

STOCHASTIC MODEL OF THE NONIDEAL FLOW MIXER*

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The flow mixer is described by use of the unidimensional stochastic model based on the earlier published general approach. It is demonstrated that on basis of the proposed model two individual models result which are most frequently used in chemical engineering for description of mixers and reactors: the dispersion model and model of the cascade of ideal mixers. On the basis of the model proposed it is also possible to derive the usual relation for calculation of the reactor conversion at macroflow.

In our recent study¹ a unidimensional stochastic model was proposed which describes the random motion of the indicating particle superimposed with respect to the also randomly moving small liquid volume in the mixer. On basis of several simplification assumptions it was demonstrated that on basis of this model the diffusion Kolmogorov's equation for spreading of scalar quantity (temperature or concentration) in turbulent regime can be derived. This approach was applied to the rather special case: homogenisation of miscible liquids in batch equipment equipped with a mechanical stirrer². Here an attempt has been made to propose a procedure how to apply the proposed model for the flow system.

THEORETICAL

General Relations

Let us assume the infinitely long mixer schematically given in Fig. 1 and let us choose the oriented unidimensional system with the axis x parallel with the axial axis of the

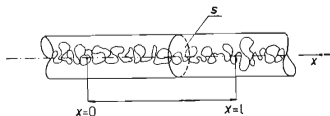


FIG. 1
Motion of Indicating Particle in Mixer

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mixer. In the moment $t = 0$ we locate in the point $x = 0$ the indicating particle which tracks the motion of the liquid flowing through the mixer.

It was demonstrated^{1,2} that — in the case when it is possible to neglect the superimposed component of motion which corresponds to molecular diffusion — it is possible to describe the random motion of the particle by use of the system of stochastic differential equations³

$$dV(t) = g[X(t), V(t), t] dt + h[X(t), V(t), t] dW(t) \quad (1)$$

$$dX(t) = V(t) dt. \quad (2)$$

In these equations is X denoting the projection of position and V the projection of the velocity of particle to the chosen axis x while both these quantities are random functions of time, W is the Wiener process⁴. The first right hand side term is characterizing the intensity of deterministic and the second one of random forces acting on the particle.

Similarly as in the case of the batch system² we will make several additional assumptions concerning these forces and the assumption on stationary flow in the system:

A1. A non-random force in the direction of the axis x acts on the particle, which is neither a function of position, nor of velocity and time. A2. A non-random force acts on the particle, which is directly proportional to the particle velocity $V(t)$ and is oriented against the direction of motion of this particle. A3. A force of non-random character acts on the particle, which is a linear function of particle velocity and acts against the direction of its motion. A4. The particle velocity is in each moment stationary random function of time.

Discussion of assumptions: The active force defined sub A1 is causing the motion of the particle in the direction of the axis x and it is possible to imagine that it is the result of pressure difference on both ends of the mixer or by the stirrer motion *etc.* The force sub A2 can be considered to be the force of laminar friction and the force defined sub A3 is the cause of turbulent resistance to the particle motion (see⁴). The made assumption is representing the fact that the intensity of turbulence and velocity of particle motion and thus also the flow velocity increases. The assumption A4 represents the fact that the particle begins to move in the liquid whose flow is (quasi) stationary *i.e.* it steadied from the moment $t = 0$.

At the given assumptions Eq. (1) can be written in the form

$$dV(t) = [\alpha - \beta V(t)] dt - (\sqrt{2})[\gamma + \delta V(t)] dW(t), \quad (3)$$

where α , β , γ , δ are coefficients which are constant at the given conditions of the operation of the mixer (*i.e.* the volumetric liquid flow rate through the equipment,

speed of mixer rotation, geometrical arrangement *etc.*). The coefficients α , β , δ possesses only the non-negative values.

Eq. (3) is the linear homogeneous equation; its solution can be written in the integral form (see Appendix)

$$V(t) = \frac{\alpha - 2\gamma\delta}{\beta + 2\delta^2} + \exp [-(\beta + \delta^2)t - (\sqrt{2})\delta W(t)] .$$

$$\cdot \left\{ V(0) - \frac{\alpha - 2\gamma\delta}{\beta + 2\delta^2} - \frac{(\sqrt{2}(\alpha\delta + \gamma\beta))}{\beta + 2\delta^2} \int_0^t \exp [+(\beta + \delta^2)s + (\sqrt{2})\delta W(s)] dW(s) \right\} . \quad (4)$$

By substitution of this expression into Eq. (2) and by its integration the explicit expression for $X(t)$ can be formally obtained.

To Eqs (2) and (3) corresponds the Kolmogorov's diffusion equation⁵

$$\frac{\partial f'}{\partial t} + v \frac{\partial f'}{\partial x} + \frac{\partial}{\partial v} [(\alpha - \beta v) f'] - \frac{\partial^2}{\partial v^2} [(\gamma + \delta v)^2 f'] = 0, \quad (5)$$

where $f'(x, v; t | x^0, v^0)$ is the transitive probability density for functions $X(t)$ and $V(t)$ at $t > 0$ at the condition that in the moment $t = 0$ these functions have got the values x^0 and v^0 (ref.¹). By giving the corresponding initial and boundary conditions is uniquely determined the solution of Eq. (5) and by the procedure proposed earlier¹ it would be possible to obtain the dependence of the expected value of the scalar quantity (concentration or temperature) on time and position (*i.e.* on local coordinate x) in the mixer. But perhaps it is not possible to find the analytical solution of Eq. (5) in a general form; this problem would have to be solved numerically.

