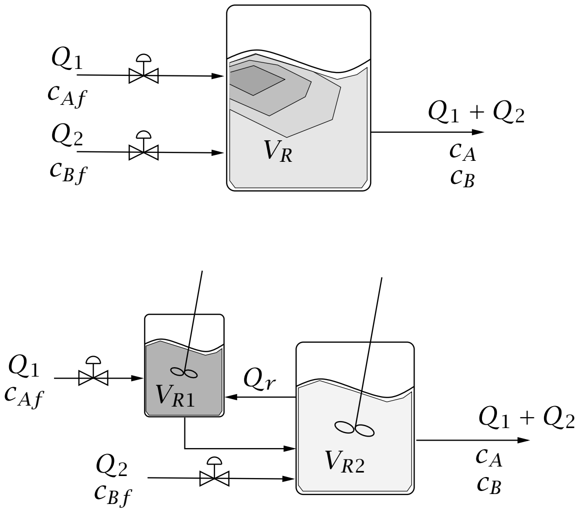

Figure 8.32: Imperfect mixing (top reactor) leads to formation of an A-rich zone, which is modeled as a small CSTR feeding a second CSTR (bottom two reactors).

8.5 Examples in Which Mixing is Critical

Returning to the topic of mixing, we would like to close the chapter by presenting a few more chemical mechanisms for which reactor mixing can play a critical role.

Example 8.5: Mixing two liquid-phase streams in a stirred tank

A classic mixing problem arises when we must bring two liquid-phase feed streams together to perform the second-order reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{C} \tag{8.59}$$

in the presence of the undesirable side reaction

$$\mathrm{A} \xrightarrow{k_2} \mathrm{D} \tag{8.60}$$

If the rate of the second degradation reaction is fast compared to the rate of mixing of the two feed streams, we can anticipate problems. To understand what happens in this situation, consider the mixing model depicted in Figure 8.32. Component A is assumed to be the limiting

Parameter	Value	Units
k_1	1	min^{-1}
k_2	2	L/mol·min
n	2	
$\theta_1 = V_{R1}/Q_2$	1	min
$\theta_2 = V_{R2}/Q_2$	2	min
$\theta = V_R/Q_2$		
$= \theta_1 + \theta_2$	3	min
$\alpha = Q_1/Q_2$	0.1	
$\rho = Q_r/Q_2$	varies	

Table 8.3: Reactor and kinetic parameters for feed-mixing example.

reactant. It is added at a low flowrate to a CSTR that contains an excess of reactant B. In the top figure we depict the ideal-mixing case in which the rate of mixing is arbitrarily fast compared to the rate of either reaction. But this ideal mixing may be impossible to achieve if the reaction rates are reasonably large. So in the bottom figure, we model the formation of an A-rich zone near the feed entry point. This small CSTR exchanges mass with a larger reactor that contains the excess of reactant B. We can vary the recycle flowrate between the two CSTRs, Q_r, and the sizes of the two reactors, V_{R1} and V_{R2}, to vary the degree of mixing. For large Q_r, we expect the two-reactor mixing model to approach the single, ideally mixed CSTR.

As discussed in Chapter 4, the conversion and yield are the usual quantities of interest in competing parallel reactions of the type given in Reactions 8.59 and 8.60. We assume the density of this liquid-phase system is constant, and define the overall conversion of reactant A and yield of desired product C as follows:

$$x_A = \frac{Q_1 c_{Af} - (Q_1 + Q_2) c_A}{Q_1 c_{Af}} \qquad y_C = \frac{(Q_1 + Q_2) c_C}{Q_1 c_{Af} - (Q_1 + Q_2) c_A}$$

Given the parameters and rate constants in Table 8.3, calculate x_A and y_C versus Q_r for the two-reactor mixing model shown in Figure 8.32, and compare the result to the single, well-mixed reactor. Then calculate the residence-time distribution $P(\theta)$ for tracer injected with the A feed stream for the two models. Discuss whether or not the residence-time distribution is a reliable indicator for problems with yield in the imperfectly mixed reactor.

Solution

The steady-state mass balance for the single, well-mixed CSTR is

$$\begin{aligned} 0 &= Q_1 c_{Af} - (Q_1 + Q_2) c_A - (k_1 c_A c_B + k_2 c_A^n) V_R \\ 0 &= Q_2 c_{Bf} - (Q_1 + Q_2) c_B - k_1 c_A c_B V_R \end{aligned}$$

Defining the following parameters

$$\alpha = \frac{Q_1}{Q_2} \qquad \theta = \frac{V_R}{Q_2} \qquad \rho = \frac{Q_r}{Q_2}$$

allows us to write these as

$$\begin{aligned} 0 &= \alpha c_{Af} - (1 + \alpha) c_A - (k_1 c_A c_B + k_2 c_A^n) \theta \\ 0 &= c_{Bf} - (1 + \alpha) c_B - k_1 c_A c_B \theta \end{aligned}$$

