Mixing Effects in Chemical Reactors–IV —Residence Time Distributions

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OBJECTIVES

At the completion of this module, the student should be able to

1. Define the residence time density function $E(t)$ and residence time distribution $F(t)$.
2. Determine $E(t)$ and $F(t)$ from measured tracer impulse and step responses.
3. Calculate the nominal mean residence time in a process unit and the mean of the residence time distribution, and state when the two quantities are equal.
4. Calculate the functions E and F in terms of reduced time $\theta = t/\bar{t}$.
5. Determine qualitatively the degree of axial mixing, bypassing, and internal recirculation in a process unit, and quantitatively the extent of stagnancy in a unit, from a measured residence time distribution.
6. Determine effective phase volumes in multiphase reactors from tracer responses.

PREREQUISITE MATHEMATICAL SKILLS

1. Calculus.

PREREQUISITE ENGINEERING AND SCIENCE SKILLS

1. Mixing in chemical reactors (Modules E4.4 and E4.5).

The performance of a continuous chemical reactor depends to a great extent on the flow and mixing patterns in the reactor. You have performed design calculations for ideal plug flow reactors and perfect mixers, for example, and you know that they may yield significantly different conversions for a specific reaction rate and a given mean residence time.

The behavior of continuous chemical reactors cannot always be described in terms of either ideal plug flow or perfect mixing. Imperfect mixing in stirred tanks, nonuniform flow velocities in tubular reactors, and diffusion in any direction in which concentrations vary make the exact relationship between feed and product variables difficult to represent mathematically. Other modules (E4.4 through E4.6) have shown how various models (mathematical representations) for nonideal reactors may be formulated and applied to reactor design and analysis. For example, a real reactor whose mixing characteristics fall between ideal plug flow and perfect mixing can be modeled as a series of perfect mixers. The same modules also demonstrate that tracer response measurements can provide the information needed to select a flow model for a reactor, and to determine the model parameters which best simulate the reactor behavior.

It is also possible, and often useful, to describe quantitatively the nature of flow and mixing in a reactor without resorting to specific models. This module introduces several concepts which form the basis of this approach.

As a simple illustration, let us first consider a chamber (system) with one inlet and one outlet, which contains thousands of white marbles (fluid molecules). Further suppose that hundreds of white marbles enter and leave the chamber each second.

Unless the marbles move uniformly through the system, the periods of time that they spend in the chamber before emerging vary about a mean value. Clearly (remembering that the chamber being discussed really represents a process system) how these times are distributed must have a significant effect on the performance of any process to be carried out in the chamber. One would therefore like to know how long each of the emerging marbles was in the chamber before emerging vary about a mean value. it emerged.

Unfortunately, simply observing the emerging marbles cannot give us this information, since they all look alike. The solution is to perform a tracer experiment. At an instant in time, which will be called $t=0$, we introduce one hundred red marbles (tracer) into the inlet stream, and then position ourselves at the outlet to observe the times at which red marbles emerge. Suppose that in a time interval from $t=5$ seconds to $t=6$ seconds we observe 15 red marbles. We now know that of the red marbles entering the reactor, a fraction 15/100 had residence times between 5 seconds and 6 seconds, since all of the red marbles entered together at $t=0$. If we assume that the red marbles behave exactly as the white ones do (i.e. that the tracer is perfect) and that the system is at steady-state, we can estimate that of *all* the marbles entering the system, 15% remain there for a period between 5 and 6 seconds. It follows that 15% of all the marbles in the exit stream were in the system for the same time interval. If we had injected 1000 marbles and observed 150 we would have greater confidence in this conclusion; still more if we had injected roughly 10^{20} marbles and counted 0.15×10^{20}, which is closer to what happens in a real tracer experiment.

We can perform the same calculation for arbitrary 1-second intervals, and plot the results versus time from injection. The plot might appear as in Figure 1. This histogram provides an estimate of the *residence time density function* for marbles in the outflow. (It can also be identified as an estimate of the system impulse response function, defined in Module E4.4.)

It is this type of information that we wish to obtain about process vessels and reactors. In this module we define a set of functions which describe residence time distributions of fluid elements in a process unit, present the relationships that exist among them, and show how to determine them from tracer experiments.

RESIDENCE TIME DENSITY FUNCTION

Definition

Let us consider a system with one inlet and one outlet (Figure 2). The *residence time density function* (or *exit age density*) of fluid elements in the system, designated $E(t)$, is formally defined as follows:

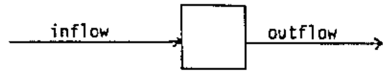


Figure 2.

$E(t)dt$ = fraction of emerging fluid elements that were in the system for a time between t and $t+dt$

The fraction of the outflow that was in the system for a time between t_1 and t_2 equals the sum of the fractions with residence times in all differential intervals between these limits, or

$$\int_{t_1}^{t_2} E(t)dt$$

The residence time distribution, $F(t)$ is:

$$\int_0^t E(t')dt' = \text{fraction of outflow with residence times less than } t$$

The residence time distribution must satisfy the following conditions:

a) $E(t)=0$ for $t<0$ since no fluid can exit before it entered
b) $E(t)\geq 0$ for $t\geq 0$ since mass fractions are always positive
c) $\int_0^\infty E(t)dt=1$

Why must this be so?

The residence time density function for a process unit might appear as shown in Figure 3 (recall the histogram of the previous section). This plot shows that almost all fluid elements remain in the system between one and four minutes, and on the average, spend approximately two minutes there. Later, a more precise definition of mean residence time will be given.

Note that since Edt is a fraction, and therefore dimensionless, E itself must have units of inverse time. (In probabilistic terms, E is a density rather than a distribution; nevertheless, let us call it a distribution, following traditional reaction engineering usage.) $E(t)$ is the fundamental indicator of the flow and mixing pattern in a process unit, and consequently, its measurement is an important step in the analysis of nonideal reactors.

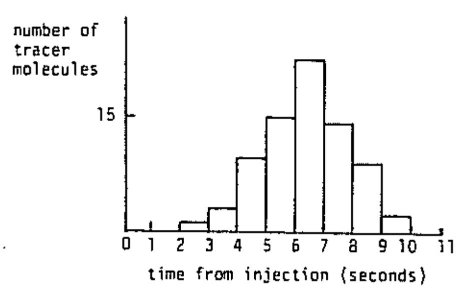


Figure 1.