But it is possible to find the explicit expression for the distribution function of the particle velocity or its probability density; as results from Eq. (3) it will neither be a function of position and according to the assumption A4 nor a function of time. To relation (3) corresponds the Kolmogorov's equation⁵ which is here given with respect to the same assumption for the stationary case in the form

$$\frac{d}{dv} \left\{ (\alpha - \beta v) f_v - \frac{d}{dv} [(\gamma + \delta v)^2 f_v] \right\} = 0, \quad (6)$$

whose solution is the expression (see Appendix)

$$f_v(v) = \frac{1}{\Gamma(b)} \exp \left(- \frac{e}{v+g} \right) \left(\frac{e}{v+g} \right)^b \frac{1}{v+g}; \quad [v \geq -g], \quad (7)$$

$$b = (\beta + \delta^2)/\delta^2; \quad e = (\alpha\delta + \gamma\beta)/\delta^3; \quad g = \gamma/\delta$$

and $\Gamma(\cdot)$ is the gamma-function. Velocity distribution can be thus described by the gamma-distribution with the reciprocal argument.

The fact that distribution (7) depends only on the argument v enables to write with respect to the assumption A4 both the initial conditions of solution of relation (5) and formally the own solution in the form

$$\begin{aligned} f_{xv}(x, v; t) &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f'(x, v; t | x^0, v^0) \delta(x^0) f_v(v^0) dx^0 dv^0 = \\ &= f_{x|v}(x; t | v) f_v(v). \end{aligned} \quad (8)$$

In Eq. (8) is $\delta(\cdot)$ denoting the Dirac function, $f_{x|v}$ the conditioned probability density for the particle position $X(t)$ in the case when its velocity is just equal to v . Relations (7) and (8) make possible to find explicitly the moments of solution $f_{xv}(x, v; t)$ (see Appendix) which are uniquely determining the looked for distribution.

Here only the expressions for the first two moments are given which are needed for the next considerations: The expected value of the velocity \bar{v} as the stationary random function and its dispersion h_{vv} are given by the relations

$$\begin{aligned} \bar{v} &= E[V(t)] = \alpha/\beta, \\ h_{vv} &= \bar{v}^2 - \bar{v}^2 = (\beta/\alpha + \gamma/\delta)^2 \delta^2 / (\beta - \delta^2). \quad [\beta > \delta^2]. \end{aligned} \quad (9)$$

Similarly there holds for the expected value \bar{x} of the particle position and for its dispersion h_{xx} for the case that the particle in the moment $t = 0$ is just located in the point $x = 0$

$$\begin{aligned} \bar{x} &= \bar{v}t, \\ h_{xx} &= \bar{x}^2 - \bar{x}^2 = [\beta t - 1 + \exp(-\beta t)] h_{vv} / \beta^2. \end{aligned} \quad (10)$$

The covariance between the position and velocity can be expressed by the relation

$$h_{xv} = \bar{x}\bar{v} - \bar{x}\bar{v} = [1 - \exp(-\beta t)] h_{vv} / \beta. \quad (11)$$

Relations for Usual Chemical Engineering Models

We will now demonstrate that two models most frequently used in chemical engineering for description of flow systems – the dispersion model and cascade model of ideal mixers (at macroflow) – see *e.g.*⁶ – are the individual cases of the model here proposed and the corresponding equations result at certain simplifications of rela-

tions given in the last paragraph. We choose in total four simplifications and we observe the consequences each of them at first separately:

$$\text{Simplification I: } \delta \equiv 0$$

$$\text{Simplification II: } \gamma \equiv 0$$

$$\text{Simplification A: } t \ll 1/\beta$$

$$\text{Simplification B: } t \gg 1/\beta$$

I. In this case the stochastic differential Eq. (3) takes the form

$$dV(t) = [\alpha - \beta V(t)] dt - (\sqrt{2})\gamma dW(t), \quad (12)$$

into which can now be for $V(t)$ substituted from Eq. (2) so that we obtain the equation in total differentials

$$dV(t) = \alpha dt - \beta dX(t) - (\sqrt{2})\gamma dW(t), \quad (12a)$$

which can be easily integrated so that the explicit expression for position of the particle as a random function of time is obtained

$$X(t) = (\alpha/\beta)t - (1/\beta)[V(t) - V(0)] - (\sqrt{2})(\gamma/\beta) W(t). \quad (13)$$

It is possible to demonstrate (see Appendix) that by solution of Eq. (12) with regard to Eq. (4) — at stationary conditions is obtained the expression

$$V(t) - V(0) = -(\sqrt{2})\gamma \int_0^t \exp[-\beta(t-s)] dW(s). \quad (14)$$

The corresponding Kolmogorov's equation (5) can be at this simplification solved explicitly⁷ and the relation for the conditional probability density can be obtained from relation (8)

$$\lim_{\delta \rightarrow 0} f_{x|v}(x; t | v) = \{\sigma_x [2\pi(1-r^2)]^{1/2}\}^{-1} \cdot \exp\{-[2\sigma_x^2(1-r^2)]^{-1} [x - \bar{x} - r(\sigma_x/\sigma_v)(v - \bar{v})]^2\}. \quad (15)$$

Also solution of Eq. (6) is given by the limiting case of distribution (7)

$$\lim_{\delta \rightarrow 0} f_v(v) = [\sigma_v \sqrt{(2\pi)}]^{-1} \cdot \exp[-(v - \bar{v})^2/(2\sigma_v^2)] \quad (16)$$

and after substitution from Eqs (15) and (16) into the right hand side of relation (8) and by integration of this relation with respect to v we obtain also explicitly the limiting distribution f_x for position of the particle

$$\lim_{\delta \rightarrow 0} f_x(x; t) = [\sigma_x \sqrt{(2\pi)}]^{-1} \exp \left[- (x - \bar{v}t)^2 / (2\sigma_x^2) \right]. \quad (17)$$

