LECTURE FOUR: Multiple Reactions

1. Batch Reactors

<u>Batch Reactors</u>

Run at non-steady state conditions

Which to choose? Batch vs. CSTR?

Figure 1. Schematics of a batch reactor and a CSTR.

Small Amount of Material	(small quantities)	(does not tie up equipment continuously)
Flexibility	+	-
Expensive Reactants	+	-
If product does not flow, Materials Handling (e.g. Polymers)	+	-
Do not have to shut down and clean, less down time	-	+
Captial costs? For size of reactor, for given conversion	+ (concentration stays higher longer)	-
Operability & Control (T, P, p4) e.g. Exothermic reaction	-	+ (Manipulate only one setpoint, steady state. You can control additional variables. Such as flow rates.)

Material Balance

$$\underset{0}{\cancel{\text{In}}} - \underset{0}{\cancel{\text{Out}}} + \text{Product} = \text{Accumulation}$$

$r_A \mathrm{V} = \frac{dN_A}{dt}$

Constant V, $r_A = \frac{dC_A}{dt}$

In terms of conversion, $C_{Ao} \frac{dX_A}{dt} = r_A$

Integrating, $t = \int_{C_{Ao}}^{C_A} \frac{dC_A}{r_A}$ or $t = C_{Ao} \int_0^{X_A} \frac{dX_A}{r_A}$

1st Order Reaction $A \xrightarrow{k} B$

$$-r_A = kC_A = kC_{Ao}(1 - x_A)$$

$$t = C_{Ao} \int_0^{x_A} \frac{dx_A}{-kC_{Ao}(1 - x_A)} \longrightarrow t = \frac{1}{k} \ln\left(\frac{1}{1 - x_A}\right)$$

$$x_A = 1 - e^{-kt}$$

90% conversion $t_{90.0\%} = \frac{1}{k} \ln\left(\frac{1}{1 - 0.9}\right) = \frac{2.3}{k}$

(order of $\frac{1}{k}$)

2nd Order Reaction $A + A \xrightarrow{k} B$

$$-r_A = kC_A^{\,2} = kC_{Ao}^{\,2}(1 - X_A)^2$$

$$t = C_{Ao} \int_0^{X_A} \frac{dX_A}{-kC_{Ao}^{\,2}(1 - X_A)^2} = \frac{1}{-kC_{Ao}} \int_0^{X_A} \frac{dX_A}{(1 - X_A)^2}$$

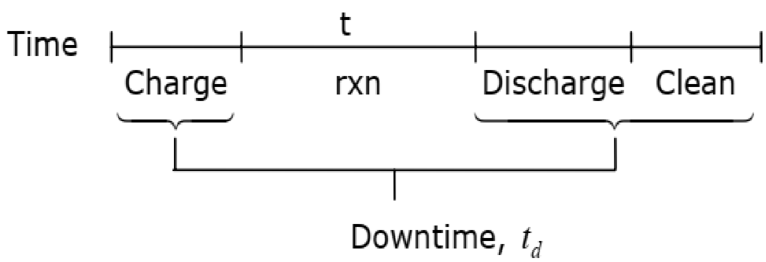
$$t = \frac{1}{kC_{Ao}} \frac{X_A}{1 - X_A} \qquad X_A = \frac{kC_{Ao}t}{1 + kC_{Ao}t}$$

If $k_{\text{first order}} = k_{\text{second order}} C_{Ao}$, which is faster?

	1	2	3	
1st order	0.63	0.86	0.95	$\}x_A$
2nd order	0.50	0.67	0.75	

For a given Damkohler number, 1st order is faster. The second order reaction has greater concentration dependence. Exponential approach (1st order) is faster.

Batch Cycle



How long should t be?
How high should X_A be?

Economic calculation: Compare economics of further conversion to a different use of equipment

Chemical consideration: Will product degrade? Assume product stable.

Product produced in one cycle $= X_A C_{Ao} \mathrm{V}$

$\mathrm{P_r}$(Rate of Production) $= \dfrac{X_A C_{Ao} \mathrm{V}}{t + t_d}$

What value of t will maximize $\mathrm{P_r}$?

If there is a maximum of $\mathrm{P_r}$ vs. t, $\dfrac{d\mathrm{P_r}}{dt} = 0$

Assume $t_d =$ constant. $0 = \dfrac{d\mathrm{P_r}}{dt} = C_{Ao}\mathrm{V}\dfrac{(t_{optimum} + t_d)\dfrac{dX_A}{dt} - X_A}{(t_{optimum} + t_d)^2}$

$$(t_{optimum} + t_d)\frac{dX_A}{dt} - X_A = 0$$

Now specify kinetics. There may be no optimum.

