Chapter 23. Reactor Performance

What You Will Learn

- Reactor performance is affected by multiple parameters.
- All of these parameters must be considered appropriately.

Chemical reactors are used to produce high-value chemicals from lower-value chemicals. Reactor performance depends on the complex interaction between four effects, as is illustrated in Figure 23.1. In order to understand fully the performance of a chemical reactor in the context of a chemical process, all four effects must be considered.

1. **Reaction Kinetics and Thermodynamics:** The influence of extensive variables (pressure, temperature, concentration) on reactor performance is defined by reaction kinetics and reaction equilibrium. These extensive variables affect the reaction rate and determine the extent to which reactants can be converted into products in a given reactor or the size of reactor needed to achieve a given conversion. Additionally, catalysts are used to increase the rate of reaction. Thermodynamics sets a theoretical limit on the extent to which reactants can be converted into products and cannot be changed by catalysts.
2. **Reactor Parameters:** These include the reactor volume, space time (reactor volume/inlet volumetric flowrate), and reactor configuration. For given kinetics, thermodynamics, reactor and heat transfer configuration, and space time, the reactor volume needed to achieve a given conversion of reactants is determined. This is the design problem. For a fixed reactor volume, the conversion is affected by the temperature, pressure, space time, catalyst, and reactor and heat transfer configuration. This is the performance problem.

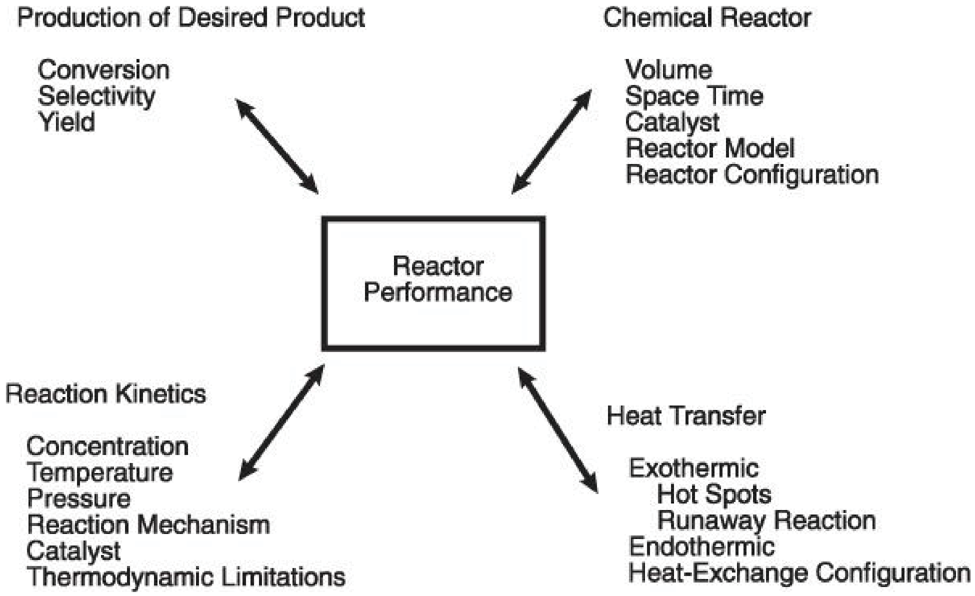


Figure 23.1. Phenomena Affecting Reactor Performance

3. **Production of Desired Product:** *Conversion*, *selectivity*, and *yield* are terms that quantify the amount of reactants reacted to form desired products. Reactor performance is expressed in terms of these parameters. For a fixed reactor volume, these parameters are functions of the temperature, pressure, reactor and heat transfer configuration, and space time.

4. **Heat Transfer in Reactor:** This important effect is often overlooked. Energy is released or consumed in chemical reactions. The rate of chemical reaction is highly temperature dependent. The key point to consider is the interaction between chemical kinetics and heat transfer (see Example 22.1). For exothermic reactions, the heat of reaction must be removed efficiently to avoid large temperature increases that can damage catalyst and to prevent runaway reaction. For endothermic reactions, heat must be supplied efficiently so that the reaction can proceed. The rate of heat transfer depends on reactor configuration (including the heat transfer configuration), the properties of the reacting stream, the properties of the heat transfer medium, and the temperature driving force.

In this chapter, the basic concepts needed for prediction of reactor performance are reviewed. Multiple reaction systems, reactor models, and heat transfer considerations are emphasized. Case studies are presented based on reactors found in the processes used as examples throughout the text and in the appendixes.