The quantities $V(t)$ and $X(t)$ thus have normal distribution whose characteristics can be found as corresponding limits of moments from Eqs (9) to (11)

$$\begin{aligned} \sigma_v^2 &= \lim_{\delta \rightarrow 0} 2h_{vv} = 2\gamma^2/\beta, \\ \sigma_x^2 &= \lim_{\delta \rightarrow 0} 2h_{xx} = [\beta t - 1 + \exp(-\beta t)] \sigma_v^2/\beta^2, \\ r^2 &= \lim_{\delta \rightarrow 0} \frac{h_{xv}^2}{h_{xx}h_{vv}} = \frac{[1 - \exp(-\beta t)]^2}{\beta t - 1 + \exp(-\beta t)}. \end{aligned} \quad (18)$$

Equation (17) is as has been demonstrated earlier¹ directly proportional to the expected value of scalar quantity (concentration or temperature) as the function of position and time in the flow mixer.

II. The parameter g in Eq. (7) is in this case equal to zero, which means that values of velocity can be only non-negative. This fact makes possible to describe by use of Eq. (8) also the "closed" flow mixers without special boundary conditions in the point $x = 0$ and $x = l$ (see Fig. 1) while in other cases (*i.e.* for $\gamma > 0$) the fundamental solution (relation (8)) can be used only for the case of the "open" *i.e.* infinitely long mixer. (The problem of boundary conditions will not be considered here).

For the case which is here considered (*i.e.* $\gamma = 0$) the residence time T of the particle in the mixer *i.e.* the time in which the particle passes from the point $x = 0$ to the point $x = l$ can be obviously easily defined. It is obviously the random variable determined as the upper integration limit at integration of relation (2)

$$1 = \int_0^T V(t) dt \quad (19)$$

with the probability density

$$f_t(t) = \lim_{\Delta t \rightarrow 0} (1/\Delta t) P\{t \leq T < t + \Delta t\}. \quad (20)$$

A. By introducing the simplification A, *i.e.* verification of validity of general relations characterizing the "behaviour" of the particle in short time intervals from their appearance in the mixer leads to the considerable simplification of integration

of Eq. (2)

$$X(t) = \int_0^t V(s) ds = V(\xi) \int_0^t ds \approx V(0) t; \quad [0 < \xi < t \ll 1/\beta]. \quad (21)$$

The position of the particle is thus – though only approximately – directly proportional to time. In this case it is possible to find the distribution $X(t)$ by the method of randomization of parameter⁸ so that we integrate at first Eq. (2a) as an ordinary one (deterministic) differential equation at constant velocity v

$$dx(t)/dt = v; \quad [x(0) = 0] \quad (2a)$$

and then we consider the velocity as the random parameter with distribution of the random variable $V(0)$. To relation (2a) corresponds a simple partial differential first order equation

$$\frac{\partial f'}{\partial t} + v \frac{\partial f'}{\partial x} = 0, \quad (5a)$$

whose solution is the Dirac function so that Eq. (8) can be easily integrated at simplification A with regard to Eq. (7) with the result

$$\begin{aligned} f_x(x; t) &= \int_{-g}^{\infty} f_{x/v}(x; t | v) f_v(v) dv = \\ &= \int_{-g}^{\infty} \delta(x - vt) \frac{1}{\Gamma(b)} \exp\left(-\frac{e}{v+g}\right) \left(\frac{e}{v+g}\right)^b \frac{dv}{v+g} = \\ &= \frac{1}{\Gamma(b)} \exp\left(-\frac{et}{x+gt}\right) \left(\frac{et}{x+gt}\right)^b \frac{1}{x+gt}, \quad [0 < t \ll 1/\beta], \end{aligned} \quad (22)$$

which is the probability density of the phenomena that the particle will just appear in the interval $[x, x + dx)$ in the moment t not far from the moment of particle entrance into the mixer.

Note: From Eq. (10) it is obvious that the expected value of function $X(t)$ is proportional to time and the variance is at the considered condition proportional to the second power of time

$$\begin{aligned} \bar{x} &= \bar{v}t \\ h_{xx} &= h_{vv}t^2/2. \quad [t \ll 1/\beta] \end{aligned} \quad (23a)$$

B. Simplification of B is not supplying in otherwise general case a more detailed information in the analytical form; the corresponding analytical solution for probability density in Eq. (8) was not found. It is only obvious (see relation (10)) that the growth of variance in this case is linear with time

$$\begin{aligned}\bar{x} &= \bar{v}t \\ h_{xx} &= h_{vv}t/\beta \cdot [t \gg 1/\beta].\end{aligned}\quad (23b)$$

Now we will consider some combinations of individual simplifications: IB. We introduce the simplification I and simplification B. From Eq. (13) it is obvious that the random motion of the particle (quantity $X(t)$) or from there resulting random changes of temperature or concentration¹ is conditioned by random changes of velocity (see the second right hand side term in Eq. (13)) and directly by the „randomisation” factor — stochastic Wiener process which is included in the third right hand side term of the same equation. We will demonstrate that it is possible to neglect the effect of random velocity changes with regard to random pulsations of the Wiener process with the greater probability the longer time t has elapsed from the beginning of the studied operation. The mentioned second term of Eq. (13) can be expressed by the stochastic integral from Eq. (14) and the third term is the integration of only the stochastic differential. We can compare both these integrals with respect to probability that their values exceed some chosen limit $\gamma(\sqrt{2t})$ (see Appendix).

$$P \left\{ \left| \int_0^t (\sqrt{2})\gamma \exp[-\beta(t-s)] dW(s) \right| > \gamma \sqrt{2t} \right\} \leq 1/(\beta t) \quad (24a)$$

$$P \left\{ \left| \int_0^t (\sqrt{2})\gamma dW(s) \right| > \gamma \sqrt{2t} \right\} \leq 1. \quad (24b)$$

It is possible to say that the third right hand side term in Eq. (13) roughly increases with the square root of time while the probability of occurrence of the equally large velocity pulsation can be at long time intervals neglected. Thus at the considered simplifications the second term in Eq. (13) can be neglected together formally with the left hand side of Eq. (12a) so that the relation holds

$$dX(t) = (\alpha/\beta) dt - (\sqrt{2})(\gamma/\beta) dW(t). \quad [t \gg 1/\beta] \quad (25)$$

But the given differentials do not correctly correspond to the definition of stochastic differential⁹.