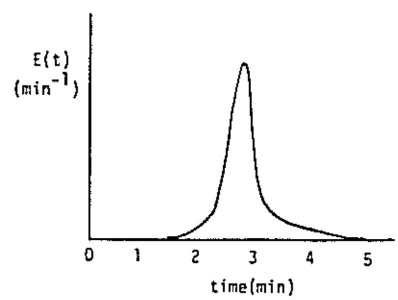


Figure 3.

Determination of $E(t)$ from a tracer impulse response

Suppose a tracer is injected at the inlet of a process unit, and the response at the outlet is monitored. The following conditions are assumed to hold:

1. Constant flow rate $q(\text{cm}^3/\text{s})$ and fluid density $\rho(\text{g}/\text{cm}^3)$.
2. Only one flowing phase.
3. "Closed" system—input and output by bulk flow only (no diffusion takes place across system boundaries).
4. Flat velocity profiles at the inlet and outlet.
5. Linearity with respect to the tracer: that is, the magnitude of the response at the outlet is directly proportional to the amount of tracer injected.
6. The tracer is completely conserved within the system, and is identical to the process fluid in its flow and mixing behavior.

In a time period from $t=0$ to $t=\Delta t$ seconds, a quantity m_i (g) of a tracer is introduced at the reactor inlet, and the tracer concentration $c(t)(\text{g}/\text{cm}^3)$ in the effluent from the reactor is measured. (Eventually, Δt will be allowed to approach 0, so that the injection is a true impulse; for now, simply assume that Δt has an infinitesimally small fixed value.) Subject to the six stated conditions, the residence time density function in the system may be determined from the measured tracer response as

$$E(t)=\frac{c(t)}{\int_0^\infty c(t)dt}=\frac{\left[\begin{array}{l}\text{Tracer concentration in the outflow}\\ \text{(or a quantity proportional to it) at time } t\end{array}\right]}{\left[\begin{array}{l}\text{Total area under tracer concentra-}\\ \text{tion (or a quantity proportional to}\\ \text{it) curve versus time as measured at}\\ \text{the outflow}\end{array}\right]} \quad (1)$$

Proceed in a stepwise manner.

a) Mass of fluid entering in Δt:

$$m_a=q(\text{cm}^3/\text{s})\ \rho(\text{g}/\text{cm}^3)\ \Delta t(\text{s})$$

b) Mass of tracer entering in Δt:

$$m_b=m_i(\text{g})$$

c) Ratio of total fluid to tracer entering in Δt:

$$\frac{m_a}{m_b}=\frac{q\rho\Delta t}{m_i}$$

Now consider an interval from an arbitrary time t (after the tracer injection), to $t+\Delta t$.

d) Mass of tracer emerging in given time interval:

$$m_d=q(\text{cm}^3/\text{s})c(\text{g}/\text{cm}^3)\Delta t(\text{s})$$

The tracer emerging in this interval had a residence time of approximately t (exactly t when Δt approaches 0). At the same time, some process fluid (which entered with the tracer, and so has the same residence time) also emerges. Assuming that the tracer and the process fluid behave identically, the ratio of process fluid with residence time t to tracer with residence time t must equal the ratio of process fluid to tracer entering the system in the initial time interval. (Reread this paragraph once or twice to make sure it is fully understood.) Thus,

e) Mass of fluid emerging with residence time t:

$$m_e=m_d\text{ (g tracer) }\frac{m_a\text{ (g fluid)}}{m_b\text{(g tracer)}}$$

$$=qc\Delta t\cdot\frac{q\rho\Delta t}{m_i}$$

f) Total mass of fluid emerging in the same time interval:

$$m_f=q\rho\Delta t$$

By definition, as $\Delta t\rightarrow dt$

g) $$E(t)dt=\frac{\left[\begin{array}{l}\text{mass of fluid emerging with residence}\\ \text{time between } t \text{ and } (t+dt)\end{array}\right]}{[\text{total mass of fluid emerging}]}$$

$$E(t)dt=\frac{m_e}{m_f}=\frac{qc(t)}{m_i}\,dt$$

Finally, dividing by dt, gives

$$E(t)=\frac{qc(t)}{m_i} \quad (2)$$

Equation 2 can used to determine $E(t)$ from a measured response function $c(t)$ if both the volumetric flow rate, q, and the mass of tracer injected, m_i, are known. One may avoid these requirements, however, by noting that since $qc(t)dt$ is the mass of tracer emerging in the interval from t to $(t+dt)$, the total quantity of the tracer must be given by the relation

$$m_i=\int_0^\infty qc(t)dt$$

$$\Downarrow$$

$$\frac{m_i}{q}=\int_0^\infty qc(t)dt \quad (3)$$

This is an expression of a material balance on the tracer (see Module E4.4). If this expression is substituted into Equation 2, the result is

$$E(t)=\frac{c(t)}{\int_0^\infty c(t)dt} \quad (1)$$

which completes the proof.

Equation 1 may be put in an even more useful form. As a rule, the concentration of tracer in the output stream is not measured directly; instead, a quantity $R_f(t)$ which is proportional to $c(t)$ is measured (R_I denotes impulse response)—perhaps a counting rate if a radiotracer is used, or a light absorbance if the tracer is a dye, or a conductance if an electrolyte is the tracer. If $c(t)=kR_I(t)$, where k is the constant of proportionality, and this expression is substituted into Equation 1, the constant cancels, leaving as the result:

$$E(t)=\frac{R_I(t)}{\int_0^\infty R_I(t)dt} \tag{4}$$

To repeat, $R_I(t)$ is the response of a system to an impulse injection of a tracer, and $E(t)$ is the residence time density function.

Example 1: Residence Time Density From a Tracer Impulse Response

An idealized response to an impulse injection of tracer is shown in Figure 4. Determine the residence time density function.

Solution:

Let us first find the normalizing factor, $\int_0^\infty R_I(t)dt$, which is equal to the area under the tracer response curve. This particular curve can be represented by:

$$R_I(t)=\begin{Bmatrix} 0.3\ (t-10) & 10\leqq t\leqq 20 \\ 0.3\ (30-t) & 20\leqq t\leqq 30 \\ 0 & \text{everywhere else} \end{Bmatrix}$$

The area under the curve is 30 (counts). From Equation 1,

$$E(t)=\frac{R_I(t)}{\int_0^\infty R_I(t)dt}=\begin{Bmatrix} 0.01\ (t-10) & 10\leqq t\leqq 20 \\ 0.01\ (30-t) & 20< t\leqq 30 \\ 0 & \text{everywhere else} \end{Bmatrix}$$

See Figure 5. Verify that $E(t)$ has the three properties of a residence time density function listed previously.

