

Figure 4. Experimental results: $(h/d_o)[1 + \beta(H/d_o)]^m$ vs. Fr_N . —: data point and least-square fitted line for $\beta = 0.45$ and $m = 1.22$. - - - : least-square fitted line for $\beta = 0.32$ and $m = 1.29$.

with the n -th power of the nozzle velocity, u_o , and decreases with the inverse of the m -th power of the effective jet diameter, d_s . The above values determined experimentally for $\beta = 0.45$ and 0.32 indicate that the choice of the entrainment coefficient does not affect our results so sensitively. However, since the calculated value of standard deviation, $(1/N \sum_i \{(h/d_o)_{\text{measured}} / (h/d_o)_{\text{calculated}} - 1\}_i^2)^{1/2}$, was 0.16 for $\beta = 0.45$ and 0.20 for $\beta = 0.32$, respectively, we concluded that $\beta = 0.45$ was a slightly better choice between the two. We also checked to make certain that the selection and assignment of the value of β between 0.32 and 0.45 did not improve the accuracy of the empirical equation.

In applying the above results, the following care should be taken.

(1) Effect of surface tension is not taken into account, and the liquid used is water only, indicating that further study is needed

before the present result can be applied with confidence to liquids other than water.

(2) The present results cannot be applied to the case of two miscible fluids or two immiscible fluids.

NOTATION

A	= constant defined in Eq. 4
d_o	= nozzle diameter
d_s	= jet diameter at the distance H from the nozzle, in the absence of a free surface
Fr_N	= Froude number defined as $u_o / \sqrt{gd_o}$
g	= gravitational acceleration
h	= height of a free surface rise
H	= distance between the nozzle and a quiescent free surface
m	= constant defined in Eq. 3
n	= constant defined in Eq. 4
N	= number of data points
Re_N	= nozzle Reynolds number defined as $u_o d_o / \nu$
u_o	= jet velocity at the nozzle
u_s	= average jet velocity at the H from the nozzle, in the absence of a free surface

Greek Letters

α	= entrainment coefficient
β	= $4\alpha = 2 \tan \theta/2$
θ	= angle of jet spread
ν	= kinematic viscosity of liquid

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Degree of Segregation and Coalescence Rate Parameter in the Random Coalescence Model for a Stirred Reactor

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Danckwerts' degree of segregation, J , has been calculated for the random coalescence model as a function of the mixing parameter. J was found to coincide with the intensity of segregation, I_s . It was possible to relate the degree of segregation to the characteristics of the turbulent field within the reactor.

The degree of segregation, J , introduced by Danckwerts (1958)

is the usual parameter by which the quality of micromixing has come to be evaluated in the literature of chemical reactors. Actually Rippin (1967) and subsequently other authors (Nishimura and Matsubara, 1970) have demonstrated that giving both the degree of segregation and residence time distribution is, in general, insufficient to identify reactor behavior unequivocally, except for the extreme cases of complete segregation or complete mixing. In other cases, the degree of segregation is only an average parameter of the reactor. It is, nevertheless, usual to compare different models

of micromixing under conditions which involve an equal value of J (Nishimura and Matsubara, 1970; Duduković, 1977).

Among the one-parameter models of micromixing in a stirred tank, the random coalescence model (Levenspiel, 1972) is of special interest because of its simplicity and physical intuitiveness. This model was introduced by Curl (1963), and Spielman and Levenspiel (1965) were the first to have used it with a technique of Monte Carlo simulation. It is also possible to relate the mixing parameter of the model with the characteristics of turbulent motion inside the reactor (Evangelista et al., 1969).

In the literature, however, no relationship is given which allows evaluation of Danckwerts' degree of segregation for the random coalescence model and lack of such relationship does restrict comparison with other models. Evangelista et al. (1969), making reference to an ideal tracer experiment, have presented as a function of the mixing parameter of the model what they designated as the "degree of segregation of Zweitering (1959)." However, as emphasized by Rao and Edwards (1973), this really corresponds not to the degree of segregation, J , but rather to the intensity of segregation parameter, I_s , which was also introduced by Danckwerts (1953, 1958).

It is worthwhile to recall the definitions of J and I_s . The degree of segregation, J , has been proposed to provide a measure of the state of micromixing, at the molecular level, of a single fluid stream, and is defined as the ratio between the variance of the median age of the molecules in a single "point" or "aggregate" in the reactor and the variance of age of all molecules present in the same reactor.

$$J = \frac{\text{Var } \alpha_P}{\text{Var } \alpha} \quad (1)$$

On the other hand, for a system with at least two components, the intensity of segregation I_s of the component A in the system is defined as

$$I_s = \frac{\text{Var } x_{AP}}{\bar{x}_A(1 - \bar{x}_A)} \quad (2)$$

where x_{AP} is the fraction of component A in a single "point," and \bar{x}_A is its average value in the whole system.

