SUPPLEMENT TO CHAPTER 7

7S.1 LOCATING THE SEPARATION SECTION WITH RESPECT TO THE REACTOR SECTION

In many, perhaps most, chemical processes, a separation section is located after the reaction section, as shown in Figure 7S.1. In this separation section, products are purified and unconverted reactants are recovered for recycle back to the reactor. In this manner, a process involving reactions with unfavorable chemical equilibrium constants, \( K_c \), at reactor conditions can achieve high overall process conversions to desired products. Important industrial examples are the hydrogenation of nitrogen to ammonia,

\[
N_2 + 3H_2 \leftrightarrow 2NH_3
\]

and the hydrogenation of carbon monoxide to methanol,

\[
CO + 2H_2 \leftrightarrow CH_3OH
\]

both of which are exothermic reactions, whose chemical equilibrium constants, therefore, decrease with increasing temperature according to the van’t Hoff equation:

\[
\left( \frac{\partial \ln K_c}{\partial T} \right)_p = \frac{\Delta H^\circ_{rxn}}{RT^2}
\]  

(7S.1)

In these two examples, the chemical equilibrium constants are both less than unity and reactor conversions are less than 50\% at temperatures high enough to achieve reasonable reaction rates. Because both reactions involve shrinkage in the number of moles (4 to 2 for the ammonia reaction and 3 to 1 for the methanol reaction), the reactor conversion can also be increased by increasing the pressure, but practical considerations limit the operating pressure. However, with the recovery and recycle of unconverted reactants, overall process conversions of 100\% are approached.
Although product purification may require extreme measures to achieve product specifications, recycle streams rarely require a significant degree of purification with respect to recycled reactants. When two or more reactants are involved, they do not have to be recovered separately for recycle unless their separation indexes (e.g., relative volatility) are separated by the product(s), as shown in the next two examples.

**EXAMPLE 7S.1 Styrene Manufacture.**

In the styrene manufacture process of Figure 9.61, the main reaction is

\[ \text{Methanol} + \text{Toluene} \rightarrow \text{Styrene} + \text{Hydrogen} + \text{Water} \]

The following side reaction also occurs:

\[ \text{Methanol} + \text{Toluene} \rightarrow \text{Ethylbenzene} + \text{Water} \]

The reactor effluent contains appreciable percentages of unreacted methanol and toluene. In this process, both styrene and ethylbenzene are products and must be purified to meet strict specifications. Water from the main reaction must be treated to the extent required for disposal to a sewer or for another use. Methanol and toluene are recovered and recycled. They are adjacent in relative volatility and, therefore, when distillation is used, they need not be separated; and because they are recycled they need not be purified to a high degree. Typically, the recycle stream might contain 5% ethylbenzene plus styrene.

**EXAMPLE 7S.2 Cumene Manufacture.**

A more complex example is the manufacture of cumene (isopropyl benzene) by the alkylation of benzene with propylene, taken from the 1997 National Student Design Competition of the AIChE. Cumene is widely used to make acetone and phenol. The fresh feeds are as follows, where the benzene feed is nearly pure, but a refinery cut of a propylene-propane mixture is used rather than a more expensive feed of nearly pure propylene.
<table>
<thead>
<tr>
<th>Component</th>
<th>Propylene feed, lbmol/hr</th>
<th>Benzene feed, lbmol/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.1800</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>4.6440</td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>1,029.2075</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>465.6127</td>
<td></td>
</tr>
<tr>
<td>1-Butene</td>
<td>0.0300</td>
<td></td>
</tr>
<tr>
<td>Isobutane</td>
<td>0.3135</td>
<td></td>
</tr>
<tr>
<td>Methylcyclopentane, MCP</td>
<td>1.1570</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>997.5130</td>
<td></td>
</tr>
<tr>
<td>Methylcyclohexane, MCH</td>
<td>0.2030</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0.1270</td>
<td></td>
</tr>
</tbody>
</table>

The main reaction, conducted with a catalyst, is:

\[
\text{Propylene} + \text{Benzene} \rightarrow \text{Isopropylbenzene (Cumene)}
\]

A number of undesirable side reactions involving the main reactants also occur, including:

\[
\begin{align*}
\text{Propylene} + \text{Benzene} & \rightarrow \text{n-Propylbenzene} \\
\text{Cumene} + \text{Propylene} & \rightarrow \text{m-Diisopropylbenzene (m-DIPB)} \\
\text{Cumene} + \text{Propylene} & \rightarrow \text{p-Diisopropylbenzene (m-DIPB)} \\
\text{Other reactions that produce alkylation heavies}
\end{align*}
\]

All of the impurities in the propylene and benzene fresh feed streams, including the large amount of propane in the propylene feed, are essentially inert, with the exception of 1-Butene, which enters into the following undesirable side reactions:

\[
\begin{align*}
\text{1-Butene} + \text{Benzene} & \rightarrow \text{t-Butylbenzene (t-BB)} \\
\text{1-Butene} + \text{Benzene} & \rightarrow \text{1-isopropyl,4-methyl Benzene (p-Cymene)}
\end{align*}
\]
Potential products and byproducts include cumene, propane, DIPBs, t-BB, p-cymene, inert light hydrocarbons, inert aromatic compounds, and water. A main objective of the process is to maximize the production of cumene and minimize the amounts of byproduct and waste streams. The cumene product must meet the following specifications:

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumene purity, wt%</td>
<td>99.97</td>
</tr>
<tr>
<td>Butylbenzenes, ppm (by wt)</td>
<td>40</td>
</tr>
<tr>
<td>Toluene, ppm (by wt)</td>
<td>15</td>
</tr>
<tr>
<td>Cymene, ppm (by wt)</td>
<td>10</td>
</tr>
<tr>
<td>Benzene and paraffins, ppm (by wt)</td>
<td>10</td>
</tr>
<tr>
<td>Others, ppm (by wt)</td>
<td>225</td>
</tr>
</tbody>
</table>

The propane byproduct is used as either fuel gas or LPG. Thus, it can contain water and light hydrocarbons. However, the aromatic content cannot exceed 0.01 wt%.

Experimental alkylation data show that the two reactions above that produce DIPBs can result in a serious loss (> 10%) of potential cumene product. To reduce this loss, two remedies are applied, the first of which is related to Heuristic 2 in Table 6.2: (1) the use of a large excess of benzene in the combined feed to the alkylation reactor, for example, a 4.0 molar ratio of benzene to propylene to reduce the DIPB formation reactions, and (2) the addition of a trans-alkylation reactor where the DIPBs are reacted with benzene to produce cumene according to the reaction:

\[ \text{DIPB} + \text{Benzene} \rightarrow 2 \text{Cumene} \]

Other reactions that produce trans-alkylation heavies

**SOLUTION**

A preliminary block flow diagram, suggested for the cumene process, is shown in Figure 7S.1. The process consists of one separation section, consisting of three columns, situated between two reactor sections, one for alkylation and one for trans-alkylation. The separations are all distillations, where approximate measures for the ease of distillation,
assuming ideal liquid solutions, are the differences between the normal boiling points of the components in the alkylation reactor effluent:

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>Molecular weight</th>
<th>Normal boiling point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>18.02</td>
<td>100</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>30.07</td>
<td>-88.6</td>
</tr>
<tr>
<td>Propylene</td>
<td>C₃H₆</td>
<td>42.08</td>
<td>-47.4</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>44.11</td>
<td>-42.1</td>
</tr>
<tr>
<td>Isobutane</td>
<td>C₄H₁₀</td>
<td>58.13</td>
<td>-11.7</td>
</tr>
<tr>
<td>l-Butene</td>
<td>C₄H₈</td>
<td>56.12</td>
<td>-6.3</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>C₆H₁₂</td>
<td>84.16</td>
<td>71.8</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>78.12</td>
<td>80.1</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>C₇H₁₄</td>
<td>98.19</td>
<td>100.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>92.16</td>
<td>110.6</td>
</tr>
<tr>
<td>Cumene</td>
<td>C₈H₁₂</td>
<td>120.2</td>
<td>152.4</td>
</tr>
<tr>
<td>n-Propylbenzene</td>
<td>C₉H₁₂</td>
<td>120.2</td>
<td>159.2</td>
</tr>
<tr>
<td>t-Butylbenzene</td>
<td>C₁₀H₁₄</td>
<td>134.2</td>
<td>169.0</td>
</tr>
<tr>
<td>p-Cymene</td>
<td>C₁₀H₁₄</td>
<td>134.2</td>
<td>177.1</td>
</tr>
<tr>
<td>m-DIPB</td>
<td>C₁₂H₁₈</td>
<td>162.3</td>
<td>203.2</td>
</tr>
<tr>
<td>p-DIPB</td>
<td>C₁₂H₁₈</td>
<td>162.3</td>
<td>210.3</td>
</tr>
<tr>
<td>Trans-alkylation heavies</td>
<td></td>
<td></td>
<td>201.7</td>
</tr>
<tr>
<td>Alkylation heavies</td>
<td></td>
<td></td>
<td>206.4</td>
</tr>
</tbody>
</table>
Figure 7S.1  Cumene Process.
Note that the fresh propylene feed contains approximately 31 mol% propane. Because propane is inert, Heuristic 3 of Table 6.2 should be considered. Propane can be removed in a separation section before or after the alkylation reactor. However, if removed before the reactor, a difficult separation between propane and propylene is required, as discussed in Section 8.2, because the boiling-point difference is only 5.3°C (relative volatility < 1.3). In the alkylation reactor, essentially all of the propylene, as well as all of the 1-butene, are reacted. Therefore, after the reactor, propylene is not present to be separated from propane. Instead, the propane, together with water and small amounts of inert light hydrocarbons in the propylene feed, are easily removed from the excess benzene in the reactor effluent in the depropanizer, C1. Here, the difference in boiling points between the key components is 112.2°C (relative volatility > 10). Following the depropanizer is a benzene-recovery distillation column, C2, where benzene is removed, with a portion recycled to the alkylation reactor and the remainder sent to the trans-alkylation reactor. The main separation is between benzene and cumene with a boiling-point difference of 72.3°C (relative volatility > 5). Finally, cumene product is recovered as the distillate in distillation column, C3, where the bottoms product, comprised of DIPBs, is sent to the trans-alkylation reactor to be converted to cumene. In the trans-alkylation reactor, a 4.0 molar ratio of benzene to total DIPBs is used, but the conversion of DIPBs is only 50%. By recycling the effluent from the trans-alkylation reactor, no net production of DIPBs is incurred. Based on laboratory experiments and other considerations, the benzene recycle to the alkylation reactor can contain up to 10 mol% impurities. However, the combined feed to the alkylation reactor must not contain more than 1.3 mol% cumene.

