

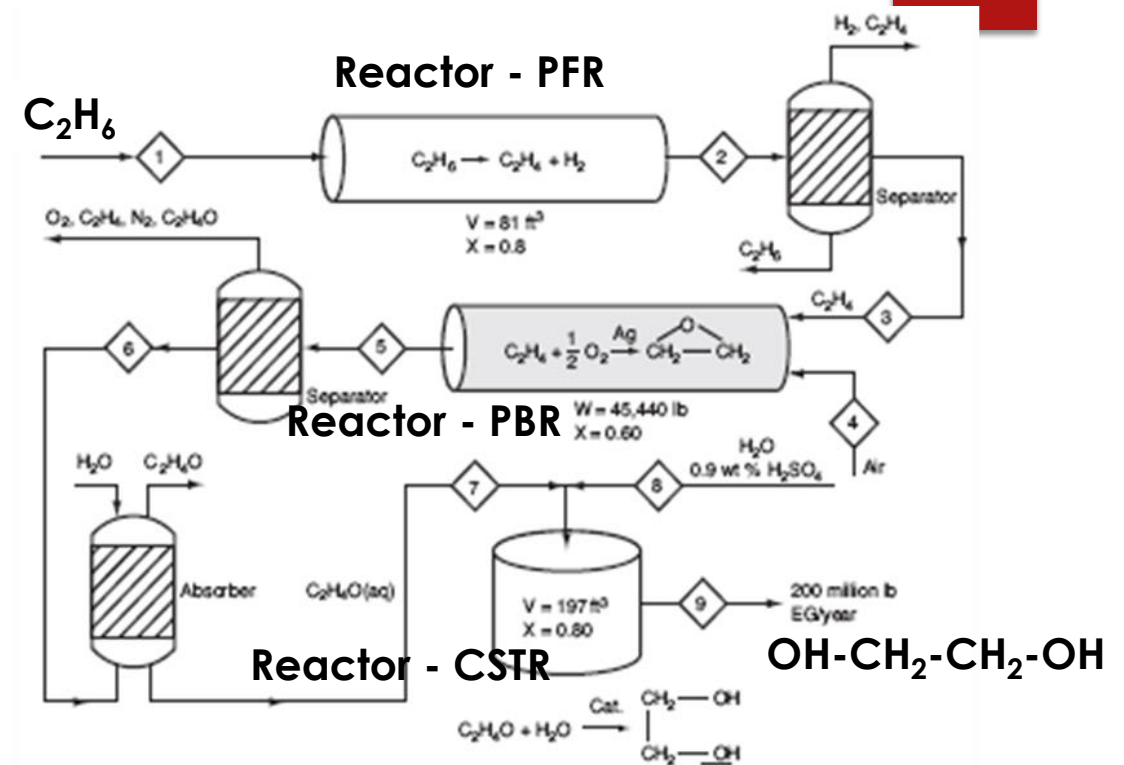
Lecture # 9 CHE331A

- Basics of reactions and ideal reactors
- Design/Analysis of CSTRs, PFRs and PBRs in terms of conversions
- Manufacture of Ethylene Glycol
- Analysis of Batch and Semi-Batch reactors

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Process Flowsheet for Ethylene Glycol Manufacture

From "Elements of Chemical Reaction Engineering", 4th Editions, H.S. Fogler, For teaching purposes only.



Batch and Semi-Batch reactor analysis

- ▶ Batch reactors are used:
 - For small production amounts and
 - Mostly for liquid phase reactions
 - However, they are not suitable for scale up
- ▶ Semi-batch reactors are also used for:
 - Small production amounts
 - Improving selectivity
 - Better control of heat being released in an exothermic reaction
 - Product removal as a purge stream



The design equation need to account for time variations

$$F_{j0} - F_j + \int r_j \cdot dV = \frac{dN_j}{dt}$$

► For Batch reactor: $F_{j0} = 0 = F_j$ and $\int r_j \cdot dV = r_j \cdot V$ (well mixed)

► Thus, $r_j \cdot V = \frac{dN_j}{dt} \rightarrow r_j = \frac{1}{V} \frac{dN_j}{dt} \rightarrow$ for constant volume $r_j = \frac{d(N_j/V)}{dt}$

► $C_j = \frac{N_j}{V}$ and

$$r_j = \frac{dC_j}{dt}$$

This is valid for constant volume systems only and can be used to calculate rates and develop rate laws



For variable volume systems the time variation of volume needs to be accounted for

