CHEMICAL REACTION ENGINEERING (SKF3223)

Chapter 6: Multiple Reaction

WAN NORHARYATI WAN SALLEH
hayati@petroleum.utm.my
RAFIZIANA MD. KASMANI
rafiziana@petroleum.utm.my

BY NC SA

ocw.utm.my

Types of multiple reaction

$$A \xrightarrow{k1} B$$
$$A \xrightarrow{k2} C$$

Parallel reaction

$$A + B \longrightarrow C + D$$
$$A + C \longrightarrow E$$

Complex reactions

$$A \longrightarrow B \longrightarrow C$$

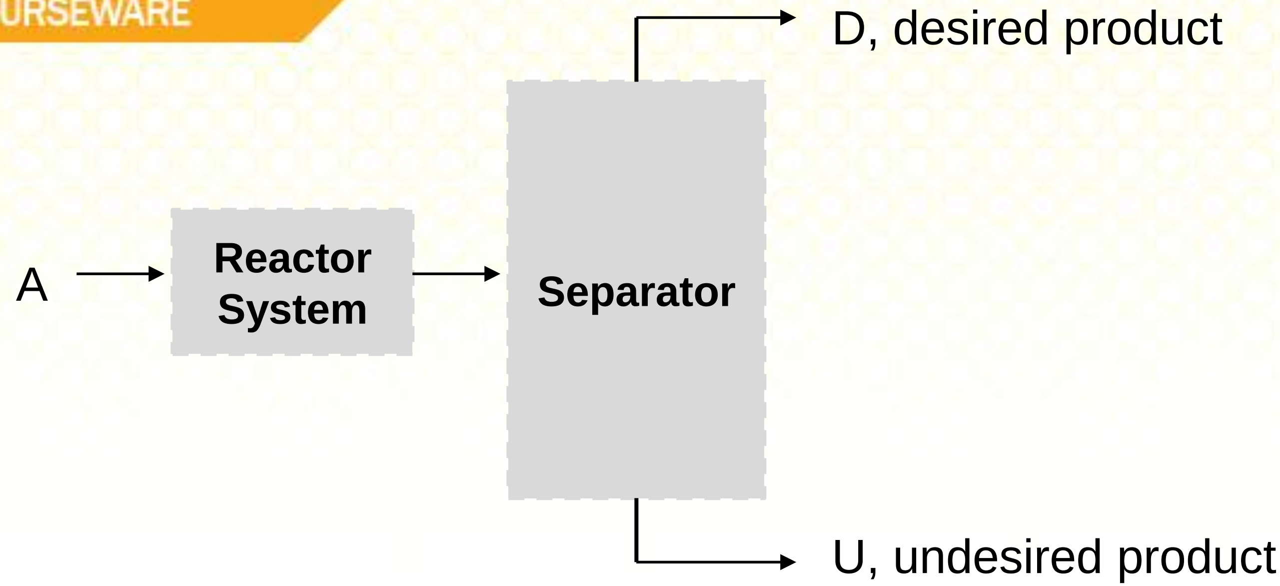
Series reaction

$$A \longrightarrow B + C$$
$$D \longrightarrow E$$

Independent reactions

$$A \rightarrow D$$

$$A \rightarrow U$$



$$A \rightarrow D \rightarrow U$$

<u>Instantaneous Selectivity</u>

$$S_{D/U} = \frac{r_D}{r_U} = \frac{\text{rate of formation of D}}{\text{rate of formation U}}$$

<u>Overall Selectivity</u>

$$\tilde{S}_{D/U} = \frac{F_D}{F_U} = \frac{\text{exit molar flow rate of desired product}}{\text{exit molar flow rate of undesired product}}$$

$$\tilde{S}_{D/U}\,(\text{batch reactor}) = \frac{N_D}{N_U}$$

Reaction Yield

Instantaneous Yield $$Y_D = \frac{r_D}{-r_A}$$

Overall Yield

For Batch system : $$\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A}$$

For flow system : $$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A}$$

- For CSTR: $\tilde{S}_{D/U} = S_{D/U}$ $\tilde{Y}_D = Y_D$
- To maximize the selectivity of D with respect to U run at high concentration of A and use PFR

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Reactor Selection

- Selectivity
- Yield
- Temperature control
- Safety
- Cost

- Different reactors and schemes for minimizing the unwanted product:
  - CSTR – liquid phase reaction
  - PFR
  - Batch
  - Semibatch
  - Series of small CSTRs
  - CSTR with recycle – exothermic reaction
  - Tubular reactor with recycle – gas phase reaction

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Parallel Reactions

$A \rightarrow D$ (desired) $r_D = k_D C_A^{\alpha 1}$

$A \rightarrow U$ (undesired) $r_U = k_U C_A^{\alpha 2}$

Rate of disappearance of A:

$$-r_A = r_D + r_U$$

$$-r_A = k_D C_A^{\alpha 1} + k_U C_A^{\alpha 2}$$

Rate selectivity Parameter :

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D C_A^{\alpha 1}}{k_U C_A^{\alpha 2}} = \frac{k_D}{k_U} C_A^{\alpha 1 - \alpha 2}$$

