Non-ideal behavior in reactors

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Different types of flow

- Two ideal flow behavior in reactors: Plug flow and Mixed flow. If there is no axial mixing(in the direction of flow) it is plug flow. In another case, if the contents of the reactor are well-mixed by agitation, it is mixed flow.
- In real reactors, i.e. in industrial reactors never the fully ideal behavior be maintained. There will be different extent of deviation from ideal flow. The calculation of conversion assuming ideal flow is not applicable for these reactors.
- These are called non-ideal reactors. We need to evaluate the deviation from ideality to determine conversion in non-ideal reactors.

The cause of deviation

- Consider a gas-liquid reaction in a stirred tank reactor, where a gaseous reactant is bubbled in continuous liquid phase. The reaction is taking place in the gas-liquid interface. The rate of reaction depends on the gas-liquid interfacial area.
- The bubbles are also not uniform size. The interfacial area will vary with the size of bubbles.
- Some bubbles also escape just entering the reactor. So contact time between gas bubbles and liquid phase will be different. The time that molecules spend inside the reactor will be not same.
- The non ideality will develop.
- We may compare the non ideal behavior with respect to PFR and CSTR.

Deviation of non ideality depends

- Creation of the stagnant region in the vessel or dead zones or partially segregated as they move
- Micro-mixing in the direction of flow or dispersion.
- Elements of fluid may move at different velocities causing channeling.
- Formation of vortices, turbulence near the inlet and outlet.

Determination of deviation

Four methods are used to determine the deviation from ideal reactor performance.

1. Segregated flow model
2. The extent of micro-mixing is considered: axial dispersion model is used.

3. Series of ideal stirred tank reactor model.

4. Recycle reactor model with various recycle ratio in an ideal plug flow reactor.

Measuring the actual RTD the number of tanks (in case 3) and recycle ratio (in case 4) can be determined.

Residence time measuring technique

- Residence time: The time required to pass a molecule through a reactor is called its residence time.
- The detail of velocity profile in a reactor should be known to predict the behavior of the vessel.
- Knowing the residence time distribution(RTD), the conversion in the reactor can be predicted.
- The assumptions for RTD analysis:

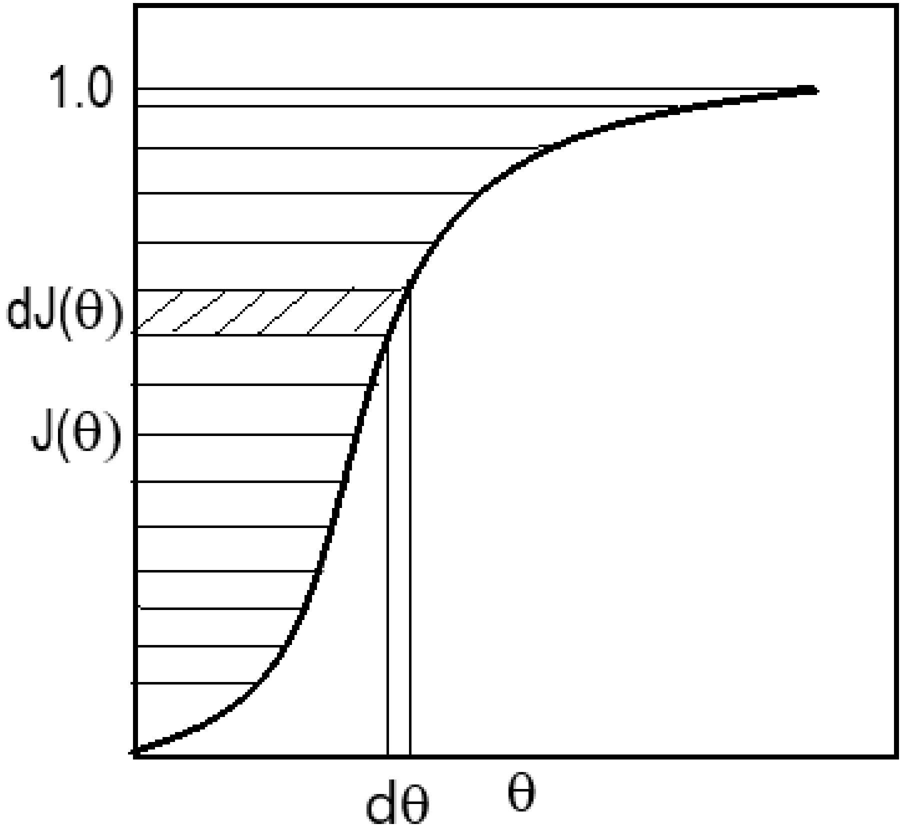
(a) Steady state flow

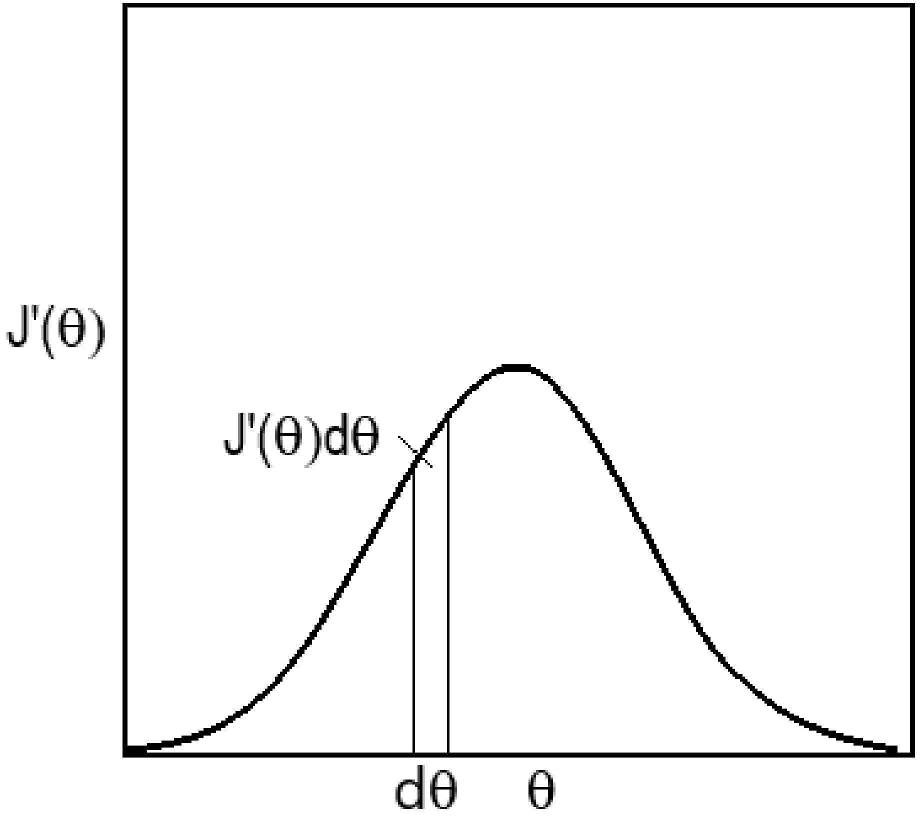
(b) No reaction in the vessel

(c) Constant density

(d) A single fluid

Let $J(\theta)$ fraction of effluent stream has a residence less than θ min, at $\theta = 0$; $J(\theta) = 0$ and $dJ(\theta)$ is the volume fraction of element has a residence time between θ and $\theta + d\theta$.





Distribution plot

Mean residence time

Mean residence time is

$$\bar{\theta} = \frac{\int_0^1 \theta dJ(\theta)}{\int_0^1 dJ(\theta)} = \int_0^1 \theta dJ(\theta) = \frac{V}{Q}$$

$$Also, \frac{dJ(\theta)}{d\theta} = J'(\theta)$$

$$So, dJ(\theta) = J'(\theta)d\theta$$

$J'(\theta)$ is called the exit age distribution. It is also designated as 'E'. The plot is called E-curve. J(θ) vs θ curve is called F-curve.

$$\bar{\theta} = \frac{\int_0^\infty \theta J'(\theta)d\theta}{\int_0^\infty J'(\theta)d\theta} = \int_0^\infty \theta J'(\theta)d\theta$$

Mean residence by using E-curve.

If $\theta J'(\theta)$ $is\ plotted\ against\ \theta, the\ area\ under\ the\ curve\ ffrom\ 0\ to\ \infty$

