1

Nonideal Flow

1.1 Introduction

Basic chemical reactors (plug flow reactor or PFR, and continuously stirred tank reactor or CSTR) are studied considering their behavior is that of an ideal reactor. Unfortunately, in practice, we often find behaviors that are far from that considered ideal. Consequently, working with them, the chemical engineer must be able to handle and diagnose the behavior of these reactors. At the time of describing the nonideal behavior of a reactor, three concepts are introduced: the residence time distributions (RTDs), the quality of the mixture (not discussed in this book), and the models that can be used to describe the reactor. These three concepts are used to describe the deviations of the mixing assumed in the ideal models and are considered as attributes of the mixture in nonideal reactors.

One way of approaching the study of nonideal reactors is to consider them, in a first approximation, as if the flow model were the one corresponding to a CSTR or a PFR. However, in real reactors, the nonideal flow model implies a minor conversion, so a method that allows for this conversion loss to be considered must be available. Therefore, a higher level of approximation implies the use of information about the RTD.

1.2 Residence Time Distribution (RTD) Function

The idea of introducing the RTD in the analysis of the behavior of reactors occurred thanks to MacMullin and Weber (in 1935), although it was Danckwerts (later, in 1953) who structured this analysis and defined most of the distributions of interest.

In an ideal PFR, all the particles (or units) of material that leave the reactor have remained in it the same time. Analogously, in an ideal (well-mixed) batch reactor, all particles are in the reactor the same period of time. The time that these units have remained in the reactor is what we call the residence time of those particles in that reactor.

The ideal reactor's PFR and batch are the only ones in which all the portions of reactants present in the reactor have the same residence time. In all other reactors, the particles entering the reactor vessel remain inside the reactor for different periods of time; that is, there exists a RTD inside the reactor.

Chemical Reactor Design: Mathematical Modeling and Applications,
First Edition. Juan A. Conesa.

For example, consider an ideal CSTR; the input flow that is introduced to the reactor at a given moment mixes instantaneously and completely with the rest of the material that already exists inside the reactor. In this way, some of the particles that enter the reactor abandon this one almost immediately with the exit current, whereas other atoms remain of almost indefinite form, since all the material is never dragged. Of course, many of the particles leave the reactor after a period close to the average residence time.

The RTD of a reactor is a feature of the mixture that is taking place inside the reactor. Thus, in an ideal PFR there is no axial mixing, and this absence is reflected in the RTD that this type of reactors exhibit. In contrast, in an ideal CSTR there is a great degree of mixing, so the RTD that these reactors exhibit is very different from that of the plug flow. However, not all RTDs are unique to one type of reactor; reactors with marked differences can give identical RTDs. Despite this, the RTD of a certain reactor presents distinctive keys with respect to the type of mixture that is taking place inside it and is one of the ways to characterize the reactor that provides more information.

1.2.1 Measurement of the RTD

The experimental measurement of the RTD is done by injecting a tracer into the reactor at a definite time ($t = 0$). This tracer is a chemical, molecule, or an inert atom. The tracer concentration is then measured at the outlet at different times. The tracer must be inert, easily detectable, with physical properties similar to those of the substances present in the reaction mixture and easily soluble in it. In addition, it should not be adsorbed on walls or other surfaces on the reactor. The objective is to reflect, as best as possible, the behavior of the substances that are flowing through the reactor. The most commonly used tracers are dyes and radioactive material, while the most commonly used injection methods are pulse input ("Dirac delta function") and step input (suddenly increase of the tracer concentration).

1.2.1.1 Pulse Input

This kind of experiment consists of introducing into the current entering the reactor, quickly and at once, an amount N_0 of tracer. The output concentration is subsequently measured as a function of time. Concentration-time curve characteristics for the input and exit of an arbitrary reactor can be observed in Figure 1.1. The concentration-time curve corresponding to the effluent is called curve C in RTD analysis.

Let us consider a system with a single input and a single output, in which a tracer is injected in pulse and in which it is transported, exclusively because of the flow (not because of dispersion), through the system. If a time increment Δt small enough is chosen so that the concentration of tracer, $C(t)$, which leaves the system between the instants "t" and "$t + \Delta t$" is constant, we can express the amount of tracer (in moles or grams), ΔM, that leaves the reactor between "t" and "$t + \Delta t$" as

$$\Delta M = C(t) \cdot Q \cdot \Delta t \tag{1.1}$$

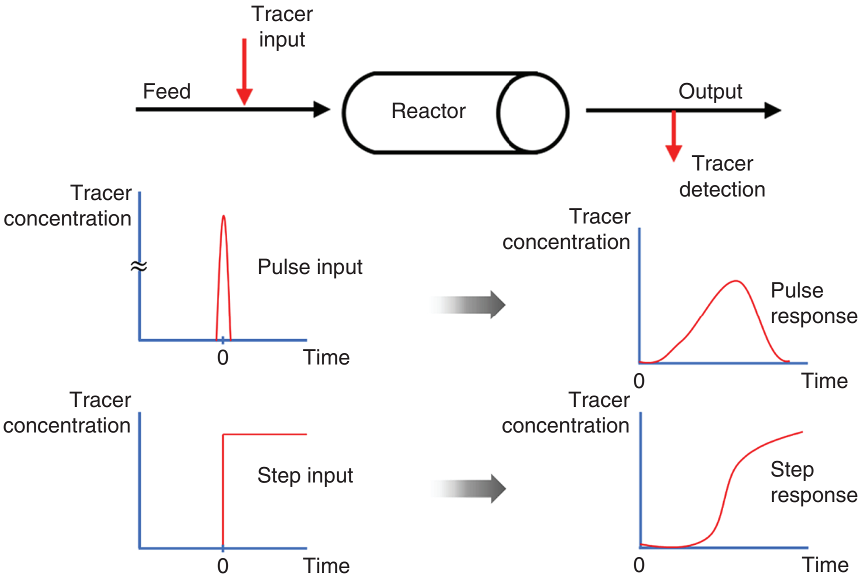


Figure 1.1 Measurement of the RTD.

That is, ΔM is the amount of tracer (in moles or grams, for example) that has remained in the reactor for a time interval comprising between "t" and "$t + \Delta t$." Dividing by the total amount of tracer injected into the reactor (M_0), we obtain the tracer fraction whose residence time in the reactor is between "t" and "$t + \Delta t$":

$$\frac{\Delta M}{M_0} = \frac{C(t) \cdot Q}{M_0} \cdot \Delta t \tag{1.2}$$

For a pulse injection, we define the RTD function, $E(t)$, as

$$E(t) = \frac{Q \cdot C(t)}{M_0} \tag{1.3}$$

This expression describes in a quantitative way how long the different elements of fluid have passed inside the reactor. In consequence:

$$\frac{\Delta M}{M_0} = E(t) \cdot \Delta t \tag{1.4}$$

If M_0 is not directly known, it may be obtained from the output concentrations, adding the different amounts of the tracer that have exited the reactor between 0 and infinity. Expressing in differential form:

$$dM = Q \cdot C(t) \cdot dt$$

and integrating, we obtain

$$M_0 = \int_0^{\infty} Q \cdot C(t) \cdot dt \tag{1.5}$$

Since the volumetric flow (Q) is generally constant, we will define $E(t)$ as

$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t) \cdot dt} \tag{1.6}$$

In that expression, the integral in the denominator is the area under the curve, $C(t)$. In this way, from the tracer concentration, C(t), it is possible to find the curve $E(t)$, as long as that curve is obtained from a perfect pulse of the input tracer.

Another way to interpret the function of residence times is in its integral form:

$$\begin{bmatrix}\text{Amount of tracer exiting the reactor after} \\ \text{passing inside it a time between } t_1 \text{ and } t_2\end{bmatrix} = \int_{t_1}^{t_2} E(t)\cdot dt \tag{1.7}$$

Now, the fraction of tracer that passed inside the reactor a time t, between 0 and infinity is equal to 1; therefore:

$$\int_0^{\infty} E(t)\cdot dt = 1 \tag{1.8}$$

The main drawback of the use of the pulse technique lies in the difficulty in achieving a tracer input to the reactor that is reasonably pulsed (as we explain in Chapter 2, deconvolution of curves). The injection should take place in a very short period compared to the residence times and the tracer dispersion between the injection point and the reactor inlet should be negligible. If these conditions are satisfied, the technique is a simple and direct way to obtain the RTD.

1.2.1.2 Step Input

During a step input experiment, a tracer is added at a steady rate to the reactor feed to give a steady input concentration of C_0 (see Figure 1.1). The concentration of the tracer in the effluent is then monitored from the time of adding the tracer until it reaches a concentration approximating that of C_0.

As stated before, the RTD curve can be easily obtained by injecting a tracer in a pulse input, but now we will formulate a more general relationship between a tracer injection (not necessarily a pulse input) and the corresponding tracer concentration in the effluent (current leaving the system).

Chapter 2 presents a more general equation establishing the relation of the concentration of a tracer leaving a reactor (C_{out}) and the input concentration (C_{in}). This is presented as the convolution integral:

$$C_{\text{out}}(t) = \int_0^{t} C_{\text{in}}(t-t')E(t')dt' \tag{1.9}$$

In this equation, $E(t)$ is the corresponding RTD for the reactor. The concentration at the input is evaluated at different times and the resulting signal C_{out} is a convolution of C_{in} and the RTD in the vessel.

In this way, in the following chapters we are able to calculate the $E(t)$ curve given any function of concentration input C_{in} and measuring C_{out}. For now, we continue with more simple techniques, considering that the inlet concentration is introduced in the form of a step input (Figure 1.1).

Let us consider a system of constant volumetric flow (Q) in which a tracer input is introduced in the form of a step, with a rate of addition of tracer to the constant input flow and which begins to occur at time $t = 0$. Before that moment, it is considered that no tracer enters with the inlet current. Under these conditions:

$$C_{\text{in}}(t) = 0 \quad \text{for } t < 0$$

$$C_{\text{in}}(t) = \text{constant} = C_0 \quad \text{for } t \geq 0$$

The tracer concentration in the feed should be maintained at this value until the concentration of tracer in the effluent is practically C_0, i.e. equal to that of the feed, at which time the test can be interrupted. Figure 1.1 shows a typical output concentration curve for this type of input.

