2. CHARACTERIZATION OF MACROMIXING

2.1 Residence Time Distributions, What are they?

In describing a flow pattern in any flow system, reactors in particular, since the hydrodynamic equations of flow are too complex to solve, it is useful to at least provide the information on what is the distribution of residence times for the outflow. Here by residence time we mean the time that a fluid element (particle) spends within the boundaries of the system (reactor). We will first define all the functions that are customarily used to characterize the flow pattern.

2.1.1 Exit Age Density Function, $E(t)$

We define a probability density function or exit age density function by

\[
E(t) \, dt = \left( \frac{\text{fraction of the outflow that has resided\}}{\text{in the system between time } t \text{ and } t + dt} \right)
\]

Clearly then $E(t)$ has units of (time\(^{-1}\)).

The key concepts associated with the above are:

1. The flowing fluid contains entities that are conserved. These entities may be molecules, atoms, particles, etc. and from now on we will call these conserved quantities fluid elements.
2. Every fluid element has some original entry point and final departure point from the system.
3. The system consists of a volume in a three dimensional space and there is no ambiguity with regard to its boundaries.
4. Fluid elements have zero age as they enter and acquire age equal to the time spent in the system. Aging stops if the fluid element leaves the system but resumes if the same element returns into the system and stops completely when the element leaves never to return again. At that point its age becomes the residence time of the element in the outflow.

The rules for a probability density function (p.d.f.) require that:

\[
E(t) \geq 0 \text{ on } t \in [0, \infty) \tag{2}
\]

\[
\int_0^\infty E(t) \, dt = 1 \tag{3}
\]

Equation (2) simply reminds us that fractions of the outflow of any residence time must be non-negative and that residence time can take only positive values. Equation (3) requires that the sum of all fractions be unity.
2.1.2 Residence Time Distribution, \( F(t) \)

The RTD, or residence time distribution, can now be defined by

\[
F(t) = \left( \text{fraction of the outflow of residence time less than } t \right) = \int_0^t E(t) \, dt
\]

and is obtained by summing all the fractions of the outflow between residence time of 0 and \( t \). In terms of probability theory, \( F(t) \) is the probability that the fluid element of the outflow has residence time less than \( t \).

2.1.3 Washout Function, \( W(t) \)

The so-called washout function, \( W(t) \), is the probability that the fluid element in the outflow has residence time larger than \( t \); it is the fraction of the outflow of residence times larger than \( t \).

\[
W(t) = 1 - F(t) = \int_t^\infty E(\tau) \, d\tau
\]

The functions defined so far (i.e. \( E(t) \), \( F(t) \), \( W(t) \)) are based on the fluid elements of the outflow as their sample space (population) and characterize the outflow. (How to determine these is a question that we will address later).

2.1.4 Internal Age Density Function, \( I(t) \)

Let us now consider the fluid elements within the system at some actual time \( t_a = 0 \) and consider how they are distributed in their ages, the age of an element being the time that elapsed since its entry to the system.

Let us define:

\[
I(\alpha) \, d\alpha = \left( \text{fraction of the fluid elements in the reactor that has an age between } \alpha \text{ and } \alpha + d\alpha \right)
\]

where \( I(\alpha) \) is the internal age density function. To relate \( I(\alpha) \) to the functions already defined we can consider the system at time \( \alpha \) and \( \Delta \alpha \) seconds later. Make a mass balance on fluid elements around age \( \alpha \)

\[
\begin{align*}
(\text{Fluid elements in the system of age about } \alpha + \Delta \alpha) & \quad - \\
(\text{Fluid elements in the system of age about } \alpha) & \quad = \\
(\text{Fluid elements fed to the system of age } \alpha \text{ to } \alpha + \Delta \alpha \text{ during time } \Delta \alpha) & \quad - \\
(\text{Fluid elements leaving the system of age } \alpha \text{ to } \alpha + \Delta \alpha \text{ during time } \Delta \alpha)
\end{align*}
\]

Since elements of any age other than zero cannot be introduced to the system (since age can only be acquired by residing in the system) the first term on the right hand side is zero. The other terms, using the definitions introduced earlier, can be expressed as follows:
\[ VI(\alpha + \Delta \alpha) \Delta \alpha - VI(\alpha) \Delta \alpha = -Q \Delta \alpha E(\tilde{\alpha}) \Delta \alpha \]  
\[ \frac{\partial}{\partial \alpha} \int_{\alpha}^{\alpha + \Delta \alpha} E(\alpha) d\alpha \]  

(7a)

where \( \alpha + \Delta \alpha \geq \tilde{\alpha} \geq \alpha \).

The limit process gives

\[ \lim_{\Delta \alpha \to 0} \frac{I(\alpha + \Delta \alpha) - I(\alpha)}{\Delta \alpha} = -\frac{Q}{V} \lim_{\Delta \alpha \to 0} E(\tilde{\alpha}) \]

\[ \frac{dI}{d\alpha} = -\frac{1}{t} E(\alpha) = -\frac{1}{t} \frac{dF}{d\alpha} = \frac{1}{t} \frac{dW}{d\alpha} \]  

(8)

The last two equalities in eq. (8) are obtained using the relationship between \( E, F, W \) defined by eqs. (4, 5). We also took the mean residence time to be \( \tilde{t} = V/Q \). The boundary condition required to solve eq. (8) is that at \( \alpha \to \infty \) \( I = 0 \) and \( W = 0, \ F = 1 \) so that

\[ I(\alpha) = \frac{1}{t} \left[ 1 - F(a) \right] = \frac{1}{t} W(\alpha) \]  

(9)

2.1.5 Mean Residence Time and Mean Age

Now it only remains to be established that the mean residence time, which is indeed the mean or first moment of the \( E \) function, is equal to \( V/Q \).

(mean residence time) = \sum (residence time \( t \) of a fluid element) \( \times \) (fraction of the elements of residence time \( t \))

\[ \tilde{t} = \int_{0}^{\infty} t E(t) dt = -\frac{V}{Q} \int_{0}^{\infty} \frac{dI}{dt} dt = \frac{V}{Q} \left[ -tI \bigg|_{0}^{\infty} + \int_{0}^{\infty} I dt \right] = \frac{V}{Q} \]  

(10)

Using eq (8) a proof given above can readily be established. Indeed \( \tilde{t} = V/Q \).

From the definition of the RTD it follows that \( \lim_{t \to \infty} I(t) = 0, \lim_{t \to \infty} F(t) = 1 \)

The mean age of the fluid in the vessel by definition is:

\[ \tilde{t}_{i} = \int_{0}^{\infty} t I(t) dt = \frac{1}{t} \int_{0}^{\infty} \int_{t}^{\infty} E(\tau) d\tau d\tau = \frac{1}{t} \int_{0}^{\infty} E(\tau) \int_{0}^{\infty} t dt = \frac{1}{2t} \int_{0}^{\infty} \tau^{2} E(\tau) d\tau \]  

(11)

We will see later that we can put to good use the moments of the \( E \) curve defined by:

\[ \mu_{n} = \int_{0}^{\infty} t^{n} E(t) dt \]  

(12)

We have already seen that \( \mu_{0} = 1, \mu_{1} = \tilde{t} \) and, therefore, in terms of the moments of the E-curve the mean age is
\[ t_I = \frac{\mu_2}{2\bar{t}} = \frac{\mu_2}{2\mu_1} \]  

It is customary to use the variance, \( \sigma^2 \), or the second central moment, which measures the spread of the curve. The central moments are defined by:

\[ \mu_{nc} = \int_0^\infty (t - \mu_1)^n E(t) \, dt \]  

so that

\[ \mu_2 = \mu_2 - \mu_1^2 = \mu_2 - \bar{t}^2 = \sigma^2 \]  

Then:

\[ \bar{t}_I = \frac{\bar{t}}{2} + \frac{\sigma^2}{2\bar{t}} = \frac{\bar{t}}{2} \left[ 1 + \sigma_D^2 \right] \]  

where \( \sigma_D^2 \) is the dimensionless variance, \( \sigma_D^2 = \sigma^2/\bar{t}^2 \). Often we will use \( \bar{\sigma}^2 \) for \( \sigma_D^2 \).

