\varepsilon}\ , \quad x^* \equiv x/L\ , \quad v^* \equiv v\bar{t}/L\ , \qquad (31)$$

and the dimensionless parameter

$$\Omega = \frac{\kappa}{2\varepsilon} \ . \qquad (32)$$

The dimensionless concentration profile inside the mixer is

$$\rho_A^*(x^*;t^*) = L\rho_A(x^*L;t^*\bar{t})/k = \frac{1}{t^*}\left[\sum_{n=0}^{\infty} f_u(u_n^+)\ \Psi_n(u_n^+) + \sum_{n=1}^{\infty} f_u(u_n^-)\ \Psi_n(u_n^-)\right] \ , \qquad (33)$$

$$(0 \leq x^* \leq 1) \ ,$$

where $u_n^{\pm} = (2n \pm x^*)/t^*$ , $\Psi_n(u) = [u\Omega/(u\Omega + 2\Omega + 1)]^n$ , and $f_u(u) = Lf_v(uL/\bar{t})/\bar{t}$.

The dimensionless probability density of the residence time is

$$f_t^*(t^*) = \bar{t}f_t(t^*\bar{t}) = \frac{2\Omega + 1}{\Omega t^*}\sum_{n=0}^{\infty} f_u[(2n+1)/t^*]\ \Psi_{n+1}[(2n+1)/t^*] \ , \quad (t^* > 0) \ . \qquad (34)$$

The variance and the asymmetry coefficient of the probability density $f_t^*(t^*)$ are (see Appendix)

$$\mu_2 = 1 + \frac{1/b - 1}{(1 + 2\Omega)^2} \ , \qquad (35)$$

$$\mu_3 = 2 + \frac{2[(1/b^2 - 1) + 2\Omega(5/b - 1)]}{(1 + 2\Omega)^3} \ . \qquad (36)$$

## RESULTS AND DISCUSSION

The derived component concentration profiles inside the mixer (Eq. (*33*), Fig. 2) and the residence time distribution functions (Eq. (*34*), Fig. 3) involve two parameters: *b* and Ω. The physical meaning of the first one was discussed earlier[5]. The quantity *b* – 1 can be interpreted as the ratio of the nonrandom to the random force acting against the particle motion. Equation (*15*) is formally identical with the residence time distribution in a cascade of the ideal mixers[11] for integer values of *b*. Hence, the parameter *b* can be considered as the "number of mixers in a cascade".

The physical meaning of parameter Ω can be clarified by means of liquid circulation within a mixer: Let symbol $\dot{V}$ denotes the volumetric flow rate of liquid through the mixer. The total volume of the closed mixer (Fig. 1*b*) is divided into two parts: the part of volume $V_p$ in which the liquid flows without circulation, and the second part of volume $V_c$ with the circulating flow. The ratio of these two volumes is assumed to be approximately constant at a steady state. The mean residence time of the liquid in the non-circulation part of the mixer volume is $1/\kappa = V_p/\dot{V}$, and in the circulation part of the mixer volume, $1/\varepsilon = V_c/\dot{V}$. By introducing these mean residence times into Eq. (*30*), the total mean residence time is obtained $\bar{t} = 1/\kappa + 1/\varepsilon = (V_p + V_c)/\dot{V}$, and with respect to Eq. (*32*), one can write $V_c/V_p = 2\Omega$. The volume $V_c$ can be divided into two parts: $V_c^+$ with the liquid moving in the positive direction of the *x*-axis, and $V_c^-$ with the liquid moving in the opposite direction. The ratio of the mixer subvolumes is then $(V_c^+ + V_c^-)/V_p$. Both numerator and denominator of this fraction can be multiplied by $\kappa$, then quantity $V_c^+\kappa = \dot{V}_c$ is equal to the volumetric flow rate in the circulating liquid stream. The product $V_c^-\kappa$ is equal to the volumetric flow rate in the circulating liquid stream in the case of an incompressible liquid. Hence

$$\Omega = \frac{\dot{V}_c}{\dot{V}} \qquad (37)$$

denotes the intensity of the liquid circulation within the mixer.