Since the input concentration (C_0) remains constant over time, we can extract it from the integral using Eq. (1.9):

$$C_{\text{out}}(t) = C_0 \int_0^t E(t^{'})dt^{'} \tag{1.10}$$

Obviating that t' is mathematically equal to t, we see that the signal at the output of this experiment is a cumulative function of $E(t)$, as it evaluates the integral of all $E(t)$ from $t = 0$ to the instant "t." This cumulative distribution is called the "F curve" and can be directly determined from a step input.

$$\left[\frac{C(t)}{C_0}\right]_{\text{step input}} = \int_0^t E(\text{t})d\text{t} = F(t) \tag{1.11}$$

Differentiating this expression, we obtain the function of RTD, $E(t)$:

$$E(t) = \frac{d}{dt}\left[\frac{C(t)}{C_0}\right]_{\text{step input}}$$

The determination of the $E(t)$ using a step input is, in general, easier to carry out experimentally than the pulse input. It has some other advantages, as in that it is not necessary to know the total amount of tracer introduced during the test period. In return, it has some disadvantages: (i) sometimes, it is not easy to maintain a constant concentration of tracer in the feed; (ii) for calculating the $E(t)$ curve, this procedure implies the differentiation of the data, which can lead, sometimes, to errors; (iii) as the feed should be maintained for a long period of time, the amount of tracer required is usually very large, so if the tracer is expensive, a pulse input is usually used.

Other techniques to introduce the tracer are possible: negative step (dilution of the food), a periodic signal, or a random signal. However, they tend to be more difficult to carry out and are discussed in the following chapters.

1.2.2 RTD Concept in Heterogeneous Systems

Just as in the homogeneous reactors, the concept of RTD is valid in heterogeneous systems, with the particularity that there will exist an RTD related to the flow of each phase involved in the reaction. For example, let us think about the flow produced in a catalytic reactor where a gaseous species is introduced on one side, and, simultaneously, the solid catalyst is introduced on the other. Figure 1.2 presents such a situation.

The experimental techniques to measure these RTD functions are equivalent to the ones used in one-phase reactors. The application of such measurements is extremely important in the design of reactors. For example, let us think of a catalyzed fluidized bed, where gas is flowing at its bottom and circulating up. The flow of the solid is very similar to that of the ideal CSTR, as the fluidized bed is supposed to be perfectly mixed due to the fact that the mass transfer is

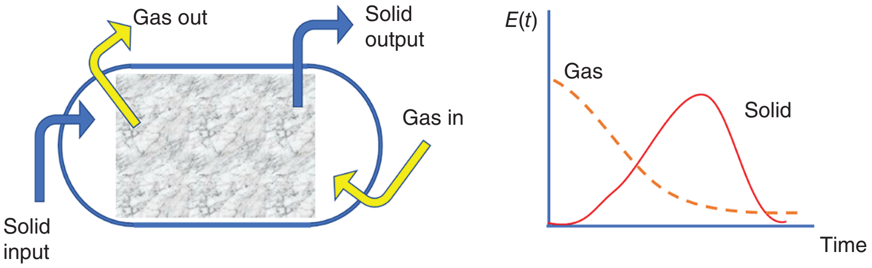


Figure 1.2 Two $E(t)$ functions are needed to characterize a reactor with two moving phases.

extremely fast. Nevertheless, the gas will flow through this bed, and will present a specific and complicated flow pattern, as we know. This pattern will depend on different factors and usually is between the plug flow and the CSTR behavior. The measurement of the precise RTD of both phases will give important information for the design and scale-up of the reactors.

1.2.3 Characteristics of RTD

Going back to the use and measurement of RTD, it is important to know some characteristics. If we consider the age of a reacting particle as the time it has remained under the conditions in which the reaction is carried out, then $E(t)$ is related to the age distribution of the effluent. In fact, the $E(t)$ is also called function of distribution of exit ages.

The fraction of the output current that has remained in the reactor for a period less than a given value, t, equals the sum over all times of the function $E(t)\cdot\Delta t$, or expressed continuously:

$$\int_0^t E(t) = \left[\begin{array}{c}\text{Fraction of output current that has remained}\\ \text{in the reactor a time less than "}t\text{"}\end{array}\right] = F(t)$$

which represents the cumulative RTD function, $F(t)$. Analogously, the integral of the $E(t)$ function from time "t" to infinity will represent the fraction of the output current that has remained in the reactor a time higher than "t."

This function $F(t)$ (cumulative distribution function) can be calculated at various "t" values using the area of the curve of the representation of $E(t)$ vs. time. An example of curve $F(t)$ for a tracer step input can be seen in Figure 1.3, where

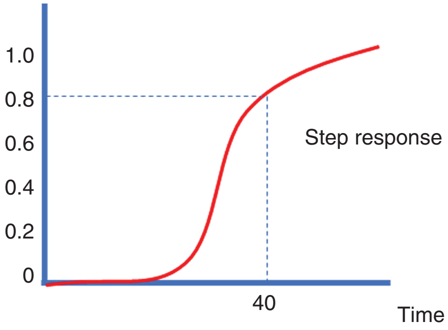


Figure 1.3 Interpretation of the cumulative distribution curve, $F(t)$.

it can be affirmed that 80% of the input tracer spends less than 40 units of time in the reactor.

1.2.3.1 Mean Residence Time

Variables described by distribution functions are characterized by their moments. Correspondingly, function $E(t)$ can also be characterized by its moments. In this sense, the mean value of the variable is equal to the first moment of the RTD function, $E(t)$. So, the mean residence time is defined as

$$t_m = \frac{\int_0^\infty t \cdot E(t)dt}{\int_0^\infty E(t)dt} = \int_0^\infty t \cdot E(t)dt \tag{1.12}$$

When studying the ideal reactors, the spatial time (τ = mass of catalyst/Q) and the average residence time ($\bar{t} = V/Q$) are usually used.

We can demonstrate that, regardless of the RTD that exists in a given reactor, ideal or not ideal, the nominal average residence time, $\bar{t} = V/Q$ is equal to the mean residence time of the RTD distribution, t_m, if the system is of constant density (where Q is constant). For doing this, let us consider a reactor completely filled with a colored fluid (for example, red bromine gas); at an instant $t = 0$, we start to inject yellow gas to replace the bromine filling the reactor. That is, the reactor volume V is equal to the volume occupied by the bromine leaving the reactor. In such a situation, during a certain time dt, the volume of bromine that will leave the reactor is $Q{\cdot}dt$, "Q" being the volumetric flow rate (considered at constant temperature and pressure). In that case, $[1 - F(t)]$ will represent the fraction of the gas that has remained in the reactor for a longer time. Since only this red gas has remained in the reactor more than "t," the volume of bromine, dV, leaving the reactor at time "dt" is

$$dV = (Q \cdot dt)[1 - F(t)] \tag{1.13}$$

If we add all the bromine that has left the reactor in the period between $0 < t < \infty$, we have

$$V = \int_0^\infty Q \cdot [1 - F(t)] \cdot dt \tag{1.14}$$

For constant volumetric flow:

$$V = Q \int_0^\infty [1 - F(t)] \cdot dt$$

$$\frac{V}{Q} = \int_0^\infty [1 - F(t)] \cdot dt \tag{1.15}$$

For the integration of the right-hand side, we will use the integration by parts, indicating that

$$\int u \cdot dv = u \cdot v - \int v \cdot du$$

Applying to Eq. (1.15):

$$\frac{V}{Q} = t[1 - F(t)]_0^\infty + \int_0^1 t \cdot dF \tag{1.16}$$

At $t = 0$, the cumulative function is zero, $F(t) = 0$, and when $t \rightarrow \infty$, $[1 - F(t)] = 0$:

$$\frac{V}{Q} = \infty \cdot (1 - 1) - 0 \cdot (1 - 0) + \int_0^1 t \cdot dF$$

In this way, the first term on the right-hand side is zero, and we can write

$$\frac{V}{Q} = \bar{t} = \int_0^1 t \cdot dF \tag{1.17}$$

On the other hand, since $dF = E(t)dt$:

$$\bar{t} = \int_0^\infty E(t) \cdot dt \tag{1.18}$$

Now, the right side of this equality is, precisely, the mean residence time, so we can conclude that spatial time and mean residence time *are equal in systems of constant density, regardless of whether the flow is ideal or not*:

$$\bar{t} = t_m \tag{1.19}$$

This result is only valid for closed systems (that is, without dispersion). The volume of the reactor can now be easily determined:

$$V = Q \cdot t_m \tag{1.20}$$

1.2.3.2 Second and Third Moments of the RTD

When comparing RTDs, it is usual to use the moments associated with the distribution instead of using the entire distribution. To this end, three are the moments that are usually used. The first moment is the average residence time, already defined. The second moment is calculated from the mean and is the variance which is defined as

$$\sigma^2 = \int_0^\infty (t - t_m)^2 \cdot E(t)dt \tag{1.21}$$

This equation corresponds to the square of the standard deviation. The magnitude of this moment gives a measure of the dispersion of the distribution, in such a way that the greater this moment, the greater the dispersion of the distribution (see Figure 1.4).

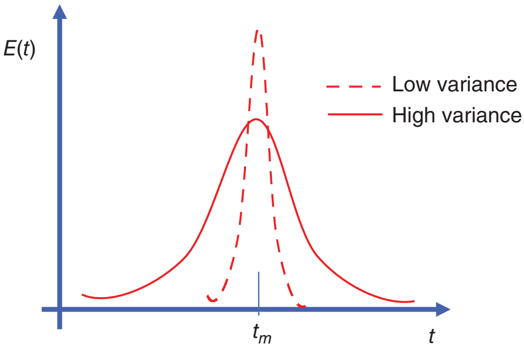


Figure 1.4 Effect of the second moment of the RTD in the curve shape. Both distributions are centered at the same t_m.

