Advance Chemical Reaction Engineering

Non-Ideal Reactors

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- Residence-Time Distribution Function
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The flow of a fluid through a vessel usually falls between the extremes of BMF (complete mixing) and PF (no axial mixing).

In a stirred tank,
- It is difficult to achieve complete instantaneous mixing at the inlet, and
- There may be “dead zones” arising from stagnation near a baffle at the wall, in which there is little or no exchange of fluid with the “active zone,” the central portion of the vessel
- These may result in significant axial mixing or dispersion.

In a packed-bed,
- Deviations from PF may show as channeling or bypassing, arising from uneven distribution of fluid across the bed, or spatial differences in the resistance to flow through the bed.
- Bypassing or short-circuiting from inlet to outlet (and internal recycling) may occur in general in a stirred tank; they occur as well in BMF, but in accountable ways so as to obtain a predictable spread in residence times.

In tubular reactor,
- PF may be difficult to achieve, particularly if frictional losses at the wall and the relative effects of diffusion and convection on the transport of material within the vessel are considered.
Introduction

- In gas liquid reactor, the reaction took place at the gas-liquid interface of the bubbles, and the product was a liquid.
- The continuous liquid phase could be regarded as perfectly mixed, and the reaction rate was proportional to the total bubble surface area.
- The surface area of a particular bubble depended on the time it had spent in the reactor.
- Because of their different sizes, some gas bubbles escaped from the reactor almost immediately, while others spent enough time in the reactor so that they were almost completely consumed.

**Residence time distribution (RTD)**

The total reaction rate is estimated by summing over all the bubbles in the reactor.

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Deviations from ideal tubular-flow performance:

- Longitudinal mixing due to vortices and turbulence
- Laminar-flow (poor radial mixing)
- Bypassing infixed-bed catalytic reactor
**Non-ideal Reactors**

- **Reactor performance in general depends on**
  
  i. The kinetics of reaction.
  
  ii. The flow pattern as represented by the RTD, and
  
  iii. Mixing characteristics within the vessel.

**Mixing Concepts and Models**

- Deviation from the two ideal flow patterns can be caused by channeling of fluid, by recycling of fluid, or by creation of stagnant regions in the vessel.

All deviations from ideal performance fall into two classifications:

i. A flow arrangement in which elements of fluid do not mix, but follow separate paths through the reactor (segregated flow) and thus these elements have different residence times.

- Elements of fluid may move through the reactor at different velocities, causing channeling and "dead spots." i.e., the elements of fluid must not completely mix locally, but remain at least partially segregated as they move through the reactor.

**Non-ideal Reactors**

ii. The extent of the local or micromixing: A flow arrangement whereby adjacent elements of fluid partially mix (micromixing). For example, there may be some mixing or diffusion in the direction of flow in a tubular reactor.

Three concepts used to describe non-ideal reactors:

i. The distribution of residence times in the system,

ii. The quality of mixing, and

iii. The model used to describe the system.
Non-ideal Reactors

- Non-ideal flow results in irregularities relating to the mixing of fluid elements of differing ages at the microscopic level.
- The RTD is not enough to determine both the extent of segregated flow in the reactor and the extent of micro mixing.
- It provides a measure of macroscopic mixing and thus it is unable to account for how fluid elements at the microscopic level interact with each other.
- Such interactions can be very important, especially in a reactor, if reaction requires two different chemical species to come together.

- The time the atoms have spent in the reactor is called the residence time of the atoms in the reactor.
- It is evident that elements of fluid taking different routes through the reactor may take different lengths of time to pass through the vessel.
- The distribution of these times for the stream of fluid leaving the vessel is called the Age Distribution Function \( E \) (units of time\(^{-1} \)), or the residence time distribution RTD of fluid.
- The Residence-time Distribution (RTD) of a reactor is a characteristic of the mixing that occurs in the chemical reactor.

**Measurement of the RTD**

- The RTD is determined experimentally by injecting an inert chemical, molecule, or atom, called a tracer, into the reactor at some time \( t = 0 \) and then
- Measuring the tracer concentration, \( C \), in the effluent stream as a function of time.
Measurement of the RTD

The tracer characteristics

- Nonreactive
- Easily detectable,
- The physical properties are similar to those of the reacting mixture
- Completely soluble in the mixture.
- Can not be adsorbed on the walls or other surfaces in the reactor.