Now, let us consider why the assumptions previously listed in the determination of $E(t)$ from a trace impulse response are necessary. Certainly Assumption 1 is required: if conditions were not steady state, then the determined function $E(t)$ would depend upon the time the tracer experiment was performed. If the process fluid density varied, one could not balance input and output in terms of volumetric flow rates.

Assumption 2 is required, because if more than one flowing phase existed, the age-density function for the tracer would depend on whether the tracer were introduced into one or both phases, and on how it distributed itself between the phases within the system. Assumption 3, of a "closed" system, is needed since in all mass balances the product qc is used for input and output terms, whereas if the system were not closed, dispersion (diffusion) terms would need to be added. (See Module E4.6). If Assumption 4 (flat velocity profiles) was not valid, the response signal would depend on how the tracer is distributed over the inlet and outlet cross sections, and its interpretation would be ambiguous.

The linearity assumption (Assumption 5) guarantees that if one doubled the mass m_i of the tracer injected, the response would double in amplitude, but its form would not change. If the system were nonlinear, $E(t)$ calculated from Equation 4 would depend on the amount of tracer injected. Finally, the assumption of a perfect tracer (Assumption 6) is needed since one is really measuring the residence time distribution of the tracer and from it, inferring the residence time distribution of the carrier fluid. If the tracer behaved differently from the carrier fluid, the two functions would not be the same.

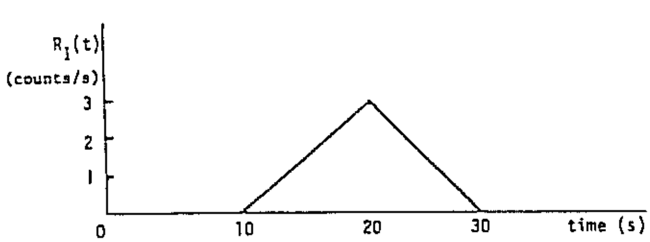


Figure 4.

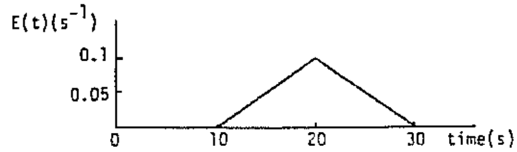


Figure 5.

Determination of Mean Residence Time

The average residence time, $\bar{t}_E$, of the fluid in the outflow (the apparent mean residence time) is by definition the mean (first moment) of the residence time density function:

$$\bar{t}_E=\int_0^\infty tE(t)dt \tag{5}$$

For example, the average residence time of the fluid in the reactor of Example 1 is:

$$\bar{t}_E=\int_0^\infty tE(t)dt=\int_{10}^{20} 0.01t(t-10)dt + \int_{20}^{30} 0.01t(30-t)dt=20 \text{ seconds}$$

If the expression for $E(t)$ of Equation 4 is substituted in Equation 5, the result is

$$\bar{t}_E=\frac{\int_0^\infty tR_I(t)dt}{\int_0^\infty R_I(t)dt} \tag{6}$$

Thus, the mean of the residence time distribution may be determined directly from a measured impulse response.

Provided that certain conditions are satisfied, the mean of the residence time density function $\bar{t}_E$ defined by Equation 5, equals the nominal mean residence time

$\bar{t}$ = volume/volumetric flow rate:

$$\bar{t}_E = \bar{t} \qquad \text{or} \qquad \int_0^\infty tE(t)dt = \frac{V}{q} \tag{7}$$

For all practical purposes, the criteria for the validity of Equation 7 are the six conditions given at the beginning of this section.

RESIDENCE TIME DISTRIBUTION (CUMULATIVE AGE DISTRIBUTION)

Definition

$F(t)$ = fraction of the fluid elements emerging in the outflow which were in the system less than time t.

The relationship between $F(t)$ and the residence time density $E(t)$ is readily established.

$$F(t) = \int_0^t E(t')dt' \tag{8}$$

Thus, the residence time or cumulative age distribution $F(t)$ can also be determined from a tracer impulse response using Equations 4 and 8. From its definition, one can readily deduce the following properties of $F(t)$:

a) $F(t) = 0$ when $t < 0$

b) $F(t) \geqq 0$ when $t \geqq 0$

c) $F(\infty) = 1$

and

d) $$\frac{dF}{dt} = E(t) > 0 \tag{9}$$

The cumulative exit age distribution is a nonnegative, monotone nondecreasing function, which has the general appearance of Figure 6.

Example 2: Determination of *F(t)* from an impulse response

An impulse response measurement was performed on a process system, and the idealized response shown in Figure 7 was obtained. Determine the cumulative age distribution for the system.

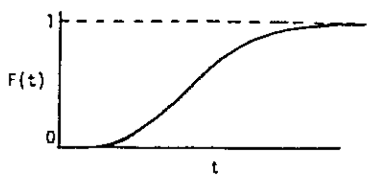


Figure 6.

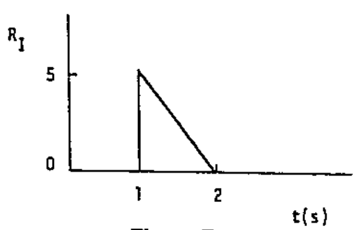


Figure 7.

Solution:

$$R_I(t) = 5(2-t) \quad 1 \leqq t \leqq 2$$
$$= 0 \qquad \text{elsewhere}$$

$$\int_0^\infty R_I\,dt = (0.5)(5)(1) = 2.5 \text{ s}$$

$$E(t) = \frac{R_I}{\int_0^\infty R_I\,dt} = 2(2-t) \quad 1 \leqq t \leqq 2$$
$$= 0 \qquad \text{elsewhere}$$

$$F(t) = \int_0^t 0dt = 0 \quad \text{for } t \leqq 1$$
$$= 0 + \int_1^t E(t')dt' = [4t' - (t')^2]_1^t$$
$$= 4t - t^2 - 3 \quad \text{for } 1 \leqq t \leqq 2$$
$$= F(2) + \int_2^t 0dt = 1 \quad \text{for } t \geqq 2$$

This is shown in Figure 8.

Determination of *F(t)* from a positive or negative tracer step response

Let us again consider a tracer response experiment, only now suppose that instead of injecting a tracer impulse, one imposes a step input by switching at ($t = 0$) from a feed of pure carrier fluid to a fluid containing a tracer at a concentration c_o (g/cm^3). If the tracer concentration $c(t)$ was monitored at the outlet, the response might appear as shown in Figure 9 (Note that if the tracer is not lost in the reactor due to irreversible adsorption, reaction, or activity decay, the response curve asymptotes to the value of the inlet tracer concentration c_o).

