Simulation of Reaction and Mixing Situations by Computer Models

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In a recent paper, Mao and Toor (*1*) presented a model for a single phase reaction system in which the turbulent mixing of segregated feed streams was simulated by allowing the diffusion of reactants *A* and *B* from an initial condition in which *A* and *B* are in alternate slabs. The results obtained with this diffusional mixing process were similar to those obtained by Kattan and Adler (*2*) who used a stochastic mixing model.

For the case where the two reactants have equal diffusivities and are in the stoichiometric ratio and when the reaction is very rapid or instantaneous, Mao and Toor (*1*, Equation 4) obtained for their diffusional model the solution

$$F = 1 - \frac{8}{\pi^2} \sum_{n=1,3,5..} \frac{1}{n^2} \exp\left(-n^2\pi^2\theta\right)$$

where F is the conversion of reactant A and θ is the dimensionless time parameter. A plot of $(1 - F)$ versus θ is given in Figure 1. From Figure 1 of Harris and Srivastava (*3*), which is included in Figure 1 of this communication, it is apparent that a very similar relationship between conversion and dimensionless time is obtained with a stochastic mixing process.

Thus, by appropriate manipulation of the parameters of either one or both models, almost identical F vs. θ response could be simulated. A suitable parameter for the stochastic model would be the fraction of the total number of model cell pairs selected for averaging per time interval, while an appropriate one for the diffusional model would be slab thickness.

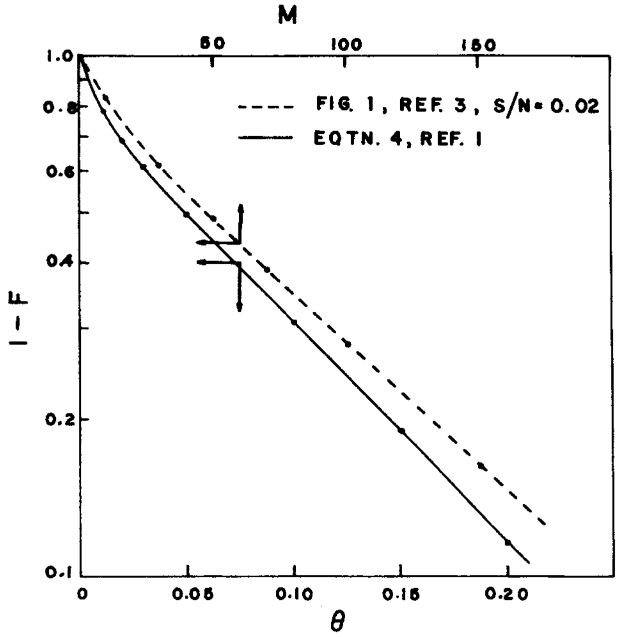

Fig. 1. Mixing characteristics of 'diffusional' and 'stochastic' models; $\beta = 1$.

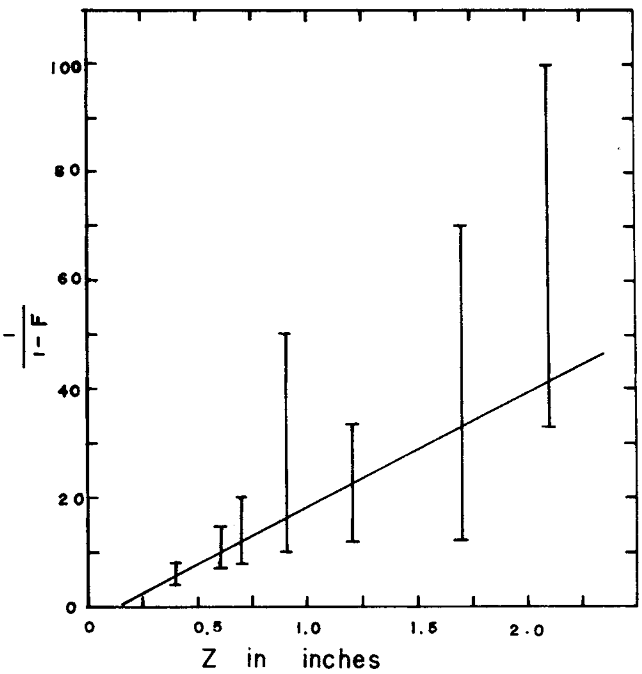

Fig. 2. Plot of Vassilatos and Toor's data (Figure 5, reference *4*) including error bars, which were shown in (Figure 2, reference *4*).

