LECTURE FIVE: Energy Balance

This lecture covers residence time distribution (RTD), the tanks in series model, combinations of ideal reactors, reactors in series and in parallel, and how the choice of reactor affects selectivity versus conversion

1. **Reactor Size Comparisons for PFR and CSTR**

PFR vs. CSTR: Size and Selectivity

Material balance:

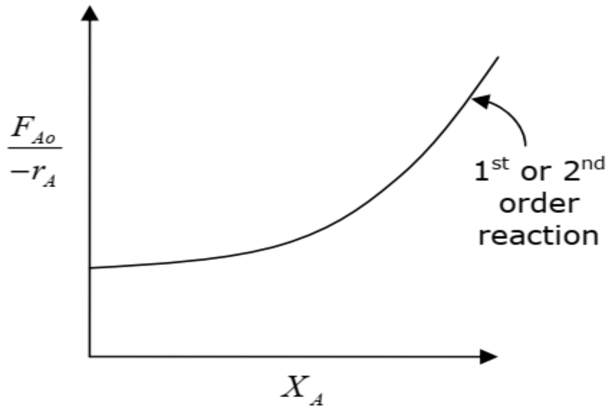
CSTR

$$V = \frac{F_{Ao}}{-r_A} X_A$$

PFR

$$V = \int_0^{X_A} \frac{F_{Ao}}{-r_A} dX_A$$

"Levenspiel Plot"



- as X_A increases, C_A decreases $-r_A$ decreases, for 1st and 2nd order, so $\frac{F_{Ao}}{-r_A}$ increases

Figure 1. General Levenspiel Plot.

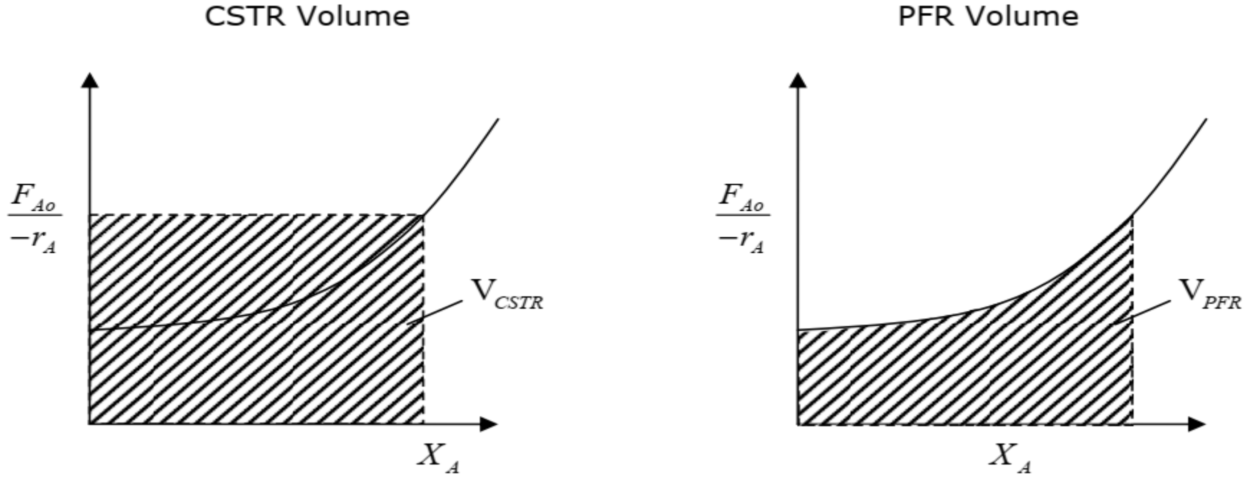


Figure 2. Levenspiel plots for a CSTR and a PFR for positive order reactions.

So PFR is always a smaller reactor for a given conversion when kinetics are positive order.

Non-monotonically positive order kinetics arise:

- Autocatalytic reactions (e.g. cell growth)
- Adiabatic or non-isothermal exothermic reactions
- Product inhibited reactions (some enzymes)

Series of Reactors

Example: 2 CSTRs

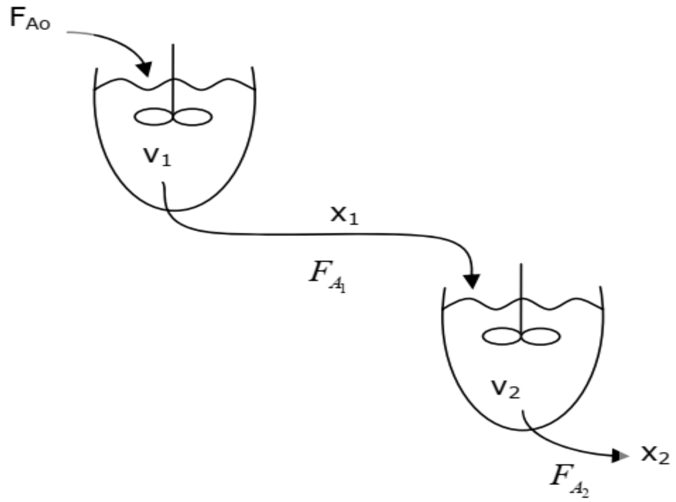


Figure 3. Schematic of two CSTRs in series.

