Turbulent micromixing in chemical reactors — a review

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Abstract

The idea of micromixing, its definition and measures are outlined. The concepts of mixing environments and mixing earliness are presented. The paper concentrates on the effects of turbulent mixing of incompressible fluids in single-phase systems on the course of chemical reactions. The processes of turbulent micromixing are discussed in detail: the fluid mechanical interpretation of turbulent micromixing (effect of fluid element deformation on the acceleration of molecular diffusion, engulfing of environment, inertial-convective disintegration of large eddies and local intermittency) is presented. It is concluded that stretching of material elements and vortices, accompanied by molecular diffusion results in the growth of the mixing zones. The growth of the zone mixed on the molecular scale is a characteristic feature of micromixing and should be included in micromixing modelling. The characteristic time constants for the consecutive stages of mixing are presented and compared with the characteristic time for chemical reaction — the numerical criteria are outlined. The two approaches, i.e. eulerian and lagrangian, are described; it is shown that each requires different methods of description and generates specific problems (closure problem, problem of environment). The applications of the micromixing theory to the most important fields of industrial practice, such as complex reactions, precipitations and polymerizations, are outlined.

Keywords: Turbulent micromixing; Reactors; Micromixing; Incompressible fluids

1. Introduction: notion and definition of turbulent micromixing

Chemical reaction is a molecular-level process and only mixing on the molecular scale can affect its course directly. Micromixing theory is concerned with those features of mixing which cause the attainment of homogeneity on the molecular level, i.e. with the reduction of the scale of unmixed blobs of fluid by breakage and deformation, and with final mixing by molecular diffusion. The chemical reaction kinetic equations can be incorporated into mixing models only locally; this can be achieved by using micromixing models.

Micromixing affects the course of fast and instantaneous chemical reactions (single and complex), changing their conversion and selectivity; these effects are observed in reactive mixing of gases and liquids in both turbulent and laminar flows. The problem is of technological importance in combustion, jet propulsion, chemical lasers, chemical reactors and environmental studies.

In chemical reactors, micromixing can change the product properties and, hence, the product quality. Such a case is observed in a precipitation process, where the size distribution of the precipitating particles is dependent on the mixing [1,2]; similarly, mixing can control the molecular weight distribution of polymer molecules [3–5].

Further examples of processes dependent on mixing on the molecular scale can be given, such as freezing or quenching of the reaction composition, nitric oxide formation in combustors, reactions in highly viscous liquids, biological reactors, etc. This paper discusses the effects of turbulent mixing of incompressible fluids in single-phase systems on the course of homogeneous chemical reactions.

The process of turbulent mixing is very complex. In this complex process, one can distinguish and describe some simpler stages of mixing [6,7], i.e. macromixing, mesomixing and micromixing. The process of mixing on the scale of the whole vessel is called 'macromixing'. This determines the environment concentrations for
mesomixing and micromixing, and conveys fluids that are undergoing meso- and micromixing through environments where the turbulence properties vary.

Mesomixing [7] reflects the coarse-scale turbulent exchange between the fresh feed and its surroundings; a fast chemical reaction is usually localized near the feed point, forming a plume of fresh feed. This plume is of a coarse scale relative to the micromixing scales but is of a fine scale relative to the scale of the system. Spatial evolution of the plume can be identified with the process of turbulent diffusion.

Another aspect of mesomixing is related to the inertial-convective process of disintegration of large eddies. Mixing by inertial-convective disintegration of large eddies proceeds without any direct effect of molecular mixing. However, there is an effect of the inertial-convective mixing on the micromixing process. The simplest models [8,9] of inertial-convective mixing assume erosive diminishing of the blobs of fresh feed, followed by micromixing — in the more complex models [10,11], the large eddies of the inertial-convective subrange determine the environment for micromixing.

Micromixing — the last of the turbulent mixing stages — consists of the viscous-convective deformation of fluid elements, followed by molecular diffusion. The effect of acceleration of the molecular diffusion by the viscous-convective process is considered to be the important feature of micromixing [12]. The process of micromixing will be considered in detail in the next sections of this paper.

2. Mixing environment and mixing earliness

To describe the degree of segregation $J_a$ defined by the age $a_p$ of the fluid at a point, Danckwerts [13] introduced the concepts of a "point", "concentration at a point" and the "age of the fluid at a point", such that

$$J_a = \var{\alpha_p} = \frac{(\alpha_p - \bar{\alpha})^2}{(\alpha - \bar{\alpha})^2}$$

where $\bar{\alpha}$ is the age of the molecules. Using this definition, Danckwerts [13] and Zwietering [14] were able to define two limiting cases of micromixing: complete segregation (mass exchange among points of different age is excluded); maximum mixedness, when mass exchange is instantaneous among those points which, consistent with the limitations of the residence time distribution (RTD), can exchange mass with each other (hence, the "points" of the same mean residual lifetime are mixed on the molecular scale). Fig. 1 shows a schematic representation of idealized reactors related to these limiting states for micromixing. The completely segregated fluid is often called a "macrofluid" and the fluid in the state of maximum mixedness a "microfluid".

**Fig. 1. Schematic representation of limiting states for mixing:**
- (a) completely segregated reactor;
- (b) maximum mixedness reactor.

Conversions calculated for the two micromixing limits determine upper and lower conversion bounds for simple, single-species reactions in premixed feed systems [15]. For given kinetics, we have

$$\frac{dc}{dt} = -R(c)$$

and the average exit concentration from the completely segregated system can be calculated from

$$\bar{c}_{out} = \int_0^\infty c_{batch}(t)f(t) \, dt$$

where $c_{batch}(t)$ is equal to the concentration in a batch reactor after time $t$. For a maximum mixedness system, we have

$$\frac{dc}{d\lambda} = R(c) + \frac{f(\lambda)}{1 - F(\lambda)} (c - c_o)$$

where $R(c)$ is the reaction rate in the residual lifetime ($\lambda$) space (for kinetics given by Eq. (2), one has $dc/d\lambda = +R(c)$).

