Decoupling of Micro- and Macromixing in Turbulent Reacting Flow

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Closure models of mean reaction terms for turbulent reacting flows have been subject of many recent studies (Heeb and Brodkey, 1990; Dutta and Tarbell, 1989; Li and Toor, 1986; Patterson, 1985). Most of these models, however, consider micromixing as a controlling step and assume complete macromixing in the reactor. Almost all of these models are one-dimensional and do not readily extend to multidimensional systems where macro- as well as micromixing are important. Recently, Ranade and Bourne (1991) have proposed a new mechanistic model that can simulate interactions of micro- and macromixing in multidimensional systems, based on the engulfment model of Baldyga and Bourne (1989). In this work, we propose to place that model in proper perspective by comparing it with other closure models recently proposed for turbulent reactive mixing. It has been recognized that rapid competing reactions of the type:

$$A + B \rightarrow R \tag{1}$$

$$B + R \rightarrow S \tag{2}$$

are particularly sensitive to micromixing and can be used to discriminate various closure models. All the discussion presented here, therefore, refers to this reaction system.

Review of Previous Work

The term macromixing is used for the process leading to equal values of average concentration in space, and its characteristic time T_{macro} can be computed using blending time correlations. The term micromixing refers to processes governing local concentration fluctuations, and its characteristic time T_{micro} depends on local turbulence properties. All available models for reactive mixing can be classified according to their assumptions on relative magnitudes of T_{micro} and T_{macro}, and the characteristic reaction time, T_{kin}.

When the rate of macromixing is slow, but that of local micromixing is fast compared to reaction rate ($T_{kin} < T_{macro}$ and $T_{kin} \gg T_{micro}$), the relevant mixing scale is intermediate between a micromixing scale and the size of reactor. Cell balance models (Patterson, 1975; Middleton et al., 1986) can give reasonable simulations for such cases. These models, however, cannot predict influence of mixing scales smaller than computational cell. When the rate of macromixing is fast, but that of local micromixing is slow compared to reaction rate ($T_{kin} > T_{macro}$ and $T_{kin} < T_{micro}$), only small-scale mixing governs the reaction rate. Included in this category are: the mass-transfer model of Harada et al. (1962); the stochastic mixing model of Kattan and Adler (1967); the slab diffusion model of Mao and Toor (1970); the IEM model of Villermaux and Devillon (1972); the ESCIMO model of Spalding (1978); the 3E model of Ritchie and Togby (1979); the 4E model of Mehta and Tarbell (1983); the EDD model of Bourne and Baldyga (1984); and the model of Baldyga and Bourne (1989). These models cannot predict the influence of mixing scales larger than integral length scales of turbulence. However, when both micro- and macromixing affect the reaction rate, none of the above models can predict the correct performance.

There have been many attempts at modeling the interactions of various mixing scales. Though some of the previously developed models can, in principle, be extended to simulate such interactions (for example, model of Kattan and Adler, 1967), no such attempt has been published. Recently, Heeb and Brodkey (1990), Dutta and Tarbell (1989), and Li and Toor (1986) have compared performances of various micromixing models. Out of these, only the closure models can potentially be extended to simulate interactions of macro- and micromixing (along with the flow simulation model) and will be considered in this work. The comparison of the model of Ranade and Bourne (1991) with these closure models will, therefore, be useful for the selection of an appropriate model for practical simulation of reactive mixing. Closures described by Brodkey and coworkers could not predict reactive mixing correctly, as can be seen from their comparisons with Li and Toor's (1986) experimental data and therefore are not considered here for comparison. The model of Li and Toor (1986) shows good agreement with their experimental data. Model parameter used in their predictions was calculated using their experimental data of very rapid reaction. Dutta and Tarbell (1989) could fit their model to Li and Toor's data, but with the use of model parameter that was obtained via fitting exercise itself. Patterson (1985) had proposed a concept of "paired interaction" to

extend the closure model of single bimolecular reaction to the reaction system represented by Eqs. 1 and 2. This model has not been tested and compared with other closure models. The model of Ranade and Bourne (1991) is compared with those of Patterson (1985), Li and Toor (1986) and Dutta and Tarbell (1989).

