LETTERS TO THE EDITOR

To the Editor:

I have found the following two errors in the paper, "Dense-Phase Feeding of Pulverized Coal in Uniform Plug Flow," Sprouse and Schuman (1983).

The denominator of Eq. 11 should read $\epsilon^2 D_p^2$ and *not* $\epsilon^3 D_p^2$. This can be clearly seen by substituting for b in Eq. 14 using Eq. 11 and considering the case of zero solids flow (i.e., $V_{s,t} = 0$). The result is

$$\frac{(P_{f,0} - P_{f,L})}{L} = \frac{150\mu(1-\epsilon)^2}{\epsilon^3 D_p^2} V_{f,t} \quad \text{(a)}$$

But, from Eq. 21 $V_{f,t}$ is the interstitial fluid velocity i.e., $V_{f,t} = U_f/\epsilon$ where U_f is the superficial velocity. Comparison of Eq. a with the Blake-Kozeny equation shows the error.

Now since Eq. 11 is obtained from Eq. 6, it follows that the denominator of Eq. 6 should read ϵD_p^2 and not $\epsilon^2 D_p^2$. This can be shown directly by substituting Eq. 6 as written into Eq. 3 and considering the case of one-dimensional gas flow in the z-direction through a stationary packed bed.

Literature Cited

Sprouse, K. M., and M. D. Schuman, "Dense-Phase Feeding of Pulverized Coal in Uniform Plug Flow," *AIChE J.*, **29**(6), 1000 (1983).

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Reply:

Professor Konrad is quite correct in reporting that the denominator of Eq. 6 should read ϵD_p^2 while the denominator of Eq. 11 should be $\epsilon^2 D_p^2$. Fortunately, these changes in Eqs. 6 and 11 do not significantly alter the final modeling results shown in Figures 4–6. Using a nonlinear least-squares curve-fitting computer program, it was found with this change in Eq. 11 that the feeder tank fluid discharge coefficient, C_D, shown in Table 2, should read "0.135" instead of "0.177." This change in the parameter C_D will produce curves nearly identical to those already shown in Figures 4–6 when using the revised Eq. 11.

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To The Editor:

Brodkey and Lewalle (1985) recently attempted to extend Toor's turbulent closure hypothesis (Toor, 1969) for single-step, second order nonpremixed reactions to the series-parallel reactions

$$A + B \xrightarrow{k_1} P \qquad (1)$$

$$B + P \xrightarrow{k_2} S \qquad (2)$$

by assuming that in the time averaged reaction rate expressions

$$\bar{r}_A = -k_1 (\bar{A}\,\bar{B} + \overline{ab}) \qquad (3)$$

$$\bar{r}_S = k_2 (\bar{B}\,\bar{P} + \overline{bp}) \qquad (4)$$

$$\bar{r}_B = \bar{r}_A - \bar{r}_S \qquad (5)$$

$$\bar{r}_P = -\bar{r}_A - \bar{r}_S \qquad (6)$$

they could take

$$\overline{bp} = \overline{ab}\left(\frac{\bar{P}}{\bar{A}}\right) \qquad (7)$$

$\bar{r}_i$ refers to time average reaction rate of species i and all other notation follows Brodkey and Lewalle.

Consider the situation in which k_1 (or better, the first Damköhler Number) increases without limit. Since $\bar{r}_A$ must remain finite, just as with a single step reaction, Eq. 3 gives

$$\overline{ab} = -\bar{A}\,\bar{B} \qquad (8)$$

and Eqs. 7, 8, and 4 give $\bar{r}_S = 0$. But this cannot be true! As k_1 increases holding k_1/k_2 constant, or equivalently the mixing is slowed, the first reaction is slowed down more than the second (Bourne & Toor, 1977) and the yield of S should reach its *maximum*, not its *minimum* value. At this limit A and B are segregated because they react instantaneously forming a reaction surface. P is produced in this surface and it must then diffuse into the surrounding fluid and react in the adjacent B region to produce S. There is no reason to expect the second-step reaction to stop as k_1 gets large (holding k_1/k_2 constant) or the mixing gets poorer. In fact it does not; the yield of S *increases* as the first Damköhler number increases.

We studied a fast series-parallel diazo-coupling reaction in a multijet tubular reactor essentially the same as that used by Brodkey and Lewalle in their calculations (Li, 1985). The yield of S *increased* as the mixing got poorer, the opposite of what is implied by Eq. 7.

At a Reynolds Number of 600, for example, we found the yield of S ($\bar{C}_S/\bar{C}_{BO}$) to be 0.13 ± 0.010 and it decreased as the Reynolds number increased. Under the conditions used, the yield would have been close to zero if the mixing had been perfect (chemical reaction control)–the unmixedness (segregation) slowed down the first reaction more than the second, increasing the yield of S. However, Eq. 9 of Brodkey and Lewalle, which uses Eq. 7, when integrated with well-known values of I_s, k_1 and k_2 predicts an S yield of 0.001.

We conclude that the hypothesis of Brodkey and Lewalle unfortunately cannot be used to predict the effect of mixing on the yield of a series-parallel reaction.

Literature Cited

Bourne, J. R., and H. L. Toor, "Simple Criteria for Mixing Effects in Complex Reactions," *AIChE J.* **23**, 602 (1977).

