HYDRO- AND GAS DYNAMICS IN TECHNOLOGICAL PROCESSES

VERIFICATION OF CHEMICAL REACTION RATE MODELS IN TURBULENT REACTING FLOWS AT SCHMIDT NUMBER CONSIDERABLY EXCEEDING 1

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Relations widely used in numerical modeling describing the average rate of a chemical reaction have been analyzed. The spontaneous distributions of the mixture fraction and reaction products measured simultaneously in different cross-sections of the jet mixer under turbulent mixing of chemically reacting incompressible liquid media served as the basis for verification.

Keywords: laser-induced fluorescence, turbulent jet, cocurrent flow, mixture fraction, segregation coefficient, chemical reaction rate, probability density function.

Introduction. Mixing of turbulent reacting flows is determined by both the convective transport of the original reactants and their chemical interaction at the molecular level (by micromixing). In the case where the chemical reaction rate is much higher than the turbulent transport rate, micromixing fully depends on the convective transport, due to which the distribution of transported substances with a concentration other than zero at each point of the considered volume is formed.

Modeling of mixing accompanied by a fast chemical reaction in turbulent flows plays an important part in developing the statistical theory of turbulent transport with account for the molecular interaction [1]. Despite the existence of a large number of phenomenological models developing the above theory, there is still no universal model for turbulent mixing of reacting flows which could provide a rigorous mathematical description of the mixing processes proceeding in them at a different rate, which is a consequence of the limited base of experimental data for chemically reacting flows.

One of the main goals of the theory under consideration is to construct models for averaged rates of chemical reactions with account for the influence on them of turbulent transport, which shows up as pulsations of scalar characteristics (concentrations of impurities, reactants, and reaction products, as well as the temperature). Initially, such models completely ignored the influence of pulsations on the chemical reaction rate ("laminar chemistry" approximation) [1, 2], then they were constructed with the use of segregation coefficients [3, 4], and finally probabilistic models appeared (the probability density function method, flamelet models, the method based on the closing of conditional moments, etc.) [5–7]. It should be noted that verification and development of models for the averaged rate of the chemical reaction were carried out mainly for chemically reacting gas flows (Schmidt number Sc $\sim$ 1), primarily in combustion problems [2, 7]. For flows of media with a Schmidt number Sc $\gg$ 1, consideration was primarily given to the features of turbulent transport and mixing different forms of gases (spectral models of mixing of Corrsin [8], Fox [9], the MTS (multi-time-scale) model [10], etc.), since micromixing in this case occurs on scales much smaller than the dissipative scales of the rate. At large Reynolds numbers the dissipative scales of the scalar are so small that at the present time they can only be resolved by experimental methods, but this is an extremely difficult problem, which explains the small number of known experimental studies of mixing of turbulent reacting flows [11–17]. Therefore, it is natural that model approximations by which the averaged rate of the chemical reaction for the case of Sc $\gg$ 1 is calculated were constructed on the basis of approximations for the case of Sc $\sim$ 1 by selecting and varying

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the values of constants and parameters entering into them (for example, by modifying [18] or [10] the known EDC model [7]). The degree of confidence of a particular approximation was determined in consultation with the sparse experimental data limited as to the position and time resolution. As a rule, for analysis of chemical processes, integral characteristics of mixing and the reaction zones (length of the reaction zone, averaged concentrations of one of the reactants or reaction products, concentrations of the transported passive impurity, etc.) were considered [18–22].

The current methods of experimental diagnostics, primarily optical ones, permit measuring instantaneous distributions of concentrations of reactants and thus obtaining also quantitative information on the change in the pulsations of concentrations and their correlations. This opens up the possibility of verifying mathematical expressions for the averaged rate of a chemical reaction. This problem is the subject of the present work in which the known model relations for the chemical reaction rate are tested for agreement with the experimental data obtained in investigating turbulent mixing of chemically reacting incompressible liquid media (the density is constant) [17]. The above-mentioned work presents a complete experimental database on the evolution of the mixture fraction and the concentrations of reactants and the reaction products, i.e., parameters needed for modeling the chemical reaction rate.

Experimental Conditions. We investigated turbulent mixing in a coaxial mixer accompanied by a fast irreversible isothermal neutralization reaction of hydrochloric acid (HCl) and alkali (NaOH). The experimental conditions were identical to the conditions described in [23] for the regime of mixing without the formation of a recirculation zone near the mixer walls.

An acid solution (concentration 1.17 mmole/liter) was fed to the center of the mixer and mixed with a cocurrent flow of the alkali (concentration 18 mmole/liter). The choice of a small stoichiometric ratio of the reaction made it possible to register its proceeding practically at once with the formation of a mixing layer of the jet and the concurrent flow. Simultaneous measurement of instantaneous distributions of the mixture fraction values and the concentration of the reaction product was made by the method of laser-induced fluorescence with the use of two dyes [17]. Both dyes were added to the acid solution. One dye, Rhodamine B, is insensitive to the chemical reaction, and the change in its concentration reflected the change in the mixture fraction. The radiation intensity of the second dye, fluorescein ($C_{20}H_{10}O_5Na_2$), is sensitive to a change in the pH number of the medium and characterized indirectly the change in the reaction product concentration. The radiation from both dyes in the mixer cross-section in the vertical symmetry plane was recorded simultaneously by two identical digital cameras in the wavelength range $l = 540$ nm and $l > 640$ nm, respectively, for Rhodamine B and the fluorescein. The quantity of the reaction product formed is equivalent to the quantity of the original media that have reacted at molecular level, i.e., it is a quantitative measure of micromixing or scalar dissipation. Thus, this method provides the possibility of measuring the micromixing without resolving the dissipative scales of the scalar.