### 2.1.6 Ideal Reactors

We can now ask the question as to what the above density and distribution functions look like for ideal reactors.

For a PFR all elements of the outflow have the same residence time equal to the mean residence time.

\[ E_{PFR}(t) = \delta(t - \bar{t}) \]  

\[ F(t) = H(t - \bar{t}) \]  

\[ W(t) = 1 - H(t - \bar{t}) \]  

\[ I(t) = \frac{1}{\bar{t}} \left[ 1 - H(t - \bar{t}) \right] \]

The mean age in the system is \( \bar{t}_I = \frac{\bar{t}}{2} \) since there is no spread of the \( E \) curve around the mean. Then the mean age is equal to half of the mean residence time.

For a CSTR, the age density function is the same as the residence time (i.e., exit age) density function of the outflow since there is perfect mixing, and the probability of exiting does not depend on the age of the fluid element.

\[ E_{CSTR}(t) = I_{CSTR}(t) \]
Using eq (8) this implies
\[
\frac{dI}{dt} = \frac{1}{\bar{t}} I
\] (18a)

We also know that \( I(t) \) must be a p.d.f. so that
\[
\int_{0}^{\infty} I(t) \, dt = 1
\] (18b)

Equations (18a) and (18b) yield readily:
\[
I_{CSTR}(t) = \frac{1}{\bar{t}} e^{-t/\bar{t}} = E_{CSTR}(t)
\] (19)
\[
F(t) = 1 - e^{-t/\bar{t}} = 1 - W(t)
\] (20)
\[
\bar{t}_{I} = \bar{t}
\] (21)

The mean age of the fluid elements in a perfectly mixed stirred tank is equal to the mean residence time of the exiting fluid. This is to be expected since the assumption of perfect mixing requires that there is no difference between the exit stream and the contents of the vessel.

### 2.1.7 Intensity Function, \( \Lambda(t) \)

The conditional probability density, or the intensity function, \( \Lambda(t) \), is defined as follows:
\[
\Lambda(t) \, dt = \text{(fraction of fluid elements in the system of age between } t \text{ and } t + dt \text{ that will exit during the next time interval } dt \text{).}
\]

\( \Lambda(t) \) can be determined from the previously defined functions by the following procedure:

\[
(\text{Elements in the system that are of age } t \text{ to } t + dt) \times (\text{Fraction of elements of age between } t \text{ and } t + dt \text{ that will exit in next interval } dt) = (\text{Elements in the outflow of residence time between } t \text{ and } t + dt \text{ collected during } dt)
\]

\[
V I(t) \, dt \cdot \Lambda(t) \, dt = (Q \, dt) E(t) \, dt
\] (22)

\[
\Lambda(t) = \frac{E(t)}{\bar{t} I(t)} = \frac{E(t)}{W(t)} = \frac{E(t)}{1 - F(t)}
\] (23)
2.1.8 Dimensionless Representation

It is customary to use dimensional time \( \theta = t/\bar{t} \). Then the set of function defined over the \( \theta \) domain are \( E_\theta, F_\theta, I_\theta, \Lambda_\theta \). Since

\[
\text{(Fraction of the fluid of residence time } t \text{ to } t + dt) = \text{(Fraction of the fluid of residence time } \theta \text{ to } \theta + d\theta) \\
E(t)dt = E_\theta(\theta)d\theta
\]

This implies

\[
E_\theta(\theta) = E(t)\frac{dt}{d\theta} = \bar{t}E(\bar{t} \theta)
\]  

Equation (24) indicates that if in the functional form for \( E(t) \) we substitute \( t = \bar{t}\theta \) and multiply the whole function with the mean residence time, \( \bar{t} \), we obtain the dimensionless \( E_\theta(\theta) \). Equation (24) is a well known relationship from probability and statistics where it is presented as the general rule for an independent variable change in a p.d.f. We are in fact compressing the independent variable by \( 1/\bar{t} \) and, hence, we have to expand the ordinate by \( \bar{t} \) in order to preserve the area under the curve to be unity i.e. \( \int_0^\infty E_\theta(\theta)d\theta = 1 \). Similarly, using well known relations from the theory of distributions we can show that

\[
F_\theta(\theta) = F(\bar{t} \theta) \quad \text{ (25a)} \\
I_\theta(\theta) = \bar{t}I(\bar{t} \theta) \quad \text{ (25b)} \\
W_\theta(\theta) = W(\bar{t} \theta) \quad \text{ (25c)} \\
\Lambda_\theta(\theta) = \bar{t}\Lambda(\bar{t} \theta) \quad \text{ (25d)}
\]

SUMMARY

Review: \( E, I, W, F, \Lambda \) and their inter-relationships

\[
\frac{dI}{dt} = -\frac{1}{\bar{t}}E = \frac{1}{\bar{t}} \frac{dW}{dt} = -\frac{1}{\bar{t}} \frac{dF}{dt}
\]

\[
F = \int_0^t E(t)dt = 1 - W
\]

\[
\Lambda = \frac{E(t)}{\bar{t} I(t)} = \frac{E(t)}{W(t)}
\]
\[
\bar{T} = \frac{V}{Q} = \int_{0}^{\infty} tE(t) \ dt
\]

\[
\mu_n = \int_{0}^{\infty} t^n E(t) \ dt \quad \sigma^2 = \frac{\mu_2 - \mu_1^2}{\mu_1^2}
\]

\[
\text{when} \quad \mu_0 = 1
\]

\[
\bar{T}_i = \int_{0}^{\infty} t I(t) \ dt = \frac{\bar{T}}{2} \left[ 1 + \frac{\sigma^2}{\mu_1} \right] \quad \theta = \frac{t}{\bar{T}}
\]

\[
PFR \Rightarrow E = \delta(t-\bar{T}) \quad CSTR \Rightarrow E(t) = \frac{1}{\bar{T}} e^{-t/\bar{T}} \quad E(t) dt = E(\theta) d\theta
\]

### 2.2 How to Obtain RTDs or Age Density Functions Experimentally

Experimentally we can obtain directly the exit age density function, \( E(t) \), residence time distribution, \( F(t) \), and internal age density function, \( I(t) \), by using tracers. By injecting, for example, a step input of tracer at time \( t = 0 \) at the inlet of the system we can monitor the distribution of residence times of the tracer elements in the outflow. This information can be inferred from some signal measured in the outflow which is proportional to tracer concentration such as light absorption or transmission, reflection, current, voltage, etc. This output signal can be interpreted in terms of the residence times of the tracer only if:

a) The system is closed, i.e., the tracer enters and leaves the system by bulk flow only, i.e., diffusion or dispersion effects are negligible in the inlet and outlet plane.

b) Tracer injection is proportional to flow, i.e., at the inlet boundary tracer injection rate is proportional to the velocity component normal to the boundary at each point of the boundary.

c) The total rate at which the tracer leaves the system is the integral of the product of the velocity times concentration integrated in a vectorial sense over the whole exit boundary.