- If $\alpha_1 > \alpha_2$ use high concentration of A. Use PFR.
  If carried out in the gas phase – run it without inerts at high pressures
  If carried out in liquid phase – use of diluents should be kept to a minimum
- If $\alpha_1 < \alpha_2$ use low concentration of A. Use CSTR and dilute feed stream

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Series Reaction – reaction in PBR

$$A \rightarrow B \rightarrow C$$

1 Rate law : $-r_A^{'} = k_1 C_A$

2 Mole balance : $\dfrac{dF_A}{dW} = r_A^{'}$

3 Stoichiometry (dilute concentrations: y_{A0}=0.001): $F_A = C_A v_0$

4 Combine : $v_0 \dfrac{dC_A}{dW} = -k_1 C_A$ $\quad \tau^{'} = \dfrac{W}{v_0} = \dfrac{\rho_b V}{v_0} = \rho_b \tau$

5 Integrating with $C_A = C_{A0}$ at W = 0: $C_A = C_{A0} e^{-k_1 \tau^{'}}$

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Series Reaction – reaction in PBR

$$A \rightarrow B \rightarrow C$$

1 Rate law : $r'_{Bnet} = r'_{Brxn1} + r'_{Brxn2}$

$r'_{Bnet} = k_1 C_A - k_2 C_B$

2 Mole balance : $\frac{dF_B}{dW} = r'_{Bnet}$

3 Stoichiometry: $F_B = C_B v_0$

4 Combine : $v_0 \frac{dC_B}{dW} = k_1 C_A - k_2 C_B$

Substituting for C_A, dividing v_0 into W : $\frac{dC_B}{d\tau'} + k_2 C_B = k_1 C_{A0} e^{-k_1 \tau'}$

5 Integrating: $C_B = k_1 C_{A0} \frac{e^{-k_1 \tau'} - e^{-k_2 \tau'}}{k_2 - k_1}$

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$$\tau'_{opt} = \frac{1}{k_1 - k_2} In \frac{k_1}{k_2} \qquad W_{opt} = \frac{v_0}{k_1 - k_2} In \frac{k_1}{k_2}$$

$$X_{opt} = \frac{C_{A0} - C_A}{C_{A0}} = 1 - e^{-k_1 \tau'_{opt}}$$

$$X_{opt} = 1 - \exp\left[- In \left(\frac{k_1}{k_2} \right)^{k_1/(k_1 - k_2)} \right] = 1 - \left(\frac{k_1}{k_2} \right)^{k_1/(k_2 - k_1)}$$

Mole balance of C: $\dfrac{dC_C}{d\tau'} = r'_C = k_2 C_B = \dfrac{k_1 k_2 C_{A0}}{k_2 - k_1} [e^{-k_1 \tau'} - e^{-k_2 \tau'}]$

$$C_C = \frac{C_{A0}}{k_2 - k_1} [k_2 [1 - e^{-k_1 \tau'}] - k_1 [1 - e^{-k_2 \tau'}]]$$

$$C_C = C_{A0} - C_A - C_B$$

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Multiple Reactions

1. Number every reaction :

$$A + B \rightarrow 3C + D \qquad (1)$$

$$A + 2C \rightarrow 3E \qquad (2)$$

2. Rate Law for every reaction :

Reaction (1) : $-r_{1A} = k_{1A} C_A C_B$

Reaction (2) : $-r_{2A} = k_{2A} C_A C_C^2$

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3 Relative Rates for every reaction :

Reaction (1) :

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-1} = \frac{r_{1C}}{3} = \frac{r_{1D}}{1}$$

$$r_{1B} = r_{1A} = -k_{1A}C_A C_B$$

$$r_{1C} = 3(-r_{1A}) = 3k_{1A}C_A C_B$$

$$r_{1D} = -r_{1A} = k_{1A}C_A C_B$$

Reaction (2) :

$$\frac{r_{2A}}{-1} = \frac{r_{2c}}{-2} = \frac{r_{2E}}{3}$$

$$r_{2C} = \frac{-2}{-1}(r_{2A}) = -2k_{2A}C_A C_C^2$$

$$r_{2E} = \frac{3}{-1}(r_{2A}) = 3k_{2A}C_A C_C^2$$

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4 Net Rates of Reaction :

$$r_A = r_{1A} + r_{2A} = -k_{1A}C_A C_B - k_{2A}C_A C_C^2$$

$$r_B = r_{1B} = -k_{1A}C_A C_B$$

$$r_C = r_{1C} + r_{2C} = 3k_{1A}C_A C_B - 2k_{2A}C_A C_C^2$$

$$r_D = r_{1D} = k_{1A}C_A C_B$$

$$r_E = r_{2E} = 3k_{2A}C_A C_C^2$$

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Applications of Algorithm

1 Reactions – follow 4 STEP

2 Mole balance – write mole balance on each species

3 Stoichiometry:

$$C_A = C_{T0}\frac{F_A}{F_T}y \qquad C_B = C_{T0}\frac{F_B}{F_T}y \qquad F_T = F_A + F_B + F_C + F_D$$

4 Pressure Drop:

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{F_T}{F_{T0}}\frac{T}{T_0} \qquad y = \frac{P}{P_0}$$

5 Combine

6 SOLVE for the Profiles of F, C, and P for example

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