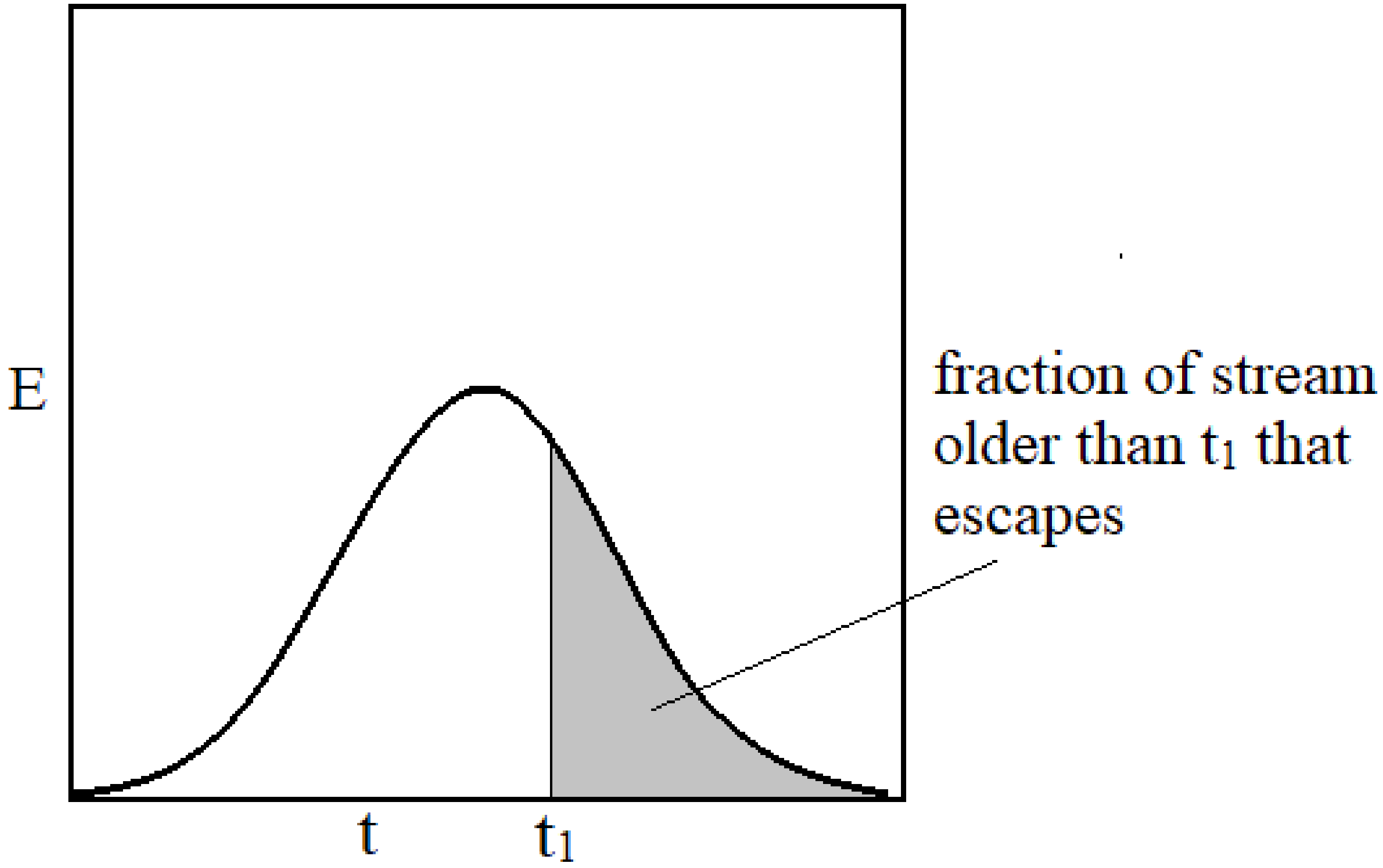
Will give the average or mean residence time $\bar{\theta}$. $\theta J'(\theta)$ may be written as tE

$$\bar{\theta} = \frac{\int_0^\infty \theta J'(\theta) d\theta}{\int_0^\infty J'(\theta) d\theta} = \int_0^\infty \theta J'(\theta) d\theta = \int_0^\infty tEdt$$

If E_i $is\ the\ axit\ age\ distribution\ at\ t_i$ and equal time interval is used.

$$\bar{t} = \sum t_i E_i \Delta t_i$$

$$\int_0^\infty E dt = 1 \qquad and \quad \int_{t_1}^\infty E dt = 1 - \int_0^{t_1} E dt$$



RTD Measurement:

- RTD is determined experimentally by using an inert chemical called a tracer.
- The characteristics of the tracer are:

i) It should be non-reactive

ii) It should be completely soluble in in the system fluid.

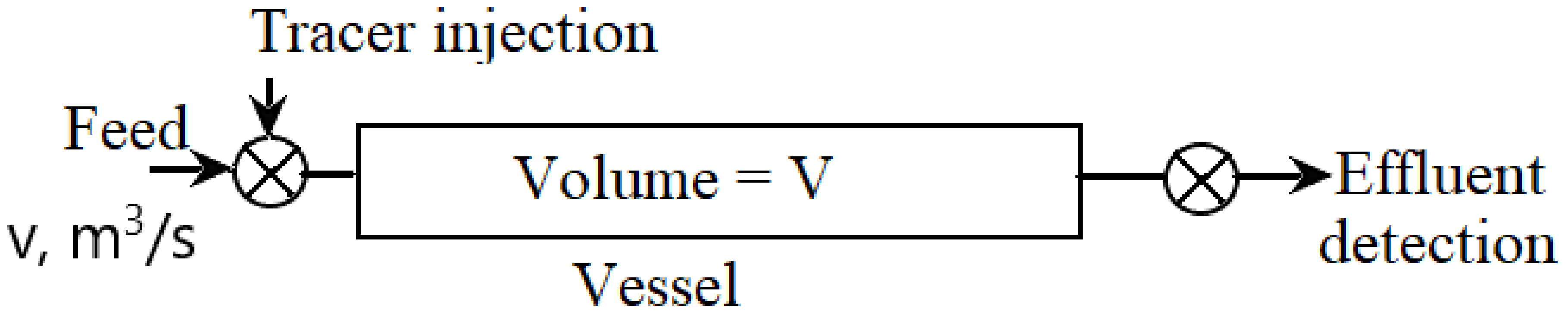
iii) Easily can be detected.