In addition, the residence time distribution of the tracer will yield the residence time distribution for the carrier fluid, which is what we want, if and only if:

a) the system is at steady state except with respect to (w.r.t.) the tracer concentration;

b) the system is linear, i.e., the response curve is proportional to the mass of tracer injected;

c) the tracer is perfect, i.e., behaves almost identically to the carrier fluid;

d) there is a single flowing phase and single homogeneous phase within the system;

e) the system has one inlet and outlet;

Under the above set of conditions we can interpret the response to a step-up tracer injection to directly obtain the \( F \) curve for the carrier fluid. Suppose we had no tracer in the inlet stream (white fluid), and
then at time $t = 0$ we started injecting the tracer (red fluid) at such a rate that its concentration at the inlet is $C_o$. The quantity of tracer elements injected per unit time is $Q C_o$. For each tracer element there are $K$ carrier fluid elements that, if tracer is perfect, behave identically to the red elements of the tracer. Hence, $K Q C_o$ white fluid elements are entering the system per unit time. We monitor at the outlet tracer concentration $C$. At each time $t$ all the red elements that we see at the outlet, $QC$, have residence times less than $t$ because they only could have entered the system between time 0 (when tracer injection started) and time $t$. For each red element of residence time $t$ there must be $K$ white elements of carrier fluid that have the same residence time since they entered with these red elements and have behaved in the same manner. By definition

$$F(t) = \frac{\text{(fraction of the outflow of residence times less than } t)}{\text{(total elements of the outflow)}}$$

$$= \frac{\text{(tracer elements) + (carrier fluid elements of the same residence time)}}{\text{(total elements of the outflow)}}$$

$$= \frac{QC + KQC}{(1 + K)QC_o}$$

The denominator above results from a simple mass balance. Per unit time we feed into the system $Q C_o$ tracer elements and $K Q C_o$ carrier fluid elements. Total rate of input must be equal to the total rate of output which, therefore, is $(1 + K) Q C_o$. Then the RTD of the carrier fluid is given by

$$F(t) = \frac{C(t)}{C_o}$$

(26)

The $E$, $W$, $I$ curves can now be evaluated from the RTD (i.e., the $F$ curve) by previously reported relationships.

The residence time density function, $E(t)$, can also be obtained directly from an impulse tracer injection. During a short time interval $dt$ at $t = 0$ we inject a pulse of $m_T$ of tracer elements (and of course for each tracer element $K$ carrier fluid elements entered). At the outlet we monitor tracer response $C$. During time period $dt$ at time $t$ we collect $QC dt$ tracer elements and $KQC dt$ elements of the carrier fluid of the same residence time. All these elements have residence time between $t$ and $t + dt$ because they entered the system between time 0 and $dt$. By definition:

$$E(t) dt = \frac{\text{(fraction of the outflow of residence time between } t \text{ and } t + dt)}{\text{(total elements collected during } dt)}$$

$$= \frac{\text{elements of the outflow of residence time between } t \text{ & } t + dt \text{ collected during interval } dt}{\text{(total elements collected during } dt)}$$
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(tracer elements in the outflow collected during time $dt$ at $t$) +

$$= \frac{Q \, C \, dt + K \, Q \, C \, dt}{m_T + K \, m_T} \tag{27}$$

Other functions $F$, $I$, $W$ can now be derived from the $E$ curve using previously reported relationships. The total mass balance on tracer in a pulse injection requires that all the tracer injected must eventually emerge, which is the same as requiring that $\int_0^\infty E(t) \, dt = 1$. This formula is used to check the tracer mass balance and ensure that the experiment is executed properly. The formula can also be used (when one is confident that tracer is indeed conserved) to determine the unknown flow rate:

$$Q = \frac{m_T}{\int_0^\infty C(t) \, dt} \tag{28}$$

Whenever the mass balance for the tracer is not properly satisfied the tracer test does not represent a proper way of determining the $E$ curve. Various pitfalls were discussed by Curl, R. and McMillan, M. L. (AIChE J., 12, 819, 1966).

The washout curve, $W(t)$, can of course be obtained from the step-up tracer test by subtracting the $F(t)$ curve from unity, $W = 1 - F$. This produces inaccurate results at large times because of subtraction of numbers of the similar order of magnitude since $\lim_{t \to \infty} F = 1$. Therefore, $W(t)$ can be obtained directly by a step-down tracer test. Imagine that at the end of the step-up test both the inlet and exit tracer concentration are $C_0$. Now at $t = 0$ we start the stop watch and reduce the inlet tracer concentration to 0. Then all the tracer elements appearing at the outflow at time $t$ are older than $t$ since they have entered the system before time 0. Due to linearity and perfect behavior of the tracer, for each tracer element there are $K$ carrier fluid elements of the same residence time. By definition:

$$W(t) = \frac{(1+K)QC}{(1+K)QC_0} \frac{C}{C_0} \tag{29}$$

The area under the washout curve gives the mean residence time:
\[ \bar{I} = \frac{V}{Q} = \int_{0}^{\infty} W(t) \, dt \]  
\[ (30) \]

Based on the previously derived relationships you should be able to prove the above.

The \( I(t) \) curve can be evaluated readily using the step-down tracer test, its integral and eq (31):

\[ I(t) = \int_{0}^{\infty} W(t) \, dt \]
\[ (31) \]

The \( I(t) \) curve is often determined directly in biomedical applications by injecting a pulse of tracer \( m_{\tau_0} \) at time 0, and by monitoring the response of the whole system (not the outflow) which is proportional to the mass of tracer remaining at time \( t \), \( m_\tau \). Then:

\[ I(t) = \frac{m_\tau(t)}{m_{\tau_0}} \]
\[ (32) \]

**Some Other Items of Interest:**

**Perfect tracer** - detectable, yet same behavior as carrier fluid and at infinite dilution.

**Radioactive tracers** - half life \( \gg \bar{I} \) (only exception positron emitters).

**Electrolytes** - conductivity meters (cast epoxy tubular body carbon ring electrodes and female pipe threaded ends with a self balancing bridge working at 1000 Hz to eliminate polarization).

**Dyes** - colorimetric detectors and spectrophotometer may give nonlinear response.
   - thermal conductivity detectors.
   - flame ionization detectors (organics)
   - \( R \) (\( CO_2, SO_2, NH_3 \) in mixture of diatomic gases) two channel design preferred.

## 2.3 How To Derive Age Density Functions

We know what the age density functions for the two ideal reactors (PFR and CSTR) look like. Using these we can derive the age density functions for a generalized compartmental model with time lags. By this we mean that if we have evidence or reason to believe that a real flow system or reactor can be represented by a set of CSTR's (well mixed compartments) and PFR's (time lags) in series or parallel we can readily derive an \( E \) curve for any such combination.

Here, and in later applications, it is very useful to use Laplace transforms defined by
\[ \bar{E}(s) = L\{E(t)\} = \int_0^\infty e^{-st} E(t) \, dt \]  

(33)

Any network of CSTR's and PFR's consists of: elements in parallel, elements in series, split points and mixing points (where points are considered to have no volume). The rules for dealing with these are explained below.

2.3.1 Systems in Parallel

Consider two parallel branches represented above. The top branch contains the fraction \( \beta \) of the total volume of the system and the bottom branch has \( (1-\beta) \) of the total volume. The splitting point \( S \) and mixing point \( M \) have no volume. Let the transfer function (Laplace transform of the unit impulse response and hence the Laplace transform of the residence time density function, \( E \)) of the top branch be \( \bar{E}_1(s) \), if that branch had all the volume of the system and all the flow passed through it. Let \( \bar{E}_2(s) \) be the Laplace transform (LT) of the impulse response of the bottom branch if all the volume was in it and all the flow ran through it. Since only volume \( \beta V \) is in the upper branch and \( \alpha Q \) flow rate passes through it, the LT of the response is \( \bar{E}_1 \left( \frac{\beta}{\alpha} s \right) \) and similarly for the bottom branch \( \bar{E}_2 \left( \frac{1-\beta}{1-\alpha} s \right) \). The overall response is obtained by the weighted average of the two, where at point \( M \) the weighting is accomplished proportionally to flow.

\[ \bar{E}(s) = \alpha \bar{E}_1 \left( \frac{\beta}{\alpha} s \right) + (1-\alpha) \bar{E}_2 \left( \frac{1-\beta}{1-\alpha} s \right) \]  

(34)

This can readily be generalized to \( M \)-branches in parallel

\[ \bar{E}(s) = \sum_{j=1}^{M} \alpha_j \bar{E}_j \left( \frac{\beta_j}{\alpha_j} s \right) \]  

(35)

where \( \alpha_j \) is the fraction of the total flow rate going through branch \( j \) and \( \beta_j \) is the fraction of the total volume of the system that is in branch \( j \).
We build block diagrams for flow pattern representation out of two ideal patterns (plug flow and complete backmixing) or their combinations. We know the \( E_\theta(\theta) \) curves for our building blocks with \( \theta = t / \bar{t} \) where \( \bar{t} \) is the total mean residence time. They are the impulse responses of a PFR and a CSTR. If the building block is a subsystem then the mean residence time is \( \bar{t}_{sub} = \frac{\beta}{\alpha} \bar{t} \) (\( \beta = \) fraction of total system's volume present in subsystem, \( \alpha = \) multiple or fraction of total system's throughput that flows through the subsystem) so that \( \theta_{sub} = \frac{t}{\bar{t}_{sub}} = \frac{\alpha t}{\beta \bar{t}} = \frac{\alpha}{\beta} \theta \). Then the subsystem's dimensionless impulse response is: \( E_\theta \left( \frac{\alpha}{\beta} \theta \right) \).