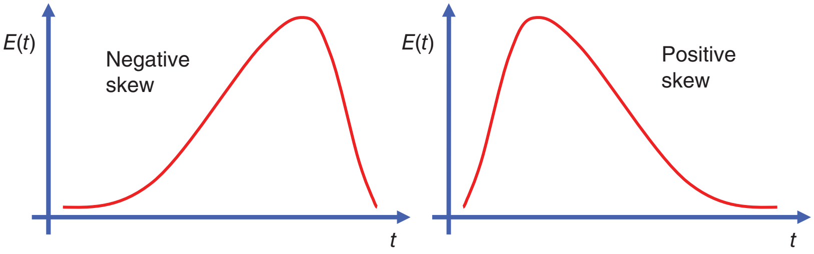


Figure 1.5 Form of the RTD curve for positive and negative skewness.

The third moment is also calculated around the average and is known as skewness. It is defined as

$$s^3 = \frac{1}{\sigma^{3/2}} \int_0^{\infty} (t - t_m)^3 \cdot E(t)dt \tag{1.22}$$

The greatness of this moment measures the extent to which the distribution with respect to the mean is displaced in one direction or another. A positive value of the skewness indicates that a tail to the right is expected in the distribution, and to the left if the skewness is negative. Figure 1.5 shows a scheme.

1.3 RTD in Ideal Reactors

1.3.1 RTD of the Batch and PFR Reactors

The RTD of these two types of reactors is the simplest we can consider, as already mentioned. All the particles (considered very small portions of the fluid, or solid particles if there is a solid moving in the reactor) that leave these reactors have stayed the same time inside the reactor. The output is then infinite at a particular time, and zero otherwise. This will produce an output function similar to that of an arrow of infinite height and zero width but presenting an area equal to one. This arrow appears at $t = V/Q = \bar{t}$. Mathematically, this arrow is represented by the Dirac delta function, in such a way that the $E(t)$ for an PFR is

$$E(t) = \delta(t - \bar{t}) \tag{1.23}$$

The delta function has the following properties:

$$\delta(x) = 0 \quad \text{when } x \neq 0$$

$$\delta(x) = \infty \quad \text{when } x = 0 \tag{1.24}$$

$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1 \tag{1.25}$$

$$\int_a^b g(x) \cdot \delta(x - \bar{t})\, dx = g(\bar{t}) \quad \text{if } a < \bar{t} < b \tag{1.26}$$

$$\int_a^b g(x) \cdot \delta(x - \bar{t})\, dx = 0 \quad \text{if } \bar{t} \notin [a, b] \tag{1.27}$$

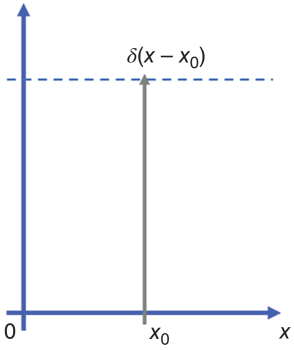


Figure 1.6 Dirac delta function, i.e. response of an ideal PFR to a pulse tracer input when "*x*" is time and the signal to a tracer is registered. In that case, x_0 would represent the average residence time.

In this way, the variance of this distribution is zero, by the fact that all values of $(t - t_m)$ are zero (all the signal is obtained at $t = t_m$). The function can be seen in Figure 1.6.

1.3.2 RTD of an ideal CSTR

The main characteristic of a CSTR is that the concentration of all substances inside the reactor are identical to those concentrations in the output stream. Imagine that an amount M_0 of inert tracer is injected into a CSTR. Once the tracer in injected, we can do a material balance for inert tracer, and we obtain

$$\begin{aligned} &\text{Input} - \text{Output} = \text{Accumulation} \\ &0 - Q \cdot C = V \cdot \frac{dC}{dt} \end{aligned} \tag{1.28}$$

Note that the input is zero (we consider the balance when the tracer has been already injected, i.e. at $t > 0$). Obviously, the generation term is also zero as the tracer is inert.

Since the reactor is perfectly agitated, C is the tracer concentration at the outlet and also at any point of the reactor. Separating variables and integrating, taking into account that $C = C_0$ for $t = 0$, we obtain

$$C(t) = C_0 \cdot \exp(-t \cdot Q/V) = C_0 \cdot \exp(-t/\bar{t}) \tag{1.29}$$

an expression that allows to obtain the concentration of the tracer in the effluent for any instant "*t*."

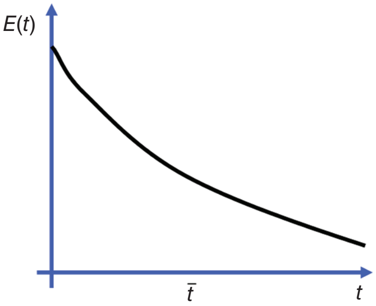
If we take into account the definition of $E(t)$ and introduce the value of $C(t)$, we obtain the RTD of an ideal CSTR:

$$E(t) = \frac{C(t)}{\int_0^\infty C(t) \cdot dt} = \frac{C_0 \cdot \exp(-t/\bar{t})}{\int_0^\infty C_0 \cdot \exp(-t/\bar{t}) \cdot dt} \tag{1.30}$$

Evaluating the integral of the denominator:

$$\begin{aligned} \int_0^\infty C_0 \cdot \exp(-t/\bar{t}) \cdot dt &= C_0 \cdot [\bar{t} \cdot \exp(-t/\bar{t})]_0^\infty \\ &= -C_0 \cdot \bar{t} \cdot [\exp(-\infty) - \exp(0)] = C_0 \cdot \bar{t} \end{aligned}$$

Figure 1.7 Response of a CSTR to a pulse tracer input.



Thus, the RTD is obtained for an ideal CSTR (Figure 1.7):

$$E(t) = \frac{1}{\bar{t}} \cdot \exp(-t/\bar{t}) \tag{1.31}$$

We have already seen that the average residence time in a reactor is given by V/Q or $\bar{t}$. This relationship can now be obtained in a simpler way by applying the definition of the average residence time of an RTD for a CSTR:

$$t_m = \int_0^\infty t \cdot E(t) \cdot dt = \int_0^\infty t \cdot \frac{1}{\bar{t}} \cdot \exp\left(-\frac{t}{\bar{t}}\right) \cdot dt = \bar{t} \tag{1.32}$$

That is to say, the nominal residence time (spatial time) $\bar{t} = V/Q$ coincides with the mean residence time that the material remains in the reactor, t_m.

To know the degree of dispersion in the reactor, we will calculate the second moment, the variance:

$$\sigma^2 = \int_0^\infty \frac{(t-\bar{t})^2}{\bar{t}} \cdot \exp\left(-\frac{t}{\bar{t}}\right) \cdot dt = \bar{t}^2 \tag{1.33}$$

That is to say, $\sigma = \bar{t}$. Or in other words, the standard deviation of the RTD coincides with the average.

1.3.3 RTD of PFR/CSTR in Series

In agitated tank reactors, there are zones, in the vicinity of the agitator, with a high degree of agitation and where an ideal CSTR could be a valid model. Nevertheless, depending on the location of the conductions, the reaction mixture can follow a somewhat tortuous path when entering, or when leaving the area perfectly agitated, or in both cases. This tortuous path can be modeled as if it behaved like a PFR. Thus, the tank-type reactor can be modeled as if it were a CSTR in series with a PFR (Figure 1.8), and the PFR can be before or after the CSTR. Next, we study the RTD for this type of reactor.

Consider, first, the system constituted by a CSTR followed by a PFR (Figure 1.8). The mean residence time in the CSTR will be called $\bar{t}_t$ and the mean residence time in the PFR, $\bar{t}_p$. If we inject a tracer pulse at the entrance of the CSTR, the concentration at the exit of the tank will vary with time according to the expression:

$$C(t) = C_0 \cdot \exp(-t/\bar{t}_t) \quad \text{(from Eq.(1.29))}$$

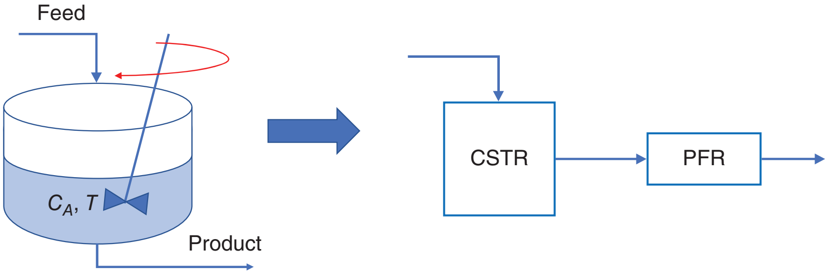


Figure 1.8 Real reactor modeled as a CSTR and a PFR in series.

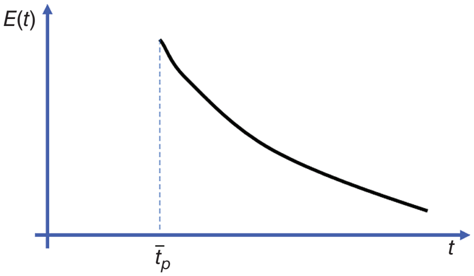


Figure 1.9 RTD for a CSTR and a PFR in series.

This output concentration will exit the PFR in series delayed by a time $\overline{t_p}$. Therefore, the RTD of the series reactor system will be given by (Figure 1.9)

$$E(t) = 0 \quad \text{if } t < \bar{t}_p$$

$$E(t) = \frac{1}{\bar{t}_t} \cdot \exp\left(-\frac{(t - \bar{t}_p)}{\bar{t}_t}\right) \quad \text{if } t \geq \bar{t}_p \tag{1.34}$$

Note that Eq. (1.34) is the same as Eq. (1.31), but the time scaling has been moved $\overline{t_p}$ units.

Let us see now the case of a CSTR preceded by a PFR. If a signal tracer is introduced into the input pulse PFR, the same signal appears at the input of the CSTR, but with a delay of $\overline{t_p}$ seconds, so the system's RTD will be the same as when the CSTR is the first reactor and is followed by a PFR. That is, the order in which both reactors are placed is not important, and the resulting RTD is the same provided that the sum of residence times in the two sections is the same.