23.1. Production of Desired Product

Consider the following reaction scheme:

$$\begin{aligned} &aA + bB \xrightarrow[rxn\ 1]{k_1} pP \xrightarrow[rxn\ 2]{k_2} uU \\ &\beta B \xrightarrow[rxn\ 3]{k_3} vV \end{aligned} \tag{23.1}$$

Equation (23.1) shows three reactions involving five species *A*, *B*, *P*, *U*, and *V*, with stoichiometric coefficients *a*, *b*, *p*, *u*, and *v*, respectively. It is assumed that *P* is the desired product and that *U* and *V* are unwanted by-products. The reaction scheme in Equation (23.1) can be used to illustrate the effects commonly observed in actual reaction kinetics.

1. A **single reaction** produces desired product. Here $k_2 = k_3 = 0$, and only the first reaction proceeds. Acetone production (Appendix B, Figure B.10.1) is an example of this situation. Hydrodealkylation of toluene to benzene behaves like this because the catalyst suppresses the undesired reactions sufficiently so that single-reaction behavior is approached.
2. **Parallel** (competing) reactions produce desired products and unwanted by-products. Here $k_2 = 0$, and no *U* is formed. Species *B* reacts to form either *P* or *V*. In the phthalic anhydride reaction sequence (Appendix C, Figure C.5), the reaction of o-xylene to form either phthalic anhydride, maleic anhydride, or combustion products (Appendix C, Table C.10, Reactions 1, 3, and 4) is an example of a parallel reaction.
3. **Series** (sequential) reactions produce desired products and unwanted by-products. Here $k_3 = 0$, and no *V* is formed. Species A reacts to form desired product *P*, which further reacts to form unwanted by-product *U*. In the phthalic anhydride reaction sequence (Appendix C, Table C.10), the reaction of o-xylene to phthalic anhydride to combustion products (Reactions 1 and 2) is an example of a series reaction.
4. **Series** and **parallel** reactions produce desired products and unwanted by products. Here, all three reactions in Equation (23.1) occur to form desired product *P* and unwanted by-products *U* and *V*. The entire phthalic anhydride sequence (Appendix C, Table C.10) as well as the cumene production reaction (Appendix C, Table C.17) are examples of series or parallel reactions.

For reaction schemes like the one shown in Equation (23.1), there are three key definitions used to quantify production of desired product.

The term **conversion** quantifies the amount of reactant reacted. The single-pass conversion (or reactor conversion) is

$$\text{Single-pass conversion} = \frac{\text{Reactant consumed in reactor}}{\text{Reactant fed to reactor}} \tag{23.2}$$

and is generally reported in terms of the limiting reactant. This is different from the overall process conversion, which is defined as

$$\text{Overall conversion} = X = \frac{\text{Reactant consumed in process}}{\text{Reactant fed to process}} \tag{23.3}$$

Most processes recover and recycle unreacted material to provide a high overall conversion.

High reactor conversions are neither necessary nor desirable for optimum reactor performance. At low reactor conversions, high overall conversions can be achieved with increased recycle.

The term **selectivity** quantifies the conversion to desired product.

$$\text{Selectivity} = \eta = \frac{\text{Rate of production of desired product}}{\text{Rate of production of undesired by-products}} \tag{23.4}$$

A high selectivity is always desirable.

Competition from undesired reactions limits conversion to the desired product.

Another term used to quantify production of the desired product is **yield**, defined as

$$\text{Yield} = \frac{\text{Moles of reactant reacted to produce desired product}}{\text{Moles of limiting reactant reacted}} \tag{23.5}$$

The terms defined in this section will be used in examples and the case studies presented later in this chapter.

23.2. Reaction Kinetics and Thermodynamics

The kinetics of a reaction quantify the rate at which the reaction proceeds. When designing a new reactor for a given conversion, a faster reaction requires a smaller volume reactor. When analyzing an existing reactor of fixed volume, a faster reaction means increased conversion. As stated previously, thermodynamics provides limits to the conversions obtainable from a chemical reaction.

23.2.1. Reaction Kinetics

The reaction rate, r_i, is defined as

$$r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{\text{moles of } i \text{ formed}}{(\text{volume of reactor})\ (\text{time})} \tag{23.6}$$

The reaction rate is an intensive property. This means that the reaction rate depends only on state variables such as temperature, concentration, and pressure, and not on the total mass of material present.