Conversions corresponding to the micromixing limits determine the upper and lower conversion bounds for simple, single species reaction in premixed feed systems. Chauhan et al. [15] have shown that, in the case of an $n$th-order reaction whose rate is described by a kinetic equation of the form

$$R(c) = k_n c^n$$

for $n < 1$, micromixing accelerates the reaction, and complete segregation and maximum mixedness form for any given RTD the lower and upper bounds on conversion respectively. For $n = 1$, the reaction is not sensitive to differences in the level of molecular mixing and, for $n > 1$, complete segregation forms the upper
bound, whereas maximum mixedness forms the lower bound of conversion.

The conclusion of Chauhan et al. [15] is actually more general: for monotonic $R(c)$, conversion is maximized by maximum mixedness and minimized by complete segregation if $d^2R/dc^2 < 0$ (the reaction is concave down). In contrast, if $d^2R/dc^2 > 0$ (so reaction is concave up), then conversion is minimized by maximum mixedness and maximized by complete segregation. For $d^2R/dc^2 = 0$, the reaction is not sensitive to micromixing.

The considerations presented above have been restricted to simple, single-species reactions in premixed feed, isothermal, steady state systems, with a constant density of reactants. The presented approach was later generalized; these generalizations concern micromixing in non-steady state systems, unpremixed feed systems, and systems with variable density for simple and complex reactions [S-21].

Another aspect of this problem is related to the following questions. If micromixing consists of molecular diffusion within and among stretching fluid elements, then what is the environment of such fluid elements? What kinds of fluid element meet in the reactor and when?

In a microfluid, the environment of any molecule is composed of molecules that will leave the system at the same instant, so the fluid elements entering the reactor are losing their identity by mixing with other fluid elements of the same life expectancy. In a macrofluid, the environment of any molecule in the system is composed of other molecules that entered the system at the same instant, so the fluid elements entering the reactor can mix only with these fluid elements, which are of the same age. Consequently, the mixing of molecules that leave together is as late as possible in the case of a macrofluid and as early as possible in the case of a microfluid; in the real system, the instant of mixing on the molecular scale depends on the rate of micromixing.

In practice, it is often assumed that the reactor interior is divided into two (or more) parts, which are in the states of maximum mixedness (microfluid) and complete segregation (macrofluid); the two-, three- and four-environment models have been constructed this way [20,22,23].

The environments are usually arranged in series, with the region maximum of mixedness (microfluid) and complete segregation (macrofluid); the two-, three- and four-environment models have been constructed this way [20,22,23].

(1) In the first group, any fluid element loses its identity immediately upon arrival at the given environment [24]. Micromixing is simulated in these models, by the simple process of mass exchange between environments, so these models are simple but not greatly related to the real mechanism of the process.

(2) In the second group of models, any fluid element loses its identity slowly, as a result of a certain mechanism of mixing; the environment of such a lump of fluid is determined at any instant by the model of complete segregation, maximum mixedness or any multi-environment model [25]. Models of the second group can be considered as predictive when the mechanism of mixing is chosen to be appropriate for the situation.

3. Fluid mechanical fundamentals of turbulent micromixing

A spectral interpretation of micromixing that distinguishes different mechanisms of micromixing at different subranges of eddy size was introduced by Pohorecki and Baldyga [8], and was further developed by Baldyga and Bourne [6,31].

Let us start the analysis from the interpretation of the spectral density functions $E(k)$ of turbulent kinetic energy and $G(k)$ of concentration fluctuations [26]. The spectral densities are demonstrated in Fig. 2 as functions of the wavenumber $k$, which is proportional to the reciprocal of the eddy size. For liquids, the spectral density of the concentration fluctuation distribution $G(k)$ can be divided into three subranges: the inertial-convective, the viscous-convective and the viscous-diffusive subranges.

In the inertial-convective subrange ($\eta_K < I < L_C$, $k_{OC} < k < k_K$), large blobs of fluid are deformed and broken up by the fluid motion, so their scale is reduced without any effect of molecular mixing. The process can be identified with the process of the inertial-convective mesomixing.

In the viscous-convective subrange ($\eta_K < I < \eta_K$, $k_K < k < k_B$), eddies are subjected to laminar strain, which depends upon the viscosity, so their scale is further reduced by viscous deformation, while molecular diffusion becomes slowly active.

The viscous-diffusive subrange ($\eta < \eta_B$, $k > k_B$) begins when laminar strain and molecular diffusion become...
of equal importance; for even smaller eddies, molecular diffusion rapidly dissipates the concentration variance.

The spectral density of the kinetic energy becomes negligible for eddies smaller than the Kolmogorov scale, so molecular diffusion becomes affected by viscous deformations only. Batchelor [27] and Townsend [28] have shown that, in Cartesian coordinates which rotate and translate with the fluid, the fluid elements are deformed in such a way that intensive elongation occurs in one direction, rapid thinning in the second direction and a moderate increase in dimension in the third direction.

The long, thin slabs are formed. The concentration gradients increase rapidly in the direction of shrinkage, molecular diffusion is accelerated in this direction, and the problem quickly becomes one dimensional, greatly simplifying the mathematical description.

The velocity \( u \) at any distance \( x \) from the slab center is proportional to \( x \), so that
\[
\dot{u} = -\frac{\psi}{\gamma} x
\]  
and the concentration distribution can be described by
\[
\frac{\partial c_i}{\partial t} - \frac{\partial c_i}{\partial x} \frac{\partial x}{\partial x} = D_i \left( \frac{\partial^2 c_i}{\partial x^2} + R_i \right)
\]  

There are different models of fluid deformation [6] but, in any case, the rate of deformation \( \Psi \) is a function of \( (\epsilon/\nu)^{1/2} \), which is the characteristic Kolmogorov rate of strain in the viscous subrange. Batchelor [27], assuming pure elongation compression kinematics, obtained
\[
\Psi = c_B \left( \frac{\epsilon}{\nu} \right)^{1/2}
\]  
where \( c_B = 0.3-0.5 \) from experimental data. Baldyga and Bourne [29] applied the theory of initial relative turbulent diffusion to estimate \( \Psi \) as
\[
\Psi = \frac{(\epsilon/\nu)^{1/2}}{(4 + \epsilon^2/\nu)^{1/2}}
\]  

The value calculated from Eq. (8) is bounded by the pure shearing and the pure elongation limits. It should be noticed that Eq. (8) shows some decrease in the deformation rate with time; this phenomenon results from reorientation of slabs, resulting from the action of vorticity and intermittency.