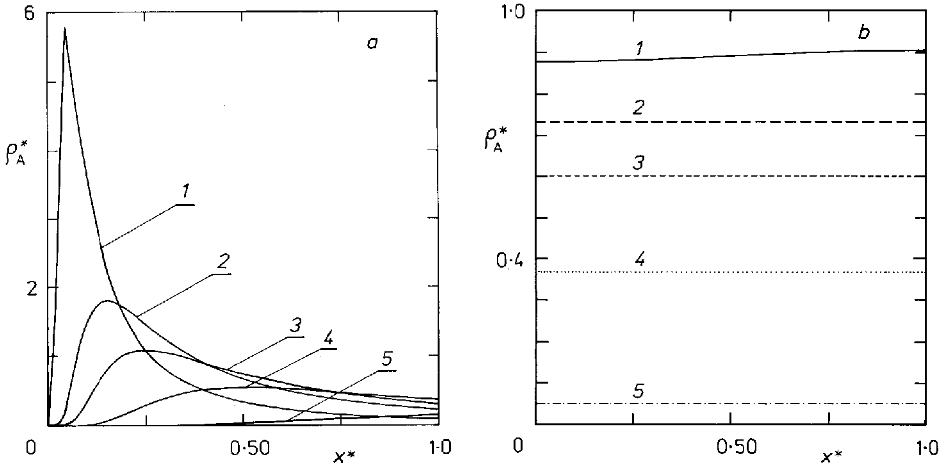

FIG. 2

Spatial profiles of component A concentration inside the closed mixer at time $t^*$ elapsed since the injection of the concentration impulse: *a* *1* $t^* = 0.1$, *2* $t^* = 0.3$, *3* $t^* = 0.5$, *4* $t^* = 1.0$, *5* $t^* = 3.0$; parameters: $\Omega = 0$, $b = 1$; *b* *1* $t^* = 0.1$, *2* $t^* = 0.3$, *3* $t^* = 0.5$, *4* $t^* = 1.0$, *5* $t^* = 3.0$; parameters: $\Omega = 30$, $b = 30$

The parameters $b$ and $\Omega$ make the model considerably flexible. The circulation intensity $\Omega$ may vary from zero to infinity, the parameter $b$ takes values greater or equal to one. For extreme values of parameters, the model converges to the simple idealized models commonly used in chemical engineering:

*1.* $\Omega \to 0$. This case describes the non-circulating flow, i.e., the open mixer (Fig. 1*a*). The circulation part of the mixer volume approaches zero, hence, the liquid residence time inside this part of the mixer is also zero. The value of the parameter $\varepsilon$ grows above all limits. The concentration profile of the component A inside the mixer is expressed by Eq. (*13*). The liquid residence time distribution at the mixer outlet is given by Eq. (*15*) and is depicted in Fig. 3*a* (curves *1* and *2*).

*1.a.* $\Omega \to 0$, $b \to \infty$. The piston flow of liquid in the mixer corresponds to these parameters. The concentration profile inside the mixer, as well as the residence time probability density, are expressed by the Dirac $\delta$-functions (see Appendix).

*1.b.* $\Omega \to 0$, $b \to 1$. According to Eq. (*15*) the residence time distribution is

$$f_t(t) = \kappa \exp(-\kappa t) \ , \qquad (38)$$

i.e., the residence time distribution in an ideal mixer with the mean residence time $1/\kappa$. The concentration profile for this case is shown in Fig. 2*a*. The probability density of residence time is depicted in Fig. 3*a* (curve *2*). Hence, the proposed model at the given