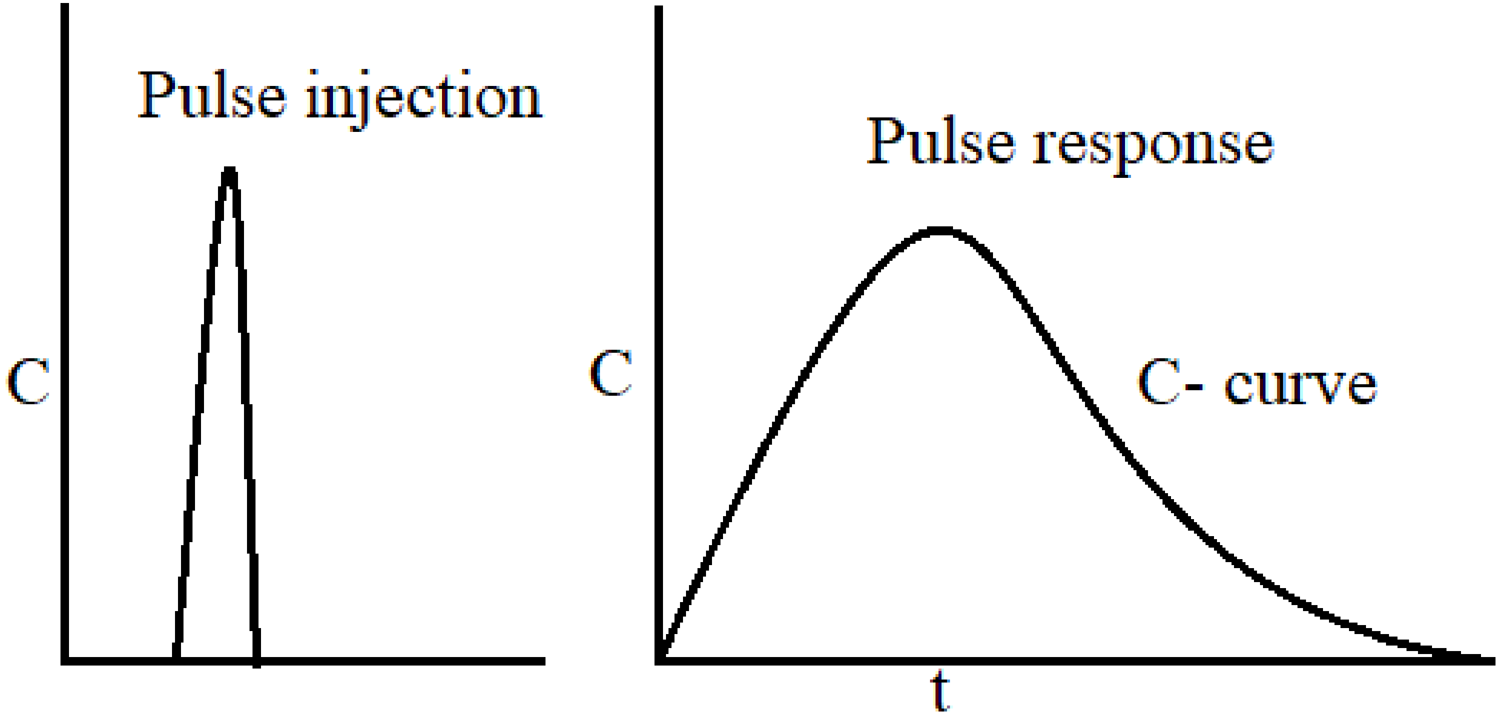
iv) It should have physical properties similar to those of system fluid.

v) It dose not adsorbed on the vessel wall.

RTD measurement:

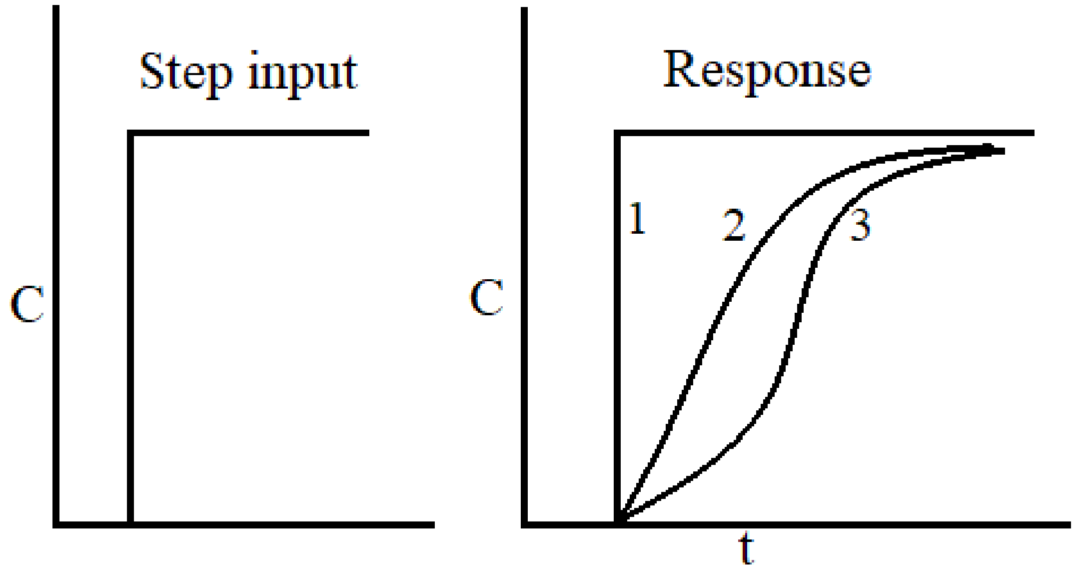
- Stimulus-response technique
- Input of tracer and the response:
- In order to determine the 'E' Curve. A tracer input is added at the inlet of the reactor as stimulus. The outlet concentration of the tracer is determined as a function of time, which is called the response.
- Various input function may be introduced at the inlet. In general, pulse and step inputs are used for this study. Sinusoidal function also may be used.


Tracer injection
Feed
v, m³/s
Volume = V
Vessel
Effluent
detection


Pulse injection
C
Pulse response
C
C- curve
t

Step input: F-Curve

Suppose a stream with a concentration C_0 flows through a reactor with volumetric flow rate Q. At θ=0 all molecules are marked to distinguish them from the molecules entered prior to θ =0. As total concentration remains same, so marked molecule concentration at the inlet is C_0. Now the marked molecule concentration is measured at the outlet by any suitable method at various time. This is C. So, $\frac{C}{C_0} = J(\theta) =$ fraction of molecules of residence less than θ

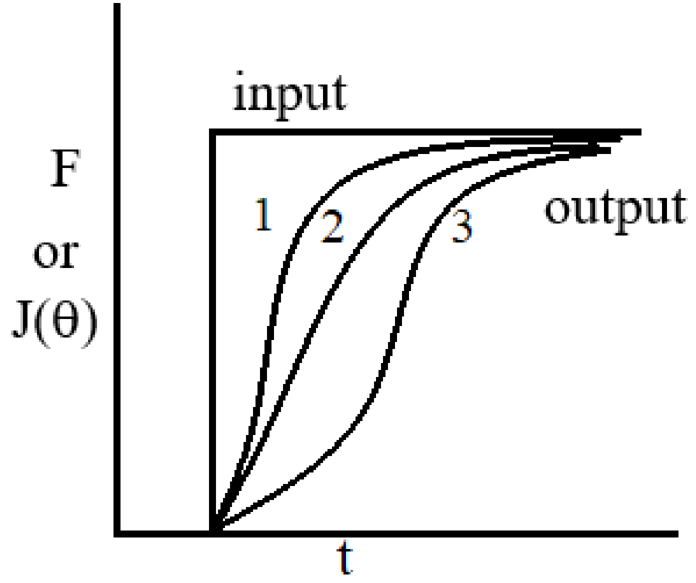


$$dJ(\theta) = Edt = J'(\theta)d\theta$$

$$Mass\ balance\ is\quad C_0QJ(\theta) = C.Q$$

$$\mathrm{F} = \frac{C}{C_0} = J(\theta)$$

The response curves are 1, 2 and 3

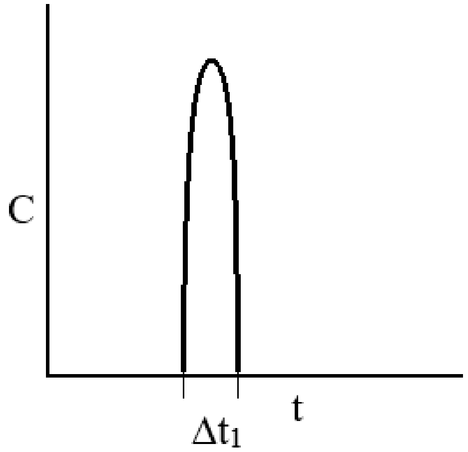


Pulse input: E-Curve

If all molecules are marked for a short span of time, say $\Delta t_0 at\ \theta = 0$,