1st order $\quad X_A = 1 - e^{-kt}$

$$\frac{dX_A}{dt} = ke^{-kt}$$

$$(t_{optimum} + t_d)ke^{-kt_{optimum}} - (1 - e^{-kt_{optimum}}) = 0$$

Can numerically solve for $t_{optimum}$.

Semi-batch Reactor

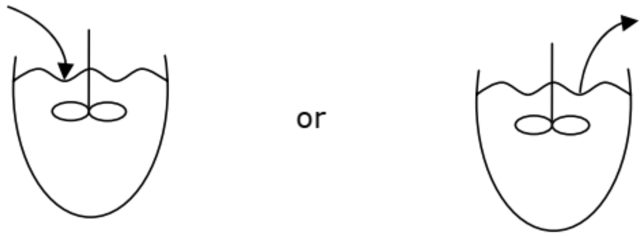


Figure 2. Schematics of two types of fed-batch reactors.

1) Why?

- To remove "poisonous" product
- Make room in reactor (expansion of product)
- If a reactant has a negative order effect on rate, add in small quantities
- Selectivity $A + B \rightarrow$ Desired
  (control) $A + A \rightarrow$ Byproduct

  Start with B, slowly feed A.

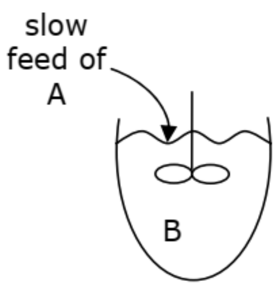


Figure 3. A fed-batch reactor with a slow feed of one reactant.

- To shift equilibrium, strip off product
- To control evolution of heat
- In biological cases
  Fed-batch - Feed in carbon source slowly to avoid overflow metabolism
  - (glucose)
  - O_2 sparingly soluble, must feed.

2) Balances

A Balance

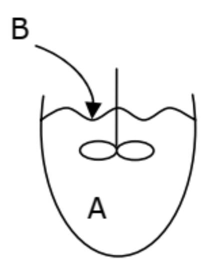


Figure 4. Fed-batch reactor with a feed of B.

In – Out + Product = Accumulation

$$r_A V(t) = \frac{d(r_A V)}{dt}$$

$$r_A \mathrm{V}(t) = \mathrm{V}\frac{dC_A}{dt} + C_A \frac{d\mathrm{V}}{dt}$$

Liquid $\mathrm{V} = \mathrm{V}_0 + v_0 t$ ← flow

$$\frac{dC_A}{dt} = r_A - \overbrace{\frac{v_0}{\mathrm{V}_0} C_A}^{\text{dilution}}$$

B Balance

$$\frac{dC_B}{dt} = r_B + \underbrace{\frac{v_0}{\mathrm{V}_0} C_{Bo}}_{\text{Addition}} - \underbrace{\frac{v_0}{\mathrm{V}_0} C_B}_{\text{Dilution}}$$

2. The Plug Flow Reactor

$$r_A = -k[A]^2$$

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

$$V_{CSTR} = \frac{X_A F_{Ao}}{k[A]_0^2 (1 - X_A)^2} \quad \text{(2}^{\text{nd}}\text{ order reaction)}$$

$$t_{react.} = \frac{X_A}{k[A]_0 (1 - X_A)}$$

$$V_{Batch}\left([A]_0\right) = ?$$

$$F_{Ao} = \frac{\text{moles A}}{\text{time}} = \frac{V_{Batch}[A]_0}{t_{react} + t_d}$$

$$V_{Batch} = \frac{F_{Ao}}{[A]_0}\left[t_d + \frac{X_A}{k[A]_0(1 - X_A)}\right]$$

Assume X_A=90%

If $t_{react} > t_d$ then

$$V_{Batch} = \frac{2F_{Ao} \cdot 0.9}{[A]_0 k[A]_0 (1 - 0.9)}$$

$$V_{CSTR} = \frac{0.9 F_{Ao}}{k[A]_0^2} \le \frac{1.8 F_{Ao}}{k[A]_0^2}$$

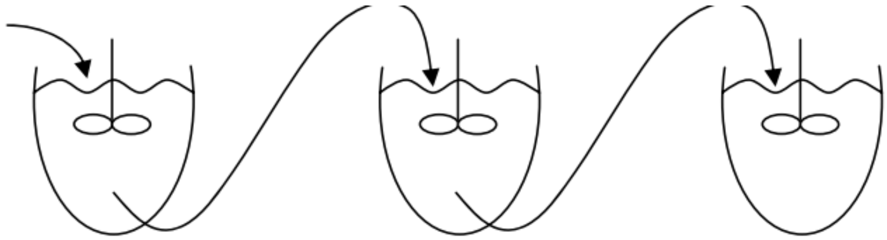


Figure 1. Three tanks in series.