► $V \neq V_0$ and in terms of limiting reactant $N_A = -N_{A0}dX$

► Thus,

$$r_A = \frac{1}{V} \frac{dN_A}{dt} = -\frac{1}{V} \frac{N_{A0}dX}{dt}$$

► We need $V = V(t)$ or $V(X)$

► For an ideal gas with $T \neq T_0$ and $P \neq P_0$ then $V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{N_T}{N_{T0}} \right)$

► From the stoichiometric table: $\frac{N_T}{N_{T0}} = 1 + \varepsilon \cdot X$

$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} (1 + \varepsilon \cdot X)$$



For ideal gas and isobaric-isothermal conditions the calculations are simplified

- ▶ Substituting for $V(X)$ in $-r_A = \frac{1}{V} \frac{N_{A0} dX}{dt}$

$$-r_A = \frac{1}{(1 + \varepsilon.X)} \frac{C_{A0} dX}{dt} \left(\frac{P}{P_0} \right) \frac{T_0}{T}$$

- ▶ For isobaric-isothermal conditions, $\varepsilon \neq 0$, and $-r_A = k.C_A^2$

- ▶ Thus, $-r_A = k.C_A^2 = k.C_{A0}^2 \frac{(1-X)^2}{(1+\varepsilon.X)^2} = \frac{1}{(1+\varepsilon.X)} \frac{C_{A0} dX}{dt} \rightarrow t = \frac{1}{k.C_{A0}} \int_0^X \frac{(1+\varepsilon.X)}{(1-X)^2} dX$

- ▶ Thus, the reaction time, t_R , can be found out by integration

$$t_R = \frac{1}{k.C_{A0}} \frac{(1 + \varepsilon)X}{(1 - X)} - \varepsilon \ln \frac{1}{1 - X}$$



Total time for batch reactor operation is longer than reaction time

- ▶ Time is required for different operations
 - Filling of the reactor, t_f
 - Heating of the reactor, t_e
 - Cleaning between different batches, t_c
 - Total cycle time: $t_t = t_f + t_e + t_R + t_c$
- ▶ Total reaction time, t_t , may be much larger than t_R in some cases
- ▶ Multiple reactors may be used in the batch mode
 - Necessary to optimize the scheduling of different operations to produce the maximum product



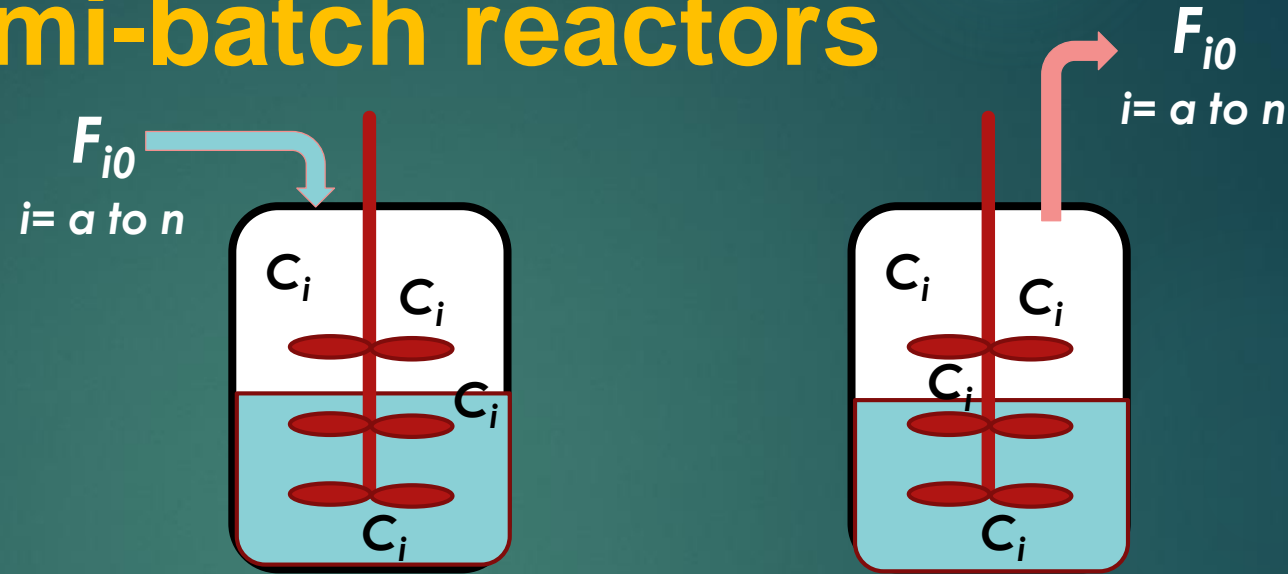
Design equations based on conversion are not always useful