To relation (25) corresponds the Kolmogorov's equation

$$\frac{\partial f'_x}{\partial t} + \frac{\alpha}{\beta} \frac{\partial f'_x}{\partial x} - \left(\frac{\gamma}{\beta}\right)^2 \frac{\partial^2 f'}{\partial x^2} = 0, \quad (26)$$

which is the usual equation of the unidimensional diffusion. The coefficient $(\gamma/\beta)^2$ has the significance of the coefficient of axial dispersion or of turbulent diffusivity as the Wiener process in Eq. (25) is in the frame of the general model¹ the reason of turbulent pulsations. (Molecular diffusion as is stated in the introduction of this paper is in all these considerations neglected).

IIA. We introduce the simplification II together with the simplification A. For this case it is easily possible to find the distribution function as the corresponding probability density of residence time T in the mixer, defined by Eq. (19). The usual procedure¹⁰ is prescribed by equation

$$f_i(t) = - \frac{d}{dt} \int_0^l f_x(x; t) dx, \quad (27)$$

but it requires formulation of the boundary conditions at the ends of the interval $[0, l]$. In our case a more simple procedure may be adopted as the velocity — *i.e.* the function $V(t)$ is non-negative and thus it is not necessary to take the boundary conditions into consideration. Moreover, from Eqs (19) and (21) results the relation

$$T = l/V(0); \quad [0 < t \ll 1/\beta], \quad (28)$$

which is the relation between the residence time and particle velocity and is thus a monotonous function. In this case it is possible on basis of the known probability density of velocity to find easily the probability density of residence time¹¹

$$f_i(t) = f_v(l/t) |dv/dt|. \quad [t = l/v]. \quad (29)$$

In Eq. (7) we thus use $g = 0$ and we also define parameter κ :

$$a \equiv e/(lb) = \alpha/[(\beta + \delta^2) l] \quad (30)$$

so that we obtain after performing the operations in Eq. (29) the looked for probability density

$$f_i(t) = \frac{\kappa b}{\Gamma(b)} \exp(-\kappa bt) (\kappa bt)^{b-1}. \quad (31)$$

It is possible to find easily the first two moments of this distribution

$$\begin{aligned}\bar{i} &= E[T] = 1/\kappa, \\ h_{ii} &= \overline{i^2} - \bar{i}^2 = 1/(\kappa^2 b).\end{aligned}\quad (32)$$

It is immediately obvious that in the case when b is a natural number Eq. (31) takes the form of a known relation for distribution of residence times in the cascade of ideal mixers. In the case $b = 1$ the equation becomes the relation for the ideal mixer.

Remark: Simultaneous application of simplification I and II leads to the relation for plug flow as *e.g.* in Eq. (3) the term with the "randomising" Wiener process disappears. Relations (2) and (3) are ordinary differential equations and the corresponding probability density is the Dirac's function

$$f_x(x; t) = \delta(x - t\alpha/\beta). \quad (33)$$

DISCUSSION

Relations derived in the last part of this study demonstrate the fact that application of stochastic differential equations has a wide application in description of chemical engineering operations. A similar solution of the problem has been attempted by King^{12,13} who considered the flow mixer as a linear system with the stochastic transfer function with the Gauss and gamma-perturbations. The physical significance of relations which he obtained was to a certain degree depreciated by a faulty use of parameter A *e.g.* in Eq. (1a) in his second paper¹³ which the autor wrongly considered to be the random residence time although it was from the same equation obvious that it had the dimension of reciprocal time.

Note: In mathematic operations is King applying the Stratonovich's method of calculation; in our study we use the procedure according to Ito which we consider to be more adequate as concerns the physical significance of description; the difference between the both calculation methods has been already explained¹⁴ in the chemical engineering literature.

The model we have proposed enables on the contrary an obvious physical explanation also from the point of view of spreading the scalar quantity (concentration or temperature) in liquid whose particles (*i.e.* small volumes) are moving with random velocities $V(t)$. The model was from the general point of view discussed both in our recent study¹ and in a concrete form in this paper in the discussion of individual assumptions. The statement that the random force described by the last term in Eq. (3) is the cause of turbulent pulsations is beside others also supported by the fact that the limiting values of dispersions in short and long time intervals (second from Eqs (23a) and (23b)) are in agreement with the relations given in the general theory of turbulence¹⁵.

In Eq. (3) there are given the random forces (actually the intensity of impulse of these forces is concerned): One of them is proportional to velocity — $\delta V(t)$ — and may be considered to be the cause of turbulence which originated by liquid flow through the mixer *i.e.* by interaction of flowing liquid with its walls and solid particles. In the diffusion Eq. (5) is the corresponding term equal to the second power of velocity which is in agreement with the familiar relation for the hydraulic resistance in turbulent flow. The second term — $\gamma dW(t)$ — is independent either of position or velocity which is due to moving mechanical parts *e.g.* rotary mixers, pulsing units *etc.* This mechanical action is then the cause of the velocity pulsation which is oriented against the main stream.