- Colored and radioactive materials are the two most common types of tracers
- The analysis for tracer should be convenient, sensitive, and reproducible

Examples of tracers are:

i. Gas-phase tracers such as He, Ne, and Ar used with thermal conductivity detectors;

ii. pH indicators such as phenol red and methylene blue;

iii. Electrolytes such as K+ and Na+ used with electrical conductivity detectors or specific-ion electrodes;

iv. Dyes (e.g., India ink) used with color intensity;

v. Radioactive isotopes such as ³H, ¹⁴C, ¹⁸O; ⁵¹Cr-labeled red-blood cells used to investigate hepatic blood flow; isotopes of iodine, thallium, and technetium used to investigate cardiac blood flow;

vi. Stereoisomers and structural analogs used for diffusion-limited processes (e.g., L versus d-glucose in biological systems).

➢ Two most used methods of injection are pulse input and step input.
Pulse Input

- An amount of tracer $N_0$ is suddenly injected in one shot into the feed stream entering the reactor in as short a time as possible.

$$C = \begin{cases} 
0 & \text{for } t < 0 \\
C_0 & \text{for } 0 < t < \Delta t_0 \\
0 & \text{for } t > \Delta t_0 
\end{cases}$$

- The outlet concentration is then measured as a function of time.

Pulse Input

- The effluent concentration-time curve is referred to as the $C$ curve in RTD analysis.

- To analyze the injection of a tracer pulse for a single-input and single-output system:
  
  i. Choose an increment of time $\Delta t$ sufficiently small that the concentration of tracer, $C(t)$ exiting between time $t$ and $t + \Delta t$ is essentially the same.
  
  ii. The amount of tracer material $\Delta N$ leaving the reactor between time $t$ and $t + \Delta t$ is then

$$\Delta N = C(t) \nu \Delta t$$

where $\nu$ is the effluent volumetric flow rate.

$\Delta N$ is the amount of material exiting the reactor that has spent an amount of time between $t$ and $t + \Delta t$ in the reactor.

- The fraction of material that has a residence time in the reactor between time $t$ and $t + \Delta t$

$$\frac{\Delta N}{N_0} = \frac{\nu C(t)}{N_0} \Delta t$$

Where $N_0$ is the total amount of material that was injected into the reactor.
Pulse Input

- Define

\[ E(t) = \frac{vC(t)}{N_0} \]

\[ \frac{\Delta N}{N_0} = E(t) \Delta t \]

\( E(t) \) is called the *residence-time distribution function.*

\( E(t)dt \) is the fraction of fluid exiting the reactor that has spent between time \( t \) and \( t + \Delta t \) inside the reactor.

\[
\left[ \frac{\text{Fraction of material leaving the reactor}}{\text{that has resided in the reactor}} \right]_{t_1 \text{ and } t_2} = \int_{t_1}^{t_2} E(t) \, dt
\]

Pulse Input

- It is the function that describes in a quantitative manner how much time different fluid elements have spent in the reactor.

\[ dN = vC(t) \, dt \quad \text{integrating,} \quad N_0 = \int_0^\infty vC(t) \, dt \]

- If the volumetric flow rate \( v \) is constant

\[ E(t) = \frac{C(t)}{\int_0^\infty C(t) \, dt} \]

- The fraction of all the material that has resided for a time \( t \) in the reactor between \( t = 0 \) and \( t = \infty \) is

\[ \int_0^\infty E(t) \, dt = 1 \]

\[ \int_{t_1}^{\infty} E \, dt = 1 - \int_0^{t_1} E \, dt \]
Pulse Input

\[
\int_0^t E(t) \, dt = \begin{bmatrix} \text{fraction of effluent} \\
\text{which has been in reactor} \\
\text{for less than time } t \end{bmatrix} = F(t)
\]

\[
\int_t^\infty E(t) \, dt = \begin{bmatrix} \text{fraction of effluent} \\
\text{which has been in reactor} \\
\text{for longer than time } t \end{bmatrix} = 1 - F(t)
\]

Example

A sample of the tracer hytane at 320 K was injected as a pulse to a reactor and the effluent concentration measured as a function of time, resulting in the following data:

<table>
<thead>
<tr>
<th>( t ) (min)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>12</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C ) (g/m³)</td>
<td>0</td>
<td>1</td>
<td>5</td>
<td>8</td>
<td>10</td>
<td>8</td>
<td>6</td>
<td>4</td>
<td>3.0</td>
<td>22</td>
<td>15</td>
<td>0.6</td>
<td>0</td>
</tr>
</tbody>
</table>

The measurements represent the exact concentrations at the times listed and not average values between the various sampling tests. (a) Construct figures showing \( C(t) \) and \( E(t) \) as functions of time, (b) Determine both the fraction of material leaving the reactor that has spent between 3 and 6 min in the reactor and the fraction of material leaving that has spent between 7.75 and 8.25 min in the reactor, (c) 3 min or less.
Example Cont.

\[ E(t) = \frac{C(t)}{\int_0^\infty C(t) \, dt} \]

\[ \int_0^\infty C(t) \, dt = \int_0^{10} C(t) \, dt + \int_{10}^{14} C(t) \, dt \]

\[ \int_0^{10} C(t) \, dt = \frac{1}{2} \{ 1(0) + 4(1) + 2(5) + 4(8) + 2(10) + 4(8) + 2(6) + 4(4) + 2(3.0) + 4(2.2) + 1(1.5) \} = 47.4 \, \text{g} \cdot \text{min/m}^3 \]

\[ \int_{10}^{14} C(t) \, dt = \frac{1}{2} \{ 1.5 + 4(0.6) + 0 \} = 2.6 \, \text{g} \cdot \text{min/m}^3 \]

\[ \int_0^\infty C(t) \, dt = 50.0 \, \text{g} \cdot \text{min/m}^3 \]
Example Cont.

\[ E(t) = \frac{C(t)}{50 \text{ g} \cdot \text{min/m}^3} = \frac{C(t)}{\int_0^\infty C(t) \, dt} \]

<table>
<thead>
<tr>
<th>( t ) (min)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>12</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C(t) ) (g/m³)</td>
<td>1</td>
<td>5</td>
<td>8</td>
<td>10</td>
<td>8</td>
<td>6</td>
<td>4</td>
<td>3</td>
<td>2.2</td>
<td>1.5</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>( E(t) ) (min⁻¹)</td>
<td>0.02</td>
<td>0.1</td>
<td>0.16</td>
<td>0.2</td>
<td>0.16</td>
<td>0.12</td>
<td>0.08</td>
<td>0.06</td>
<td>0.044</td>
<td>0.03</td>
<td>0.012</td>
<td>0</td>
</tr>
</tbody>
</table>

- The shaded area represents the fraction of material leaving the reactor that has resided in the reactor between 3 and 6 min.

Example Cont.

\[ \int_3^6 E(t) \, dt = \text{shaded area} \]

\[ = \frac{3}{8} \Delta t(f_1 + 3f_2 + 3f_3 + f_4) \]

\[ = \frac{3}{8}(1[0.16 + 3(0.2) + 3(0.16) + 0.12] = 0.51 \]

51\% of the material leaving the reactor spends between 3 and 6 min in the reactor.

- Because the time between 7.75 and 8.25 min is very small relative to a time scale of 14 min

The average value of \( E(t) \) between these times is \( 0.06 \text{ min}^{-1} \)

\[ E(t) \, dt = (0.06 \text{ min}^{-1})(0.5 \text{ min}) = 0.03 \]

3.0\% of the fluid leaving the reactor has been in the reactor between 7.75 and 8.25 min.
Example Cont.

- The fraction of material that has been in the reactor for a time $t$ or less, that is, the fraction that has spent between 0 and $t$ minutes in the reactor

$$\int_0^t E(t) \, dt = 20\%$$

**Pulse Input**

Inlet \[\xrightarrow{}\] PFR \[\xrightarrow{}\] Outlet

- Concentration vs. Time
  - Before $t_0$ (Input)
  - After $t_1$ (Output)
Pulse Input

Inlet → CSTR → Outlet

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Step Tracer Experiment

- A constant rate of tracer is added to a feed that is initiated at time $t = 0$. Before this time no tracer was added to the feed

$$C_0(t) = \begin{cases} 
0 & t < 0 \\
(C_0) \text{ constant} & t \geq 0
\end{cases}$$

- The concentration of tracer in the feed to the reactor is kept at this level until the concentration in the effluent is indistinguishable from that in the feed; the test may then be discontinued.