We can solve numerically the two equations for the two unknowns c_A, c_B. The concentration of C in the outflow is determined from the change in the concentration of B,

$$(Q_1 + Q_2) c_C = Q_2 c_{Bf} - (Q_1 + Q_2) c_B$$

Using this relationship and the defined parameters gives for conversion and yield,

$$x_A = \frac{\alpha c_{Af} - (1 + \alpha) c_A}{\alpha c_{Af}} \qquad y_C = \frac{c_{Bf} - (1 + \alpha) c_B}{\alpha c_{Af} - (1 + \alpha) c_A}$$

For the two-reactor system, we write mass balances for each reactor. Let $c_{A1}, c_{A2}, c_{B1}, c_{B2}$ be the unknown A and B concentrations in the two-reactors, respectively. The mass balances are

Reactor 1:

$$\begin{aligned} 0 &= Q_1 c_{Af} - (Q_1 + Q_r) c_{A1} + Q_r c_{A2} - (k_1 c_{A1} c_{B1} + k_2 c_{A1}^2) V_{R1} \\ 0 &= -(Q_1 + Q_r) c_{B1} + Q_r c_{B2} - k_1 c_{A1} c_{B1} V_{R1} \end{aligned}$$

Reactor 2:

$$\begin{aligned} 0 &= (Q_1 + Q_r) c_{A1} - Q_r c_{A2} - (Q_1 + Q_2) c_{A2} - (k_1 c_{A2} c_{B2} + k_2 c_{A2}^2) V_{R2} \\ 0 &= Q_2 c_{Bf} + (Q_1 + Q_r) c_{B1} - Q_r c_{B2} - (Q_1 + Q_2) c_{B2} - (k_1 c_{A2} c_{B2}) V_{R2} \end{aligned}$$

We can summarize this case using the previously defined variables as four equations in four unknowns

$$
\begin{aligned}
0 &= \alpha c_{Af} - (\alpha+\rho)c_{A1} + \rho c_{A2} - (k_1 c_{A1} c_{B1} + k_2 c_{A1}^2)\theta_1 \\
0 &= -(\alpha+\rho)c_{B1} + \rho c_{B2} - k_1 c_{A1} c_{B1}\theta_1 \\
0 &= (\alpha+\rho)c_{A1} - \rho c_{A2} - (1+\alpha)c_{A2} - (k_1 c_{A2} c_{B2} + k_2 c_{A2}^2)\theta_2 \\
0 &= c_{Bf} + (\alpha+\rho)c_{B1} - \rho c_{B2} - (1+\alpha)c_{B2} - (k_1 c_{A2} c_{B2}\theta_2
\end{aligned}
$$

Figures 8.33 and 8.34 show the yield and conversion for the two cases as a function of Q_r. The conversion is not adversely affected by the poor mixing. In fact, the conversion in the two-reactor system is higher than the single, well-mixed reactor. Notice, however, that at low values of Q_r, which corresponds to poor mixing at the feed location, the yield changes from *more than 90% to less than 15%.* Low yield is a qualitatively different problem than low conversion. If the conversion is low, we can design a separation system to remove the unreacted A and recycle it, or use it as feed in a second reactor. With low yield, however, the A has been irreversibly converted to an undesired product D. The raw material is lost and cannot be recovered. It is important to diagnose the low yield as a reactor mixing problem, and fix the problem at the reactor. A yield loss cannot be recovered by downstream processing.

Next we compute the outcome of injecting a unit step change in a tracer in the A feed stream. We solve the transient CSTR balances and calculate the tracer concentration at the outlet. Because the tracer does not take part in any reactions, this can be done analytically or numerically. The result is shown in Figure 8.35. We see the familiar single CSTR step response. For the two-reactor mixing model, when $\rho = 0$, which corresponds to the poorest mixing and lowest yield, the step test does reliably indicate the poor mixing. At the end of this chapter and also in Chapter 9 we show how to use this step response to determine the best value of ρ to model the mixing. When ρ is reasonably large, $Q_r = Q_2$, and the single CSTR and two-reactor cases have similar yields and step responses.

Notice in all three step responses, the tracer concentration reaches only $c_{Is} = 0.091 = \alpha/(1+\alpha)$ because we inject tracer in only one of the two feed streams. □

This example is one of the classic sets of reactions in which mixing has a significant impact on the reactor performance and the product yield. It deserves careful study because it builds intuition and leads us to ask good questions when confronted with more complex cases.