Mao and Toor (*1*) with their diffusional model, like Kattan and Adler (*2*) and Harris and Srivastava (*3*) with their stochastic mixing model, were able to simulate the experimental results of Vassilatos and Toor (*4*). The simulation obtained by Kattan and Adler was the closest to these experimental results, but they manipulated the representation of the mixing rate of the model to fit the experimental findings of reference *4*. Both models represent the mixing step as a first order process after an initial nonlinear response, while Vassilatos and Toor (*4*) considered that the mixing rate in their apparatus was second order, after an initial first order period of short duration. Too much emphasis, however, should not be placed on their mixing data, as it is subject to a high degree of error, particularly at conversions close to unity. A plot of Vassilatos and Toor's data, with error bars included, is shown in Figure 2.

Although the diffusional and stochastic models have been used successfully to simulate the data of Vassilatos and Toor (*4*) for the case where both the mixing and reaction rates must be considered, some of their properties, which are discussed herein, are inconsistent with available experimental data, and hence the application of the models is limited.

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The mixing order for real systems has not been firmly established at this stage, but most of the experimental values that have been reported differ considerably from those predicted by the models. Keeler, Petersen, and Prausnitz (*5*), for flow behind a square mesh grid, and Gibson and Schwarz (*6*), for flow behind a biplane grid, obtained a mixing order of 7/3. O'Brien (*7*) in a theoretical work for a second order chemical reaction, calculated a turbulent mixing order of 15/11 as $t \to \infty$, while Corrsin (*8*) and Lee (*9*) predicted a variable value for the mixing order. This latter prediction has been supported qualitatively by some experimental work by Keeler et al. (*5*) and Uberoi and Wallis (*10*) who found that decreasing the scale of turbulence decreased the rate of scalar decay.

Another inconsistency, which emphasizes the empirical nature of the existing models, is that they do not satisfy the relation

$$(1 - F) = \Gamma^0/\Gamma_0^0 \qquad (1)$$

developed by Toor (*12*) for mixing with an instantaneous chemical reaction and the reactants in the stoichiometric ratio. Equation (1) has been substantiated by the experimental work of Keeler et al. (*5*). From this relation, Γ^0/Γ_0^0 and $(1 - F)$ are interchangeable for the above conditions. Hence, it should be possible to obtain the mixing characteristics of the model by simulating mixing with an instantaneous chemical reaction and following the conversion as a function of time, or by simulating the equivalent mixing process without reaction and following the root-mean-square concentration fluctuation as a function of time.

When these two approaches are used, it is found that differing results are obtained. For the stochastic model, the mixing rate obtained when simulating mixing without reaction is given by

$$\frac{d(\Gamma^0/\Gamma_0^0)}{dt} = k_s(\Gamma^0/\Gamma_0^0) \qquad (2)$$

Yet if an instantaneous reaction, with reactants in the stoichiometric ratio is simulated, the process is better represented by

$$\frac{d(1 - F)}{dt} = J_s(1 - F)^P \qquad (3)$$

where $P \to 1$ at $t > r$ and $J_s \to k_s$ at $t > r$.

Equation (2) is unaffected by alterations in the initial concentration distributions, while in Equation (3) the value of P at $t < r$ changes as the initial distribution of reactant concentrations within the N cells is changed. Plots for various distributions (Table 1) of $(1 - F)$ against dimensionless time are included in Figure 3. By manipulating the initial concentration distribution, it is possible to obtain $P = 1$ and $J_s = k_s$ for the entire range of the process. The distributions that give these results ('skew' and 'blank') were established by considering a simple analytical analysis of the first steps of the mixing process (see Appendix 1), which highlights the discrepancy between Equations (2) and (3). The simulation of Vassilatos and Toor's (*4*) data for the intermediate case, achieved by using a skew distribution of the initial reactant concentrations, was not significantly different from that obtained by Harris and Srivastava (*3*) and Kattan and Adler (*2*).