Mathematical Model

Mixing and chemical reaction between two miscible fluids proceeds through following steps:

Step 1. Convection by mean velocity
Step 2. Turbulent dispersion by large eddies
Step 3. Reduction of segregation length scale
Step 4. Laminar stretching of small eddies
Step 5. Molecular diffusion and chemical reaction

Therefore, to construct an approximate, but tractable, model of reactive turbulent flows requires two distinct models: one for simulating turbulent transport terms ($\overline{u_i u_j}$, $\overline{u_i c}$); the other for simulating mean reaction terms. This work concentrates on developing the model for mean reaction terms, assuming that some available models provide an acceptable description of the turbulent transport. Consider a turbulent fluid in which two initially segregated reactants mix together. Ranade and Bourne (1991) proposed to decouple macromixing from micromixing at length scales of computational grid following the practice in large eddy simulations (where the grid size is selected using the requirement that eddies smaller than grid should behave as locally isotropic). Thus, we propose to select the size of grid element in such a way that the third step (scale reduction to Kolmogorof's scale) in mixing process can be eliminated as a controlling step by making it fast. Characteristic time for step 3 is given as (Corrsin, 1964; Rosensweig, 1964):

$$T_3 = (L_s^2/\epsilon)^{1/3} \tag{3}$$

If this time scale is shorter than the residence time of computational element, then each computational element can be visualized as mixed cell with segregation scale of the order of Kolomogorof's scale. Schumann (1973) recommends about 30 grids for Reynold's number greater than 2×10^5 in each direction for the subgrid motions to behave locally isotropic. Results reported by Schumann (1975) and Horiuti and Kuwahara (1982), however, show that coarser grids also can give good results. Thus, proper choice of grid element allow us to construct a decoupled model. Each computational element can be visualized as a composite of a large number of coherent fluid packets. Mass exchange between such small fluid lumps will occur through steps 4 and 5 listed above. Large-scale processes (steps 1 and 2) affect these small-scale mass exchanges indirectly by transporting such coherent fluid packets to another location (though without changing their concentrations). Broadwell and Breidenthal (1982) have also used similar concepts to develop a simple model for mixing in turbulent shear layers.

The mass exchange between small fluid packets can be modeled using the engulfment model of Baldyga and Bourne (1989). They have showed that for systems with $Sc < 4{,}000$, diffusivity does not affect reaction significantly. following them it can be assumed that there are no concentration gradients within such small fluid (Kolomogorof's scale) packets. Population of such lumps within each computational cell is divided into N subgroups, each associated with unique concentration. Time constant for this small-scale mass exchange between these subgroups can be estimated either from Baldyga and Bourne's (1989) analysis as:

$$T_{ms} = (\nu/\epsilon)^{1/2}\ (1.0/0.05776) \tag{4}$$

or modified form of Corssin's equation for small-scale eddies (Pohoreki and Baldyga, 1983) as:

$$T_{ms} = (\nu/\epsilon)^{1/2}\ \{1./[3.08(\ln Sc - 1.27)]\} \tag{5}$$

Extending two subgroup models of Baldyga and Bourne (1989), we can write mass exchange between N subgroups within each cell as:

$$de_j/dt = E\, e_j\, e_{j+1} + 2E\, e_{j+1} \sum_{i}^{j-i} e_i - E\, e_j \sum_{\neq j,\, j+1}^{N} e_i \tag{6}$$

$$de_j C_{mj}/dt = E\, e_j\, e_{j+1}\, C_{mj+1} + 2E\, e_{j+1} \sum_{i}^{j-1} e_i (C_{mi} + C_{mj+1}) - E\, e_j\, C_{mj} \sum_{\neq j,\, j+1}^{N} e_i + e_j\, R_{mj} \tag{7}$$

where C_{mj} is concentration of the mth species in jth subgroup and the engulfment rate, and E is reciprocal of T_{ms}.