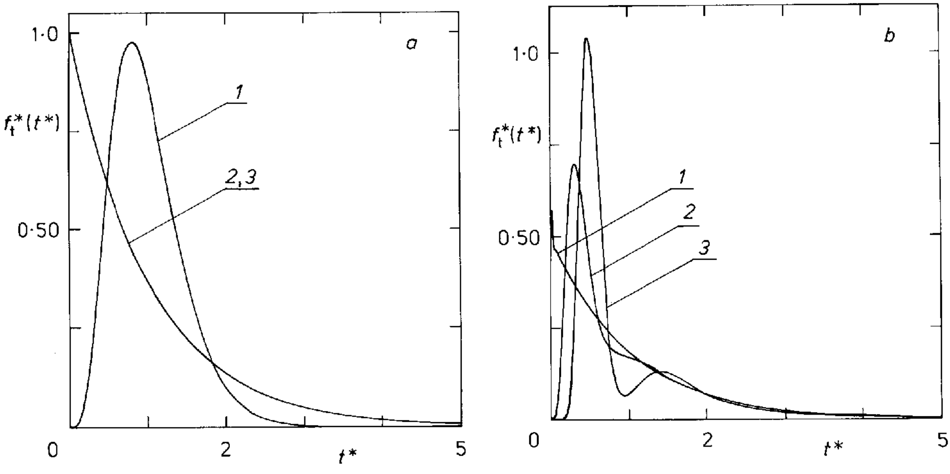

FIG. 3

The residence time probability density function: *a* *1* $\Omega = 0$, $b = 5$, *2* $\Omega = 0$, $b = 1$, *3* $\Omega = 200$, $b = 1$; *b* *1* $\Omega = 50$, $b = 1$, *2* $\Omega = 1$, $b = 5$, *3* $\Omega = 0.5$, $b = 15$

parameter values supposes a passage of the particles through the mixer without mutual mixing. An ideal mixer with the liquid macroflow[11] corresponds to this situation.

Hitherto, we have considered the zero intensity of the liquid circulation inside the mixer. At non-zero circulation intensity, the transversal liquid mixing inside the mixer takes place.

*2.* $\Omega \to \infty$. The concentration of component A takes a constant value throughout the mixer and decreases with increasing time (see Appendix)

$$\rho_A(x;t) = \frac{k}{L} \exp(-\varepsilon t) \ . \qquad (39)$$

The residence time distribution has the form of the exponential function

$$f_t(t) = \varepsilon \exp(-\varepsilon t) \ , \qquad (40)$$

with the mean residence time $1/\varepsilon$. In this case the model describes an "actual" ideal mixer, i.e., a mixer with the liquid microflow. This case is depicted in Figs 2*b* and 3*a* (curve *3*). Figure 2*b* shows that already at $\Omega = 30$ the concentration profile along the mixer is almost flat after a very short time elapsed since the injection of the component A impulse. Immediately after the beginning of the mixing process, the effect of this impulse is clearly visible; the characteristic exponential form of the residence time distribution is attainable at very high values of the circulation intensity ($\Omega \approx 200$) – Fig. 3*a* (curve *3*). At $\Omega \approx 50$ the effect of the injected impulse is still visible (Fig. 3*b*, curve *1*).

A case of the weakly circulating flow is shown in Fig. 3*b* (curve *2*). A passage of the only slightly dispersed impulse through the mixer is clearly remarkable. The model is capable of describing even multimodal residence time distributions (Fig. 3*b*, curve *3*).

Obviously, the proposed model under the above-adopted simplifying assumptions combines the gamma-distribution[5,11] with the models involving recycle streams[12]. This combination enables us to describe a very wide set of actual systems encountered in chemical engineering.

Certain problems arise when estimating the model parameters from the measured residence time distribution curves. The second and the third moment of the dimensionless residence time distribution (Eq. (*34*)) are shown in Fig. 4. The values of the moments undergo remarkable changes at only low values of $\Omega$ (approximately for $\Omega < 2$). Equations (*35*) and (*36*) may be used for the evaluation of $b$ and $\Omega$ using moments evaluated from experimental data. A consequent accuracy improvement by means of the proper non-linear regression method[13] using Eq. (*34*) is possible. At higher $\Omega$ values this approach is inappropriate because of the ambiguity of initial guess selection. Therefore, Eq. (*37*) is recommended for the estimation of $\Omega$ using the additional experimental data on the liquid circulation, obtained, e.g., in experiments with a flow-follower[14]. In this region of $\Omega$ values, the $b$ value does not influence the concentration fluctuations inside the mixer markedly.

