

## Lecture: Selecting Reactor Types

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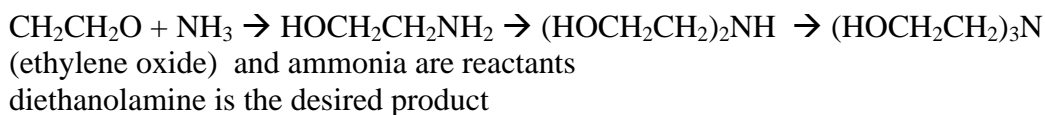
This lecture is coordinated with Chapter 6 Sections 1-3 of Fogler.

### Types of Multiple Reactions

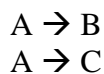
#### 1. series



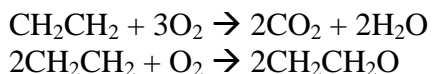
example



#### 2. parallel

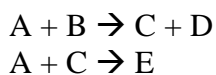


example



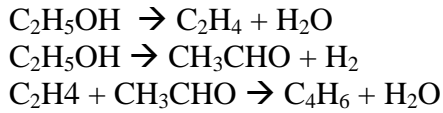
You want to avoid complete combustion of ethylene.

#### 3. complex



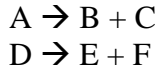
elements of series and parallel reactions

example

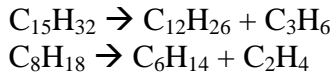


products of parallel reactions are reactants for the next reaction in the series

4. independent



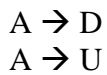
example



There are many reactions in cracking of crude oil to form gasoline.

### Desired and Undesired reactions

parallel



series



process:

typically react then separate

Goals:

form as little U as possible

Selectivity:

$$S_{D/U} \equiv \frac{r_D}{r_U} = \frac{\text{rate of production of } D}{\text{rate of production of } U} \text{ at steady state}$$

overall selectivity

$$\tilde{S}_{D/U} \equiv \frac{F_D}{F_U} = \frac{\text{exit flowrate of } D}{\text{exit flowrate of } U}$$

$$\tilde{S}_{D/U} \equiv \frac{N_D}{N_U} = \frac{\text{moles of } D}{\text{moles of } U} \text{ for batch reactor}$$

See Figure 6-2, page 308.

For simple parallel and simple series reaction in a CSTR at steady state,

$$S_{D/U} = \tilde{S}_{D/U}$$

### Reaction yield

$$Y_D \equiv \frac{r_D}{-r_A} \text{ at steady state}$$

or

$$Y_D \equiv \frac{F_D}{F_{A,in} - F_A} \text{ at steady state}$$

$$Y_D \equiv \frac{N_D}{N_{A,o} - N_A} \text{ for batch reactor}$$

### Parallel Reactions (Section 6.2)

$A \rightarrow D$  with reaction rate  $k_D$

$A \rightarrow U$  with reaction rate  $k_U$

rate laws

$$r_D = k_D C_A^{|v_{A,1}|}$$

$$r_U = k_U C_A^{|v_{A,2}|}$$

selectivity

$$S_{D/U} \equiv \frac{r_D}{r_U} = \frac{k_D C_A^{|v_{A,1}|}}{k_U C_A^{|v_{A,2}|}} = \frac{k_D}{k_U} C_A^{|v_{A,1}| - |v_{A,2}|} = \frac{k_D}{k_U} C_A^a$$

We want a high selectivity for D.

### Designing Constraints for Concentration

Case 1.  $a > 0$

Keep a high concentration.

liquids - Don't use dilutants

gases - pressurize

reactor type - BR or PFR

because they keep the reactant concentration higher than the CSTR

Case 2.  $a < 0$

Keep a low concentration.

liquids - Use dilutants

gases - low pressure

reactor type - CSTR

because they keep the reactant concentration lower than the BR or PFR

### Designing Constraints for Temperature

$$k_D = k_{D,o} \exp\left(-\frac{E_{a,D}}{RT}\right)$$

$$k_U = k_{U,o} \exp\left(-\frac{E_{a,U}}{RT}\right)$$

$$\begin{aligned} S_{D/U} &\equiv \frac{r_D}{r_U} = \frac{k_D C_A^{|v_{A,1}|}}{k_U C_A^{|v_{A,2}|}} = \frac{k_D}{k_U} C_A^{|v_{A,1}| - |v_{A,2}|} = \frac{k_D}{k_U} C_A^a = \frac{k_{D,o} \exp\left(-\frac{E_{a,D}}{RT}\right)}{k_{U,o} \exp\left(-\frac{E_{a,U}}{RT}\right)} C_A^a \\ &= \frac{k_{D,o}}{k_{U,o}} \exp\left(-\frac{(E_{a,D} - E_{a,U})}{RT}\right) C_A^a \end{aligned}$$