For solid catalyzed reactions, the reaction rate is often defined based on the mass of catalyst present, *W*:

$$r_i = \frac{1}{W}\frac{dN_i}{dt}\rho_b = \frac{1}{V}\frac{dN_i}{dt} \qquad (23.7)$$

where ρ_b is the bulk catalyst density (mass catalyst/volume reactor). The density of solid catalyst is defined as ρ_{cat} (mass catalyst particle/volume catalyst particle). So the bulk density of the catalyst, ρ_b, is defined as

$$\rho_b = (1 - \varepsilon)\rho_{cat} \qquad (23.8)$$

Here, ε is the void fraction in the reactor; so $(1 - \varepsilon)$ is volume of catalyst/volume of reactor.

If a reaction is an elementary step, the kinetic expression can be obtained directly from the reaction stoichiometry. For example, in Equation (23.1), if the first reaction is an elementary step, the rate expression is

$$-r_A = k_1 c_A^{\alpha} c_B^{\beta} \qquad (23.9)$$

For catalytic reactions, the rate expressions are often more complicated because the balanced equation is not an elementary step. Instead, the rate expression can be obtained by an understanding of the details of the reaction mechanism. The resulting rate expressions are often of the form

$$r_i = \frac{k_1 \prod_{i=1}^{n} c_i^{\alpha_i}}{\left[1 + \sum_{j=1}^{m} K_j c_j\right]^{\gamma}} \qquad (23.10)$$

Equation (23.10) describes a form of Langmuir-Hinshelwood kinetics. The constants (k_1 and K_j) in Equation (23.10) are catalyst specific. The constants in Equation (23.10) must be obtained by fitting reaction data.

In heterogeneous catalytic reacting systems, reactions take place on the surface of the catalyst. Most of this surface area is internal to the catalyst pellet or particle. The series of resistances that can govern the rate of catalytic chemical reaction are as follows:

1. Mass film diffusion of reactant from bulk fluid to external surface of catalyst
2. Mass diffusion of reactant from pore mouth to internal surface of catalyst
3. Adsorption of reactant on catalyst surface
4. Chemical reaction on catalyst surface
5. Desorption of product from catalyst surface
6. Mass diffusion of product from internal surface of catalyst to pore mouth
7. Mass diffusion from pore mouth to bulk fluid

Each step offers a resistance to chemical reaction. Reactors often operate in a region where only one or two resistances control the rate. For a good catalyst, the intrinsic rates are so high that internal diffusion resistances are usually controlling.

For solid catalyst systems, reactor performance is usually controlled by resistances to mass transfer.

The temperature dependence of the rate constants in Equations (23.9) and (23.10) is given by the Arrhenius equation

$$k_i = k_o e^{-\frac{E}{RT}} \qquad (23.11)$$

where k_o is called the **pre-exponential factor**, and E is the **activation energy** (units of energy/mol, always positive). Equation (23.11) reflects the significant temperature dependence of the reaction rate. For gas-phase reactions, the concentrations can be expressed or estimated from the ideal gas law, so $c_i = P_i/RT$. This is the origin of the pressure dependence of gas-phase reactions. As pressure increases, so does concentration, and so does the reaction rate. The temperature dependence of the Arrhenius equation usually dominates the opposite temperature effect on the concentration.

As temperature increases, the reaction rate always increases, and usually significantly.

23.2.2. Thermodynamic Limitations

Thermodynamics provides limits on the conversion obtainable from a chemical reaction. For an equilibrium reaction, the equilibrium conversion may not be exceeded.

Thermodynamics sets limits on possible conversions in a reacting system.

The limitations placed on conversion by thermodynamic equilibrium are best illustrated by Example 23.1.

Example 23.1.

Methanol can be produced from syngas by the following reaction:

$$CO + 2H_2 = CH_3OH$$

For the case when no inerts are present and for stoichiometric feed, the equilibrium expression has been determined to be

$$K = \frac{X(3-2X)^2}{4(1-X)^3 P^2} = 4.8 \times 10^{-13} \exp(11{,}458/T) \qquad \text{(E23.1)}$$

where X is the equilibrium conversion, P is the pressure in atmospheres, and T is the temperature in Kelvin. Construct a plot of equilibrium conversion versus temperature for four different pressures: 15 atm, 30 atm, 50 atm, and 100 atm. Interpret the significance of the results.

The plot is shown on Figure E23.1. By following any of the four curves from low to high temperature, it is observed that the equilibrium conversion decreases with increasing temperature at constant pressure. This is a consequence of Le Chatelier’s principle, because the methanol formation reaction is exothermic. By following a vertical line from low to high pressure, it is observed that the equilibrium conversion increases with increasing pressure at constant temperature. This is also a consequence of Le Chatelier’s principle. Because there are fewer moles on the right-hand side of the reaction, increased conversion is favored at high pressures.