Calibration of acidic solutions of each dye and of their mixture (titration) has shown that in all cases there was a linear change in the radiation intensity of the dyes in each range of wavelengths for alkali solutions [17]. This enabled us to use the simple relations for determining the concentration of the reaction product Y_P and the values of the mixture fraction f:

$$\frac{Y_P}{Y_P^{\max}} = \frac{I_i}{I_m^{\max}}, \quad f = \frac{I_i}{I_R^{\max}}.$$

The maximum radiation intensity of fluorescein in a mixture with two impurities $I_m^{\max}$ was measured during calibration at the wavelength $l = 540$ nm, and the maximum radiation intensity of the rhodamine solution $I_R^{\max}$ was measured in the spectral range $l > 640$ nm.

The experimental conditions (small stoichiometric ratio, small concentration of acid, excess alkali) meant that the chemical reaction could be registered only at distances up to $x/D \leq 3$. Downstream, the change in the radiation of both dyes characterized only the turbulent transport [17].

For theoretical analysis, we considered the simplified kinetic scheme of the neutralization reaction

$$A + n\,B \xrightarrow{\ \omega\ } (n+1)\,P,$$
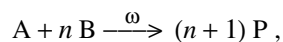
where A and B are the reactants (A is acid, B is alkali); P is the reaction product. The instantaneous rate of the chemical reaction was defined as

$$\omega(x_i, t, Y_A, Y_B) = -K^* \frac{Y_A Y_B}{Y_{A0} Y_{B0}}, \tag{1}$$

where $K^* = K Y_{B0}$ and $n = 1$ in the considered case.

Apparently, for the chemical reaction to proceed, it is essential that at a certain instant of time both substances A and B be present in the investigated region of the flow, i.e., the proceeding of the chemical reaction is determined by the turbulent transport in the flow, as a result of which the two initially homogeneous but segregated substances are brought into contact. To analyze the mixing process, we used the theory of conservative scalars, an example of which is the mixture fraction f [3, 24]:

$$f = \frac{nY_A - Y_B + Y_{B0}}{nY_{A0} + Y_{B0}} = f_{st}\left(r_{eq}\frac{Y_A}{Y_{A0}} - \frac{Y_B}{Y_{B0}} + 1\right) = \frac{(n+1)Y_A + Y_P}{(n+1)Y_{A0}} = 1 - \frac{(n+1)Y_B + nY_P}{(n+1)Y_{B0}}, \tag{2}$$

with a domain of definition $f \in [0, 1]$, where f acquires a value equal to 0 in the flow of the pure reactant B and $f = 1$ in the flow of the pure reactant A. In accordance with relations (2), to determine the change in the concentrations of the reactants Y_A and Y_B and the reaction product Y_P, it is enough to know the values of two quantities — the mixture fraction f and one of the concentrations, for example, of the reaction product Y_P. In this case, the instantaneous values of the reactant concentrations are determined [24] as

$$Y_A / Y_{A0} = f - \frac{Y_P}{(n+1)Y_{A0}}, \quad Y_B / Y_{B0} = (1-f) - \frac{n}{(n+1)}\frac{Y_P}{Y_{B0}} \tag{3}$$

and the chemical equivalence ratio r_{eq} gives the stoichiometric value of the mixture fraction f_{st} calculated from the condition that the chemical reaction proceeds at a stoichiometric ratio between the reactants A and B, i.e., under the conditions that $nY_A - Y_B = 0$, $f_{st} = Y_{B0}/(nY_{A0} + Y_{B0}) = 1/(r_{eq} + 1)$. It is clear that at mixture fraction values equal to the stoichiometric value of f_{st} the considered process proceeds most intensely with the formation of the maximum quantity of the reaction product. Because of the nonlinearity of expression (1), the rate of the chemical reaction decreases markedly upon deviation from stoichiometric conditions.

The instantaneous distributions of the reactant concentrations determined from the experiment permit calculating the distributions of pulsations of these concentrations y'_A and y'_B ($y'_A = Y_A - \overline{Y}_A$ and $y'_B = Y_B - \overline{Y}_B$), as well as the change in their correlation $\overline{y'_A y'_B}$ needed for calculating the averaged rate of the chemical reaction.

Consider the Reynolds-averaged rate of the chemical reaction (1):

$$\overline{\omega}(t, x_i, Y_A, Y_B) = -K^* \frac{\overline{Y}_A \overline{Y}_B}{Y_{A0} Y_{B0}}(1 + I_s), \tag{4}$$

where $I_s = \dfrac{\overline{y'_A y'_B}}{\overline{Y}_A \overline{Y}_B}$ and determines the degree of homogeneity of the mixture [3, 24]. The segregation coefficient distributions over the cross-section of the mixer were determined at different distances along its length from experimental measurements and reflected the influence of the turbulent mixing on the molecular one. In the case of ideal mixing of the mixture where concentration pulsations are equal to zero ($I_s = 0$), the change in the chemical reaction rate is proportional to the change in the product of $\overline{Y}_A$ and $\overline{Y}_B$. The existence of concentration pulsations of the reactants influences the chemical reaction rate: when their correlation is negative ($I_s < 0$) the rate of the chemical reaction decreases. From relation (4) it follows that the chemical reaction does not proceed if $I_s = -1$, i.e., when the reactants are completely segregated.

The segregation coefficients I_s can be calculated with the use of various hypotheses. The possible variants of the approximate relation (4) for $\overline{\omega}(t, x_i, Y_A, Y_B)$ are considered below.

Modeling of the Average Rate of a Fast Chemical Reaction. *Model with empirical determination of the form of the averaged rate of the chemical reaction.* Apparently, the application of the approximation $\overline{\omega} = -K^* \dfrac{\overline{Y}_A \overline{Y}_B}{Y_{A0} Y_{B0}}$ ($I_s = 0$)

("laminar chemistry" approximation) [1, 2] ignores the influence of turbulent pulsations on the chemical processes and can only be used for chemical analysis as a limiting case — the case of infinitely fast mixing [1, 7].