Our object is to determine the fraction of the outflow emerging at time t with a residence time less than t; that is, the fraction that entered the reactor after the switch to the tracer feed was

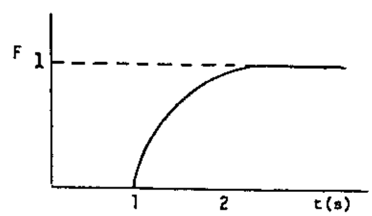


Figure 8.

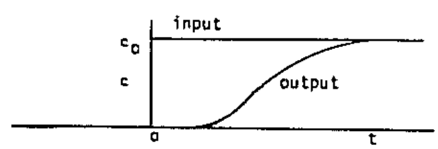


Figure 9.

performed. Let us first consider a time interval from t to $(t+dt)$.

a) Mass of tracer entering in dt:

$$m_a=q\left(\frac{\text{cm}^3}{\text{s}}\right)c_o\left(\frac{\text{g}}{\text{cm}^3}\right)dt\ (\text{s})$$

b) Total mass of fluid entering in dt:

$$m_b=q\left(\frac{\text{cm}^3}{\text{s}}\right)\rho\left(\frac{\text{g}}{\text{cm}^3}\right)dt\ (\text{s})$$

where ρ is the process fluid density.

Next, consider the outflow in a time interval from t to $(t+dt)$.

c) Tracer in outflow:

$$m_c=q\left(\frac{\text{cm}^3}{\text{s}}\right)c\left(\frac{\text{g}}{\text{cm}^3}\right)dt(s)$$

As noted, the tracer must have a residence time of t or less. It is also apparent that any carrier fluid that entered at the same time as the tracer must also have a residence time less than t; moreover, if the tracer and carrier have the same residence time distribution (which, one assumes here they do), one may write

$$\frac{\left(\begin{array}{l}\text{total fluid in outflow with}\\ \text{residence time}<t\end{array}\right)}{(\text{tracer in outflow})}=\frac{(\text{total fluid entering})}{(\text{tracer entering})}$$

from which, one obtains

d) Mass of fluid in outflow residence time less than t:

$$m_d=m_c\frac{m_b}{m_a}=qc\frac{\rho}{c_o}dt$$

e) Total mass of fluid in outflow:

$$m_e=q\left(\frac{\text{cm}^3}{\text{s}}\right)\rho\left(\frac{\text{g}}{\text{cm}^3}\right)dt\ (\text{s})$$

f)

$$F(t)=\frac{\left(\begin{array}{l}\text{Mass of fluid in outflow with}\\ \text{residence time}<t\end{array}\right)}{(\text{Total mass of fluid in outflow})}=\frac{m_d}{m_e} \qquad (10)$$

$$\Downarrow$$

$$F(t)=c/c_o$$

Finally, suppose that instead of measuring the tracer concentration c directly, a signal R_s proportional to it was measured, so that $c=kR_s$ (and $c_o=kR_{so}$). Substituting for c and c_o in Equation 10, the proportionality constant k cancels, leaving us with the result

$$F(t)=\frac{R_s(t)}{R_{so}} \qquad (11)$$

Thus, one may determine the cumulative age distribution $F(t)$ from a measured step response $R_s(t)$, simply by normalizing the response by its asymptotic value R_{so}.

Sometimes it is more convenient to switch off the flow of a tracer at a given instant; i.e., to impose a *negative step input*, as in Figure 10. It is not difficult to show that the F curve may be obtained from such a response as

$$F(t)=1-\frac{R_{-s}(t)}{R_{-so}} \qquad (12)$$

Once $F(t)$ is known, the residence time distribution $E(t)$ may be calculated from Equation 9

$$E(t)=dF/dt \qquad (9)$$

as the slope of the F curve. To perform this calculation requires graphical or numerical differentiation of a tracer response curve; this is usually a highly inaccurate procedure, and it is therefore preferable to determine $E(t)$ directly from an impulse response if at all possible.

The mean residence time can be determined from a step response, without first having to calculate $E(t)$, using the relationship shown in Figure 11

$$\bar{t}_E=\int_o^\infty [1-F(t)]dt \qquad (13)$$

Try to derive Equation 13 from Equations 5 and 9.

Note: In some references, $F(t)$ is defined as the unit step response, or the response of a step input normalized by its asymptotic value, and another function is defined as the cumulative age distribution. The two are equivalent, as long as the six conditions stated at the beginning of the previous section are satisfied.

Example 3: Step Response Analysis

Determine $F(t)$, $\bar{t}$, and $E(t)$ from the step response in Figure 12.

Solution:

$$R_{so}=10 \Rightarrow F(t)=\frac{R_s}{R_{so}}=0,\ t\leqq 2$$

$$=t-2,\ 2\leqq t\leqq 3$$

$$=1,\ t>3$$

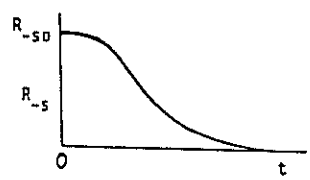


Figure 10.

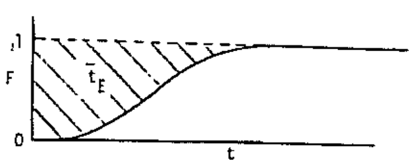


Figure 11.

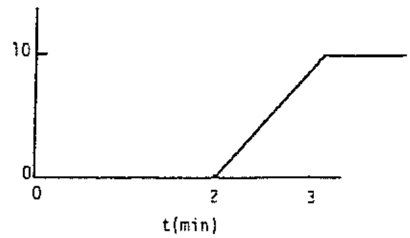


Figure 12.

See Figure 13a, where

$\bar{t} = \bar{t}_E =$ shaded area.

$= (1)(2) + (0.5)(1)(3-2) = 2.5$ min

$E(t) = dF/dt = 0 \quad t < 2$

$= 1 \quad 2 \leqq t \leqq 3$

$= 0 \quad t > 3$

See Figure 13b.

REDUCED TIME

A reduced (dimensionless) time is often used so that systems of different sizes may be compared on the same basis. Here let us assume that the true volume of the system and the throughput rate, and hence the nominal mean residence time, $\bar{t} = (V/q)$ are known. The reduced (dimensionless) time is defined as

$$\theta = t/\bar{t} \tag{14}$$

The age density $E(\theta)$ and cumulative age distribution $F(\theta)$ are defined as before: $E(\theta)d\theta$ is the fraction of emerging fluid elements which were in the system for a reduced time interval between θ and $(\theta + d\theta)$, and $F(\theta)$ is the fraction with reduced residence times less than θ.