More generally speaking we are stating that if the dimensionless response of a system with volume \( V \) and flow rate \( Q \) that exhibits a certain flow pattern is \( E_\theta(\theta) \), then the impulse response of the same system when it is a subsystem, i.e. a building block within a larger system) (containing fraction \( \beta \) of the volume of the whole system and with flow rate of \( \alpha Q \) going through it) is given by \( E_\theta \left( \frac{\alpha}{\beta} \theta \right) \).

The dimensional impulse response of the subsystem then is given by

\[
E_\theta(\theta_{sub})d\theta_{sub} = E_{sub}(t)dt
\]  

(36)

When \( \alpha = \beta = 1 \) we get the whole system's response.

\[
E(t) = \frac{1}{\bar{t}} E_\theta \left( \frac{t}{\bar{t}} \right)
\]  

(37)

Thus, by replacing \( \bar{t} \) by \( \beta \bar{t} / \alpha \) we get \( E_{sub}(t) \) from \( E(t) \). Now the previously stated relation for the Laplace transforms follows.

\[
L \{ E(t) \} = \int_0^\infty e^{-st} E(t) dt = \frac{1}{\bar{t}} \int_0^\infty e^{-st} E_\theta \left( \frac{t}{\bar{t}} \right) dt = \overline{E}(s)
\]  

(38)

\[
L \{ E_{sub}(t) \} = \frac{\alpha}{\beta \bar{t}} \int_0^\infty e^{-st} E_\theta \left( \frac{\alpha t}{\beta \bar{t}} \right) dt = \frac{1}{\bar{t}} \int_0^\infty e^{-\left[\frac{\beta}{\alpha}\right] u} E_\theta \left( \frac{u}{\bar{t}} \right) du = \overline{E}_{sub} \left( \frac{\beta}{\alpha} s \right)
\]  

(39)

by replacing \( s \) with \( \frac{\beta}{\alpha} s \) in \( \overline{E}(s) \) we get \( \overline{E}_{sub} \).

Also:

\[
L \{ E_\theta(\theta) \} = \int_0^\infty e^{-s\theta} E_\theta(\theta) d\theta = \overline{E_\theta}(s)
\]  

(40)
\[ L \{E_{\theta_{ab}}(\theta)\} = \int_{0}^{\infty} e^{-s\theta} E_{\theta}(\frac{\alpha}{\beta} \theta) d\theta = \frac{\beta}{\alpha} \int_{0}^{\infty} e^{-\frac{\beta}{\alpha} u} E_{\theta}(du) = \frac{\beta}{\alpha} E_{\theta_{ab}}(\frac{\beta}{\alpha}) \]  

(41)

However the mean of \( E_{\theta_{ab}} \) is not 1 but \( \frac{\beta}{\alpha} \).

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**Example**

1. 2-CSTR's of different volume in two parallel branches:

   ![Diagram of 2-CSTR's](image-url)

   \[ Q_1 + Q_2 = Q \]
   \[ \alpha = \frac{Q_1}{Q} \]
   \[ V_1 + V_2 = V \]
   \[ \beta = \frac{V_1}{V} \]

   Now \( \bar{E}(s) = \alpha \bar{E}_1(\frac{\beta}{s}) + (1-\alpha) \bar{E}_2(\frac{1-\beta}{s}) \)

   where \( \tilde{t}_1 = \frac{\beta}{\alpha} \tilde{t} \), \( \tilde{t}_2 = \frac{(1-\beta)}{(1-\alpha)} \tilde{t} \)

   \[ \bar{E}_1(s) = \bar{E}_2(s) = \frac{1}{1 + \tilde{t}_i s} \]  ;  \( i = 1 \) or 2

   \[ \bar{E}(s) = \alpha \frac{1}{1 + \frac{\beta}{\alpha} \tilde{t} s} + (1-\alpha) \frac{1}{1 + \frac{1-\beta}{\alpha} \tilde{t} s} \]

   \[ E(t) = L^{-1} \{ \bar{E}(s) \} = \frac{\alpha}{\beta \tilde{t}} e^{\frac{\alpha t}{\beta \tilde{t}}} + \frac{(1-\alpha)^2}{(1-\beta) \tilde{t}} e^{\frac{(1-\alpha)t}{(1-\beta) \tilde{t}}} \]

---

### 2.3.2 Systems in Series

Let us now consider a system in series consisting of two elements as shown below.
Let the transfer function of the first one be $\bar{E}_1(s)$ and of the second one $\bar{E}_2(s)$. If the first one contains a fraction $\beta$ of the total volume of the system then the system’s response in the Laplace domain (transfer function) is given by

$$\bar{E}(s) = \bar{E}_1(\beta s) \times \bar{E}_2((1-\beta)s)$$

(42)

In time domain this is:

$$E(t) = \int_0^t \frac{1}{\beta} E_1\left(\frac{\tau}{\beta}\right) \frac{1}{1-\beta} E_2 \left(\frac{t - \tau}{1-\beta}\right) d\tau$$

(43)

This is the well known convolution theorem for linear systems.

The above rule can be readily generalized to $N$ subsystems in series, each containing a fraction $\beta_j$ of the total volume of the system. The overall transfer function is given by

$$\bar{E}(s) = \prod_{j=1}^{i} \bar{E}_j(\beta_j s)$$

(44)

where $\bar{E}_j(s)$ is the Laplace transform of the impulse response of the $j$-th individual subsystem as if it contained the whole volume of the system.

---

**Example:**

Find the $E$-curve of $N$-equal sized CSTRs in series.

We know that for a single stirred tank of volume $V$ and with flow rate $Q$ the impulse response is given by

$$E_1(t) = \frac{1}{t} e^{-\frac{t}{\tau}}$$

so that the transfer function is

$$\bar{E}_1(s) = \frac{1}{1 + \frac{s}{\tau}}$$

where $\tau = V / Q$

For $N$ equal size stirred tanks in series each tank contains $\beta_j = \frac{1}{N}$ fraction of the total volume. Hence

$$\bar{E}_j(\beta s) = \bar{E}_j\left(\frac{s}{N}\right) = \frac{1}{1 + \frac{t}{N}}$$

$$\bar{E}_j(\beta s) = \bar{E}_j\left(\frac{s}{N}\right) = \frac{1}{1 + \frac{t}{N}}$$
The overall transfer function is obtained by eq (44):

\[
\overline{E}(s) = \prod_{j=1}^{N} \frac{1}{1 + \left(\frac{i}{N} \cdot \frac{s}{s}ight)} = \frac{1}{\left(1 + \left(\frac{i}{N} \cdot \frac{s}{s}\right)\right)^{N}}
\]

The overall impulse response then is obtained by inversion of the Laplace transform

\[
E(t) = L^{-1} \left\{ \frac{1}{\left(1 + \left(\frac{i}{N} \cdot \frac{s}{s}\right)\right)^{N}} \right\} = \left(\frac{N}{i}\right)^{N} L^{-1} \left\{ \frac{1}{\left(\frac{s}{s} + \frac{N}{i}\right)^{N}} \right\}
\]

\[
= \left(\frac{N}{i}\right)^{N} \frac{i^{N-1}}{(N-1)!} e^{-Nt/i}
\]

The dimensionless E-curve is

\[
E_{\theta}(\theta) = \dot{E}(\dot{\theta}) = \frac{N^{N}}{(N-1)!} \dot{\theta}^{N-1} e^{-N\theta}
\]

We can now use the above to derive the responses of N-CSTR's of equal size in series, CSTR's and PFR's in parallel and systems with recycle.

