Closure Equations for Single and Multiple Reactions in a CSTR

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In a recent paper, Dutta and Tarbell (1989) derived several first-order closure models for the nonlinear reaction terms in turbulent plug flow reactors by exploiting analogies between "mechanistic models" and "direct turbulence models." In this note, we extend their approach to a continuous stirred tank reactor (CSTR) with unmixed feed streams, a configuration in which significant deviations from maximum mixedness can be encountered if the turbulent mixing time scale is large. For a single bimolecular reaction, our result is particularly noteworthy since the fractional conversion is computed very simply as the solution to an algebraic quadratic equation. We also show that our single reaction calculation is in excellent agreement with the Monte Carlo results of the coalescence-redispersion (CRD) model presented by Spielman and Levenspiel (1965). We conclude by applying the closure ideas to multiple reactions where the effects of poor mixing are known to influence the product selectivity ratio (Chang et al., 1986).

Single Reaction Case

Let us consider the single reaction

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

which is being carried out in an isothermal, constant volume, constant flow rate CSTR with separate feed streams for A and B, and a bimolecular reaction rate ($r = kC_AC_B$). The continuity equation for species A in this reactor is

$$\partial C_A/\partial t + \nabla \cdot \vec{N}_A = - r \tag{2}$$

where C_A is the molar concentration of A, $\vec{N}_A$ is the molar flux of A and r is the molar rate of reaction—all being instantaneous local quantities. Following Rosensweig (1966), we define an average concentration within the reactor volume V

$$\bar{C}_A = (1/V) \int_V C_A \, dV \tag{3}$$

and decompose the local concentration field into the sum of a volume-averaged component and a local fluctuating component.

$$C_A = \bar{C}_A + c_A \tag{4}$$

Note that by definition

$$\bar{c}_A = 0 \tag{5}$$

To develop an evolution equation for $\bar{C}_A$ we integrate Eq. 2 over the reactor volume to obtain

$$V (d\bar{C}_A/dt) + \int_V \nabla \cdot \vec{N}_A \, dV = - V\bar{r} \tag{6}$$

where $\bar{r}$ is the volume-averaged reaction rate

$$\bar{r} = k(\bar{C}_A\bar{C}_B + \overline{c_Ac_B}) \tag{7}$$

Application of the divergence theorem to the second term in Eq. 6 leads to

$$\int_V \nabla \cdot \vec{N}_A \, dV = \int_S (\vec{N}_A \cdot \vec{n}) \, dS \tag{8}$$

where S is the surface bounding V and $\vec{n}$ denotes the unit normal vector directed outward at each point on S. Since $\vec{N}_A \cdot \vec{n}$ is nonzero only at the entrance and exit pipes, we have

$$\int_S (\vec{N}_A \cdot \vec{n}) \, dS = q\bar{\bar{C}}_A - q\bar{C}_{A0} \tag{9}$$

with q representing the total volumetric flow rate (see Eq. 11), $\bar{C}_{A0}$ denoting the mixed feed concentration and $\bar{\bar{C}}$ identifying the efflux-averaged concentration of the exit stream (Rosen-1966), for which a definition follows:

$$\bar{\bar{C}}_A = [\int_{S_e} C_A \, \vec{v} \cdot \vec{n} \, dS] / [\int_{S_e} \vec{v} \cdot \vec{n} \, dS] \tag{10}$$

S_e is the surface where the exit pipe intersects V, and clearly

$$q = \int_{S_e} \vec{v} \cdot \vec{n} \, dS \tag{11}$$

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Further analytical progress can be made only if we assume

$$\overline{\overline{C}}_A = \overline{C}_A \tag{12}$$

which is a statement of the standard stirred tank assumption that the effluent stream is at the average concentration of the tank. Invoking Eq. 12, we arrive at the evolution equation for the mean concentration of species A in the CSTR:

$$\tau\,(d\overline{C}_A/dt) = \overline{C}_{A0} - \overline{C}_A - \bar{r}\tau \tag{13}$$

Similarly for species B

$$\tau\,(d\overline{C}_B/dt) = \overline{C}_{B0} - \overline{C}_B - \bar{r}\tau \tag{14}$$

where $\tau = V/q$ is the mean residence time.

Equations 13 and 14 are not closed because of the appearance of the correlation $\overline{c_A c_B}$ in $\bar{r}$. It is possible, however, to close the system at the level of the mean equations (Eqs. 13 and 14) by providing a relationship between $\overline{c_A c_B}$ and the mean concentrations $\overline{C}_A$ and $\overline{C}_B$ (a first-order closure model).