Modeling of fast chemical reactions in turbulent flows is often carried out in the basis of vortex dissipation with the use of the EDC model [1, 7, 9, 18, 24]. The given model is an extension of the EBU model describing the chemical reaction of premixed mixtures [25]. The EDC model uses the dependence of time scales of the reaction on the dissipation time of turbulent vortices transporting reactants and reaction products.

The model of [18] is valid for fast chemical reactions in which there is excess content of the reactant B, i.e., a limitation on the concentration of the reactant deficient for the reaction in the mixture is specified in it. The standard EDC model was developed and used for strongly exothermal reactions (for combustion problems) [7]. For isothermal reactions in liquids, the following variant of the model can be used [18]:

$$\bar{\omega} = -C_1 \tau_s^{-1} \min\left(\frac{\overline{Y}_A}{Y_{A0}}, \frac{1}{r_{eq}}, \frac{\overline{Y}_B}{Y_{B0}} \right), \quad C_1 = 4 \, . \tag{5}$$

In calculation codes, the EDC model [9]

$$\bar{\omega} = -\min\left(K^* \frac{\overline{Y}_A \overline{Y}_B}{Y_{A0} Y_{B0}}, C_2 \tau_s^{-1} \right) \tag{6}$$

is also used. The model constant C_2 is usually chosen in accordance with experimental data.

Independent of the variant for the EDC model, an important control process is mixing, but at the same time the concentration pulsations are not included in it explicitly. Their influence is taken into account by empirical parameters depending on the turbulence characteristics (time scale of mixing τ_s). For gas flows (Sc ~ 1), assumptions that the time scales of mixing τ_s (scalar dissipation) are proportional to the time scale of dissipation of the kinetic energy of turbulence are valid. However, for liquids the Schmidt number Sc >> 1 and the rates of these processes differ considerably, and, therefore, it is necessary to take into consideration the pulsation dynamics of the concentrations of the reactants or the mixture fraction.

Model based on the determination of the segregation coefficient. Models including the determination of the segregation coefficient I_s (works of Toor [3] or Patterson [4, 26]) are based on the assumption that mixing controls the rate of a chemical reaction, and the dynamics of the change in pulsations of reactants is analogous to the dynamics of pulsations of the mixture fraction. In such an event, the values of $\bar{\omega}$ and I_s are determined in terms of the average and pulsation characteristics of mixing: $\overline{Y}_A$, $\overline{Y}_B$, σ_A^2, σ_B^2, $\bar{f}$, and σ^2. Then, according to the Toor model [3], the segregation coefficient $I_s = -\sigma^2/[\bar{f}(1-\bar{f})]$, and according to the Patterson model [26], $I_s = -\dfrac{\sigma_A^2 \sigma_B^2}{\overline{Y}_A^2 \overline{Y}_B^2}$. In the other Patterson model [4], $I_s = -C_3 \dfrac{\sigma^2 \sigma^2}{\overline{Y}_A^2 \overline{Y}_B^2}$, where $C_3 = Y_{B0}^2/Y_{A0}^2$ and it is assumed that the dispersion of the reactant concentrations is equal to the dispersion of the mixture fraction, $\sigma_A^2 = \sigma_B^2 = \sigma^2$, which is used in calculating the segregation coefficient.

Probability density function method. It is not necessary to construct approximate expressions for $\bar{\omega}$ or I_s if we use the joint probability density function (PDF) $F(x_i, t, \Gamma_A, \Gamma_B)$ of random variables Y_A and Y_B [5–7]:

$$\bar{\omega}(x_i, t, Y_A, Y_B) = \iint_{\Gamma_A, \Gamma_B} \omega(x_i, t, \Gamma_A, \Gamma_B) F(x_i, t, \Gamma_A, \Gamma_B) d\Gamma_A d\Gamma_B \, , \tag{7}$$

$$I_s(x_i, t) = \frac{1}{\overline{Y}_A \overline{Y}_B} \iint_{\Gamma_A, \Gamma_B} y_A' y_B' F(x_i, t, \Gamma_A, \Gamma_B) d\Gamma_A \Gamma_B \, , \tag{8}$$

where Γ_A and Γ_B are probabilistic variables of concentrations of reactants Y_A and Y_B, respectively. Such an approach permits obtaining expressions for $\overline{\omega}$ and I_s with account for all correlations of the concentration. However, we have to "invent" the form of multidimensional PDFs for real turbulent flows with the use of more or less reliable physical representations or solve the corresponding differential equations. Even in the case where we restrict ourselves to the "laminar chemistry" approximation, i.e., the equality for $\overline{\omega} = -K\overline{Y}_A\overline{Y}_B$ is written, actually the simplest form of the PDF

$$F(x_i,\ t,\ Y_\alpha) = \prod_{\alpha=1}^{n} \delta\,(Y_\alpha - \overline{Y}_\alpha)\ \text{is used.}$$

Model of an infinitely fast reaction. The model considers a chemical reaction to be completed as soon as the reactants come in molecular contact. An infinitely fast reaction can be expressed quantitatively by the approximation $Y_A(x_i,\ t)Y_B(x_i,\ t) = 0$, i.e., the two reactants do not exist simultaneously at one point and at one and the same instant of time, since such a reaction will annihilate them. Consequently, it is assumed that the reactants A and B in the flow are fully separated (complete segregation) [24]. The reactant B ($Y_B = 0$) is absent from regions where $f > f_{st}$ and, vice versa, the reactant A ($Y_A = 0$) is not present in regions where $f < f_{st}$ because as soon as they are mixed in the stoichiometric ratio needed for the reaction, they react instantaneously and completely.