Figure 2*b* shows that at higher Ω values, Danckwerts' boundary condition[2] prescribing zero concentration derivative at the mixer outlet is well fulfilled. Figure 2*a*, on the contrary, shows that this condition can easily be corrupted, especially at high values of *b* when the model approaches the plug-flow.

## CONCLUSIONS

1. The presented stochastic model enabled us to improve the accuracy of the commonly used diffusion model, and the validity of general considerations disclosed in previous paper[1] was proved.

2. Together with the boundary conditions introducing the possibility of circulation of diffusing particles into the model, the model makes possible the unambiguous definition of the residence time of each particle. The probability of returning the particle back into the system from the outside of the mixer is equal to zero. Therefore, the residence time distribution may be correctly defined.

3. The model, for extreme values of the parameters, tends to all models commonly used in chemical engineering for description of flow systems.

In a paper under preparation[15], the application of this model to an evaluation of the reacting component conversion in an isothermal continuous flow chemical reactor will be shown.

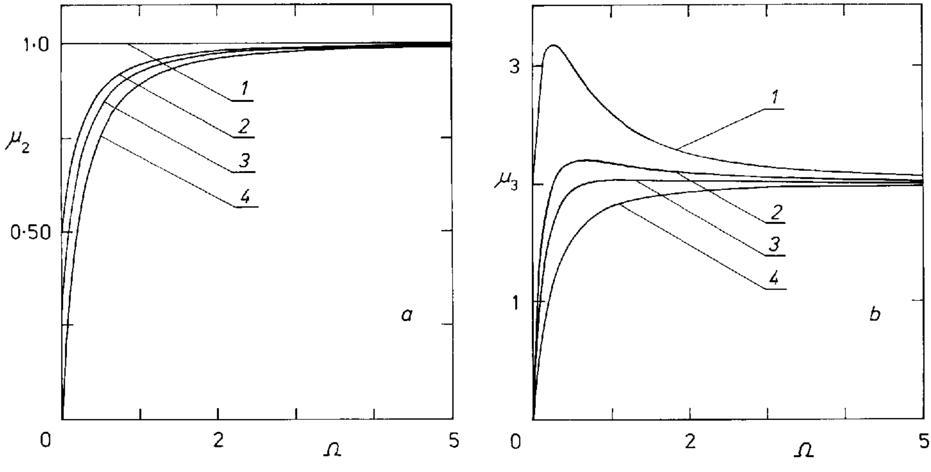

FIG. 4
The second central moment of the residence time distributions: *a* *1* *b* = 1, *2* *b* = 2, *3* *b* = 3, *4* *b* = 30; *b* *1* *b* = 1, *2* *b* = 2, *3* *b* = 3, *4* *b* = 30

## APPENDIX

### *Derivation of the Residence Time Distribution Function*

When the Dirac impulse of the component concentration is imposed on the mixer inlet, then during the initial period of the mixing process, Eqs (*24*) represent the solution of Eqs (*18*) owing to the validity of the following conditions (with respect to the boundary conditions (*20*))

$$\lim_{x \to 0+} f_0^+ = \delta(x) \ ,$$
$$\lim_{x \to L-} \delta(x - 2L + vt) = \lim_{x \to L-} \delta(x - vt) \ ,$$
$$\lim_{x \to 0+} \delta(x - 2L + vt) = \lim_{x \to 0+} \delta(x + 2L - vt) \ , \ldots$$

The Laplace transforms of the functions in Eqs (*24*) are

$$g_n^+(s) = \int_0^\infty \delta(x + 2nL - vt) \exp(-st) \, \mathrm{d}t = \exp[-s(2nL + x)/v]/v \ ,$$

$$g_n^-(s) = \int_0^\infty \delta(x - 2nL + vt) \exp(-st) \, \mathrm{d}t = \exp[-s(2nL - x)/v]/v \ . \qquad (A1)$$