Large-scale mixing and transport of these small, coherent fluid packets within reactor can be simulated using population balance models. However, it is convenient to formulate equations in the volume fractions rather than number density framework. If each computational cell is considered macromixed, that is, spatial fluctuations of volume fractions within the cell are neglected, the large-scale mixing process can be modeled using usual convective-dispersion transport equation (Ranade and Bourne, 1991):

$$\partial e_j/\partial t + \partial (U_i e_j)/\partial x_i = \partial (\Gamma\ \partial e_j/\partial x_i)/\partial x_i + S_e \tag{8}$$

$$\partial e_j C_{mj}/\partial t + \partial (U_i e_j C_{mj})/\partial x_i = \partial (\Gamma\ \partial e_j C_{mj}/\partial x_i)/\partial x_i + S_C \tag{9}$$

The turbulent mass diffusivity (Γ) in these equations can be assumed to be equal to the turbulent momentum diffusivity (which can be computed from suitable turbulence model) as a first approximation. The source terms in the above equations are results of small-scale mixing within each computational element. Therefore, these source terms are the righthand sides of Eqs. 6 and 7. Equations 8 and 9, along with appropriate boundary conditions (zero gradient at impermeable walls with feed inlets as mass sources), form the complete model for turbulent reactive mixing. The details of the solution of these equations are described by Ranade and Bourne (1991).

Discussion

The mathematical model described above provides a flexible, yet simple, framework for the simulation of reactive mixing. This model reduces to previously established models under limiting conditions. If local micromixing time, T_{ms}, is very small, each computational cell will act as a completely mixed cell and the model will reduce to that of Middleton et al. (1986).

If convection and turbulent dispersion is high enough to eliminate large-scale gradients, this model reduces to that of Baldyga and Bourne (1989). Both of these models show good agreement with a wide range of experimental data and require no further comparisons to demonstrate their validity. Therefore, instead of repeating those comparisons with experimental data in the micromixing controlling regime here, we compared the predictions of our model with those of other models using identical parameters. Model predictions will be compared with experimental data in the region where previous models are not applicable (that is, when interaction between macro- and micromixing is present).

Before presenting quantitative comparisons with other models, it should be noted that unlike other models, the present model can be readily extended to multidimensional systems where incomplete macromixing is present. Ranade and Bourne (1991) have shown that this model also satisfies two important limits: the slow reaction (pure mixing) limit and the fast reaction limit. It should also be noted that the results of this model will be sensitive to the initial volume ratio of the segregated reactants: this has been observed experimentally. Models of Patterson (1985), Li and Toor (1986) and Dutta and Tarbell (1989) do not possess this important property. Preliminary computational results using our model indicate that an increase in the number of subgroups beyond three has no significant effect on predictions in the micromixing regime. Therefore, we have used three subgroups for the following comparisons (only sample comparisons are presented).

Micromixing regime

When only micromixing is controlling, the concentration equations for the reaction scheme represented by Eqs. 1 and 2 can be written as:

$$dY_A/d\theta = r_A = -D_1\ (Y_A Y_B + \overline{Y_A' Y_B'}) \tag{10}$$

$$dY_S/d\theta = r_S = D_2\ (Y_B Y_R + \overline{Y_B' Y_R'}) \tag{11}$$

$$dY_B/d\theta = r_A - r_S \tag{12}$$

$$dY_R/d\theta = -r_A - r_S \tag{13}$$

Initially, no R and S were assumed to be present. Thus, the profiles of dimensionless concentrations (Y) with respect to dimensionless time (as predicted by Li and Toor's and Dutta and Tarbell's 4E closure models) will depend only on the Damkohler numbers (D_1 and D_2) and ratio of initial concentrations of A and B. Ranade and Bourne's (1991) model will also require initial conditions on volume fractions. Since other models are not sensitive to the volume fractions of segregated streams, all the computations using Ranade and Bourne's model are based on equal initial volume fractions of A and B (0.5 each).