However, this is not the only thing that should be considered; in case the reaction that takes place in the system is of the second order, the conversion that would be obtained with both dispositions would be different, as the conversion depends on the concentration. Contrarily, a first-order reaction will produce the same conversion both for PFR + CSTR and CSTR + PFR. This means that the RTD is not a complete description of what happens in a reactor or reactor system. The RTD is unique for a particular reactor; however, the reactor or reactor system is not unique to a particular RTD. In this way, in nonideal reactors, the RTD gives information that is not enough to characterize their behavior, and we need more information.

1.4 Modeling the Reactor with the RTD

On many occasions, the flow inside a reactor is not adjusted either to the complete mixture or to the plug flow, so when trying to use the RTD to predict the conversion that we are going to obtain, we find that the ideal models so far no longer serve us. There will, therefore, be a need to model the real reactor with some type of combination of ideal reactors or introduce new models. In these models, the adjustable parameter is usually evaluated on the basis of the RTD analysis obtained with a tracer test. We classify the models according to the number of adjustable parameters that are extracted from the information provided by the RTD.

1.4.1 Models with One Parameter: Tanks-in-series and Dispersion Models

In these models, we use a single parameter to bear in mind the nonideal behavior of a particular reactor. The parameter is determined by analyzing the measured RTD in a tracer test, as mentioned before.

For modeling the nonideal behavior of CSTRs, usually a dead zone volume (V_d), where the reaction does not take place, is used. Also, it is usual to consider the existence of a part of the fluid that passes through the reactor in short circuit and therefore does not react. In the case of tubular reactors, there are two models that usually represent the flow: the tanks-in-series model and the dispersion model. Both are one-parameter models, being the number of tanks in the first one, n_t, and the dispersion coefficient, D_e, in the last one.

For both types of distributions, once the value of the parameter is known, we will be able to calculate the conversion and or the concentrations at the output of the reactor.

In the case of a nonideal tubular reactor, usually it is assumed that the fluid moves in a plug flow through the reactor, so that each atom passes through the reactor the same time, and that the velocity profile is flat and there is no axial mixing. Both statements are false, to a greater or lesser extent, in all tubular reactors. Two approaches are often used to compensate for failures in the two ideal assumptions. In one case, the real reactor is modeled as a series of CSTRs of the same size. In the other (dispersion model), an axial dispersion is superimposed on the piston flow.

1.4.1.1 Tanks-in-series Model

In this model, we analyze the RTD of a particular tubular reactor to determine the number of CSTRs in series that will present an RTD approximately the same as the actual RTD. Next, we apply the balance equations valid for the ideal CSTR in order to calculate the conversion. We first consider the case of three tanks (Figure 1.10), developing the equations for the expression of the RTD, and then generalize it for "n_t" reactors connected in series. In this way, we obtain an equation that permits to calculate the number of tanks that best correlates the data of the actual RTD.

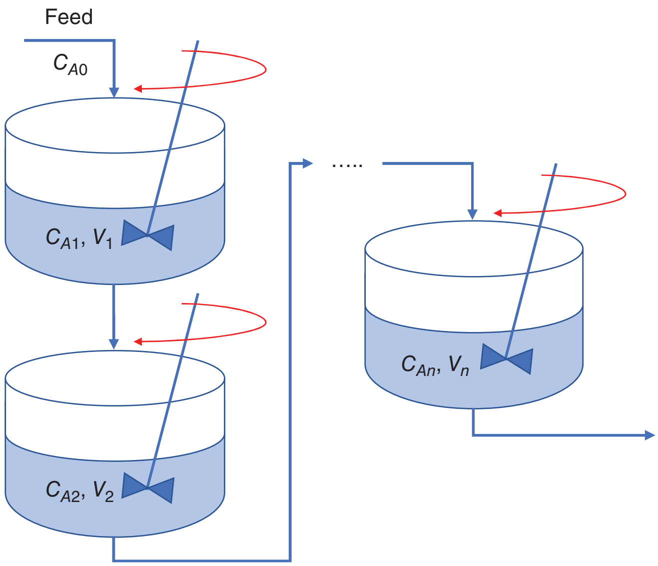


Figure 1.10 Tanks-in-series model.

If an impulse tracer signal is injected into the first tank, the tracer fraction that leaves the third reactor system after remaining in the system for a time between t and $t + dt$ is given by $E(t) \cdot dt$, which can be estimated from the concentration obtained in a pulse tracer experiment:

$$E(t) = \frac{C_{A3}(t)}{\int_0^\infty C_{A3}(t) \cdot dt} \tag{1.35}$$

In this expression, $C_{A3}(t)$ is the concentration of the tracer at the outlet of the third reactor. Now, we must obtain how this concentration varies with time. For a unique CSTR, the mass balance will be

$$\frac{V_1 \cdot dC_{A1}}{dt} = -Q \cdot C_{A1} \tag{1.36}$$

Integrating, we obtain the expression of the tracer concentration at the exit of that reactor:

$$C_{A1} = C_{A0} \exp\left(-Q \cdot \frac{t}{V_1}\right) = C_{A0} \exp\left(-\frac{t}{\bar{t}_1}\right) \tag{1.37}$$

Since the volumetric flow is constant $Q = Q_0$ and that the volume of all the reactors is the same ($V_1 = V_2 = V_3$), the average times will be identical ($\bar{t}_1 = \bar{t}_2 = \bar{t}_3 = \bar{t}_i$), $\bar{t}_i$ being the residence time in each one of the reactors, not in the whole system. Posing a balance of the tracer in the second reactor:

$$\frac{V_2 dC_{A2}}{dt} = Q \cdot C_{A1} - Q \cdot C_{A2} \tag{1.38}$$

Taking into account the expression that we have previously obtained for C_{A1}, we arrive at the differential equation:

$$\frac{dC_{A2}}{dt} + \frac{C_{A2}}{\bar{t}_2} = C_{A0} \exp\left(-\frac{t}{\bar{t}_1}\right) \tag{1.39}$$

which can be solved using an integration factor together with the initial condition $C_{A2} = 0$ for $t = 0$:

$$C_{A2} = \frac{C_{A0}t}{\bar{t}_i} \cdot \exp\left(-\frac{t}{\bar{t}_i}\right) \tag{1.40}$$

Using the same procedure for the third reactor, we obtain the expression for the tracer concentration at the exit of the third tank (and, therefore, of the system):

$$C_{A3} = \frac{C_{A0}t^2}{2\bar{t}_i^2} \cdot \exp\left(-\frac{t}{\bar{t}_i}\right) \tag{1.41}$$

Substituting in the equation for the curve $E(t)$:

$$E(t) = \frac{C_3}{C_0} = \frac{t^2}{2\bar{t}_i^2} \cdot \exp\left(-\frac{t}{\bar{t}_i}\right) \tag{1.42}$$

If we generalize for n_t equal tanks in series:

$$E(t) = \frac{t^{n_t-1}}{(n_t-1)!\bar{t}_i^{n_t}} \cdot \exp\left(-\frac{t}{\bar{t}_i}\right) \tag{1.43}$$

since $\bar{t}_i = \bar{t}/n_t$, where $\bar{t}$ is the quotient of the total volume of the system by the volumetric flow rate Q.

Figure 1.11 shows the RTD for different CSTR numbers in series. As n_t increases, the behavior is closer to piston flow.

The number of reactors in series can be calculated from the dimensionless variance σ^2:

$$\sigma^2 = \int_0^\infty (t-\bar{t})^2 \cdot E(t)dt = \ldots = \frac{\bar{t}^2}{n_t} \tag{1.44}$$

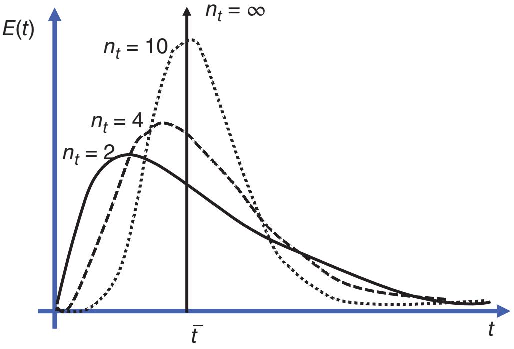


Figure 1.11 Response to a pulse tracer input in function of the number from tanks according to the tanks-in-series model. In the figure, $\bar{t}$ represents the average residence time of the whole system.

That is an expression that gives us the number of tanks needed to model the nonideal reactor as a series of n_t CSTR connected in series.

Let us now calculate the conversion of a reaction in the tanks in series. If the reaction is of the first order:

$$\text{1st reactor}: C_{A1} = \frac{C_{A0}}{1 + \bar{t}_1 k} \tag{1.45}$$

$$\text{2nd reactor}: C_{A2} = \frac{C_{A1}}{1 + \bar{t}_2 k} = \frac{C_{A0}}{(1 + \bar{t}_1 k)(1 + \bar{t}_2 k)} \tag{1.46}$$

As all residence times are equal, $\bar{t}_i$, and the temperature is constant ($k_1 = k_2 = k$), we can generalize the expression as

$$C_{An} = \frac{C_{A0}}{(1 + \bar{t}_i k)^{nt}} \tag{1.47}$$

Therefore, we can express the conversion as

$$X_A = 1 - \frac{1}{(1 + \bar{t}_i \cdot k)^{n_t}} \tag{1.48}$$

In general, the value of n_t obtained from the variance is considered as a non-integer number when calculating the conversion. In this sense, equations of the model can be applied to fractional number of tanks. Nevertheless, if the reaction is not of the first order, sequential molar balances must be made in each reactor (see Example 1.3 in the following sections).

1.4.1.2 The Dispersion Model

In this model, it is considered that there is a dispersion of the material overimposed to the flow, and that this dispersion is governed by an expression analogous to that of Fick for diffusion, which is superimposed on the plug flow. Thus, in addition to the term ($u{\cdot}S$) due to the flow of the mass of fluid, each component of the mixture will be transported through any section of the reactor with an additional rate [$D_e{\cdot}S{\cdot}(dC/dz)$] due to molecular and turbulent diffusion. At first glance, this simple model could only serve the effects of axial mixing. However, it can be seen that it serves to compensate also for the effects of radial mixing and those due to non-flat velocity profiles. These variations in concentration may be due to different speeds and flow paths, as well as to molecular and turbulent diffusion.