Ottino [30] defined the local efficiency of elongation as the ratio of the real \( \Psi \) value in a certain mixing situation to \( \Psi_{\text{max}} \) where
\[
\Psi_{\text{max}} = \left( \frac{1}{2} \frac{\nu}{\epsilon} \right)^{1/2}
\]  

The average efficiency coefficients can be used to characterize the energetical usefulness of different mixers and reactors.

Let us consider now a single slab of contaminant embedded in turbulent liquid. The slab initially shrinks. When the slab thickness becomes so small that the shrinkage is compensated for by molecular diffusion, the thickness becomes stable and equal to the Batchelor scale, i.e.
\[
\eta_B = \left( \frac{D_i}{\nu} \right)^{1/2} \approx \eta_K \text{Sc}^{-1/2}
\]  
while the slab length and the volume of the material spot increase.

The time of decreasing of the slab thickness from the Kolmogorov scale \( \eta_K \) to the Batchelor scale \( \eta_B \) (assuming no molecular diffusion) is given by
\[
t_{\text{Ds}} = -\frac{1}{\nu} \ln \left( \frac{\eta_B}{\eta_K} \right) \approx \left( \frac{\nu}{\epsilon} \right)^{1/2} \ln(\text{Sc})
\]  

and can be interpreted as the characteristic time for diffusion and shear. However, a more precise definition is given by Baldyga and Bourne [6] as
\[
t_{\text{Ds}} = 2 \left( \frac{\nu}{\epsilon} \right)^{1/2} \text{arc sinh}(0.05 \text{Sc})
\]  

The long, thin slabs formed by elongation and shrinkage are twisted and convoluted, as a result of the action of turbulent vorticity. Baldyga and Bourne [31] have shown that the shrinking slabs become embedded within stretching vortices; the vortices of scale \( \delta_w \approx 12 \eta_K \) are stable because of the balance between the work of stretching and the viscous dissipation — this mechanism is analogous to that which explains the Batchelor microscale. The stretching process of the vortex tubes of scale \( \delta_w \) is accompanied by the incorporation of the fluid from the environment; such convection with velocity \( u_i = \Psi \eta_K \) (Fig. 3) is what is called "engulfment" [31, 32]. The lamellar structures are formed and the diffusional mixing shown in Fig. 4 proceeds in lamellae which thin under the action of vortex stretching.

Thus, the spots of substance \( i \) (inert tracer or reactant) grow at the expense of the environment according to
\[
\frac{di}{dt} = \dot{E} V_i
\]  
\[
E = 0.058 \left( \frac{\epsilon}{\nu} \right)^{1/2}
\]  

The characteristic time constant for mixing by engulfment is roughly equal to \( E^{-1} \); the exact definition is
\[
\tau_w \approx 12 \left( \frac{\nu}{\epsilon} \right)^{1/2}
\]  

The structure of these spots, at least initially, is lamellar; however, for not too high Schmidt numbers, diffusional mixing between deformed slabs is faster than the rate
Fig. 3. Vortex stretching causes engulfing of fluid from environment.

Fig. 4. Concentration profiles during reaction and diffusion of substances A and B in thinning lamellae: (a) lamellar structure; (b) concentration profiles.

of incorporation of the fluid from the environment and the spots quickly lose their lamellar character [12].

In the discussion presented above, the micromixing process is explained and interpreted using the spectral approach to the fine-scale turbulence. The fine-scale turbulence is usually interpreted by using the theory of energy cascade [33]. This theory assumes that there is no direct interaction between large and small eddies, but that there is a cascade of energy from larger to smaller eddies. The local value of the rate of energy dissipation ($\epsilon$) does not fluctuate about its mean value $\langle \epsilon \rangle$. The theory results in the well-known kinetic energy spectrum equation

$$E(k) = 1.5 \langle \epsilon \rangle^{2/3} k^{-5/3}$$  \hspace{1cm} (16)

for the inertial subrange ($k$ is the wavenumber of an eddy; $k \approx (1/l)$).

However, the analysis of Kolmogorov and Obukhov [34,35] has shown that the physical basis of the energy cascade model is incomplete. They found that there is marked variability of the instantaneous energy dissipation rate field; this phenomenon is called “fine-scale intermittency” or “internal intermittency”.

One should be aware that, in the three-dimensional isotropic turbulence, the velocity, vorticity and Reynolds stress fields also have an “intermittent” character. Intermittency modifies Eq. (16) to give

$$E(k) = \langle \epsilon \rangle^{2/3} k^{-5/3} (kL)^{-\delta} \hspace{1cm} \delta \approx 0.06$$  \hspace{1cm} (17)

Because $\delta$ is small, the difference between Eqs. (16) and (17) has often been neglected. For engineering scaling up purposes, the proportionality of $L$ to the equipment size implies a difference in the structure of turbulence between the laboratory and industrial scales.

For the largest eddies ($k \approx L^{-1}$), there is almost no difference between Eqs. (16) and (17), so the effect of local intermittency on the mesomixing processes (including both inertial-convective and dispersive mesomixing) should be negligible. The largest effect of intermittency occurs when $k \approx \eta_k^{-1}$; thus, it is likely to be important for micromixing or finely divided materials suspended in a turbulent fluid. Using the model of local intermittency proposed by Novikov and Stewart [36], in the version modified by Frisch et al. [37] (the so-called $\beta$ model), Baidyga and Bourne have shown how to modify the micromixing equations to account for the effect of intermittency [38]. The energy dissipation rate $\epsilon$ exhibits spatial and temporal fluctuations; the modification of the micromixing equations allows us to use the local and temporal mean value $\langle \epsilon \rangle$, which is actually an ensemble average.