Substituting these functions into the transformed Eq. (*22*), one obtains the relation

$$g_c = g_c(x,s,v) = \left\{ \exp(-sx/v) \sum_{n=0}^{\infty} Q^n + \exp(sx/v) \sum_{n=1}^{\infty} Q^n \right\} /v =$$

$$= \left[ \exp(-sx/v) + 2 \cosh(sx/v) \frac{Q}{1 - Q} \right] /v \ , \qquad (A2)$$

where $Q = q \exp(-2sL/v)$. The sums in Eq. (*A2*) can be evaluated as the geometrical progression sums as the probability $q$ in a flow mixer must be always less then one. Substituting from Eqs (*A2*) and (*9*) into Eq. (*23*), using a replacement $v = L/z$, and with respect to Eq. (*29*), the following relation is obtained

$$g_x(x,s) = \int_0^\infty g_c(x,s;v) \, f_v(v) \, \mathrm{d}v =$$

$$= \frac{1}{L}\int_0^\infty z f_t(z) \left\{ \exp(-r) + \frac{\cosh(r)\exp(-sz)}{\varepsilon z \exp(sz) + \sinh(sz)} \right\} \mathrm{d}z \ , \qquad (A3)$$

where $r = szx/L$ and $f_t(z)$ is defined in Eq. (*15*). An original coresponding to this function is given in Eq. (*25*). Equation (*14*) after the Laplace transformation reads as folows

$$g_t(s) = -s\int_0^L g_x(x,s)\,\mathrm{d}x + \lim_{t\to 0}\int_0^L f_x(x,t)\,\mathrm{d}x \ ; \qquad (A4)$$

the last integral is equal unity for, at the given initial condition, the relation $\lim\limits_{t\to 0} f_x(x,t) = \delta(x)$ holds. On putting $g_x(x,s)$ from Eq. (*A3*) into Eq. (*A4*), changing order of integration, and using the variable $r$ defined post Eq. (*A3*), we obtain

$$g_t(s) = -\int_0^\infty f_t(z)\int_0^{sz} \left\{ \exp(-r) + \frac{\cosh(r)\exp(-sz)}{\varepsilon z\exp(sz) + \sinh(sz)} \right\} \mathrm{d}r\,\mathrm{d}z + 1 \ . \qquad (A5)$$

Solving the inner integral and adopting certain rearrangements, we can write

$$g_t(s) = \int_0^\infty \frac{f_t(z)\varepsilon z}{\varepsilon z\exp(sz) + \sinh(sz)}\,\mathrm{d}z \ . \qquad (A6)$$

The original to $g_t(s)$ is given by Eq. (*28*). Statistical moments of the distribution (*A6*) may easily be derived using a relation$^9$

$$m_k = \int_0^\infty t^k f_t(t)\,\mathrm{d}t = (-1)^k \frac{\mathrm{d}^k}{\mathrm{d}s^k} g_t(s)\,|_{s=0} \ . \qquad (A7)$$

The first (negative) derivative of $g_t(s)$ with respect to $s$ at $s = 0$ results in the relation

$$m_1 = \frac{\kappa b}{\Gamma(b)}\int_0^\infty (\kappa b z)^{b-1}\exp(-\kappa b z)[z + 1/\varepsilon]\,\mathrm{d}z = \frac{\Gamma(b+1)}{\Gamma(b)\kappa b} + \frac{1}{\varepsilon} = \frac{1}{\kappa} + \frac{1}{\varepsilon} \ , \qquad (A8)$$

hence, the validity of Eq. (*30*) is proved. The second and the third moments of function $g_t(s)$ are

$$m_2 = \frac{b+1}{\kappa^2 b} + \frac{4}{\varepsilon\kappa} + \frac{2}{\varepsilon^2} \ , \qquad (A9)$$

$$m_3 = \frac{(b+2)\,(b+1)}{b^2\kappa^3} + \frac{13(b+1)}{b\kappa^2\varepsilon} + \frac{18}{\kappa\varepsilon^2} + \frac{6}{\varepsilon^3} \;. \tag{A10}$$