$$the\ total\ concentration\ of\ marked\ molecules = M = C_0Q\Delta t_0$$

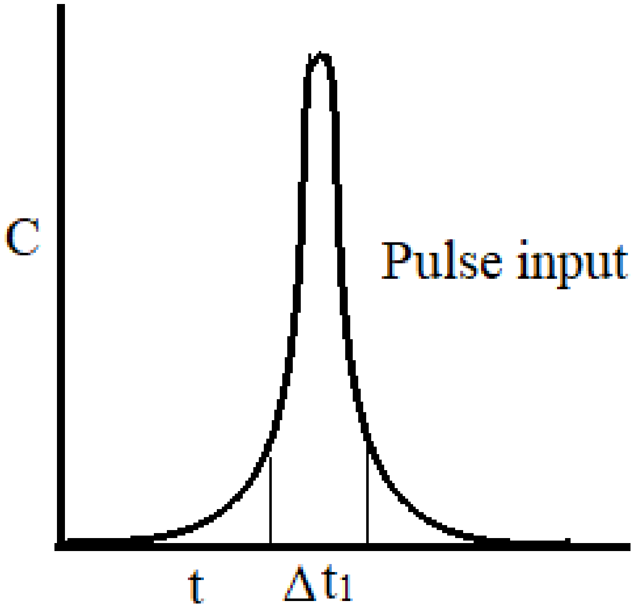
$$C = \{ \begin{array}{ll} 0 & for\ t < 0 \\ C_0 & 0 < t < \Delta t_0 \\ 0 & t > \Delta t_0 \end{array}$$

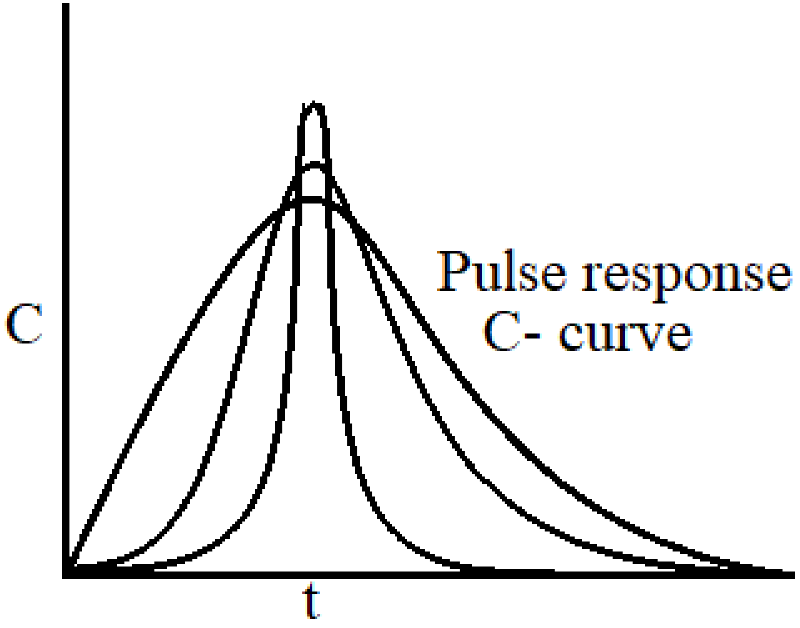


At the outlet we get C versus θ or t, which is called the response curve(C − Curve)
No. molecules leaving in the period θ $to\ \theta + d\theta = CQd\theta$ and $dJ(\theta) is\ the\ fraction\ of\ molecules\ residing\ within$ θ $to\ \theta + d\theta = J'(\theta)d\theta$

$So, MJ'(\theta)d\theta = CQd\theta$

$$j'(\theta) = \frac{C_{pulse}Q}{M} = \mathrm{E} \quad Where, M = Q\int_0^\infty C_{pulse}d\theta$$





$$j'(\theta) = \frac{C_{pulse}Q}{Q\int_0^\infty C_{pulse}d\theta}$$

The relation between step and pulse response

We have $J'(\theta)|_{step} = \frac{dJ(\theta)}{d\theta} = \frac{d(C/C_0)}{d\theta}$

For pulse $J'(\theta) = \frac{C_{pulse}Q}{M}$

$$C_{pulse} = \frac{M}{Q}J'(\theta) = \frac{C_0 Q \Delta t_0}{Q}J'(\theta)$$

$$\frac{C_{pulse}}{C_0} = \Delta t_0 J'(\theta) = \Delta t_0 \frac{d(C/C_0)}{d\theta} \propto \frac{d}{d\theta}J(\theta)\,|_{step}$$

Thus the response curve for a pulse input is proportional to the derivative to the response curve of step input.