To convert a function of real time $f(t)$ to the corresponding function of reduced time $f(\theta)$ the following rules should be followed:

a) If $f(t)$ contains units of $(\text{time}),^{-1}$ as does the function $E(t)$, then

$f(t)dt = f(\theta)d\theta$

since the fraction with age between t and $(t+dt)$ is numerically equal to the fraction with reduced age between θ and $(\theta + d\theta)$. Hence,

$$f(\theta) = f(t)\frac{dt}{d\theta} = \bar{t}f(t) \tag{15}$$

In particular:

$$E(\theta) = \bar{t}E(t) \tag{16}$$

Observe that $E(\theta)$ is dimensionless [unlike $E(t)$, which has units of inverse time].

b) If $f(t)$ does not contain units of time, then:

$f(\theta) = F(t)$

In particular:

$$F(\theta) = F(t) \tag{17}$$

$E(\theta)$ and $F(\theta)$ are related simply as follows:

$$E(\theta) = dF(\theta)/d\theta \tag{18}$$

$$F(\theta) = \int_o^\theta E(\theta)d\theta \tag{19}$$

Example 4: Evaluation of $E(\theta)$ and $F(\theta)$

A radiotracer impulse is injected at the inlet of a reactor, and the response at the outlet is measured. The count rate R (counts/s), after corrections for background and decay are applied as shown in Figure 14a, where the reactor volume is 20 liters, and the throughput rate is 2 L/min. Determine the density function $E(\theta)$.

Solution:

First determine $E(t)$ using Equation 4.

$$E(t)\ (\text{min}^{-1}) = \frac{R(t)}{\int_o^\infty R(t)dt}$$

Now, from Equation 16, $E(\theta) = \bar{t}E(t)$, and $\bar{t} = 20(1)/(2(\text{L/min}) = 10$ min. Combining these results, obtains

$$E(\theta) = \bar{t}E(t) = \frac{10R}{\int_o R(t)dt}$$

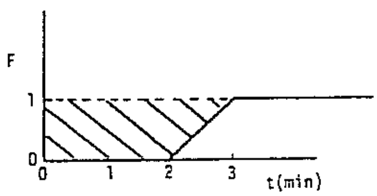


Figure 13a.

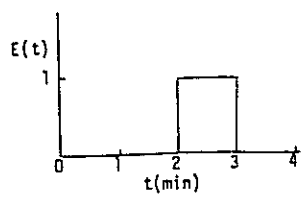


Figure 13b.

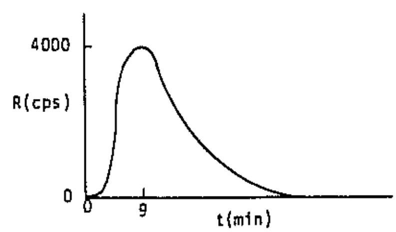


Figure 14a.

The area under the $R(t)$ curve may be calculated by graphical or numerical integration. Suppose the result is

$$\int_0^{\infty} R(t)dt = 25{,}000 \text{ cps} \cdot \text{min}$$

Then,

$$E(\theta) = \frac{10R}{25{,}000} = 4.0 \times 10^{-3} R$$

The value of $E(\theta)$ at the peak maximum and the corresponding reduced time are

$$E_{max} = 4.0 \times 10^{-3} R_{max} = 16$$

$$\theta_{max} = t_{max} / \bar{t} = 9 \text{ min}/10 \text{ min} = 0.9$$

The curve might appear as shown in Figure 14b.

DEVIATION FROM IDEAL FLOW PATTERNS, STAGNANT ZONES, BYPASSING, INTERNAL RECIRCULATION

Deviation from ideal flow patterns is most often determined by examining the shape of the $E(\theta)$ curve, since this function is readily obtainable from impulse tracer responses. $E(\theta)$ curves for systems with various degrees of axial mixing are shown in Figures 15a-15d. The shape of the E curve may also suggest the existence of stagnant zones, bypassing and internal recycling, as illustrated in Figure 16. However, the E-curve does not necessarily reveal the occurrence of these phenomena; for example, a unimodal (one peak) E-curve may still be obtained in systems with bypassing and/or recycling.

In Module E4.5, it was shown that the stagnant volume fraction of a process unit may be obtained from an impulse response test in the following way. Suppose the impulse response appears as in Figure 17. Further suppose that the true reactor volume V and the volumetric flow rate through the reactor q (and therefore the true mean residence time $\bar{t} = V/q$) are known. Let V_e be the effective volume of the reactor—the total volume minus the stagnant volume—and say that $\bar{t}_E = V_e/q$ is the apparent mean residence time. The percentage of the reactor which is stagnant is

$$PS = \frac{V - V_e}{V} \times 100\% = \frac{\bar{t} - \bar{t}_E}{\bar{t}} \times 100\% \qquad (20)$$

The question remains, how does one determine $\bar{t}_E$?

One may say that the portion of the response excluding the tail (i.e. up to the dashed line of the above plot) is essentially the impulse response of the active portion of the reactor. Hence, one eliminates (*truncates*) the tail, and substitutes the remainder of the response into Equation 6 to calculate $\bar{t}_E$. Once $\bar{t}_E$

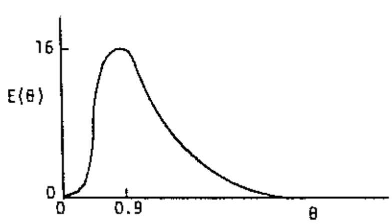


Figure 14b.

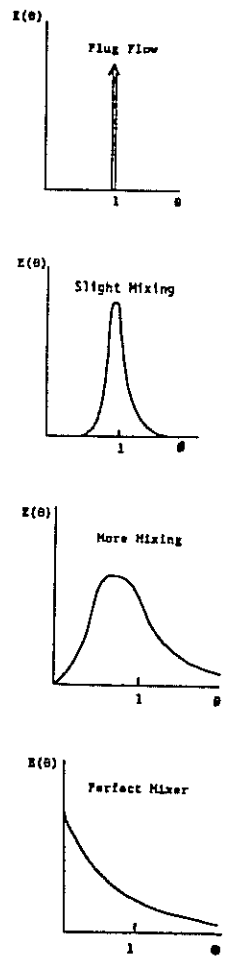


Figure 15 a-d.

