CHAPTER 8

Nonideal Flow in Reactors

8.1 | Introduction

In Chapter 3, steady-state, isothermal ideal reactors were described in the context of their use to acquire kinetic data. In practice, conditions in a reactor can be quite different than the ideal requirements used for defining reaction rates. For example, a real reactor may have nonuniform flow patterns that do not conform to the ideal PFR or CSTR mixing patterns because of corners, baffles, nonuniform catalyst packings, etc. Additionally, few real reactors are operated at isothermal conditions; rather they may be adiabatic or nonisothermal. In this chapter, techniques to handle nonideal mixing patterns are outlined. Although most of the discussion will center around common reactor types found in the petrochemicals industries, the analyses presented can be employed to reacting systems in general (e.g., atmospheric chemistry, metabolic processes in living organisms, and chemical vapor deposition for microelectronics fabrication). The following example illustrates how the flow pattern within the same reaction vessel can influence the reaction behavior.

EXAMPLE 8.1.1

In order to approach ideal PFR behavior, the flow must be turbulent. For example, with an open tube, the Reynolds number must be greater than 2100 for turbulence to occur. This flow regime is attainable in many practical situations. However, for laboratory reactors conducting liquid-phase reactions, high flow rates may not be achievable. In this case, laminar flow will occur. Calculate the mean outlet concentration of a species A undergoing a first-order reaction in a tubular reactor with laminar flow and compare the value to that obtained in a PFR when $(kL)/u = 1$ (u = average linear flow velocity).

■ Answer

The material balance on a PFR reactor accomplishing a first-order reaction at constant density is:

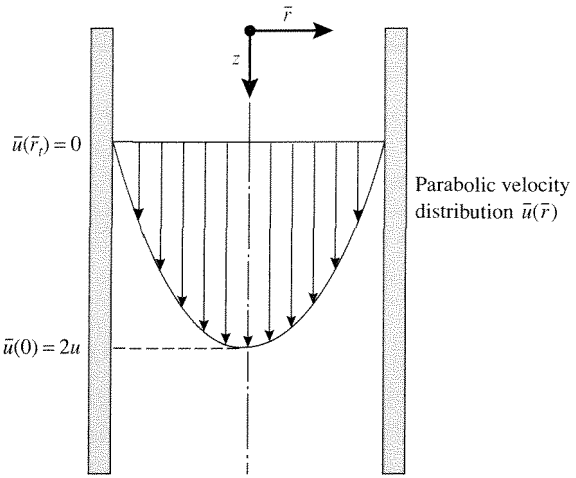


Figure 8.1.1 | Schematic representation of laminar velocity profile in a circular tube.

$$\frac{dF_A}{dV_R} = \nu \frac{dC_A}{dV_R} = \frac{uA_C}{A_C}\frac{dC_A}{dz} = u\frac{dC_A}{dz} = -kC_A$$

Integration of this equation with $C_A = C_A^0$ at the entrance of the reactor ($z = 0$) gives:

$$C_A = C_A^0 \exp\left[-\frac{kz}{u}\right]$$

For laminar flow:

$$\bar{u}(\bar{r}) = 2u\left[1 - \left(\bar{r}/\bar{r}_t\right)^2\right]$$

where $\bar{r}_t$ is the radius of the tubular reactor (see Figure 8.1.1).

The material balance on a laminar-flow reactor with negligible mass diffusion (discussed later in this chapter) is:

$$\bar{u}(\bar{r})\frac{\partial C_A}{\partial z} = -kC_A$$

Since $\bar{u}(\bar{r})$ is not a function of z, this equation can be solved to give:

$$C_A(\bar{r}) = C_A^0 \exp\left[-\frac{kz}{\bar{u}(\bar{r})}\right]$$

To obtain the mean concentration, $\overline{C}_A$, $C_A(\bar{r})$ must be integrated over the radial dimension as follows:

$$\bar{C}_A = \frac{\int_0^{\bar{r}'} C_A(\bar{r})\bar{u}(\bar{r})2\pi\bar{r}d\bar{r}}{\int_0^{\bar{r}'} \bar{u}(\bar{r})2\pi\bar{r}d\bar{r}}$$

Thus, the mean outlet concentration of A, $\bar{C}_A^L$, can be obtained by evaluating $\bar{C}_A$ at $z = L$. For $(kL)/u = 1$ the outlet value of C_A from the PFR, C_A^P, is 0.368 C_A^0 while for the laminar-flow reactor $\bar{C}_A^L = 0.443\ C_A^0$. Thus, the deviation from PFR behavior can be observed in the outlet conversion of A: 63.2 percent for the PFR versus 55.7 percent for the laminar-flow reactor.

8.2 | Residence Time Distribution (RTD)

In Chapter 3, it was stated that the ideal PFR and CSTR are the theoretical limits of fluid mixing in that they have no mixing and complete mixing, respectively. Although these two flow behaviors can be easily described, flow fields that deviate from these limits are extremely complex and become impractical to completely model. However, it is often not necessary to know the details of the entire flow field but rather only how long fluid elements reside in the reactor (i.e., the distribution of residence times). This information can be used as a diagnostic tool to ascertain flow characteristics of a particular reactor.

The "age" of a fluid element is defined as the time it has resided within the reactor. The concept of a fluid element being a small volume relative to the size of the reactor yet sufficiently large to exhibit continuous properties such as density and concentration was first put forth by Danckwerts in 1953. Consider the following experiment: a tracer (could be a particular chemical or radioactive species) is injected into a reactor, and the outlet stream is monitored as a function of time. The results of these experiments for an ideal PFR and CSTR are illustrated in Figure 8.2.1. If an impulse is injected into a PFR, an impulse will appear in the outlet because there is no fluid mixing. The pulse will appear at a time $t_1 = t_0 + \tau$, where τ is the space time ($\tau = V/\nu$). However, with the CSTR, the pulse emerges as an exponential decay in tracer concentration, since there is an exponential distribution in residence times [see Equation (3.3.11)]. For all nonideal reactors, the results must lie between these two limiting cases.

In order to analyze the residence time distribution of the fluid in a reactor the following relationships have been developed. Fluid elements may require differing lengths of time to travel through the reactor. The distribution of the exit times, defined as the $E(t)$ curve, is the residence time distribution (RTD) of the fluid. The exit concentration of a tracer species $C(t)$ can be used to define $E(t)$. That is:

$$E(t) = \frac{C(t)}{\int_0^\infty C(\bar{t})d\bar{t}} \tag{8.2.1}$$

such that:

$$\int_0^\infty E(\bar{t})d\bar{t} = 1 \tag{8.2.2}$$

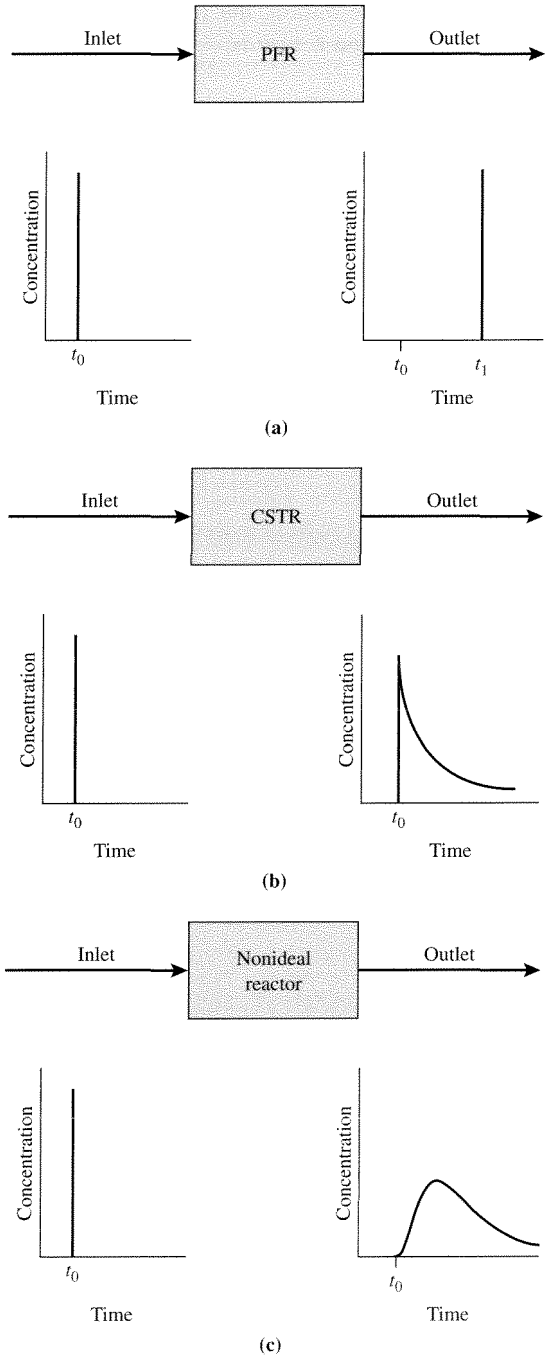


Figure 8.2.1 |
Concentrations of tracer species using an impulse input. **(a)** PFR ($t_1 = t_0 + \tau$). **(b)** CSTR. **(c)** Nonideal reactor.