RTD of known mixing condition: CSTR

- Mass balance in CSTR: Step function

$$C_0 Q\Delta\theta - CQ\Delta\theta = V\Delta C$$

$$\Delta C = change\ in\ concentration\ inside\ the\ reactor\ in\ \Delta\theta$$

$$C_0 = initial\ concentration\ , C = effluent\ concentration$$

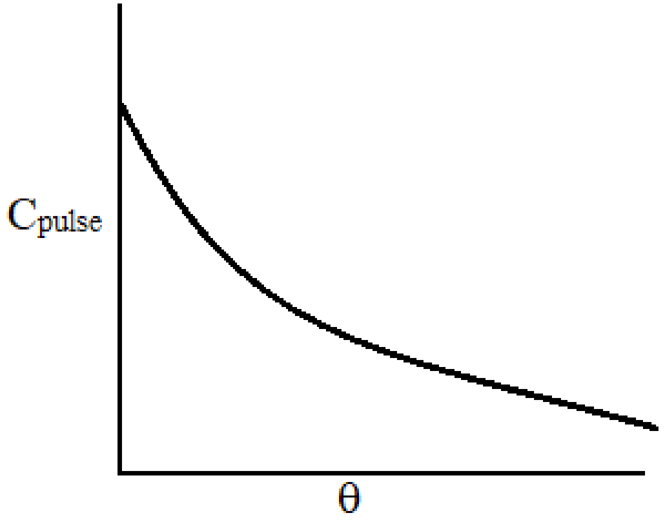
$$\frac{dC}{d\theta} = \frac{Q}{V}(C_0 - C) = \frac{1}{\bar{\bar{\theta}}}(C_0 - C)$$

With the condition $C = 0\ at\ \theta \leq 0$, integrating

$$\int_0^C \frac{dC}{(C_0 - C)} = \frac{1}{\bar{\bar{\theta}}}\int_0^\theta d\theta$$

$$-ln\left[\frac{C_0 - C}{C_0}\right] = \frac{\theta}{\bar{\bar{\theta}}}\ \ or, \qquad \left(\frac{C}{C_0}\right)_{step} = J(\theta) = 1 - e^{-\frac{\theta}{\bar{\bar{\theta}}}}$$

- The response curve for ideal CSTR is $\left(\frac{C}{C_0}\right)_{step} = J(\theta) = 1 - e^{-\frac{\theta}{\bar{\theta}}}$
- If $\theta = \bar{\theta}$, $J(\theta) = 1 - e^{-1} = 0.631$
- So, 63.1 % effluent stream has a residence time less than average residence time $\overline{\theta}$.
- For pulse function, $J'(\theta) = \frac{1}{\bar{\theta}} e^{-\frac{\theta}{\bar{\theta}}}$
- $C_{pulse} = \frac{M}{Q} J'(\theta) = C_0 \Delta t_0 \frac{1}{\bar{\theta}} e^{-\frac{\theta}{\bar{\theta}}}$
- At $\theta = 0$, C_{pulse} $has\ a\ maximum\ value$



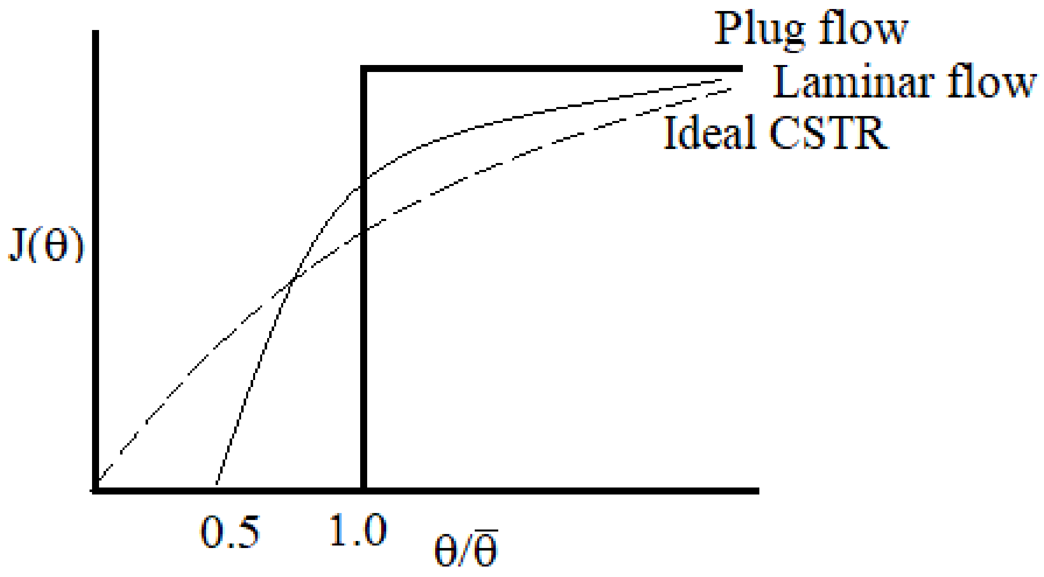
Segregated model: Laminar flow in a tubular reactor

- The velocity profile $u(r) = \frac{2Q}{\pi R^2}\left[1 - \left(\frac{r}{R}\right)^2\right]$
- $\theta = \frac{L}{u} = \frac{V/Q}{2\left[1-\left(\frac{r}{R}\right)^2\right]}$
- $\frac{\theta}{\overline{\theta}} = \frac{1}{2\left[1-\left(\frac{r}{R}\right)^2\right]}$
- The fraction stream in $r \ \ and \ \ r + \Delta r, is \ dJ(r)$ has the residence time in between $\theta \ and \ \theta + \Delta\theta$.
- $dJ(r) = dJ(\theta) = \frac{u(2\pi r dr)}{Q}$
- $dJ(\theta) = \frac{4}{R^2}\left[1 - \left(\frac{r}{R}\right)^2\right] r dr$

$$rdr = \frac{\bar{\theta}}{4\theta^2} R^2 d\theta$$

$$\frac{dJ(\theta)}{d\theta} = J'(\theta) = \frac{1}{2}\frac{\bar{\theta}^2}{\theta^3} \qquad E - curve$$

$\theta_{min} = \frac{V}{2Q} = \frac{1}{2}\bar{\theta}$ at the center of the tube where the velocity is maximum.