A cardinal rule, implied in Heuristic 4 of Table 6.2, that must be adhered to when developing a process flowsheet, is to provide exits from the process for all inert species that enter the process as impurities in the fresh feed(s) or are formed in irreversible side reactions. In the cumene process, these species include water and ethane, which are more volatile than propane; isobutane, MCP, MCH, and toluene, which are more volatile than cumene; and n-propylbenzene, tBB, and p-cymene,
which are more volatile than the DIPBs. Based on the product specifications for the propane and cumene products, calculations show that the total amounts of these species produced do not leave with one or both products. Consequently, two alternatives, suggested in Heuristic 4 of Table 6.2, must be evaluated. The first is to add separators to the process flowsheet. When too expensive, the second includes one or more purge or drag streams, resulting in the loss of reactant(s), product(s), or both. Two drag streams, one from the distillate of the benzene recovery column and one from the bottoms of the cumene recovery column, are used, leading to a benzene loss of about 2% and a cumene loss of less than 1%. Inclusion of drag streams and the resulting material balance calculations are the subjects of Exercise 7.6 at the end of this chapter.

Chemical processes, especially those utilizing a catalyst in the chemical reactor, may require a feed separation section, as shown in Figure 8.1, to purify the fresh feed before it enters the reactor. In this separation section, catalyst poisons are removed as well as components, other than reactants for the main reaction(s), that may enter into undesirable side reactions in the reactor section. In general, inert chemicals can be removed in separation sections either before or after the reactor, wherever the separation index is more favorable, as discussed above for the cumene process. However, when removed after the reactor, a larger reactor is required because of the higher flow rate and lower reactant concentrations. As an example, consider the manufacture of sulfuric acid. The feed stocks are air and either sulfur or sulfide ores, where the first reaction is the oxidation of sulfur or sulfide to sulfur dioxide, the second reaction is the catalytic oxidation of SO\textsubscript{2} to SO\textsubscript{3}, and the third reaction is the absorption of SO\textsubscript{3} in water to form sulfuric acid. Before the first reactor, moisture must be removed from the entering air to avoid corrosion and allow the use of carbon steel. Before entering the second reactor, dust, fluorides, and arsenic and vanadium compounds must be removed from the feed gas to prevent catalyst poisoning.
What should be done when the fresh feed contains an appreciable percentage of product chemicals? This occurs most frequently in isomerization reactions involving light paraffin hydrocarbons, as illustrated in Example 6.2. Suppose the reaction is \( A \leftrightarrow B \). In this case, it is important to remove the product B from the fresh feed before it enters the reactor so as to increase the rate of reaction and achieve the highest equilibrium conversion possible. However, because reactor conversion is usually incomplete for isomerization reactions, A is commonly separated from B, with A recovered and recycled. Unless other chemicals formed in the reactor interfere with the A-B separation, the two A-B separators are combined, with the resulting separator placed before the reactor. Exercise 7.7 considers separator placement for a pentane isomerization process.

### 7S.2 TRADEOFFS IN PROCESSES INVOLVING RECYLE

Reactions with very large chemical equilibrium constants (e.g., \( > 10,000 \)) at reactor conditions of temperature and pressure provide an opportunity for approaching 100% conversion during a single pass through the reactor. In addition, when the feed contains stoichiometric proportions of the reactants with no impurities and the reaction leads to only one product, then in principle no separation section is needed. One such situation exists. It is the manufacture of anhydrous hydrogen chloride gas from pure, evaporated chlorine and a stoichiometric amount of pure, electrolytic hydrogen by the reaction:

\[
\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}
\]

The only pieces of equipment required are a reactor, compressors, and heat exchangers. Such a process is rare. Even when 100% reactor conversion is theoretically possible, the optimal reactor conversion is less than 100% and a separation section is necessary. The main reason for this is the rapid decline in reaction rate as the reacting mixture is depleted of reactants. Thus, in most processes where a chemical reactor is required, consideration must be given to the tradeoffs between the cost of the reactor section and the cost of the separation section that follows it.
A number of factors affect the tradeoff between the reactor and separation sections, many of which are introduced in Chapters 4-8. These include:

1. The fractional conversion in the reactor of the limiting reactant. This directly affects the need for and cost of the separation section.

2. The entering temperature to and mode of operation (adiabatic, isothermal, programmed temperature profile, etc.) for the reactor. This affects heating and/or cooling costs and reactor effluent composition when side reactions are possible.

3. Reactor pressure, particularly for gas-phase reactions where the number of reactant molecules is greater than the number of product molecules. In this case, reaction kinetics may favor a higher pressure, but at the higher cost of gas compression.

4. Use of an excess of one reactant to minimize side reactions and/or increase the rate of reaction. This increases the cost of the separation system.

5. Use of an inert diluent in an adiabatic reactor to reduce the change in temperature. This increases the cost of the separation system.

6. Use of a gas or liquid purge stream to avoid difficult separations. This reduces the cost of the separation system, but results in the loss of reactants and may increase the cost of the reactor section, depending on the purge-to-recycle ratio (ratio of purge flow rate to recycle flow rate).

The use of process simulation, in conjunction with optimization, as discussed in Chapter 24, allows one to determine optimal values of reactor conversion, entering temperature, mode of operation, pressure, molar ratio of reactants in a combined reactor feed, diluent ratio, and purge-to-recycle ratio.
7S.3 OPTIMAL REACTOR CONVERSION

Return to the toluene hydrodealkylation process in Section 5.3, with the reaction kinetics in Example 7.2. To illustrate the effect of achieving a high conversion on reactor size, simplify the combined reactor feed by eliminating methane and neglect biphenyl formation. Also, to avoid carbon formation, assume a molar ratio of hydrogen to toluene of 5 for the combined feed to the reactor. At typical reactor conditions, the reverse reaction is considered to be negligible and Eq. (7.31) gives the forward reaction rate, $r_f$, where the Arrhenius equation for the rate constant, $k_f$, as a function of temperature is taken from the paragraph below Eq. (7.31). Thus,

$$
    r_f = -\frac{dC_{\text{toluene}}}{dt} = k_f C_{\text{H}}^{1/2} C_{\text{toluene}} = 6.3 \times 10^{10} \exp \left( \frac{-52,000}{RT} \right) C_{\text{H}}^{1/2} C_{\text{toluene}} \tag{7S.2}
$$

where, $R = 1.987$ cal/mol-K; concentrations, $C_i$, are in kmol/m$^3$; time, $t$, is in sec; and temperature, $T$, is in K. Next, the volume of both isothermal and adiabatic PFRs is computed for a series of conversions from 1% to 99%, for the following feed conditions:

- Temperature, °F: 1,200
- Pressure, psia (0 pressure drop): 500
- Component flow rates, lbmol/hr:
  - Hydrogen: 2,500
  - Toluene: 500

The calculations can be performed with any process simulator. Using the CHEMCAD program, the results for the isothermal case, plotted as reactor volume against fractional conversion of toluene, are shown in Figure 7S.2, with the adiabatic case in Figure 7S.3. For the isothermal case, the reactor volume increases almost linearly as
conversion increases to 0.4. The volume then increases more rapidly until at conversions near 0.8, the volume turns up sharply. The reactor volume is 4,080 ft³ at a conversion of 0.9, but twice that at a conversion of 0.99.