With this definition, the fraction of the exit stream that has residence time (age) between t and $t + dt$ is:

$$E(t)dt \tag{8.2.3}$$

while the fraction of fluid in the exit stream with age less than t_1 is:

$$\int_0^{t_1} E(\bar{t})d\bar{t} \tag{8.2.4}$$

EXAMPLE 8.2.1

Calculate the RTD of a perfectly mixed reactor using an impulse of n moles of a tracer.

■ Answer

The impulse can be described by the Dirac delta function, that is:

$$\delta(t - t_0) \begin{cases} = 0, & t \neq t_0 \\ \neq 0, & t = t_0 \end{cases}$$

such that:

$$\int_{-\infty}^{\infty} \delta(t - t_0)dt = 1$$

The unsteady-state mass balance for a CSTR is:

$$\underset{\text{accumulation}}{V\frac{dC}{dt}} = \underset{\text{input}}{\text{n}\delta(t)} - \underset{\text{output}}{\text{v}C}$$

where t_0 in the Dirac delta is set to zero and:

$$\int_{-\infty}^{\infty} \delta(t)dt = 1$$

Integration of this differential equation with $C(0) = 0$ gives:

$$\text{(a)} \qquad \tau\frac{dC}{dt} + C = \left(\frac{\text{n}}{\text{v}}\right)\delta(t)$$

$$\text{(b)} \qquad \int_0^t d[C\exp(\bar{t}/\tau)] = \left(\frac{\text{n}}{\text{v}}\right)\int_0^t \frac{\delta(\bar{t})}{\tau}\exp(\bar{t}/\tau)d\bar{t}$$

$$\text{(c)} \qquad C\exp(\bar{t}/\tau)\Big|_0^t = \left(\frac{\text{n}}{\text{v}}\right)\int_0^t \frac{\delta(\bar{t})}{\tau}\exp(\bar{t}/\tau)d\bar{t}$$

(d) $$C(t)\exp(t/\tau) - C(0)\exp(0) = \left(\frac{n}{v}\right)\int_0^{t'} \frac{\delta(\bar{t})}{\tau}\exp(\bar{t}/\tau)d\bar{t}$$

(e) $$C(t) = \left(\frac{n}{v}\right)\exp(-t/\tau)\int_0^{t'} \frac{\delta(\bar{t})}{\tau}\exp(\bar{t}/\tau)d\bar{t}$$

(f) another property of the Dirac delta function is:

$$\int_{-\infty}^{\infty} \delta(t - t_0) f(t)dt = f(t_0)$$

(g) $$C(t) = \left(\frac{n}{v}\right)\frac{\exp(-t/\tau)}{\tau}\exp(0/\tau)$$

(h) $$C(t) = \left(\frac{n}{v}\right)\frac{\exp(-t/\tau)}{\tau}$$

(i) $$E(t) = \frac{C(t)}{\left(\frac{n}{v}\right)\int_0^{\infty}\frac{\exp(-\bar{t}/\tau)}{\tau}d\bar{t}}$$

(j) $$E(t) = \frac{\frac{\exp(-t/\tau)}{\tau}}{-\exp(-t/\tau)|_0^{\infty}}$$

(k) $$E(t) = \frac{\exp(-t/\tau)}{\tau}$$

Thus, for a perfectly mixed reactor (or often called completely backmixed), the RTD is an exponential curve.

VIGNETTE 8.2.1

The concept of using a "tracer" species to measure the mixing characteristics is not limited to chemical reactors. In the area of pharmacokinetics, the time course of renal excretion of species originating from intravenous injections in many ways resembles the input of a pulse of tracer into a chemical reactor. Normally, a radioactive labeled (^{2}H, ^{14}C, ^{32}P, etc.) version of a drug is used to follow the pharmacokinetics of the drug in animals and humans. Analyses like those presented in this chapter and in other portions of the text are used to ascertain clearance times and other parameters of importance. Good coverage of these topics can be found in M. Rowland and T. N. Tozer, *Clinical Pharmacokinetics, Concepts and Application,* 3rd ed., Lippincott, Williams and Wilkins, Philadelphia, 1995.

Two types of tracer experiments are commonly employed and they are the input of a pulse or a step function. Figure 8.2.1 illustrates the exit concentration curves and thus the shape of the $E(t)$-curves (same shape as exit concentration curve) for an impulse input. Figure 8.2.2 shows the exit concentration for a step input of tracer. The $E(t)$-curve for this case is related to the time derivative of the exit concentration.

By knowing the $E(t)$-curve, the mean residence time can be obtained and is:

$$\langle t \rangle = \frac{\int_0^\infty \bar{t}E(\bar{t})d\bar{t}}{\int_0^\infty E(\bar{t})d\bar{t}} = \int_0^\infty \bar{t}E(\bar{t})d\bar{t} \tag{8.2.5}$$

EXAMPLE 8.2.2

Calculate the mean residence time for a CSTR.

■ Answer

The exit concentration profile from a step decrease in the inlet concentration is provided in Equation (3.3.11) and using this function to calculate the $E(t)$-curve gives:

$$E(t) = \frac{\exp(-t/\tau)}{\tau}$$

Therefore application of Equation (8.2.5) to this $E(t)$-curve yields the following expression:

$$\langle t \rangle = \frac{1}{\tau}\int_0^\infty \bar{t}\exp(-\bar{t}/\tau)d\bar{t}$$

Since:

$$\int_0^\infty x\exp(-x)dx = 1$$

$$\langle t \rangle = \frac{1}{\tau}\int_0^\infty \tau^2(\bar{t}/\tau)\exp(-\bar{t}/\tau)d(\bar{t}/\tau) = \tau$$

As was shown in Chapter 3, the mean exit time of any reactor is the space time, τ.

The RTD curve can be used as a diagnostic tool for ascertaining features of flow patterns in reactors. These include the possibilities of bypassing and/or regions of stagnant fluid (i.e., dead space). Since these maldistributions can cause unpredictable conversions in reactors, they are usually detrimental to reactor operation. Thus, experiments to determine RTD curves can often point to problems and suggest solutions, for example, adding or deleting baffles and repacking of catalyst particles.