A related problem was solved by Rosensweig (1964, 1966) using statistical turbulence concepts similar to those of Corrsin (1957). Rosensweig showed that the decay of variance of a nonreactive tracer in a constant volume, constant flow rate, stirred vessel of the type we have described above is given by:

$$\overline{c_A^2} = I_s(\overline{C}_{A0})^2 \tag{15}$$

where the intensity of segregation, I_s, is related to the turbulent mixing (micromixing) time scale by:

$$I_s = 1/(1 + \tau/\tau_m) \tag{16}$$

In Eq. 15, the overbar denotes a volume average, c_A is the fluctuating concentration of the tracer (cf. Eq. 4) and $\overline{C}_{A0}$ the mixed feed concentration. In Eq. 16, τ_m is the turbulent mixing time scale, for which Rosensweig's isotropic turbulence theory provides the estimate

$$\tau_m \approx (L_s^2/\epsilon)^{1/3} \tag{17}$$

from a basis of both the 3E and CRD models in the pure mixing (slow reaction) asymptote:

$$\overline{c_A c_B} = -I_s\,(\overline{C}_{A0}\overline{C}_B + \overline{C}_{B0}\overline{C}_A - \overline{C}\,\overline{C}_B) \tag{18}$$

where I_s again is the intensity of segregation. They showed that Eq. 18 reduces to the proper limits in the case of no reaction:

$$\overline{c_A c_B} = -I_s\,\overline{C}_{A0}\overline{C}_{B0} \tag{19}$$

and infinite reaction rate (slow mixing):

$$\overline{c_A c_B} = -\overline{C}_A\overline{C}_B \tag{20}$$

In addition, Eq. 18, when combined with the appropriate plug flow material balances, provided good predictions of a wide range of experimental data for both single and multiple reactions.

Building upon the established analogy between the 3E/CRD models and Rosensweig's stirred tank, we will apply Eq. 18 to the CSTR while using Eq. 16 to calculate the intensity of segregation. The closed model for the turbulent CSTR is then defined by Eqs. 7, 13, 14, 16 and 18. Note that we are assuming that the turbulent mixing time scale τ_m computed from variance decay experiments in a nonreactive environment can be used to describe mixing in a reacting situation—an assumption validated elsewhere (see references in Dutta and Tarbell, 1989). In what follows, first we use the steady-state version of the closed equations to determine the influence of turbulent mixing on the single reaction given in Eq. 1 and subsequently we consider a multiple reaction situation.

Upon scaling the mean species concentrations with the individual feed stream concentrations ($\xi = \overline{C}_A/\overline{C}_{A0}$, $\eta = \overline{C}_B/\overline{C}_{B0}$, $\beta = \overline{C}_{B0}/\overline{C}_{A0}$) and substituting Eq. 18 into the steady-state versions of Eqs. 13 and 14, we obtain the following equation for the mean concentration of reactant A:

$$k\tau\overline{C}_{A0}(1 + I_s)\xi^2 + \{1 + k\tau\overline{C}_{A0}\,[\beta - 1 - 2I_s]\}\xi - k\tau\overline{C}_{A0}I_s(\beta - 1) - 1 = 0 \tag{21}$$

The solution of this quadratic equation is:

$$\xi = \{k\tau\overline{C}_{A0}\,[2I_s + 1 - \beta] - 1 + \sqrt{[1 + k\tau\overline{C}_{A0}(\beta - 1 - 2I_s)]^2 + 4k\tau\overline{C}_{A0}(1 + I_s)[k\tau\overline{C}_{A0}I_s(\beta - 1) + 1]}\}/[2k\tau\overline{C}_{A0}\,(1 + I_s)] \tag{22}$$

where L_s is the integral length scale of the concentration field and ϵ is the turbulent kinetic energy dissipation rate.

Mehta and Tarbell (1983a) showed that two popular "mechanistic" mixing models, the three environment (3E) model and the coalescence-dispersion (CRD) model are analogous to Rosensweig's turbulent mixing tank, because they produce Eqs. 15 and 16 for the variance decay of a nonreactive tracer. This analogy allows the estimation of the micromixing parameter of the models from turbulence properties (Chang et al., 1986).