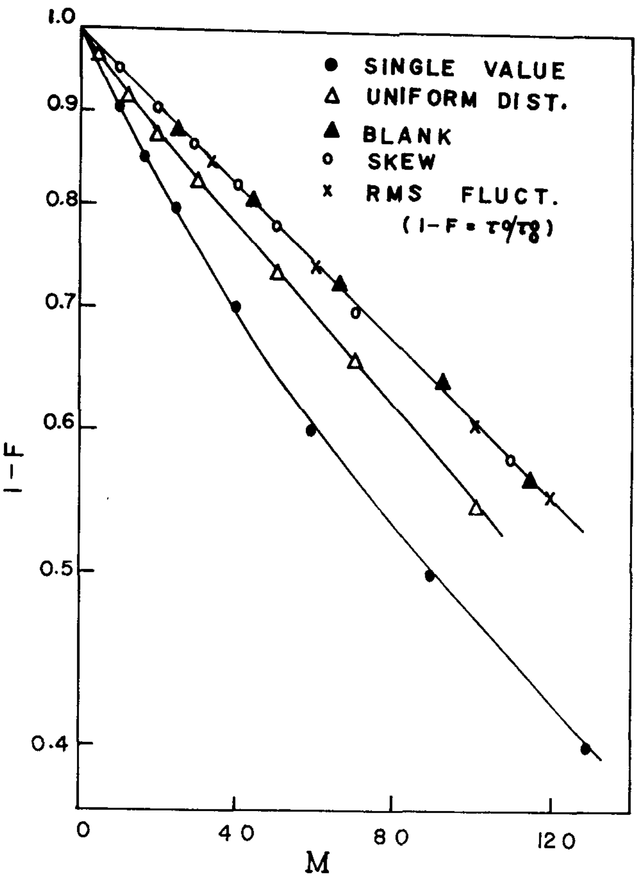

Fig. 3. Variation of mixing characteristics of the stochastic model with different initial distributions of reactants within the N cells; $\beta = 1$ and $S/N = 0.01$.

For a model to be used to predict the behavior of a real situation, there must be similitude (i.e., geometric, dy-

TABLE 1. FEED DISTRIBUTIONS

1. Single value	$A_{oi} = 2.0, B_{oi} = 0.0$	$i = 1 \to N/2$
	$A_{oi} = 0.0, B_{oi} = 2.0$	$i = N/2 + 1 \to N$
2. Uniformly distributed	$A_{oi} = \frac{8i}{N}, B_{oi} = 0.0$	$i = 1 \to N/2$
	$A_{oi} = 0.0, B_{oi} = \frac{8i - 8\left(\frac{N}{2}\right)}{N}$	$i = N/2 \to N$
3. Skew	$A_{oi} = 7.0, B_{oi} = 0.0$	$i = 1 \to N/10$
	$A_{oi} = 0.0, B_{oi} = 7.0$	$i = N/10 + 1 \to N/5$
	$A_{oi} = 0.75, B_{oi} = 0.0$	$i = N/5 + 1 \to 3N/5$
	$A_{oi} = 0.0, B_{oi} = 0.75$	$i = 3N/5 + 1 \to N$
4. Blanks	$A_{oi} = 4.0, B_{oi} = 0.0$	$i = 1 \to N/4$
	$A_{oi} = 0.0, B_{oi} = 4.0$	$i = N/4 + 1 \to N/2$
	$A_{oi} = 0.0, B_{oi} = 0.0$	$i = N/2 + 1 \to N$

The total number of model cells was always 1,000, and $\overline{A} = \overline{B} = 1.0$ in every case.

namic and chemical similarity) between the real system and the model. In view of the foregoing discussion it is clear that this similarity does not exist for either the stochastic or diffusional models. Mao and Toor (*13*) in a recent work have undertaken a dimensional analysis of the fundamental equations describing the system, which enables a greater insight into the physical situation and could prove useful for further model studies.