As seen in Figure 7S.3, the effect of conversion on reactor volume for the adiabatic case is very different from the isothermal case in Figure 7S.2. At all conversions, the reactor volume is less for the adiabatic case. Furthermore, the difference in reactor volumes widens as the conversion is increased. For example, at a 50% conversion, the isothermal reactor volume is 2.25 times that of the adiabatic reactor. At a
99% conversion, the ratio becomes 8. The adiabatic case benefits by the increase in temperature with increasing conversion. The exothermic heat of reaction is considerable at between 21,000 and 22,000 Btu/lbmol of toluene reacted. However, the large excess of hydrogen acts as a heat carrier, curtailing the adiabatic rise in temperature. Nevertheless, the temperature increases by approximately 2.2°F per 1% increase in conversion. Thus, at 99% conversion, the reactor outlet temperature is 1,423°F. As the conversion increases, the concentration of toluene in Eq. (7S.2) decreases, causing the rate of reaction to decrease. The decrease of the hydrogen concentration is not nearly as pronounced because of its large excess in the reactor feed. In the adiabatic case, the decrease in toluene concentration with conversion is offset by the increase in the rate constant with temperature because the activation energy is moderately high at 52,000 cal/mol. This results in an approximate doubling of the rate constant with every 50°F increase in temperature. Thus, in Figure 7S.3 for the adiabatic case, unlike the isothermal case, the increase in reactor volume is less than linear up to an inflection point at a conversion of approximately 50%. Only beyond a conversion of 90% does the reactor volume turn up sharply.

When striving for high reactor conversions, it may be necessary to consider the reverse reaction even when the reaction is considered to be irreversible. This is the case for the hydrodealkylation of toluene. A rate equation for the reverse reaction can be derived from the rate equation for the forward reaction, given by Eq. (7S.2), by assuming that the two rate equations are consistent with the chemical-reaction equilibrium constant. Assume that the gas reacting mixture is ideal at the high temperature of the reaction. Then, the chemical equilibrium constant can be expressed in terms of concentrations and equated to the ratio of the rate constants by:

\[
K_c = \frac{C_{CH_4}C_{benzene}}{C_{H_2}C_{toluene}} = \frac{k_f}{k_b}
\] (7S.3)
But in chemical equilibrium, the rate of the forward reaction is equal to the rate of the backward reaction. Therefore, from Eq. (7S.2), with an as yet undetermined dependence of component concentrations on the backward rate,

\[ k_f C_{\text{H}_2}^{1/2} C_{\text{toluene}} = k_b C_{\text{H}_2}^\alpha C_{\text{toluene}}^\beta C_{\text{CH}_4}^\gamma C_{\text{benzene}}^\delta \]  

(7S.4)

To determine the exponents, \( \alpha, \beta, \gamma, \) and \( \delta, \) combine Eqs. (7S.3) and (7S.4),

\[ \frac{k_f}{k_b} = \frac{C_{\text{H}_2}^\alpha C_{\text{toluene}}^\beta C_{\text{CH}_4}^\gamma C_{\text{benzene}}^\delta}{C_{\text{H}_2}^{1/2} C_{\text{toluene}}} = \frac{C_{\text{CH}_4} C_{\text{benzene}}}{C_{\text{H}_2} C_{\text{toluene}}} \]  

(7S.5)

By equating exponents in Eq. (7S.5), \( \alpha = -1/2, \beta = 0, \gamma = 1, \) and \( \delta = 1. \) Therefore, the form of the rate equation for the backward reaction is,

\[ r_b = k_b C_{\text{H}_2}^{1/2} C_{\text{CH}_4} C_{\text{benzene}} \]  

(7S.6)

To determine the Arrhenius expression for \( k_b \) from Eq. (7S.3), an expression for \( K_c \) as a function of temperature is needed. Based on the correlations of Yaws (1977), the standard Gibbs free energy of reaction, \( \Delta G_{rx}^o, \) in cal/mol, as a function of the absolute temperature, \( T, \) in K, for the hydrodealkylation of toluene,

\[ \text{H}_2 + \text{C}_7\text{H}_8 \rightarrow \text{CH}_4 + \text{C}_6\text{H}_6 \]

is given by:

\[ \Delta G_{rx}^o = -11,200 - 2.1 T \]  

(7S.7)

From thermodynamics, \( \Delta G_{rx}^o \) is related to the chemical-reaction equilibrium constant by the equation:
\[ K_c = \exp \left( \frac{-\Delta G^0}{RT} \right) \]  \hspace{1cm} (7S.8)

Combining Eqs. (7S.7) and (7S.8) and substituting 1.987 for \( R \), gives:

\[ K_c = \exp \left( \frac{5.636}{T} + 1.057 \right) = 2.878 \exp \left( \frac{5.636}{T} \right) \]  \hspace{1cm} (7S.9)

From Eq. (7S.3), using the temperature-dependent expressions for \( k_f \) in Eq. (7S.2) and \( K_c \) in Eq. (7S.9),

\[ k_b = \frac{k_f}{K_c} = \frac{6.3 \times 10^{10} \exp \left( \frac{-52,000}{RT} \right)}{2.878 \exp \left( \frac{5.636}{T} \right)} = 2.19 \times 10^{10} \exp \left( \frac{-63,200}{RT} \right) \]  \hspace{1cm} (7S.10)

Combining Eqs. (7S.6) and (7S.10), the rate law for the backward reaction becomes,

\[ r_b = 2.19 \times 10^{10} \exp \left( \frac{-63,200}{RT} \right) C_{H_2}^{1/2} C_{CH_4} C_{benzene} \]  \hspace{1cm} (7S.11)

When the reactor calculations are repeated for up to 99% conversion of toluene, taking into account the reverse reaction, reactor volumes for both isothermal and adiabatic cases increase only slightly (< 1%). This is largely due to the large concentration of hydrogen, which according to Eq. (7S.11) decreases the rate of the reverse reaction. Reaction equilibrium calculations for this example give a 99.98% conversion for the isothermal case and a 99.96% conversion for the adiabatic case. However, when only the stoichiometric quantity of hydrogen is used in the feed, the equilibrium isothermal conversion decreases to 97.3%.
7S.4 RECYCLE TO EXTINCTION

In many chemical processes, the main reaction is accompanied by one or more side reactions that produce byproducts. When the main reaction is irreversible or has a large chemical-reaction equilibrium constant, but one or more of the side reactions are so-called reversible reactions with chemical-reaction equilibrium constants on the order of one or less, the possibility of increasing the overall yield of the desired product(s) from the main reaction by eliminating the net production of byproduct(s) exists. This is accomplished by applying a concept sometimes referred to as recycle to extinction. The concept must be applied with care and must be supported by reaction rates that are sufficiently high. This is particularly true when the main reaction is catalyzed because the catalyst may not support the side reaction(s). Experimental verification is essential.

The recycle to extinction concept is introduced briefly in Example 6.4 and in Section 8.1, illustrated for the toluene-hydrodealkylation process in Figure 8.4. Two alternatives are considered: (1) production of the byproduct, and (2) recovery and recycle to extinction of the byproduct. In this process, the main reaction is the hydrogenation of toluene to the main product, benzene, and methane:

\[ \text{H}_2 + \text{C}_7\text{H}_8 \rightarrow \text{CH}_4 + \text{C}_6\text{H}_6 \]

As shown in Section 7S.2, this reaction, while not completely irreversible at typical reactor operating conditions, has a chemical-reaction equilibrium constant high enough to give conversions greater than 99%. When the main reaction is carried out thermally, in the absence of a catalyst, it is accompanied by the following side reaction that produces the byproduct, biphenyl:

\[ 2 \text{C}_6\text{H}_6 \leftrightarrow \text{H}_2 + \text{C}_{12}\text{H}_{10} \]

The chemical-reaction equilibrium constant for this reaction is written as:
\[
K_c = \frac{C_{\text{H}_2}C_{\text{biphenyl}}}{C_{\text{benzene}}^2}
\] (7S.12)

Although not always considered, a further reaction to triphenyl also occurs,

\[
C_6H_6 + C_{12}H_{10} \leftrightarrow H_2 + C_{18}H_{14},
\]

with a chemical-reaction equilibrium constant written as:

\[
K_c = \frac{C_{\text{H}_2}C_{\text{triphenyl}}}{C_{\text{benzene}}C_{\text{biphenyl}}}
\] (7S.13)

From Hougen and Watson (1947), the chemical-reaction equilibrium constant for Eq. (7S.12) ranges from 0.045 to 0.32 over a temperature range of 700 to 1,400°F, while for Eq. (7S.13), the constant increases from 0.23 to 0.46 over the same temperature range.

When the biphenyl and triphenyl byproducts are recovered and recycled to the reactor, they build to their equilibrium concentrations at the reactor outlet, as determined from Eqs. (7S.12) and (7S.13), such that no net production of either biphenyl or triphenyl occurs. In effect, the byproducts are recycled to extinction. In this manner, the production of undesirable byproducts is eliminated and the overall yield of the main product(s) is increased. A disadvantage of recycle of the byproducts to extinction is that the byproducts and unconverted reactants increase the cost of recycling. However, the cost of the separation system downstream of the reactor may be reduced when the byproducts are recovered together with one or more of the reactants in a single recycle stream. This occurs in the toluene hydrodealkylation process where the biphenyl and triphenyl are recovered with toluene.