Let us imagine a pulse injection of tracer to a tubular reactor of section "S." During the movement of the fluid through the reactor, the pulse widens and becomes more diluted. The molar flow rate of the tracer (n_T), both by dispersion and convection, is

$$n_T = u \cdot S \cdot C_T + \left(-D_e \frac{\partial C_T}{\partial z}\right) \cdot S \tag{1.49}$$

In this expression, "z" is the spatial dimension where the fluid is moving, D_e is the effective dispersion coefficient (m^2/s) and "u" is the superficial velocity.

Note that the term corresponding to the dispersion of the component "*A*" is based on Fick's law for diffusion. If we do an inert tracer balance in a differential volume:

$$\text{In} - \text{Out} = \text{Accumulation}$$

$$-dn_T = dV \cdot \frac{dC_T}{dt} = S \cdot dz \cdot \frac{dC_T}{dt} \tag{1.50}$$

and, using partial derivatives:

$$-\frac{\partial n_T}{\partial z} = S \cdot \frac{\partial C_T}{\partial t} \tag{1.51}$$

Substituting for n_T (Eq. (1.49)) and dividing by the cross-section S:

$$D_e \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial(u \cdot C_{T)}}{\partial z} = \frac{\partial C_T}{\partial t} \tag{1.52}$$

If we divide by $(u{\cdot}L)$:

$$\frac{D_e}{u \cdot L}\frac{\partial^2 C_T}{\partial z^2} - \frac{\partial C_T}{L \cdot \partial z} = \frac{\partial C_T}{u \cdot L \cdot \partial t} \tag{1.53}$$

The parameter D_e/uL is the so-called ***recipient dispersion module*** or the Peclet–Bodenstein module (Bo $= D_e/uL$) that measures the degree of axial dispersion. When this module tends to zero, the system is close to piston flow, and when it tends to infinity (large dispersion), we have complete mixing. In the case of a packed bed, the module would be $(\varepsilon{\cdot}D_e/u{\cdot}d_p)$, where d_p is the particle diameter and ε the porosity of the bed.

Equation (1.52) is only solvable for small values of Bo number, usually Bo < 0.01. In that case, the dispersion modifies the input signal in the reactor, but the tracer widening does not vary in the measuring point with time, in such a way that the boundary conditions are well known. In this situation, the expression for the RTD curve of the reactor is

$$E = \frac{1}{\bar{t} \cdot \sqrt{4 \cdot \pi \cdot \text{Bo}}} \cdot \exp\left[-\frac{\left(1 - \frac{t}{\bar{t}}\right)^2}{4 \cdot \text{Bo}}\right] \tag{1.54}$$

$$t_m = \bar{t} = \frac{V}{Q} \tag{1.55}$$

$$\sigma^2 = 2 \cdot \text{Bo} \tag{1.56}$$

Nevertheless, if the value of the Bodenstein module Bo is higher than 0.01, the response of the tracer to the impulse is wide and passes through the measuring point so slowly that it can change its form during the time of measuring. This produces an asymmetrical *E* curve that, on some occasions, does not have an analytical expression for the *E* curve.

In this case, the *E* curve also depends on what happens in the input and output sections of the reactor vessels. We consider two cases: closed boundary conditions (where there is plug flow behavior outside of the system), and open boundary conditions (where the flow is not affected when passing through the system).

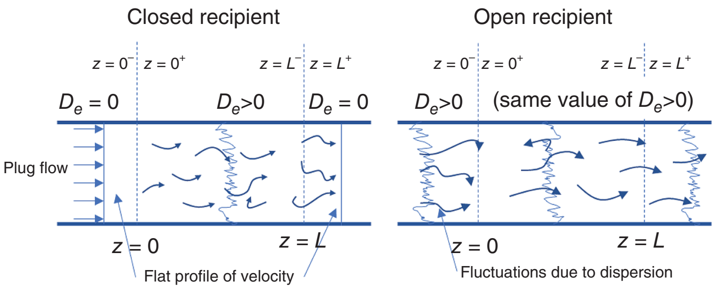


Figure 1.12 Effect of the dispersion on the velocity profile.

For simplifying all possibilities, let us consider only two cases: the closed–closed containers in which there is neither dispersion nor radial variation of the concentration, both upstream and downstream of the reaction zone; and *open–open containers* in which there is dispersion both before and after the reaction zone. Both cases are shown in Figure 1.12, where it is observed that the fluctuations of the concentration due to dispersion overlap the piston flow velocity profile. A closed–open container would have no dispersion at the entrance but only at the exit of the reaction zone.

Boundary Conditions for a Closed–Closed Vessel (Bo > 0.01) In this case, immediately before the reactor entrance zone ($z = 0^-$) and immediately after the exit zone ($z = L^+$), we have piston flow (without dispersion). However, between $z = 0^+$ and $z = L^-$, there is dispersion and convection by the flow movement. The corresponding boundary condition at the input is

$$n_T(0^-, t) = n_T(0^+, t) \tag{1.57}$$

Substituting the value n_T of at each side, we obtain

$$uSC_T(0^-, t) = -SD_e \left[\frac{\partial C_T}{\partial z}\right]_{z=0^+} + uSC_T(0^+, t) \tag{1.58}$$

Taking into account that at the input $C_T(0^-, t) = C_{T0}$ (known concentration):

$$C_{T0} = -\frac{D_e}{u}\left[\frac{\partial C_T}{\partial z}\right]_{z=0^+} + C_T(0^+, t) \tag{1.59}$$

Also, at the exit of the reactor considered, we can write $C_T(L^-, t) = C_T(L^+, t)$, this being later the measured exit concentration. In this way, when $z = L$:

$$\begin{aligned} C_T(L^-, t) &= C_T(L^+, t) \\ \left(\frac{\partial C_T}{\partial z}\right)_{z=L} &= \frac{C_T(L^-, t) - C_T(L^+, t)}{\partial z} = 0 \end{aligned} \tag{1.60}$$

The combination of Eqs. (1.59) and (1.60) are known as the Danckwerts' boundary conditions.

On the other hand, the initial condition of the reactor at $t = 0$ is

$$t = 0, z > 0 \; C_T\,(0^+, 0) = 0 \tag{1.61}$$

The injected tracer mass (M_0) is given by

$$M_0 = u \cdot S \cdot \int_0^{\infty} C_T(0^-, t) \cdot dt \tag{1.62}$$

In the closed–closed case, we do not have an analytical expression for the E curve, but the curve can be calculated by numerical methods and, also, we can calculate exactly its mean and variance. Bischoff and Levenspiel (in 1963) found the following relationships for the mean residence time and variance for this case:

$$\bar{t} = t_m$$

$$\left(\frac{\sigma}{t_m}\right)^2 = 2 \cdot \mathrm{Bo} - 2 \cdot \mathrm{Bo}^2 \cdot \left[1 - \exp\left(-\frac{1}{\mathrm{Bo}}\right)\right] \tag{1.63}$$

Experimentally, the dispersion module can be calculated from the values of t_m and σ^2 obtained from the RTD, substituting in the previous expression.

Boundary Conditions for an Open–Open Container (Bo > 0.01) These conditions would be applicable in the case of a packed bed in which the tracer was injected at a point downstream of the inlet, a distance around two to three times the diameter, and whose concentration was measured at a certain distance before the exit. A solution of the differential equation (Eq. (1.52)) could be obtained in the case of a pulse injection.

For an open–open system, the boundary condition at the input is

$$n_T(0^-, t) = n_T(0^+, t) \tag{1.64}$$

Note that the expression is the same as that obtained in the previous case. If the dispersion coefficient is the same at the entrance as in the reaction zone, we will have

$$-D_e \left[\frac{\partial C_T}{\partial z}\right]_{z=0^-} + u \cdot C_T(0^-, t) = -D_e \left[\frac{\partial C_T}{\partial z}\right]_{z=0^+} + u \cdot C_T(0^+, t) \tag{1.65}$$

As we can imagine, the derivatives at $z = 0^+$ and $z = 0^-$ are the same, as no discontinuity is included in the model, so:

$$C_T(0^-, t) = C_T(0^+, t) \tag{1.66}$$

while on the exit:

$$-D_e \left[\frac{\partial C_T}{\partial z}\right]_{z=L^-} + u \cdot C_T(L^-, t) = -D_e \left[\frac{\partial C_T}{\partial z}\right]_{z=L^+} + u \cdot C_T(L^+, t) \tag{1.67}$$

$$C_T(L^-, t) = C_T(L^+, t) \tag{1.68}$$

In addition to these boundary conditions, many other modifications may occur. For example, the dispersion coefficient can have different values in each of the three regions (before the entrance, in the reaction zone, and after the output) and/or the tracer can be injected at a point other than $z = 0$. However, we consider only the case that the dispersion coefficient is the same for any value of z and that the pulse tracer is injected at the point $z = 0$ at time $t = 0$.

In the open–open case, there exists an analytical solution of the differential equation, with an expression of the E curve that is not much complicated:

$$E = \frac{1}{\sqrt{4 \cdot \pi \cdot \mathrm{Bo} \cdot t/\bar{t}}} \cdot \exp\left[-\frac{\left(1-\frac{t}{\bar{t}}\right)^2}{4 \cdot t \cdot \mathrm{Bo}/\bar{t}}\right] \tag{1.69}$$

The corresponding average residence time is

$$t_m = \bar{t} \cdot (1 + 2 \cdot \mathrm{Bo}) \tag{1.70}$$

where $\bar{t}$ is based on the volume (and flow rate) between $z = 0$ and $z = L$; that is, the reactor volume measured with a calibrated apparatus. Note that, as a result of the previous equations, the average residence time in the open system is longer than the one corresponding to the closed system. The variance will be

$$\left(\frac{\sigma}{t_m}\right)^2 = 2 \cdot \mathrm{Bo} + 8 \cdot \mathrm{Bo}^2 \tag{1.71}$$

In the next two chapters, we discuss the numerical solution to these partial differential equations systems and we present the problem of calculating the conversion in systems with dispersion.