Returning now to the closure problem for $\overline{c_A c_B}$, Dutta and Tarbell (1989) derived the following first-order closure model

For an infinitely fast reaction, we take the limit $k\tau\overline{C}_{A0} \to \infty$ to arrive at the simple expression:

$$\xi = \{2I_s + 1 - \beta + \sqrt{[4I_s^2\beta + (1-\beta)^2]}\}/[2(1 + I_s)] \tag{23}$$

which for stoichiometric feed streams ($\beta = 1$) reduces to

$$\xi = 2I_s/(1 + I_s) \tag{24}$$

In Figure 1 we compare Eq. 24 with the Monte Carlo results

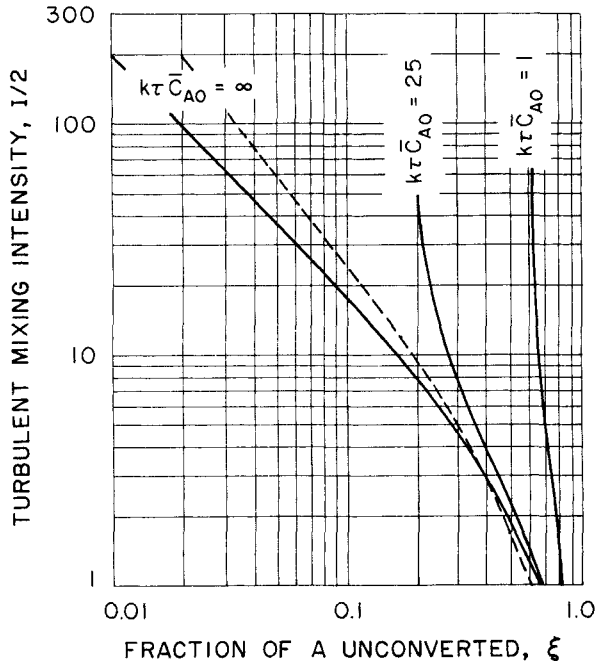

Figure 1. Closure prediction (Eq. 24, —) vs. Monte Carlo results of Spielman and Levenspiel (1965) for the CRD model (---).

The infinitely fast single reaction $A + B \rightarrow R$ occurs in an unmixed feed stream CSTR ($\beta = 1$)

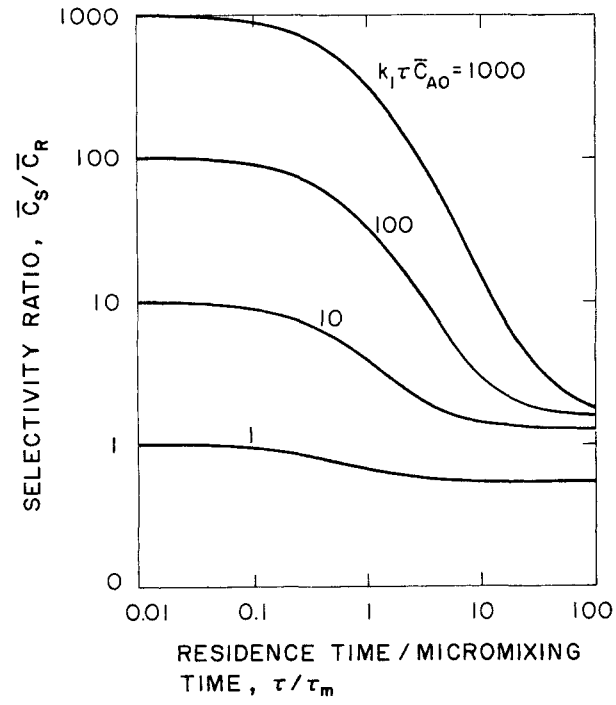

Figure 2. Effect of turbulent mixing time scale on selectivity ratio for different values of $k_1\tau\bar{C}_{A0}$ ($k_1 = k_2$).

The multiple reaction scheme $A + B \rightarrow R$, $R + B \rightarrow S$ occurs in an unmixed feed stream CSTR ($\beta = 1$)

of Spielman and Levenspiel (1965) for the CRD model in the limit $k\tau\bar{C}_{A0} \rightarrow \infty$. In addition, we display our closure computations for two different finite values of $k\tau\bar{C}_{A0}$. The parameter I in Figure 1 is the turbulent mixing parameter of the CRD model and it is related to I_s via the equation (Chang et al., 1986)

$$I_s = 1/(1 + I/2) \tag{25}$$

It is clear that the simple algebraic equation (Eq. 24) compares quite favorably with the results of tedious Monte Carlo simulations of the CRD model over the entire range of reactant conversion. Although Figure 1 does not directly compare the predictions of our algebraic closure model and experimental data, it should be realized that the CRD model has been shown to provide excellent predictions of a wide variety of experimental mixing-reaction data (Patterson, 1981; Chang et al., 1986).

