Similar agreement was observed in other experiments as is evident from the fact that average deviations in the total number of moles evaporated $(A + B)$ of +3.1, +3.0, and −0.7% were found for the three systems over a large number of runs. It should be noted at this point that careful consideration has been given to the question of the sensitivity of the predictions of the Gilliland equations to small errors in the measured diffusion coefficients D_{AC} and D_{BC} and in the semiempirically determined values of D_{AB}. This analysis has indicated that the observed agreement between theory and experiment would not be significantly affected by errors in the diffusion coefficients of the order of the difference between experimental and modified HBS values. Thus it is felt that these comparisons provide further evidence of the validity of the Stefan-Maxwell equations in multicomponent systems, and in the presence of a significant convective flux.

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A Stochastic Mixing Model for Homogeneous, Turbulent, Tubular Reactors

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A stochastic mixing model is developed for turbulent flow in homogeneous plug-flow reactors. The model is based on random coalescence and redispersion of fluid elements. Of special significance is its applicability when mixing and reaction rates are comparable, as well as when either rate dominates. The model's parameters may be determined by measuring conversion with instantaneous reactions. Experimental results reported by others are successfully simulated.

Mixing is an important factor in many chemical reaction processes, both heterogeneous and homogeneous. This paper considers homogeneous reactions occurring in turbulent flow tubular reactors where the reactants are fed separately. If the rate of reaction is very rapid compared with the rate of mixing, or vice versa, then the performance of the reactor can be calculated by well-developed techniques (*1* to *3*). However, the general case where the rate of reaction and the rate of mixing are comparable has not been extensively studied.

Of particular importance to this paper is the experimental work of Vassilatos and Toor (*4*). They measured conversion in an isothermal tubular reactor, using reactions which were rapid, intermediate, and slow in comparison with the rate of mixing. For the limiting cases of rapid and slow reactions, they successfully predicted conversion, but they experienced difficulty in predicting the results of intermediate speed reactions.

A simple stochastic mixing model is developed here for turbulent tubular reactors. It is shown capable of simulating the experimental results reported by Vassilatos and Toor. The model is based on random collisions and redispersions between elements of fluid. These notions have been used previously by others, especially Curl (*5*) and

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Chen Ming-heng et al. (*6*), who presented analytical developments, and Spielman and Levenspiel (*7*), who presented a Monte Carlo study of the continuous stirred-tank reactor.

THE MODEL

The essential features of mixing which should be embodied in the model are long-range mixing caused by the motion of eddies and short-range mixing caused by molecular diffusion. Long-range mixing is incorporated by randomly coalescing and redispersing lumps of fluid. Short-range mixing is provided by averaging intensive variables immediately after each coalescence.

The following assumptions are made in developing the model:

1. The chemical reaction occurring does not affect the hydrodynamic behavior of the system.
2. Plug flow exists, and axial diffusion is negligible.
3. Homogeneity on a coarse scale is reached close to the entrance.
4. The fluid in the reactor is divided into a large number of lumps, constant in number and equal in size.
5. All intensive variables are uniform within each lump.
6. Lumps located at the same axial position coalesce randomly, two at a time, and redisperse instantaneously to form two new lumps which are identical.
7. Rates of coalescence and redispersion are only a function of axial position.

The model considers the fluid entering the reactor during a short time interval δt to be divided into N lumps. These lumps flow through the reactor experiencing coalescence and redispersion. Let the total number of coalescences experienced by these N lumps between the entrance and any axial position z be denoted by $n(z)$. It is convenient to define a *mixing characteristic* $\eta(z)$ by

$$\eta(z) = \frac{n(z)}{N} \tag{1}$$

The function $\eta(z)$ describes the mixing within the reactor as a function of position and may be interpreted as half of the average number of collisions experienced by lumps while flowing from the entrance to position z.

It is possible to determine $\eta(z)$ by measuring the root-mean-square fluctuation of a tracer which is being introduced steadily into one of the reactant streams (*3*). Alternately, $\eta(z)$ can be found by measuring the conversion of a very rapid reaction, since rapid reactions are controlled by the rate of mixing (*1*, *2*). This is accomplished by comparing the conversion determined experimentally as a function of axial position with the conversion simulated by the model as a function of the number of coalescences.