1.4.2 Models with Two Parameters

1.4.2.1 Two CSTR with Exchange of Matter

Consider the case that there is a strongly agitated region near the agitator of an CSTR. Nevertheless, outside this region, the agitation is lower (Figure 1.13). Both regions have an important exchange of material. We also consider that the entrance and exit pipes are connected to the zone of greatest agitation. Each zone will be modeled as a CSTR, both being connected and there is material transfer between them.

If we propose a molar balance on the tracer, with a pulse injected at $t = 0$, for each of the tanks, we obtain

Accumulation = Input − Output (there is no tracer generation)

$$V_1 \frac{dC_{T1}}{dt} = Q_1 C_{T2} - (Q_0 C_{T1} + Q_1 C_{T1}) \;\; \text{(in the first tank)} \tag{1.72}$$

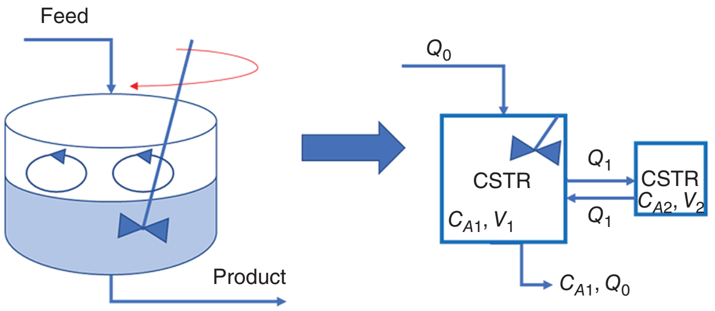


Figure 1.13 Real reactor and modeling using two CSTR.

$$V_2 \frac{dC_{T2}}{dt} = Q_1 C_{T1} - Q_1 C_{T2} \text{ (in the second tank)} \tag{1.73}$$

where C_{T1} and C_{T2} are, respectively, tracer concentrations in both reactors. These two differential equations are coupled and should be solved simultaneously.

In this model, the two adjustable parameters are the flow rate exchanged (Q_1) and the volume of the most agitated region (V_1). Remember that the measured volume (V) is the sum of V_1 and V_2. We will call β the fraction of the total flow that is transferred between both reactors:

$$Q_1 = \beta \cdot Q_0 \tag{1.74}$$

and α the fraction of the total volume that corresponds to the most agitated area:

$$V_1 = \alpha \cdot V \rightarrow V_2 = (1 - \alpha) \cdot V \tag{1.75}$$

On the other hand, the average time ($\bar{t}$) is given by the quotient V/Q_0.

The initial conditions ($t = 0$) for this model are (i) $C_{T1} = (C_{T1})_0$, and (ii) $(C_{T2})_0 = 0$

An analytical solution is possible in this case, and is as follows:

$$\left[\frac{C_{T1}}{(C_{T1})_0}\right]_{\text{pulse}} = \frac{(\alpha m_1 + \beta + 1)\exp\left(\frac{m_2 t}{\bar{t}}\right) - (\alpha m_2 + \beta + 1)\exp\left(\frac{m_1 t}{\bar{t}}\right)}{\alpha(m_1 - m_2)} \tag{1.76}$$

being:

$$m_1, m_2 = \left[\frac{1 - \alpha + \beta}{2\alpha(1 - \alpha)}\right]\left[-1 \pm \sqrt{1 - \frac{4\alpha\beta(1 - \alpha)}{(1 - \alpha + \beta)^2}}\right] \tag{1.77}$$

However, for more complicated models, an approximate solution would be necessary.

Equation (1.76) shows that, if tank 1 is small compared to 2 (α small) and the transfer speed between both reactors is small (β small), the second exponential term tends to 1 during the first part of the response to an impulse injection. During the second part, the first exponential term tends to 0. If we represent the logarithm of the tracer concentration vs. time, the response curve will tend to a straight line at both ends of the curve and the parameters will be obtained from the slopes (m_1 for $t \rightarrow \infty$ and m_2 for $t \rightarrow 0$) and the cut points of both lines (for $t \rightarrow \infty$, the cut point is $- \{\alpha m_2 + \beta + 1\}/\alpha\{m_1 - m_2\}$).

1.4.2.2 CSTR with Dead Volume and Short Circuit

In this case, the real CSTR is modeled as the combination of an ideal CSTR of volume V_t, a dead zone of volume V_d, and a bypass (short circuit) of volumetric flow rate Q_b (Figure 1.14). Using a tracer injection, we will calculate the parameters of the model V_t and Q_t, since the total volume and the volumetric flow are known.

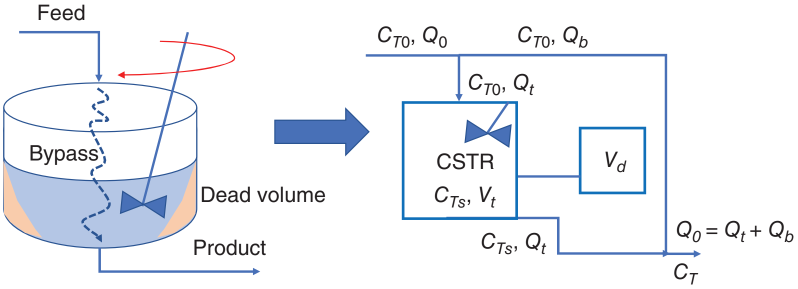


Figure 1.14 Real reactor and modeling using a single CSTR with dead volume and short circuit.

In this case, the derivation of the equations is simpler if we consider the injection of a tracer in positive step. Let us use the scheme in Figure 1.14; the balance in nonstationary regime (at $t > 0$, some tracer is still entering the system) of nonreactive tracer in the volume of reactor V_t, is

$$Q_t \cdot C_{T0} - Q_t \cdot C_{Ts} = \frac{dM_{Ts}}{dt} = V_t \frac{dC_{Ts}}{dt} \tag{1.78}$$

Remembering that for a positive step entry it is fulfilled that:

$$t < 0 \rightarrow C_T = 0$$
$$t \geq 0 \rightarrow C_T = C_{T0}$$

The tracer balance at the point of union of both currents will be

$$C_T = \frac{Q_b \cdot C_{T0} + Q_t \cdot C_{Ts}}{Q_0} \tag{1.79}$$

If we define:

$$V_t = \alpha V \quad \text{and} \quad Q_b = \beta Q_0, \qquad \text{with } \bar{t} = V/Q_0$$

Integrating and replacing in the expression of tracer balance in the reactor, we get

$$\frac{C_{Ts}}{C_{T0}} = 1 - \exp\left[-\frac{1-\beta}{\alpha}\left(\frac{t}{\bar{t}}\right)\right] \tag{1.80}$$

So, the expression of the tracer concentration that leaves the system will be

$$\frac{C_T}{C_{T0}} = 1 - (1-\beta) \cdot \exp\left[-\frac{1-\beta}{\alpha}\left(\frac{t}{\bar{t}}\right)\right] \tag{1.81}$$

If we reorder the equation, we can obtain the parameters of the model (Q_t and V_t or similarly α and β) from a plot of the tracer concentration at the output as a function of time. Representing $\ln[C_{T0}/(C_{T0} - C_T)]$ vs. time, if the model is correct, a straight line of slope $(1-\beta)/\bar{t}$ should be obtained α and an ordinate in the origin of value $\ln[1/(1-\beta)]$.

In order to have in mind the possible RTD curves obtained with this model, Figure 1.15 shows three curves corresponding to three different cases: the ideal

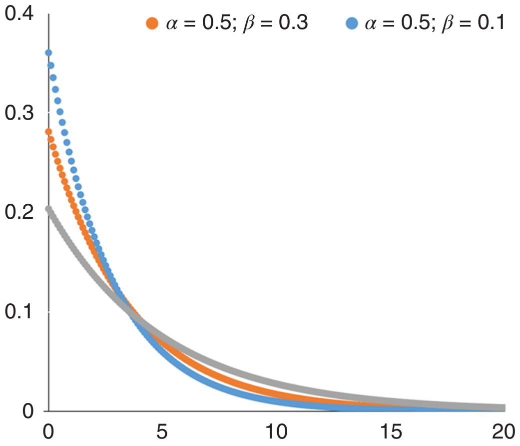


Figure 1.15 $E(t)$ predicted by this model with different values of the parameters, and the one for ideal CSTR for comparison.

CSTR, a reactor where $\alpha = 0.5$ and $\beta = 0.3$ and the other reactor with $\alpha = 0.5$ and $\beta = 0.1$; all of them with the same average residence time of five minutes. As we can see, the differences are quite small and, in practice, it is difficult to affirm without a little more information if the system has or not a dead volume and/or bypass.

1.5 Other Models of Real Reactors Using CSTR and PFR

So far, we have discussed about various reactor models. All of them are based on physical observations, which, in almost all the stirred tanks, are based on the existence of a well-mixed zone in the proximity of the agitator, usually represented by a CSTR. The region out of this well-agitated area can be modeled in various ways. The simplest form is using a model implying a CSTR connected to a dead zone; if it is suspected that some of the feed to the reactor may short out, a bypass current is added.

When the models do not satisfactorily represent the deviations of the ideal flow, we have to try more complicated models. In these models, it is assumed that the real reactor is constituted by a series of regions (flow in piston, flow dispersed in piston, flow in complete mixture, dead volumes) interconnected with each other in different ways (flow in bypass, with recirculation or cross-flow).

The simple types of these models are shown in Figure 1.16, where the form of the tracer response, in terms of E or F curves, for different models can be seen.

Example 1.1 *Tubular Reactor*

A tubular reactor was designed in order to obtain a conversion of 98% and process $0.03\ \text{m}^3/\text{s}$. The reaction is a first-order irreversible isomerization. The reactor is 3 m long, with a cross-sectional area of $0.1\ \text{m}^2$. In the newly constructed reactor, a tracer pulse test gave the following data: $t_m = 10$ s and $\sigma^2 = 65\ \text{s}^2$. What conversion can be expected in the real reactor?