A second example where recycle to extinction should be considered is the hydrolysis of ethylene to ethyl alcohol:

\[
C_2H_4 + H_2O \rightarrow C_2H_5OH
\]
which is accompanied by a reversible side reaction that produces diethylether and water,

\[
2 \text{C}_2\text{H}_5\text{OH} \leftrightarrow (\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O}
\]

for which the chemical-reaction equilibrium constant at typical reactor conditions is 0.2. By recovering and recycling diethylether and water, the overall yield of alcohol is increased.

A third example is the steam reforming of methane (or natural gas) in the presence of a nickel-supported catalyst to produce synthesis gas (CO + H₂), an intermediate that can be used to produce acetic acid, ammonia, gasoline, or methanol. The main reaction is:

\[
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3 \text{H}_2
\]

Typically, the reactor operation at adiabatic conditions gives an outlet temperature of approximately 800°C, which limits the extent of the reaction to that of chemical equilibrium, with an equilibrium constant of 126.8, with compositions in partial pressures in atm. Reactor pressure is generally set by the available pressure of the methane and may be as high as 30 atm.

In the presence of the catalyst, a number of side reactions occur as discussed by Rase (1977). However, the only one of significance is the water-gas shift reaction:

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2
\]

At 800°C, the chemical-reaction equilibrium constant for this reaction is 0.929, with compositions in partial pressures in atm. When CO₂ is recovered and recycled to extinction, is the overall yield of synthesis gas increased? This is the subject of Example 7S.3.
EXAMPLE 7S.3  Steam Reforming of Naphtha.

The fresh feed to a steam reformer is 13.5 kmol/hr of methane and 86.5 kmol/hr of steam. If the outlet conditions of the reactor are 800°F and 12.2 atm and chemical equilibrium is achieved for both the steam reforming and water-gas shift reactions, determine the kmol/hr of synthesis gas produced when:

(a) the CO₂ produced is not recovered and recycled.

(b) the CO₂ is recovered from the reactor effluent and recycled to extinction.

SOLUTION

(a) At 800°F, the two chemical equilibrium equations are:

\[
\frac{n_{CO} n_{H_{2}}}{n_{CH_{4}} n_{H_{2}O} \left( \frac{P}{n_{total}} \right)^2} = 126.8
\]

\[
\frac{n_{CO_{2}} n_{H_{2}}}{n_{CO} n_{H_{2}O}} = 0.929
\]

where \(P = 12.2\) atm and \(n_i\) are in kmol/hr. Since these two equations contain five unknowns, three atom-balance equations are needed. They are:

- **Carbon balance:** \(13.5 = n_{CH_{4}} + n_{CO} + n_{CO_{2}}\)
- **Hydrogen balance:** \(2(86.5) + 4(13.5) = 227.0 = 2 n_{H_{2}} + 4 n_{CH_{4}} + 2 n_{H_{2}O}\)
- **Oxygen balance:** \(86.5 = n_{H_{2}O} + n_{CO} + 2 n_{CO_{2}}\)

where the left-hand sides are in kg-atom/hr of the elements, C, H, and O in the fresh feed. Solving these five equations gives:
From these results, 95.5% of the methane is reacted. The production of synthesis gas is \(5.521 + 46.061 = 51.582\) kmol/hr.

(b) For recycle of CO\(_2\) to extinction, the CO\(_2\) in the reactor effluent is recycled and added to the fresh feed to give a combined feed. At chemical equilibrium, the flow rate of CO\(_2\) in the reactor effluent is the same as that in the combined feed. The two chemical equilibrium equations remain the same, but the three atom balance equations become:

- \(\text{Carbon balance: } 13.5 + n_{\text{CO}_2} = n_{\text{CH}_4} + n_{\text{CO}} + n_{\text{CO}_2}\)
- \(\text{Hydrogen balance: } 2(86.5) + 4(13.5) = 227.0 = 2n_{\text{H}_2} + 4n_{\text{CH}_4} + 2n_{\text{H}_2\text{O}}\)
- \(\text{Oxygen balance: } 86.5 + 2n_{\text{CO}_2} = n_{\text{H}_2\text{O}} + n_{\text{CO}} + 2n_{\text{CO}_2}\)

Solving the revised equations gives:

<table>
<thead>
<tr>
<th>Component</th>
<th>Combined feed, kmol/hr</th>
<th>Reactor effluent, kmol/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>13.5</td>
<td>0.549</td>
</tr>
<tr>
<td>Water</td>
<td>86.5</td>
<td>73.544</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0</td>
<td>38.859</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>0</td>
<td>12.946</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>22.763</td>
<td>22.763</td>
</tr>
<tr>
<td>Total</td>
<td>122.763</td>
<td>148.661</td>
</tr>
</tbody>
</table>

7S-20
Observe that there is no net production of CO$_2$. The percent conversion of methane is slightly greater at 95.9%, with the production of synthesis gas slightly increased to 12.946 + 38.859 = 51.805 kmol/hr. Note that in case (a), the production of CO$_2$ from CO by the water-gas shift reaction gives an additional mole of H$_2$ for every mole of CO$_2$ produced. Thus, by eliminating the net production of CO$_2$, less H$_2$ is produced. The usual benefit of the increased yield of the main product(s) by recycle to extinction is not achieved in this case. However, in case (b), CO$_2$ is not emitted to the atmosphere where it contributes to global warming. This is considered in more detail by Mulholland and Dyer (1999).

7S.5 SNOWBALL EFFECTS IN THE CONTROL OF PROCESSES INVOLVING RECYCLE

In recent years, chemical engineers engaged in process design in industry have become increasingly aware of the need to understand the interaction of process design and process control when developing a control system for an entire chemical plant. When the process does not involve recycle, the development of the control system is relatively straightforward because the process can be treated in a sequential manner. However, the majority of chemical processes involve recycle, for which the development of a feasible and efficient control system, particularly for a reactor-separator-recycle network, is not at all straightforward. This is due to the possibility of the so-called snowball effect, which refers to a situation where a small disturbance, for example, in the fresh feed rate to a reactor, causes a very large change in the flow rate of the recycle stream. When this occurs, either the reactor or the separation system, or both, may not be able to handle the increased load. Whether or not the snowball effect occurs depends on the design of the control system, which is the subject of Sections 12.3 (Example 12.11) and 12S.5 (Case Study 12S.3).
As discussed in Section 7.5, the ideal PFR model, which ignores axial heat and mass transfer, and assumes zero velocity, temperature, and concentration gradients in the radial direction, can sometimes be in serious error. Section 7.5 shows the impact of fully-developed laminar flow under isothermal conditions using analytical solutions. In this section, further analytical solutions are discussed and computational fluid dynamics (CFD) is applied to flows in straight- and curved-tube reactors under laminar flow where analytical solutions do not exist. In Example 7S.4, comparisons are made among chemical reaction conversions in: (1) straight circular tubes under plug flow, (2) straight circular tubes under fully-developed laminar flow, (3) coiled (helical) tubes, and (4) figure-8 (lemniscate) tubes. This example shows the significant impact of fluid mechanics on reaction conversions. It demonstrates that the conventional plug-flow assumption is inaccurate when calculating reaction conversions in straight tube reactors, but becomes more accurate for flows which induce significant amounts of radial mixing.

**EXAMPLE 7S.4**

For the liquid-phase saponification of ethyl acetate by sodium hydroxide in an aqueous solution to produce ethyl alcohol and sodium acetate:

\[
\text{EtAc} + \text{NaOH} \rightarrow \text{EtOH} + \text{NaAc}
\]

Determine and compare the reaction conversions in three different tubular reactors operating in the viscous-flow regime.

The conditions are as follows:

- Feed at 0.05 mol/L of sodium hydroxide and 0.05 mol/L of ethyl acetate.
- Tube radius at 2 cm (0.7874 in).
Temperature is 30°C.
Isothermal operation.
Density of the reacting fluid (assumed to be pure water) is 996 kg/m$^3$ and viscosity of the reacting fluid is 0.000798 Pa-s at 30°C.
Diffusivity of ethyl acetate and NaOH in the reacting fluid at 1.2×10$^{-5}$ cm$^2$/s.
Inlet volumetric flow rate of solution at 2 L/min (assumed to remain constant).
Second-order irreversible reaction (first-order in each reactant) with rate constant,
k = 8.9 L/mol-min.

Note that these specifications are comparable to those of Seader and Southwick (1982).
Select a reactor volume and compare the conversion for each of the following reactor models:

(a) Plug flow in a straight tube.
(b) Fully-developed laminar flow in a straight tube.
(c) A coiled tube wrapped around a mandrel of 23 cm (9.06 in) radius with 5 cm (1.969 in) pitch per revolution.
(d) A Bernoulli lemniscate (figure-8) coil wrapped around two mandrels side-by-side, each of 23 cm (9.06 in) radius with 5 cm (1.969 in) pitch per half revolution.

SOLUTION

Geometric Considerations

Table 7S.1 shows the Reynolds number ($Re = D\rho u_{mean}/\mu$) and Dean number ($De = Re(R_t/R_c)^{1/2}$), where $D$ is the inside tube diameter, $\rho$ is the fluid density, $u_{mean}$ is the mean axial velocity, $\mu$ is the fluid viscosity, $R_t$ is the inside tube radius, $R_c$ is $R_t + R_m$, and $R_m$ is the mandrel radius. Note that in all cases the flow regime is laminar.