Step Tracer Experiment

- Because the inlet concentration is a constant with time, $C_o$,

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

$$\left[ \frac{C_{\text{out}}}{C_0} \right]_{\text{step}} = \int_0^t E(t') \, dt' = F(t)$$

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

- The positive step is usually easier to carry out experimentally than the pulse test,

- It has the additional advantage that the total amount of tracer in the feed over the period of the test does not have to be known as it does in the pulse test.
One possible drawback in this technique is that it is sometimes difficult to maintain a constant tracer concentration in the feed.
Step Tracer Experiment

Normalized RTD Function

- Defined \( \Theta \equiv \frac{t}{\tau} \) and \( E(\Theta) \equiv \tau E(t) \)

\( \Theta \) : represents the number of reactor volumes of fluid based on entrance conditions that have flowed through the reactor in time \( t \).

The nominal holding time (space time) \( \tau = \frac{V}{v} \)

- The purpose of creating this normalized distribution function is that the flow performance inside reactors of different sizes can be compared directly.
- if the normalized function \( E(\Theta) \) is used, all perfectly mixed CSTRs have numerically the same RTD.
- If the simple function \( E(t) \) is used, numerical values of \( E(t) \) can differ substantially for different CSTRs.

\[ \int_0^\infty E(\Theta) \, d\Theta = 1 \]
Pulse Input in an Ideal CSTR

- The impulse can be described by the Dirac delta function,

\[
\delta(x) = \begin{cases} 
0 & \text{when } x \neq 0 \\
\infty & \text{when } x = 0
\end{cases}
\]

such that:

\[
\int_{-\infty}^{\infty} \delta(x) \, dx = 1
\]

- The unsteady-state mass balance on an inert tracer that has been injected as a pulse at time \( t = 0 \) into a CSTR:

\[
V \frac{dC}{dt} = n\delta(t) - vC
\]

accumulation input output

- For \( t \) other than zero

\[
in - out = \text{accumulation}
\]

\[
0 - uc = +v \frac{dC}{dt}
\]

Pulse Input in CSTR

integrating with \( C = C_0 \) at \( t = 0 \)

\[
C(t) = C_0 e^{-t/\tau}
\]

\[
E(t) = \frac{C(t)}{\int_0^\infty C(t) \, dt} = \frac{C_0 e^{-t/\tau}}{\int_0^\infty C_0 e^{-t/\tau} \, dt}
\]

\[
E(t) = \frac{e^{-t/\tau}}{\tau}
\]

\[
E(\Theta) = e^{-\Theta}
\]

Recall \( \Theta = t/\tau \)

The RTD is an exponential curve.
Pulse Input in CSTR

CSTR response to a pulse tracer input.

- The mean residence time in a reactor is defined as
  \[ t_m = \frac{\int_0^\infty tE(t) \, dt}{\int_0^\infty E(t) \, dt} = \int_0^\infty tE(t) \, dt \]

- For a CSTR with pulse input
  \[ t_m = \int_0^\infty tE(t) \, dt = \int_0^\infty \frac{t}{\tau} e^{-t/\tau} \, dt = \tau \]

Step Tracer in a CSTR

\[ \tau \frac{dC}{dt} = C_o - C \]

accumulation input output

- The exit concentrations from an ideal CSTR that has experienced a step increase in feed concentration
  \[ \left[ \frac{C_{out}}{C_0} \right]_{step} = \int_0^t E(t') \, dt' = F(t) \quad \left( \frac{C}{C_0} \right)_{step} = 1 - \exp\left[ -t/\tau \right] \]
The Cumulative Distribution Function

- The fraction of the exit stream that has resided in the reactor for a period of time shorter than a given value \( t \) is equal to the sum over all times less than \( t \) of \( E(t) \)

\[
\int_0^t E(t) \, dt = \left[ \begin{array}{c} \text{fraction of effluent} \\ \text{which has been in reactor} \end{array} \right] \text{ for less than time } t = F(t)
\]