Multiple Reaction Case

We consider the parallel consecutive reaction scheme

$$A + B \rightarrow R \tag{26}$$

$$B + R \rightarrow S \tag{27}$$

in a CSTR with A and B fed in separate feed streams. For this scheme, the additional correlation $\overline{c_R c_B}$, arising from the second reaction, must be closed. This is accomplished by analogy with Eq. 18 after noting that $\bar{C}_{R0} = 0$. The result is:

$$\overline{c_R c_B} = -I_s(\bar{C}_{B0}\bar{C}_R - \bar{C}_R\bar{C}_B) \tag{28}$$

Introducing Eq. 28 along with Eq. 18 into the averaged material balances for species A and B, and taking the reaction stoichiometry into account lead to the following system of closed equations:

$$1 = \xi + \beta k_1\tau\bar{C}_{A0}\{\xi\eta - I_s[\xi + \eta - \xi\eta]\} \tag{29}$$

$$1 = \eta + k_1\tau\bar{C}_{A0}\{\xi\eta - I_s[\xi + \eta - \xi\eta]\} + k_2\tau\bar{C}_{A0}\{\eta\chi - I_s[\chi - \eta\chi]\} \tag{30}$$

$$\chi = 2(1 - \xi) - \beta(1 - \eta) \tag{31}$$

In these equations, $\chi = \bar{C}_R/\bar{C}_{A0}$ and the other symbols retain their earlier meaning. k_1 and k_2 are the rate constants for the first and the second reaction, respectively.

A useful asymptotic limit for the selectivity ratio, $\bar{C}_S/\bar{C}_R$, can be derived from these equations when $\tau_m \rightarrow \infty$ (or $I_s \rightarrow 1$), that is, when mixing is very poor. The result, which is obtained by first expressing the selectivity in terms of ξ (or η) and then noting that $\xi, \eta \rightarrow 1$ as $I_s \rightarrow 1$, is given by:

$$\bar{C}_S/\bar{C}_R \rightarrow \beta k_2\tau\bar{C}_{A0} = k_2\tau\bar{C}_{B0} \text{ as } \tau_m \rightarrow \infty \tag{32}$$

Some numerical results for the selectivity ratio as a function of the mixing time scale for different values of the parameter $k_1\tau\bar{C}_{A0}$ ($k_1 = k_2$, $\beta = 1$) are plotted in Figure 2 for demon-

stration purposes. A qualitative discussion of the effect of micromixing on product selectivity is given in Levenspiel (1972). From Figure 2 we see that poor mixing tends to enhance the selectivity ratio $\overline{C}_S/\overline{C}_R$, a result consistent with conclusions based on the qualitative analysis in Levenspiel (1972). We note that the extent of enhancement increases as the reactions progressively become more mixing-limited and $\overline{C}_S/\overline{C}_R$ approaches the limit of Eq. 32 as $\tau/\tau_m \to 0$. We are unable to compare our predictions for multiple reactions in a CSTR with data because well defined experiments with unambiguous kinetics have not yet been described in the literature.

The closure scheme presented in this paper results in an extremely simple algebraic model of turbulent mixing in a CSTR with a single parameter (τ_m) that has a physical basis. It may be useful in the design and analysis of unmixed feed stream CSTRs. However, a note of caution in application of this model to real reactors is in order. The stirred tank assumption (Eq. 12), which underlies the entire development of the paper, requires that the time scale for macromixing, τ_M, be small compared to the time scales for micromixing (τ_m) and reaction (τ_r). τ_M can be taken as the blending time in a mixing tank (Oldshue, 1985), which is on the order of the reciprocal of the impeller rotation speed at high Reynolds numbers ($> 10^4$). The advantage of this model over the classical CSTR model is that situations where $\tau_r \leq \tau_m$ can be described.

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Notation

A,B,R,S = reactants or products
c = fluctuating component of turbulent concentration field of species
C = turbulent concentration of species
$\overline{C}$ = mean (volume-averaged) concentration of species
$\overline{\overline{C}}$ = efflux-averaged concentration of species
I,I_s = mixing parameter of CRD model and intensity of segregation
k,k_1,k_2 = rate constants
L_s = integral length scale of concentration field
$\vec{n},\vec{N}$ = unit outward normal and molar flux of species
$r(\overline{r})$ = local (average) reaction rate
S,S_e = surface bounding reactor volume and cross-section of exit pipe
t = time
q = total volumetric flow rate
$\vec{v},V$ = local velocity field and volume of reacting fluid

Greek letters

β = stoichiometric ratio
ϵ = turbulent kinetic energy dissipation per unit mass
ξ,η,χ = dimensionless mean species concentrations
τ = reactor residence time
τ_m = turbulent mixing (micromixing) time scale
τ_M = macromixing time scale
τ_r = reaction time scale

Subscripts

A,B,R,S = species
0 = feed stream value

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