To compare the product conversions, the mean residence times in the four reactors must be equal. Reactors with the same axial centerline length and same mean inlet fluid
velocity have the same mean residence time regardless of their centerline path, since the cross-section of each reactor is circular with a constant radius involving incompressible fluids. This satisfies continuity, giving reactors of equal volume, having equal axial centerline length (and equal circular radius).

Table 7S.1 Dimensionless Parameters

<table>
<thead>
<tr>
<th>Model</th>
<th>Re</th>
<th>De</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plug flow – straight tube</td>
<td>1,329</td>
<td>0</td>
</tr>
<tr>
<td>Fully-developed laminar flow – straight tube</td>
<td>1,329</td>
<td>0</td>
</tr>
<tr>
<td>Helical coiled tube</td>
<td>1,329</td>
<td>376</td>
</tr>
<tr>
<td>Figure-8 (lemniscate) tube</td>
<td>1,329</td>
<td>376</td>
</tr>
</tbody>
</table>

For this problem, one full helical revolution and half a lemniscate (figure-8) revolution determine the centerline length. These geometries have a centerline length:

\[
L_c = 2\pi \sqrt{(R_i + R_m)^2 + (P_t / 4)^2} = 2\pi \sqrt{(2 + 23)^2 + (5/4)^2} = 157.3 \text{ cm} \tag{7S.14}
\]

where \(P_t\) is the tube pitch. The second term corrects the length of the centerline path due to tilting, as shown in Figure 7S.4. To compare conversions, the straight tube reactors are 157.3 cm in length. Note that the volume of the tubes is \(\pi R_i^2 L_c = \pi(2)^2(157.3) = 1,977 \text{ cm}^3\).

Figure 7S.4 Dimensions of curved tubes.
General Approach

Analytical solutions are used when they exist. When no analytical solution exists, a CFD solution is obtained using COMSOL. The geometry of the reactor is drawn to as high a precision as possible using the tools in the Draw Mode. Geometric symmetries are exploited to decrease the computation times and increase the density of the mesh. The reactor model is described in the appropriate multi-physics modes. Then a mesh is generated, generally with higher density at the boundaries. The solution is obtained using a carefully selected solver. The solution is analyzed and displayed using the plots and tools available in the Post-Processing mode. When problems arise with this procedure, as they often do, the COMSOL help guides provide many tips and strategies. As in all numerical problems, the density of the mesh is limited by the memory of the computer, and a balance is struck between the computation time and the density of the mesh.

(a) Plug Flow in a Straight Tube

The saponification reaction has the form:

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

The reaction is second order and irreversible, and assumed to be isothermal. Using the plug flow assumption, the radial velocity and diffusivity are zero, and the axial velocity is constant in the radial and axial directions. The intrinsic rate of consumption of reactant A (ethyl acetate) is:

$$r_A = u_{\text{mean}} \left(- \frac{dC_A}{dZ} \right) = kC_A c_B$$

and for reactant B (sodium hydroxide) is:

$$r_B = u_{\text{mean}} \left(- \frac{dC_B}{dZ} \right) = kC_A c_B$$

where $Z$ is the axial coordinate, $k$ is the reaction rate constant, and $C_A$ and $C_B$ are the concentrations of A and B. The inlet concentrations and intrinsic rates of consumption of both reactants are equal. Consequently, throughout the reactor:

$$C_A = C_B, \quad r = r_A = r_B$$

and:
\[ r = u_{\text{mean}} \left( -\frac{dc_A}{dZ} \right) = u_{\text{mean}} \left( -\frac{dc_B}{dZ} \right) = kc_A^2 \]  

(7S.18)

Only reactant A will be considered subsequently, allowing for more efficient numerical computations. The conversion of reactants A and B, \( X \), is:

\[ X = 1 - \frac{c_A}{c_{A0}} \]  

(7S.19)

where \( c_{A0} \) is the inlet concentration of reactant A. Substituting Eq. (7S.19) into (7S.18):

\[ r = u_{\text{mean}} \left( \frac{dX}{dZ} \right) = kc_{A0} \left( 1 - X \right)^2 \]  

(7S.20)

Integrating from \( Z = 0 \) to \( L \):

\[ X_{\text{PFR}} = \frac{1}{\left( 1 + \frac{u_{\text{mean}}}{kc_{A0}L} \right)} \]  

(7S.21)

where \( L \) is the tube length. For a similar derivation, see Churchill (2005). Substituting the specifications, \( X_{\text{PFR}} = 30.54\% \) – as shown in Table 7S.2.

**b) Fully-Developed Laminar Flow in a Straight Tube**

Analytical solutions can also be found for laminar flow in a straight tube with no radial mixing; i.e., negligible diffusion. This idealized reactor is referred to as laminar with zero diffusion \( (D = 0 \text{ m}^2/\text{s}) \), i.e., LD0. The axial velocity, \( u_r \), is:

\[ \frac{u(R)}{u_{\text{mean}}} = 2 \left( 1 - \left( \frac{R}{R_i} \right)^2 \right) \]  

(7S.22)

where \( R \) is the radial coordinate. As above, \( c_A = c_B \), but Eq. (7S.20) becomes:

\[ r[R] = 2u_{\text{mean}} \left( 1 - \left( \frac{R}{R_i} \right)^2 \right) \left( \frac{\partial X[R]}{\partial Z} \right) = kc_{A0} \left( 1 - X[R] \right)^2 \]  

(7S.23)
which is a partial-differential equation in coordinates \( Z \) and \( R \). Integrating with respect to \( Z \):

\[
X_{LD0}(R) = \frac{1}{2u_{\text{mean}} \left( 1 - \left( \frac{R}{R_t} \right)^2 \right)} \left( 1 + \frac{k c_{A0} L}{1 - \varphi \ln \left( 1 + \frac{1}{\varphi} \right)} \right) \tag{7S.24}
\]

The mixed-mean conversion is:

\[
\bar{X}_{LD0} = 2\pi \int_0^R X_{LD0}(R) u(R) RdR \tag{7S.25}
\]

Substituting Eqs. (7S.22) and (7S.24), gives:

\[
\bar{X}_{LD0} = 2\varphi \left( 1 - \varphi \ln \left( 1 + \frac{1}{\varphi} \right) \right) \tag{7S.26}
\]

where

\[
\varphi = \frac{k c_{A0} L}{2u_{\text{mean}}} \]

See, also, Churchill (2005). Substituting the specifications, \( \bar{X}_{LD0} = 27.41\% \) — as shown in Table 7S.4.

In general, the mass balance for species A with finite molecular diffusion is:

\[
2u_{\text{mean}} \left( 1 - \left( \frac{R}{R_t} \right)^2 \right) \left( \frac{\partial c_A}{\partial Z} \right) = D \left( \frac{\partial^2 c_A}{\partial R^2} + \frac{1}{R} \left( \frac{\partial c_A}{\partial R} \right) + \left( \frac{\partial^2 c_A}{\partial Z^2} \right) \right) - k c_A^2 \tag{7S.27}
\]

In this case, the diffusivities are equal; that is \( D = D_A = D_B \), and consequently, \( c_A = c_B \). This PDE, which is similar to Eq. (7.62), does not have an analytical solution, and consequently, COMSOL is used to obtain the solutions. For the product concentrations, when \( D = D_C = D_D, c_C = c_D \), and a similar PDE is included.
For this straight tube, axial symmetry applies. Finite-element analysis is implemented from the centerline to the tube wall. On the Model Navigator, the Axial symmetry (2D) Space dimension is chosen. Then, the path, Application Modes → COMSOL Multiphysics → Fluid Dynamics → Incompressible Navier-Stokes → Steady State Analysis, is followed, as shown in Figure 7S.5.

[Image of Model Navigator dialog box]

Figure 7S.5 Model Navigator dialog box

Next, in Draw Mode, a rectangle is drawn having a width of 0.02 m ($R = 2$ cm) and a height of 1.573 m ($L = 157.3$ cm), with its bottom left corner at the origin, as shown in Figure 7S.6.
Then, the constants, are entered following the path *Options → Constants* to give the *Constants* dialog box in Figure 7S.7. These constants are saved using the save button in the lower left corner.

**Figure 7S.6** *Rectangle* dialog box

**Figure 7S.7** *Constants* dialog box
Next, using the path, *Options → Expressions → Global Expressions*, the expression for the laminar velocity profile, named *laminar_profile*, is entered into the *Global Expressions* dialog box in Figure 7S.8.

![Global Expressions dialog box](image)

**Figure 7S.8 Global Expressions dialog box**

The *Subdomain Settings – Convection and Diffusion (cd)* dialog box, accessed either by right-clicking the mode under the *Model Tree* on the left side of the screen or using the *Physics* tab, are entered, as shown in Figure 7S.9. The diffusivity, $D$, is entered as *isotropic*. The intrinsic reaction rate ($R$ in COMSOL) is $-kc^2$. The $r$-velocity is set to 0 m/s and the $z$-velocity is set to *laminar_profile*.