CONCLUSIONS

The closeness of the simulations of Vassilatos and Toor's (*4*) data produced by the diffusional and stochastic models is most likely due to the similarity between the mixing process represented by both models, rather than being related to the physical situation as suggested by Mao and Toor (*1*). In fact, this similarity suggests that further study should be given to the numerical solution of diffusional equations by stochastic representation.

While an analytical solution does not appear imminent (*11*), the use of computer models to solve the problem should continue despite the shortcomings of the models developed to date. To be consistent with the information at present established, a model of the physical system would need the following properties:

1. That $\tau^0/\tau_0^0 = (1 - F)$ for an instantaneous reaction with the reactants in the stoichiometric ratio.
2. That the mixing rate could be made to vary as the scale of turbulence is changed.

In view of this rather limited information, it is clear that further progress on analyzing turbulent mixing and mixing with chemical reaction is strongly dependent on additional worthwhile experimental data. Once the physical behavior is well characterized, further work on modelling the process would be warranted.

ACKNOWLEDGMENT

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NOTATION

A, B = concentration of species A and B
F = conversion of A
N = total number of cells in stochastic model
k = reaction rate constant
J_s, k_s = mixing rate constants
t = time
R.M.S. = root mean square
τ^0 = R.M.S. concentration fluctuation of species A
θ, M = dimensionless time
n = integer
r = finite value of time
P = a variable with a value between 1.0 and 2.0
Pr = probability
S/N = mixing rate parameter for stochastic model
β = $\overline{B}_0/\overline{A}_0 b$ where b = stoichiometric coefficient

Subscript

o = initial value
i = refers to any cell location

Superscript

— = bulk average value

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APPENDIX 1: ANALYSIS OF DISCREPANCY BETWEEN PLOTS OF τ^0/τ_0^0 AND $(1 - F)$ FOR STOCHASTIC MODEL

Consider the system to be divided into N cells with the feed distribution used in references 2 and 3, as

$$N/2 \text{ cells have } A = 2.0 \text{ and } B = 0.0$$

$$N/2 \text{ cells have } A = 0.0 \text{ and } B = 2.0$$

hence $\overline{A} = 1.0$ and $\overline{B} = 1.0$.

If two cells are chosen at random, the probability of choosing one cell containing some A and one cell containing some B, before any mixing has occurred, is

$$Pr = \left(\frac{N}{N}\right)\left(\frac{N/2}{N}\right) = ½$$

For the case of a instantaneous reaction, the contribution to the overall conversion for such a selection (an effective mixing trial) is $2/N$. Considering all possible selections of two cells from the array, the probable conversion per selection (mixing trial) can be expressed for the first step as

$$(1 - F) = ½\,(1 - 2/N) = ½\left(\frac{N-2}{N}\right) \quad (1)$$

For the analogous case using R.M.S. concentration fluctuations as a measure of the degree of mixing

$$\tau_0^0 = \sqrt{\frac{(2.0 - 1.0)^2 N/2 + (0.0 - 1.0)^2 N/2}{N}} = 1.0$$

After the first effective mixing trial

$$\tau^0 = \sqrt{\frac{(2.0 - 1.0)^2(N/2 - 1) + (0.0 - 1.0)^2(N/2 - 1) + 2(1.0 - 1.0)^2}{N}} = \sqrt{\frac{N-2}{N}}$$

Hence the expected value of τ^0/τ_0^0 for the first mixing trial is

$$\tau^0/\tau_0^0 = ½\sqrt{\frac{N-2}{N}} \quad (2)$$

Expressions (1) and (2) are only equivalent for $N = 2$ or as $N \to \infty$. As the feed distribution is changed, the initial conversion per mixing trial changes while the value of τ^0/τ_0^0 remains constant. The distributions 'skew' and 'blank' (Table 1) were derived by considering those distributions which gave an initial conversion per mixing trial of $½\sqrt{\frac{N-2}{N}}$. Clearly there are an infinite number of combinations of different 'skew' and 'blank' distributions which will lead to a first order mixing rate because it was found that, if the mixing is forced to be first order in the initial stages, a steady first order rate exists for the entire process.