To give some examples, engulfment parameter $E$ defined by Eq. (14) should be modified to

$$\langle E \rangle = 0.058 \left( \frac{\langle \epsilon \rangle}{\nu} \right)^{1/2} \left( \frac{\eta_k}{L} \right)^{0.5(3-D_p)} D_\beta \approx 2.8$$  \hspace{1cm} (18)

whereas the characteristic time constant for diffusion and shear ($t_{ds}$) reads as

$$\langle t_{ds} \rangle = 2 \left( \frac{\nu}{\langle \epsilon \rangle} \right)^{1/2} \left( \frac{\eta_k}{L} \right)^{-0.5(3-D_p)} \text{ arc sinh}(0.05 Sc)$$  \hspace{1cm} (19)

The $\beta$ model of intermittency oversimplifies the description of the phenomenon, while the multifractal model of intermittency, which is more exact and more complex than the $\beta$ model, gives more exact estimation of the correct factors in the micromixing equations [32]; however, the character of correction is the same. The modifications have some consequences for the scaling up of reactors when complex reactions are considered [32,38].

One can conclude that engulfment, deformation and molecular diffusion affected by the local intermittency constitute the micromixing process.

Stretching of material elements and vortices, accompanied by molecular diffusion, results in the growth of
the mixing zones; the growth of the zone mixed on the molecular scale (in the lagrangian frame) is a characteristic feature of micromixing and should be included in modelling [12,31,39,40].

4. Problems of meso- and macromixing

Competition between micromixing and chemical reaction determines a direct effect of mixing on chemical reaction. The additional inhomogeneity related to the meso- and macromixing processes has only an indirect effect; however, although indirect, this effect can be very strong.

Let us consider the inhomogeneity that appears at higher feed rates in the region of the feeding point. The plume of fresh feed is of a coarse scale relative to the micromixing scales, but is of a fine scale relative to the scale of the system; the turbulent (or eddy) diffusion of this plume is called mesoscale mixing or mesomixing [7]. Fig. 5(a) shows the development of the plume of fresh feed \( \delta \), fed into the system through the pipe of internal diameter \( 2a \).

Let us consider the simplest case when the feed pipe represents a point source. This assumption is possible if

\[ a \ll L_D \ll D \]

where \( D \) is the scale of the system and

\[ L_D = \left( \frac{\dot{V}_i}{\bar{u}} \right)^{1/2} \]

is the characteristic length scale for dispersion. In the simplest case of a point source and for \( D_\text{r} = \text{const} \) and \( \bar{u} = \text{const} \), the distribution of the volume fraction of \( i \)-rich feed is

\[ X_i^\delta(r, x) = \frac{\dot{V}_i}{4\pi D \bar{u}} \exp \left( -\frac{\bar{u} r}{4D \bar{u}} \right) \]

which determines the environment for micromixing. The characteristic time constant for mesomixing was defined [7] by

\[ \tau_D = \frac{\dot{V}_i}{\bar{u} D_\text{r}} \]

If \( a \ll D \) and \( a = L_D \) or \( a > L_D \) then the feed pipe is a local finite source [41]. The case of a finite source was recently considered in detail [41]; here, it is enough to point out that the single time constant (23) does not characterize the process completely.

The use of another parameter is necessary — this can be the velocity ratio [41]

\[ U = \frac{u_i}{\bar{u}} \]

where \( u_i \) is the velocity through the feed pipe and \( \bar{u} \) is the mean velocity of the flow surrounding the feed point. One can also define a second time-scale as

\[ \tau_{D1} = \frac{a^2}{D_\text{r}} \]

and apply both \( \tau_D \) and \( \tau_{D1} \) to characterize the process.

The turbulent diffusivity \( D_\text{r} \) can be related to the kinetic energy of turbulence (\( k \)) and its dissipation rate \( \epsilon \) by [7]

\[ D_\text{r} = 0.1 \frac{k^2}{\epsilon} \]

or to the rate of energy dissipation and a turbulent macroscale \( L \) as

\[ D_\text{r} = 0.12 \epsilon^{1/3} L^{4/3} \]

Eq. (27) follows from Eq. (26) after substituting for \( k \) from

\[ \epsilon = 0.85 \frac{k^{3/2}}{L} \]
In the Rushton turbine discharge, the turbulent microscale \( L \) is approximately equal to 0.52\( w \) [42] (\( w \) being the height of an impeller blade; in the case of the Rushton turbine, \( w \approx 0.2 \, d \)), so \( D_t \) in the turbine discharge can be calculated [7] from
\[
D_t \equiv 6 \times 10^{-3} \epsilon_1^{1/3} d^{4/3}
\]  
where \( \epsilon_1 \) is the local energy dissipation in the turbine discharge.

Another model of mesomixing by turbulent dispersion was proposed by David and Villermaux for batch and semibatch processes [40]. The authors assumed that the growth of the cloud of contaminant (or "reacting cloud") is described by a simplified diffusive mechanism
\[
\frac{dL_{\text{C}}^2}{dt} = k' \tag{30}
\]
or
\[
\frac{dV_{\text{C}}}{dt} = \frac{3}{2} k' V_{\text{C}}^{1/3} = D_t V_{\text{C}}^{1/3} \tag{31}
\]
so that
\[
\frac{1}{V_{\text{C}}} \frac{dV_{\text{C}}}{dt} = \left( \frac{D_t}{V_{\text{C}}} \right)^{2/3} \tag{32}
\]
where \( L_{\text{C}} \) is the linear dimension of the cloud and \( V_{\text{C}} \) is the cloud's volume, assumed to be equal to \( L_{\text{C}}^3 \) for the sake of simplicity.

This simple model can be very useful for the estimation of mesomixing effects in the case of pulse injection of one reactant (B) into the system containing another reactant (A). However, when solution B is fed continuously into the system and a jet or a plume of the partially homogenized B is formed, the concentration gradients in the radial direction are much larger than the gradient in the direction of flow, so the radial dispersion is much faster than the longitudinal dispersion. Consequently, the simple relation \( V_{\text{C}} \approx L_{\text{C}}^3 \) should not, in our opinion, be applied any more.