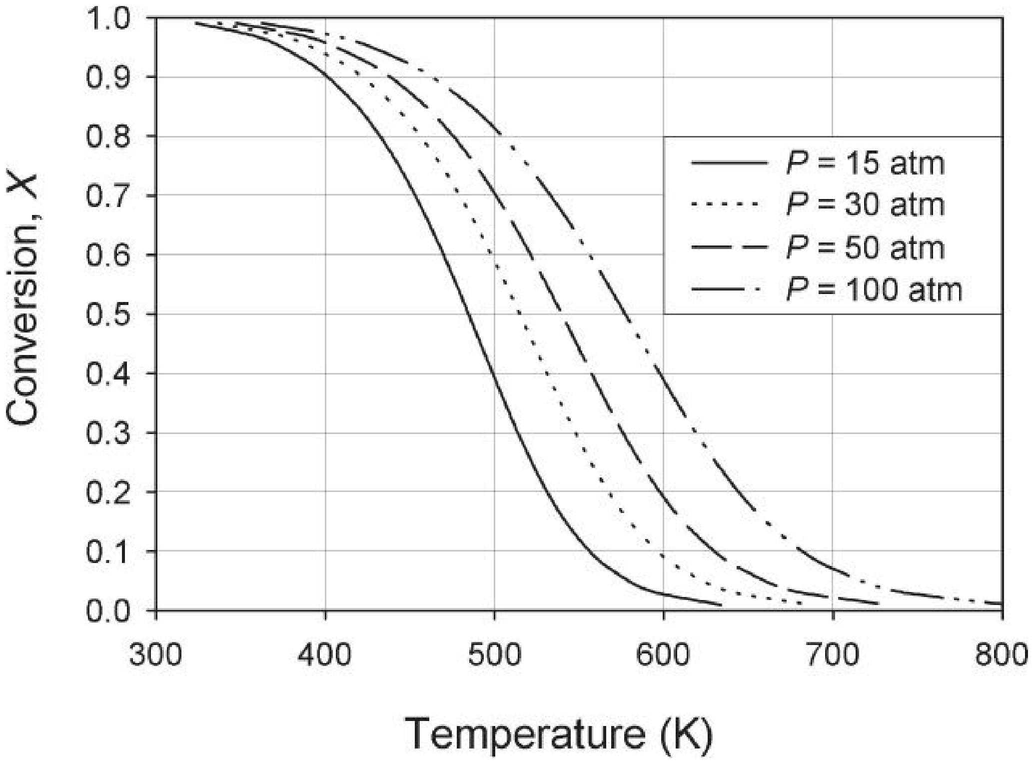


Figure E23.1. Temperature and Pressure Dependence of Conversion for Methanol from Syngas

From thermodynamic considerations alone, it appears that this reaction should be run at low temperatures in order to achieve maximum conversion. However, as discussed in Section 23.2.1, because the rate of reaction is a strong function of temperature, this reaction is usually run at higher temperatures, with low single-pass conversion, in order to take advantage of the faster kinetics. As discussed in Section 23.1, despite a low single-pass conversion in the reactor, a large overall conversion is still achievable by recycling unreacted reactants.

23.3. The Chemical Reactor

For continuous flow reactors, the two ideal models are the plug flow reactor and the continuous stirred tank reactor. In the plug flow reactor (PFR), which is basically a pipe within which the reaction occurs, the concentration, pressure, and temperature change from point to point. The performance equation is

$$\frac{V}{F_{Ao}} = \frac{\tau}{c_{Ao}} = \int_0^{X_A} \frac{dX_A}{-r_A} \qquad (23.12)$$

In the continuous stirred tank reactor (CSTR), the reactor is assumed to be well mixed, and all properties are assumed to be uniform within the reactor. The performance equation is

$$\frac{V}{F_{Ao}} = \frac{\tau}{c_{Ao}} = \frac{X_A}{-r_A} \qquad (23.13)$$

where

V = volume of the reactor
F_{Ao} = molar flow of limiting reactant A
τ = space time (reactor volume/inlet volumetric flowrate)

c_{Ao} = inlet concentration of A

X_A = conversion of A

r_A = rate of reaction of A

Equations (23.12) and (23.13) must be solved for a given rate expression to get the actual relationship between the indicated parameters. However, several generalizations are possible. The reactor volume and conversion change in the same direction. As one increases, so does the other; as one decreases, so does the other. As the reaction rate increases, the volume required decreases, and vice versa. As the reaction rate increases, the conversion increases, and vice versa. It has already been discussed how temperature, pressure, and concentration affect the reaction rate. Their effect on conversion and reactor volume is derived from their effect on reaction rate. Example 23.2 illustrates these qualitative generalizations.

