Lecture # 15 CHE331A

Design of Multiple Reactions in Isothermal Reactors

Definition of Selectivity and Yield

Parallel, Series, Complex and Independent Reactions

Reactor schemes and conditions for improving selectivity

Reactor Design for Multiple reactions

GOUTAM DEO

CHEMICAL ENGINEERING DEPARTMENT

IIT KANPUR

Design and Analysis of Reactors where multiple reactions take place

▶ For example: $A + B \rightarrow C$ and $A + 3C \rightarrow D$

▶ Mole balance equations for a Batch or Flow reactors

▶ For each species 'i':

- $\frac{dN_i}{dt} = r_i V$ (Batch Reactor)

- $V = \frac{F_{i0} - F_i}{-r_i}$ (CSTR) $\frac{dF_i}{dV} = r_i$ (PFR) $\frac{dF_i}{dW} = r_i'$ (PBR)

▶ Need to determine reaction rate for multiple reactions

Multiple reactions continued

▶ Number of reactions: $A + B \rightarrow C$ and $A + 3C \rightarrow D$

▶ Rate laws: $-r_{1A} = k_{1A}C_AC_B$ for 1st reaction

$\qquad\qquad -r_{2A} = k_{2A}C_AC_C^3$ for 2nd reaction

▶ Net rate for species 'i': $\boldsymbol{r_i} = \sum_{j=1}^{n} r_{ji}, \Rightarrow$ here $i = 4 \ and \ j = 2$

$\boldsymbol{r_A} = r_{1A} + r_{2A}$ $\boldsymbol{r_B} = r_{1B} + r_{2B}$ $\boldsymbol{r_C} = r_{1C} + r_{2C}$ $\boldsymbol{r_D} = r_{1D} + r_{2D}$

▶ Relations between Rates: $\dfrac{r_{1A}}{-1} = \dfrac{r_{1B}}{-1} = \dfrac{r_{1C}}{1}$ $\dfrac{r_{2A}}{-1} = \dfrac{r_{2C}}{-3} = \dfrac{r_{2D}}{1}$

$\qquad\qquad -r_{1A} = -r_{1B} = r_{1c}$ and $-r_{2A} = -\dfrac{1}{3}r_{2C} = r_{1D}$

Multiple reactions continued some more

▶ Net rate for species 'i': $r_i = \sum_{j=1}^{n} r_{ji}, \Rightarrow$ here $i = 4 \; and \; j = 2$

$$-r_A = -r_{1A} - r_{2A} = k_{1A}C_AC_B + k_{2A}C_AC_C^3 \quad \Rightarrow \quad -r_A = k_{1A}C_AC_B + k_{2A}C_AC_C^3$$

$$-r_B = -r_{1B} - r_{2B} = k_{1A}C_AC_B + 0 \quad\quad\quad \Rightarrow \quad -r_B = k_{1A}C_AC_B$$

$$r_C = r_{1C} + r_{2C} = k_{1A}C_AC_B - 3k_{2A}C_AC_C^3 \quad \Rightarrow \quad r_C = k_{1A}C_AC_B - 3k_{2A}C_AC_C^3$$

$$r_D = r_{1D} + r_{2D} = 0 + k_{2A}C_AC_C^3 \quad\quad\quad\quad \Rightarrow \quad r_D = k_{2A}C_AC_C^3$$

▶ These are the rate laws to be used in the mole balance equations

$$\frac{dN_i}{dt} = r_iV \quad \text{(Batch)} \quad\quad\quad V = \frac{F_{i0} - F_i}{-r_i} \quad \text{(CSTR)}$$

$$\frac{dF_i}{dV} = r_i \quad \text{(PFR)} \quad\quad\quad \frac{dF_i}{dW} = r_i' \quad \text{(PBR)}$$

Maximizing the Selectivity for the Trambouze Reactions – Example 6-2 of Fogler (4th Edition)

► Reactant *A* decomposes by 3 simultaneous liquid-phase reactions to form 3 products. One of the products *B* is the desired product and two of them, *X* and *Y*, are undesired products. $C_{A0} = 0.4M$ and $\dot{v}_0 = 2\frac{dm^3}{s}$

► Rate Laws:

○ $A \xrightarrow{k_1} X$ $-r_{1A} = r_X = k_1$ $k_1 = 0.0001\frac{mol}{dm^3.s}$ @ 300K

○ $A \xrightarrow{k_2} B$ $-r_{2A} = r_B = k_2 C_A$ $k_2 = 0.0015\frac{1}{s}$ @ 300K

○ $A \xrightarrow{k_3} Y$ $-r_{3A} = r_Y = k_3 C_A^2$ $k_3 = 0.008\frac{dm^3}{mol.s}$ @ 300K

► $E_1 = 10,000\frac{kcal}{mol}$; $E_2 = 15,000\frac{kcal}{mol}$; $E_2 = 20,000\frac{kcal}{mol}$

► Determine conditions (reactor type, temperature, conc.) to maximize B.