$$V_1 = \frac{F_{Ao}}{-r_{A_1}} X_1$$

2nd reactor:

$$\text{In} + \text{Out} + \text{Prod} = \cancelto{0}{\text{Acc}}$$

$F_{A_1} - F_{A_2} + r_{A_2} V_2 =$ Steady state

$$F_{A_2} = F_{A_0} - X_2 F_{A_0} \quad \rightarrow \quad V_2 = \frac{F_{A_0}}{-r_{A_2}}(X_2 - X_1)$$

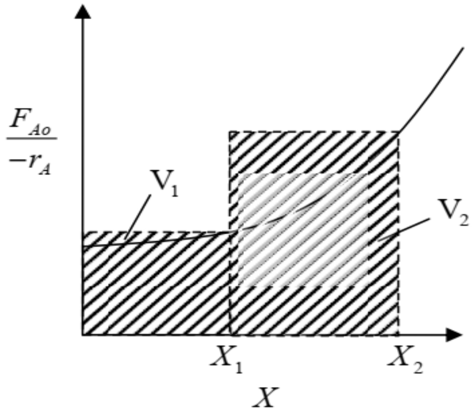
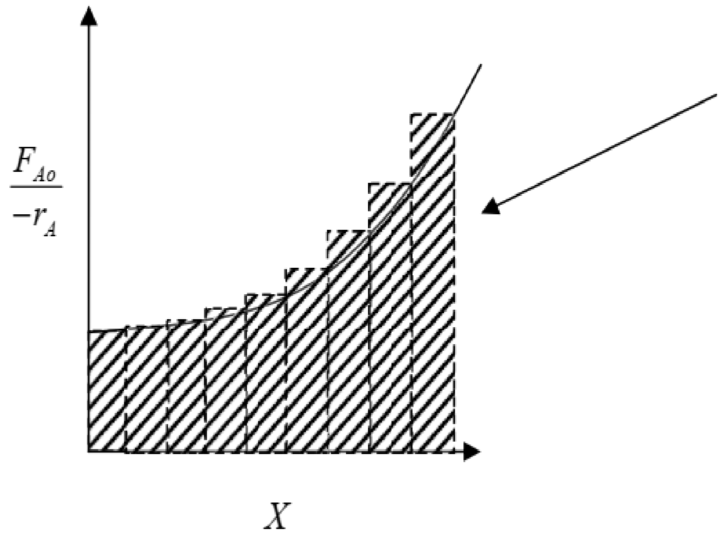


Figure 4. Reactor volumes for 2 CSTRs in series.



Multiple CSTRs begin to approximate a single PFR

Figure 5. Reactor volumes for multiple CSTRs in series.