- Also

\[
\int_t^\infty E(t) \, dt = \left[ \begin{array}{c} \text{fraction of effluent} \\ \text{which has been in reactor} \end{array} \right] \text{ for longer than time } t = 1 - F(t)
\]

where \( F(t) \) is the cumulative distribution function

\[
dF = E(t) \, dt
\]

- \( F(t) \) at 3 min was 0.20, meaning that 20% of the molecules spent 3 min or less in the reactor.
Tubular Reactors with Laminar Flow

- Tubular reactor with *laminar flow* has been mentioned as a good approximation to segregated flow.
- Segregated flow is a flow arrangement in which elements of fluid do not mix, but follow separate paths through the reactor and thus these elements have different residence times.
- If the dispersion due to molecular diffusion is neglected, the approximation is exact.
- For laminar flow,

\[
U = U_{\text{max}} \left[ 1 - \left( \frac{r}{R} \right)^2 \right] = 2U_{\text{avg}} \left[ 1 - \left( \frac{r}{R} \right)^2 \right] = \frac{2v_0}{\pi R^2} \left[ 1 - \left( \frac{r}{R} \right)^2 \right]
\]

where \( U_{\text{max}} \) is the centerline velocity, \( U_{\text{avg}} \) is the average velocity through the tube.

Tubular Reactors with Laminar Flow

The time of passage of an element of fluid at a radius \( r \) is

\[
t(r) = \frac{L}{U(r)} = \frac{\pi R^2 L}{v_0} \frac{1}{2[1 - (r/R)^2]}
\]

\[
= \frac{\tau}{2[1 - (r/R)^2]}
\]

The volumetric flow rate of fluid out between \( r \) and \((r + dr)\), \( dv \), is

\[
dv = U(r) 2\pi rdr
\]

The fraction of total fluid passing between \( r \) and \((r + dr)\) is \( dv/v_0 \), i.e.

\[
\frac{dv}{v_0} = \frac{U(r)2(\pi rdr)}{v_0}
\]
Tubular Reactors with Laminar Flow

The fraction of fluid between \( r \) and \( (r + dr) \) that has a flow rate between \( u \) and \( (u + dv) \) spends a time between \( t \) and \( (t + dt) \) in the reactor is

\[
E(t) dt = \frac{dv}{v_0}
\]

But

\[
t(r) = \frac{L}{U(r)} = \frac{\pi R^2 L}{v_0} \frac{1}{2[1 - (r/R)^2]} \]

\[
dt = \frac{r}{2R^2} \left[ 1 - \left( \frac{r}{R} \right)^2 \right]^{1/2} \left( \frac{\tau/2}{\left[1 - \left( \frac{r}{R} \right)^2 \right]} \right)^2 r \, dr
\]

\[
dt = \frac{4t^2}{\tau R^2} r \, dr
\]

Tubular Reactors with Laminar Flow

\[
E(t) dt = \frac{dv}{v_0} = \frac{L}{t} \left( \frac{2\pi r \, dr}{v_0} \right) = \frac{L}{t} \left( \frac{2\pi r}{v_0} \right) \frac{\tau R^2}{4t^2} dt = \frac{\tau^2}{2t^3} dt
\]

\[
E(t) = \frac{\tau^2}{2t^3}
\]

The minimum time the fluid may spend in the reactor is

\[
t = \frac{L}{U_{\text{max}}} = \frac{L}{2 U_{\text{avg}} \left( \frac{\pi R^2}{2v_0} \right)} = \frac{V}{2v_0} = \frac{\tau}{2}
\]

the complete RTD function for a laminar flow reactor is

\[
E(t) = \begin{cases} 
0 & t < \frac{\tau}{2} \\
\frac{\tau^2}{2t^3} & t \geq \frac{\tau}{2}
\end{cases}
\]

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Tubular Reactors with Laminar Flow

The cumulative distribution function for $t \geq \tau/2$ is

$$F(t) = \int_0^t E(t) dt = 0 + \int_{\tau/2}^t E(t) dt = \frac{\tau^2}{2t^3} \int_{\tau/2}^t dt = \frac{\tau^2}{2t} \int_{\tau/2}^t \frac{dt}{t^3} = 1 - \frac{\tau^2}{4t^2}$$