In the example on nonideal stirred tank that follows the section on systems with recycle we will show how to determine the parameters of the model from the experimentally determined E-curve and how to use this in assessing reactor performance.
2.3.3 Systems with Recycle

Once you have mastered the derivation of the transfer function for subsystems in series and subsystems in parallel, you should be able to handle systems with recycle. The only new “rule” is the splitting rule where by if you split a stream each of the outgoing streams possesses the same transfer function.

Let us consider a general recycle system depicted below:

Flow rate $Q$ flows through a recycle system (the system within the dashed box is the system with recycle) of total volume $V$. Internally, at point $M$ flow rate $Q$ is joined by recycle flow rate, $RQ$, so that the flow rate of $(R+1)Q$ flows through the forward branch of the system that contains volume $\beta V$. At splitting point $S$, $R, Q$, is recycled through the recycle branch of volume $(1-\beta)\beta$ which flow rate $Q$ leaves the system. The transfer function of the forward branch is $G_1$ (we mean by it $\frac{BV}{(R+1)^2}$). The transfer function of the recycle flow branch is $G_2$, i.e. $\frac{(1-\beta)\beta}{R}$. The transfer function of the total system is $E(s)$.

Applying what we have learned so far, we note that for a normalized impulse injection of $\delta(t)$ the transfer function for the inlet is 1. The mass balance in the Laplace domain yields

$$\left( 1 + R G_2 E \right) G_1 = (R + 1) E$$

This response $(R + 1)E$ is obtained by the product (i.e. convolution in the time domain) of the transfer function for the forward path, $G_1$, and the transfer function for the inlet stream after mixing point $M$. The later is the sum of the transfer function for the fresh inlet stream (i.e. 1) and the product (i.e. convolution in time domain) of the transfer function for the recycle branch, $G_2$, and the transfer function for the exit stream, $E$, multiplied by $R$ due to flow rate being $RQ$.

We can now solve eq (45) for the transfer function of the system $E$:

$$E = \frac{\overline{G_1}}{\overline{R + 1 - R \overline{G_1} \overline{G_2}}}$$

(46a)
Which can also be written as:

\[ \bar{E} = \frac{1}{R+1} \frac{G_1}{1 - \frac{R}{R+1} \overline{G}_1 \overline{G}_2} \]  \hspace{1cm} (46b)

We recall that \( \overline{G}_1 \), \( \overline{G}_2 \) are functions of \((\beta s/R + 1)\) and \((1 - \beta)s/R\), respectively.

To get the impulse response in the time domain, inversion of equation (46a) or (46b) can be attempted using the usual rules for Laplace transform inversion.

Often it is necessary to expand equation 46(b) by binomial theorem to get:

\[ \bar{E} = \frac{1}{R+1} \left( \sum_{n=0}^{\infty} \left( \frac{R}{R+1} \right)^n \right) \overline{G}_1^n \overline{G}_2^n \]

Which can be rearranged to the following form:

\[ \bar{E} = \frac{1}{R} \sum_{n=0}^{\infty} \left( \frac{R}{R+1} \right)^n \overline{G}_1^n \cdot \overline{G}_2^{n-1} \]

(47)

(48)

To obtain the impulse response in the time domain one can now invert the series in equation (48) term by term.

**Example**

Consider a recycle system with volume \( \beta V \) in the forward branch and volume \( (1 - \beta)V \) in the recycle branch as sketch below. Plug flow occurs in both branches so that

\[ \overline{G}_1 = e^{-\beta \bar{z} s/(R+1)} \]

\[ \overline{G}_2 = e^{-(1 - \beta)\bar{z}/R} \]

According to equation (48)

\[ \bar{E} = \frac{1}{R} \sum_{n=1}^{\infty} \left( \frac{R}{R+1} \right)^n e^{\frac{\beta \bar{z} s}{R+1}} e^{-\frac{(1 - \beta)\bar{z}}{R} (n-1) s} \]

Inversion, term by term, yields

\[ E(t) = \frac{1}{R} \sum_{n=1}^{\infty} \left( \frac{R}{R+1} \right)^n \delta \left( t - \frac{\beta \bar{z} n}{R+1} - \frac{(1 - \beta) \bar{z} (n-1)}{R} \right) \]
Let us write out explicitly the first three terms

\[ E(t) = \frac{1}{R+1} \delta \left( t - \frac{\beta \bar{t}}{R+1} \right) + \frac{R}{(R+1)^2} \delta \left( t - \frac{2\beta \bar{t}}{R+1} - \frac{(1-\beta)\bar{t}}{R} \right) + \frac{R^2}{(R+1)^3} \delta \left( t - \frac{3\beta \bar{t}}{R+1} - \frac{2(1-\beta)\bar{t}}{R} \right) + \cdots \]

This response looks as shown below:

\[ E(t) \]

\[ \frac{1}{R+1} \]

\[ \frac{R}{(R+1)^2} \]

\[ \frac{R^2}{(R+1)^3} \]

\[ t_{a_1} \]

\[ t_{a_2} \]

\[ t_{a_3} \]

\[ t_{a_n} \]

\[ t \]

Where

\[ t_{a_1} = \frac{\beta \bar{t}}{R+1} \]

\[ t_{a_2} = \frac{2\beta \bar{t}}{R+1} + \frac{(1-\beta)\bar{t}}{R} \]

\[ t_{a_3} = \frac{3\beta \bar{t}}{R+1} + \frac{2(1-\beta)\bar{t}}{R} \]

\[ t_{a_n} = \frac{n\beta \bar{t}}{R+1} + \frac{(n-1)(1-\beta)\bar{t}}{R} \]

Now, mentally perform a tracer experiment in which you injected normalized mass of tracer of unity (i.e. \( m_T/Q = 1 \)). The first time the tracer appears at the exit is at \( t_{a_1} = \beta \bar{t}/R+1 \), which is the time it takes to transverse volume \( \beta V \) at flow rate \( (R+1)\bar{Q} \). (Recall \( \bar{t} = V/Q \) always!). The tracer is carried by \((R+1)\bar{Q}\), only \( Q \) exits and \( R\bar{Q} \) is recycled. So the amount of tracer carried out by the outflow at \( t_{a_1} \) is \( 1/(R+1) \). Hence \( 1/(R+1) \) is the area under that delta function at \( t_{a_1} \).

For the tracer to appear the second time, it must transverse the volume in the recycle branch \((1-\beta)V \) at flow rate \( R\bar{Q} \), which takes \((1-\beta)V/R\bar{Q} \) and then transverse to forward branch again, which takes
another \( t_{a_1} \). So \( t_{a_2} = 2 t_{a_1} + \frac{(1 - \beta) V}{R} \). The amount of tracer that now arrives at the exit is \( \left(\frac{R}{R+1}\right) \)
(remember \( 1/(R+1) \) left at the first passage time) and again only the fraction \( \frac{1}{R+1} \) is recycled. So the area under the second delta function at \( t_{a_2} \) is \( \frac{R}{(R+1)^2} \). The rest follows by analogy.