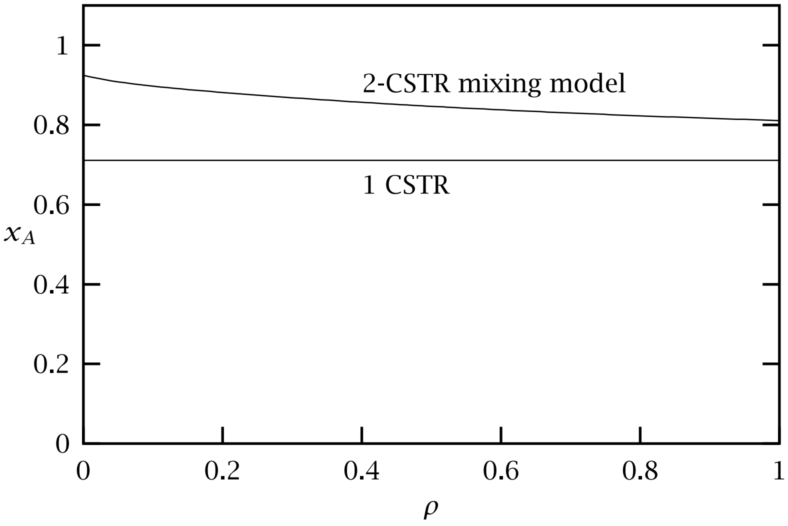

Figure 8.33: Conversion of reactant A for single, ideal CSTR, and as a function of internal flowrate, $\rho = Q_r/Q_2$, in a 2-CSTR mixing model.

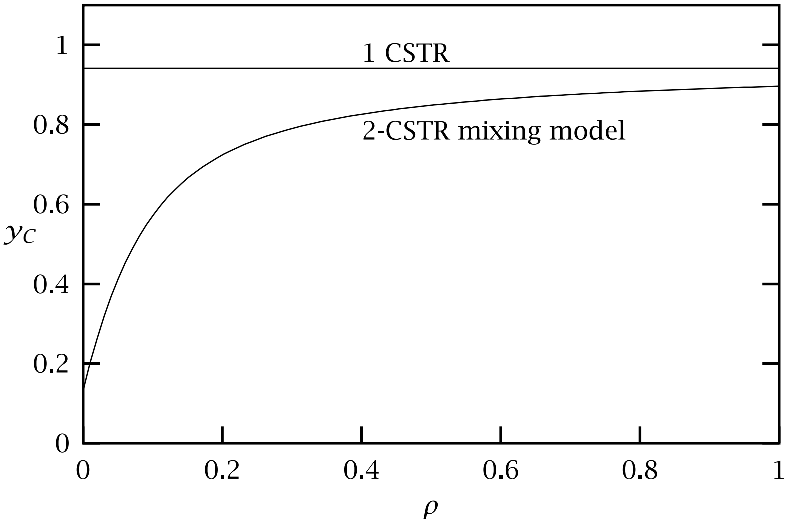

Figure 8.34: Yield of desired product C for single, ideal CSTR, and as a function of internal flowrate, $\rho = Q_r/Q_2$, in a 2-CSTR mixing model.

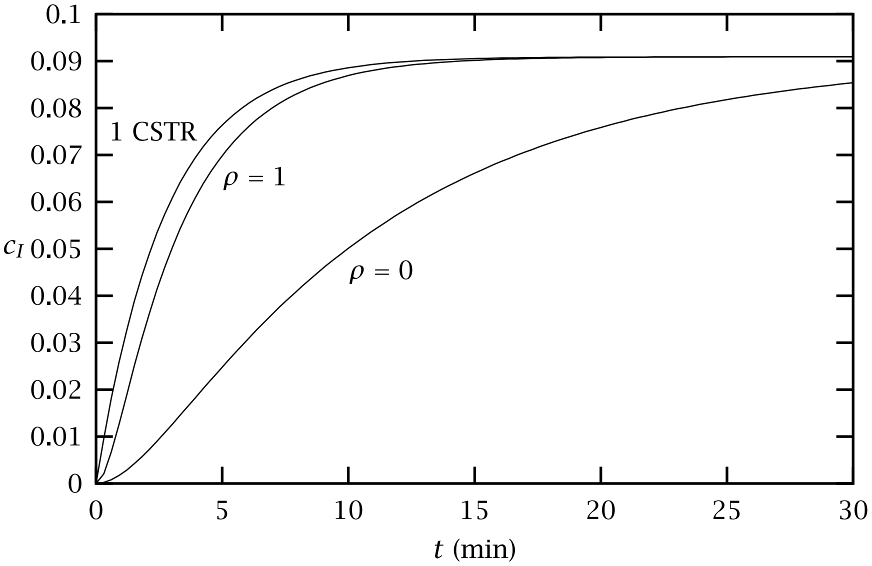

Figure 8.35: Step response for single, ideal CSTR, and 2-CSTR mixing model with $\rho = 0, 1$.

For example, Villa et al. [23] discuss similar issues that arise in more complex polymerization reaction engineering problems.

Example 8.6: Maximizing yield in dispersed plug flow

Consider the following two liquid-phase reactions in which B is the desired product

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}, \qquad r_1 = k_1 c_A \tag{8.61}$$

$$2\mathrm{B} \xrightarrow{k_2} \mathrm{C}, \qquad r_2 = k_2 c_B^2 \tag{8.62}$$

The second reaction can represent the first step in a polymerization process of species B, which is undesirable in this case.

Because the second reaction is second order in B, it is desirable to keep the *average* B concentration in the reactor low, to avoid yield losses, but achieve high B concentration near the reactor exit to maximize the production rate. Intuitively the CSTR is a bad choice, because it maintains the same B concentration everywhere in the reactor. A PFR