The number of lumps N used in the model is not necessarily related to the number or size of physical lumps present. However N should be chosen large enough to represent well the continuous concentration distribution of the lumps. The minimum value of N, $N_{\min}$, is determined experimentally in accordance with the criterion that further increases in N do not change the simulated results significantly. Simulations with $N \geqq N_{\min}$ yield the same results, except for random fluctuations, confirming that conversion is only a function of the mixing characteristic $\eta(z)$. In practice N is selected large enough to reduce random fluctuations to an acceptable level.

Chemical reactions are incorporated in the model by changing the concentration of each chemical species in each lump between coalescences in accordance with the governing kinetic reaction rate expressions.

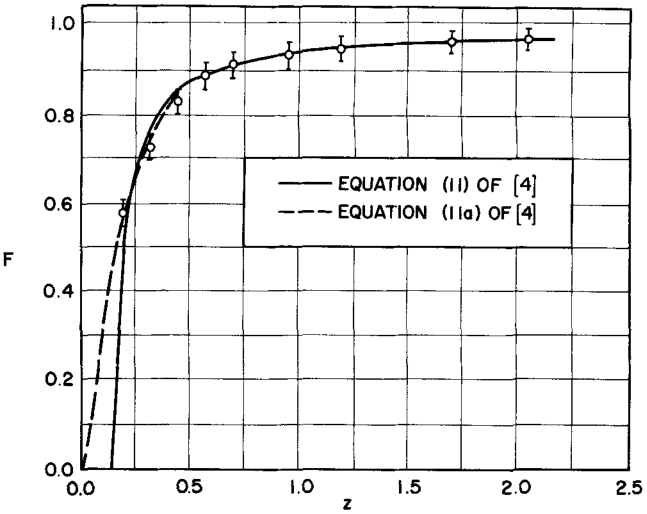

Fig. 1. Experimental conversion vs. axial position for very rapid reactions (*4*) (β = 1.0).

APPLICATION

The model is applied to simulate the experimental results reported by Vassilatos and Toor (*4*). Their mixing device consisted of one hundred parallel stainless steel tubes about 4 in. long and 0.05 in. I.D. These tubes fed a 1.25 in. I.D. Lucite tubular reactor. Two dilute aqueous reactant streams were introduced through alternate tubes. In the reactor the flow was turbulent with a velocity of 15.85 in./sec. The reactant streams entered the reactor at 29.9°C. after passing through constant temperature baths. Conversion was measured at several downstream stations by measuring the slight temperature rise associated with the reaction. The reactions were irreversible, second order, and had a wide range of reaction rates from 4.7×10^1 to 1×10^{11} liters/(mole)(sec.). The ratio of reactants fed was varied from stoichiometric ($\beta = 1.0$) to nonstoichiometric ($\beta > 1.0$) by changing the concentration of the excess reactant in its feed stream.

Mixing Characteristic

The mixing characteristic $\eta(z)$ of Vassilatos and Toor's reactor can be determined conveniently from their data for very rapid reactions. Figure 1 gives conversion F as a function of axial position z for a reaction rate constant $k_r = 1 \times 10^{11}$ [our Figure 1 corresponds to Vassilatos and Toor's Figure 2 (*4*)]. These data were taken under stoichiometric feed conditions ($\beta = 1$).

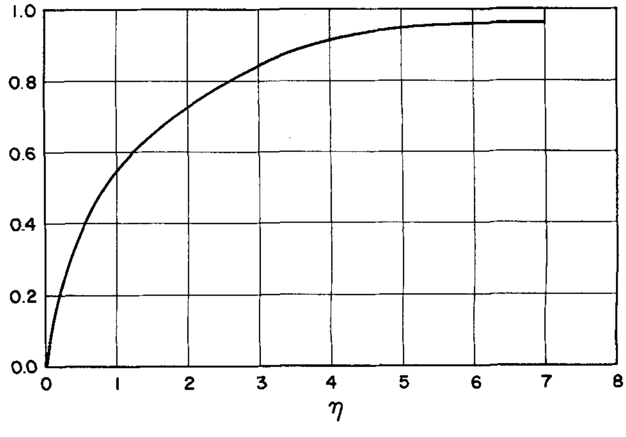

Fig. 2. Simulated conversion vs. mixing parameter for very rapid reactions (β = 1.0).