We note that if we had only the response curve we could tell how much volume the recycle system has associated with the forward and recycle branch. The difference

\[
t_{a_n} - t_{a_{n-1}} = \frac{\beta \bar{\tau}}{R + 1} + \frac{(1 - \beta) \bar{\tau}}{R} = \text{const}
\]

Since \( t_{a_1} = \frac{\beta \bar{\tau}}{R + 1} \)

We know that if

\[
t_{a_n} - t_{a_{n-1}} = t_{a_1}
\]

All the volume is in the forward stream i.e. \( \beta = 1 \), Otherwise

\[
t_{a_n} - t_{a_{n-1}} = t_{a_1} - \frac{(1 - \beta) \bar{\tau}}{R} \quad (*)
\]

By dividing the areas under the first peak \( A_1 = \frac{1}{R + 1} \) with the area under the second peak \( A_2 = \frac{R}{(R + 1)^2} \)

we get

\[
\frac{A_1}{A_2} = \frac{R + 1}{R} \quad (**)
\]

We can use eqs (*) and (**) to get estimates for \( \beta \) and \( R \).
Example of a Nonideal Stirred Tank Reactor

A reactor of volume $V = 25 \, m^3 (25,000 \, \text{lit})$ with flow rate $Q = 1000 \, \text{lit/min} = 1 \, m^3/\text{min}$ which was designed to operate as a CSTR and give very high conversion for a 2nd order irreversible reaction ($A \rightarrow \text{product}$) is operating poorly at $x_A = 0.75$. A pulse of $m_i = 250 g$ of tracer is injected instantaneously into the reactor. At the outlet the following exit concentration is measured for the tracer. Initially rapid fluctuations within the first five seconds of very high tracer concentration are observed. Afterwards the following data is obtained:

<table>
<thead>
<tr>
<th>$t$(min)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$(mg/lit)</td>
<td>6.21</td>
<td>3.52</td>
<td>2.15</td>
<td>1.10</td>
<td>0.70</td>
<td>0.40</td>
<td>0.23</td>
<td>0.13</td>
</tr>
</tbody>
</table>

a) How can we model the old reactor?
b) If we had a perfect CSTR what volume do we need for $x_A = 0.75$?
c) What volume of a perfect CSTR do we need to get conversion that currently is produced by the well mixed region?

The rapid initial rise of tracer concentration in the outflow seems to suggest bypassing. The slope of $\ln C$ vs $t$ is

$$\text{slope} = - \frac{\ln (1.06 / 0.01)}{85} = -0.0549$$

We cannot a priori discard the possibility of stagnancy either. Use Cholette and Cloutier model schematically presented in the figure below.

$V_m = \text{volume of a perfectly mixed region (CSTR)}$

$V_d = \text{‘dead’ volume, not accessible to flow}$

Let $V_m = \beta V$ where $V = V_m + V_d$.

Fraction of the flow that bypasses is $(1 - \alpha)$. Then the transfer function for the above system is given by

$$\bar{E} = 1 - \alpha + \frac{\alpha}{1 + \frac{\beta}{\alpha} \bar{t}_S}$$

and the impulse response is:
\[ E(t) = (1 - \alpha) \delta(t) + \frac{\alpha^2}{\beta t} e^{\frac{-\alpha}{\beta t}} \]

where \( \bar{t} = \frac{V}{Q} \).

If we recognize that \( C(t) = \frac{m_i E(t)}{Q} \), then:

\[
C(t) = \frac{m_i}{Q} \left[ (1 - \alpha) \delta(t) + \frac{\alpha^2}{\beta t} e^{\frac{-\alpha}{\beta t}} \right]
\]

If we plot on semilog paper

\[
\ln C = \ln \left( \frac{m_i (\alpha^2)}{\beta t} \right) - \frac{\alpha}{\beta t} t , \text{ then } -\text{slope} = 0.055 = \frac{\alpha}{\beta t} \text{slope} = |s|
\]

Extrapolation of the exponential to \( t = 0 \) gives

\[
I = C_{\exp}(0) = \frac{m_i (\alpha^2)}{\beta t} = 10.7 \text{ (mg/L)} = 10.7 \times 10^{-3} \text{(g/L)}
\]

\[
\frac{C_{\exp}(0)}{|s|} = \frac{m_i (\alpha)}{Q} = \frac{I}{|s|}
\]

\[
\alpha = \frac{Q}{m_i} \frac{I}{|s|}
\]

\[
\alpha = \frac{Q}{m_i} \frac{C_{\exp}(0)}{|s|} = \frac{1000}{250} \frac{10.7 \times 10^{-3}}{0.055} = 0.778
\]

\[
\alpha \approx 0.78
\]

\[
1 - \alpha = 0.22 \text{ of the flow bypasses the vessel}
\]

From the information given we have the mean residence time:

\[
\bar{t} = \frac{25}{1} = 25 \text{ min}
\]

Hence, we can find now the fraction of the total volume, \( \beta \), that is actively mixed.

\[
\frac{\alpha}{\beta t} = 0.055 \quad \beta = \frac{\alpha}{0.055 \bar{t}} = \frac{0.78}{0.055 \times 25} = 0.567 \approx 0.57
\]

\[
\beta \approx 0.57
\]

\[
V_{\text{active}} = 0.57 \times 25 = 14.25 \text{ m}^3
\]

\[
V_{\text{dead}} = 10.75 \text{ m}^3
\]

Now we need to set the CSTR design equation in order to find the unknown rate parameters:
\[
\frac{V_{\text{active}}}{Q_{\text{active}}} = \frac{\beta V}{(\alpha)Q} = \frac{C_{\text{Ao}} x_{\text{Ar}}}{kC_{\text{Ao}} (1 - x_{\text{Ar}})^2}
\]

Now \( x_{\text{Ar}} \) is the actual conversion produced by the reactor found in the stream leaving the active section of the reactor before mixing with the bypass stream

\[
kC_{\text{Ao}} = \frac{x_{\text{Ar}}}{(1 - x_{\text{Ar}})^2} \frac{\alpha}{\beta t}
\]

However, we must first relate this conversion \( x_{\text{Ar}} \) to the conversion produced by the reactor as a whole. This requires a balance around the mixing point \( M \). The stream \( \alpha Q \) arriving from the reactor has conversion \( x_{\text{Ar}} \), the stream bypassing the reactor has conversion of zero. This balance can be represented by:

\[
(1 - \alpha)F_{\text{Ao}} + \alpha F_{\text{Ao}} (1 - x_{\text{Ar}}) = F_{\text{Ao}} (1 - x_A)
\]

\[
1 - \alpha + \alpha (1 - x_{\text{Ar}}) = 1 - x_A
\]

\[
1 - \alpha x_{\text{Ar}} = 1 - x_A \text{ so that } x_{\text{Ar}} = \frac{x_A}{\alpha}
\]

We are told that \( x_A = 0.75 \). Then, for \( x_A = 0.75 \) and \( \alpha = 0.78 \)

\[
x_{\text{Ar}} = \frac{0.75}{0.78} = 0.96
\]

\[
kC_{\text{Ao}} = \frac{0.96}{(1 - 0.96)^2} \frac{0.78}{0.57 \times 25} = 32.8 \text{ (min}^{-1})
\]

Recall that \( V = \frac{Q x_A}{kC_{\text{Ao}} (1 - x_A)} \), Then

\[
V_{\text{new}} (x_A = 0.75) = \frac{1,000 \times 0.75}{32.8 (1 - 0.75)^2} = 366 \text{ (lit) } = 0.37 \text{ m}^3
\]

\[
V_{\text{new}} (x_A = 0.96) = \frac{1000 \times 0.96}{32.8 (1 - 0.96)^2} = 18,293 \text{ lit } = 18.3 \text{ m}^3
\]
2.3.4 Bypassing and Stagnancy

Let us consider now a single CSTR with bypassing. If the portion of the flow that bypasses is \((1 - \alpha)\) the schematic of the system is as follows:

![Schematic of the system](image)

and the impulse response and its transform are given below by eqs. (48) and (49). We expand the transform (see eq (49)) to evaluate its moments, and we tabulate below the dimensionless variance of the system as a function of the fraction of flow that bypasses which is \((1 - \alpha)\). Clearly, the dimensionless variance is larger than one for a CSTR with bypassing indicating pathological behavior.

\[
E(t) = (1 - \alpha) \delta(t) + \frac{\alpha^2}{\tau} e^{-\alpha t/\tau} \quad (49)
\]

\[
\tilde{E}(s) = 1 - \alpha + \frac{\alpha}{1 + \frac{s}{\alpha}} = 1 - \alpha + \alpha \left( 1 - \frac{\tilde{t}}{\tilde{\alpha}} s + \frac{\tilde{t}^2}{\tilde{\alpha}^2} s^2 \right) = 1 - \tilde{t} s + \frac{\tilde{t}^2}{\tilde{\alpha}} s^2 + O(s^3) \quad (50)
\]