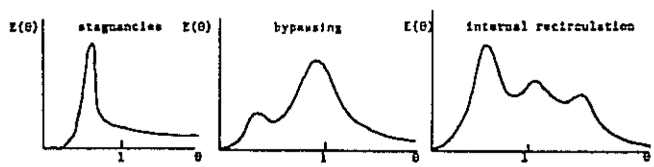


Figure 16.

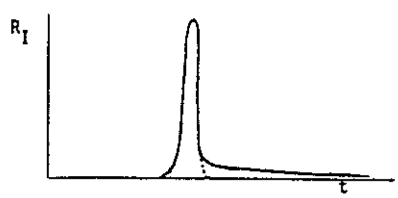


Figure 17.

is known, the percentage stagnancy may be determined from Equation 20.

Example 5: Detection of Stagnancy

A tracer is injected at the inlet of an 1100 liter process unit, through which 340 L/min are flowing. The mean residence time calculated from the truncated tracer response is $\bar{t}_E = 2.5$ min. Estimate the percentage of the reactor volume which is stagnant.

Solution:

$$\bar{t} = V/q = (1100\ \text{L})/(340\ \text{L/min}) = 3.24\ \text{min}$$

$$PS = \frac{3.24 - 2.5}{3.24} \times 100\% = 22.8\%$$

Therefore, only about 77% of the reactor volume is being utilized effectively. Modification of the process unit design to improve mixing should be considered.

Considerable approximation is necessarily involved in stagnancy calculations: it is impossible to know exactly where to truncate the response, and more fundamentally, the "volume of the stagnant zone" is a fictional quantity to begin with. However, the engineer is only interested in knowing whether 60% or 80% of 100% of his reactor is being used effectively (whether it is 60% or 61% is of no practical concern), so that the approximations do not represent a real drawback to the method.

Example 6: Age Distribution Functions From Discrete Tracer Data in a Partially Stagnant System

The results of an impulse response experiment are presented in Table 1. The concentration of the tracer was monitored at one minute intervals at the outlet following an injection of 3800g of tracer. The flow rate through the reactor was maintained at 100(L/min) and the reactor volume is 800 liters. Find $E(t)$ and $F(t)$ for this vessel.

Solution:

From Figure 18, one can see that the tracer impulse response has a prolonged tail and therefore some stagnancy exists in the system. Note that with discrete

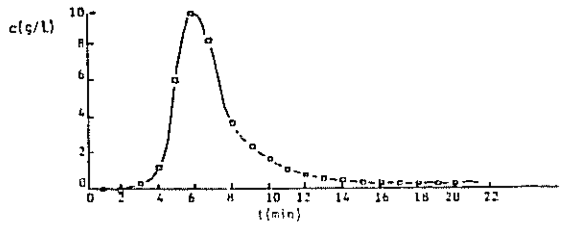


Figure 18.

data, one cannot be certain about the exact location of the peak.

First, let us determine whether the tracer material balance is satisfied (Equation 3):

$$\frac{m_i}{q} = \int_0^\infty c(t)dt$$

Given, is that $m_i/q = 38$(g · min)/L. The integral on the right may be calculated by Simpson's rule:

$$\int_0^\infty c(t)dt \approx \frac{\Delta t}{3}[c_o + 4c_1 + 2c_2 + 4c_3 + \ldots 4c_{n-1} + c_n]$$

$$= 36.47\ \frac{\text{g} \cdot \text{min}}{\text{L}}$$

The basic material balance is thus satisfied within 4%, and the determined area under the curve could be used directly for normalization and evaluation of the $E(t)$ curve. However, the contribution of the unmeasured tail of the tracer response curve to the total mass balance is often much larger, and the tail has to be approximated in some manner. Although this is not necessary in our example, let us use this opportunity to illustrate the procedure.

A commonly used method is to fit the data in the tail with an exponential function, $A\ \exp(-kt)$. The data past the peak are plotted versus time on a semilog plot, as shown in Figure 19. The linearity of the plot confirms the exponential functionality of the tail; the function parameters are $k = 0.23$ (min^{-1}) and $A = 12.55$ (g/L).

Now calculate the area under the curve using

Table 1.

t(min)	c(g/l)	t(min)	c(g/L)	t(min)	c(g/L)	t(min)	c(g/L)
1	0.0	6	10.0	11	1.0	16	0.3
2	0.0	7	8.0	12	0.8	17	0.3
3	0.2	8	3.5	13	0.6	18	0.2
4	1.0	9	2.2	14	0.5	19	(0.15)
5	6.0	10	1.5	15	0.4	20	(0.10)
						21	(0.10)

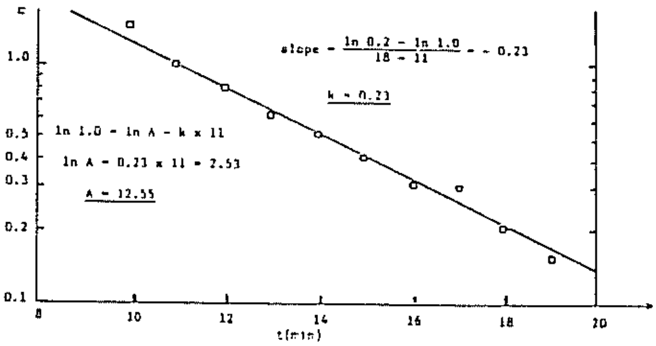


Figure 19.

Simpson's rule:

$$\int_o^\infty c(t)dt \simeq \frac{\Delta t}{3}[c_1+4c_2+2c_3+\ldots 4c_{10}+c_{11}]$$

$$+\int_{11}^\infty Ae^{-kt}dt = 32.60+4.34=36.94\ \frac{\text{g}\cdot\text{min}}{\text{L}}$$

Now, by dividing each value of c in Table 1 by 36.94, obtain age density $E(t)$. The apparent mean residence time $\bar{t}_E$ can then be found as:

$$\bar{t}_E=\int_o^\infty tE(t)dt$$

$$=\frac{\Delta t}{3}[t_1E(t_1)+4t_2E(t_2)+2t_3E(t_3)+\ldots+t_{11}E(t_{11})]$$

$$+\int_{..}^\infty Ate^{-kt}dt=7.5\text{ min}$$

The nominal mean residence time is $V/q=8$ min, which implies that about 6% of the volume of the vessel may be considered stagnant.

EXTENSION TO MULTIPHASE SYSTEMS

Many of the reactors encountered in practice involve heterogeneous systems with two or more phases, such as fluidized and moving bed reactors, gas-liquid packed or bubble column contactors, etc. The extension of the methods described in this module to such systems is straightforward.