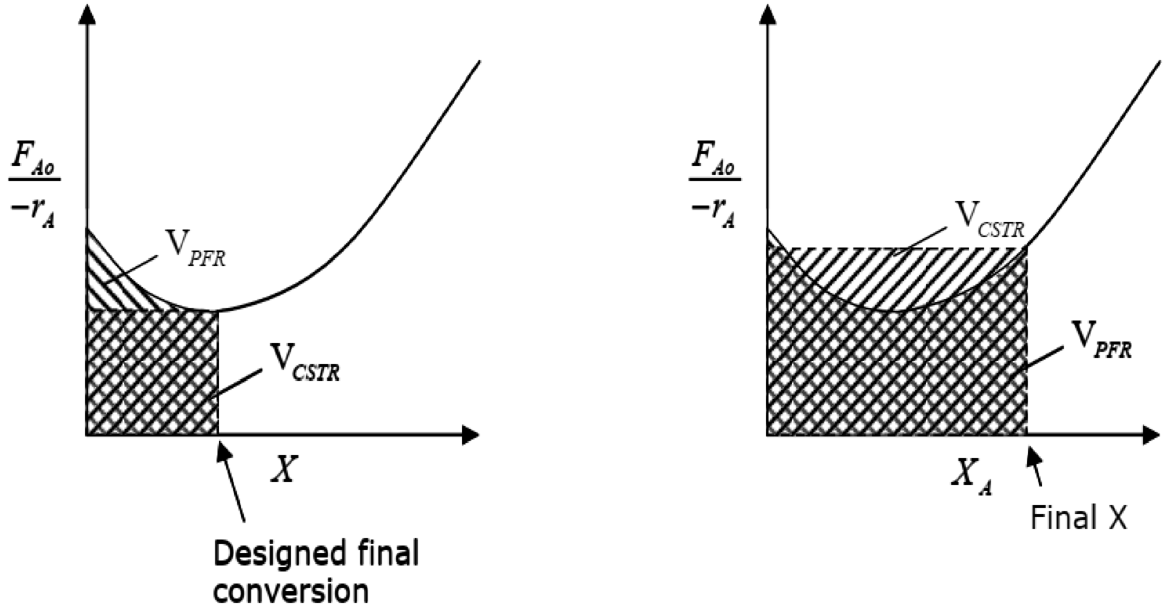


Figure 6. Levenspiel plots comparing CSTR and PFR volumes for changing kinetics. Left: The CSTR has the smaller volume. Right: The PFR eventually has the smaller volume.

Choice of PFR vs CSTR depends on conversion. Choose the reactor that has the smallest volume →reduce cost.

Reactors:

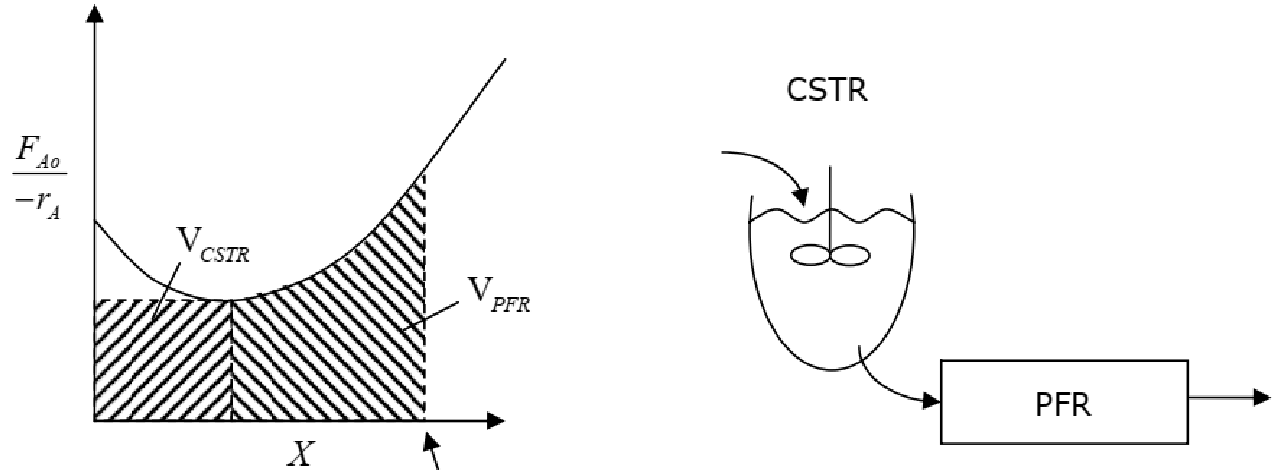


Figure 7. To achieve the desired conversion with smaller reactor volumes, use a combination. In this case, use a CSTR then a PFR. By doing so, the reactor volume is less than the area underneath the curve.

For competing parallel reactions, selectivity for desired product can dominate the choice.

<u>Example</u> $A \rightarrow D \qquad r_D = k_d C_A^{\alpha_1}$ D = Desired, U = Undesired

$A \rightarrow U \qquad r_U = k_u C_A^{\alpha_2}$

Define "selectivity" $S_{D/U} = \frac{r_D}{r_U} = \frac{k_d}{k_u} C_A^{(\alpha_1 - \alpha_2)}$

If $\alpha_1 > \alpha_2$, as C_A increases, $S_{D/U}$ increases

-Favors PFR because C_A starts at C_{Ao} then drops whereas CSTR concentrations are always at lower C_A.

If $\alpha_1 < \alpha_2$, as C_A increases, $S_{D/U}$ decreases

-CSTR favored

If $\alpha_1 = \alpha_2$ then $S_{D/U} = \frac{k_d}{k_u}$, no dependence on C_A

-Therefore no CSTR/PFR preference.