Brodkey, R. S., and J. Lewalle, "Reactor Selectivity Based on First-order Closures of the Turbulent Concentration Equations," *AIChE J.* **31**, 111 (1985).

Li, K. T., "Turbulent Mixing with Complex Reactions in Unpremixed Tubular Reactors," Ph.D. Dissertation, Carnegie-Mellon University (1985).

Toor, H. L., "Turbulent Mixing of the Two Species with and without Chemical Reaction," *Ind. Eng. Chem. Fund.* **8**, 655 (1969).

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Reply:

Toor and Li have proposed some possible problems with the closure hypothesis by Brodkey and Lewalle (1985) for the series-parallel reactions

$$A + B \xrightarrow{k_1} P$$

$$B + P \xrightarrow{k_2} S \qquad (1)$$

The closure suggested was

$$\overline{bp} = \overline{ab}\,(\overline{P}/\overline{A}) \qquad (2)$$

which when used along with the one-dimensional mass conservation equations and Toor's hypothesis applied to both reactions in Eq. 1, forms a possible solution to the turbulent mixing problem.

Toor and Li discuss the situation where k_1 increases without limit. They cite the k_1/k_2 ratio as being constant, but in actuality analyze the problem as if k_2 were constant. If k_1 increases without limit and k_1/k_2 is held constant, then k_2 must also increase without limit. Thus in order to have a finite rate of production of S, the term $(\overline{B}\,\overline{P} + \overline{bp})$ must be zero in order for

$$\bar{r}_S = \infty \cdot (0) = \mathit{finite}. \qquad (7)$$

Thus Toor and Li's first argument is invalid as proposed. In fact, we will, in a later note, show that the closure Eq. 2 is a direct consequence of applying Toor's hypothesis to the second reaction when k_2 approaches infinity.

The experimental yield of S $(\overline{C}_S/\overline{C}_{B_o})$ of 0.13 ± 0.010 for a Reynolds number of 600 must be assumed correct, for unless proven otherwise, is an experimental fact. Our calculated value of 0.0024 using the closure Eq. 2 must be considered a failure of the closure. Thus, we must conclude that Toor's hypothesis fails when applied to series-parallel reactions with very large k_1/k_2 ratios. The actual value reported in Li (1985) for the rate constant ratio is 2,086. The rate constant k_1 has a value of 7.3×10^6 L/mol/s, which is classified as a very fast reaction by Mao and Toor (1971) and Vassilatos and Toor (1965). This type of reaction is diffusion controlled (or limited) since as fast as the reactants are brought into close proximity, reaction occurs (the time constant for diffusion is much greater than the time constant for reaction one). The rate constant for the second reaction, k_2, is reported as 3,500 L/mol/s, which is classified as rapid according to Toor (the time constant for diffusion is about the same as the time constant for reaction two). Rapid reactions are kinetic and diffusion controlled (limited) since the reactants are brought into close proximity by diffusion at about the same rate as they react.

Vassilatos and Toor (1965) state that a reaction is very fast if N_{RM} is much greater than one, rapid if order of one, and slow if much less than one. N_{RM} is defined as

$$N_{RM} = k_R/k_M \qquad (8)$$

where R and M refer to reaction and mixing and k_M is in the range of 10,000 to 20,000 L/mol/s. This is equivalent to a ratio of time constants. The two reactions have values of N_{RM} of 730 and 0.350, respectively (using k_M of 10,000). Assuming that all component diffusivities are equal, A and B react almost instantaneously and form a reaction surface. The species P is produced at this surface and will diffuse away from it. The rate of diffusion is much less than the rate of reaction one, while it is greater than the rate of reaction two. The diffusion will cause more P to be produced before any S is produced. This situation can continue until the time constant of the second reaction is reached and then S is produced. This suggests that the amount of S produced will be small compared to the amounts of P produced and A and B consumed. This is as observed, but from this, one cannot conclusively give a range for S. Apparently, the predicted fractional yield of 0.0024 is too low for this case since Li's experiment gives 0.13.

We are still pursuing our random cell model simulation and plan to apply it to the extreme kinetics cited above. The results of this simulation should reveal more about the low calculated yield values for S and why Toor's hypothesis fails when applied to the second reaction. For now, we can only agree with Toor and Li and conclude that Toor's hypothesis fails for this case. This does not invalidate the hypothesis for less extreme kinetic situations, which need further investigation by both experimentation and simulation.

Literature Cited

Brodkey, R. S., and J. Lewalle, "Reactor Selectivity Based on First-order Closures of the Turbulent Concentration Equations," *AIChE J.*, **31,** 111 (1985).

Li, K. T., "Turbulent Mixing with Complex Reactions in Unpremixed Tubular Reactors," Ph.D. Dissertation, Carnegie-Mellon University (1985).

Mao, K. W., and H. L. Toor, "Second-order Chemical Reactions with Turbulent Mixing," *Ind. Eng. Chem. Fund.*, **10,** 192 (1971).

Toor, H. L., "Turbulent Mixing of Two Species with and without Chemical Reaction," *Ind. Eng. Chem. Fund.*, **8,** 655 (1969).

Vassilatos, G., and H. L. Toor, "Second-order Chemical Reactions in a Nonhomogeneous Turbulent Fluid," *AIChE J.*, **11,** 666 (1965).

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