The selectivity factor for the Trambouze Reactions and it optimization

▶ $S_{B/XY} = \dfrac{r_B}{r_X + r_Y} = \dfrac{k_2 C_A}{k_1 + k_3 C_A^2}$ 　　　Thus, $S_{B/XY}$ is a function of C_A only

▶ An optimum value of $S_{B/XY}$ can be obtained by finding the derivative of the function above with respect to C_A and set it to zero

▶ $\dfrac{dS_{B/XY}}{dC_A} = 0 = \dfrac{k_2\left[k_1 + k_3 (C_A^*)^2\right] - k_2 C_A^* [2 k_3 C_A^*]}{\left[k_1 + k_3 C_A^*\right]^2}$ 　　where C_A^* is the optimum C_A

▶ Thus, $C_A^* = \sqrt{\dfrac{k_1}{k_3}} = \sqrt{\dfrac{0.0001 \left(mol/_{dm^3 . s}\right)}{0.008 \left(dm^3/_{mol.s}\right)}} = 0.112 \; {dm^3}/_{mol}$

Optimum concentration can assist in deciding on the Choice of the Reactor

▶ For a CSTR we can operate at the resulting $C_A^*(= 0.112)$ so that $S_{B/XY}$ is at this optimum value

▶ For PFR/PBR the value of C_A^* is not constant since the concentrations vary along the length – reactor will not operate optimally

▶ $S_{B/XY} = \dfrac{k_2 C_A^*}{k_1 + k_3 \left(C_A^*\right)^2} = \dfrac{k_2}{2\sqrt{k_1 k_3}} = 0.84$

▶ Designing a CSTR to achieve C_A^* we use: $V = \dfrac{F_{A0} - F_A}{-r_A} = \dot{v}_0 \dfrac{C_{A0} - C_A^*}{-r_A^*}$

▶ $-r_A = k_1 + k_2 C_A + k_2 C_A^2 = 0.0001 + 0.0015 * 0.112 + 0.008 * 0.112^2$

$$-r_A = 3.6835 * 10^{-4} \frac{mol}{dm^3.s}$$

The volume and conversion of the CSTR can be determined

▶ $V = \dot{v}_0 \frac{C_{A0} - C_A^*}{-r_A^*} = 2 * \frac{0.4 - 0.112}{3.6835 * 10^{-4}} = 1564 \text{ dm}^3$ and $X = \frac{C_{A0} - C_A^*}{C_{A0}} = 0.72$

▶ Effect of temperature can be determined by analyzing the E_i's

▶ $S_{B/XY} = \frac{k_2 C_A^*}{k_1 + k_3 (C_A^*)^2} = \frac{k_2}{2\sqrt{k_1 k_3}} = \frac{A_2}{2\sqrt{A_1 A_3}} \exp\left[-\frac{E_2 - 0.5(E_1 + E_3)}{RT}\right]$

▶ But, $\frac{E_2 - 0.5(E_1 + E_3)}{RT} = \frac{15000 - 0.5(10000 + 20000)}{RT} = 0$

▶ Thus, $S_{B/XY}$ is temperature insensitive $\rightarrow$ increase in temp will reduce V

▶ For $X > 0.72$ additional considerations are required

For conversions greater than 0.72 we can use another reactor

▶ $X > 0.72$ can be achieved with the CSTR followed by a PFR

  ○ Concentration will gradually decrease with use of a PFR instead of dropping immediately to lower values

  ○ Thus, reactor system is: $CSTR \left(with\ C_A^* \right) + \int_{C_A^*}^{C_A^f} PFR$

▶ For designing the PFR and finding the overall selectivity the exit concentrations or molar flowrates of B, X and Y are required

▶ Outlet molar flowrates & concentrations are determined from the species mol balance equations:

$$F_{B,\ X\ or\ Y} = \left(r_{B,\ X\ or\ Y} \right) . V \qquad \text{with } V = 1564 \text{ dm}^3$$

Design of the PFR following the CSTR

▶ CSTR outlet stream: $F_{B,X \text{ or } Y} = (r_{B,X \text{ or } Y}).V$ with $V = 1564 \text{ dm}^3$

▶ $F_X = k_1.V = 0.0001 * 1564 = 0.156 \, {}^{mol}/_s$

▶ $F_B = k_2.C_A^*.V = 0.0015 * 0.112 * 1564 = 0.263 \, {}^{mol}/_s$

▶ $F_Y = k_3.(C_A^*)^2 V = 0.008 * 0.112^2 * 1564 = 0.157 \, {}^{mol}/_s$

$C_{A0} = 0.4M$

$\dot{v}_0 = 2 \dfrac{dm^3}{s}$

C_A^* C_A^* C_A^* C_A^*

F_i^{CSTR} i = A, X, B, Y

F_i^{PFR} i = A, X, B, Y

▶ For increasing X to 0.9

▶ $C_{A,f} = (1 - 0.9) * 0.4 = 0.04$

▶ 4 ODEs from mole balance of A, B, X and Y need to be solved

▶ $C_{A,B,X,Y} \; vs \; V \; or \; \tau$ obtained $\rightarrow$ $V \; or \; \tau$ determined from $C_{A,f} = 0.04$