Consider the asymptotes

high temperature asymptote

$$\lim_{T \rightarrow \infty} S_{D/U} = \lim_{T \rightarrow \infty} \frac{k_{D,o}}{k_{U,o}} \exp\left(-\frac{(E_{a,D} - E_{a,U})}{RT}\right) C_A^a = \frac{k_{D,o}}{k_{U,o}} C_A^a$$

low temperature asymptote

$$\lim_{T \rightarrow 0} S_{D/U} = \lim_{T \rightarrow 0} \frac{k_{D,o}}{k_{U,o}} \exp\left(-\frac{(E_{a,D} - E_{a,U})}{RT}\right) C_A^a = \begin{cases} 0 & \text{if } E_{a,D} > E_{a,U} \\ \infty & \text{if } E_{a,D} < E_{a,U} \end{cases}$$

Case 3.  $E_{a,D} > E_{a,U}$

Run at a high temperature

Case 4.  $E_{a,D} < E_{a,U}$

Run at a low temperature

Optimization Example. See Example 6—2 on page 312-315.

$A \rightarrow X$	zeroth order in A
$A \rightarrow B$	first order in A
$A \rightarrow Y$	second order in A

We want B.

$$S_{B/XY} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2}$$

The maximum selectivity occurs at a particular value of A

Design the CSTR to Run at that particular value by controlling residence time.

We can find the maximum value of  $C_A$  by

$$\frac{dS_{B/XY}}{dC_A} = 0$$

$$C_A^{\max} = \sqrt{\frac{k_1}{k_3}}$$

$$S_{B/XY}^{\max} = \frac{r_B}{r_X + r_Y} = \frac{k_2 \sqrt{\frac{k_1}{k_3}}}{k_1 + k_3 \left(\sqrt{\frac{k_1}{k_3}}\right)^2} \approx 0.84$$

Find volume of CSTR to give this concentration.

$$\frac{dC_A}{dt} = 0 = \frac{F_{in}}{V} C_{A,in} - \frac{F_{out}}{V} C_A + \nu_{A,1} r_1 + \nu_{A,2} r_2 + \nu_{A,3} r_3$$

$$V = - \frac{F_{in} C_{A,in} - F_{out} C_A}{\nu_{A,1} r_1 + \nu_{A,2} r_2 + \nu_{A,3} r_3}$$

Find the conversion.

$$X_A = \frac{F_{in} C_{A,in} - F_{out} C_A}{F_{in} C_{A,in}}$$

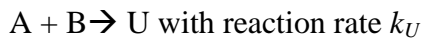
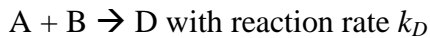
The conversion is about 72%.

If you require higher conversion, then follow the optimized CSTR with a PFR.

### Reactor Selection

See Figure 6.3 on page 318.

Consider



rate laws

$$r_D = k_D C_A^{\nu_{A,1}} C_B^{\nu_{B,1}}$$

$$r_U = k_U C_A^{\nu_{A,2}} C_B^{\nu_{B,2}}$$

selectivity

$$S_{D/U} \equiv \frac{r_D}{r_U} = \frac{k_D C_A^{\nu_{A,1}} C_B^{\nu_{B,1}}}{k_U C_A^{\nu_{A,2}} C_B^{\nu_{B,2}}} = \frac{k_D}{k_U} C_A^{|\nu_{A,1}| - |\nu_{A,2}|} C_B^{|\nu_{B,1}| - |\nu_{B,2}|} = \frac{k_D}{k_U} C_A^a C_B^b$$

Case 1.  $a > 0$ ,  $b > 0$

Keep a high concentration of A and B.

liquids - Don't use dilutants

gases - pressurize

reactor type - BR or PFR

because they keep the reactant concentration higher than the CSTR

Case 2.  $a > 0$ ,  $b < 0$

Keep a high concentration of A and a low concentration of B.

reactor type –

semi-batch in which B is fed slowly into a large amount of A

membrane reactor or PFR with sidestream feed of B

a series of small CSTRs with A fed to first reactor and B fed to each reactor.

Case 3.  $a < 0, b < 0$

Keep a low concentration of A and B

liquids - Use dilutants

gases – low pressure

reactor type –

CSTR

PFR with high recycle ratio

Case 4.  $a < 0, b > 0$

Keep a high concentration of B and a low concentration of A.