![Subdomain Settings – Convection and Diffusion (cd) dialog box – c tab](image)

**Figure 7S.9 Subdomain Settings – Convection and Diffusion (cd) dialog box – c tab**
Click *Artificial Diffusion*... to give the *Artificial Diffusion* dialog box in Figure 7S.10. To provide numerical stability, the COMSOL Help Guides recommend that the Petrov-Galerkin/Compensated method under streamline diffusion be used, with the tuning parameter at 0.25.

![Artificial Diffusion dialog box](image)

Figure 7S.10 *Artificial Diffusion* dialog box

To enter the initial concentrations of species A at each mesh point, the *Init* tab of the *Subdomain Settings – Convection and Diffusion (cd)* dialog box is used. As shown in Figure 7S.11, the *Initial value* everywhere is \( c_0 \).

![Subdomain Settings – Convection and Diffusion (cd) dialog box – Init tab](image)

Figure 7S.11 *Subdomain Settings – Convection and Diffusion (cd) dialog box – Init tab*
Next, the boundary conditions for the mass balance of species A are set in the *Boundary Settings – Convection and Diffusion (cd)* dialog box in Figure 7S.12, accessed in either the *Model Tree* or using the *Physics* tab. Note that for fully-developed laminar flow, the axial velocity as a function of radius is set in Figure 7S.8 and boundary conditions are not needed. The concentration boundary conditions are:

1. At the inlet, boundary 2 assigned by COMSOL, the *Concentration* of species A is defined as \( c_0 = c0 \text{ mol/m}^3 \), as shown in Figure 7S.12.

![Figure 7S.12](image1)

(a)

![Figure 7S.12](image2)

(b)

Figure 7S.12 *Boundary Settings – Convection and Diffusion (cd)* dialog box
2. At the outlet, boundary 3, the \textit{Convective flux} boundary condition is selected. This sets \( n \cdot (-D \nabla c_A) = 0 \), where \( n \) is the unit vector orthogonal to the tube outlet, as shown in Figure 7S.12b.

3. At the tube centerline, boundary 1, the \textit{Axial symmetry} boundary condition is selected, as shown in Figure 7S.12c. This sets \( \frac{\partial c_A}{\partial R} = 0 \) at the centerline.

Figure 7S.12 \textit{Boundary Settings – Convection and Diffusion (cd)} dialog box (Cont’d.)
4. At the outside tube wall, boundary 4, the *Insulation/Symmetry* boundary condition is selected, as shown in Figure 7S.12d. This sets $\frac{\partial c_A}{\partial R} = 0$ at the wall.

Now that the model is specified, a mesh appropriate for the computer memory and speed is defined. To create a free mesh in COMSOL, which is suitable for the straight-tube reactor, follow the path *Mesh → Free Mesh Parameters* to use *Predefined mesh sizes* or set a *Custom mesh size*. Here, the predefined mesh sizes are not effective, and consequently, a custom mesh size is defined, as shown in Figure 7S.13. Note that the COMSOL User’s Guide should be consulted for further explanations of the mesh settings.

![Free Mesh Parameters dialog box](image)

Figure 7S.13 *Free Mesh Parameters* dialog box
A mesh with 78,684 elements is generated by COMSOL. Using a front view of the tube outlet, the mesh is shown in Figure 7S.14. Note that the centerline of the tube is at $R = 0$ and the tube wall is at $R_t = 0.02$ m. Also note that the path Options $\rightarrow$ Preferences $\rightarrow$ Visualizations was used to increase the Line width from 1 to 2.

Next, the finite-element solver is selected following the path, Solve $\rightarrow$ Solver Parameters, which gives the Solver Parameters dialog box in Figure 7S.15. The Stationary, rather than Transient, analysis type is selected on the left side of the screen. The solver, $\text{Direct (UMFPACK)}$, is chosen and its settings are not changed. Note that direct solvers are usually faster than iterative solvers, but have greater memory constraints. Because there is only one state variable, $c_A$, and the mesh is 2-dimensional and not dense, relatively little memory is needed, and consequently, a direct solver is
preferable. The COMSOL User’s Guide should be consulted for a more detailed explanation of the solver choice.

Figure 7S.15 Solver selection

To use the initial values in Figure 7S.11, follow the path Solve → Solver Manager → Initial Value. Using the Solver Manager dialog box in Figure 7S.16, select the options Initial value expression and Use setting from Initial value frame.

A solution is obtained in 17 seconds on an Intel® Core™ 2 Duo CPU E8400 @ 3.00 GHz and 2.99 GHz with 3.25 GB of RAM. Figure 7S.17, which is generated using the path, Postprocessing → Plot Parameters, shows a 2-D projection of $c_A$ that varies between 0.05 and 0.0101 mol/L. Note that the scale of the radial dimension is 20 times greater than that of the axial dimension. Figure 7S.18 shows the radial $c_A$ profiles at the inlet and
outlet of the tube, which are generated using the path, *Postprocessing → Cross-Section Plot Parameters.*

![Solver Manager dialog box](image)

*Figure 7S.16* Solver Manager dialog box

![2-D projection of $c_A$ in the front view of the tubular reactor](image)

*Figure 7S.17* 2-D projection of $c_A$ in the front view of the tubular reactor
The reactant conversion (concentration) at the tube wall is highest (lowest). This is because the velocity is lower near the wall, giving a higher residence time.

To calculate the mixed-mean reactant conversion, \( \bar{X}_{LD1} \), the normal total flux, denoted in COMSOL as \( ntflux_c_cd \), is radially integrated at both the inlet and outlet boundaries to give the flow rate of reactant in mol/s. Note that LD1 refers to laminar flow with \( D = 1.2 \times 10^{-5} \) cm²/s. This is accomplished following the path Postprocessing → Boundary Integration, with the Compute surface integral option selected, as shown in Figure 7S.19. Note that the normal total flux is integrated because the fluid velocity varies radially.
The inlet flow rate of the two reactants is 0.001667 mol/s and the outlet flow rate is 0.001209 mol/s. $\bar{X}_{LD1}$ is:

$$
\bar{X}_{LD1} = \left(1 - \frac{ntflux_{c_{ad}} out}{ntflux_{c_{ad}} in}\right) \times 100\% = \left(1 - \frac{.001209 \text{mol}}{.001667 \text{mol}} \times \frac{s}{s}\right) \times 100\% = 27.47\% \quad (7S.28)
$$

This is marginally higher than the conversion calculated for fully-developed laminar flow with no diffusion, 27.41\%, indicating that the diffusivity is not sufficiently large to substantially affect the conversion. Clearly, the conversion increases with diffusivity, approaching that for the plug flow model in the limit of infinite diffusivity. To show this effect, the diffusivity is changed in either the Subdomain Settings or the Constants dialog boxes. To avoid numerical problems at high diffusivities, the axial velocity profile is changed from laminar_profile to $U_{mean}$.

The outlet concentration profiles for $D = 0, 1.2\times10^{-5}, 1.2\times10^{-3}$ cm$^2$/s, and for the plug flow case are shown in Figure 7S.20, with the conversions shown in Table 7S.4. Note that the case for $D = 1.2\times10^{-3}$ cm$^2$/s is referred to as LD100; that is, laminar flow with $D = 100(1.2\times10^{-5})$ cm$^2$/s. These conversions are in close agreement with the analytical solutions.

(c) Flow Through a Coil Wrapped Around a Mandrel (Helix)

Solutions for this geometry are significantly more difficult to obtain than for flow in a straight tube. No analytical solutions exist and the numerical methods are more sophisticated. To get started, it is recommended that the following approach be used.

Solve the momentum balances first on a coarse mesh so that the fast direct solver UMFPACK can be used. Then, solve the species balance using the Convection and Diffusion application mode with analytical continuation in the rate constant, $k$, varying from 0 to 8.9 L/mol-min, to reach an approximate solution. Then, increase the number of elements and use the slower iterative solver, GMRES, for increasingly dense meshes. Finally, estimate the conversion by extrapolation to zero element size.
Figure 7S.20 Outlet reactant concentration as $D$ varies

On the Model Navigator, select the 3D Space dimension. Then, follow the path, Application Modes → COMSOL Multiphysics → Fluid Dynamics → Incompressible Navier-Stokes → Steady State Analysis. Note that the steady-state Convection and Diffusion application mode is added later. Then, load the constants saved previously and enter a 3D laminar profile in the Global Expressions dialog box, as shown in Figure 7S.21. Note that the coordinate system is defined in the bottom left corner of Figure
7S.25. This is a rectangular coordinate system, rather than the cylindrical system used for the straight tube.

![Global Expressions dialog box](image1)

Figure 7S.21 Global Expressions dialog box

Next, following the path Draw → Work-Plane Settings, create the Geom2 Work-Plane by selecting the z-x plane with $y = 0$, as shown in Figure 7S.22. Note that the $x$ and $y$ coordinates of Geom2 correspond to the $z$ and $x$ coordinates of Geom1, the 3D geometry, respectively.