Li and Toor's (1986) closure model for the $\overline{Y_B' Y_R'}$ (Eq. 25 in their article) require the knowledge of mixing with very fast (acid-base) reaction. Li and Toor (1986) have used the experimental data in their calculations. In this note, we have used Toor's (1969) model for single, bimolecular, fast reaction to compute the necessary information. This model of Toor (1969), Patterson's (1985, his Eq. 29) closure model and the 4E closure model (Eqs. 71 and 81 in their article) of Dutta and Tarbell (1989) require the decay of intensity of segregation. This decay is modeled as:

$$I_s = \exp(-\theta) \tag{14}$$

When only micromixing is controlling, Ranade and Bourne's (1991) model reduces to Eqs. 6 and 7. Equations representing large-scale mixing (Eqs. 8 and 9) need not be solved. Relationship between the volume fractions and concentrations of each subgroup and the averaged concentrations is given by Ranade and Bourne (1991).

This discussion allows one to predict the yield of final product (X_S) in the reaction scheme represented by Eqs. 1 and 2 using the closure models of Patterson (1985), Li and Toor (1986) and Dutta and Tarbell (1989), and the model of Ranade and Bourne (1991). The predictions were made for different values of D_1/D_2 ratios (in the range 100 to 2,000), C_{B0}/C_{A0} ratios (in the range (0.5 to 2.) and D_2 (in the range 2×10^{-3} to 2×10^{-2}). The range for D_2 values is that covered by Li and Toor (1986). More efficient mixers will have more intense turbulence, and therefore, the lower end of the D_2 range will be of more interest. The trends in the predicted values were almost the same for all values of D_2 in the studied range. Therefore, here we present the comparisons only for the one value of D_2 (4×10^{-3}) to save space. Moreover, the trends in the predictions of various models do not change significantly with respect to dimensionless time. Therefore, it would be sufficient to compare the predictions at any one value of dimensionless time.

In Figure 1, predictions of Ranade and Bourne's (1991) model are compared with those of Dutta and Tarbell (1989), Li and Toor (1986) and Patterson (1985) for different D_1/D_2 ratios at $\theta = 6$. Figure 2 shows different C_{B0}/C_{A0} ratios at constant D_1/D_2 ratio and at $\theta = 4.75$. Predictions of our model agree closely with those of Li and Toor's closure model (within reported accuracy of experimental data). For the same overall concentrations of A and B, decrease in the initial volume fraction of B should result in an increase in the yield of S. Only the present model could reproduce such trend. Though predictions of Li and Toor's closure model and our model are almost the same for the micromixing regime, it should be noted that Li and Toor's closure model is specifically tailored for this reaction scheme (Eqs. 1 and 2) and cannot be extended to other reaction schemes. Our model can handle any reaction scheme without any modificiation (except in the R_{mj} term). The application of Li and Toor's model to reactors with incomplete macromixing (with 3D flow), however, will be quite tedious and has not been demonstrated (especially for semibatch reactor where incomplete macromixing will be unavoidable at higher feed rates). In the following section, we compare predictions of our model with whatever scanty experimental data available for the cases of incomplete macromixing.

Interaction between macro- and micromixing

Most of the experimental data available for reacting turbulent flows are carefully collected to eliminate interactions of micro- and macromixing (Baldyga and Bourne, 1989). Recently, Thoma (1989) has purposefully collected data of competing reactions in stirred semibatch reactor in the operating