Instead, assuming only radial dispersion of the cloud, one obtains
\[
\frac{dV_{\text{C}}}{dt} = D_t \tag{33}
\]
or
\[
\frac{1}{V_{\text{C}}} \frac{dV_{\text{C}}}{dt} = \left( \frac{D_t}{V_{\text{C}}} \right) \tag{34}
\]

Another aspect of mesomixing is related to the inertial-convective process. Here, the concentration variance of the inertial-convective subrange (an integral of the spectral density \( G(k) \); Fig. 2) decays by the disintegration of large eddies without any direct effect of molecular mixing. The time constant \( t_{\text{ms}} \) that characterizes the inertial-convective mixing is given [43,44] by
\[
t_{\text{ms}} \equiv \frac{3}{2} k_{oc}^{-2/3} \epsilon^{-1/3} = \frac{3}{2} \left( \frac{5}{\pi} \right) L_{\text{C}}^{2/3} \epsilon^{-1/3} \tag{35}
\]
where \( L_{\text{C}} \) represents an integral scale of turbulence. However, there is an indirect effect of the inertial-convective mixing on the mixing on the molecular scale.

The simplest models [8,9] of inertial-convective mixing assume "erosive" diminishing of the blobs of fresh feed, followed by micromixing. However, the mechanism of mixing in the inertial-convective subrange is more complex. The large passive scalar eddies are created by the active, energy-containing eddies, so reflect their scale. Moving randomly, these eddies tend to supply the local mixture properties to the new environment and to produce largescale segregation — the microscale inhomogeneity is embedded within large eddies. Thus, the structure of large eddies determines the environment for micromixing. The general macroscopic population balance equation can be used to evaluate the structure of large eddies [10]:
\[
\frac{D_{\text{var}}}{Dt} = a \left( D_t \frac{\partial (\text{var} \, X)}{\partial x_i} \right) + R_p - R_D \tag{36}
\]
with the production term [45]
\[
R_p = -2 \bar{\nu} \epsilon'_{ij} \frac{\partial \bar{X}}{\partial x_j} = \text{const} \, \nu_T \left( \frac{\partial \bar{X}}{\partial x_j} \right)^2 \tag{37}
\]
and the dissipation term
\[
R_D = \frac{(\text{var} \, X)}{t_{\text{ms}}} \tag{38}
\]
Here, the variance \( \text{var} \, X \) is a function of the large eddies structure. The relationship of Eqs. (36)–(38) to turbulent dispersion is obvious.

The process of macromixing refers to those large-scale flow processes that cause the realization of large-scale distributions, such as the residence time distribution or distribution of mean concentration in the eulerian frame. The macromixing process can be well characterized by the macroscopic flow pattern and by the distribution of the rate of energy dissipation in the system. As a simple characteristic of macromixing in a stirred tank, one can use the circulation time \( t_c \). The circulation time equals the tank volume divided by the circulation capacity, i.e.
\[
t_c = c_1 \frac{V_c}{Nd^3} \tag{39}
\]
Another time constant necessary to characterize the variation of energy dissipation rate is a time-scale for the energy dissipation field:
5. Competition between reaction and mixing: numerical criteria

Before modelling, it is very useful to identify which of the sequence of the mixing processes can directly or indirectly affect the course of chemical reaction. Reactions can be classified by comparing the characteristic times for mixing and reaction. For the nth-order chemical kinetics, the characteristic time constant of chemical reaction is

$$t_R = \frac{1}{k_n C_{A_0} n^{-1}}$$  \hspace{1cm} (41)$$

Using $t_M$ to denote the characteristic mixing time ($t_M$ can be equal to $t_C$, $\tau_D$, $t_{ms}$, $t_{Ds}$ or $\tau_w$), one can classify the reaction from the point of view of competition between reaction and mixing. Therefore, the reaction is instantaneous if $t_M = t_R$; fast if $t_M \approx t_R$; and slow if $t_M \ll t_R$.

The effect of mixing should be observed in the first two cases. It should be noted that the reaction can be slow when compared with micromixing, but fast or instantaneous when comparing with mesomixing or macromixing. Thus, the relationships between the time constants of different mixing subprocesses are very important.

A comparison of Eq. (15) with Eqs. (11), (12) or (19) shows that, for not very high Schmidt numbers, even in the case of instantaneous reaction, engulfment is the rate-determining step; according to Baldyga and Bourne [12], engulfment controls micromixing for $Sc \ll 4000$.

Comparing the characteristic time constant for mesomixing ($t_D$) with the time constant for engulfment, Baldyga and Bourne [7] have shown that the relative rate of dispersive mesomixing and micromixing (by engulfment) can be measured by the ratio $Q$ of these constants, i.e.

$$Q = \frac{EV}{uD_i}$$  \hspace{1cm} (42)$$

Mesomixing controls when $Q \gg 1$ (Fig. 5(c)), micromixing is most important when $Q \ll 1$ (Fig. 5(b)) and both mechanisms have to be considered when $Q \approx 1$.

In the case of a local finite source, one should consider also the second time constant for mesomixing, i.e. $\tau_D$. The relative rate of dispersive mesomixing and micromixing should be measured in this case also by $Q$, i.e.

$$Q_1 = \frac{E \varphi^2}{D_i}$$  \hspace{1cm} (43)$$

Again, mesomixing controls when $Q_1 \gg 1$, micromixing controls when $Q_1 \ll 1$ and both mechanisms have to be considered when $Q_1 \approx 1$.

The relative importance of inertial–convective mesomixing and micromixing can be estimated using the parameter $M$ defined by Baldyga and Rohani [39] as

$$M = \frac{E \tau_{ms}}{t_C}$$  \hspace{1cm} (44)$$

Inertial–convective mesomixing controls when $M \gg 1$, micromixing controls when $M \ll 1$ and both mechanisms are important when $M \approx 1$. Mesomixing affects micromixing by changing the local environment, whereas micromixing increases the mixed volume to be dispersed by mesomixing.

Macromixing can affect the mesomixing and micromixing processes as follows.

(1) When the feed time $t_f$ to the semibatch stirred tank reactor or the mean residence time $t$ in the CSTR are of the order of the circulation time $t_C$ in the system (see Eq. (39)) or shorter, the relevant scale of inhomogeneity is macroscopic over the whole vessel. The system cannot be described as being well mixed on the macroscale in this case and the macromixing model should be used to determine the environment concentrations for mesomixing and micromixing.

(2) For sufficiently slow addition ($t \gg t_C$ or $t_i \gg t_C$), one can assume uniform concentration of the bulk.