Define a fractional yield

$$\phi = \frac{dC_D}{-dC_A} = \frac{k_d C_A^{\alpha_1}}{k_d C_A^{\alpha_1} + k_u C_A^{\alpha_2}}$$

Overall fractional yield $\Phi = \dfrac{\text{All } D \text{ produced}}{\text{All } A \text{ consumed}}$

For a CSTR: $\Phi = \phi\big|_{\text{Exit } C_A}$

$$\Delta C_A = C_{A_0} - C_{A_f}$$

For a PFR: $\Phi = \dfrac{1}{\Delta C_A} \displaystyle\int_{C_{A0}}^{C_{At}} \phi \, dC_A$

If $\alpha_1 = \alpha_2$

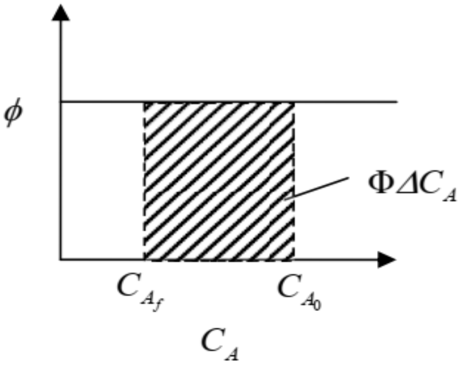


Figure 8. Fractional yield versus concentration. Selectivity does not depend on C_A.

If $\alpha_1 > \alpha_2$

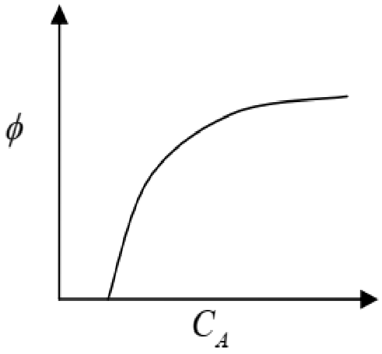


Figure 9. Fractional yield versus concentration when $\alpha_1 > \alpha_2$.

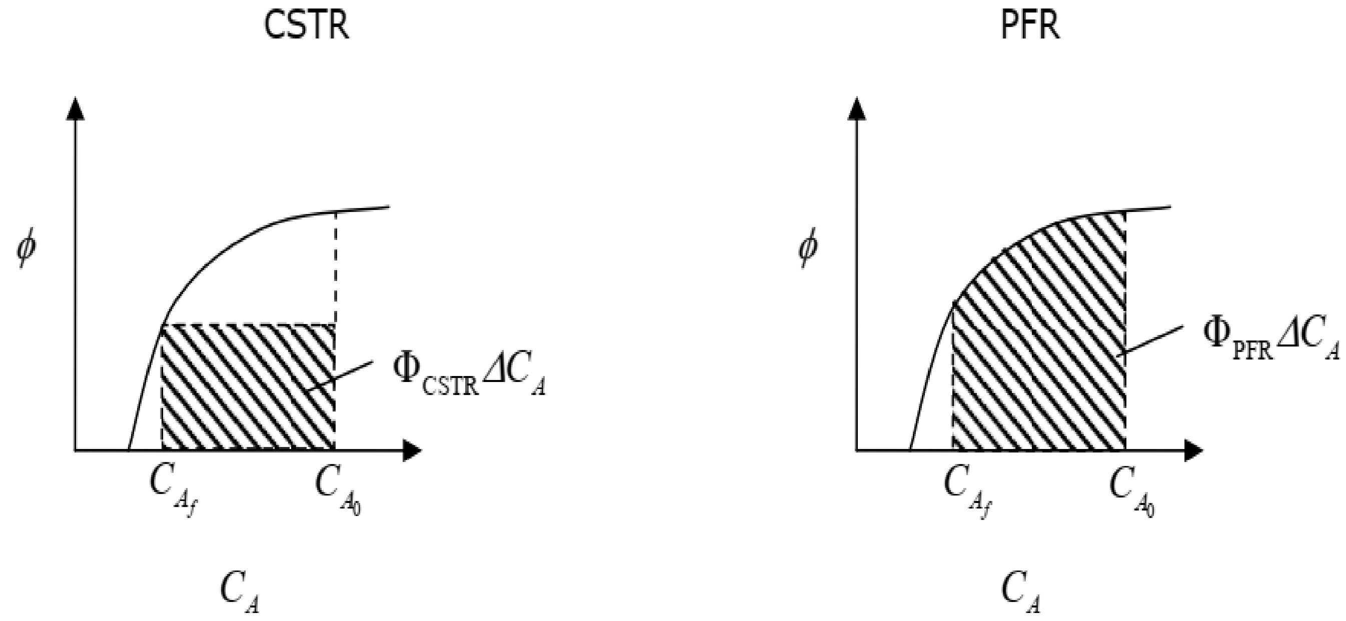


Figure 10. Comparison of overall fractional yield for a CSTR and a PFR when $\alpha_1 > \alpha_2$.