The model here proposed makes also possible to limit the region of validity of the models usually used in chemical engineering *e.g.* their discussion from more general positions:

a) *Dispersion model* (Eq. (26)) holds only for longer time intervals (or longer mixers) *i.e.* for cases where there are already no transient effect. Thus it is not correct from the point of view of our concept to try to describe the ideal mixer by use of the dispersion model (see *e.g.*¹⁶) *i.e.* to try to express by this model the behaviour of the system also in short time intervals.

Note: But it would be formally possible to correct the “usual” equation of uni-dimensional diffusion for all time intervals $t > 0$: it is possible to demonstrate that Eq. (17) with respect to Eq. (18) is the solution of diffusion equation in which is the dispersion coefficient a function of time

$$\frac{\partial f_x}{\partial t} + \bar{v} \frac{\partial f_x}{\partial x} - \frac{\sigma_v^2}{2\beta} [1 - \exp(-\beta t)] \frac{\partial^2 f_x}{\partial x^2} = 0. \quad (34)$$

b) *Model of the “cascade of ideal mixers”* (relation (31)) makes possible on the contrary the description of transfer phenomena but it is not suitable for description of longer operations. Eq. (31) is the gamma-distribution which holds for each value b greater or equal to one while its both parameters have from the point of view of the proposed model an obvious physical significance: the parameter κ , introduced by Eq. (30) is as results from the first Eq. (32) the reciprocal mean residence time of the particle in the mixer and is obviously the greater, the greater is the active force characterized by the coefficient α . The laminar and turbulent resistance to the motion (expressed here by the coefficients β and δ) on the contrary decrease the value of this parameter, *i.e.* they prolong the mean residence time. The parameter b defined by Eq. (7) represents the ratio of the total resistance against the particle motion to the turbulent resistance. It is obvious that in the case the laminar resistance can be neglected (*i.e.* if $\beta \ll \delta^2$) the coefficient b converges to one (*i.e.* the mixer is approaching by its character the ideal mixer) in the reverse case (*i.e.* for plug flow) it increases to infinity.

Thus according to this concept – the gamma distribution of the residence time in the mixer with parameter b which becomes noninteger values is not of the purely mathematic or empirical model as is quoted by Wen and Fan¹⁷. A physical interpretation of the gamma distribution has been already attempted from other positions in our recent study¹⁸ where also some experiments were mentioned confirming its suitability at description of residence time distributions. There was also determined the effect of experimental conditions on parameters of the model.

c) *Character of flow in the mixer.* We demonstrate, from the point of view of calculation of conversion in the chemical reactor, that the resulting probability density (Eq. (31)) corresponds to the description of the flow mixer at macroflow. We again use the method of randomization of the parameter.

We write Eq. (5a) for a system of particles¹ and assume validity of the law of large numbers *i.e.* we interchange the probability density for the occurrence of one particle by the concentration c of these particles. We moreover assume that the number of these particles is changing due to the (isothermal) chemical reaction:

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} + \Phi(c) = 0, \quad (35)$$

where $\Phi(c)$ is the reaction rate.

In the case the second term in Eq. (35) is equal to zero the equation describes the time dependence of the reaction rate in the ideally mixed batch reactor. On the contrary if the first term is equal to zero the plug flow reactor is concerned where the change of concentration with position is here formally equal to the change of concentration with time with the exception of the scale of the independent variable which is given by the reciprocal value of velocity. Thus we can approximately interchange the requirement of very short time interval for randomisation of the velocity, by the requirement of very short length of the mixer $t = l/v \ll 1/\beta$.

Solution of Eq. (35) for plug flow is the relation

$$\int_{c_0}^{c_1} \frac{dc}{\Phi(c)} \equiv F(c_1) = -l/v, \quad (36)$$

where c_1 is the concentration at the outlet and c_0 at the inlet of reactor. From the left hand side of Eq. (36) is explicitly expressed c_1 and the relation for conversion Y can be written¹⁹

$$Y = 1 - c_1/c_0 = 1 - F^{-1}(-l/v)/c_0, \quad (37)$$

where $F^{-1}(\cdot)$ is the inversion function to the integral in Eq. (36).

Let us now assume that the velocity v is the random parameter with the probability density $\varphi_v(v)$ situated on the positive part of the axis (i.e. for $v \geq 0$). It is obvious that the probability density, defined by Eq. (7) for values of parameter g equal to zero is a special case of distribution $\varphi_v(v)$. Now we randomize the parameter v in Eq. (37) and obtain equation for the average conversion

$$\bar{Y} = 1 - \int_0^{\infty} F^{-1}(-l/v) \varphi_v(v) dv. \quad (38)$$

As at the given conditions Eq. (28) holds, it is possible to interchange the distribution of velocities by the distribution of residence times according to the procedure suggested by Eq. (29) and finally the relation for conversion is obtained

$$\bar{Y} = 1 - \int_0^{\infty} F^{-1}(-t) \varphi_v(l/t) \left| \frac{dv}{dt} \right| dt = 1 - \int_0^{\infty} \frac{c(t)}{c_0} \varphi_t(t) dt, \quad (39)$$

where $c(t)$ is with respect to the assumption following Eq. (35), the concentration in the batch reactor and $\varphi_t(t)$ the probability density of residence times in the flow reactor which is uniquely determined by the function $\varphi_v(v)$. The shape of function $\varphi_t(t)$ can be easily determined by the empirical method of measurement of response to the δ -impulse.