Let us consider the two-phase system, shown in Figure 20. Phase II is stagnant while Phase I flows through the system with flow rate q. Suppose at $t=o$ one injects a quantity of tracer 1, which remains confined to Phase 1, and that $R_1(t)$ is the measured

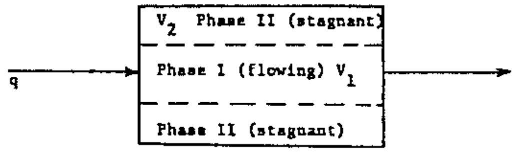


Figure 20.

response. From Equation 6,

$$\bar{t}_1=\frac{V_1}{q}=\frac{\int_o^\infty tR_1(t)dt}{\int_o^\infty R_1(t)dt} \tag{21}$$

Now an impulse of another tracer which distributes itself between both phases is injected, with a partition coefficient K:

$$K=\frac{c_{2e}^{\text{II}}}{c_{2e}^{\text{I}}} \tag{22}$$

where C_{2e}^{I} is the equilibrium concentration of tracer 2 in Phase I and C_{2e}^{II} is that in Phase II. Then, if it can be assumed that the equilibrium distribution between the two phases is established very rapidly, the following expression can be written for the mean residence time of tracer 2:

$$\frac{V_1+KV_2}{q}=\frac{\int_o^\infty tR_2(t)dt}{\int_o^\infty R_2(t)dt} \tag{23}$$

This provides a useful way of determining effective volumes in multiphase reactors. Note that the right-hand sides of Equations 21 and Equation 23 are the means of density functions: $E_1(t)$ is clearly the differential RTD for the flowing phase—how would one interpret $E_2(t)$?

NOMENCLATURE

c	=	tracer concentration in the outflow
c_o	=	inlet tracer concentration for step inputs
E	=	exit age (residence time) density function
F	=	residence time distribution (cumulative age distribution)
f	=	probability density function
K	=	partition coefficient
m	=	fluid mass
m_i	=	mass of tracer injected in an impulse injection
p_S	=	percentage of stagnant reactor volume
q	=	volumetric flow rate
R_I	=	impulse response
R_s	=	step response
R_{-s}	=	step-down response
t	=	time
$\bar{t}_E$	=	first moment of the exit age density function and mean residence time
$\bar{t}$	=	mean residence time
V	=	reactor volume
V_e	=	effective (active) reactor volume

Greek Letters

θ	=	dimensionless time
ρ	=	fluid density

SUGGESTED COMPLEMENTARY READING

1. Levenspiel, O., "Chemical Reaction Engineering," 2nd Edition, Chapter 9, John Wiley & Sons, New York (1972).

STUDY PROBLEMS

1. What is the physical significance of the function $E(t)$ for a flow reactor? (You may express your answer in terms of $E(t)dt$.) What about $F(t)$?

2. Explain how to determine $E(t)$ for a system from a measured tracer impulse response $R_I(t)$. How would you estimate the effective mean residence time from $E(t)$?

3. Explain how to determine $F(t)$ for a system from a measured tracer step response. How could one determine $E(t)$ from $F(t)$?

4. A hypothetical age density function is shown in Figure 21.
   a) Does the function satisfy the three conditions required of an E function?
   b) What fraction of the emerging fluid was in the reactor less than 1 minute? Between 1 minute and 2 minutes? Between 1 minute and 3 minutes?

5. A hypothetical cumulative age distribution is shown in Figure 22.
   a) What fraction of the emerging fluid was in the reactor for 15 minutes or less.
   b) Sketch the E curve for this reactor.

6. Under what conditions would you expect the mean of the residence time density,

$$\bar{t}_E = \int_0^\infty tE(t)dt$$

calculated from a measured impulse response, to differ from the nominal mean residence time V/q?

7. The residence time densities in Figure 23 were obtained from impulse response measurements on different systems. The systems for which they were obtained are described below. Match the responses to the systems.
   a) A tubular reactor, close to ideal plug flow.
   b) A well-mixed continuous stirred tank reactor.
   c) A tubular reactor containing an orifice, on either side of which the fluid is relatively stagnant.
   d) A poorly packed reactor in which a channel has formed, through which a portion of the fluid passes much more rapidly than the bulk of the fluid.
   e) A catalytic reactor in which a fraction of the outlet stream is recycled back to join the feed stream.

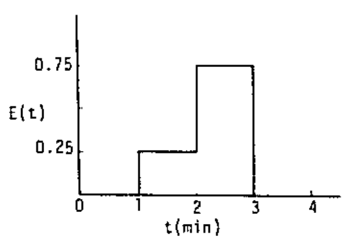


Figure 21.

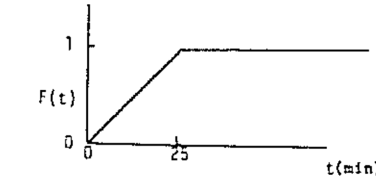


Figure 22.

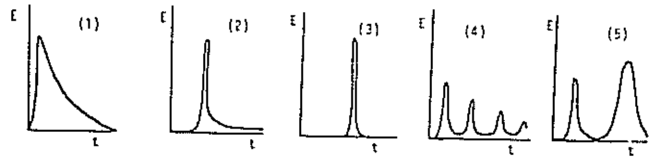
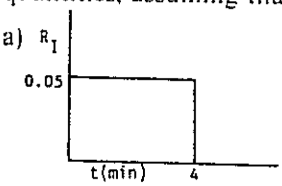


Figure 23.

HOMEWORK PROBLEMS

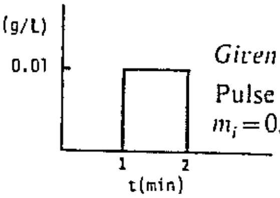
1. The following frames show measured impulse responses. For each one, determine and sketch the required distributions and calculate the requested quantities, assuming that $\bar{t}_E = \bar{t}$.

a)



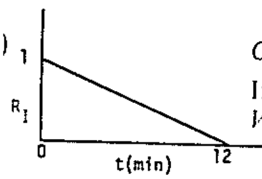
Given	*Required*
Pulse Input	V, $\bar{t}$, $E(t)$
	$F(t)$
$q = 5$ L/min	

b)



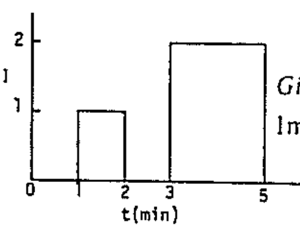
Given	*Required*
Pulse Input	q, V, $E(t)$, $E(\theta)$
$m_i = 0.050_g$	

c)