An important consequence of the assumption of an infinitely fast chemical reaction is the fact that the instantaneous concentration of the reactants $Y_\alpha = Y_\alpha(t)$ is a function of only the conservative variable — the mixture fraction f. Therefore, the problem of determining the interaction between turbulence and chemical processes is greatly simplified because the statistics of all chemical variables can be obtained from knowledge of the f value statistics, since the instantaneous values of concentrations yield linear dependences on the mixture fraction [24]:

$$\frac{Y_{A\infty}}{Y_{A0}} = 0\ ,\quad \frac{Y_{B\infty}}{Y_{B0}} = 1 - \frac{f}{f_{st}}\ ,\quad \frac{Y_{P\infty}}{(n+1)\,Y_{A0}} = f\ \ \text{at}\ \ f < f_{st}\ ,$$

$$r_{eq}\frac{Y_{A\infty}}{Y_{A0}} = \frac{f}{f_{st}} - 1\ ,\quad \frac{Y_{B\infty}}{Y_{B0}} = 0\ ,\quad r_{eq}\frac{Y_{P\infty}}{(n+1)\,Y_{A0}} = f - 1\ \ \text{at}\ \ f > f_{st}\ . \tag{9}$$

The application of the PDF $F(x_i,\ t,\ \Gamma)$ of the mixture fraction f takes into account the influence of turbulent pulsations on the statistical scalar moments. The averaged concentrations are equal to $\overline{Y}_{\alpha\infty} = \int_0^1 Y_{\alpha\infty}(\Gamma)F(x_i,\ t,\ \Gamma)d\Gamma$ or, according to definitions (3) and (9), to:

$$\frac{\overline{Y}_{P\infty}}{(n+1)\,Y_{A0}} = \int_0^1 \min\,(f,\,(1-f)/r_{eq})\,F\,(x_i,\ t,\ \Gamma)\,d\Gamma\ ,\quad \frac{\overline{Y}_{A\infty}}{Y_{A0}} = \overline{f} - \frac{\overline{Y}_{P\infty}}{(n+1)\,Y_{A0}}\ ,\quad \frac{\overline{Y}_{B\infty}}{Y_{B0}} = 1 - \overline{f} - \frac{r_{eq}\overline{Y}_{P\infty}}{(n+1)\,Y_{A0}}\ . \tag{10}$$

In the considered case, the averaged rate $\overline{\omega}$ cannot be calculated from formula (4), since by virtue of the assumptions made and definitions (9), it is obvious that $\overline{y'_A y'_B} = -\overline{Y}_A\overline{Y}_B$ and, therefore, $I_s = -1$. In modeling, the average concentrations of the reactants and reaction products are calculated. With account for the finite rate of the chemical reaction the given approximation is used as one of the limiting cases for calculating the averaged concentrations of the reactants and reaction products.

Model for a fast finite-rate reaction. Consider the statistical information needed for determining the mixture fraction used to predict the chemical reaction rate (4). The segregation coefficient I_s is defined as

$$I_s = \frac{\overline{y'_A y'_B}}{\overline{Y}_A\overline{Y}_B} = \frac{\overline{Y_A Y_B}}{\overline{Y}_A\overline{Y}_B} - 1\ ,$$

where the correlation, according to definitions (3), is equal to

$$\frac{\overline{Y_A Y_B}}{Y_{A0} Y_{B0}} = \iint \left(\Gamma - \frac{\Gamma_P}{(n+1)\,Y_{A0}} \right) \left(1 - \Gamma - r_{eq} \frac{\Gamma_P}{(n+1)\,Y_{A0}} \right) F\,(x_i,\,t,\,\Gamma,\,\Gamma_P)\,d\Gamma d\Gamma_P\,. \tag{11}$$

As mentioned above, the correlation $\overline{Y_A Y_B}$ can be calculated with the use of the method of the joint PDF $F(x_i,\,t,\,\Gamma,\,\Gamma_P)$ for determining the unknown statistical moment (11). With the use of the method described in [9], to find $\overline{Y_A Y_B}$, let us write the value of the reaction product concentration as

$$\overline{Y_P} = \iint \Gamma_P F\,(x_i,\,t,\,\Gamma,\,\Gamma_P)\,d\Gamma d\Gamma_P\,. \tag{12}$$

According to the Bayes theorem [27], for the joint PDF the relation $F(x_i,\,t,\,\Gamma,\,\Gamma_P) = F(x_i,\,t,\,\Gamma_P\,|\,\Gamma)F(x_i,\,t,\,\Gamma)$, where $F(x_i,\,t,\,\Gamma_P\,|\,\Gamma)$ is the conditional PDF of the concentration Y_P, i.e., the PDF under the condition that the mixture fraction f takes on a value equal to Γ, is valid. Then definition (12) transforms to the form

$$\overline{Y_P} = \iint \Gamma_P F\,(x_i,\,t,\,\Gamma_P\,|\,\Gamma)\,F\,(x_i,\,t,\,\Gamma)\,d\Gamma d\Gamma_P = \int_0^1 \overline{Y_P\,|\,\Gamma}\,F\,(x_i,\,t,\,\Gamma)\,d\Gamma\,,$$

where $\overline{Y_P\,|\,\Gamma}$ is the conditional concentration of the reaction product, $\overline{Y_P\,|\,\Gamma} = \int (\Gamma_P F(x_i,\,t,\,\Gamma_P\,|\,\Gamma)d\Gamma_P$. The quantity $\overline{Y_P\,|\,\Gamma}$ acquires values 0 and $Y_{P\infty}$ for two limiting cases: $Y_P = 0$ — mixing without a reaction and $Y_P = Y_{P\infty}$ — mixing at an infinitely fast reaction, respectively. Consequently, for the finite rate of the reaction the domain of definition of $\overline{Y_P\,|\,\Gamma}$ is the interval $(0,\,Y_{P\infty})$. The authors of [28] proposed a linear interpolation $\overline{Y_P\,|\,\Gamma} = \chi Y_{P\infty}(\Gamma)$, where the interpolation parameter χ is chosen so that the equality $\overline{Y_P} = \int_0^1 \overline{Y_P\,|\,\Gamma}F(x_i,\,t,\,\Gamma)d\Gamma = \chi \overline{Y_{P\infty}}$ holds and, therefore, $\chi = \overline{Y_P}/\overline{Y_{P\infty}}$.