It is possible to calculate the conversion of reactor by use of Eq. (39) for macroflow¹⁹. With respect to function $f_t(t)$ which is the special case of function $\varphi_t(t)$, Eq. (31) describes the residence time distribution in the reactor at macroflow. It is possible to prove easily (see Appendix) that for first and second order reactions, the familiar relations for calculation of conversion in the ideal mixer¹⁹ are obtained

$$\begin{aligned} \bar{Y} &= 1 - 1/(1 + k_1 \bar{t}) & [\phi(c) = k_1 c] \\ \bar{Y} &= 1 - \omega \exp(\omega) \text{ei}(\omega), & [\phi(c) = k_2 c^2] \end{aligned} \quad (40)$$

where $\text{ei}(\cdot)$ denotes the integral exponential, k_1, k_2 reaction rate constants and parameter ω is given by the relation

$$\omega = e/(k_2 c_0 l).$$

d) *Relation between the mean velocity and mean residence time of the particle in the mixer.* From Eq. (28) results that the residence time of particles is obviously, at the given conditions, indirectly proportional to its velocity. But as is obvious from Eqs (30), (32) and (9) this statement does not hold for mean values of these quantities between which the relation holds

$$\bar{t} = l/\bar{v} + \delta^2 l/\alpha.$$

Thus the question arises which of these quantities can be expressed by the macroscopic characteristic *i.e.* by the volumetric flow rate \dot{V} of liquid through the systems.

From simplification II and simplification B results that the mixer must be fully filled by the considered stream-pipes while through each of them liquid flows with a constant velocity v , accurately in the given stream-pipe the value of velocity can vary in the interval $[v, v + dv)$. The infinitesimal volumetric flow rate through such stream-pipe can be expressed by the relation

$$d\dot{V}(v) = \dot{V} \varphi_v(v) dv, \quad (41)$$

while the probability density $\varphi_v(v)$ is defined by the statement preceding Eq. (38). Evidently from the equation of continuity can be inferred:

$$d\dot{V}(v) = v dS(v), \quad (42)$$

where dS is the infinitesimal cross-sectional area of the corresponding stream-pipe. Both right hand sides of Eqs (41) and (42) are equal. After separation of variables and integration the relation is obtained

$$\int_0^{\infty} (1/v) \varphi_v(v) dv = S/\dot{V}. \quad (43)$$

Physical significance of the procedure becomes more obvious when integration is substituted by summation *i.e.* if a system of n particles with the same mass is considered. Then the "linear" calculation of the mean velocity

$$\bar{v} = \sum_{i=1}^n v_i = \sum_{i=1}^n l_i/t \quad [t = \text{const.}] \quad (44)$$

determines the velocity of the inertia centre (centre of gravity) of the system of particles in the given moment t , while the symbol l_i determines the length of trajectory of the i -th particle. The "reciprocal" calculation which is approximating the integral in Eq. (43) is given by the relation

$$\overline{(1/v)} = \sum_{i=1}^n 1/v_i = \sum_{i=1}^n t_i/l = \bar{t}/l \quad [l = \text{const.}], \quad (45)$$

where t_i is the residence time of the i -th particle in the mixer with the constant length l .

The liquid flow rate through the mixer is thus directly proportional to the mean residence time of liquid in the mixer.

Note: It is worth mentioning that the simple triangular distribution with the probability density

$$\varphi_v(v) = mv, \quad [0 \leq v \leq v_{\max}], \quad (46)$$

where m is the constant and v_{\max} the upper limit of velocity, leads, at the use of the proposed procedure, to the familiar parabolic velocity profiles in the pipe with the circular cross section at laminar flow²⁰

$$v/v_{\max} = 1 - \varrho^2/R^2, \quad [0 \leq \varrho \leq R] \quad (47)$$

where R is the radius of the pipe (see Appendix).

Finally it is possible to conclude that the model here proposed makes possible to judge from a more general point of view the "unidimensional" models most frequently used for description of reactors and mixers. It is thus possible to assume that they enable description of some situations in which the proposed models do fail. Of course it includes one parameter more and in the general case it is not supplying the analytical solution.

APPENDIX

a) *Solution of the stochastic differential* Eq. (3) is given in literature²¹ for a more general case when the coefficients α , β , γ , δ are functions of time. In our case is this solution simplified to the form

$$\begin{aligned} V(t) = & \exp [-(\beta + \delta^2) t - (\sqrt{2})\delta W(t)] \{ V(0) + (\alpha - 2\gamma\delta) \cdot \\ & \int_0^t \exp [(\beta + \delta^2) s + (\sqrt{2})\delta W(s)] ds - \\ & - (\sqrt{2})\gamma \int_0^t \exp [(\beta + \delta^2) s + (\sqrt{2})\delta W(s)] dW(s) \}. \end{aligned} \quad (D-1)$$

According to the rules of calculus with stochastic differentials²² there holds for the first integral in Eq. (D-1)

$$\begin{aligned} & (\beta + 2\delta^2) \int_0^t \exp [(\beta + \delta^2) s + (\sqrt{2})\delta W(s)] ds = \\ & = \exp [(\beta + \delta^2) t + (\sqrt{2})\delta W(t)] - 1 - (\sqrt{2})\delta \int_0^t \exp \end{aligned}$$

$$\cdot [(\beta + \delta^2)s + (\sqrt{2})\delta W(s)] dW(s). \quad (D-2)$$

After substitution from Eq. (D-2) into Eq. (D-1) and algebraic arrangements we obtain Eq. (4) given earlier in this paper, which reduces for $\delta = 0$ to the form

$$V(t) = \alpha/\beta + \exp(-\beta t) [V(0) - \alpha/\beta - (\sqrt{2})\gamma \int_0^t \exp(\beta s) dW(s)]. \quad (D-3)$$

To be able to find the relation for the stationary form of function $V(t)$ we move the time axis to the left for an interval τ , which will increase to infinity. We obtain

$$\begin{aligned} \lim_{\tau \rightarrow \infty} [V(t + \tau) - V(\tau)] &= \lim_{\tau \rightarrow \infty} \{ \exp[-\beta(t + \tau)] \cdot [V(0) - \alpha/\beta - \\ &- (\sqrt{2})\gamma \int_0^{t+\tau} \exp(\beta s) dW(s)] - \exp(-\beta\tau) \cdot \\ &\cdot [V(0) - \alpha/\beta - (\sqrt{2})\gamma \int_0^\tau \exp(\beta s) dW(s)] \}. \end{aligned} \quad (D-4)$$

The functions $\exp(-\beta\tau)$ are converging to zero so that the effect of initial conditions disappears. If we move again the origin of the time axis into the moment $\tau = 0$ we obtain

$$V(t) - V(0) = -(\sqrt{2})\gamma \exp(-\beta t) \int_0^t \exp(\beta s) dW(s), \quad [\text{steady state}] \quad (D-5)$$

which after arrangement leads to Eq. (14).