Given	*Required*
Impulse input	$E(t)$, q
$V = 500$ L	

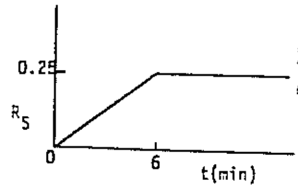
d)



Given	*Required*
Impulse input	$\bar{t}$, $E(t)$, $F(t)$

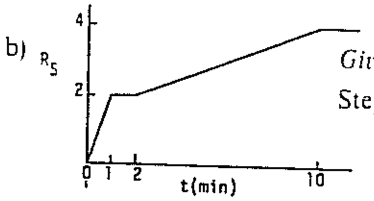
2. The following frames show measured step responses. For each one, determine and sketch the required distributions and calculate the requested quantities, assuming that $\bar{t}_E = \bar{t}$.

a)



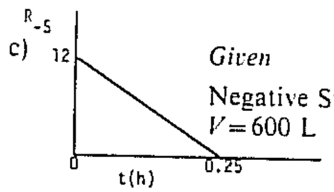
Given	*Required*
Step input $q = 4$ L/min	$F(t)$, $E(t)$, V

b)



Given	*Required*
Step input	$F(t)$, $E(t)$, $\bar{t}$

c)



Given	*Required*
Negative Step Input $V = 600$ L	$F(t)$, $E(t)$, $\bar{t}$, q

3. Two grams of tracer are injected instantaneously into a flow reactor and the exit tracer concentration is monitored and shown in Figure 24. The flow rate is known to be 1.0 (L/min).

   a) Is the tracer material balance equation satisfied?
   b) Calculate the active volume of the system if the total volume is 3 liters, and the percentage of the volume that is stagnant.

4. A packed column 15 m high with a $1.0 m^2$ cross section ($\epsilon = 0.5$) is used for gas-liquid contacting. Gas flows at $0.5 \ m^3/s$ through the unit and liquid flows at $0.05 \ m^3/s$. We would like to know the volume fraction occupied by flowing gas, free flowing liquid and stagnant liquid trapped in the packing. A pulse of nonvolatile tracer is introduced into the entering liquid, and a step input of noncondensable tracer is injected at the gas inlet. The tracer concentrations are measured at the liquid and gas outlets. Using the data given in Figures 25 and 26, find the desired volume fractions, and sketch the gas and liquid residence time distributions.

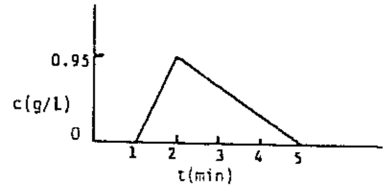


Figure 24.

5. Table 2 shows the impulse response obtained in a 10 liter liquid-phase reactor. Determine $\bar{t}(=\bar{t}_E)$ by numerical integration, and then generate plots of $E(t)$ and $F(t)$ versus t. Use the trapezoidal rule for integration.

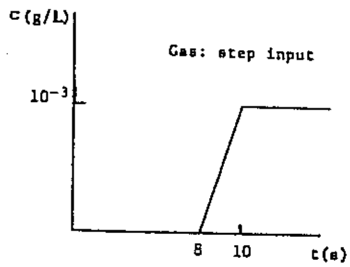


Figure 25.

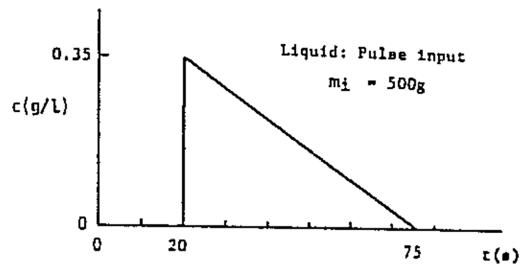


Figure 26.

Table 2.

t(min)	0	1	2	3	4	5	6	7	8	9	10
c(g/L)	0	0	0.1	0.2	1.2	7.0	12.0	9.0	7.0	5.8	5.0
t(min)	15	20	25	30	45	60	75	90	120		
c(g/L)	3.5	2.8	2.3	1.9	1.0	0.5	0.3	(0.1)	(0)		

SOLUTIONS TO THE STUDY PROBLEMS

1. $E(t)dt$ is the fraction of the emerging fluid which was in the reactor for a time between t and $(t + dt)$. $F(t)$ is the fraction which was in the reactor for a time less than t.

2. Integrate the response graphically or numerically to determine the area under the curve

$$\int_0^\infty R_I(t)dt$$

Then calculate the E function as

$$E(t) = \frac{R_I(t)}{\int_0^\infty R_I(t)dt}$$

and determine $\bar{t}$ from Eq. (5).

3. Use Eq.(16) to determine $F(t)$ from a positive step response, or Eq.(17) to determine F from a negative step response. $E(t)$ can be calculated as the slope of the $F(t)$ curve.

4. (a) $E(t)=0$ for $t<0$, $E(t)\geq 0$ for $t\geq 0$, and

$$\int_0^\infty E(t)dt = 0.25(2-1)+0.75(3-2)=1\text{, therefore, } \underline{\text{yes}}.$$

(b) $\boxed{\text{None.}}$

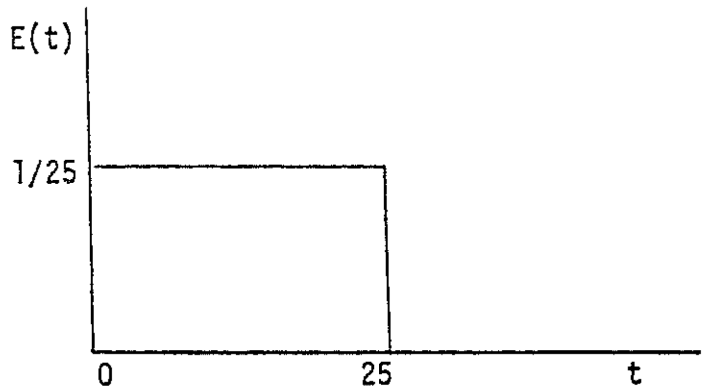
$$\int_1^2 E(t)dt = \boxed{0.25}\qquad \int_1^3 E(t)dt = \boxed{1.0}$$

5. (a) $F(t) = t/25,\ t\leq 25$

$\qquad = 1.0 \quad t>25$

Fraction $\leq 15 = F(15) = 15/25 = \boxed{0.6}$

(b)



6. If a significant portion of the reactor volume is stagnant, then $\bar{t} \neq \bar{t}_E$.

7. 1b, 2c, 3a, 4e, 5d