As a result, in our case the segregation coefficient can be written as $I_s = \dfrac{\overline{y_A' y_B'}}{\overline{Y_A}\,\overline{Y_B}} = \dfrac{\overline{Y_A Y_B}}{\overline{Y_A}\,\overline{Y_B}} - 1$, where the correlation

$$\frac{\overline{Y_A Y_B}}{Y_{A0} Y_{B0}} = \int_0^1 \left(\Gamma - \chi \frac{Y_{P\infty}\,(\Gamma)}{(n+1)Y_{A0}} \right) \left(1 - \Gamma - \chi \frac{r_{eq} Y_{P\infty}\,(\Gamma)}{(n+1)Y_{A0}} \right) F\,(x_i,\,t,\,\Gamma)\,d\Gamma\,. \tag{13}$$

Thus, the only unknown quantity remaining, as in the case of an infinitely fast reaction, is the PDF $F(x_i,\,t,\,\Gamma)$ of the mixture fraction.

At different times and depending on the type of problems to be solved, several approximate analytic representations were proposed for the PDF of scalars, whose concrete form contains, as parameters, statistical moments of the PDF itself [1, 5–7, 9]. For the PDF $F(x_i,\,t,\,\Gamma)$ of one random scalar variable f, we can give, as an example, representations in the form of a sum of two δ-functions, a truncated Gauss distribution, the β-PDF, etc., which are determined with the use of two averaged parameters of turbulent mixing — the averaged value of the scalar and its dispersion.

The influence of the analytical form of the PDF on the value of the segregation coefficient I_s calculated from equality (13) has been established with the application of both the PDF $F(x_i,\,t,\,\Gamma)$ on the basis of experimental data and the β-PDF. The latter function is given by the relation $F(x_i,\,t,\,\Gamma) = \beta(f)/\Phi(a,\,b)$, where $\beta(f) = f^{a-1}\,(1-f)^{b-1}$; $a = \overline{f}\left[\dfrac{\overline{f}(1-\overline{f})}{\sigma^2} - 1 \right]$; $b = a\dfrac{1-\overline{f}}{\overline{f}}$; $\Phi(a,\,b) = \int_0^1 f^{a-1}(1-f)^{b-1}df$ [29]. Then, to find the interpolation parameter χ, the values of the averaged concentration of the product at an infinitely fast reaction from the first equality of (10) are defined as

$$\frac{r_{eq} \overline{Y_{P\infty}}}{(n+1)\,Y_{A0}} = 1 - \overline{f} + f_{st}^{-1} \Phi_{st}\,(a+1,\,b)\,\frac{a}{a+b} - \Phi_{st}\,(a,\,b)\,,$$
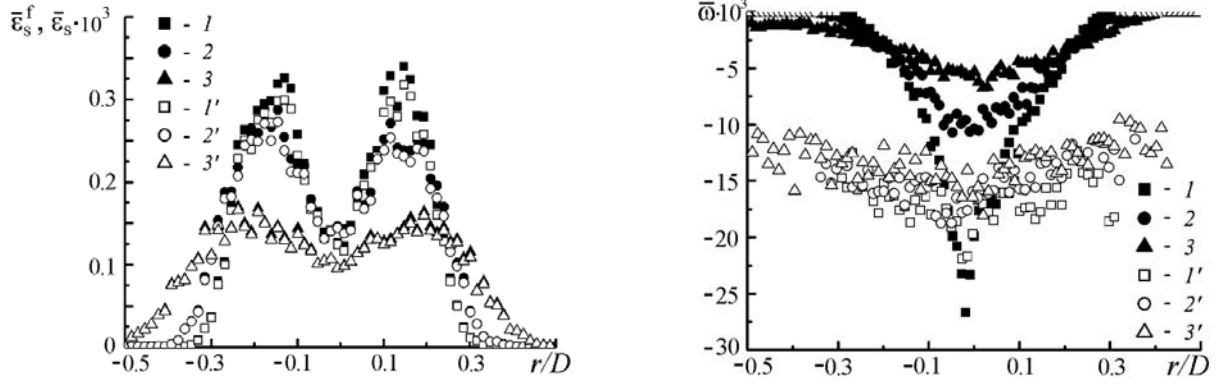
Fig. 1. Dissipation of the mixture fraction $\bar{\varepsilon}_s^f$ (solid symbols) and dissipation of mixture fraction pulsations $\bar{\varepsilon}_s$ (open symbols) as a function of the transverse coordinate r/D for various cross-sections of the mixer: 1, 1′) $x/D = 1.5$; 2, 2′) 2; 3, 3′) 3.

Fig. 2. Averaged rate of the chemical reaction determined by the EDC model (model (5)) (open symbols), model (6) (solid symbols) as a function of the transverse coordinate r/D for various cross-sections of the mixer: 1, 1′) $x/D = 1.5$; 2, 2′) 2; 3, 3′) 3.

where $\Phi_{st}(p,\ q) = \dfrac{1}{\Phi(p,q)}\displaystyle\int_0^{f_{st}} f^{p-1}(1-f)^{q-1}df$ is an incomplete β-function.