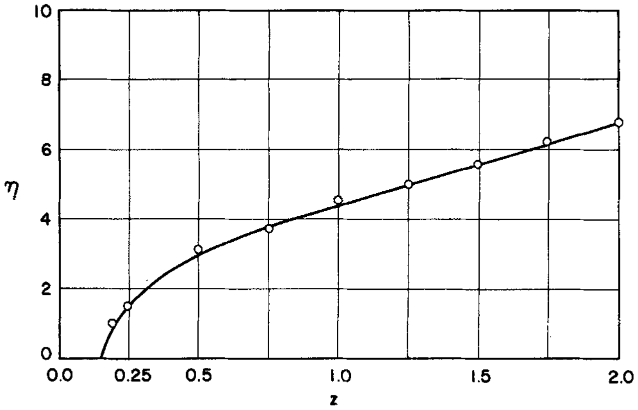

Fig. 3. Mixing characteristic.

Table 1. Simulated Experiments of Vassilatos and Toor (4)

Speed of reaction	Reactants	k_r	β	C_{Ao}
Slow	CH_3COOH-NaOH	4.7×10^1	1.56	0.01
Intermediate	CO_2-2 NaOH	1.24×10^4	1.26	0.007
			2.52	0.007
Very rapid	HCl-NaOH	1×10^{11}	1.0	0.02
			1.4	0.02
			2.0	0.02
			3.0	0.02

With the same feed conditions and reaction kinetics used, a model simulation displayed in Figure 2 is performed yielding conversion as a function of η. For this simulation $N = 300$ was found to be a sufficiently large number of lumps. Since in the experiments the reactants were fed in alternate jets at equal flow rates, $N/2 = 150$ lumps of each reactant were used as the initial condition of the simulation. This simulation is particularly easy to perform since it is independent of kinetic details. Only the stoichiometry, the ratio of reactants fed, and the mixing are important when the reaction is very rapid.

Comparing Figures 1 and 2 at equal values of F yields the mixing characteristic $\eta(z)$, Figure 3. This figure reflects several interesting aspects of the mixing.

From the geometry of the mixer, the entering jets are expected to maintain their identity and not intermix appreciably for a short distance. By extrapolation, $\eta(z)$ is estimated to be zero for $z \leqq 0.15$ in., indicating that the jets first begin to impinge and intermix intensively at approximately $z = 0.15$ in. This is in good agreement with free jet theory (8, 9) which predicts the point of impingement to be $z = 0.166$ in.

It is also expected that the intensity of mixing, expressed in the model by $d\eta/dz$, should be greatest at the point of jet impingement and should decrease monotonically to a lower value characteristic of fully developed flow at points farther downstream. The mixing characteristic Figure 3 is in agreement with these expectations.

Reactor Simulation

With the mixing characteristic $\eta(z)$ determined, conversion for any type of known kinetics and feed stoichiometric ratio can be simulated. Consider second-order reactions of the type studied by Vassilatos and Toor:

$$aA + bB \rightarrow \text{products} \tag{2}$$

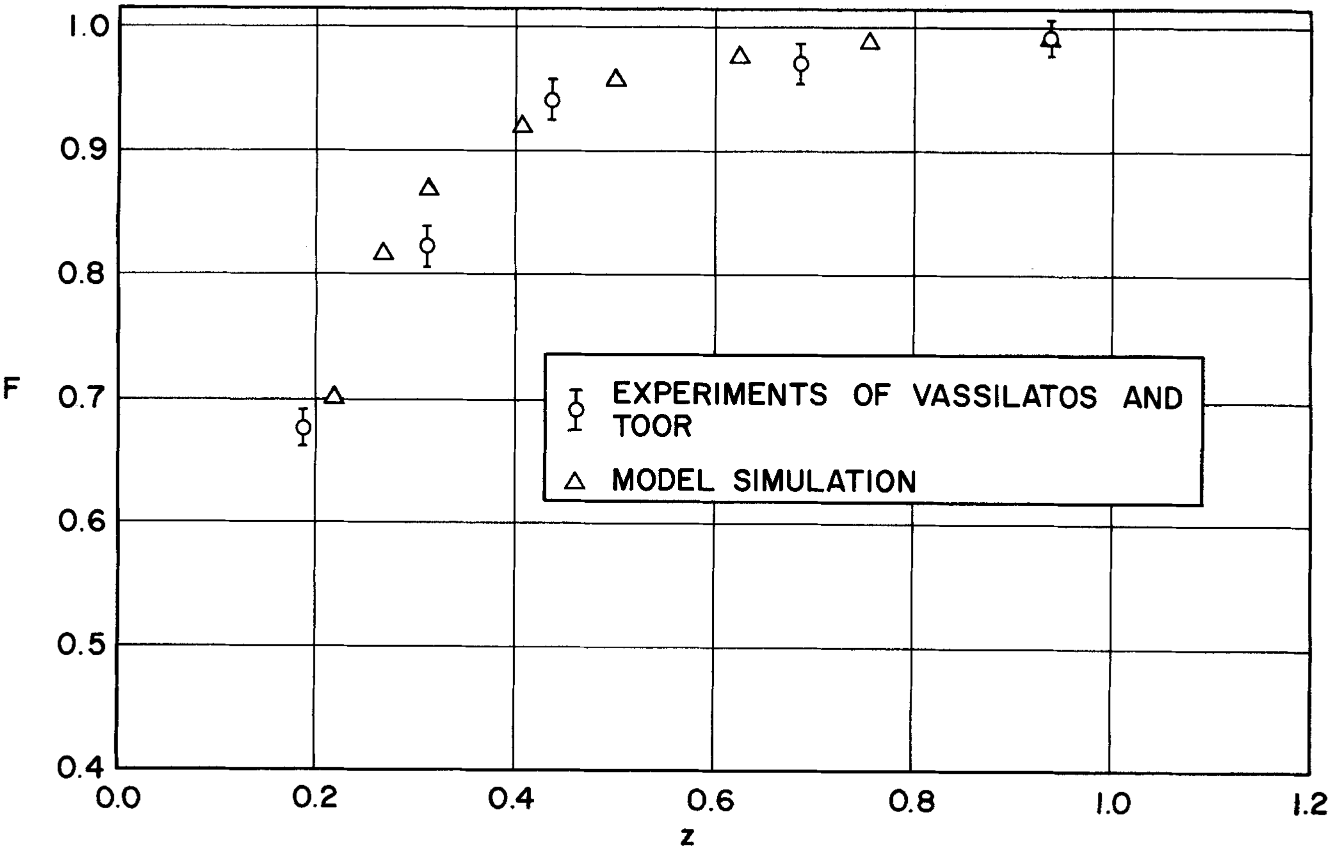

Fig. 4. Conversion vs. axial position for very rapid reactions ($\beta = 1.4$).