Example 23.2.

Discuss qualitatively the effect of temperature and pressure on the space time and conversion in a chemical reactor.

Gas-Phase Reaction: From the Arrhenius equation in Equation (23.11), the reaction rate constant increases exponentially with temperature. From the ideal gas law, the concentration decreases less drastically. From Equations (23.12) and (23.13), at constant pressure, if the reaction rate increases, at constant conversion, a smaller reactor volume (and space time) is required. At constant reactor volume and space time, the conversion increases.

From a typical reaction rate expression such as Equation (23.9), as the pressure increases, so do the concentration and the reaction rate. Therefore, the same trends are observed as with temperature. However, the quantitative effect is not as great, because the concentration dependence on pressure is not exponential.

Liquid-Phase Reaction: For a liquid-phase reaction, temperature and pressure do not affect concentration. Therefore, there is no effect of pressure on reactor performance for a liquid-phase reaction. Because the temperature effect is determined by the Arrhenius equation only, the reaction rate increases exponentially with temperature.

The PFR is a hypothetical system. PFRs are elementary models for packed-bed reactors. The PFR model excludes the effects of axial mixing resulting from molecular movement and fluid turbulence while assuming radial mixing is complete. This mixing takes place between adjacent fluid elements of approximately the same conversion. Reactors approximating PFRs are often built using many small-diameter tubes (less than 3 in) of significant length (20 to 30 ft) operated at high fluid velocity with small space times. This minimizes axial fluid mixing, limits radial temperature profiles, and provides needed heat transfer area. Tubes are arranged in a bundle characteristic of those found in many heat exchangers. If heat exchange is not desired in the reaction zone, a single or series of larger-diameter packed beds can be used.

The CSTR is also a hypothetical system in which there is perfect mixing so that temperature, pressure, concentration, and reaction rate are constant over the reactor volume. Reactors approximating CSTRs are used for liquid-phase reactions. This represents a theoretical limit because perfect mixing can only be approached. Transit time for fluid elements varies. The exit stream is at the same temperature, pressure, and conversion as the reactor contents. Feed is mixed with the reactor contents that have a high conversion. As a result, the CSTR requires a higher volume than a PFR when operated isothermally at the same temperature and conversion for simple, elementary reactions.

Reactors are modeled using different combinations and arrangements of CSTRs and PFRs. Intermediate degrees of mixing are obtained that can be used to model various real reactor systems. Some of these models are shown in Figure 23.2 and described below.

System (a) is a PFR for an exothermic reaction. The concentration and temperature vary from point to point in the reactor. This model is used to simulate the cumene reactor in Appendix C.

System (b) is a CSTR. The temperature and concentration are constant within the reactor.

System (c) consists of a PFR and CSTR in parallel. By increasing the ratio of CSTR feed rate to PFR feed rate, the degree of mixing is increased. By increasing the ratio of PFR feed rate to CSTR feed rate, dead space (regions that are not well mixed) in a CSTR can be simulated.

System (d) consists of a series of CSTRs in series. The degree of mixing is less than that in a single CSTR. Although each reactor is completely mixed, there is no mixing between each section. In the limit of an infinite number of CSTRs in series, PFR behavior is approached.

System (e) consists of an isothermal PFR with a bypass stream. In a fluidized bed, solid catalyst is circulated within the bed; however, the fluid moves through the bed essentially in plug flow. Maldistribution of fluid, due to the formation of bubbles and voids, and channeling may cause some fluid to bypass the catalyst. This model is used in catalytic fluidized bed applications or in any other application where the solid does not react. A portion of the reactants forms an emulsion phase with little mixing (plug flow). The remaining fluid forms bubbles that move upward at a higher velocity, contact only a small portion of the solid catalyst, and do not react as much as in the emulsion phase. An important feature of the fluidized bed is that it operates isothermally as a result of the mixing of the solids. The model shown in System E is a crude approximation of what happens in a real fluidized bed, but it predicts the trends found in fluidized beds. This model is used to simulate the acrylic acid reactor in Appendix B.