These parameters, J and I_s , are obviously entirely distinct from each other (Brodkey, 1966, 1967; Rao and Edwards, 1973), even if both have the value zero for completely micromixed systems, and the value 1 for completely segregated systems. There are frequent references to the parameter J in the theory of chemical reactors with premixed feed, while I_s has been used predominantly to characterize turbulent mixing of streams not previously mixed (Brodkey 1966, 1967).

Takao and Nurakami (1976) have recently compared J and I_s for various two-zone reactor models suggested in the literature. These authors have verified that in many cases the two parameters in fact coincided, while in other cases, however, for example in the model suggested by Rippin (1967), this did not happen.

Hence, an autonomous derivation of the degree of segregation, J , is generally imposed. Because of the analytical complexity which the model of random coalescence carries by its very nature of discrete stochastic model, which involves population balances expressed by integro-differential equations of difficult solution, we have had recourse in the present case to a direct simulation of the model employing the Monte Carlo technique.

SIMULATION TECHNIQUE

The degree of segregation has been calculated directly on the basis of definition (Eq. 1) for various values of the coalescence parameter, I , defined as the number of coalescences which an aggregate undergoes, on the average, in its residence in the reactor.

The random coalescence model, originally proposed for a bi-phasic liquid-liquid system (Curl, 1963; Rietema, 1964), considers,

in fact, a fluid as consisting of a great number of aggregates of equal size, which can collide by chance occasionally with each other, immediately rearranging themselves into two new aggregates, each with characteristics corresponding to the mean of the original aggregates. Each aggregate behaves like a closed homogeneous system, in the time interval between two successive collisions. A constant stream of aggregates is fed to the reactor, and a stream of equal capacity leaves it. The aggregates present in the reactor have equal probability of exit, which leads to the well-known exponential distribution of residence time of continuous, perfectly-mixed reactors.

Monte Carlo simulation has been carried out by three distinct methods, which differ from one another by the diverse criteria of ordering the time sequence of the random events within the reactor, but which have yielded substantially identical results.

The first method, which closely follows the original technique of Spielman and Levenspiel (1965), and which has also been recently used (Marconi and Vatisas, 1980), is based on equal spacing in time of the coalescence-redispersion events, as well as the intake-outgo events of the aggregates.

The discretization of time can be avoided, however, by random generation of the time interval between two consecutive events, which, being independent and with uniform probability in time, give rise to an exponential distribution of the intervals of quiescence. Shah et al. (1977) have emphasized that this technique is preferable especially when populations with a limited number of elements are simulated.

A second simulation method, which precisely uses the random intervals of quiescence, has therefore been developed. In this method, constancy in time is maintained for the number of aggregates present in the reactor. From this it follows that the entrance of a fresh aggregate is still synchronous with the exit of one of the aggregates present in the reactor and selected by chance. Entrance and exit hence comprise a unique event, in fact, and the probability density of the intervals of quiescence, θ_q , is given by

$$f(\theta_q) = \frac{1}{n_f + nI/2} e^{-(n_f + nI/2)\theta_q} \quad (3)$$

where n , the number of aggregates present in the reactor, is constant, and coincides with n_f , the number of aggregates fed in a time equal to the average residence time. The intervals of quiescence, distributed according to Eq. 3, are generated at random each time, with the standard method of inversion of a uniform distribution (Abramowitz and Stegun, 1965). The choice whether the subsequent event is ingress-exit or coalescence-redispersion occurs in a random manner on the basis of the respective probabilities, which stand in the ratio $2n_f/(nI)$.

Shah et al. (1977) have suggested removal of the constraint of synchronism between entrance and exit of the aggregates, leaving the number of aggregates present in the reactor subject to statistical fluctuations. Although, in the specific case studied, the physical nature of the system under examination does not fully justify this removal of the constraint, it remains interesting to test this variant also by comparison with the preceding method.

A third method of simulation has therefore been established, according to which the probability density of the intervals of quiescence is given by

$$f(\theta_q) = \frac{1}{n_f + nI/2 + n} e^{-(n_f + nI/2 + n)\theta_q} \quad (4)$$

where n is variable with time and thus subject to fluctuations.

In all three simulation procedures mentioned above, the aggregates are considered as each constituted of a number, m , of molecules, and the entry time of each molecules present in the reactor is retained. The redispersion which follows the random coalescence of two aggregates is realized through the equiprobable choice of m among $2-m$ molecules at hand. The m molecules chosen, and the remaining m , constitute respectively the two new aggregates.