Results of the Calculations. For the EDC models (5) and (6), the basic parameter is the time scale τ_s given in terms of the experimentally obtained averaged characteristics of mixing — dispersion σ^2 and dissipation $\bar{\varepsilon}_s$ of mixing fraction pulsations, $\tau_s = \sigma^2/\bar{\varepsilon}_s$. The dispersion was determined directly from the instantaneous realizations of the mixing fraction. Determining the dissipation $\bar{\varepsilon}_s$ requires information on the statistics of the gradient of the scalar fields. In the present work, which is still within the framework of the conditions of the experiment performed and which possess single-point statistics of the scalars, we determined the local complete dissipation $\varepsilon_s^f = 2\dfrac{\nu}{Sc}|\nabla f|^2$ of the mixture fraction on the basis of the Taylor hypothesis for calculating the local axial gradient of the mixture fraction with the aid of the time derivative of the measured intensity of the signal [30]:

$$\varepsilon_s^f = 2\,\frac{\nu}{Sc}\left(2\left(\frac{\partial f}{\partial r}\right)^2 + \frac{1}{U_{ax}^2}\left(\frac{\partial f}{\partial t}\right)^2\right). \tag{14}$$

The error in calculating by formula (14) due to the introduction of the Taylor hypothesis does not exceed 10% [30]. As is seen from Fig. 1, the dissipation $\bar{\varepsilon}_s^f$ of the mixture fraction correlates fairly well with the change in the dissipation of mixing fraction pulsations calculated as

$$\bar{\varepsilon}_s = 2\,\frac{\nu}{Sc}\left(2\overline{\left(\frac{\partial f'}{\partial r}\right)^2} + \frac{1}{U_{ax}^2}\overline{\left(\frac{\partial f'}{\partial t}\right)^2}\right) = \bar{\varepsilon}_s^f - \bar{\varepsilon}_s^{ave},$$

where the averaged field dissipation $\bar{\varepsilon}_s^{ave} = 2\dfrac{\nu}{Sc}\left(2\left(\dfrac{\partial \bar{f}}{\partial r}\right)^2 + \dfrac{1}{U_{ax}^2}\left(\dfrac{\partial \bar{f}}{\partial t}\right)^2\right)$, which confirms the fact that the contribution of gradients of the averaged mixing fraction to the scalar dissipation is small, i.e., $\bar{\varepsilon}_s^f \approx \bar{\varepsilon}_s$.
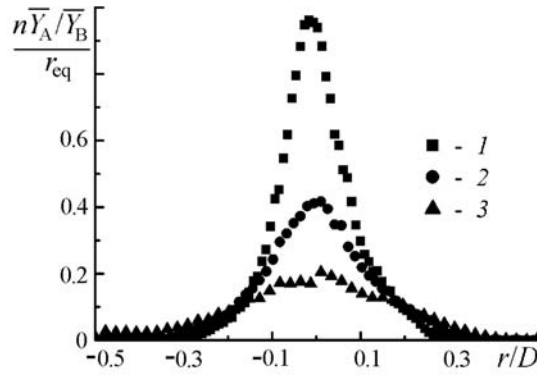
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Fig. 3. Concentration ratio of the reactants normalized to r_{eq} as a function of the transverse coordinate r/D for various cross-sections of the mixer: 1) x/D = 1.5; 2) 2; 3) 3.
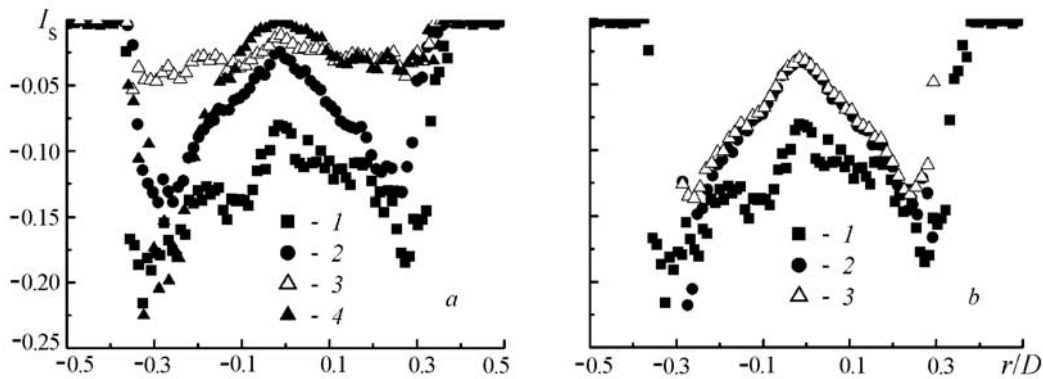

Fig. 4. Segregation coefficient as a function of the transverse coordinate r/D at x/D = 1.5: (a) 1) experimental data; 2) Toor model [3]; 3) Patterson model [26]; 4) Patterson model [4]; (b) 1) experimental data; 2) model (13) with the β-PDF.

The obtained distributions of dissipation $\overline{\varepsilon}_s$ were used to calculate the chemical reaction rate $\overline{\omega}$ by the EDC models (5) and (6) (the reaction constant $K = 10^8$ (Fig. 2). As is seen, there is a wide difference in the reaction rate in using the above models. The chemical reaction proceeds most vigorously (EDC model (5)) in the vicinity of the mixer axis and it is practically zero near the walls, which agrees well with the reaction product profile measured in the experiment in [17]. The chemical reaction rate is maximal at a distance x/D = 1.5, where the maximum production of reaction products is observed because the stoichiometric content of reactants in the mixture $\dfrac{n\overline{Y}_A/\overline{Y}_B}{r_{eq}} \approx 1$ has been attained (Fig. 3).

