Lecture: Selecting Reactor Types

David J. Keffer
Department of Chemical and Biomolecular Engineering
The University of Tennessee, Knoxville
dkeffer@utk.edu
last updated: November 7, 2011

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

Types of Multiple Reactions

1. series

$A \rightarrow B \rightarrow C$

example

$CH_2CH_2O + NH_3 \rightarrow HOCH_2CH_2NH_2 \rightarrow (HOCH_2CH_2)_2NH \rightarrow (HOCH_2CH_2)_3N$
(ethylene oxide) and ammonia are reactants
diethanolamine is the desired product

2. parallel

$A \rightarrow B$
$A \rightarrow C$

example

$CH_2CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
$2CH_2CH_2 + O_2 \rightarrow 2CH_2CH_2O$

You want to avoid complete combustion of ethylene.

3. complex

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

elements of series and parallel reactions example

$C_2H_5OH \rightarrow C_2H_4 + H_2O$
$C_2H_5OH \rightarrow CH_3CHO + H_2$
$C_2H4 + CH_3CHO \rightarrow C_4H_6 + H_2O$

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

4. independent

$A \rightarrow B + C$
$D \rightarrow E + F$

example

$C_{15}H_{32} \rightarrow C_{12}H_{26} + C_3H_6$
$C_8H_{18} \rightarrow C_6H_{14} + C_2H_4$

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

Desired and Undesired reactions

parallel

$A \rightarrow D$
$A \rightarrow U$

series

$A \rightarrow D \rightarrow U$

process:
typically react then separate

Goals:
form as little U as possible

Selectivity:

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

overall selectivity

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

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

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

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

or

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

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

Parallel Reactions (Section 6.2)

A → D with reaction rate k_D

A → U with reaction rate k_U

rate laws

$$r_D = k_D C_A^{|\nu_{A,1}|}$$
$$r_U = k_U C_A^{|\nu_{A,2}|}$$

selectivity

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

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

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

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

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

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

Consider the asymptotes

high temperature asymptote

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

low temperature asymptote

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

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 → X	zeroth order in A
A→ B	first order in A
A→ 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

A + B → D with reaction rate k_D

A + B→ U with reaction rate k_U

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)

$A \rightarrow B$
$B \rightarrow C$

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 simply, 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.

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

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

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.