The integral in (D-5) is now compared with the integral

$$(\sqrt{2})\gamma W(t) = \int_0^t (\sqrt{2})\gamma dW(s), \quad (D-6)$$

which is the last right hand side term of Eq. (13). In general the relation^{2,3} holds

$$P \left\{ \left| \int_0^t f(s) dW(s) \right| > p \right\} \leq P \left\{ \int_0^t f^2(s) ds > q \right\} + q/p^2, \quad (D-7)$$

where f is the subintegral function and p, q are suitably selected terms. Into this equation we at first substitute from (D-5) while we select $p = \gamma(\sqrt{2}t)$ so that it holds

$$\begin{aligned}
 P \left\{ \left| \int_0^t (\sqrt{2})\gamma \exp[-\beta(t-s)] dW(s) \right| > \gamma \sqrt{(2t)} \right\} &\leq \\
 \leq P \left\{ 2\gamma^2 \int_0^t \exp[-2\beta(t-s)] ds > q \right\} + q/(2\gamma^2 t) &= \\
 = P\{(\gamma^2/\beta) [1 - \exp(-2\beta t)] > q\} + q/(2\gamma^2 t). &\quad (D-8)
 \end{aligned}$$

It is obvious that the probability on the right hand side of relation (D-8) is equal to zero if we choose the quantity $q = 2\gamma^2/\beta$ which leads to the relation (24a). Similarly, we obtain after substitution from Eq. (D-6) into (D-7)

$$P \left\{ \left| \int_0^t (\sqrt{2})\gamma dW(s) \right| > \gamma \sqrt{(2t)} \right\} \leq P \left\{ 2\gamma^2 \int_0^t ds > q \right\} + q/(2\gamma^2 t). \quad (D-9)$$

If we put $q = 2\gamma^2 t$ the probability on the right hand side of Eq. (D-9) is equal to zero so that we obtain Eq. (24b).

b) *Solution corresponding to the Kolmogorov's equation and corresponding moments.* At the assumption that the relation holds,

$$\lim_{v \rightarrow \infty} v f_v(v) = \lim_{v \rightarrow \infty} v^2 \frac{df_v}{dv} = 0$$

is the first integral in Eq. (6) equal to zero so that the relation is obtained

$$(\alpha - \beta v) f_v = \frac{d}{dv} [(\gamma + \delta v)^2 f_v]. \quad (D-10)$$

If we substitute $u = v + \gamma/\delta$ we obtain the solution

$$f_v(u) = K \exp(-e/u) 1/u^{b+1}, \quad (D-11)$$

where the parameters of solution b, e were defined by Eq. (7). The integration constant K is determined from the condition

$$\int_0^\infty f_v(u) du = 1.$$

The probability density $f_v(\cdot)$ is obviously defined only for nonnegative values of the quantity u . After reverse substitution for u the relation (7) is obtained.

It is also possible to prove that the n -th central moment of the considered distribu-

tion is given by the relation

$$\int_{-g}^{\infty} (v - \bar{v})^n f_v(v) dv = \frac{(\alpha/\beta + \gamma/\delta)^n}{\Gamma(b)} \sum_{i=0}^n [(-1)^i (b-1)^{n-1} \Gamma(b-n+i)], \quad [b > n] \quad (D-12)$$

where \bar{v} is the first moment of the same distribution, which is given in the first Eq. (9).

An arbitrary moment of order $m+n$ of $f_{xv}(x, v; t)$ from Eq. (8) is obtained with respect to Eq. (5)

$$\begin{aligned} \frac{\partial}{\partial t} \int_{-\infty}^{+\infty} \int_{-g}^{+\infty} x^m v^n f_{xv} dv dx + \int_{-\infty}^{+\infty} \int_{-g}^{+\infty} x^{m+1} v^n \frac{\partial f_{xv}}{\partial x} dx dx + \\ + \int_{-\infty}^{+\infty} \int_{-g}^{+\infty} x^m v^n \frac{\partial}{\partial v} [(\alpha - \beta v) f_{xv}] dv dx - \\ - \int_{-\infty}^{+\infty} \int_{-g}^{+\infty} x^m v^n \frac{\partial^2}{\partial v^2} [(\gamma + \delta v)^2 f_{xv}] dv dx = 0. \end{aligned} \quad (D-13)$$

At integration we assume that all primitive functions do converge to zero at the increase of the corresponding arguments to infinity. For second moments we then obtain the relations

$$\begin{aligned} \bar{v}^2 &= (\alpha/\beta + \gamma/\delta)^2 \beta/(\beta - \delta^2), \quad (D-14) \\ d\bar{v}x/dt - \bar{v}^2 - \alpha\bar{x} + \beta\bar{v}\bar{x} &= 0, \\ \frac{d\bar{x}^2}{dt} - 2\bar{v}\bar{x} &= 0. \end{aligned}$$

The last two equations are obtained at the initial conditions $\bar{v}\bar{x}(0) = \bar{x}^2(0) = 0$, as the position of the particle in the initial moment is independent of its velocity.