### *Simplification of Equations (A3) and (A6) at Extreme Parameter Values*

*1.a.* $\varepsilon \to \infty$. The second term after the summation mark inside the braces in Eq. (*A3*) is equal zero in this case. Putting $y = z(sx/L + \kappa b)$ we obtain

$$\lim_{\varepsilon\to\infty} g_x(x,s) = \frac{(\kappa b)^b}{L\Gamma(b)\,(sx/L+\kappa b)^{b+1}} \int_0^\infty \exp(-y)\, y^b\, \mathrm{d}y = \frac{b}{e}\left(\frac{e/x}{s+e/x}\right)^{b+1}, \;\; e = \kappa bL \;. \tag{A11}$$

The original to this expression is given in Eq. (*13*). Using Eq. (*A4*) or directly Eq. (*A6*) we can derive, in an analogous way, the relation

$$\lim_{\varepsilon\to\infty} g_t(s) = \left(\frac{\kappa b}{\kappa b + s}\right)^b \;. \tag{A12}$$

The original to this expression is given in Eq. (*15*).

*1.b.* $\varepsilon \to \infty$, $b \to \infty$. By an rearrangement of Eq. (*A11*) we get

$$\lim_{\varepsilon,b\to\infty} g_x(x,s) = \lim_{b\to\infty} \frac{1}{\kappa L}\left[\left(\frac{\kappa bL/x}{s+\kappa bL/x}\right)^{\kappa bL/x}\right]^{x/\kappa L} = \frac{1}{\kappa L}\exp\left(-\frac{sx}{\kappa L}\right), \tag{A13}$$

$$\lim_{\varepsilon,b\to\infty} g_t(s) = \exp(-s/\kappa) \;. \tag{A14}$$

The originals to these transforms are

$$\begin{gathered} \rho_A(x;t) = k\delta(x - \kappa Lt) \;, \\ f_t(t) = \delta\left(t - \frac{1}{\kappa}\right) . \end{gathered} \tag{A15}$$

*2.* $\kappa \to \infty$. Comparing Eqs (*15*) and (*A3*), one can recognize that the expressions in front of the braces in Eq. (*A3*) may be written in the form

$$\frac{1}{L\Gamma(b)}\,(\kappa bz)^b \exp(-\kappa bz) = \frac{zf_t(z)}{L} \;. \tag{A16}$$

The Laplace transform of this relation (according to Eq. (*A11*) in case of κ growing above all limits) is given by the relation

$$\lim_{\kappa\to\infty}(z/L)g_t(s) = \lim_{\kappa\to\infty}(z/L)\left(\frac{\kappa b}{\kappa b + s}\right)^b = \frac{z}{L} \;. \qquad (A17)$$

The original corresponding to a constant is the Dirac δ-function, hence

$$\lim_{\kappa\to\infty} z f_t(\mathrm{z})/L = \lim_{\omega\to 0}\delta(z-\omega) \;, \qquad (A18)$$

where ω is a formal parameter. Substituting from Eqs (*A16*) and (*A18*) into Eq. (*A3*) and after rearranging and performing the integration and the limit evaluation we have

$$\lim_{\kappa\to\infty} g_x(x,s) = \lim_{\omega\to 0}\frac{\omega}{L}\left[\exp\left(-s\omega x/L\right) + \frac{2\cosh\left(s\omega x/L\right)\exp\left(-2s\omega\right)}{1+2\varepsilon\omega-\exp\left(-2s\omega\right)}\right] =$$

$$= \frac{1}{L}\lim_{\omega\to 0}\frac{2\omega}{1+2\varepsilon\omega-\exp\left(-2s\omega\right)} = \frac{1}{L(\varepsilon+s)} \;. \qquad (A19)$$

The original to this function is given in Eq. (*39*). Adopting Eq. (*A4*), we can finally obtain the Laplace transform of the residence time probability density at κ → ∞

$$\lim_{\kappa\to\infty} g_t(s) = -\frac{s}{L}\int_0^L \frac{\mathrm{d}x}{\varepsilon+s} + 1 = \frac{\varepsilon}{\varepsilon+s} \;. \qquad (A20)$$

The backward transform is given in Eq. (*40*).