The mean residence time $t_m$ is

$$t_m = \int_{\tau/2}^\infty tE(t) dt = \frac{\tau^2}{2} \int_{\tau/2}^\infty \frac{dt}{t^2} = \frac{\tau^2}{2} \left[ -\frac{1}{t} \right]_{\tau/2}^\infty = \frac{\tau}{2}$$

The dimensionless form of the RTD function is

$$E(\Theta) = \begin{cases} 0 & \Theta < 0.5 \\ \frac{1}{2\Theta^3} & \Theta \geq 0.5 \end{cases}$$

\[ E(\Theta) \]

\[ \Theta \]

0.2 0.4 0.6 0.8 1.0 1.2 1.4

1.0 1.5 2.0 2.5 3.0

Tubular Reactors with Laminar Flow

$$F(\Theta) = 0 + \int_{\frac{1}{4}}^{\Theta} E(\Theta) d\Theta = \int_{\frac{1}{4}}^{\Theta} \frac{d\Theta}{2\Theta^3} = \left( 1 - \frac{1}{4\Theta^2} \right)$$

$$F(\Theta) = \begin{cases} 0 & \Theta < \frac{1}{2} \\ \left( 1 - \frac{1}{4\Theta^2} \right) & \Theta \geq \frac{1}{2} \end{cases}$$
Example

Calculate the mean residence time and the variance for the reactor characterized in the previous example by the RTD obtained from a pulse input at 320 K.

\[
E(t) = \frac{C(t)}{50 \text{ g} \cdot \text{min/m}^3} = \int_{0}^{\infty} C(t) \, dt
\]

\[
t_m = \int_{0}^{\infty} tE(t) \, dt = \int_{0}^{10} tE(t) \, dt + \int_{10}^{\infty} tE(t) \, dt
\]

Example Cont.

\[
t_m = \int_{0}^{h} f(x) \, dx = \frac{h_1}{3} (f_1 + 4f_2 + 2f_3 + 4f_4 + \cdots + 4f_{n-1} + f_n) + \frac{h_2}{3} (f_{n+1} + 4f_{n+2} + f_{n+3})
\]

\[
t_m = \frac{1}{3} [1(0) + 4(0.02) + 2(0.2) + 4(0.48) + 2(0.8) + 4(0.8) + 2(0.72) + 4(0.56) + 2(0.48) + 4(0.40) + 1(0.3)]
\]

\[
+ \frac{2}{3} [0.3 + 4(0.14) + 0]
\]

\[
= 4.58 + 0.573 = 5.15 \text{ min}
\]
To evaluate reactor behavior in general we have to know four factors:

1. The kinetics of the reaction
2. The RTD of fluid in the reactor
3. The earliness or lateness of fluid mixing in the reactor
4. Whether the fluid is a micro or macro fluid

Prediction of Reactor Conversion

Different models can be used, classified according to the number of adjustable parameters:

1. **Zero adjustable parameters**
   a. Segregation model
   b. Maximum mixedness model

2. **One adjustable parameter**
   a. Tanks-in-series model
   b. Dispersion model

3. **Two adjustable parameters**
   Real reactors modeled as combinations of ideal reactors
Segregation Model

- In a "perfectly mixed" CSTR, the entering fluid is assumed to be distributed immediately and evenly throughout the reacting mixture.
- This mixing is assumed to take place even on the micro scale and elements of different ages mix together thoroughly to form a completely micro mixed fluid.
- The segregation model used to consider the early and late mixing of a microfluid (macro-mixing)
- Little clumps of fluid staying for different lengths of time in the reactor (given by the E function).
- Each clump reacts away as a little batch reactor, thus fluid elements will have different compositions.

\[
\begin{align*}
\text{Small } \tau & \quad \text{Large } \tau \\
\text{(a)} & \\
\end{align*}
\]