(3) The macro-convection through the different environments with varying energy dissipation rate $\langle \varepsilon \rangle$ should be considered when any time constant for mesomixing or micromixing is smaller than $\tau_e$ or of the order of $\tau_e$. For example, when $\tau_w \ll \tau_e$, the local value of $\langle \varepsilon \rangle$ can be used in the engulfment equations; when $\tau_w \gg \tau_e$, the average value in the tank $\langle \varepsilon \rangle$ can be applied; and, when $\tau_w = \tau_e$, the exact profile of $\langle \varepsilon \rangle$ should be used for calculations.

(4) There is an interesting effect of a flow field on mesomixing when flow converges or diverges. Converging flow results in increasing concentration gradients on the mesoscale, whereas diverging flow has the opposite effect [7].

6. Micromixing models

The process of mixing can be observed and described from eulerian or lagrangian perspectives.

With regard to the lagrangian approach, the concepts of residence time distribution and micromixing have been introduced and developed using the lagrangian or material frame approach. Using the lagrangian frame perspective, one can follow the history of a fluid element, describing the elementary processes that form the overall micromixing or mesomixing process: disintegration of eddies, engulfing, deformation, molecular diffusion, etc.
Using residence time distribution functions together with suitable multi-environment models, one is able to make predictions for a certain fluid element distinguished among others present in the system, or at least to find limits for various environments in the system. However, such an approach does not permit the prediction of spatial distributions in the system.

Another possibility is to link the eulerian coordinate system \((x, y, z)\) for \(u(x, y, z)\) and \(e(x, y, z)\) to the lagrangian framework for micromixing [46]. When the turbulent dispersion — especially in the direction of flow — can be neglected, the streamlines of a steady state flow determine the trajectories of fluid elements such that

\[
\frac{dx}{u(x, y, z)} = \frac{dy}{u_y(x, y, z)} = \frac{dz}{u_z(x, y, z)} = dt \tag{45}
\]

Solutions of Eq. (45) for any element whose initial position was \((x_0, y_0, z_0)\) give the following: its position \(x(t, x_0, y_0, z_0)\) and similarly for \(y\) and \(z\); its velocity \(u(x, t, x_0, y_0, z_0)\) and similarly for \(u_x\) and \(u_y\); its energy dissipation \(e(t, x_0, y_0, z_0)\). The full mechanism of micromixing, included in the engulfment-deformation-diffusion (EDD) model [31], can now be applied. In such a case, the chemical kinetics are incorporated into the mixing model using Eq. (6).

When engulfment controls the micromixing process, the diffusion step can be neglected and the chemical kinetics can be introduced directly into the engulfment equations. Taking into account slowing down of the reaction zone growth by engulfment of the same fluid (self-engulfment), Baldyga and Bourne [12] gave the general E-model equations

\[
\frac{dV_i}{dt} = \langle E \rangle V(1 - X_i) \tag{46}
\]

\[
\frac{dc_i}{dt} = \langle E \rangle (1 - X_i)(c_i - c_i) + R_i \tag{47}
\]

Eq. (47) shows how the processes of mesomixing and micromixing interact. Mesomixing determines the local composition of the environment for any fluid element in the system, i.e. the local average concentrations \(c_i\) of species in the environment and the local volumetric distribution \(X_i\) of fluids containing these species.

The micromixing parameter \(E\) determines the intensity of mass exchange between the relevant fluid element of concentration \(c_i\) and its surroundings of concentration \(\langle c_i \rangle\). Mesomixing controls the process when a fluid element is surrounded by the fluid elements of the same composition \(X_i \approx 1, c_i = \langle c_i \rangle\), micromixing is most important when the fluid element is surrounded by fluid elements of different composition \(X_i \approx 0, c_i \neq \langle c_i \rangle\) and both mechanisms affect the process when these conditions are not fulfilled.

David and Villermaux [40] suggested using either engulfment or a turbulent dispersion mechanism for the growth of the reacting cloud; the relevant mechanism is the one which would lead to the smallest cloud volume if it were to occur alone (limiting mechanism).

Within the cloud, there are fluid elements which are deformed and which exchange material with each other. David and Villermaux [40] suggested representation of this exchange by the interaction by exchange with the mean (IEM) model [47,48]:

\[
\frac{dc_i}{dt} = \frac{c_i - c_i}{\tau_M} + R_i \tag{48}
\]

Points, having negligible mass and uniform concentration \(c_i\), exchange mass with the whole population in the cloud, which has the average concentration \(\bar{c}_i\), according to the linear rate expression \((c_i - \bar{c}_i)\tau_i\), where \(\tau_i\) is the micromixing time constant. Using Eq. (48) instead of Eq. (6) considerably simplifies the model. However, one should be aware that, in the case of complex reactions, the IEM predicts results which do not agree with the experimental data [63]; this is because the IEM neglects the growth of the reaction zone.

An interesting extension of the E-model approach has been presented by Ranade and Bourne [49]. They combined the micromixing E model with the fluid mechanical "k-ε" model to simulate mixing in agitated reactors. The interaction between the micromixing and the larger-scale mixing was possible using population balance models, similar to the general population balance equations for micromixing developed by Baldyga and Rohani [39].

In this review, only the models based directly on the turbulence theory have been discussed in detail; a similar method of linking can be applied to some other micromixing models, including the coalescence-redispersion [48] and the shrinking aggregate models [6].

With regard to the eulerian approach, to describe the reactive mixing in the physical space, the eulerian or fixed frame perspective is used. In the eulerian approach, the averaging procedure, typical for turbulence description, causes a loss of information about the local mixing and the age distribution. To solve the set of differential equations that describe the process, additional information is necessary; this is called the "closure problem".