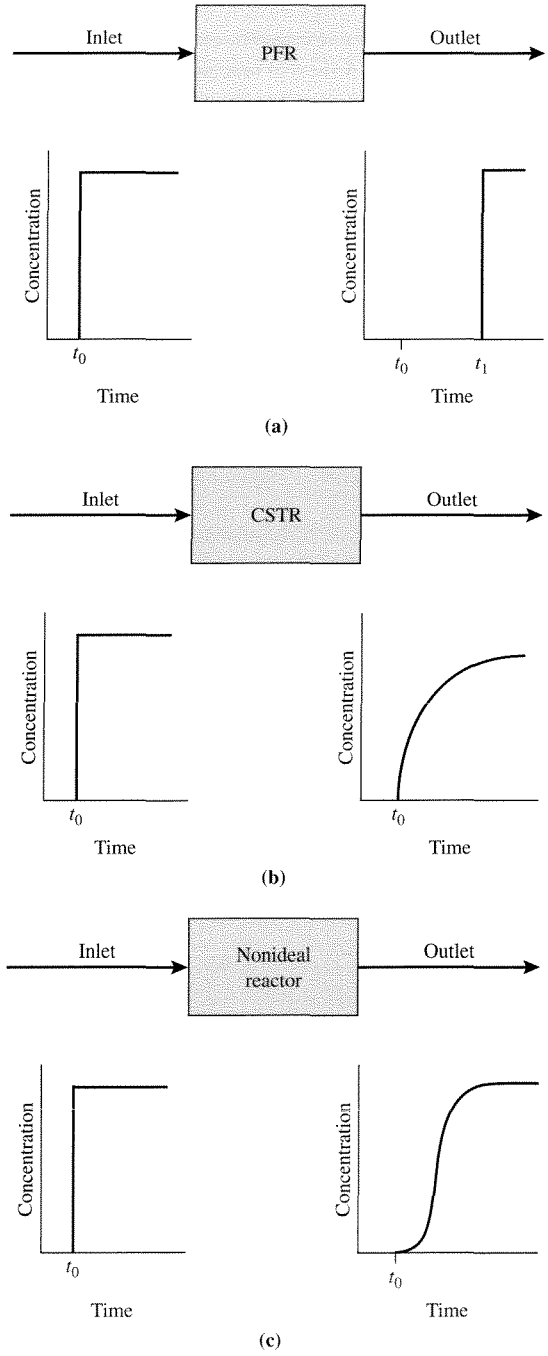


Figure 8.2.2 |
Concentrations of tracer species using a step input. **(a)** PFR ($t_1 = t_0 + \tau$). **(b)** CSTR. **(c)** Nonideal reactor.

EXAMPLE 8.2.3

In Section 3.5 recycle reactors and particularly a Berty reactor were described. At high impeller rotation speed, a Berty reactor should behave as a CSTR. Below are plotted the dimensionless exit concentrations, that is, $C(t)/C^0$, of cis-2-butene from a Berty reactor containing alumina catalyst pellets that is operated at 4 atm pressure and 2000 rpm impeller rotation speed at temperatures of 298 K and 427 K. At these temperatures, the cis-2-butene is not isomerized over the catalyst pellets. At $t = 0$, the feed stream containing 2 vol % cis-2-butene in helium is switched to a stream of pure helium at the same total flow rate. Reaction rates for the isomerization of cis-2-butene into 1-butene and trans-2-butene are to be measured at higher temperatures in this reactor configuration. Can the CSTR material balance be used to ascertain the rate data?

■ Answer

The exit concentrations from an ideal CSTR that has experienced a step decrease in feed concentration are [from Equation (3.3.11)]:

$$C/C^0 = \exp[-t/\tau]$$

If the RTD is that of an ideal CSTR (i.e., perfect mixing), then the decline in the exit concentration should be in the form of an exponential decay. Therefore, a plot of $\ln(C/C^0)$ versus time should be linear with a slope of $-\tau^{-1}$. Using the data from the declining portions of the concentration profiles shown in Figure 8.2.3, excellent linear fits to the data are obtained (see Figure 8.2.4) at both temperatures indicating that the Berty reactor is behaving as a CSTR at 298 K $\leq T \leq$ 427 K. Since the complete backmixing is achieved over such a large temperature range, it is most likely that the mixing behavior will also occur at slightly higher temperatures where the isomerization reaction will occur over the alumina catalyst.

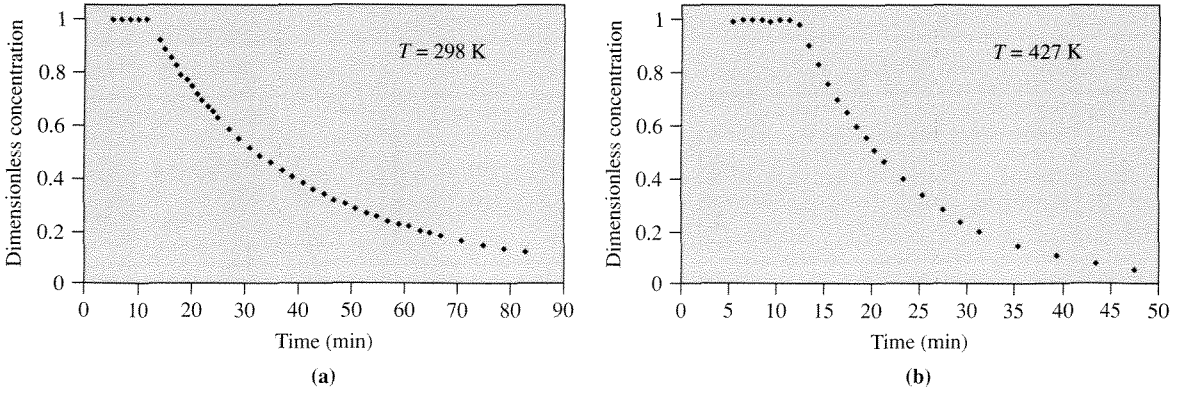


Figure 8.2.3 | Dimensionless concentration (C/C^0) of cis-2-butene in exit stream of Berty reactor as a function of time. See Example 8.2.3 for additional details.

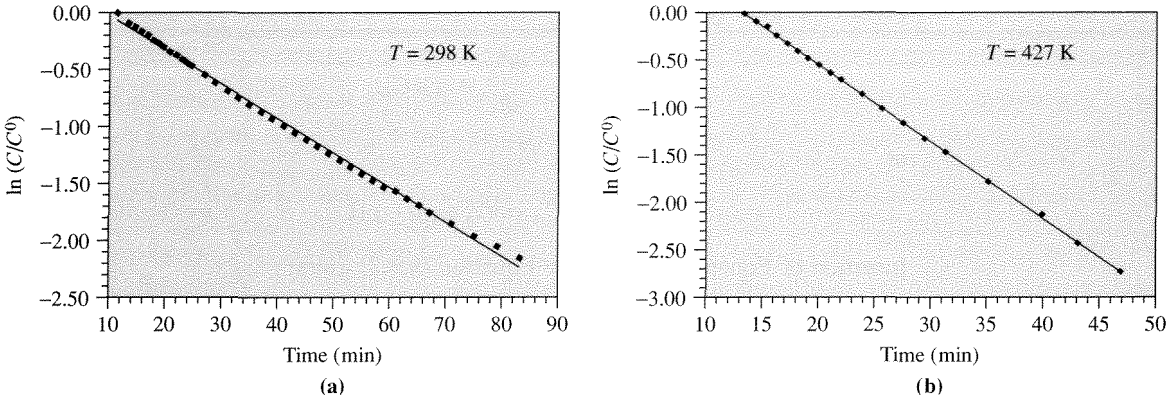


Figure 8.2.4 | Logarithm of the dimensionless concentration of cis-2-butene in exit stream of Berty reactor as a function of time. See Example 8.2.3 for additional details.

8.3 | Application of RTD Functions to the Prediction of Reactor Conversion

The application of the RTD to the prediction of reactor behavior is based on the assumption that each fluid element (assume constant density) behaves as a batch reactor, and that the total reactor conversion is then the average conversion of all the fluid elements. That is to say:

$$\begin{bmatrix}\text{mean concentration}\\ \text{of reactant in}\\ \text{reactor outlet}\end{bmatrix} = \sum \begin{bmatrix}\text{concentration of}\\ \text{reactant remaining in}\\ \text{a fluid element of age}\\ \text{between } t \text{ and } t+dt\end{bmatrix}\begin{bmatrix}\text{fraction of exit stream}\\ \text{that consists of fluid}\\ \text{elements of age}\\ \text{between } t \text{ and } t+dt\end{bmatrix} \tag{8.3.1}$$

where the summation is over all fluid elements in the reactor exit stream. This equation can be written analytically as:

$$\langle C_A \rangle = \int_0^\infty C_A(\bar{t})E(\bar{t})\,d\bar{t} \tag{8.3.2}$$

where $C_A(t)$ depends on the residence time of the element and is obtained from:

$$\frac{dC_A}{dt} = -\upsilon_A \mathrm{r}(C_A) \tag{8.3.3}$$

with

$$C_A(0) = C_A^0$$

For a first-order reaction:

$$\frac{dC_A}{dt} = -kC_A \tag{8.3.4}$$

or

$$C_A = C_A^0 \exp[-kt] \tag{8.3.5}$$

Insertion of Equation (8.3.5) into Equation (8.3.2) gives:

$$\langle C_A \rangle = \int_0^\infty C_A^0 \exp[-k\bar{t}]E(\bar{t})d\bar{t} \tag{8.3.6}$$