Downstream, the $\overline{\omega}$ values decrease because of the deviation from the stoichiometric conditions as a consequence of the reactant A deficit for the reaction to proceed (Figs. 2, 3). It should be noted that in the experiment the reaction product production varied slightly in the range of distances $1.5 \le x/D \le 2.0$, i.e., it is obvious that the model overestimates both the reaction rate and the consumption of acid.

The change in the chemical reaction rate obtained by the EDC model (6) points to the fact that the reaction proceeds throughout the width of the jet with an approximately equal intensity for various cross-sections of the mixer (Fig. 2). However, this contradicts the known experimental data on mixing of nonreacting and reacting media in coaxial flows [17, 23].

For models of the averaged rate of the chemical reaction, the necessary parameter for closing is the segregation coefficient I_s. Figures 4–6 present the results of comparing the experimental values of I_s with the values calculated by the models with the use of the measurement data for $\overline{Y}_A$, $\overline{Y}_B$, $y'_A y'_B$, σ_A, σ_B, $\overline{f}$, and σ^2.
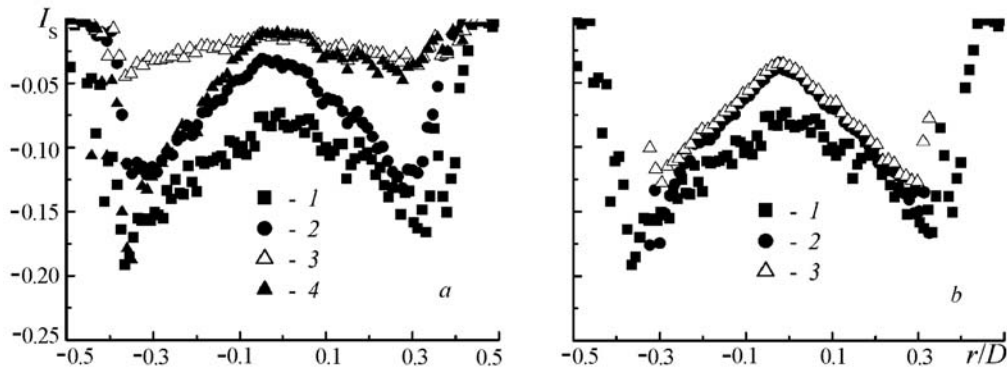
520

Fig. 5. Segregation coefficient as a function of the transverse coordinate r/D at $x/D = 2$. Symbols 1–4 are same as in Fig. 4.
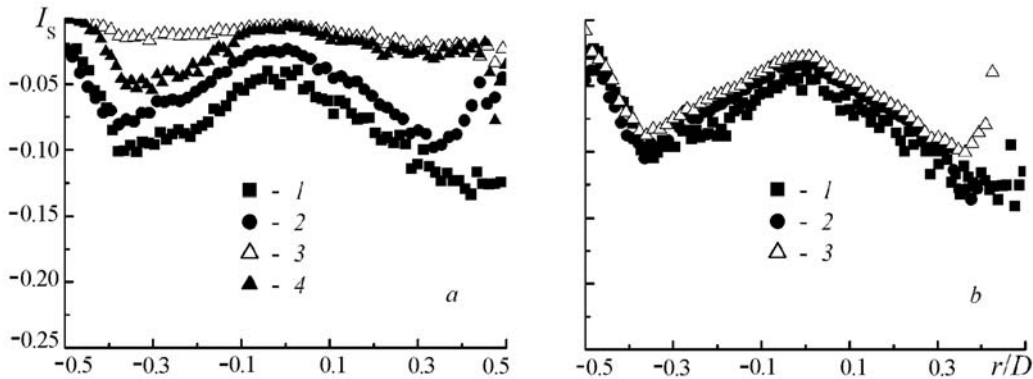

Fig. 6. Segregation coefficient as a function of the transverse coordinate r/D at $x/D = 3$. Symbols 1–4 are same as in Fig. 4.

All the approximations considered above are consistent in terms of the possible range of the change in the segregation coefficient (Figs. 4–6): the I_s distributions lie between the asymptotic curves of the infinitely fast reaction ($I_s = -1$) and the infinitely fast mixing ($I_s = 0$). There are differences in the degree of their agreement with the experimental distributions.

The segregation coefficients calculated by the Patterson model [26] (Figs. 4–6a, curve 3) where average concentrations of reactants and their dispersions are used correlate weakly with the concentrations calculated on the basis of direct measurements $\left(I_s = \dfrac{\overline{y'_A y'_B}}{\overline{Y}_A \overline{Y}_B} \right)$. The reaction rate depends weakly on the spatial cross-sectional coordinate, and the fact of prevailing mixing of reactants at the cocurrent flow-jet interface is ignored. This is a result of the fact that the maximum of alkali pulsations in the experiment was registered in the mixing layer while the maximum of acid pulsations was observed on the flow axis [17]. A low level of pulsations of reactants leads to segregation coefficients close to zero, which must point to complete mixing of the media. However, at a distance of $1.5 < x/D < 2.0$ mixing layers with maximum production of the reaction product coalesce, and a low level of pulsations results from the fact that a small number of reactants present in the considered region of the flow enter into the reaction. This fact can be explained by the influence of the structure of the turbulent flow on the chemical reaction: the mixing layer is formed by vortices in which the original substances (acid and alkali) are brought into contact, and the structure of vortices inhibits the reaction [17]. Investigation of the scalar field microstructure has shown that dissipation in vortices takes place at the boundary between their shear layers containing the substance being mixed with various concentrations (in the case of mixing different substances the layers contain different media) [31]. Thus, the use for calculating the segregation coefficient of dispersion values of the original reactant distorts the real stage of the chemical reaction, overestimating its rate.