## SYMBOLS

(Numbers in brackets refer to the equation with the first occurrence of the respective symbol)

| | |
|---|---|
| $b$ | parameter of gamma-distribution (*11*) |
| $e$ | constant proportional to mean particle velocity (*9*), m $\mathrm{s}^{-1}$ |
| $f$ | probability density function for position and velocity (*4*), $\mathrm{m}^2\,\mathrm{s}^{-1}$ |
| $f_t^*$ | dimensionless probability density function for residence time (*34*) |
| $f_c$ | probability density function for position and velocity (*22*), $\mathrm{s}^{-1}$ |
| $f_t$ | probability density function for residence time (*14*), $\mathrm{s}^{-1}$ |
| $f_x$ | probability density function for position (*12*), $\mathrm{m}^{-1}$ |
| $f_v$ | probability density function for velocity (*9*), $\mathrm{m}^{-1}$ s |

| | |
|---|---|
| $f_V(v;(t\|x)$ | conditional probability density function for velocity (*4*), m$^{-1}$ s |
| $k$ | component mass related to mixer cross-section (*4*), kg m$^{-2}$ |
| $L$ | length of reactor or mixer (*15*), m |
| $m_k$ | $k$-th moment of residence time (*A7*), s$^k$ |
| $n$ | number of particle reverberations at outlet wall (*19*) |
| $p$ | probability of particle escape from mixer (*16*) |
| $q$ | probability of particle reverberation back into mixer (*16*) |
| $t$ | time (*1*), s |
| $\bar{t}$ | mean residence time (*30*), s |
| $t^*$ | dimensionless time (*31*) |
| $v^*$ | dimensionless velocity of particle (*31*) |
| $V$ | random velocity of particle (*1*), m s$^{-1}$ |
| $\dot{V}$ | volumetric flow rate (*37*), m$^3$ s$^{-1}$ |
| $\dot{V}_c$ | circulation flow rate (*37*), m$^3$ s$^{-1}$ |
| $V_c$ | mixer volume fraction with liquid circulation (Fig. 1), m$^3$ |
| $V_p$ | primary part of mixer volume (Fig. 1), m$^3$ |
| $v$ | velocity of particle (*3*), m s$^{-1}$ |
| $W$ | Wiener process (*1*), s$^{1/2}$ |
| $w$ | parameter in Eq. (*17*), m s$^{-1}$ |
| $X$ | random position of particle (*2*), m |
| $x$ | spatial coordinate (*3*), m |
| $x^*$ | dimensionless spatial coordinate (*31*) |
| $\alpha$ | constant of active force (*1*), m s$^{-2}$ |
| $\beta$ | constant of friction force (*1*), s$^{-1}$ |
| $\gamma$ | constant of random force (*1*), m s$^{-3/2}$ |
| $\Gamma$ | gamma function (*9*) |
| $\delta$ | constant of random force of friction (*1*), s$^{-1/2}$ |
| $\varepsilon$ | reciprocal mean residence time in circulation part of mixer (*30*), s$^{-1}$ |
| $\kappa$ | reciprocal mean residence time in non-circulation part of mixer (*15*), s$^{-1}$ |
| $\mu_i$ | $i$-th central moment of dimensionless residence time (*35*) |
| $\Psi_n$ | functions defined in Eq. (*23*) |
| $\rho_A$ | component A concentration (*4*), kg m$^{-3}$ |
| $\rho_A^*$ | dimensionless component A concentration (*33*) |
| $\Omega$ | circulation intensity (*32*) |

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