Prediction of Reactor Conversion

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

\[
\left( \frac{\text{mean concentration of reactant in exit stream}}{C_{A}} \right)_{\text{at exit}} = \left( \frac{\text{concentration of reactant remaining in an element of age between } t \text{ and } t + dt}{C_{A0}} \right) \left( \text{fraction of exit stream which is of age between } t \text{ and } t + dt \right)
\]

where the summation is over all fluid elements in the reactor exit stream

\[
\left( \frac{C_{A}}{C_{A0}} \right)_{\text{at exit}} = \int_{0}^{\infty} \left( \frac{C_{A}}{C_{A0}} \right) \cdot E \, dt
\]

where \( C_{A}(t) \) depends on the residence time of the element

\[
\frac{dC_{A}}{dt} = -\nu \tau(C_{A})
\]
Prediction of Reactor Conversion

with \( C_A(0) = C_A^0 \)

For a first-order reaction:

\[
\frac{dC_A}{dt} = -kC_A \quad \Rightarrow \quad C_A = C_A^0 \exp[-kt]
\]

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

For the ideal CSTR \( E(t) = \frac{e^{-t/\tau}}{\tau} \)

then

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

or

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

By Integration

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

Similarly,

\[
\bar{X} = \int_0^\infty X(t) E(t) dt
\]
Prediction of Reactor Conversion

- For a first-order irreversible reaction in an isothermal batch reactor

\[
\frac{dX}{dt} = k(1 - X)
\]

\[
X(t) = 1 - e^{-kt}
\]

\[
\overline{X} = \int_0^\infty (1 - e^{-kt})E(t) \, dt
\]

- For the CSTR

\[
\overline{X} = \int_0^\infty (1 - e^{-kt}) \frac{1}{\tau} e^{-t/\tau} \, dt = \frac{k\tau}{1 + k\tau}
\]

Prediction of Reactor Conversion

- for first-order reactions

\[
\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = e^{-kt}
\]

- for second-order reactions

\[
\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = \frac{1}{1 + kC_{A0}t}
\]

- for an \(n\)th-order reaction

\[
\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = [1 + (n - 1)C_{A0}^{-1}kt]^{1/n}
\]
Example

Calculate the mean conversion in the reactor we have characterized by RTD measurements in Examples 13-1 and 13-2 for a first-order, liquid-phase, irreversible reaction in a completely segregated fluid:

\[ \text{A} \longrightarrow \text{products} \]

The specific reaction rate is 0.1 min\(^{-1}\) at 320 K.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>12</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(t) (g/m(^3))</td>
<td>10</td>
<td>5</td>
<td>2</td>
<td>10</td>
<td>6</td>
<td>3</td>
<td>2.2</td>
<td>1.5</td>
<td>0.6</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Because each globule acts as a batch reactor of constant volume

\[ X = 1 - e^{-kt} = 1 - e^{-0.1t} \]

Example Cont.

\[ \bar{X} = \int_{0}^{\infty} X(t)E(t) \, dt \]

Table E13-5.1: Processed Data to Find the Mean Conversion \( \bar{X} \)

<table>
<thead>
<tr>
<th>t (min)</th>
<th>( E(t) ) (min(^{-1}))</th>
<th>( X(t) )</th>
<th>( X(t)E(t) ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.020</td>
<td>0.095</td>
<td>0.0019</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
<td>0.181</td>
<td>0.0180</td>
</tr>
<tr>
<td>3</td>
<td>0.160</td>
<td>0.259</td>
<td>0.0414</td>
</tr>
<tr>
<td>4</td>
<td>0.200</td>
<td>0.330</td>
<td>0.0660</td>
</tr>
<tr>
<td>5</td>
<td>0.160</td>
<td>0.393</td>
<td>0.0629</td>
</tr>
<tr>
<td>6</td>
<td>0.120</td>
<td>0.451</td>
<td>0.0541</td>
</tr>
<tr>
<td>7</td>
<td>0.080</td>
<td>0.503</td>
<td>0.0402</td>
</tr>
<tr>
<td>8</td>
<td>0.060</td>
<td>0.551</td>
<td>0.0331</td>
</tr>
<tr>
<td>9</td>
<td>0.044</td>
<td>0.593</td>
<td>0.0261</td>
</tr>
<tr>
<td>10</td>
<td>0.030</td>
<td>0.632</td>
<td>0.01896</td>
</tr>
<tr>
<td>12</td>
<td>0.012</td>
<td>0.699</td>
<td>0.0084</td>
</tr>
<tr>
<td>14</td>
<td>0.000</td>
<td>0.75</td>
<td>0</td>
</tr>
</tbody>
</table>
Example Cont.