c) *Calculation of conversion by randomisation of the parameter.* In Eq. (36) we put $\Phi(c) = k_1 c$ and we obtain the familiar relation

$$c_1/c_0 = \exp(-k_1 l/v). \quad (D-15)$$

From Eq. (D-15) and from relation (7) at $g = 0$ we substitute into Eq. (38) for calculation of conversion

$$\bar{Y} = 1 - \int_0^{\infty} \exp\left(-\frac{k_1 l}{v}\right) \cdot \frac{1}{\Gamma(b)} \exp\left(-\frac{e}{v}\right) \left(\frac{e}{v}\right)^{b-1} \frac{e}{v^2} dv. \quad (D-16)$$

After introduction of the integration variable $t = l/v$ and integration the relation is obtained

$$\bar{Y} = 1 - \left(\frac{e}{e + k_1 l} \right)^b = 1 - \left(\frac{\chi b}{\chi b + k_1} \right)^b, \quad (D-17)$$

with regard to Eq. (30). For ideal mixer we put $b = 1$ and from the first of Eqs (32) results the first relation (40).

If we use $\Phi(c) = k_2 c^2$, we obtain the familiar relation

$$c_1/c_0 = [1 + lk_2 c_0/v]^{-1}. \quad (D-18)$$

By randomisation in the same way and with $b = 1$ i.e. when we consider only the ideal mixer we obtain

$$\bar{Y} = 1 - \int_0^\infty [1 + lk_2 c_0/v]^{-1} \exp(-e/v) (e/v^2) dv. \quad (D-19)$$

By introduction of a new integration variable $y = 1 + k_2 c_0 l/v$ the relation is obtained

$$\bar{Y} = 1 - \frac{e}{k_2 c_0 l} \exp\left(\frac{e}{k_2 c_0 l}\right) \int_1^\infty \exp\left(-\frac{ye}{k_2 c_0 l}\right) \frac{dy}{y}. \quad (D-20)$$

If we use $\omega = e/(k_2 c_0 l)$ we obtain the right hand side of Eq. (40).

d) *Velocity profile in the pipe of circular cross-section.* We evaluate at first the constant m in Eq. (46)

$$1 = m \int_0^{v_{\max}} v dv = mv_{\max}^2/2$$

and substitute into Eq. (41)

$$d\dot{V}(v) = \dot{V}(2v/v_{\max}^2) dv. \quad (D-21)$$

At the assumption of cylindrical symmetry in the annulus with the infinitesimal area $dS = 2\pi q dq$ the liquid flows with the same velocity. If we substitute this area into Eq. (42) and the used expression is put equal to the right hand side of relation (D-21) we obtain

$$\dot{V}(2v/v_{\max}^2) dv = -2\pi q v dq. \quad (D-22)$$

The negative sign denotes that the velocity decreases with increasing radius. After separation of variables we solve this differential equation for boundary conditions $v(R) = 0$, so that we obtain

$$(v/v_{\max}^2) \dot{V} = (\pi/2)(R^2 - \rho^2). \quad (D-23)$$

In Eq. (D-23) we put $v(0) = v_{\max}$ and we express the volumetric flow rate \dot{V} . So we obtain Eq. (47).

LIST OF SYMBOLS

- b parameter in Eq. (7) characterizing the ratio of total resistance with respect to the turbulent resistance to motion of the particle
- c concentration, mol m^{-3}
- e parameter in Eq. (7), ms^{-1}
- F^{-1} inversion function
- f probability density
- g parameter in Eq. (7) — minimum velocity, ms^{-1}
- $g()$ function characterizing a nonrandom force, ms^{-2}
- h second central distribution moment
- $h()$ function characterizing a random force, $\text{ms}^{-3/2}$
- k reaction rate constant
- l length of mixer, m
- n number of particles in the system
- R radius of pipe, m
- r correlation coefficient
- S cross sectional area of the mixer, m^2
- T residence time in the mixer, s
- t time, s
- V random velocity, ms^{-1}
- v velocity, ms^{-1}
- \dot{V} volumetric flow rate, $\text{m}^3 \text{s}^{-1}$
- W Wiener process, $\text{s}^{1/2}$
- X random position of particles, m
- x local (axial) coordinate, m
- Y degree of conversion
- α parameter in Eq. (3) characterizing the active force, ms^{-2}
- β parameter in Eq. (3), characterizing the force of laminar friction s^{-1}
- γ parameter in Eq. (3), characterizing the turbulence due to mechanical motion, $\text{ms}^{-3/2}$,
- δ parameter in Eq. (3) characterizing turbulence due to liquid flow, $\text{s}^{-1/2}$

Φ	chemical reaction rate, mol m ⁻³ s ⁻¹
φ	probability density for non-negative values
κ	parameter in Eq. (31) reciprocal value of mean residence time s ⁻¹
σ^2	variance of normal distribution
ϱ	radial coordinate, m
\bar{u}	mean (expected) value of quantity u

Subscripts

i	related to the i -th element
t	related to time
v	related to velocity
x	related to position
0	related to the inlet of the mixer
l	related to the outlet of the mixer
1	related to the first order reaction
2	related to the second order reaction

The Used Special Functions

$$ei(y) = \int_1^{\infty} \exp(-yu) \frac{du}{u} \quad \text{integral exponential}$$

$$\Gamma(y) = \int_0^{\infty} \exp(-u) u^{y-1} du \quad \text{gamma function}$$

$$\delta(y) = \lim_{\sigma \rightarrow 0} \frac{1}{\sqrt{(2\pi)\sigma}} \exp\left(-\frac{y^2}{2\sigma^2}\right) \quad \text{Dirac function}$$

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