Take for example the ideal CSTR. If the $E(t)$-curve for the ideal CSTR is used in Equation (8.3.6) the result is:

$$\langle C_A \rangle = \frac{C_A^0}{\tau}\int_0^\infty \exp(-k\bar{t}) \exp(-\bar{t}/\tau)d\bar{t}$$

or

$$\frac{\langle C_A \rangle}{C_A^0} = \frac{1}{\tau}\int_0^\infty \exp\left[-\left(k + \frac{1}{\tau}\right)\bar{t}\right]d\bar{t}$$

that gives after integration:

$$\frac{\langle C_A \rangle}{C_A^0} = \frac{1}{\tau}\left[-\left(\frac{1}{k + \frac{1}{\tau}}\right) \exp\left[-\left(k + \frac{1}{\tau}\right)t\right]\Bigg|_0^\infty\right] = \frac{1}{k\tau + 1} \tag{8.3.7}$$

Notice that the result shown in Equation (8.3.7) is precisely that obtained from the material balance for an ideal CSTR accomplishing a first-order reaction. That is:

$$\mathrm{v}C_A^0 = \mathrm{v}C_A + VkC_A$$

or

$$\frac{C_A}{C_A^0} = \frac{1}{k\tau + 1} \tag{8.3.8}$$

Unfortunately, if the reaction rate is not first-order, the RTD cannot be used so directly to obtain the conversion. To illustrate why this is so, consider the two reactor schemes shown in Figure 8.3.1.

Froment and Bischoff analyze this problem as follows (G. F. Froment & K. B. Bischoff, *Chemical Reactor Analysis and Design*, Wiley, 1979). Let the PFR and CSTR have space times of τ_1 and τ_2, respectively. The overall RTD for either system will be that of the CSTR but with a delay caused by the PFR. Thus, a tracer experiment cannot distinguish configuration (I) from (II) in Figure 8.3.1.

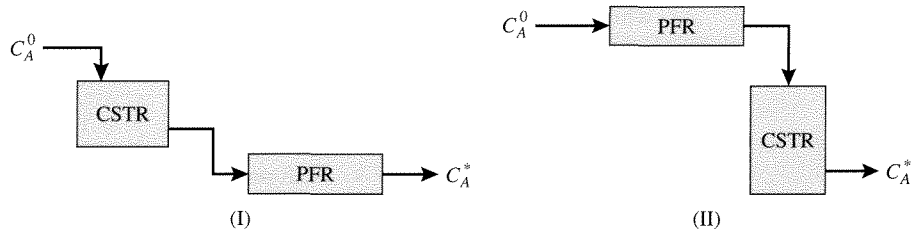


Figure 8.3.1 |
PFR and CSTR in series. (I) PFR follows the CSTR, (II) CSTR follows the PFR.

A first-order reaction occurring in either reactor configuration will give for the two-reactor network:

$$\frac{C_A^*}{C_A^0} = \frac{e^{-k\tau_1}}{1 + k\tau_2} \tag{8.3.9}$$

This is easy to see; for configuration (I):

$$C_A = \frac{C_A^0}{1 + k\tau_2} \qquad \text{(CSTR)}$$

$$\frac{C_A^*}{C_A} = \exp[-k\tau_1] \qquad \text{(PFR)}$$

or

$$\frac{C_A^*}{C_A^0} = \frac{e^{-k\tau_1}}{1 + k\tau_2}$$

and for configuration (II):

$$\frac{C_A}{C_A^0} = \exp[-k\tau_1] \qquad \text{(PFR)}$$

$$\frac{C_A^*}{C_A} = \frac{1}{1 + k\tau_2} \qquad \text{(CSTR)}$$

or

$$\frac{C_A^*}{C_A^0} = \frac{e^{-k\tau_1}}{1 + k\tau_2}$$

Now with second-order reaction rates, configuration (I) gives:

$$\frac{C_A^*}{C_A^0} = \frac{-1 + \sqrt{\left(\dfrac{1 + 4(kC_A^0\tau_2)}{1 + kC_A^0\tau_1}\right)}}{2kC_A^0\tau_2} \tag{8.3.10}$$

while configuration (II) yields:

$$\frac{C_A^*}{C_A^0} = \frac{-1+\sqrt{1+4kC_A^0\tau_2}}{2kC_A^0\tau_2 + kC_A^0\tau_1\left(-1+\sqrt{1+4kC_A^0\tau_2}\right)} \tag{8.3.11}$$

If $kC_A^0 = 1$ and $\tau_2/\tau_1 = 4$, configurations (I) and (II) give outlet dimensionless concentrations (C_A^*/C_A^0) of 0.25 and 0.28, respectively. Thus, while first-order kinetics (linear) yield the same outlet concentrations from reactor configurations (I) and (II), the second-order kinetics (nonlinear) do not. The reasons for these differences are as follows. First-order processes depend on the length of time the molecules reside in the reactors but not on exactly where they are located during their trajectory through the reactors. Nonlinear processes depend on the encounter of more than one set of molecules (fluid elements), so they depend both on residence time and also what they experience at each time. The RTD measures *only* the time that fluid elements reside in the reactor but provides *no information* on the details of the mixing. The terms *macromixing* and *micromixing* are used for the RTD and mixing details, respectively. For a given state of perfect macromixing, two extremes in micromixing can occur: complete segregation and perfect micromixing. These types of mixing schemes can be used to further refine the reactor analysis. These methods will not be described here because they lack the generality of the procedure discussed in the next section.

In addition to the problems of using the RTD to predict reactor conversions, the analysis provided above is only strictly applicable to isothermal, single-phase systems. Extensions to more complicated behaviors are not straightforward. Therefore, other techniques are required for more general predictive and design purposes, and some of these are discussed in the following section.

8.4 | Dispersion Models for Nonideal Reactors

There are numerous models that have been formulated to describe nonideal flow in vessels. Here, the axial dispersion or axially-dispersed plug flow model is described, since it is widely used. Consider the situation illustrated in Figure 8.4.1. (The steady-state PFR is described in Chapter 3 and the RTD for a PFR discussed in Section 8.2.)

The transient material balance for flow in a PFR where no reaction is occurring can be written as:

$$\underset{\text{(accumulation)}}{A_C \partial z \frac{\partial C_i}{\partial t}} = \underset{\text{(in)}}{uA_C C_i} - \underset{\text{(out)}}{\left[uA_C C_i + \partial(uA_C C_i)\right]} \tag{8.4.1}$$

or

$$\frac{\partial C_i}{\partial t} = -\frac{\partial}{\partial z}(uC_i) \tag{8.4.2}$$

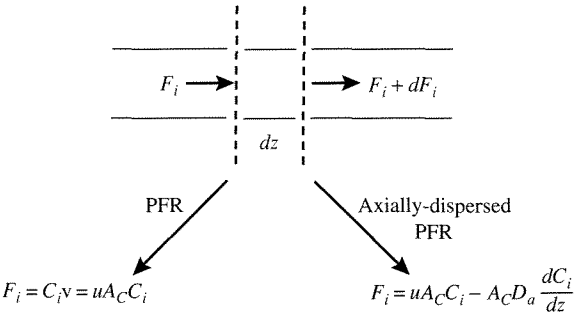


Figure 8.4.1 |
Descriptions for the molar flow rate of species i in a PFR and an axially-dispersed PFR. A_C: cross-sectional diameter of tube, u: linear velocity, D_a: axial dispersion coefficient.

where A_C is the cross-sectional area of the tube. If u = constant, then:

$$\frac{\partial C_i}{\partial t} = -u\frac{\partial C_i}{\partial z} \tag{8.4.3}$$

Now if diffusion/dispersion processes that mix fluid elements are superimposed on the convective flow in the axial direction (z direction), then the total flow rate can be written as:

$$F_i = uA_C C_i - A_C D_a \frac{dC_i}{dz} \tag{8.4.4}$$

(convection) (dispersion)