PFR is preferred because $\Phi_{PFR} > \Phi_{CSTR}$, therefore the yield of D per mol A consumed is higher.

If $\alpha_1 < \alpha_2$

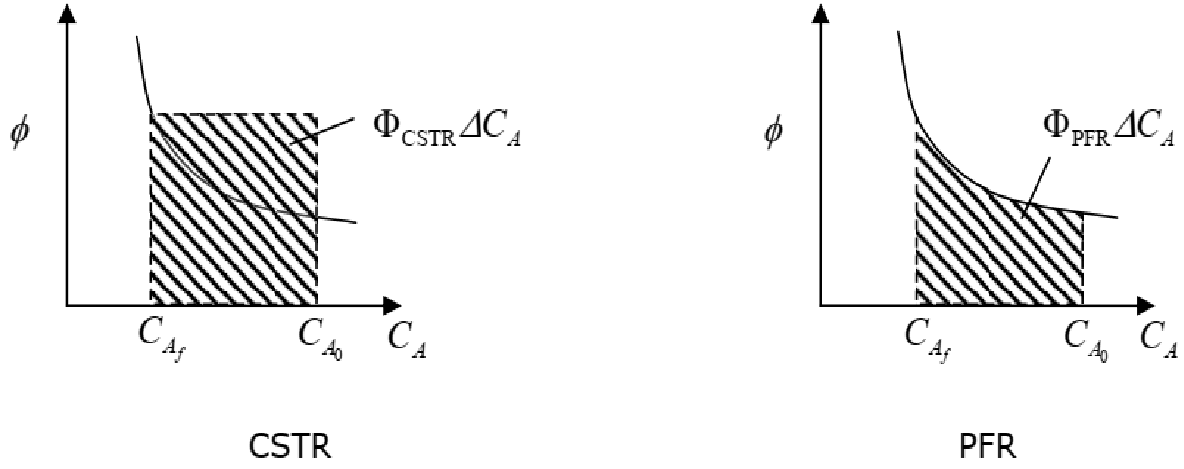


Figure 11. Comparsion of overall fractional yield for a CSTR and a PFR when $\alpha_1 > \alpha_2$.

$$\Phi_{PFR} < \Phi_{CSTR}$$

2. **Nonideal Reactor Mixing Patterns**

Non-Ideal Mixing

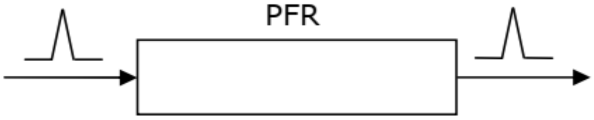


Figure 1. Ideal PFR with pulse input. A pulse input will yield an output profile that is a pulse input.

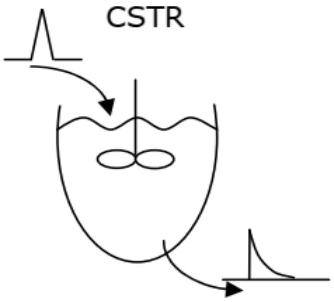


Figure 2. Ideal CSTR with pulse input. A pulse input will yield an output profile that is a sharp peak with a tail.

Real mixed tank

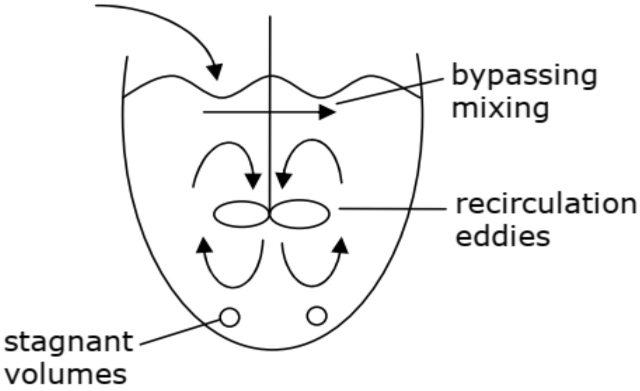


Figure 3. A real mixed tank. In a real mixed tank there are portions that are not well mixed due to stagnant volumes, recirculation eddies, and mixing bypasses.

In a real PFR there is back-mixing and axial dispersion. In a packed bed reactor (PBR) channeling can occur. This is where the fluid channels through the solid medium.

Residence Time Distribution

A useful diagnostic tool is the residence time distribution (RTD). The residence time is how long a particle stays in the reactor once entering.

$E(t)\,dt \equiv$ Probability that a fluid element entering the vessel at t=0 exits between time t and t+dt.

Probability density function for exit time, t, as a random variable.