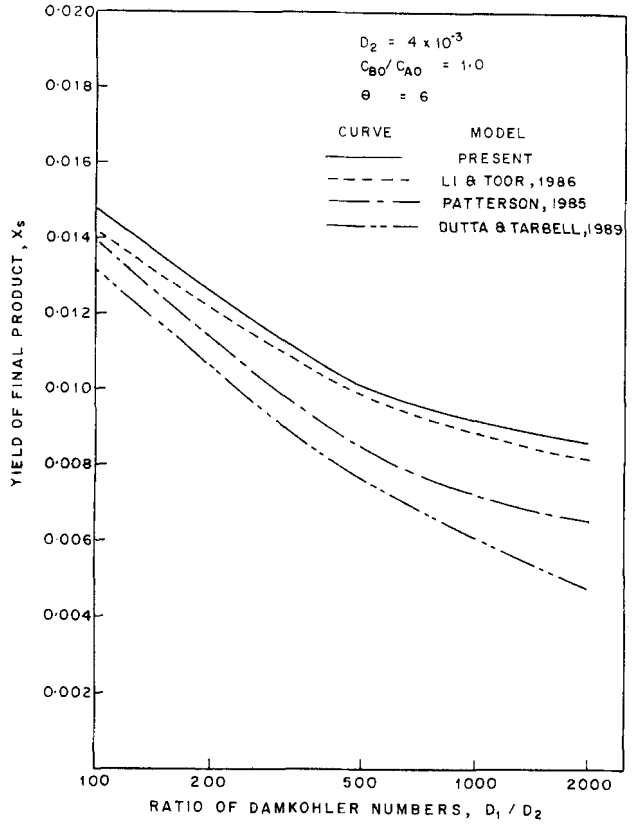

Figure 1. Comparison of closure models, effect of ratio of Damköhler numbers, D_1/D_2.

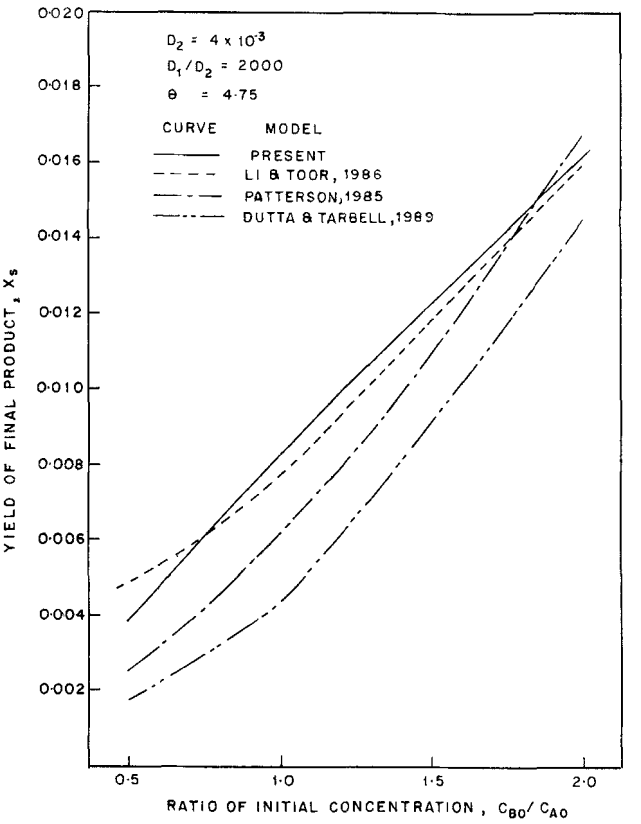

Figure 2. Comparison of closure models, effect of ratio of initial concentrations, C_{B0}/C_{A0}.

region where interactions between micro- and macromixing are significant. Thoma et al. (1991) compared experimental data with the predictions of one-dimensional version of the present model. However, their model is not capable of simulating strong interactions between micro- and macromixing. Ranade and Bourne (1991) simulated these micro- and macromixing interactions in stirred reactor. Figure 3 compares predictions of the yield of a final product, X_S, from Ranade and Bourne's (1991) model with the experimental data when strong interactions exist (at very short feed addition times). For this comparison, we simulated flow in stirred tank (with disc turbine impeller) with the $k-\epsilon$ model of turbulence (using the code FIAT, described by Ranade et al., 1991). A new code RIAT (reactions in agitated tanks) was constructed using the fractional step approach of Oran and Boris (1987). Thoma et al. (1991) present details of experimental arrangements. Details of grid arrangement, boundary conditions and further information on RIAT can be found in Ranade and Bourne (1991). It can be seen that model predictions compare well with experimental data (taken from Thoma, 1989, for four-feed points with the feed time of 20 s in the 0.3-m stirred reactor with disc turbine). Thus, the model of Ranade and Bourne (1991), which gives almost same predictions as that of Li and Toor's (1986) closure model for the micromixing controlled regime, can also be used to simulate the reactive mixing involving interactions of micro- and macromixing. Since the primary purpose of this work is to compare the new mechanistic approach of Ranade and Bourne (1991) for simulating turbulent reacting flows with other closure models, we did not include a detailed comparison with experimental data. Unavailability of data on the intermediate degree of macro- and micromixing also restricts the scope of such comparisons.