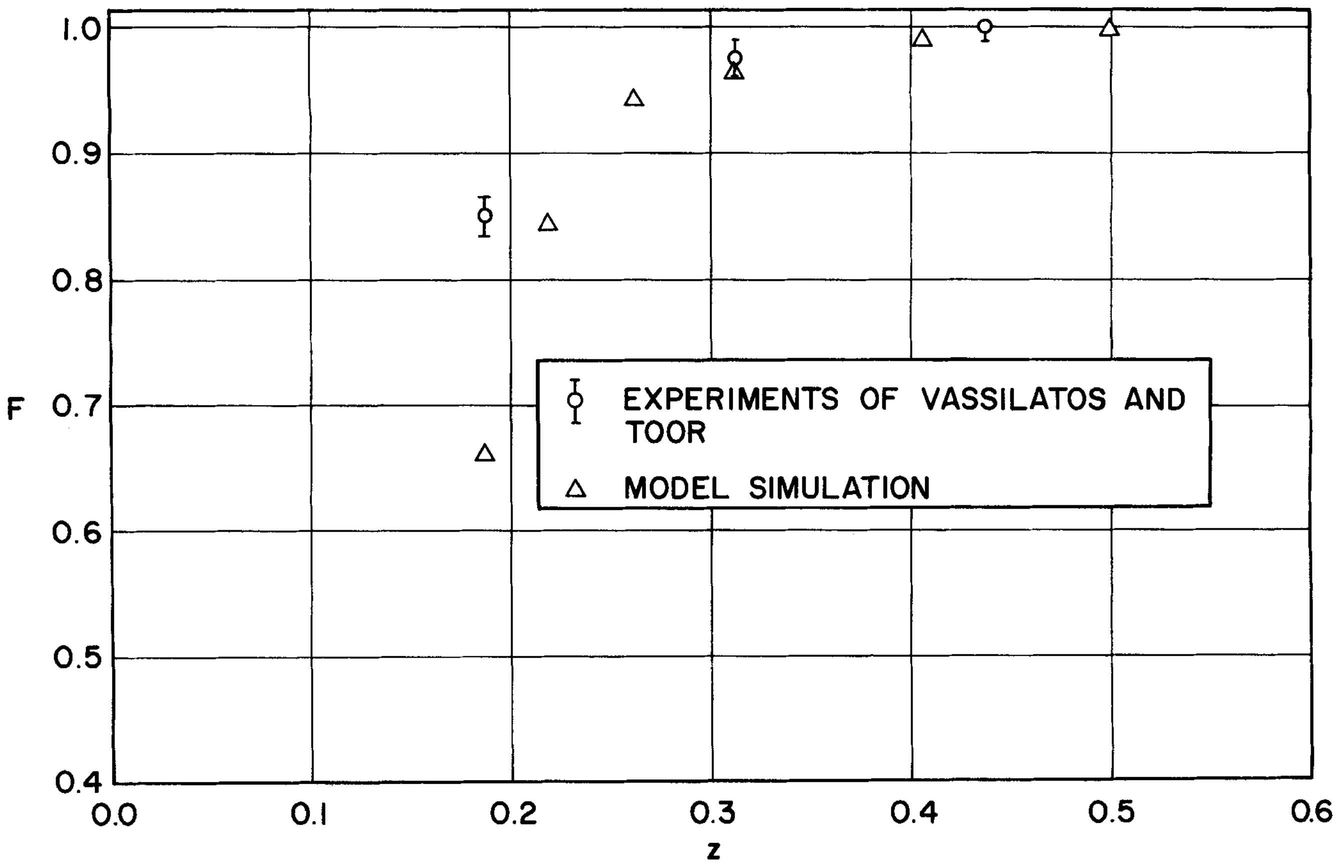

Fig. 5. Conversion vs. axial position for very rapid reactions ($\beta = 3.0$).