In most cases, we dealt with a sample system consisting of 300 aggregates, each represented by 300 molecules, which has yielded results with good stability characteristics.

EVALUATION OF RESULTS

The results of simulation tests of stochastic systems with discrete models require a statistical analysis which allows evaluation of the reliability of the estimation and the importance of the random fluctuations.

We let $X_j(t)$ be the value assumed at time t by the property X of the system in the course of the j -th simulation test. Performing the simulation S times, starting always from time zero in a certain initial state, and continuing to time t with various parts of pseudorandom number sequences, we obtain S -independent observations which, for an ergodic process, if t is sufficiently long, are not related to the starting state. In every case, from independent observations, the estimations, from S values, of the mean $\bar{X}(t)$ and the variance $\text{Var}[X(t)]$, as well as the confidence interval of the mean, are those which are customary, and reported in every standard statistics text. Supposing that $\{X_j(t)\}$ is normally distributed, which is assured by the central limit theorem if S is sufficiently large, we then have, in fact,

$$\bar{X}(t) = \frac{1}{S} \sum_{j=1}^S X_j(t) \quad (5)$$

$$\text{Var}[X(t)] = \frac{1}{S-1} \sum_{j=1}^S [X_j(t) - \bar{X}(t)]^2 \quad (6)$$

$$\Pr\left[|\bar{X}(t) - \mu(t)| < t_\alpha \sqrt{\frac{\text{Var}[X(t)]}{S}}\right] = 1 - \alpha \quad (7)$$

where t_α is Student's ratio of distribution t , corresponding to the confidence level α and with $S-1$ degrees of freedom. More precise criteria of estimation exist if $\{X_j(t)\}$ does not turn out to be normally distributed (Scheffé, 1959).

In the case which the stationary behavior of the system is of interest, the estimation criterion shown above may still not be practical and, especially if the transient is long enough, the calculation times for obtaining S -independent observations could be prohibitive. It is useful, then, to take advantage of the characteristic which stationary processes enjoy, whose properties, eventually constant in stationary states, are estimatable through the time average as well as the ensemble average. In such a case, it will be sufficient to carry out a unique simulation, obtaining data at successive time intervals after having neglected the first ones, which are anomalous because they correspond to the transient. This provides a series of observations so arranged that, in general, they will be autocorrelated and hence cannot be correctly estimated by the equivalents of Eqs. 5-7.

Fishman (1967, 1971; Fishman and Kiviat, 1967) has proposed various estimation methods particularly suitable to analysis of time series obtained through simulation tests. With respect to the estimation of the confidence interval of the mean, the informational content of a series of autocorrelated observations is inferior to that which the same number of observations would carry if they were independent. Fishman (1967) has also suggested a technique for calculating the number of independent equivalent observations and the autocorrelation time τ^* , and has shown that the autocorrelated sequence is equivalent to the sequence obtained by taking into consideration only observations taken at intervals of time $2\tau^*$, which thereby turn out to be independent.

The autocorrelation time is, therefore, half the minimum time interval which must separate two observations in order that these turn out not to be autocorrelated.

This analysis technique has been applied to the simulation test performed with the methods previously described. The result has been that for all values of the mixing parameter $I/2$ considered, we steadily obtained $\theta^* \approx 0.25$.

The possibility of having an estimation of θ^* at one's disposal on the basis of a few preliminary tests (even if subject to verification) before the conclusion of the simulation makes it particularly easy to carry out the test and reach the desired confidence interval of the mean, with the sole restriction being the computer time needed for continuing simulation up to the strictly necessary time.

No appreciable difference, indeed, has been noted among the three distinct techniques used for simulation. In the specific case

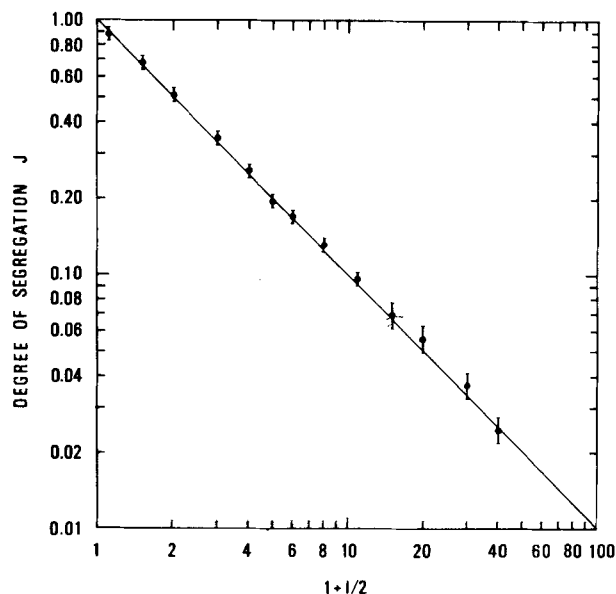


Figure 1. Degree of segregation J vs. coalescence rate parameter I : 98% confidence limits for J are reported.

at hand, the method recommended by Shah et al. (1977) has not yielded equally significant results on a smaller system (i.e., a system made up with a smaller number of aggregates), although they (Shah et al., 1977) maintained that this was the case in the problem considered by them.