$\int_0^t E(t)\,dt$ Probability that fluid element exits before time t.

$\int_t^\infty E(t)\,dt$ Probability of exiting at time later than t.

mean t $= \int_0^\infty tE(t)\,dt = \tau$

normalized $= \int_0^\infty E(t)\,dt = 1$

variance $= \sigma^2 = \int_0^\infty (t-\tau)^2 E(t)\,dt$ (measures the broadness of the distribution)

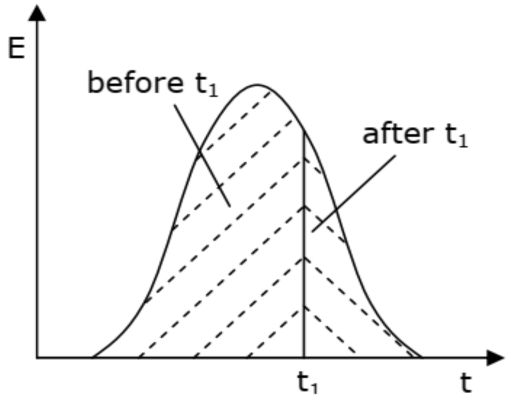


Figure 4. E(t) versus t. At a given time point, some material has exited and some material will still exit at a later time.

Experimental Determination of E(t)

Inflow should be something measurable
-Absorbance
-Fluorescence
-pH
-salt-conductivity
-radioactivity

Use one of two types of input concentration curves:

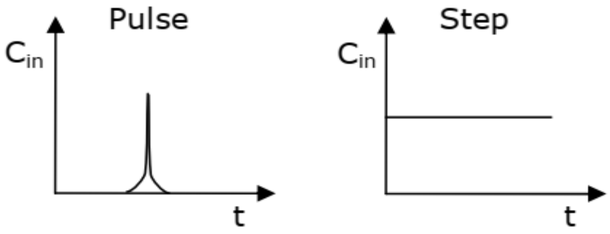


Figure 5. Two types of input. A pulse input is a spike of infinite height but zero width, ideally. A step input is a constant concentration over a period of time.

A pulse input allows for easy interpretation because all materials enter the reactor at once.

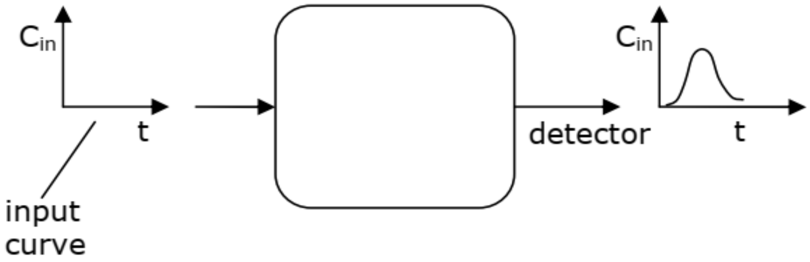


Figure 6. Schematic of a residence-time distribution experiment. The input curve enters the reactor; a detector detects concentration changes in the output stream.

$$E(t)=\frac{C_{out}(t)}{\int_0^t C_{out}(t)\,dt}$$

PFR (Ideal)

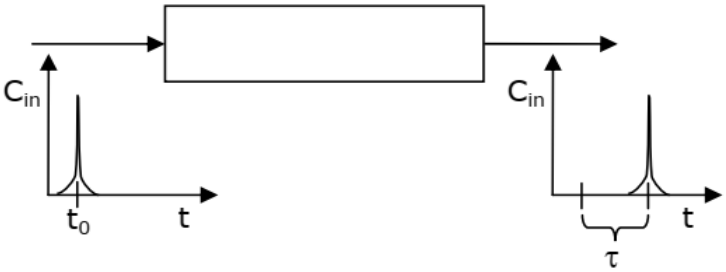


Figure 7. Pulse input in ideal PFR. A pulse input in an ideal PFR becomes a pulse output.

$$E(t)=\delta(t-\tau)$$

$$\delta(x)=\begin{cases}=0 & x\neq 0\\ =\infty & x=0\end{cases}$$

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

$$\int_{-\infty}^{\infty}f(x)\delta(x-a)\,dx=f(a)$$

CSTR (Ideal)