$$[A]_{CSTR} = [A]_{in} + r_A \frac{V}{v_0}$$

If $r_A = -k[A]$

$$[A]_{out} = \frac{[A]_{in}}{1+Da} = \frac{[A]_{in}}{1+\frac{kV}{v_0}}$$

If n CSTRs are in series:

each volume $= \frac{V}{n}$

$$[A]_{out} = \frac{[A]_{in}}{1+\left(\frac{kV}{nv_0}\right)^n}$$

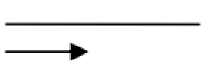
→improves productivity:
concentration of A in 1st one is higher than would be in one large CSTR

$$[A]_{out\ Batch} = [A]_0 e^{\frac{-kV}{v_0}}$$

$$\frac{kV}{v_0} = 3 \Rightarrow 95\% \text{ conversions}$$

$$[A]_{out\ CSTR\ series} = \frac{[A]_0}{\left(1+\frac{3}{n}\right)^n}$$

N	X_A
1	.75
10	.93
100	.948



PFR

Figure 2. Diagram of a plug flow reactor.

Plug Flow Reactor (behaves like an infinite number of infinitely small CSTRs)

$$F_{Ain} - F_{Aout} + r_A\left(\Delta V\right) = 0 \quad \text{CSTR}$$

$$\left(\frac{F_{Ain} - F_{Aout}}{\Delta V}\right) = -r_A$$

$$\frac{dF_A}{dV} = -r_A \quad \text{design equation for PFR}$$

$$\frac{dF_A}{dV} = r\left(C_A, C_B, \ldots\right)$$

$$= -kC_A C_B \quad \text{(for example)}$$

$$F_A = C_A v_0$$

$$\frac{dF_A}{dV} = -k\frac{F_A}{v_0}\frac{F_B}{v_0}$$

This can be expressed as: $\frac{d\underline{Y}}{dt} = F\left(t, \underline{Y}\right)$ where t is replaced by V.

Example:

$$A + B \underset{k_{rev}}{\overset{k}{\rightleftharpoons}} C$$

$$\frac{d}{dV}\underbrace{\begin{pmatrix} F_A \\ F_B \\ F_C \end{pmatrix}}_{\underline{Y}} = \underbrace{\begin{pmatrix} -\dfrac{kF_AF_B}{v_0^2} + \dfrac{k_{rev}F_C}{v_0} \\ -\dfrac{kF_AF_B}{v_0^2} + \dfrac{k_{rev}F_C}{v_0} \\ +\dfrac{kF_AF_B}{v_0^2} - \dfrac{k_{rev}F_C}{v_0} \end{pmatrix}}_{F(t,\underline{Y})}$$

Figure 3. Diagram of a plug flow reactor showing flow in the z-direction.

$$dV = area \cdot dz$$

Mass flow rate is constant

$$(v\rho A) = const.$$

$$\rho = \sum C_i W_i$$

For a liquid, $\frac{d\rho}{dz} = 0$

$$\frac{d(v\rho A)}{dz} = \rho A \frac{dv}{dz} + \rho v \frac{dA}{dz} + Av \frac{d\rho}{dz} = 0$$

Rearrange:

$$\frac{dv}{dz} = -v\left(\frac{1}{A}\frac{dA}{dz} + \frac{1}{\rho}\frac{d\rho}{dz}\right)$$

For a normal pipe $\frac{dA}{dz} = 0$ and for a liquid $\frac{d\rho}{dz} = 0$

Therefore: $\frac{dv}{dz} = 0 \Rightarrow v = v_0$

(We can't assume this for gases!)

For a PFR:

$$\frac{dF_A}{dV} = r_A$$

$$F_A = v[A]$$

$$\frac{d(vC_A)}{dV} = r_A$$

For liquids, v is constant so we can take it out of the differential.

$$r_A = \frac{v}{area}\frac{dC_A}{dz}, \text{ for liquids}$$

$$\frac{dC_A}{dz} = \frac{area}{v_0} r_A$$

Instead of t_{react} we have z_{react}!

$$t_{pipe} = \frac{area \cdot length}{v_0}$$

$$t_{PFR} = \frac{area \cdot z}{v_0} = \frac{X_A}{k[A]_0(1 - X_A)}$$

Flow is driven by the pressure drop across the pipe.

Figure 4. Diagram of a pipe showing pressure upstream and downstream.

$$PV = NRT$$

$$\sum C_i = \frac{P}{RT}$$

$$C_i = \frac{P}{RT}\frac{F_i}{\sum_n F_n}$$ turns F's into concentrations

$\rho = \sum C_i W_i$, W_i is molecular weight of i.

$$v = \frac{\text{mass flowrate}^{\leftarrow const.}}{\rho(z)}$$