Note that D_a is called the *axial-dispersion coefficient*, and that the dispersion term of the molar flow rate is formulated by analogy to molecular diffusion. Fick's First Law states that the flux of species A (moles/area/time) can be formulated as:

$$N_A = -D_{AB}\frac{dC_A}{dz} + uC_A \tag{8.4.5}$$

for a binary mixture, where D_{AB} is the molecular diffusion coefficient. Since axial dispersion processes will occur by molecular diffusion during laminar flow, at this condition the dispersion coefficient will be the molecular diffusion coefficient. However, with turbulent flow, the processes are different and D_a must be obtained from correlations. Since D_a is the molecular diffusion coefficient during laminar flow, it is appropriate to write the form of the dispersion relationship as in Equation (8.4.4) and then obtain D_a from correlations assuming this form of the molar flow rate expression. Using Equation (8.4.4) to develop the transient material balance relationship for the axially-dispersed PFR gives:

$$\underset{\text{(accumulation)}}{A_C \partial z \frac{\partial C_i}{\partial t}} = \underset{\text{(in)}}{\left(uA_C C_i - A_C D_a \frac{\partial C_i}{\partial z}\right)} - \left[\underset{\text{(out)}}{\left(uA_C C_i - A_C D_a \frac{\partial C_i}{\partial z}\right)} + \underset{\text{(out)}}{\partial\left(uA_C C_i - A_C D_a \frac{\partial C_i}{\partial z}\right)}\right] \tag{8.4.6}$$

or for constant u and D_a:

$$\frac{\partial C_i}{\partial t} + u\frac{\partial C_i}{\partial z} = D_a \frac{\partial^2 C_i}{\partial z^2} \tag{8.4.7}$$

If $\theta = t/\langle t\rangle = (tu)/L$ (L: length of the reactor), $Z = z/L$ and $Pe_a = (Lu)/D_a$ (axial Peclet number), then Equation (8.4.7) can be written as:

$$\frac{\partial C_i}{\partial \theta} + \frac{\partial C_i}{\partial Z} = \frac{1}{Pe_a}\frac{\partial^2 C_i}{\partial Z^2} \tag{8.4.8}$$

The solution of Equation (8.4.8) when the input (i.e., C_i at $t = 0$) is an impulse is:

$$C_i = \left(\frac{Pe_a}{4\pi\theta}\right)^{\frac{1}{2}} \exp\left[\frac{-(1-\theta)^2 Pe_a}{4\theta}\right] \tag{8.4.9}$$

Thus, for the axially-dispersed PFR the RTD is:

$$E(\theta) = \left(\frac{Pe_a}{4\pi\theta}\right)^{\frac{1}{2}} \exp\left[\frac{-(1-\theta)^2 Pe_a}{4\theta}\right] \tag{8.4.10}$$

A plot of $E(\theta)$ versus θ is shown in Figure 8.4.2 for various amounts of dispersion. Notice that as $Pe_a \to \infty$ (no dispersion), the behavior is that of a PFR while as $Pe_a \to 0$ (maximum dispersion), it is that of a CSTR. Thus, the axially-dispersed reactor can simulate all types of behaviors between the ideal limits of no backmixing (PFR) and complete backmixing (CSTR).

The dimensionless group Pe_a is a ratio of convective to dispersive flow:

$$Pe_a = \frac{Lu}{D_a} = \frac{\text{convective flow}}{\text{dispersive flow}} \text{ in the axial direction} \tag{8.4.11}$$

The Peclet number is normally obtained via correlations, and Figure 8.4.3 illustrates data from Wilhelm that are plotted as a function of the Reynolds number for packed beds (i.e., tubes packed with catalyst particles). Notice that both the Pe_a and Re numbers use the particle diameter, d_p, as the characteristic length:

$$Pe_a = \frac{d_p u}{D_a}, \qquad Re = \frac{d_p u \rho}{\bar{\mu}}$$

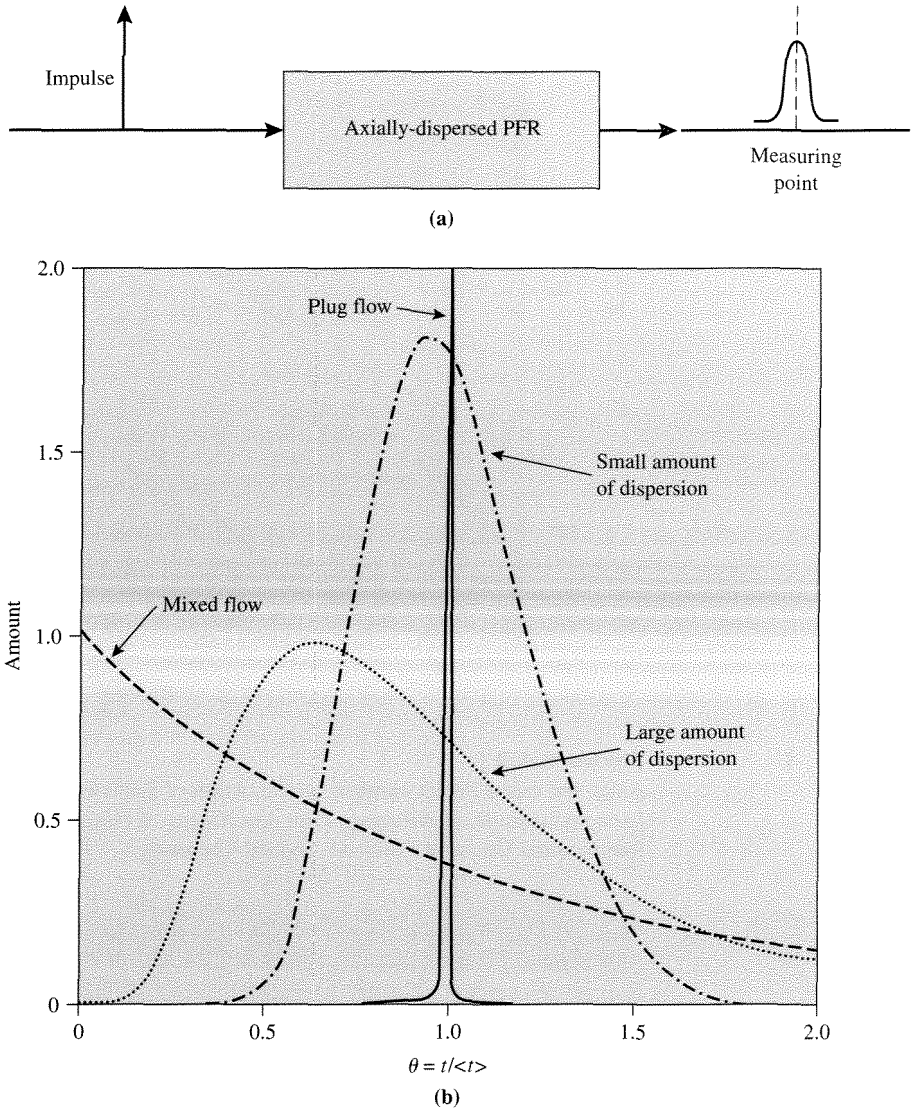


Figure 8.4.2 |
(**a**) Configuration illustrating pulse input to an axially-dispersed PFR. (**b**) Results observed at measuring point.

It is always prudent to check the variables used in each dimensionless group prior to their application. This is especially true with Peclet numbers, since they can have many different characteristic lengths.