Transient material balance:
In-Out+Production=Accumulation

Since all the material is added at once, In=0. The tracer used is non-reactive. Therefore there is no production. This gives:

$$0 - \nu_0 C + 0 = V\frac{dC}{dt}$$

$$C(t) = C_0 e^{-t/\tau}, \quad \tau = \frac{V}{\nu_0}$$

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

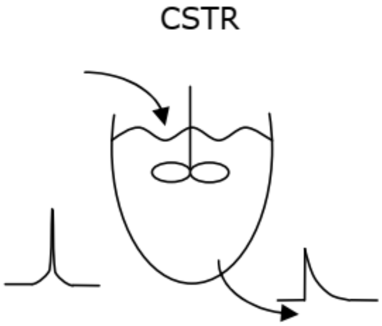


Figure 8. Pulse input in an ideal CSTR. In an ideal CSTR, a pulse input leads to a sharp peak with a tail.

$$\text{mean residence time} = \int_0^\infty \frac{te^{-t/\tau}}{\tau}\,dt = \tau$$

CSTR (non-ideal mixing)

Bypassing: Divide input into 2 streams

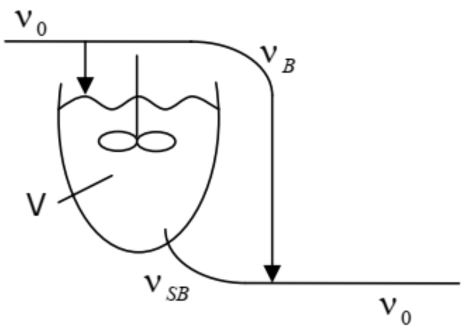


Figure 9. A bypass is modeled by dividing the input stream into two streams, one of which does not enter the reactor.

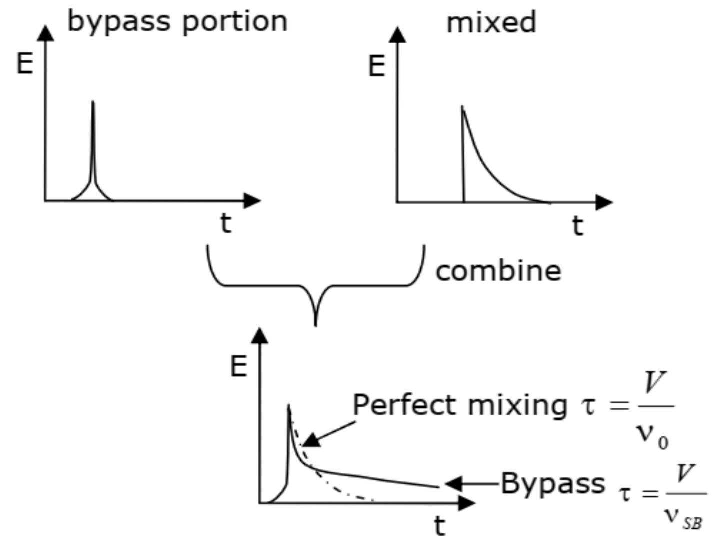


Figure 10. Residence-time distribution determination for a bypass.

Dead volumes: Stagnant regions not getting mixed

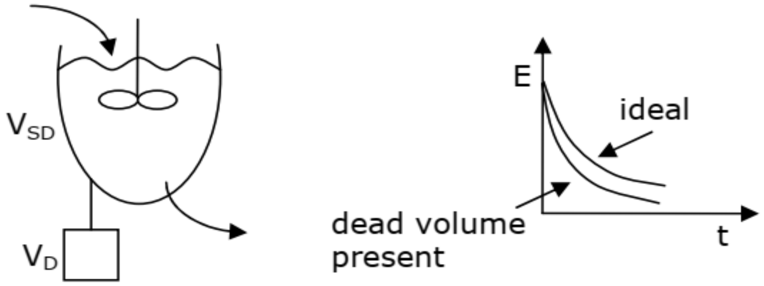


Figure 11. Residence-time distribution for dead volumes**.** When a dead volume is present, a decreased amount of material is observed in the output stream.

measureable $V=V_{SD}+V_D$

$$\tau_{SD} = \frac{V_{SD}}{\nu_0} < \tau_{ideal}$$

PFR (Non-ideal)

Channeling

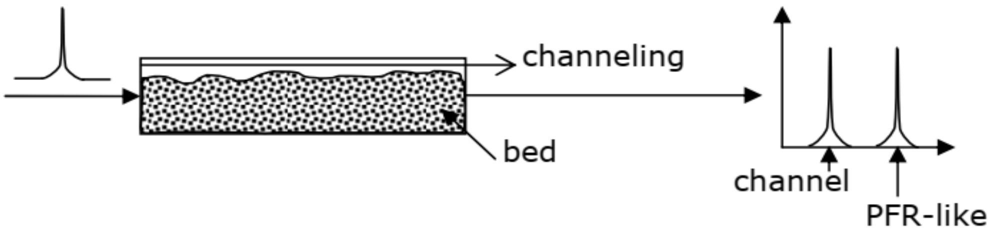


Figure 12. Channeling. In channeling, the residence-time distribution will show peaks for each channel as well as the one for the main portion of the reactor.