![Work-Plane Settings dialog box](image2)

Figure 7S.22 Work-Plane Settings dialog box

On the work-plane, Geom2, a circle of radius 0.02 m is drawn centered at the origin. Then, switch to Mesh Mode, which produces a very fine mesh, and re-mesh the circle to reduce the memory demand, as shown in Figure 7S.23. Next, revolve the geometry to
generate one-half revolution of the helix using the *Revolve Mesh* dialog box in Figure 7S.24.

Figure 7S.23 *Geom2 work-plane in Mesh Mode*

![Revolve Mesh dialog box](image)

Figure 7S.24 *Revolve Mesh* dialog box
In the default 3D view in the *Draw Mode*, the resulting half of a helical turn is shown in Figure 7S.25.

![Figure 7S.25 Half-helix in Draw Mode](image)

The geometric *Composite Object, CO1*, is mirrored about the $x$-$z$ plane at $y = 0$, as shown in Figure 7S.26.

![Figure 7S.26 Mirror dialog box](image)
Using the *Rotate* dialog box, shown in Figure 7S.27, the resulting, geometric *Composite Object, CO2*, is rotated $2 \tan^{-1}(-0.025/0.5) = -5.72481$ degrees about $(0.5, 0, -0.025)$.

Figure 7S.28 shows one full helical turn, as seen in the default 3D view in *Draw Mode*.

![Figure 7S.27 Rotate dialog box](image1)

![Figure 7S.28 One full helical turn in Draw Mode](image2)
In the Subdomain Settings – Incompressible Navier-Stokes (ns) dialog box, shown in Figure 7S.29, the density and viscosity are set to the specifications in Figure 7S.7.

The initial velocities, at zero, are shown in Figure 7S.30. Note that specifying a nonzero initial velocity profile, while desirable, is difficult because of the helical geometry.
The boundary conditions are:

- At the inlet, the *Boundary type* is set to *Inlet*, the *Boundary condition* is set to *Velocity*, and the y-velocity is entered as *laminar profile*. The other velocities remain at 0 m/s.
- At the single interior boundary connecting the two *subdomains*, the *Boundary condition* *Continuity* is selected.
- At the outlet, the *Boundary type* is set to *Outlet* and the *Boundary condition* is set to *No viscous stress*.
- All other boundaries remain as *Boundary type Wall*, with the *Boundary condition* *No slip*.

Pressure must be entered at a single point to complete the specifications. COMSOL recommends a point on the outlet boundary to ensure numerical stability. In the *Point Settings – Incompressible Navier-Stokes (ns)* dialog box, accessed either through the *Model Tree* or the *Physics* tab, the pressure of the point located at the outside edge of the outlet, point 2, is set to *Pref*, as shown in Figure 7S.31.

![Figure 7S.31 Point Settings – Incompressible Navier-Stokes (ns) dialog box](image)
Next, a free mesh is created with the specifications in Figure 7S.32.

![Free Mesh Parameters dialog box](image)

**Figure 7S.32** *Free Mesh Parameters* dialog box

The mesh has 13,629 elements, with the inlet shown in Figure 7S.33.

![Inlet mesh in Mesh Mode](image)

**Figure 7S.33** Inlet mesh in *Mesh Mode*
The Navier-Stokes equations are solved using the Direct (UMFPACK) solver. A solution is found in 125 seconds. Then, a Convection and Diffusion application mode is added following the path Multiphysics → Model Navigator. The subdomain settings are shown in Figure 7S.34.

![Subdomain Settings – Convection and Diffusion (cd) dialog box – c tab](image.png)

Petrov-Galerkin/Compensated streamline diffusion is turned on, using the Artificial Diffusion... button, and the tuning parameter remains at 0.25. The initial conditions are set to \( c_0 \).

The boundary conditions are:

- At the inlet, the Concentration is defined as \( c_0 = c_0 \) mol/m³.
- At the single interior boundary, the boundary condition is set to Continuity.
- At the outlet, the boundary condition is set to Convective flux.
- At all other boundaries, the boundary conditions are set to Insulation/Symmetry.
At this point, analytical continuation is specified using the *Solver Parameters* dialog box, as shown in Figure 7S.35. The *Parametric segregated* solver is selected. $k$ is entered as the *Parameter name*, to be varied from 0 to $1.48 \times 10^{-4}$ m$^3$/mol-s, as defined under *Parameter values*. Here, the range(-8,0.5,-4) indicates that $k$ increases from $10^{-8}$, $10^{-7.5}$, ..., $10^{-5}$, $10^{-4.5}$, $10^{-4}$ m$^3$/mol-s. Under *Segregated groups*, $u$, $v$, $w$, and $p$ are segregated from the variable $c$. Also, for Groups 1 and 2, under *Linear solver*, depress the *Settings*... button, and select the *Direct (UMFPACK)* solver. The *Tolerance* is left at $1e-3$.

![Solver Parameters dialog box]

Figure 7S.35 *Solver Parameters* dialog box

In the *Solver Manager* dialog box, shown in Figure 7S.36, the solution to the Navier-Stokes equations, obtained using a course mesh, is stored by clicking *Store solution*. For
subsequent values of $k$, the latest solution is used to initiate a solution of the Navier-Stokes equations, followed by a solution of the species balance.

![Solver Manager dialog box](image)

Figure 7S.36 Solver Manager dialog box

The solution for $1.48 \times 10^{-4}$ m$^3$/mol-s (8.9 L/mol-min) is computed in 19 minutes. Next, a finer mesh is defined by decreasing the Maximum element size in the Free Mesh dialog box. The solver type is switched to Segregated stationary and the Tolerance is decreased to 1e-4 for both groups. The GMRES solver is used for moderately dense meshes and the BICGSTAB solver is used to solve the Navier-Stokes equations for the densest meshes. For all mesh sizes, the Direct (UMFPACK) solver is used to solve the species balance. For the iterative solvers, the Maximum number of iterations and the Number of iterations before restart are both increased to 300, as shown in Figure 7S.37. Because this model is nonsymmetrical, Incomplete LU is selected as the Preconditioner – see Figure 7S.38. A higher Drop tolerance is more memory efficient, but may result in divergence from a solution. Solutions are obtained for Drop tolerances approaching 0.011. The Pivot threshold is set to 0.1 and the Number of iterations is set to 3. For more details, consult
the COMSOL Help Guides. Solutions are found for decreasing Maximum element sizes until memory is insufficient. The latest solution is stored in the Solver Manager to initialize calculations for the next smaller mesh size.

Figure 7S.37  Linear System Solver Settings dialog box for Group 1

Figure 7S.38  Preconditioner settings for Group 1
The graphics that follow were generated with a mesh having 40,646 elements, the densest mesh for which a solution was computed. Note that the vertical slice plots are nearly orthogonal to the tilted centerline of the pipe. At the inlet, the fluid is in fully-developed flow from a straight tube; i.e., having a parabolic velocity profile. In the entrance region, the fluid is distorted by centrifugal force in the turn. The axial velocity profiles at the inlet, $\frac{1}{4}$ turn, $\frac{1}{2}$ turn, $\frac{3}{4}$ turn, and the outlet, are shown in Figure 7S.39. The abscissa of the slice plots for the helix and lemniscate (part (d)) are $r_{m1}$ and $r_{m2}$, which denote the distance to a point in the tube from the centerline of the first and second mandrel, respectively, in the x-y plane. The left side of each graphic is the innermost edge of the tube touching the mandrel.

The axial velocity does not change substantially from the $\frac{1}{4}$ turn to the outlet, indicating that the fluid is close to fully-developed laminar flow through most of the turn. Secondary motion, that is, motion in the plane orthogonal to the centerline is seen in the helix. The secondary motion at the tube outlet is shown in the arrow plot in Figure 7S.40. Two recirculation patterns are seen, which relieve the pressure gradient created by the centrifugal force – one in the top half and the other in the bottom half of the tube. Secondary motion is strongest (having larger arrows) in the center of the recirculation patterns and weakest at the inner and outer edges.

The reactant concentration profile is shown at the inlet, $\frac{1}{4}$ turn, $\frac{1}{2}$ turn, $\frac{3}{4}$ turn, and outlet in Figure 7S.41.
Figure 7S.39  Axial velocity profile cross sections
The highest conversion occurs at the innermost edge of the cross-section, where axial velocity is low and little recirculation occurs, giving a long residence time. The lowest conversion occurs in the bottom and top lobes where recirculation is the strongest and the axial velocity is moderate to fast. The secondary motion causes both radial and azimuthal mixing, which levels the concentration profile, approaching the plug flow profile. Note that for fully-developed laminar flow in a straight tube, there is a ring of slow moving flow, having high conversion, along the wall and fast moving flow, having low conversion, about the centerline. There is no such ring in the helical case. The flow along roughly 75% of the wall is recirculated to the middle of the tube, resulting in a more even profile. Its mixed-mean conversion is higher than a straight tube with negligible diffusion, as shown in the next paragraphs.
Figure 7S.41  Reactant concentration profile cross sections
Mixed-mean conversions at the outlet are calculated for a range of mesh sizes and are given in Table 7S.2. A semi-log plot of the conversion as a function of the inverse of the number of elements in the mesh is shown in Figure 7S.42. Here, the ordinate, $y$, is $\ln(X)$ and the abscissa, $x$, is the inverse of the number of elements. $R^2$ is the sum of the square of deviations of $\ln(X)$ on the linear regression line from the conversions in Table 7S.2.