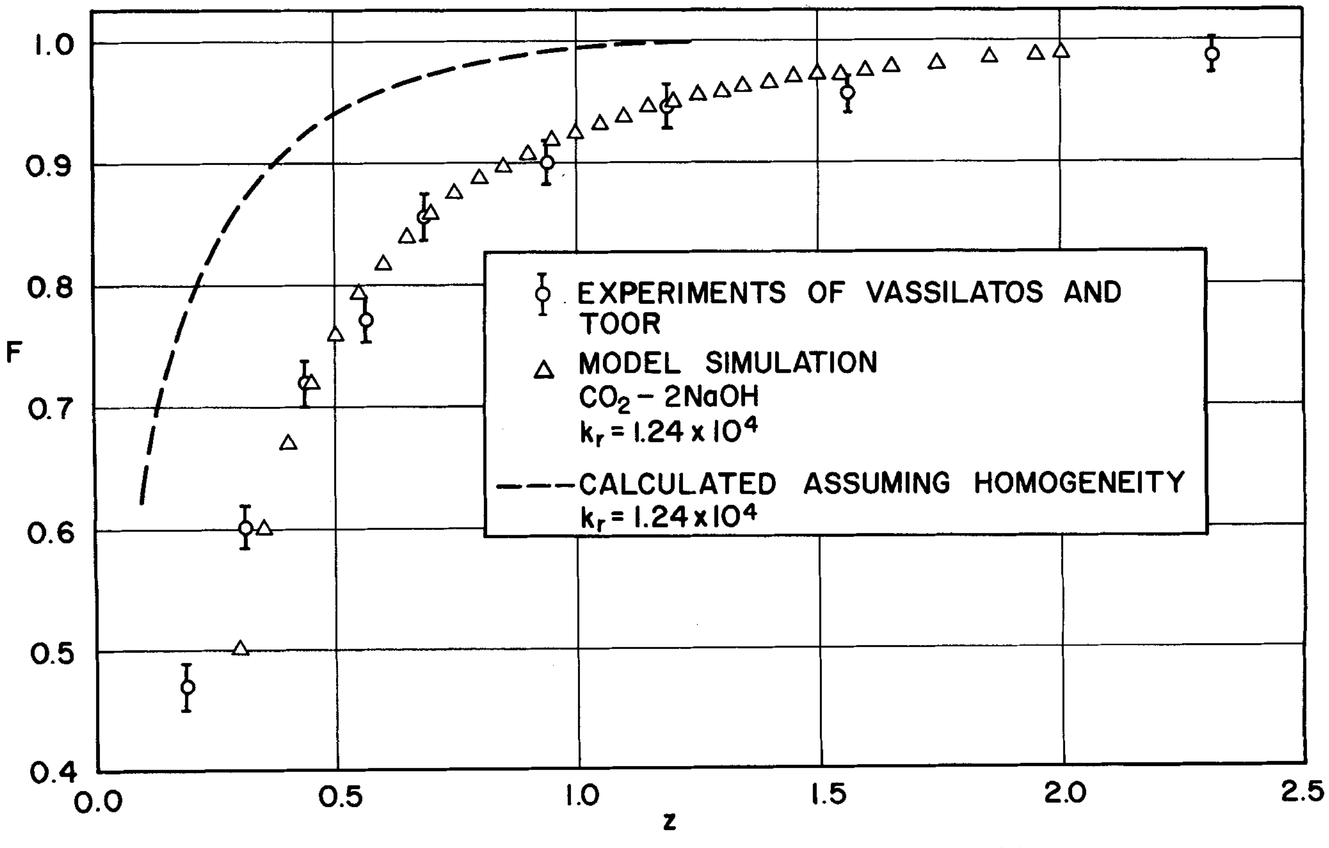

Fig. 6. Conversion vs. axial position for intermediate speed reactions ($\beta = 1.26$).

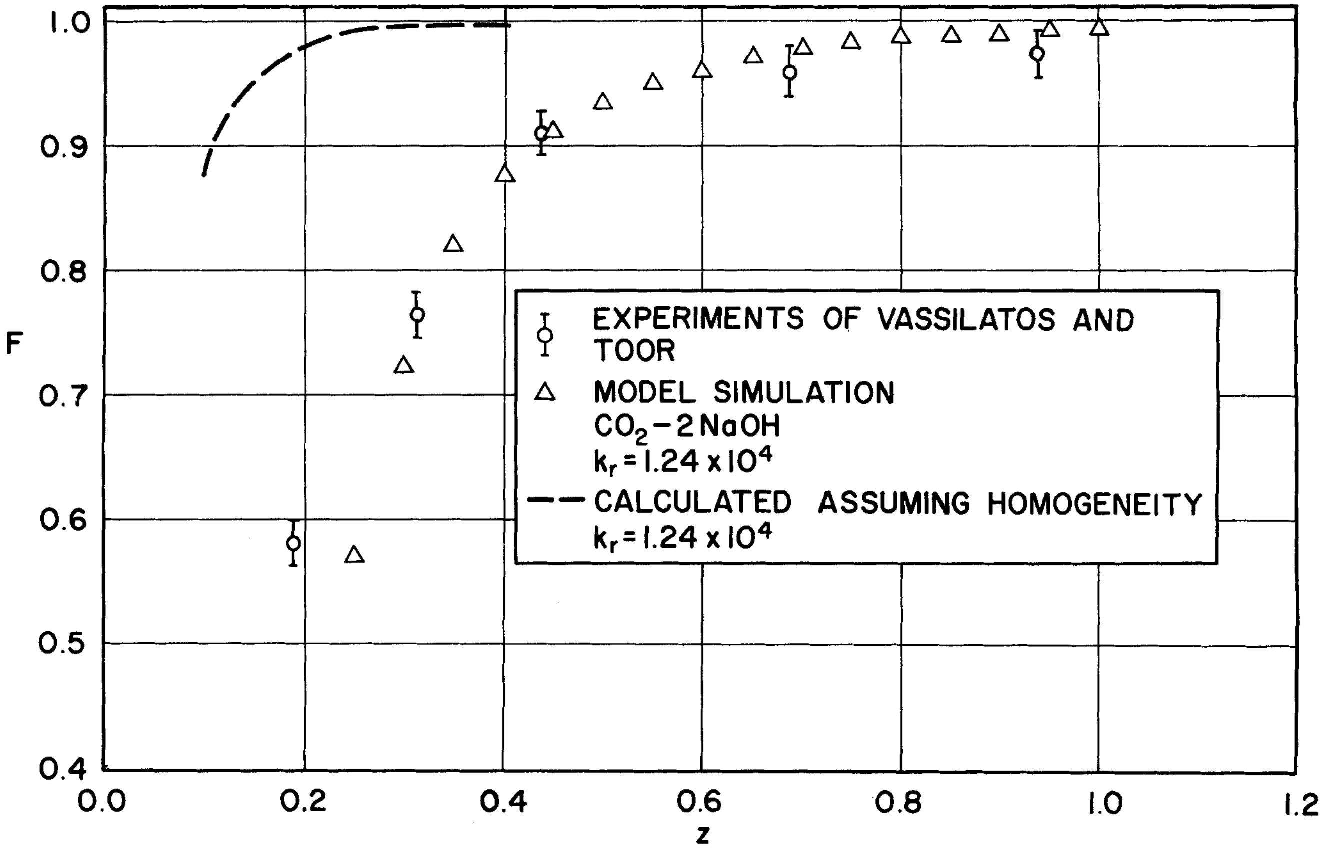

Fig. 7. Conversion vs. axial position for intermediate speed reactions ($\beta = 2.52$).