Notice that in packed beds, $Pe_a = 2$ for gases with turbulent flow $Re = (d_p u\rho)/\overline{\mu} > 40$, while for liquids Pe_a is below 1. Additionally, for unpacked tubes,

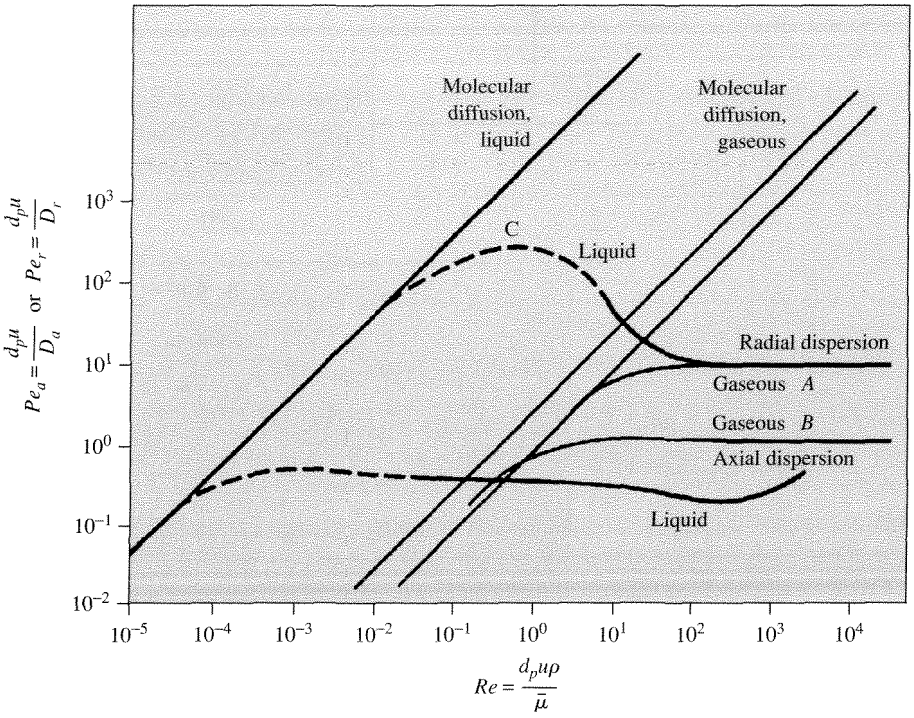


Figure 8.4.3 |
Axial and radial Peclet numbers as a function of Reynolds number for packed-beds. [Adapted from R. H. Wilhelm, *Pure App. Chem.*, **5** (1962) 403, with permission of the International Union of Pure and Applied Chemistry.]

$Pe_a(d_t u/D_a)$ is about 10 with turbulent flow ($Re = (d_t u\rho)/\bar{\mu}$ greater than 2100) (not shown). Thus, all real reactors will have some effects of dispersion. The question is, how much? Consider again Equation (8.4.7) but now define $Pe_a = d_e u/D_a$ where d_e is an effective diameter and could be either d_p for a packed bed or d_t for an open tube. Equation (8.4.7) can be then written as:

$$\frac{\partial C_i}{\partial \theta} + \frac{\partial C_i}{\partial Z} = \frac{1}{Pe_a}\left(\frac{d_e}{L}\right)\frac{\partial^2 C_i}{\partial Z^2} \tag{8.4.12}$$

If the flow rate is sufficiently high to create turbulent flow, then Pe_a is a constant and the magnitude of the right-hand side of the equation is determined by the aspect ratio, L/d_e. By solving Equation, (8.4.12) and comparing the results to the solutions of the PFR [Equation (8.4.3)], it can be shown that for open tubes, $L/d_t > 20$ is sufficient to produce PFR behavior. Likewise, for packed beds, $L/d_p > 50$ (isothermal) and $L/d_p > 150$ (nonisothermal) are typically sufficient to provide PFR characteristics. Thus, the effects of axial dispersion are minimized by turbulent flow in long reactors.

VIGNETTE 8.4.1

B. G. Anderson et al. [*Ind. Eng. Chem. Res.*, **37** (1998) 815] obtained *in situ* images of pulses of ^{11}C-labeled alkanes that were passing through packed beds of zeolites by using positron emission tomography (PET). PET is a technique developed primarily for nuclear medicine that is able to create three-dimensional images of gamma-ray emitting species within various organs of the human body. By using PET, Anderson et al. could obtain complete concentration profiles of ^{11}C-labeled alkanes as a function of time in a packed-bed reactor upon introduction of a pulse of the tracer alkane. Using analyses similar to those illustrated in this chapter, the following data were obtained:

Zeolite	T (°C)	Axial dispersion coeff. (m^2/s)
H-Mordenite	230	1.1×10^{-4}
H-Beta	230	2.1×10^{-4}
H-ZSM-22	170	1.2×10^{-4}
H-Ferrierite	170	1.0×10^{-4}

The measured axial dispersion coefficients are around 1×10^{-4} m^2/s. The reactor was 4 mm in diameter and the volumetric flow rate was 150 mL/min. Assuming a void volume of 0.5 and $Pe = 2$, D_a is calculated to be approximately 1×10^{-4} m^2/s. Thus, the value calculated with the information presented in Figure 8.4.3 is in good agreement with the experimental findings.

8.5 | Prediction of Conversion with an Axially-Dispersed PFR

Consider (so that an analytical solution can be obtained) an isothermal, axially-dispersed PFR accomplishing a first-order reaction. The material balance for this reactor can be written as:

$$D_a \frac{d^2C_A}{dz^2} - u\frac{dC_A}{dz} - kC_A = 0 \tag{8.5.1}$$

If $y = C_A/C_A^0$, $Z = z/L$, and $Pe_a = uL/D_a$, then Equation (8.5.1) can be put into dimensionless form as:

$$\frac{1}{Pe_a}\frac{d^2y}{dZ^2} - \frac{dy}{dZ} - \left(\frac{kL}{u}\right)y = 0 \tag{8.5.2}$$

The proper boundary conditions used to solve Equation (8.5.2) have been exhaustively discussed in the literature. Consider the reactor schematically illustrated in Figure 8.5.1. The conditions for the so-called "open" configuration are:

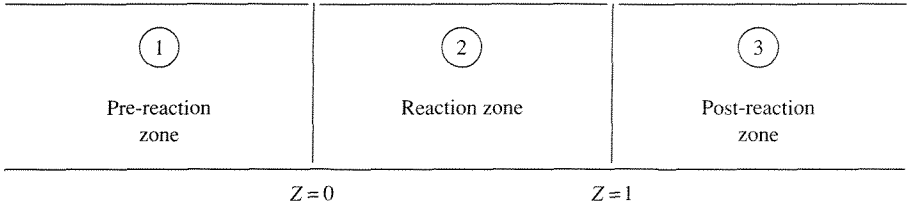


Figure 8.5.1 |
Schematic of hypothetical reactor.

$$\left.\begin{array}{ll} Z = -\infty, & y = 1 \\ Z = +\infty, & y = \text{is finite} \\ Z = 0, & y(0_-) = y(0_+) = y(0) \\ Z = 1, & y(1_-) = y(1_+) \end{array}\right\} \tag{8.5.3}$$

Note that the use of these conditions specifies that the flux continuity:

$$\left[uC_A - D_{a_1}\frac{dC_A}{dz}\right]\Bigg|_{0_-} = \left[uC_A - D_{a_2}\frac{dC_A}{dz}\right]\Bigg|_{0_+}$$

gives:

$$D_{a_1}\frac{dC_A}{dz} = D_{a_2}\frac{dC_A}{dz}$$

That is to say that if the dispersion coefficients in zones 1 and 2 are not the same, then there will be a discontinuity in the concentration gradient at $z = 0$. Alternatively, Danckwerts formulated conditions for the so-called "closed" configuration that do not allow for dispersion in zones 1 and 3 and they are:

$$\begin{aligned} uC_A\big|_{0_-} &= \left[uC_A - D_a\frac{dC_A}{dz}\right]\Bigg|_{0_+} \\ \frac{dC_A}{dz}\Bigg|_{L_-} &= 0 \end{aligned} \tag{8.5.4}$$

The Danckwerts boundary conditions are used most often and force discontinuities in both concentration and its gradient at $z = 0$.

EXAMPLE 8.5.1 |

Consider an axially-dispersed PFR accomplishing a first-order reaction. Compute the dimensionless concentration profiles for $L/d_p = 5$ and 50 and show that at isothermal conditions the values for $L/d_p = 50$ are nearly those from a PFR. Assume $Pe = d_p u/D_a = 2$, $d_p = 0.004$ m and $k/u = 25\ \text{m}^{-1}$.