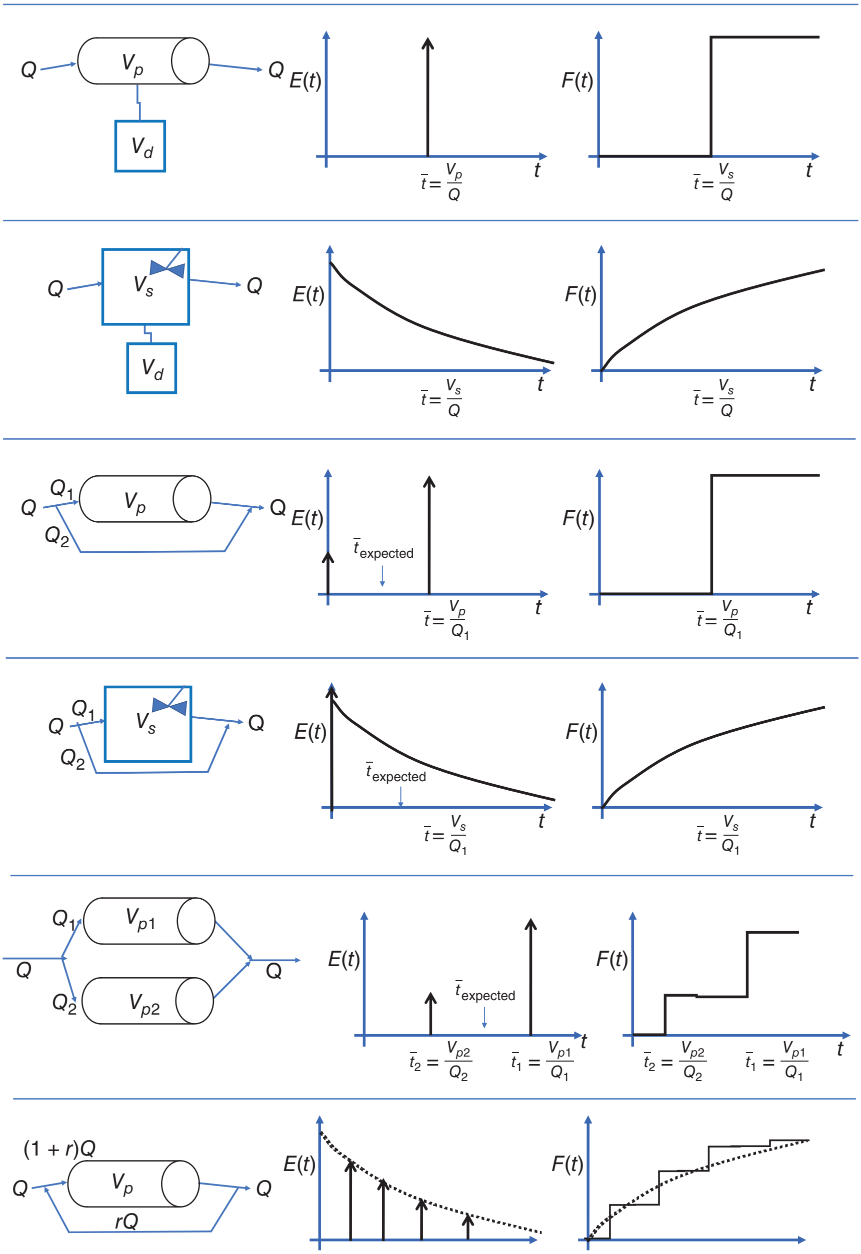


Figure 1.16 Combinations of ideal reactors used to model real reactors.

Solution

During the design of the reactor, a plug flow must be assumed. In this case, the molar balance of the reacting species "A," for a first-order reaction, gives

$$X_A = 1 - \exp(-k\bar{t})$$

In the present case:

$$\bar{t} = \frac{V}{Q} = \frac{0.1 \cdot 3}{0.03} = 10 \text{ s}$$

Coinciding with the value of t_m. From the previous equations: $k = 0.39\ \text{s}^{-1}$

Assuming a dispersion model for the real reactor, Eq. (1.63) is fulfilled, so:

$$\left(\frac{\sigma}{t_m}\right)^2 = 2 \cdot \text{Bo} - 2 \cdot \text{Bo}^2 \cdot \left[1 - \exp\left(-\frac{1}{\text{Bo}}\right)\right]$$

Iterating, we can find the value of the dispersion module: $\text{Bo} = (D_e/u{\cdot}L) = 0.667$

We have not seen in the previous sections the equations for the balances in reacting systems. Let us see this now. If we consider a tubular reactor in which we simultaneously have dispersion and reaction and we can do a molar balance of component A, in a range Δz of the reactor:

Input − Output + Generation = Accumulation

$$n_A - (n_A + dn_A) + r_A dV = 0$$

$$-\frac{1}{S}\frac{dn_A}{dz} + r_A = 0 \tag{1.82}$$

$$S \cdot dz = dV$$

Combining this expression with the molar flow of substance A:

$$n_A = -D_e S \frac{\delta C_A}{\delta z} + uSC_A \tag{1.83}$$

we obtain a differential equation of the second order:

$$\frac{D_e}{u}\frac{d^2\,C_A}{dz^2} - \frac{dC_A}{dz} + \frac{r_A}{u} = 0 \tag{1.84}$$

which is only linear when the reaction rate is of order 0 or 1.

When the kinetics is of the first order ($r_A = -kC_A$), the following expression is obtained:

$$\frac{D_e}{u}\frac{d^2\,C_A}{dz^2} - \frac{dC_A}{dz} - \frac{kC_A}{u} = 0 \tag{1.85}$$

which considers the flow, dispersion, and reaction. The solution of this second-order differential equation can be done analytically. If we consider a closed–closed system, we will apply the Danckwerts' boundary conditions at the input and at the exit of the reactor:

- Taking into account that at the input $C_A(0^-,t) = C_{A0}$(known concentration).

$$C_{A0} = -\frac{D_e}{u} \cdot \left.\frac{\partial C_A}{\partial z}\right|_{z=0^+} + C_A(0^+, t)$$

- At the exit of the reactor considered, we can write $C_A(L^-, t) = C_A(L^+, t)$, this being later the measured exit concentration. In this way, when $z = L$:

$$\left(\frac{\partial C_A}{\partial z}\right)_{z=L} = 0$$

Finally, the solution for the conversion in the reactor can be expressed by

$$1 - X_A = \frac{4a \cdot \exp\left(\frac{1uL}{2D_e}\right)}{(1+a)^2 \cdot \exp\left(\frac{auL}{2D_e}\right) - (1-a)^2 \cdot \exp\left(-\frac{auL}{2D_e}\right)} \tag{1.86}$$

where $a = [1 + 4(\bar{t} \cdot k) \cdot (D_e/uL)]^{1/2}$. This expression allows knowing the conversion that would be obtained for a first-order reaction to be carried out in a tubular reactor or in a bed reactor packed with dispersion.

For the system of the example, the value of "a" results to be 3.376 and the conversion in the real reactor is 0.88

Example 1.2 ***Reaction in a Complex System***

The second-order reaction $2A \rightarrow B$ is going to be carried out in a CSTR showing both a short circuit and a stagnant region. The tracer concentration at the outlet of this reactor is shown in the table, when a step input with initial concentration of tracer equivalent to 10 mg/l was used.

Time (min)	0	2	4	6	7	8	10	12	14	16	18	20
C_T (mol/l)	3.0	5.3	7.2	8.0	8.3	8.6	9.2	9.7	9.7	9.8	9.9	10

The measured volume of the reactor is 1 m^3 and the flow rate to the reactor is 0.1 m^3/min. The reaction rate constant is 150 l/(kmol min). The feeding contains a concentration of A at the input of 2 kmol/m^3. Calculate the conversion that can be expected in this reactor.

Solution

Let us first have a look of the experimental results. The graph C_T-time corresponding o the data is shown in Figure 1.17a.

As we have seen, Eq. (1.81) shows that the tracer concentration for a step input in this model can be expressed by

$$\frac{C_T}{C_{T0}} = 1 - (1-\beta) \cdot \exp\left[-\frac{1-\beta}{\alpha}\left(\frac{t}{\bar{t}}\right)\right] \tag{1.87}$$

From the data in the table, it is easy to calculate the slope and intercept of the representation $\ln(C_T/(C_{T0} - C_T))$ vs. t. The slope would correspond to $\left(-\frac{1-\beta}{\alpha\bar{t}}\right)$ and the intercept to $\ln(1/(1-\beta))$. In Figure 1.17b, we can see the corresponding straight line. Taking into account an intercept of –0.4549 and a slope of 0.2875, as solution of the model we find $\alpha = 0.3$ and $\beta = 0.3$ bearing in mind that the experimental value of average residence time $\bar{t} = \frac{V}{Q} = \frac{1}{0.1} = 10$ minutes should be used as it was defined for the whole system.