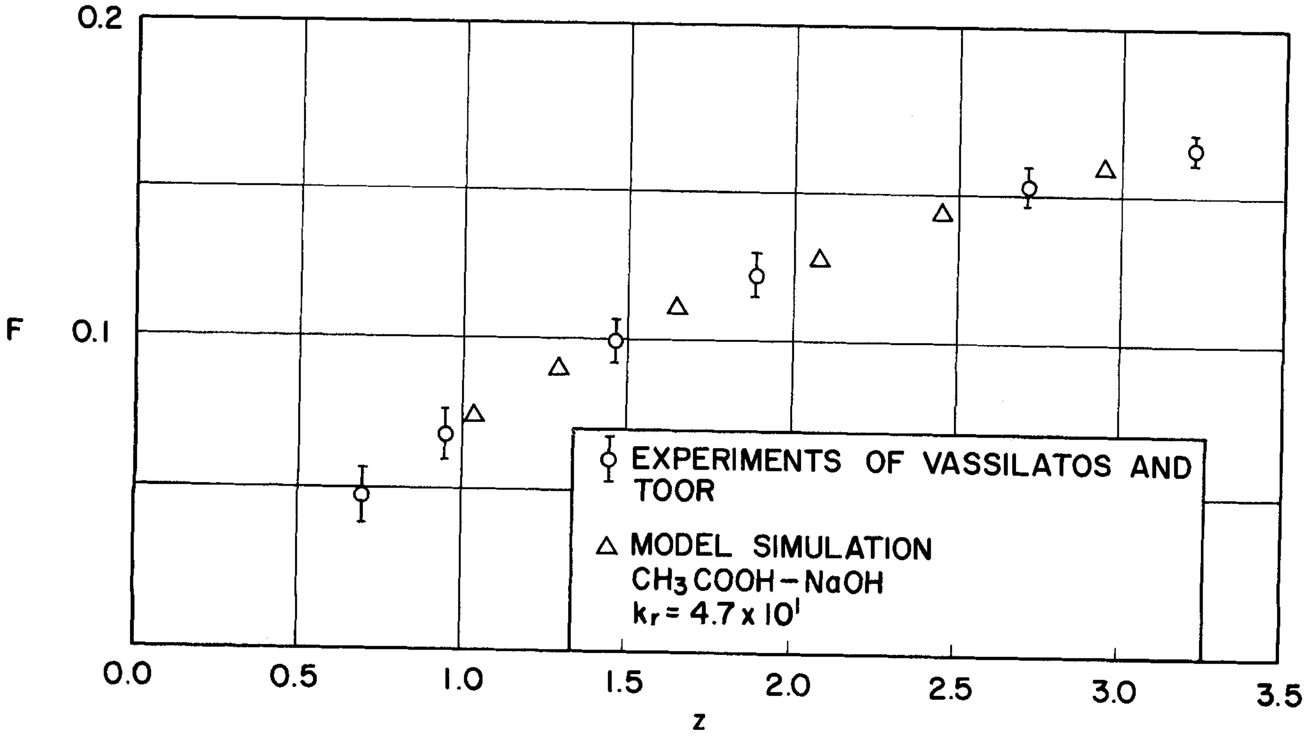

Fig. 8. Conversion vs. axial position for very slow reactions ($\beta = 1.56$).

With a digital computer used, three hundred cells are defined, each representing a small lump of fluid. Initially the concentrations of A and B in the cells are given by

$$\left.\begin{aligned} C_{Ai} &= 2\,C_{Ao} \\ C_{Bi} &= 0 \end{aligned}\right\} i = 1, 2, \ldots, \frac{N}{2}$$

$$\left.\begin{aligned} C_{Ai} &= 0 \\ C_{Bi} &= \frac{2b}{a}\,\beta\,C_{Ao} \end{aligned}\right\} i = \frac{N}{2} + 1, \frac{N}{2} + 2, \ldots, N$$

$$\text{where } N = 300$$

since in the experiments to be simulated half the entering fluid contained only A and the other half contained only B.