By a simple technique that is illustrated later, we have evaluated the moments from the above Laplace transform expansion as:

\[
\mu_0 = 1
\]

\[
\mu_1 = \tilde{t}
\]

\[
\mu_2 = \frac{2\tilde{t}^2}{\alpha}
\]

\[
\sigma_E^2 = \frac{2\tilde{t}^2}{\alpha} - \tilde{t}^2 = \frac{\tilde{t}^2 (2 - \alpha)}{\alpha} \quad \text{and} \quad \frac{\sigma_E^2}{\tilde{t}^2} = \frac{2 - \alpha}{\alpha}
\]

<table>
<thead>
<tr>
<th>(1 - \alpha)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{1 - \alpha}{\tilde{t}^2})</td>
<td>1.22</td>
<td>1.5</td>
<td>1.86</td>
<td>2.33</td>
<td>3</td>
<td>4</td>
<td>5.67</td>
<td>9</td>
<td>19</td>
</tr>
</tbody>
</table>

Now let us consider a single CSTR with 'dead' volume. Such dead volume cannot be reached by tracer or by reactant molecules.
Let $V_d = \beta V$, so $\beta$ is the fraction of the total reactor volume that is for all practical purposes inaccessible. Now the impulse response of the system is:

$$E(t) = \frac{1}{1 - \beta} e^{-\frac{t}{(1 - \beta)\gamma}}$$

and its Laplace transform is

$$E(s) = \frac{1}{1 + (1 - \beta)\gamma} = 1 - (1 - \beta)\gamma s + (1 - \beta)^2 \gamma^2 s^2 + O(s^3)$$

Recall that

$$E(s) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \mu_n s^n$$

Hence,

$$\mu_0 = 1$$

(54a)

$$\mu_1 = (1 - \beta)\gamma$$

(54b)

$$\mu_2 = 2(1 - \beta)^2 \gamma^2$$

(54c)

$$\sigma_E^2 = \frac{\mu_2 - \mu_1^2}{\mu_1^2} = 1$$

(54d)

Now we detected the presence of dead volume not from the value of the variance but from the fact that $\mu_1 < \gamma$, i.e. the central volume principle is violated. We may note, however, that the central volume principle is never violated and, while a fraction $\beta$ of the volume of the system may be difficult to reach, i.e. is relatively "stagnant", as long as that volume is a physical part of the flow system under consideration it is never "dead", i.e. it will be reached by at least a few elements of the fluid and, hence, elements of the tracer if not by flow then at least by diffusion. The fascinating feature of the central volume principle, which is little known, is that the zeroth moment of the tracer impulse concentration at any point of a closed system is constant and equal to $m_T/Q$ where $m_T$ is the mass of the instantaneous tracer injection and $Q$ is the volumetric flow rate through the system. This means that the area under the concentration response to an impulse injection is constant anywhere in the system (i.e. at all points of the system) and it implies that at points where the tracer concentration response rises rapidly, high values will be of short duration, while where the response is barely detectable, it lasts seemingly forever! This makes sense, as it says that if a point is readily accessible and easy to get to, it is also easy to get out of and the converse is also true - if it is hard to get to a point it is equally hard to get out. With this in mind let us say that our system has a stagnancy
\( V_d = \beta V \) which exchanges its contents very slowly with the main well mixed region \( V_m \) at a rate \( \alpha Q \) with \( \alpha \leq 1 \).

By setting up differential mass balances for the tracer in region \( V_m \) and \( V_d \), normalizing tracer concentrations in \( V_m \) and \( V_d \) by multiplying with \( Q/m_T \) to get the impulse response, and by applying the LaPlace transform and solving the equations in the LaPlace domain you should be able to show that

\[
\bar{E}(s) = \frac{1 + \beta \bar{t}s}{1 + \left(1 + \frac{\beta}{\alpha}\right) \bar{t}s + \frac{\beta(1 - \beta)}{\alpha} \bar{t}^2 s^2}
\]  

(55)

By expanding the denominator via binomial series, multiplying the result with the numerator and grouping items with equal power of \( s \) you should be able to get:

\[
\bar{E}(s) = 1 - \bar{t}s + \left(1 + \frac{\beta^2}{\alpha}\right) \bar{t}^2 s^2 + 0(s^3)
\]  

(56)

From the above series we readily identify the moments of the E-curve

\[
\mu_0 = 1
\]  

(57a)

\[
\mu_1 = \bar{t}
\]  

(57b)

\[
\mu_2 = 2\left(\frac{\beta^2}{\alpha} + 1\right)\bar{t}^2
\]  

(57c)

Hence the dimensionless variance of the E-curve is

\[
\sigma_E^2 = \frac{\mu_2 - \mu_1^2}{\mu_1^2} = 1 + 2 \frac{\beta^2}{\alpha} > 1
\]  

(58)

Clearly no matter what volume fraction \( \beta \) is relatively stagnant, the dimensionless variance is always greater than one. The quantity \( \sigma_E^2 - 1 \) is proportional to the square of the stagnant volume fraction and inversely proportional to the ratio of the exchange flow rate \( \alpha Q \) between the ideally mixed region, \( V_m \), and stagnant region, \( V_d \), and the flow rate \( Q \) through the system, i.e. inversely proportional to \( \alpha \). However, while the dimensionless variance is larger than one, indicating pathological behavior, the central volume principle is satisfied and \( \mu_1 = \bar{t} \). Hence, regarding stagnancy we can adopt a simple empirical rule. We will get an indication of stagnancy (dead volume) either from the fact that \( \mu_1 < \bar{t} \), in which case the variance can be anything, or if our data are accurate enough and \( \mu_1 = \bar{t} \), one can detect stagnancy from \( \sigma_E^2 > 1 \).
You should note that if $\alpha \to \infty$, that is if the exchange flow rate $\alpha \, Q$ between $V_m$ and $V_d$ is infinitely faster than flow rate through the system itself, $Q$, we recover $\sigma_E^2 = 1$ and as evident from the expression for $E(s)$ we recover the perfect mixer response. After all infinitely fast (instantaneous) mixing between all regions of the system is the definition of the perfect CSTR, so we should not be surprised by this result.

It should be clear from the above discussion, however, that just from the fact that the dimensionless variance is larger than one we cannot tell whether we deal with stagnancy or bypassing. To be able to distinguish between the two we should examine the shape of the E-curve and especially of the intensity fraction $\Lambda$.

It is tempting to talk about bypassing, if pathology is detected at small times, (e.g. a peak at small times) and of stagnancy, if pathology is present at large times (e.g. a peak at very large times). However, small and large time are ill defined. It may be tempting to say that if the problem is caused by fluid residing less than the characteristic reaction time, $\tau_R$, in the vessel we have a bypassing problem, and if the problem is caused by fluid of residence times order of magnitude larger than $\tau$, then stagnancy is the culprit.

This argument can be summarized as follows:

$$k \, C_{ao}^{n-1} \, \bar{t} \gg 1 \quad \text{stagnancy model is justified}$$

$$k \, C_{ao}^{n-1} \, \bar{t} \ll 1 \quad \text{bypassing model is justified}$$

One can argue that stagnancy is justified if there is a significant fraction of the outflow with the residence times $t$ much larger than characteristic reaction times i.e.

$$\int_{t=1}^{\infty} E(t)dt > 0.1 \quad \text{(59a)}$$

$$1 - F\left(\frac{1}{kC_a^{n-1}}\right) > 0.1 \quad \text{(59b)}$$

Bypassing is then considered as a model if there is a significant fraction of fluid that emerges at times much less than the characteristic reaction time.
\[
\int_{t=0}^{t} \frac{1}{kC_0 e^{kt}} E(t) \, dt > 0.1 \quad (60a)
\]
\[
F(t_r) > 0.1 \quad (60b)
\]

However, if one adopts these definitions then even PFR can exhibit bypassing if \( t < t_r \), and CSTR can exhibit both bypassing or stagnancy as illustrated below:

\[
E_{CSTR}(t) = \frac{1}{t} e^{-t/t} \quad (61)
\]
\[
\int_{t_r}^{\infty} E_{CSTR}(t) \, dt = -e^{-t/t} \bigg|_{t_r}^{\infty} = e^{-t_r/t} > 0.1
\]

which certainly is true whenever

\[
\frac{t}{t_r} < \ln 10 \quad \text{which would then indicate "stagnancy".} \quad \text{Similarly, bypassing would be indicated whenever}
\]

\[
e^{-t/t} \bigg|_{0}^{t_r} = 1 - e^{-t_r/t} > 0.1
\]
\[
0.9 > e^{-t_r/t} \quad \text{i.e. for all } \frac{t}{t_r} > \ln \left( \frac{1}{0.9} \right).
\]

To preclude considering stagnancy and bypassing for a perfect mixer (CSTR), and to reserve stagnancy and bypassing for pathological systems only, we say that only systems that are pathological \( \left( \sigma^2 > 1, \quad \text{or} \quad \frac{d\Lambda}{dt} > 0 \right) \) exhibit either stagnancy or bypassing depending on the criteria above.