- ▶ Working in terms of N_A , N_B or F_A , F_B , *etc.* is sometimes better
 - For example, membrane reactors and multiple reactions taking place in the gas phase → Multiple ODEs formed
- ▶ Mole balance → Rate law → Stoichiometry for single species is modified
 - Mole balance all species → Rate law → relate mole balances
 - If required concentration → terms of molar flowrates (flow reactors)
 - For isothermal gas-phase reactions use: $C_A = C_{T0} \frac{F_A}{F_T} \frac{P}{P_0}$, *etc*
 - For liquid-phase use C_A , C_B , C_C *etc.*



Analysis of Semi-batch reactors

► Two types



- Analysis of the first type of reactor with reaction $A + B \rightarrow C$
- Constant molar feed of only B and only A initially present in the reactor

$$C_{A0} = \frac{N_{A0}}{V_0} \text{ no B or C} \quad F_{B0} \neq 0 \text{ and } F_{A0} = 0 = F_{C0} \quad V = V(t)$$

- Mass balance to find out $V(t)$: $\frac{dm}{dt} = \dot{m} \rightarrow \dot{m} = \rho_0 \dot{v}_0$ and $m = \rho_0 \cdot V$

$$\frac{d(\rho_0 \cdot V)}{dt} = \rho_0 \dot{v}_0 \Rightarrow \boxed{\frac{dV}{dt} = \dot{v}_0}$$



Mole balance equations need to be modified due to unsteady state conditions

► $\frac{dV}{dt} = \dot{v}_0 \Rightarrow V(t) = V_0 + \dot{v}_0 \cdot t$ since at $t = 0 \Rightarrow V = V_0$

► Mole balance for A: $0 - 0 + r_A \cdot V(t) = \frac{dN_A}{dt} = \frac{d(C_A V)}{dt}$

$$r_A \cdot V(t) = V(t) \frac{dC_A}{dt} + C_A \frac{dV}{dt}$$

► Since $\frac{dV}{dt} = \dot{v}_0 \Rightarrow r_A \cdot V(t) = V(t) \frac{dC_A}{dt} + C_A \cdot \dot{v}_0$ and

$$\frac{dC_A}{dt} = r_A - \frac{C_A \cdot \dot{v}_0}{V(t)}$$

► Not always possible to separate variable, e.g., $-r_A = k \cdot C_A C_B$



Mole balance of B and C is also an unsteady state case

- ▶ Mole balance for B: $F_{B0} - 0 + r_B \cdot V(t) = \frac{dN_B}{dt} = \frac{d(C_B V)}{dt}$
- ▶ $F_{B0} + r_B \cdot V(t) = V(t) \frac{dC_B}{dt} + C_B \frac{dV}{dt}$ with $F_{B0} = \dot{v}_0 C_{B0}^{in}$ and $\frac{dV}{dt} = \dot{v}_0$
- ▶ $C_{B0}^{in} \cdot \dot{v}_0 + r_B \cdot V(t) = V(t) \frac{dC_B}{dt} + C_B \cdot \dot{v}_0$

$$\frac{dC_B}{dt} = r_B + \frac{(C_{B0}^{in} - C_B) \dot{v}_0}{V(t)}$$

- ▶ Similarly, mole balance for C:

$$\frac{dC_C}{dt} = r_C - \frac{C_C \dot{v}_0}{V(t)}$$

with $V(t) = V_0 + \dot{v}_0 \cdot t$



ODEs need to be solved to find the conversion of A and the concentrations vs. time

- ▶ ODEs: $\frac{dC_A}{dt} = r_A - \frac{C_A \cdot \dot{v}_0}{V(t)}$ $\frac{dC_B}{dt} = r_B + \frac{(C_{B0}^{in} - C_B) \dot{v}_0}{V(t)}$ $\frac{dC_C}{dt} = r_C - \frac{C_C \dot{v}_0}{V(t)}$
- ▶ with $V(t) = V_0 + \dot{v}_0 \cdot t$, $C_A = C_{A0}$, and $(C_{B0})_{CV} = 0 = C_{C0}$
- ▶ Rate law: $-r_A = k \cdot C_A \cdot C_B$
- ▶ Stoichiometry: $\frac{r_A}{-1} = \frac{r_B}{-1} = \frac{r_C}{1} \Rightarrow r_A = r_B = -r_C$
- ▶ Conversion of A: $X = \frac{N_{A0} - N_A}{N_{A0}}$
- ▶ $N_{A0} = C_{A0} \cdot V_0$ and $N_A = C_A \cdot V$
- ▶ Known parameters: $C_{A0}, C_{B0}^{in}, V_0, \dot{v}_0, k$