The distance traveled downstream Δz by the N cells between coalescence is specified by $\frac{1}{N}\,\frac{d\eta}{dz}$. Each coalescence and redispersion is performed by picking two cells at random and instantaneously averaging their concentrations. Between each coalescence the concentrations in all N cells are changed in accordance with the reaction kinetics. For a second-order reaction whose stoichiometry is specified by Equation (2), these changes are

$$\Delta C_{Ai} = \frac{C_{Bi} - \dfrac{b}{a} C_{Ai}}{\dfrac{C_{Bi}}{C_{Ai}} \exp\left[\left(C_{Bi} - \dfrac{b}{a} C_{Ai}\right) k_r\,\Delta z/u\right] - \dfrac{b}{a}} - C_{Ai} \tag{3a}$$

$$\Delta C_{Bi} = \frac{b}{a}\,\Delta\,C_{Ai} \tag{3b}$$

$$i = 1, 2, \ldots, N$$

The actual calculations were shortened without appreciable loss of accuracy by performing all of the coalescences taking place in a space increment $\Delta z = 0.005$ in. at once, and then changing the concentrations in all cells in accordance with Equations (3a) and (3b) with the larger increment $\Delta z = 0.005$ in. used.

Without loss of generality, A may be taken to be the limiting reactant, in which case the conversion F is defined by

$$F = \frac{C_{Ao} - \overline{C}_A}{C_{Ao}} \tag{4}$$

where

$$\overline{C}_A = \frac{1}{N} \sum_{i=1}^{N} C_{Ai}$$

A number of representative reactions from the experiments of Vassilatos and Toor have been simulated. Table 1 summarizes the parameters of the simulated runs. Figures 4, 5, 6, 7, and 8 compare the experimental results with the model simulations. The range of uncertainty in the experimental data is estimated by the vertical bars through the data points. This estimate is based on the variations reported in Figure 2 of Vassilatos and Toor (4). Homogeneous conversions are given for reference in Figures 6 and 7 by dashed lines. Generally good agreement is seen to be obtained over a wide range of reaction velocities and feed stoichiometric ratios.

SUMMARY AND CONCLUSIONS

A stochastic mixing model has been developed for homogeneous turbulent flow in tubular reactors. The model is based on random coalescence and redispersion of fluid elements. The intensity of coalescence is specified by a continuous function of position. This continuous function, called the *mixing characteristic*, can be determined either from root-mean-square tracer fluctuation tests or from conversion measurements made with fast reactions.

The model's usefulness is demonstrated by simulating the tubular reactor of Vassilatos and Toor. The mixing characteristic of the reactor is determined from its fast reaction data. The model simulations are in good agreement with their experiments, which cover a wide range of reaction velocities and feed stoichiometric ratios. Of special significance is the ability of the model to predict results for reactions of intermediate velocities where both mixing and reaction rates are comparable.

The application reported here is limited to single, second-order reactions between two chemical species. However, the model can be used for systems where any number of chemical species are reacting and where questions of selectivity as well as conversion are of importance. The model can be extended to simulate conversion in reactors having arbitrary residence time distributions. Results of this extension will be reported shortly.

NOTATION

A, B = reactants, see Equation (2)
a, b = stoichiometric coefficients defined by Equation (2)
C_{Ai}, C_{Bi} = concentration of A, B in i^{th} cell or lump of fluid, g.-moles/liter
C_{Ao}, C_{Bo} = average feed concentration of A, B (rate of A, B fed divided by total volumetric flow), g.-moles/liter
$\Delta C_{Ai}, \Delta C_{Bi}$ = incremental change in concentration of A, B in i^{th} cell due to chemical reaction, see Equations (3a) and (3b), g.-moles/liter
F = fractional conversion defined by Equation (4), dimensionless
k_r = homogeneous chemical rate constant, liters/(g.-mole)(sec.)
N = number of cells used in the model, dimensionless
$n(z)$ = number of coalescences experienced by the N cells between the entrance and position z, dimensionless
u = average axial velocity, in./sec.
z = axial position measured from the entrance, in.

Greek Letters

β = feed stoichiometric ratio = $a\,C_{Bo}/b\,C_{Ao}$, dimensionless
Δz = increment in z, in.
δt = short time increment during which N cells enter the reactor, sec.
$\eta(z)$ = mixing characteristic defined by Equation (1), dimensionless

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