**Example**

Let us consider again the ill fated mixed reactor of our Example problem that was represented by the Cholette-Cloutier model.

Characteristic reaction time is:

\[
\tau_r = \frac{1}{kC_{A0}} = \frac{1}{32.8} = 0.03 \text{ min} = 1.8 \text{ s}
\]

Characteristic design process time

\[
\tilde{t} = \frac{V}{Q} = \frac{25}{1} = 25 \text{ min}
\]
Actual characteristic process time

\[ \tilde{t}_p = \frac{V_a}{Q_a} = \frac{0.57 \times 25}{0.78 \times 1} = 18.3 \text{ min} \]

An actual ideal CSTR has in the outflow the following fraction of fluid of residence times between 0 and \( \tau_R \)

\[
\int_0^{\tau_R} E_{\text{CSTR}}(t) dt = \frac{1}{\tilde{t}} \int_0^{\tau_R} e^{-t/\tilde{t}} dt = 1 - e^{-\tau_R/\tilde{t}}
\]

\[ = 1 - e^{-0.03/25} = 1 - e^{-0.0012} \]

\[ = 1 - 0.9988 = 0.001 \]

Our flow pattern in the above example problem yields an outflow with the fraction of residence times between 0 and \( \tau_R \) of:

\[
\int_0^{\tau_R} E(t) dt = \int_0^{\tau_R} (1 - \alpha) \delta(t) dt + \int_0^{\tau_R} \frac{\alpha^2}{\beta t} e^{-\alpha \tau_R / \beta t} dt
\]

\[ = 1 - \alpha + \alpha \left( 1 - e^{-\alpha \tau_R / \beta t} \right) \]

\[ = 1 - 0.78 + 0.78 \left( 1 - e^{-0.78 \times 0.03 / 0.57 \times 25} \right) \]

\[ = 0.22 + 0.78 \left( 1 - e^{-0.001642} \right) \]

\[ = 0.22 + 0.78 (1 - 0.9984) = 0.22 + 0.001 = 0.221 \]

Since this is much larger than 0.001, and we know that the system is pathological, i.e. \( \tilde{t}_p^2 > 1 \), it is clear that bypassing contributed significantly to our problem of low conversion.

Now let us examine the effect of stagnancy, which we suspect since \( \mu_t < \tilde{t} \)

\[
\int_{\tau_k}^{\infty} E(t) dt = \int_{\tau_k}^{\infty} (1 - \alpha) \delta(t) dt + \int_{\tau_k}^{\infty} \frac{\alpha^2}{\beta t} e^{-\alpha \tau_k / \beta t} dt
\]

\[ = 0 + \alpha e^{\frac{\alpha \tau_k}{\beta t}} = 0.78 e^{-0.001642} = 0.779 \]

Indeed stagnancy also contributes to the problem.

Ultimately, the best way to check for pathological behavior (e.g. bypassing or stagnancy) is by examination of the intensity function, \( \Lambda(t) \)

Lack of undesirable behavior is indicated by

\[
\frac{d^2 \Lambda}{dt^2} \geq 0 \quad (63)
\]
Fluid passes through the vessel in a regular fashion. The longer the fluid element has been in the vessel (the larger its age) the more probable that it will exit in the next time interval.

Bypassing. Some fluid has increased probability of leaving at a very young age. Rest of the fluid behaves normally.

Stagnancy. After main flow leaves, the probability of the fluid caught in the dead zones to exit decreases until very large ages are reached at which point all fluid must ultimately leave.

Note that the above definition of stagnancy via the $\Lambda$ function will not detect an entirely 'dead' volume as used initially as our example for a single CSTR with dead volume on page 29. This we can only detect from the fact that the central volume principle is not satisfied ($\mu_i < i$).

For a CSTR

For a PFR

Additional ways of dealing with stagnancy via the introduction of the holdup function have been discussed by Tester and Robinson in the AIChE Journal in the 1980s.

Example of Determination of System Parameters by Matching Experimentally Determined $E$ Curve with Model Predicted One via the Method of Moments.

We illustrate here the Method of Moments which we have used above in our examples of CSTR with stagnancy and bypassing.

Recall $\bar{E}(s) = \int_0^x e^{-st} E(t) \, dt$

Taylor Series Expansion around $s = 0$ yields:

$$\bar{E}(s) = \sum_{n=0}^{\infty} \frac{q^n \bar{E}}{ds^n} (s = 0) \frac{s^n}{n!}$$
\[
\frac{dE}{ds} \bigg|_{s=0} = E(s = 0) = \int_0^\infty E(t) dt = \mu_o
\]

\[
\frac{dE}{ds} \bigg|_{s=0} = \left(-\int_0^\infty te^{-st} E(t) dt \right)_{s=0} = \int_0^\infty t E(t) dt = -\mu_1
\]

Hence,
\[
\mu_n = (-1)^n \frac{d^n E}{ds^n} \bigg|_{s=0}
\]

\[
E(s) = \sum_{n=0}^\infty (-1)^n \frac{\mu_n}{n!} s^n = \mu_0 - \mu_1 s + \frac{\mu_2}{2} s^2 - \frac{\mu_3}{6} s^3 \quad \text{(A)}
\]

\[
E(s) = \sum_{n=0}^\infty \frac{d^n E}{ds^n}(0) \frac{s^n}{n!} \quad \text{(B)}
\]

By comparison of (A) and (B) moments can be obtained. For our stirred tank with bypassing and stagnancy example,

\[
E = 1 - \alpha + \frac{\alpha}{1 + \frac{\beta}{\alpha} \tilde{i} s}
\]

\[
\tilde{E} = 1 - \alpha + \alpha \left[1 - \frac{\beta \tilde{i}}{\alpha} s + \frac{\beta^2}{\alpha^2} \tilde{i}^2 s^2 \right]
\]

\[
\tilde{E} = 1 - \beta \tilde{i} s + \frac{\beta^2}{\alpha} \tilde{i}^2 s^2
\]

\[
\mu_0 = 1 \quad \mu_1 = \beta \tilde{i}
\]

\[
\mu_2 = \frac{2 \beta^2 \tilde{i}^2}{\alpha}
\]

\[
\sigma^2 = \frac{2 \beta^2 \tilde{i}^2}{\alpha} - \beta^2 \tilde{i}^2 = \frac{\beta^2 \tilde{i}^2}{\alpha} [2 - \alpha]
\]

\[
\sigma_D^2 = \frac{\sigma^2}{\mu_1^2} = \frac{\beta^2 \tilde{i}^2 \left[2 - \alpha \right]}{\alpha} = \frac{2 - \alpha}{\alpha} = \frac{2 - 0.78}{0.78} = 1.56
\]

From the tracer experiment we get experimentally
\[
\tilde{i}_{exp} = \beta \tilde{i}
\]

\[
\frac{\sigma_D^2_{\tilde{i}_{exp}}}{\tilde{i}_{exp}^2} = \frac{2 - \alpha}{\alpha} = 1.56
\]