DISCUSSION

The degree of segregation, J , for the random coalescence model has been estimated for several values of the coalescence parameter I . Each simulation test has been purposed up to a duration which allowed collection of a number of equivalent independent observations large enough in order to keep the 98% confidence limits for J within the range $\pm 5\%$ of the best estimate of J itself ($\pm 10\%$ for $I \geq 28$, in order to save computer time).

The law of the dependence of the degree of segregation on the coalescence parameter is shown in Figure 1, where best estimates and 98% confidence limits are reported. For the considered values of I , we can strictly justify the relationship

$$J = \frac{1}{1 + I/2} \quad (8)$$

represented in the diagram by the straight line drawn. Evangelista et al. (1969) have derived the same expression (Eq. 8) for the segregation intensity I_s . Although it should be regarded as a statement of an empiric nature, and not as a rigorous demonstration, it may be maintained for all practical purposes, at least in the limits of the considered values of I , that in the random coalescence model, the degree of segregation and the intensity of segregation assume the same values, given by Eq. 8. This, moreover, is also yielded by other models (Takao and Nurakami, 1976). Among these is the model proposed by Costa and Trevissoi (1972a, 1972b) for which, when the mixing parameter are equalized, $2\alpha\tau = I/2$, a relationship entirely coinciding with Eq. 8 is valid both for the degree of segregation and for the intensity of segregation (Takao et al., 1979).

Through Eq. 8, or equivalently, and in still more immediate terms, through the statement that $J = I_s$, it is possible to relate the degree of segregation with the characteristics of turbulent motion in the reactor.

In fact, although the turbulent region in a stirred reactor is usually very far from being homogeneous and isotropic (cf., for example, Rao and Brodkey, 1972), we may apply Kolmogoroff's theory of local isotropy for high Reynolds number values. On this basis, Evangelista et al. (1969) have shown that the mixing parameter can be expressed as

$$I/2 = \frac{12 D}{\lambda_s^2} \tau \quad (9)$$

where D is the molecular diffusivity, and λ_s is the microscale for the turbulent mixing. In a similar manner, the intensity of segregation may be expressed as

$$I_s = \frac{1}{1 + \frac{12 D}{\lambda_s^2} \tau} \quad (10)$$

Brodkey (1966, 1967) arrived at the same expression (Eq. 10) for the intensity of segregation in a stirred reactor, by referring to the assumption made by Rosensweig (1964) on the conservation of scalar inhomogeneities in a steady operating reactor.

An analogous expression to Eq. 9 has also been suggested by Costa and Trevisoi (1972b) for the model proposed by them. They recall some observations of Corrsin (1964) reported by Brodkey (1966, 1967) which permit Eq. 9 and hence Eq. 10 to be expressed in terms of quantities more readily examined, such as power dissipated per unit mass of fluid, physical characteristics of the fluid, and the geometry of the system.

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NOTATION

A	= chemical species A
D	= molecular diffusion coefficient, cm^2/s
$f(\theta_q)$	= probability density of the intervals of quiescence
I	= coalescence rate parameter, dimensionless
I_s	= intensity of segregation, Eq. 2, dimensionless
J	= Danckwerts' degree of segregation, Eq. 1, dimensionless
m	= number of sample molecules in an aggregate
n	= number of aggregates present in the reactor
n_f	= number of aggregates fed to the reactor during time τ
S	= number of independent observations
t	= time, s
t	= student's ratio of distribution t (with $S-1$ degrees of freedom), corresponding to the confidence level α , dimensionless
X	= property X
\bar{x}_A, x_{Ap}	= average fraction of component A , fraction of component A in a single point, dimensionless
α	= confidence level, dimensionless
α	= mass exchange parameter of the model proposed by Costa and Trevisoi (1972a, 1972b), s^{-1}
α, α_p	= molecular age, average age of the molecules in a single point, s
θ	= t/τ , dimensionless time
θ_q	= interval of quiescence, dimensionless
θ^*	= τ^*/τ , dimensionless autocorrelation time
λ_s	= microscale for the turbulent mixing, cm
μ	= population mean
τ	= space-time, s
τ^*	= autocorrelation time, s

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