Table 7S.2 Conversions for Varying Mesh Sizes

<table>
<thead>
<tr>
<th>Maximum Element Size</th>
<th>No. of Elements</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0105</td>
<td>25,922</td>
<td>33.313</td>
</tr>
<tr>
<td>0.01015</td>
<td>28,321</td>
<td>32.893</td>
</tr>
<tr>
<td>0.01</td>
<td>31,844</td>
<td>32.353</td>
</tr>
<tr>
<td>0.009275</td>
<td>34,044</td>
<td>32.173</td>
</tr>
<tr>
<td>0.0095</td>
<td>37,088</td>
<td>31.753</td>
</tr>
<tr>
<td>0.0092</td>
<td>40,646</td>
<td>31.513</td>
</tr>
</tbody>
</table>

Figure 7S.42 Semi-log plot of conversion as a function of the inverse of the number of elements with linear regression statistics
The y-intercept, at 3.3512, corresponds to the limit of zero element size; i.e., the exact solution. Then:

$$\bar{X}_{Hel} = e^{3.3512} = 28.54\%.$$  

As seen in Table 7S.4, this conversion is higher than that for fully-developed laminar flow in a straight tube, but less than that assuming plug flow in a straight tube. The radial mixing due to secondary motion moves the conversion closer to that for plug flow.

(d) Flow Through a Coil Wrapped Around Two Mandrels in a Figure-8

The steps to compute a solution for this geometry are identical to those for helical flow (c), except that geometric Composite Object, CO2, is mirrored about the y-z plane at $x = 0.5$, following the rotation in Figure 7S.27. This creates the object, CO3, and CO2 is deleted. The resulting geometry is shown in Figure 7S.43 from the default 3D view in Draw Mode.

![Figure 7S.43 Lemniscate in Draw Mode](image)

The flow through the first half of the lemniscate is identical to that for the helix, and consequently, only the second-half turn is examined next.

The axial velocity profile at the start of the second turn, at ¼, ½, and ¾ of the second turn, and at its outlet, are shown in Figure 7S.44. The right side of each plot represents the inside edge (touching the mandrel) of the tube.
Figure 7S.44  Axial velocity profile cross sections

(a) Start of the Second Turn

(b) ¼ of the Second Turn

(c) ½ of the Second Turn

(d) ¾ of the Second Turn

(e) Outlet of the Second Turn
The peak of the axial velocity profile swings from one side of the tube to the other during the second turn. As shown next, this has a substantial effect on the concentration profile due to irregular fluid motion. At the tube outlet, the secondary motion is more irregular than that at the outlet of the helix, as seen in Figure 7S.40. Note that, for comparison, the secondary motion after the first turn is shown in Figure 7S.46.

Figure 7S.45  Secondary motion at the outlet shown by an arrow plot

Figure 7S.46  Secondary motion after the first turn
The recirculation at the outlet of the helix is less regular than that at the outlet of the Figure-8. Hence, the conversion is increased due to irregular secondary motion causing increased radial and azimuthal mixing in the second turn.

The reactant concentration profiles at the start of the second turn, at \( \frac{1}{4}, \frac{1}{2}, \) and \( \frac{3}{4} \) of the second turn, and at its outlet, are shown in Figure 7S.47. The left side of each plot represents the inside edge (touching the mandrel) of the tube.

The concentration profile is leveled throughout the second turn as the peak of the axial velocity profile swings from one side to the other. Also, the region of lowest conversion switches from one side of the tube to the other. The highest concentrations remain around the lobes at the top and bottom of the tube in the recirculation zones, giving a higher conversion as shown next. Figure 7S.47(e) should be compared with Figure 7S.41(e).

Conversions at the outlet calculated over a range of decreasing mesh sizes are given in Table 7S.3.

<table>
<thead>
<tr>
<th>Maximum Element Size</th>
<th>No. of Elements</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01015</td>
<td>28,400</td>
<td>32.113</td>
</tr>
<tr>
<td>0.0101</td>
<td>30,378</td>
<td>31.993</td>
</tr>
<tr>
<td>0.00975</td>
<td>34,006</td>
<td>31.753</td>
</tr>
<tr>
<td>0.0096</td>
<td>35,489</td>
<td>31.573</td>
</tr>
<tr>
<td>0.0094</td>
<td>38,872</td>
<td>31.513</td>
</tr>
</tbody>
</table>

A semi-log plot of the conversion as a function of the inverse of the mesh size is shown in Figure 7S.48.

From the y-intercept, at \( y = 3.3945 \), the conversion at the outlet of the lemniscate is:

\[
X_{\text{Lem}} = e^{3.3945} = 29.80\%.
\]
Figure 7S.47  Reactant concentration profile cross sections

(a) Start of the Second Turn
(b) ¼ of the Second Turn
(c) ½ of the Second Turn
(d) ¾ of the Second Turn
(e) Outlet
As shown in Table 7S.4, this conversion is higher than that for the helix.

**Conclusion**

For the specifications herein, using the plug flow assumption to calculate the reactant conversion at the outlet of a straight tube under fully-developed laminar flow results in:

\[
\left( \frac{X_{\text{PFR}} - X_{\text{LDI}}}{X_{\text{LDI}}} \right) = \left( \frac{30.54\% - 27.47\%}{27.47\%} \right) = 11.2\%
\]

overestimation of the conversion. This discrepancy varies with the reactor tube length, but is not significantly affected as the reaction rate constant increases. In this section, it has been shown that curvature-induced radial mixing levels the reactant concentration profile to more closely resemble that computed using the plug flow assumption. The helix converts:
\[
\left( \frac{X_{\text{Hel}} - X_{\text{LD1}}}{X_{\text{LD1}}} \right) = \left( \frac{28.54\% - 27.47\%}{27.47\%} \right) = 3.90\%
\]

more reactant than the straight tube under fully-developed laminar flow – and the lemniscate converts:

\[
\left( \frac{X_{\text{Lem}} - X_{\text{LD1}}}{X_{\text{LD1}}} \right) = \left( \frac{29.80\% - 27.47\%}{27.47\%} \right) = 8.48\%
\]

more than the straight tube under fully-developed laminar flow. Both of these curved tubes induce substantial amounts of radial mixing due to secondary motion in the fluid flow. Table 7S.4 compares the mixed-mean conversions calculated in Section 7S.6.

Table 7S.4 Reactant Conversion

<table>
<thead>
<tr>
<th>Case</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{\text{LD0}}$</td>
<td>27.41%</td>
</tr>
<tr>
<td>$X_{\text{LD1}}$</td>
<td>27.47%</td>
</tr>
<tr>
<td>$X_{\text{LD100}}$</td>
<td>28.25%</td>
</tr>
<tr>
<td>$X_{\text{Hel}}$</td>
<td>28.54%</td>
</tr>
<tr>
<td>$X_{\text{Lem}}$</td>
<td>29.80%</td>
</tr>
<tr>
<td>$X_{\text{PFR}}$ ($X_{\text{LDx}}$)</td>
<td>30.54%</td>
</tr>
</tbody>
</table>

For process design, where the objective is to specify the reactor centerline length needed to achieve a given conversion, the plug flow assumption is particularly hazardous. Rearranging Eq. (7S.21) yields an explicit equation for $L_{\text{PFR}}$ as a function of $X_{\text{PFR}}$ for a plug flow reactor:

\[
L_{\text{PFR}} = \left( \frac{X_{\text{PFR}}}{1 - X_{\text{PFR}}} \right) \left( \frac{u_{\text{mean}}}{kC_{A0}} \right)
\]  

For example, when a mixed-mean conversion of 60% ethyl acetate is required at the outlet of a tubular saponification reactor, Eq. (7S.28) gives $L_{\text{PFR}} = 5.37$ m. Solving Eq. (7S.26) iteratively for $L$ gives $L_{\text{lam}} = 6.74$ m. The PFR model predicts a reactor centerline length that is:
\[
\left( \frac{L_{\text{Lam}} - L_{\text{PFR}}}{L_{\text{Lam}}} \right) = \left( \frac{6.74\text{m} - 5.37\text{m}}{6.74\text{m}} \right) = 20.3\%
\]

shorter than required. Using 5.37 m as the reactor centerline length, gives \( \bar{X}_{\text{LD0}} = 0.547 \) from Eq. (7S.26). If an engineer used the PFR model to design the saponification reactor, it would give:

\[
\left( \frac{\bar{X}_{\text{PFR}} - \bar{X}_{\text{LD0}}}{\bar{X}_{\text{LD0}}} \right) = \left( \frac{60\% - 54.7\%}{54.7\%} \right) = 9.7\%
\]

less conversion than is required. Agrawal (2001) showed that the relative errors for a 1\textsuperscript{st} order reaction are even higher than those seen in these materials for a 2\textsuperscript{nd} order reaction. In light of both of these analyses, the plug flow assumption should be used cautiously when designing tubular reactors. In laminar flow, curved-tube reactors are better modeled using the non-conservative plug flow model than straight tube reactors. These results do not apply to turbulent flow.

REFERENCES