The use of the mixture fraction dispersion (Patterson model [4]) for calculating the segregation coefficient leads to a qualitative improvement in agreement between experimental and model values of I_s (Figs. 4–6a, curve 4). Evidently, the measured values of the mixture fraction and its pulsations contain information on a higher concentration of reactants, i.e., on a higher potential of the chemical reaction.

The Toor approximation [3] where, to calculate the segregation coefficient, the values of the mixture fraction and its dispersion are used, markedly improves the agreement with experimental distributions (Figs. 4–6a, curve 2). Thus, the application of statistical characteristics of the mixture fraction is preferable for modeling the chemical reaction. This is confirmed by calculations of the segregation coefficient with use of the PDF $F(x_i, t, \Gamma)$ of the mixture fraction in models taking into account the final rate of the reaction (Figs. 4–6b, curves 2, 3). The advantage of the latter models over the models of Toor and Patterson [4] shows up most vividly in the cross-section $x/D = 3.0$, i.e., at a distance from the coalescence point of the mixing layers. The results presented in Figs. 4–6b also show that for the considered flow the β-PDF is a fairly reliable model for the approximation of the experimental PDF of the mixture fraction. The maximum value of the segregation coefficient I_s was observed in the mixing layer of the jet and the concurrent flow at $|r/D| \approx 0.1$–0.4 for both experimental and calculated distributions. The wide difference of the maximum experimental values of I_s from the asymptotic value ($I_s = -1$) points to the fact that turbulence considerably decelerates the chemical reaction in the flow. As mentioned above, only a small number of reactants enter into the reaction and their segregation regions still exist.

However, the models using the PDF of the mixture fraction for calculating the coefficient I_s also predict a higher rate of the reaction on the flow axis, which leads to segregation coefficients close to zero. Such a disadvantage of the models is a consequence of the assumption that in the presence of two reactants the reaction proceeds until one of them disappears. But in fact only small volumes of acid and alkali directly contacting each other at the boundaries of the shear layers in vortices enter into the reaction. The agreement between the calculated and experimental values of I_s in the mixing layers reflects the fact that the mixture fraction values in this region of the turbulent flow are relatively small and, consequently, the influence of the vortex structure of the flow on the chemical reaction is insignificant. On the flow axis where the mixture fraction values increase, the influence of the vortex structure of the flow is stronger.

Downstream, the values of the mixture fraction decrease monotonically as a result of mixing and the sizes of vortices responsible for the mixing increase simultaneously (the scalar integral scale increases as the flow is developed, [23]). Evidently, in larger vortex structures larger volumes of reactants will enter into the reaction, and the approach of the mixture fraction to its asymptotic value decreases the difference in the number of reactants that have entered into the reaction calculated from the condition of an infinitely fast reaction. Apparently, these two facts form the basis of a good correlation between the experimental values of the segregation coefficient and the calculated values obtained with the use of the PDF $F(x_i, t, \Gamma)$ of the mixture fraction.

Conclusions. We have analyzed relations widely used in numerical modeling to describing the averaged rate of a chemical reaction using the instantaneous distributions of the mixture fraction and the reaction product measured simultaneously in various cross-sections of the mixer in investigating the turbulent mixing of chemically reacting incompressible liquid media. It has been shown that all models overestimate the reaction rate.

It should be noted that nevertheless models using information on changes in the scalar dissipation, the mixture fraction and dispersion, and the PDF of the mixture fraction are advantageous. The model relations constructed on the basis of reactant dispersions do not provide even a qualitative representation of the production dynamics of reaction products.

A disadvantage of all the models considered is the application of single-point statistical information on mixing and reaction. Moreover, these models do not take into account the specific feature of the chemical reaction proceeding in vortex structures — its localization between the shift layers of these structures and, consequently, the slower formation of the reaction product as compared to that following from the model assumption about the instantaneous consumption of the volumes of reactants coming in molecular contact, i.e., the models should take into account the dynamics of the change in the scalar dissipation.

NOTATION

a, b, β-PDF parameters; C_1, C_2, C_3, constants; D, mixer diameter; F, probability density function; f, mixture fraction; f_{st}, stoichiometric value of the mixture fraction; $\bar{f}$, averaged value of the mixture fraction; I_i, instantaneous intensity of radiation; I_m^{max}, maximum radiation intensity of fluorescein in a mixture with two additives; I_R^{max}, maximum radiation intensity of the Rhodamine solution; I_s, segregation coefficient; K, reaction constant; K^*, parameter of the chemical reaction rate; l, wavelength; n, stoichiometric coefficient; p, q, β-function parameters; r, transverse coordinate of the mixer; r_{eq}, chemical equivalence ratio; Sc, Schmidt number; t, time; U_{ax}, longitudinal component of the averaged velocity on the mixer axis; x, coordinate along the mixer; x_i, spatial coordinates; Y, concentration; Y_P^{max}, maximum concentration of reaction products formed at a stoichiometric ratio of reactants; y', concentration pulsation; Γ, Γ_A, Γ_B, Γ_P, probabilistic variables of the mixture fraction f, concentration of the reactants A and B and the reaction product P, respectively; δ, Dirac function; ε_s, scalar dissipation rate; ν, kinematic viscosity coefficient; σ^2, σ_A^2, σ_B^2, dispersions of the mixture fraction and concentrations of the reactants A and B, respectively; τ, time scale of mixing; Φ, β-function; χ, interpolation parameter; ω, chemical reaction rate. Subscripts: $^-$, averaging sign; $|$, condition sign; 0, parameter in the initial cross-section of the mixer; ∞, parameter of the infinitely fast reaction; A, B, parameters of the reactants; ave, averaged; ax, axial; eq, equivalent; f, full dissipation parameter; i, realization number; m, parameters of the mixture of substances; max, maximum; P, reaction product parameter; R, Rhodamine parameter; s, segregation; st, stoichiometric; α, concentration index.

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