■ Answer

The material balance for the axially-dispersed PFR is:

$$\frac{d^2y}{dZ^2} - Pe_a\,(L/d_p)\frac{dy}{dZ} - \left(\frac{L^2kPe_a}{ud_p}\right)y = 0$$

or

$$\frac{d^2y}{dZ^2} - (500L)\frac{dy}{dZ} - (12500L^2)y = 0$$

The solution to this equation using the Danckwerts boundary conditions of:

$$1 = y - \frac{1}{Pe_a}\left(\frac{d_p}{L}\right)\frac{dy}{dZ} \quad \text{at } Z = 0$$

$$\frac{dy}{dZ} = 0 \quad \text{at } Z = 1$$

gives the desired form of y as a function of Z and the result is:

$$y = \bar{\alpha}_1 \exp(524LZ) + \bar{\alpha}_2 \exp(-23.9LZ)$$

where $\bar{\alpha}_1$ and $\bar{\alpha}_2$ vary with L/d_p. The material balance equation for the PFR is:

$$-u\frac{dC_A}{dz} = kC_A$$

or

$$\frac{dy}{dZ} = -\left(\frac{Lk}{u}\right)y$$

with

$$y = 1 \quad \text{at } Z = 0$$

The solution to the PFR material balance gives:

$$y_{PF} = \exp[-(kLZ)/u] = \exp[-25LZ]$$

Note that the second-term of y is nearly (but not exactly) that of the expression for y_{PF} and that the first-term of y is a strong function of L. Therefore, it is clear that L will significantly affect the solution y to a much greater extent than y_{PF} and that $y \neq y_{PF}$ even for very long L. However, as shown in Figure 8.5.2, at $L/dp = 50$, $y \approx y_{PF}$ for all practical matters. Notice that $y \neq 1$ at $Z = 0$ because of the dispersion process. There is a forward movement of species A because of the concentration gradient within the reaction zone. The dispersion always produces a lower conversion at the reactor outlet than that obtained with no mixing (PFR)—recall conversion comparisons between PFR and CSTR.

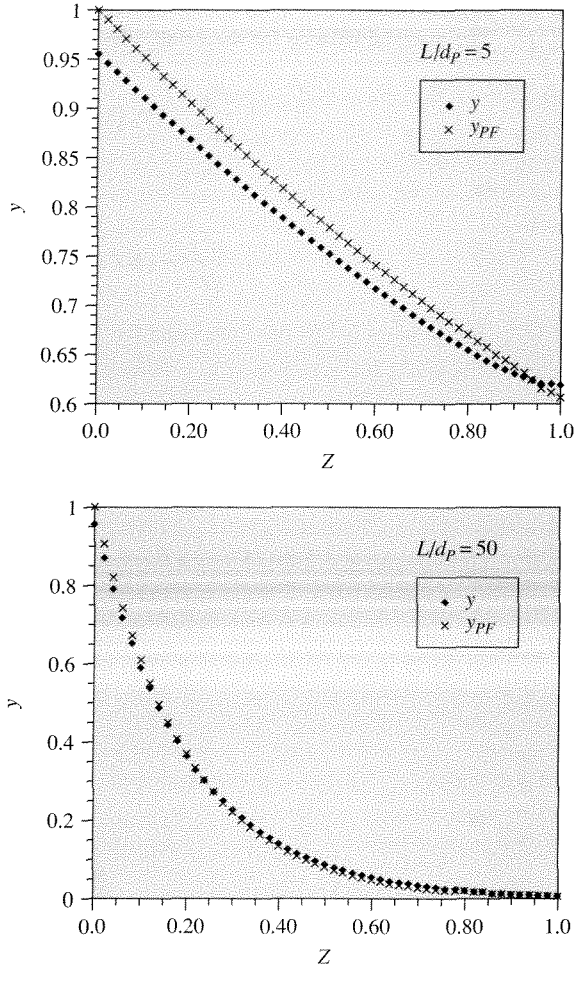


Figure 8.5.2 | Dimensionless concentration profiles for axially-dispersed (y) and plug flow (y_{PF}) reactors.

VIGNETTE 8.5.1

Y. Park et al. [*Biotech. Bioeng.*, **26** (1984) 457] analyzed a fixed-film bioreactor for the continuous production of penicillin. The bioreactor (Figure 8.5.3, left) was modeled in the two extremes of contacting patterns (Figure 8.5.3, right). Notice from the results shown in Figure 8.5.4 that the productivity of penicillin at any substrate feed concentration, So, is higher for the CSTR configuration. Thus, it would be important to know the exact mixing pattern within the bioreactor and to modify it to resemble more closely a CSTR reactor.

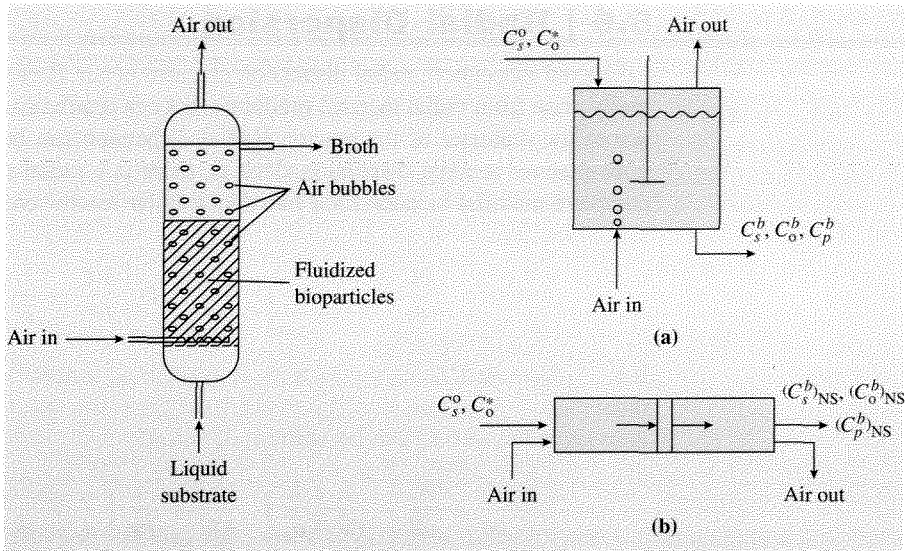


Figure 8.5.3 | Schematic of bioreactor and two extremes used for modeling the contacting pattern. **(a)** Complete backmix. **(b)** Plug flow. [Reproduced from "Analysis of a Continuous, Aerobic Fixed-Film Bioreactor. I. Steady-State Behavior," by Y. Park, M. E. Davis, and D. A. Wallis, *Biotech. Bioeng.*, **26** (1984) 457, copyright © 1984 Wiley-Liss, Inc., a subsidiary of John Wiley and Sons, Inc.]

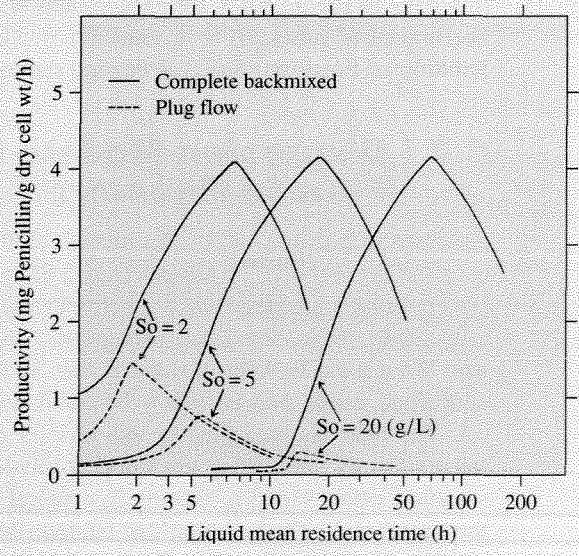


Figure 8.5.4 | Comparison of performance of completely backmixed and plug flow contacting patterns. [Reproduced from "Analysis of a Continuous, Aerobic Fixed-Film Bioreactor. I. Steady-State Behavior," by P. Park, M. E. Davis, and D. A. Wallis, *Biotech. Bioeng.*, **26** (1984) 457, copyright © 1984, Wiley-Liss, Inc., a subsidiary of John Wiley and Sons, Inc.]