Let us consider a second-order, irreversible chemical reaction in a turbulent flow, i.e. \(A + B \rightarrow \text{product}\). The concentration field is described by the differential balance equation

\[
\frac{\partial c_a}{\partial t} + u_j \frac{\partial c_a}{\partial x_j} = D_a \frac{\partial^2 c_a}{\partial x_j^2} - k_2 c_A c_B \tag{49}
\]

where \(a = A, B\) and \(k_2 = \text{const.}\). If \(c_a\) and \(u_j\) are divided into average and fluctuating components, i.e.
and the resulting equations are Reynolds averaged, one obtains

\[
\frac{\partial \bar{c}_a}{\partial t} + u_j \frac{\partial \bar{c}_a}{\partial x_j} = \frac{\partial}{\partial x_j} \left[ \left( D_t + D_a \right) \frac{\partial \bar{c}_a}{\partial x_j} \right] - k_2 (\bar{c}_a \bar{c}_n + \bar{c}_A \bar{c}_B) \tag{52}
\]

In Eq. (52), the turbulent diffusion concept was used, i.e.

\[
-u_j \frac{\partial \bar{c}_a}{\partial x_j} = D_t \frac{\partial \bar{c}_a}{\partial x_j} \tag{53}
\]

Turbulent diffusivity is usually modelled with the use of the “k-ε” model, as given by Eq. (26). Under the assumption of the insensitivity of \( D_t \) to chemical reaction, \( D_t \) calculated from Eq. (26) can be used in Eq. (52).

In fact, there is an effect of chemical reactions on turbulent diffusivities \([51,52]\). Using a mixing length model, Toor \([52]\) presented a simple method to account for this effect. In this method, an apparent flux which can enhance or hinder the normal turbulent fluxes should be added to the convective diffusion equation. The apparent flux is likely to have little effect on the mean concentration field but the problem requires further study.

The closure approximation for the reaction term \( \bar{c}_A \bar{c}_B \) should now be considered. The differential covariance balance reads

\[
\frac{\partial \left( \bar{c}_A \bar{c}_B \right)}{\partial t} + u_j \frac{\partial \left( \bar{c}_A \bar{c}_B \right)}{\partial x_j} = - \frac{\partial}{\partial x_j} \left( u_j \left( \bar{c}_A \bar{c}_B \right) \right) - u_j \frac{\partial \bar{c}_A}{\partial x_j} \frac{\partial \bar{c}_B}{\partial x_j} \] 

\[+ - 2D_a \left( \frac{\partial \bar{c}_A}{\partial x_j} \right) \frac{\partial \bar{c}_B}{\partial x_j} + D_a \frac{\partial^2 \bar{c}_A \bar{c}_B}{\partial x_j^2} \]

\[+ \frac{k_2}{\left( \bar{c}_A + \bar{c}_B \right)^2} \left( \bar{c}_A \bar{c}_B + \bar{c}_A \bar{c}_B \right) \]

\[+ \left( \bar{c}_A \right)^2 \left( \bar{c}_B \right)^2 + \left( \bar{c}_A \right) \left( \bar{c}_B \right) \left( \bar{c}_A \right) \left( \bar{c}_B \right) \] 

\[= \frac{2}{\pi} \left( \bar{c}_A \bar{c}_B \right) \] 

where \( \bar{c}_{A0} \) and \( \bar{c}_{B0} \) are the mixed feed concentrations and \( \bar{I}_s \) is the intensity of segregation defined by the concentration variance

\[
\bar{I}_s = \frac{\left( \bar{C}_A \right)^2}{\bar{C}_{A0} \bar{C}_{B0}} = \frac{\left( \bar{C}_B \right)^2}{\bar{C}_{A0} \bar{C}_{B0}} \tag{56}
\]

with \( \bar{C}_A \) and \( \bar{C}_B \) being the concentration fractions:

\[
\bar{C}_i = \bar{c}_i / \bar{c}_{i0} \]

In the papers of Baldyga and Rohani \([39]\) and Kosály \([55]\), it was shown that Toor’s hypothesis is not true when the initial probability density function (PDF) is not gaussian; in fact, in a typical unpremixed feed reactor, the PDF is of bimodal shape, determined by the initial conditions. Kosály has shown that, for an instantaneous reaction, we have

\[
\frac{\bar{c}_A \bar{c}_B}{\bar{c}_{A0} \bar{c}_{B0}} = \frac{2}{\pi} \left( \bar{I}_s \right) \tag{57}
\]

However, it can easily be shown that this equation is valid only for the symmetrical PDF distribution, which becomes asymptotically gaussian; what happens in the case of the volume ratio of reactant solutions being equal to unity \([56]\). For other values of the reactant volume ratio, the results are different from that given by Eq. (56). No simple closure of the type of Eqs. (56) and (57) — valid for any value of Damköhler number — is possible, even for equal volumes of reactant solutions and a stoichiometric ratio equal to unity. Hence, Toor’s hypothesis can be used only as a first estimate.

Much more difficult closure problems arise when complex reactions are considered; in this case, both conversion and selectivity can be mixing dependent. The classical example of complex reactions is the competitive-consecutive reaction system

\[
A + B \rightarrow R \tag{58}
\]

\[
R + B \rightarrow S \tag{59}
\]

with

\[
\bar{R}_1 = k_1 \bar{c}_A \bar{c}_B = k_1 \left( \bar{c}_A \bar{c}_B + \bar{c}_A \bar{c}_B \right) \tag{60}
\]

\[
\bar{R}_2 = k_2 \bar{c}_B \bar{c}_R = k_2 \left( \bar{c}_B \bar{c}_R + \bar{c}_B \bar{c}_R \right) \tag{61}
\]
The simplest way to close the balance equations is to neglect $c_{R}^{c_{R}}$ and to apply Toor's hypothesis to $c_{A}^{c_{A}}$ [57]. Such an approach can be valid only if the second reaction is very slow. Brodkey and Lewalle [58] extended Toor's closure to the second reaction; their estimate of $c_{b}^{c_{b}}$ was

$$
\frac{c_{b}^{c_{b}}}{c_{R}^{c_{R}}} = \frac{c_{A}^{c_{A}}}{c_{A}}
$$

(62)

It is easy to show that, if this hypothesis is true, then the final selectivity (i.e. when the limiting reactant has fully reacted) should be independent of the intensity of mixing and equal to the selectivity in the chemical regime.

Several moment closures for complex reactions have been proposed recently in the literature [59-62]; all these closures predict insensitivity of the product distribution to the volume ratio of reagent solutions, in contradiction to the experimental results [63]. This conclusion agrees well with the results of Heeb and Brodkey [62]. They observed no agreement when simulating the covariance terms using a statistical simulation program and comparing the results with the closure formulae.