Apart from the predictive value of this model, it can be used to gain an understanding about the process of reactive mixing by simulating finer details of the mixing process. For example, experimental observations for semibatch reactor (Thoma, 1989)

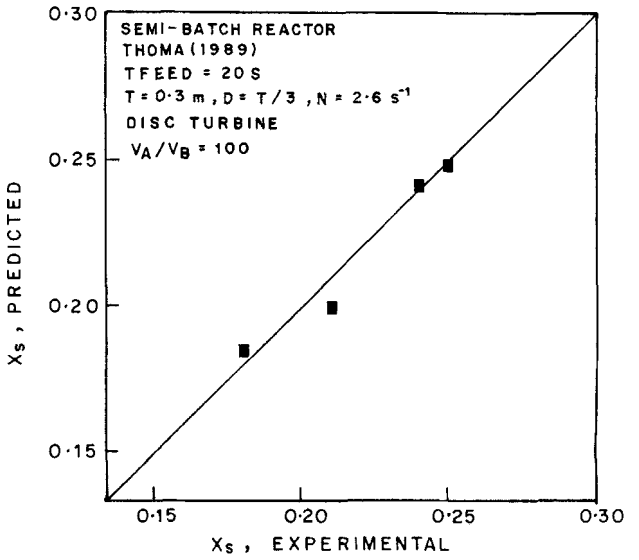

Figure 3. Comparison of model predictions with experimental data in presence of strong interactions between micro- and macromixing.

have shown that the yield, X_S (in the considered reaction scheme, Eqs. 1 and 2), develops through a minimum during the batch time instead of monotonic increase expected by simple models. The present model, however, can predict such a minimum. Further understanding about relative contributions of turbulent dispersion, engulfment and mean flow in reactive mixing can also be obtained by simply conducting more numerical experiments using the present model.

Conclusions

A simple framework has been developed to decouple influences of large- and small-scale mixing on turbulent reactive mixing (Ranade and Bourne, 1991). This generalized model reduces to previously established models of micromixing and macromixing under limiting conditions. Model predictions in the micromixing controlling regime agree with those of the closure model of Li and Toor (1986). Comparisons between model predictions and experimental data in the region of incomplete macromixing show promising agreement.

Notation

A = reactant, Eqs. 1
B = reactant, Eqs. 1 and 2
c = fluctuating concentration
C = mean concentration
C_{mj} = concentration of mth species in jth subgroup
C_{A0} = initial mean concentration of A
C_{B0} = initial mean concentration of B
D_1 = Damköhler number of 1st reaction, k_1C_{B0}/E
D_2 = Damköhler number of 2nd reaction, k_2C_{B0}/E
e = volume fraction
E = engulfment rate, $1/T_{ms}$
I_s = intensity of segregation
k = turbulent kinetic energy per unit mass and rate of reaction
k_1 = rate constant for reaction 1
k_2 = rate constant for reaction 2
L_s = integral scale of concentration fluctuations
N = number of subgroups
R = intermediate product, Eqs. 1 and 2
R_{mj} = production rate of mth species in jth subgroup
S = final product, Eq. 2
Sc = Schmidt number
S_C = source term for e_jC_{mj}, Eq. 7
S_e = source term for e_j, Eq. 6
t = time
T_{kin} = characteristic time of kinetics
T_{macro} = characteristic time of macromixing
T_{micro} = characteristic time of micromixing
T_{ms} = characteristic time of engulfment, Eqs. 4 and 5
u = fluctuating component of velocity
U = mean velocity
X_S = yield of S
Y_k = dimensionless concentration of species k, C_k/C_{B0}
Y_k' = dimensionless fluctuating concentration of species k

Greek letters

Γ = turbulent dispersion coefficient
ϵ = turbulent energy dissipation rate per unit mass
ν = kinematic viscosity
θ = dimensionless time, t/T_{ms}

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