\[ \int_0^\infty X(t) E(t) \, dt = \int_0^1 X(t) E(t) \, dt + \int_1^{14} X(t) E(t) \, dt \]
\[ = \frac{1}{3} [0 + 4(0.0019) + 2(0.018) + 4(0.0414) + 2(0.066) + 4(0.0629) + 2(0.0541) + 4(0.0402) + 2(0.0331) + 4(0.0261) + 0.01896] + \frac{1}{3} [0.01896 + 4(0.0084) + 0] \]
\[ = (0.350) + (0.035) = 0.385 \]

Example

The concentration readings in the Table represent a continuous response to a pulse input into a closed vessel which is to be used as a chemical reactor. **Calculate the mean residence time of fluid in the vessel \( t \), and tabulate and plot the exit age distribution \( E \).**

<table>
<thead>
<tr>
<th>Time ( t ), min</th>
<th>Tracer Output Concentration, ( C_{\text{pulse}} ) gm/liter fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>35</td>
<td>0</td>
</tr>
</tbody>
</table>

➢ **If a vessel is to be used as a reactor for a liquid decomposing with rate**

\[-r_A = kC_A, \quad k = 0.307 \text{ min}^{-1}\]

Find the fraction of reactant unconverted in the real reactor and compare this with the fraction unconverted in a plug flow reactor of the same size.
Example Cont.

For a first-order irreversible reaction in an isothermal batch reactor

\[ X(t) = 1 - e^{-kt} \]

\[ k = 0.307 \text{ min}^{-1} \]

\[ \bar{X} = \int_0^{35} X(t)E(t) \, dt = 0.9455 \]

<table>
<thead>
<tr>
<th>Time, min</th>
<th>0.0000</th>
<th>5.0000</th>
<th>10.0000</th>
<th>15.0000</th>
<th>20.0000</th>
<th>25.0000</th>
<th>30.0000</th>
<th>35.0000</th>
<th>Integ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cout, gm/L</td>
<td>0.0000</td>
<td>3.0000</td>
<td>5.0000</td>
<td>5.0000</td>
<td>4.0000</td>
<td>2.0000</td>
<td>1.0000</td>
<td>0.0000</td>
<td>100.0000</td>
</tr>
<tr>
<td>E(t), 1/min</td>
<td>0.0000</td>
<td>0.0300</td>
<td>0.0500</td>
<td>0.0500</td>
<td>0.0400</td>
<td>0.0200</td>
<td>0.0100</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>t*E(t)</td>
<td>0.0000</td>
<td>0.1500</td>
<td>0.5000</td>
<td>0.7500</td>
<td>0.8000</td>
<td>0.5000</td>
<td>0.3000</td>
<td>0.0000</td>
<td>14.6667</td>
</tr>
<tr>
<td>kt</td>
<td>0.0000</td>
<td>1.5350</td>
<td>3.0700</td>
<td>4.6050</td>
<td>6.1400</td>
<td>7.6750</td>
<td>9.2100</td>
<td>10.7450</td>
<td></td>
</tr>
<tr>
<td>1- Exp(-kt)</td>
<td>0.0000</td>
<td>0.7845</td>
<td>0.9536</td>
<td>0.9900</td>
<td>0.9978</td>
<td>0.9995</td>
<td>0.9999</td>
<td>1.0000</td>
<td></td>
</tr>
<tr>
<td>(1-Exp(kt))*E(t)</td>
<td>0.0000</td>
<td>0.0235</td>
<td>0.0477</td>
<td>0.0495</td>
<td>0.0399</td>
<td>0.0200</td>
<td>0.0100</td>
<td>0.0000</td>
<td>0.9455</td>
</tr>
</tbody>
</table>
Example Cont.

For the plug flow reactor

\[ \tau = C_A^0 \int_0^{X_A} \frac{dX_A}{-r_A} = -\frac{1}{k} \int \frac{dC_A}{C_A^0} \frac{dC_A}{C_A} = \frac{1}{k} \ln \frac{C_A^0}{C_A} \]

\[ X(t) = 1 - \frac{C_A}{C_A^0} = 1 - e^{-k\tau} = 1 - e^{-(0.307)(15)} = 0.99 \]