The popular moment closures are rather useless when complex reactions are to be modelled. The alternative approach is to use the PDF closure methods. These methods are usually based on the presumed PDFs (normal [64], clipped normal [65], spiked [66] and sawtooth distributions [67]); the most promising is the method based on the $\beta$ distribution function (see Refs. [10,54,68,69] for single reactions and Refs. [56,70] for complex reaction systems). The particular shape of the PDF can also be calculated [71-73]; however, the equations for the PDF are again not closed and require specific closure or modelling. The PDF methods predict well the effect of the volume ratio of the reagent solutions on the product distribution of complex reactions [56,70].

7. Applications of micromixing models

The most interesting effects of micromixing can be observed in the cases of fast complex processes. Good examples are complex reactions, polymerization reactions and precipitation processes.

7.1. Complex reactions

The micromixing mechanism presented in this paper was applied with success to predict the course of the competitive-consecutive [7,31] and parallel reactions [74]. Much more complex reaction schemes, including the effect of pH gradients on the coupling between 1-naphthol and diazotized sulphanilic acid [12] and the reaction of the diazotized sulphanilic acid with the mixture of 1-naphthol and 2-naphthol [75], were also well described.

The effect of an increase in the secondary product of the competitive-consecutive reactions with the increase of the volume ratio of reagent solutions (provided that all the initial average concentrations of substrates are kept constant!) was used as the test effect for the micromixing models. Using this effect, Baldyga and Bourne showed the inadequacy of the IEM for describing complex reactions. It was also proved that the $E$ model [63] and EDD model [31] pass the volume ratio test. The results of a simulation presented by Chang et al. [76] (see Table III p. 150 in Ref. [76]) show that the coalescence-redispersion model developed by Curl [77] and the four-environment model (4E) [23] pass this test, whereas the three-environment model (3E) and the IEM do not.

7.2. Polymerizations

Micromixing models are capable of predicting the initiator consumption and the occurrence of hot spots in high pressure polymerization [78]. The effects of mixing on the number- and weight-average degree of polymerization in free radical polymerization in solution can be successfully modelled using micromixing theory [79].

7.3. Precipitations

The idea of the effect of mixing on precipitation, through the modelling of the supersaturation distribution, was introduced by Danckwerts [80] when he first discussed micromixing phenomena. Later, Becker and Larson [81] presented a numerical study of the well-mixed (maximum of mixedness) and completely segregated crystallizers. Pohorecki and Baldyga calculated [82] the effect of micromixing on the crystal size by using the micromixing models and compared the predictions with the results of measurements [83]. Nowadays, the micromixing models make it possible to predict the supersaturation profiles and the size distributions of the precipitated particles, and to explain the effect of mixing on the morphology of the product [1,2,84]. In the case of protein precipitation, the model of micromixing describes the impact of mixing on protein solubility [85].

7.4. Other applications

The engulfment micromixing models have been successfully applied recently to study pulped fibre suspension mixing [86] and to simulate micromixing effects in a tubular flow reactor under simulated microgravity [87]. The examples presented confirm the validity and
universality of micromixing models based on the theory of turbulence — the particular models can be used, without modifications, to describe many different processes in various physical situations.

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Appendix A: nomenclature

\[ a \]
feed pipe radius

\[ c_B \]
constant

\[ c, c_i \]
concentration, concentration of substance \( i \)

\[ d \]
impeller diameter

\[ D_n, D_\alpha \]
molecular diffusivity

\[ D_t \]
turbulent diffusivity

\[ E \]
engulfment parameter

\[ E(k) \]
three-dimensional energy spectrum function

\[ f(t) \]
density of residence time distribution

\[ F(t) \]
cumulative residence time distribution

\[ G(k) \]
spectrum of concentration fluctuation field

\[ I_S \]
intensity of segregation defined by concentration variance

\[ J_\alpha \]
degree of segregation defined by age of the fluid at the point

\[ k \]
wavenumber, kinetic energy

\[ k_1, k_2 \]
second-order reaction rate constant

\[ k_n \]
\( n \)th-order reaction rate constant

\[ k_{OC} \]
characteristic wavenumber of large eddies

\[ k_B \]
Batchelor wavenumber

\[ k_K \]
Kolmogorov wavenumber

\[ l \]
size of fluid elements

\[ L \]
scale of large eddies

\[ L_C \]
integral scale for concentration fluctuations

\[ L_D \]
characteristic length scale for dispersion

\[ M=Et_{ms} \]
ratio of characteristic times for inertial–convective mesomixing and micromixing

\[ N \]
stirrer rotational speed

\[ r \]
radius

\[ R \]
reaction rate

\[ R_D \]
dissipation of unmixedness of large scale production of unmixedness of large scale

\[ R_P \]
Schmidt number

\[ t \]
time

\[ t_C \]
circulation time

\[ t_{DS} \]
characteristic time for diffusion and shear

\[ t_f \]
feed time

\[ t_M \]
charactertic mixing time

\[ t_{ms} \]
characteristic time constant for inertial–convective mixing in liquids

\[ t_R \]
characteristic reaction time

\[ t_s \]
time-scale for the energy dissipation field

\[ t \]
mean residence time

\[ Q=EV_t/\mu D_i \]
ratio of characteristic times for dispersion and micromixing

\[ Q_1=Fa^2/D_i \]
ratio of characteristic times for dispersion and micromixing for a local finite source

\[ U \]
velocity ratio

\[ \bar{u} \]
local average velocity

\[ V_C \]
tank volume

\[ \dot{V} \]
volumetric flow rate

\[ x_i, x_j \]
cartesian coordinates

\[ X \]
volume fraction of non-reacting tracer in eddies with size \( L_C \)

\[ \alpha \]
age of molecules

\[ \alpha_p \]
age at a point

\[ \delta_k \]
characteristic dimension of vortices

\[ \epsilon \]
rate of energy dissipation

\[ \epsilon_C \]
rate of concentration variance dissipation

\[ \eta_B \]
Batchelor microscale

\[ \eta_K \]
Kolmogorov microscale

\[ \lambda \]
residual lifetime

\[ \nu \]
kinematic viscosity

\[ \tau_D \]
characteristic time constant for mesomixing

\[ \tau_{D1} \]
characteristic time constant for a local finite source

\[ \tau_w \]
characteristic time constant for mixing by engulfment

\[ \Psi \]
deformation parameter

References