Non-ideal reactor models

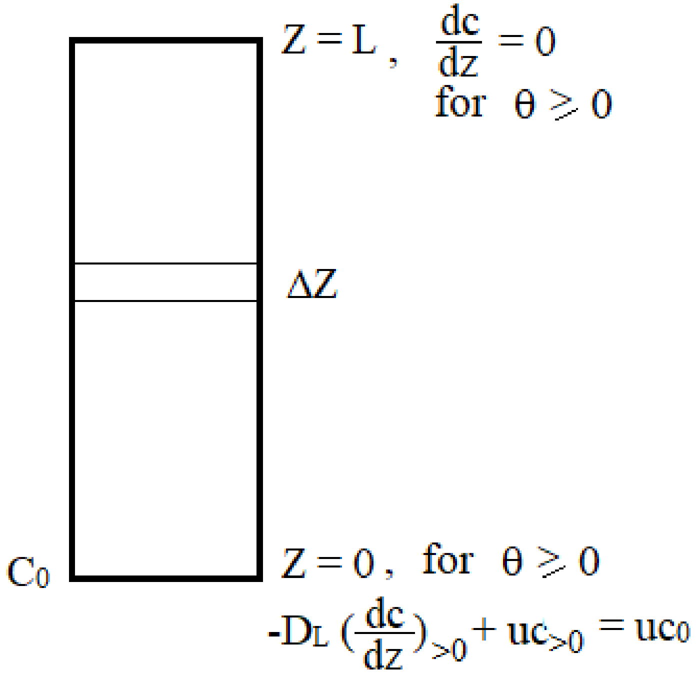
- Dispersion model
- Stirred-tank in series model
- Recycle reactor model

Dispersion model(dispersed plug flow model)
In a tubular flow assume the axial velocity u and concentration are Constant across the diameter.

A step input C_0 is introduced at θ=0.

$$\left[\left(-D_L\frac{\partial C}{\partial z}+uC\right)\pi r_0^2\right]_z\Delta\theta-\left[\left(-D_L\frac{\partial C}{\partial z}+uC\right)\pi r_0^2\right]_{z+\Delta z}\Delta\theta=\pi r_0^2\Delta z\Delta C$$

- Dividing by $\Delta z \Delta\theta$ *and limit* $\Delta z \rightarrow 0$
- $D_L \dfrac{\partial^2}{\partial z^2} - u\dfrac{\partial C}{\partial z} = \dfrac{\partial C}{\partial \theta}$
- $I.C.\;\; C = 0\ at\ z > 0 \;\;\; for\ \theta = 0$
- $C = C_0\ at\ z < 0 \;\;\; for\ \theta = 0$



The equation can be solved by modified B.C as

$$C = C_0\ \ at\ \ z = -\infty\ for\ \theta \geq 0$$
$$C = 0\ \ at\ \ z = \infty\ for\ \theta \geq 0$$

$$Assuming, C^* = \frac{C}{C_0}, \qquad \propto = \frac{z - u\theta}{\sqrt{4D_L\theta}}\ \ we\ get$$

$$\frac{d^2C^*}{d\alpha^*} + 2\alpha\frac{dC^*}{d\alpha} = 0$$

$$\frac{d^2C^*}{d\alpha^*} + 2\alpha\frac{dC^*}{d\alpha} = 0$$

$BCs,$ $\qquad C^* = 1, for \ \propto = -\infty$

$\qquad C^* = 0, for \ \propto = \infty$

$Solution\ is\ ,$

$$\left(\frac{C}{C_0}\right)_{step} = \frac{1}{2}\left[1 - erf\left(\frac{1}{2}\sqrt{\frac{uL}{D_L}}\ \frac{1-\theta/(L/u)}{\sqrt{\theta/(L/u)}}\right)\right]$$

$$\bar{\theta} = \frac{L}{u}$$

$$J(\theta) = \left(\frac{C}{C_0}\right)_{step} = \frac{1}{2}\left[1 - erf\left(\frac{1}{2}\sqrt{\frac{uL}{D_L}}\ \frac{1-\theta/\bar{\theta}}{\sqrt{\theta/\bar{\bar{\theta}}}}\right)\right]$$

$F - Curves\ are\ obtained\ for\ different\ \ D/(uL)$

F- Curves for different D/uL

D/uL is the Dispersion Number

D/uL = 0 , it is plug flow reactor
D/uL = ∞, it is ideal CSTR