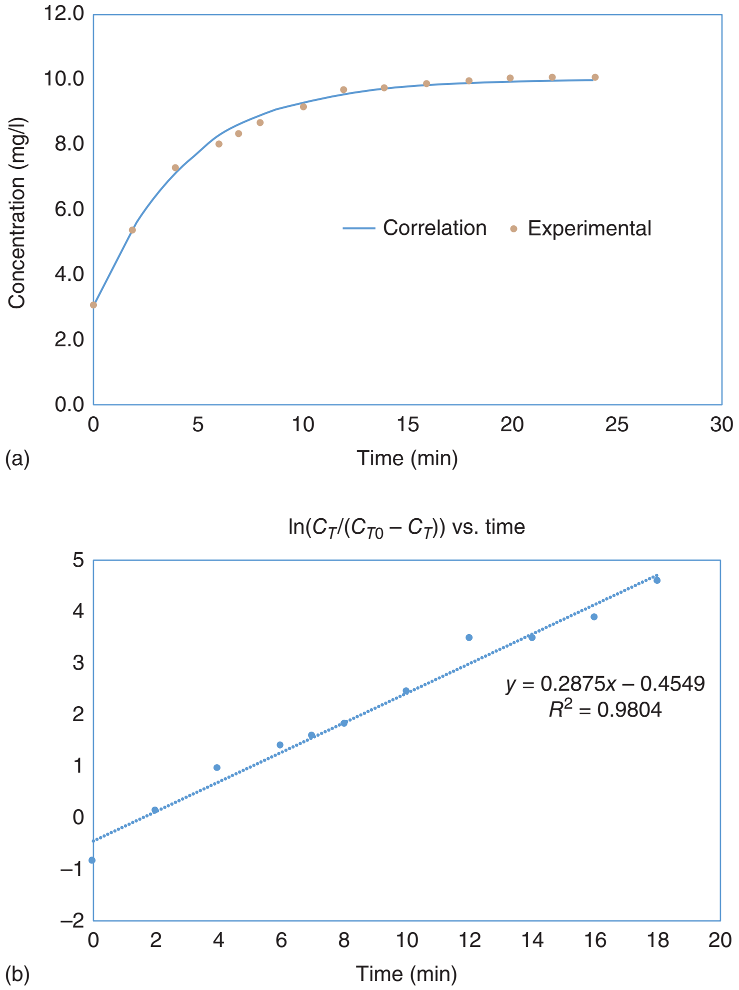


Figure 1.17 (a) Concentration of tracer obtained in a step input experiment and (b) calculation of the parameters.

For the system with reaction, let us see how to obtain the conversion with this model in the case of the first-order reaction (not in this case, but will be useful). For a first-order reaction, the molar balance of A in the reactor where the reaction takes place (V_t) gives

$$Q_t C_{A0} - Q_t C_{As} - k C_{As} V_t = 0$$

$$C_{As} = \frac{C_{A0}(1-\beta)Q_0}{(1-\beta)Q_0 + \alpha V k}$$

If we do a reagent balance A in the point where the short circuit current and the output current of the reactor are mixed, we will obtain

$$C_{A0} Q_b + C_{As} Q_t = C_A (Q_b + Q_t)$$

Clearing C_A, the concentration at the exit of the system:

$$C_A = \frac{Q_b C_{A0} + C_{As} Q_t}{Q_0} \tag{1.88}$$

So, finally:

$$\frac{C_A}{C_{A0}} = 1 - X_A = \beta + \frac{(1-\beta)^2}{(1-\beta) + \alpha \bar{t} k} \tag{1.89}$$

the expression that allows to calculate the conversion based on the parameters of the model.

As in Example 1.2, the reaction is second order, we can write:

$$Q_t C_{A0} - Q_t C_{As} - k C_{As}^2 V_t = 0 \tag{1.90}$$

Rearranging:

$$\frac{V_t \cdot k}{Q_t} \cdot C_{As}^2 + C_{As} - C_{A0} = 0 \tag{1.91}$$

Let us be aware that the flow rate and volume in the previous equations are those in the well-stirred part of the reactor, in such a way that:

$$\frac{V_t}{Q_t} = \frac{\alpha V}{(1-\beta) Q_0} = \frac{\alpha}{(1-\beta)} \bar{t}$$

and clearing, the value of C_{As} results to be

$$C_{As} = \frac{-1 + \sqrt{1 + 4 \frac{\alpha}{1-\beta} \bar{t} k C_{A0}}}{2 \frac{\alpha}{1-\beta} \bar{t} k} \tag{1.92}$$

Using the data in the example, the concentration at the exit of the CSTR is 0.927 kmol/m^3. The value of C_A at the exit of the system can be calculated from Eq. (1.80). Finally, in the example, $C_A = 1.249$ kmol/m^3

Example 1.3 ***Second-order Reaction in a Series of CSTRs***

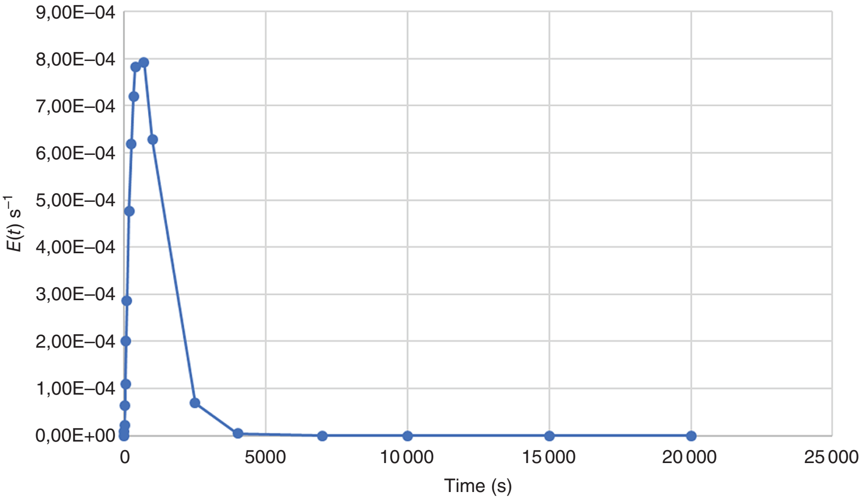
An irreversible second-order reaction occurs in an isothermal, but not ideal, CSTR. The reactor volume is 1000 l and the flow velocity of the reagent stream is 1 l/s. At reactor temperature, $k = 0.005$ l/(mol s). The concentration of A in the feed stream is 1 mol/l. The DTR is obtained by a tracer test in this reactor at the desired feed rate and reaction temperature. Calculate the conversion that can be obtained with the tanks-in-series model.

RTD data obtained:

t (s)	0	5	10	25	40	70	100	175	250	325
$E(t)$ (s^{-1})	9.712 $18\cdot10^{-6}$	2.206 $86\cdot10^{-5}$	6.411 $68\cdot10^{-5}$	0.000 1090 4	0.000 199 787	0.000 286 936	0.000 476 181	0.000 619 435	0.000 719 564	9.712 $18\cdot10^{-6}$
t (s)	400	700	1000	2 500	4 000	7 000	10 000	15 000	20 000	
$E(t)$ (s^{-1})	0.000 782 749	0.000 791 834	0.000 627 888	6.954 $06\cdot10^{-5}$	4.508 $28\cdot10^{-6}$	1.200 $36\cdot10^{-8}$	2.505 $25\cdot10^{-11}$	6.80 $646\cdot10^{-16}$	1.60 $549\cdot10^{-20}$	

Solution

First of all, we can plot the data obtained with the tracer.



As we can see, the curve is similar to a CSTR, but small differences can be accounted with the use of the tanks-in-series model. From the data, it is easy to calculate:

$$t_m = \int_0^{\infty} t \cdot E(t) \cdot dt = 1129 \text{ s}$$

$$\sigma^2 = \int_0^{\infty} (t - t_m)^2 \cdot E(t) \cdot dt = 5.420 \cdot 10^5 \text{ s}^2$$

We can calculate the number of tanks in the model, that is, $n_t = t_m{}^2/\sigma^2 = 2.221$ tanks.

We have seen in the previous sections the equations for the balances in reacting systems or first order. In that case, Eq. (1.48) with $n_t = 2.221$ would give us the expected conversion. Let us see what occurs if the system is nth order. If we consider a single tank reactor (of volume V_1) we can do a molar balance of component A:

$$\frac{V_1}{n_{A0}} = \frac{C_{A0} - C_A}{C_{A0}(r_A)} = \frac{C_{A0} - C_{A1}}{C_{A0}(k \cdot C_{A1}^n)} \tag{1.93}$$

If the system has a constant density:

$$\bar{t}_1 = \frac{V}{Q} = \frac{C_{A0} - C_{A1}}{(k \cdot C_{A1}^n)} \tag{1.94}$$

$$C_{A1} = \frac{C_{A0}}{(1 + k\bar{t}_1 C_{A1}^{n-1})} \tag{1.95}$$

As we can check, the concentration at the exit can be calculated from this nonlinear equation, and an approximation can be used.

In a second reactor connected in series with this, we would have

$$C_{A2} = \frac{C_{A0}}{(1 + k\bar{t}_1 C_{A1}^{n-1})(1 + k\bar{t}_2 C_{A2}^{n-1})} \tag{1.96}$$

For n_t tanks in series, the product in the denominator would have n_t factors and the intermediate concentrations C_{A1}, C_{A2}, … are needed.

In the present example, a value of $n_t = 2.221$ tanks would represent the system, but it is not possible to do the balance in a part of a reactor. In such situations, the best solution is to take the nearest integer to n_t or take both limits, in the present case $n_t = 2$ and $n_t = 3$.

Assuming two tanks $\bar{t}_i = \bar{t}/2$, i.e. all tanks of the same volume, we have $\bar{t}_i = 500$ s

We can now calculate C_{A1} using (Eq. (1.95)) with the corresponding values of k and n. Easily, the equation gives $C_{A1} = 0.461$ mol/l. If a second reactor is considered, (Eq. (1.96)) would give us $C_{A2} = 0.274$ mol/l, that is, a conversion of 0.723.

On the other hand, if three tanks are considered, the residence time in each tank is 333.3 s and the solution $C_{A1} = 0.533$ mol/l, $C_{A2} = 0.326$ mol/l, and $C_{A3} = 0.245$ mol/l. The final conversion would be 0.754.

Example 1.4 ***Nonideal CSTR***

In an isothermal nonideal CSTR, an irreversible second-order reaction is carried out. The values of flow rate, volume, and rate constant are known, and the RTDs has been measured with a tracer. Indicate the equations necessary to determine the concentration at the output of the reactor as a function of the input flow (or average residence time), if the reactor is modeled: (a) as three equal CSTRs in series, or (b) as three equal CSTRs in parallel.

Solution

(a) If the three reactors are connected in series, the equations just discussed in previous example are valid, so the concentration at the exit of each reactor will be given by Eqs. (1.95) and (1.96). The one corresponding to the third reactor is equivalent.

(b) On the contrary, if the reactors are connected in parallel, each of them will have a flow rate equal to 1/3 of the total. The concentration at the exit of the reactors will be the same in all three. And the mix of three currents of the same concentration in the same proportion, will give a current with exactly the same concentration, calculated by Eq. (1.95) bearing in mind the volume and the flow rate at each reactor.

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