Axial Dispersion

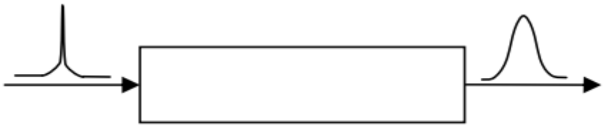


Figure 13. A pulse input can become an axially dispersed pulse output in a non-ideal PFR.

There are two common models for dispersion in a tubular reactor:
-Tanks in a series
-Taylor dispersion model (based on the Peclet number)

To model the PFR as several tanks in a series, break the reactor volume, V, into n CSTRs of volume $\frac{V}{n}$ each.

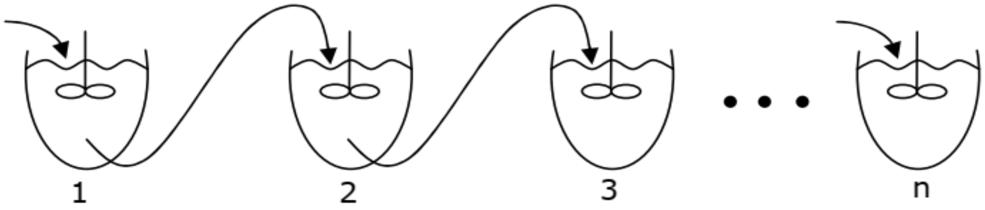


Figure 14. n tanks in series. The output of tank 1 is the input to tank 2. The output is sampled at tank n for dispersion.

$$E(t)=\frac{t^{n-1}}{(n-1)!\tau_i^{n}}e^{-t/\tau_i}\ ,\ \tau_i=\frac{\tau}{n}$$

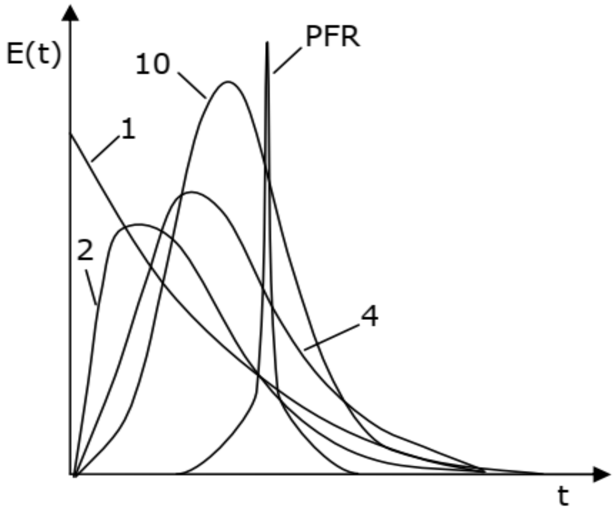


Figure 15. E(t) plots for 1, 2, 4, and 10 tanks and a PFR. Notice how the E(t) curve approaches the PFR pulse as more tanks are used.

The numbers above represent numbers of CSTRs. Without enough CSTRs, the peak is not a good approximation to the narrow peak for a PFR when there is a pulse input.

$$\sigma^2 = \frac{\tau^2}{n}$$

$$n = \frac{\tau^2}{\sigma^2}$$

We can physically measure τ and we can determine σ from experimentally measuring E(t).

RTD (residence time distribution) are useful for diagnosis, but not for reactor design.

To calculate conversion, the most straightforward tactic is to model the non-ideal system as compartmental combinations of ideal reactors.

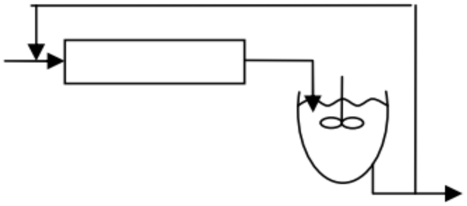


Figure 16. Recirculation. Recirculation can be modeled by a PFR followed by a CSTR with a recycle stream.

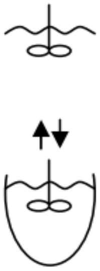


Figure 17. Partially dead volumes. Dead volumes can be modeled as separate CSTRs that exchange material with each other.

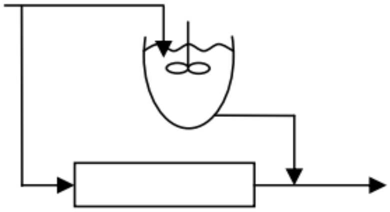


Figure 18. Bypass. A bypass can be modeled as a CSTR along one route with a PFR along the bypass route.