8.6 | Radial Dispersion

Like axial dispersion, radial dispersion can also occur. Radial-dispersion effects normally arise from radial thermal gradients that can dramatically alter the reaction rate across the diameter of the reactor. Radial dispersion can be described in an analogous manner to axial dispersion. That is, there is a radial dispersion coefficient. A complete material balance for a transient tubular reactor could look like:

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} = D_a\frac{\partial^2 C}{\partial z^2} + D_r\left[\frac{\partial^2 C}{\partial \bar{r}^2} + \frac{1}{\bar{r}}\frac{\partial C}{\partial \bar{r}}\right] \tag{8.6.1}$$

If $\theta = t/\langle t\rangle = (tu)/L$, $Z = z/L$, $\bar{R} = \bar{r}/d_e$ (d_e is d_p for packed beds, d_t for unpacked tubes), $Pe_a = (ud_e)/D_a$ and $Pe_r = (ud_e)/D_r$ (D_r is the *radial-dispersion coefficient*), then Equation (8.6.1) can be written as:

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial Z} = \frac{1}{Pe_a}\left(\frac{L}{d_e}\right)^{-1}\frac{\partial^2 C}{\partial Z^2} + \frac{1}{Pe_r}\left(\frac{L}{d_e}\right)\left[\frac{\partial^2 C}{\partial \bar{R}^2} + \frac{1}{\bar{R}}\frac{\partial C}{\partial \bar{R}}\right] \tag{8.6.2}$$

The dimensionless group Pe_r is a ratio of convective to dispersive flow in the radial direction:

$$Pe_r = \frac{d_e u}{D_r} = \frac{\text{convective flow}}{\text{dispersive flow}} \text{ in radial direction} \tag{8.6.3}$$

Referring to Figure 8.4.3, for packed beds with turbulent flow, $Pe_r = 10$ if $d_e = d_p$. For unpacked tubes, $d_e = d_t$ and $Pe_r \approx 1000$ with turbulent flow (not shown). Solution of Equation (8.6.1) is beyond the level of this text.

8.7 | Dispersion Models for Nonideal Flow in Reactors

As illustrated above, dispersion models can be used to described reactor behavior over the entire range of mixing from PFR to CSTR. Additionally, the models are *not* confined to single-phase, isothermal conditions or first-order, reaction-rate functions. Thus, these models are very general and, as expected, have found widespread use. What must be kept in mind is that as far as reactor performance is normally concerned, radial dispersion is to be maximized while axial dispersion is minimized.

The analysis presented in this chapter can be used to describe reaction containers of any type—they need not be tubular reactors. For example, consider the situation where blood is flowing in a vessel and antibodies are binding to cells on the vessel wall. The situation can be described by the following material balance:

$$u\frac{\partial C}{\partial z} = D_a\frac{\partial^2 C}{\partial z^2} + D_r\left(\frac{\partial^2 C}{\partial \bar{r}^2} + \frac{1}{\bar{r}}\frac{\partial C}{\partial \bar{r}}\right) \tag{8.7.1}$$

with

$$uC_0 = uC - D_a \frac{\partial C}{\partial z} \qquad \text{at } z = 0, \text{ all } \bar{r}$$

$$\frac{\partial C}{\partial z} = 0 \qquad \text{at } z = L, \text{ all } \bar{r}$$

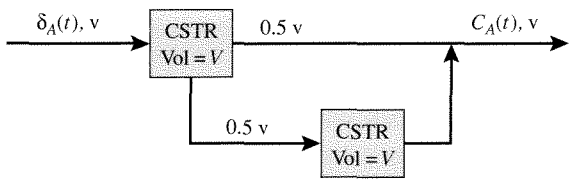
$$\frac{\partial C}{\partial \bar{r}} = 0 \qquad \text{at } \bar{r} = 0, \text{ all } z$$

$$-D_r \frac{\partial C}{\partial \bar{r}} = \overline{AB} \qquad \text{at } \bar{r} = \bar{r}_t, \text{ all } z$$

where C is the concentration of antibody, $\bar{r}_t$ is the radius of the blood vessel and $\overline{AB}$ is the rate of antibody binding to the blood vessel cells. Thus, the use of the dispersion model approach to describing flowing reaction systems is quite robust.

Exercises for Chapter 8

1. Find the residence time distribution, that is, the effluent concentration of tracer A after an impulse input at $t = 0$, for the following system of equivolume CSTRs with a volumetric flow rate of liquid into the system equal to v:



   How does the RTD compare to that of a single CSTR with volume $2V$?

2. Sketch the RTD curves for the sequence of plug flow and continuous stirred tank reactors given in Figure 8.3.1.

3. Consider three identical CSTRs connected in series according to the diagram below.

   (a) Find the RTD for the system and plot the E curve as a function of time.

   (b) How does the RTD compare to the result from an axially-dispersed PFR (Figure 8.4.2)? Discuss you answer in terms of the axial Peclet number.

   (c) Use the RTD to calculate the exit concentration of a reactant undergoing first-order reaction in the series of reactors. Confirm that the RTD method

gives the same result as a material balance on the system (see Example 3.4.3).

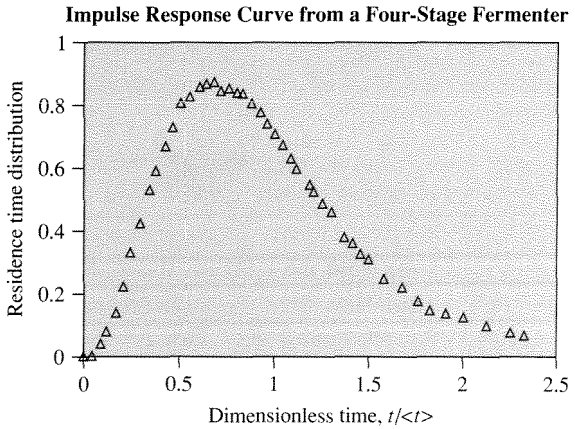
4. Calculate the mean concentration of A at the outlet ($z = L$) of a laminar flow, tubular reactor ($\overline{C}_A^L$) accomplishing a second-order reaction (kC_A^2), and compare the result to that obtained from a PFR when $[(C_A^0 kL)/u] = 1$. Referring to Example 8.1.1, is the deviation from PFR behavior a strong function of the reaction rate expression (i.e., compare results from first- and second-order rates)?
5. Referring to Example 8.2.3, compute and plot the dimensionless exit concentration from the Berty reactor as a function of time for decreasing internal recycle ratio to the limit of PFR behavior.
6. Consider the axially-dispersed PFR described in Example 8.5.1. How do the concentration profiles change from those illustrated in the Example if the second boundary condition is changed from:

$$\frac{dy}{dZ} = 0 \qquad \text{at} \quad Z = 1$$

to

$$y = 0 \qquad \text{at} \quad Z = \infty$$

7. Write down in dimensionless form the material balance equation for a laminar flow tubular reactor accomplishing a first-order reaction and having both axial and radial diffusion. State the necessary conditions for solution.
8. Falch and Gaden studied the flow characteristics of a continuous, multistage fermentor by injecting an impulse of dye to the reactor [E. A. Falch and E. L. Gaden, Jr., *Biotech. Bioengr.*, **12** (1970) 465]. Given the following RTD data from the four-stage fermentor, calculate the Pe_a that best describes the data.



$t/<t>$	RTD	$t/<t>$	RTD
0.000	0.000	0.950	0.745
0.050	0.001	0.990	0.710
0.090	0.040	1.035	0.675
0.120	0.080	1.080	0.630
0.170	0.140	1.110	0.600
0.210	0.220	1.180	0.550
0.245	0.330	1.200	0.525
0.295	0.420	1.240	0.485
0.340	0.530	1.290	0.460
0.370	0.590	1.365	0.380
0.420	0.670	1.410	0.360
0.460	0.730	1.450	0.325
0.500	0.810	1.490	0.310
0.540	0.830	1.580	0.250
0.590	0.860	1.670	0.220
0.630	0.870	1.760	0.180
0.670	0.875	1.820	0.150
0.710	0.850	1.910	0.140
0.750	0.855	2.000	0.125
0.790	0.845	2.120	0.100
0.825	0.840	2.250	0.080
0.870	0.810	2.320	0.070
0.920	0.780		

9. Using the value of the Pe_a determined in Exercise 8, compute the concentration profile in the reactor for the reaction of catechol to *L*-dopa catalyzed by whole cells according to the following rate of reaction:

$$r = -\frac{dC_S}{dt} = \frac{r_{max} C_S}{K_m + C_S}$$

where C_S is the concentration of substrate catechol. This reaction is discussed in Example 4.2.4. The values of the various parameters are the same as those determined by the nonlinear regression analysis in Example 4.2.5, that is, $C_S^0 = 0.027$ mol L^{-1}, $r_{max} = 0.0168$ mol L^{-1} h^{-1}, and $K_m = 0.00851$ mol L^{-1}. Assume that the mean residence time of the reactor is 2 h.

10. Using the same rate expression and parameter values given in Exercise 9, compute the concentration profile assuming PFR behavior and compare to the results in Exercise 9.