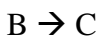
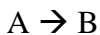
reactor type –

semi-batch in which A is fed slowly into a large amount of B

membrane reactor or PFR with sidestream feed of A

a series of small CSTRs with B fed to first reactor and A fed to each reactor.

### Series Reactions (Section 6.3)



B is desired product.

If first reaction is fast and second reaction is slow, we want a short residence time.

If first reaction is slow and second reaction is fast, difficult to get B.

Calculation of optimal residence time to get the optimum yield of the intermediate product.

Solve for a long PFR. Observe maximum in B. Use that reactor length.

If the reactions are relatively simple, you may be able to calculate the optimum reactor size analytically as is done in Example 6-4 on page 321-324.

Start with the mole balances for A and B.

$$\frac{dC_A}{dz} = \frac{v_{A,1}r_1 + v_{A,2}r_2}{v_z}$$

$$\frac{dC_B}{dz} = \frac{v_{B,1}r_1 + v_{B,2}r_2}{v_z}$$

In this example  $\nu_{A,1} = -1$  and  $\nu_{A,2} = 0$  and  $\nu_{B,1} = 1$  and  $\nu_{B,2} = -1$ . The rate laws are elementary, so the mole balances become

$$\frac{dC_A}{dz} = \frac{-k_1 C_A}{v_z}$$

$$\frac{dC_B}{dz} = \frac{k_1 C_A - k_2 C_B}{v_z}$$

Integrating the first ODE yields

$$C_A = C_{A,in} \exp\left(\frac{-k_1 z}{v_z}\right)$$

Substitution of the first ODE into the Second ODE yields

$$\frac{dC_B}{dz} = \frac{k_1 C_{A,in} \exp\left(\frac{-k_1 z}{v_z}\right) - k_2 C_B}{v_z}$$

Isolate CB on the LHS.

$$\frac{dC_B}{dz} + \frac{k_2}{v_z} C_B = \frac{k_1}{v_z} C_{A,in} \exp\left(\frac{-k_1 z}{v_z}\right)$$

use the integrating factor

$$\exp\left(\frac{k_2}{v_z} z\right) \cdot \left(\frac{dC_B}{dz} + \frac{k_2}{v_z} C_B\right) = \exp\left(\frac{k_2}{v_z} z\right) \frac{k_1}{v_z} C_{A,in} \exp\left(\frac{-k_1 z}{v_z}\right)$$

$$\frac{d \exp\left(\frac{k_2}{v_z} z\right) C_B}{dz} = \frac{k_1}{v_z} C_{A,in} \exp\left(\left(-\frac{k_1}{v_z} + \frac{k_2}{v_z}\right) z\right)$$

$$d \left[ \exp\left(\frac{k_2}{v_z} z\right) C_B \right] = \frac{k_1}{v_z} C_{A,in} \exp\left(\left(-\frac{k_1}{v_z} + \frac{k_2}{v_z}\right) z\right) dz$$

Integrate



$$\exp\left(\frac{k_2}{v_z} z\right) C_B - C_{B,in} = \frac{\frac{k_1}{v_z} C_{A,in}}{\left(-\frac{k_1}{v_z} + \frac{k_2}{v_z}\right)} \left[ \exp\left(\left(-\frac{k_1}{v_z} + \frac{k_2}{v_z}\right) z\right) - 1 \right]$$

If  $C_{B,in} = 0$  and we simplify

$$C_B = \frac{k_1}{k_2 - k_1} C_{A,in} \left[ \exp\left(-\frac{k_1}{v_z} z\right) - \exp\left(-\frac{k_2}{v_z} z\right) \right]$$

To optimize,

$$\frac{dC_B}{dz} = 0 = \frac{k_1}{k_2 - k_1} C_{A,in} \left[ -\frac{k_1}{v_z} \exp\left(-\frac{k_1}{v_z} z^{\max}\right) + \frac{k_2}{v_z} \exp\left(-\frac{k_2}{v_z} z^{\max}\right) \right]$$

Solve for  $z^{\max}$

$$0 = -k_1 \exp\left(-\frac{k_1}{v_z} z^{\max}\right) + k_2 \exp\left(-\frac{k_2}{v_z} z^{\max}\right)$$

$$\frac{k_1}{k_2} = \exp\left(\frac{k_1}{v_z} z^{\max} - \frac{k_2}{v_z} z^{\max}\right)$$

$$z^{\max} = \frac{v_z}{k_1 - k_2} \ln\left(\frac{k_1}{k_2}\right)$$

You can get all the concentrations, conversions, yields, and selectivities by evaluating the concentrations at this optimized reactor length.