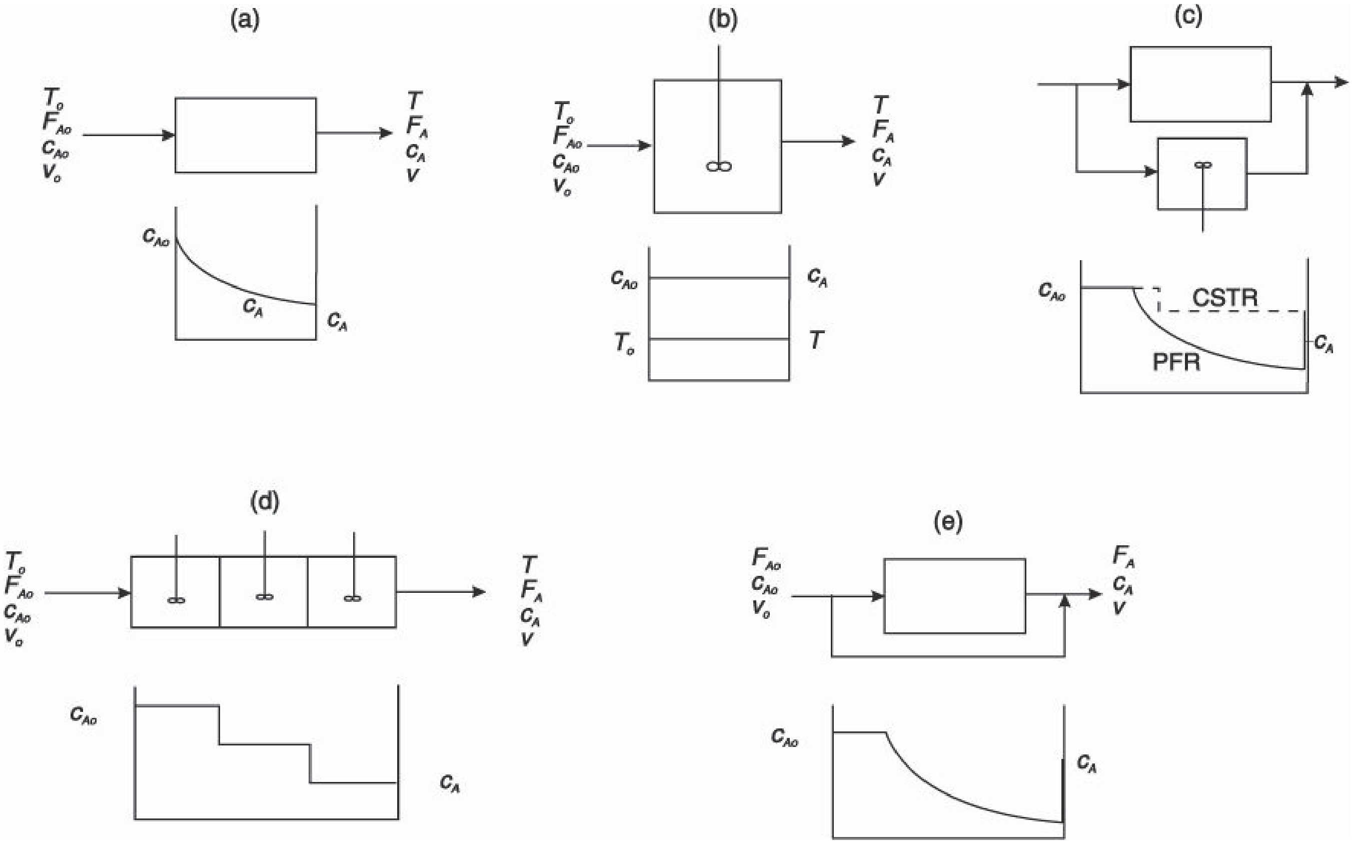


Figure 23.2. Mixing Patterns with Characteristic Concentration Profiles

As the reactor model becomes more complex, it becomes more difficult to solve Equations (23.12) and (23.13) to predict reactor performance. Because process simulators are already programmed to do this, they are a logical choice for analyzing reactor performance, especially because real reactors must be simulated in the context of an entire process. For the chemical reactor, the required input data include identification of the dominant reactions that take place, the form of the reaction rate, and values of the kinetic constants. All these may change with operating conditions, and a given set of values applies only to a limited range of operations. They must be obtained experimentally. If the experimental data are flawed or the simulation operating conditions are outside the range of the experimental studies, the answer obtained can lead to poor prediction of reactor performance. The computer can do the calculations but is unable to recognize the reliability of the input.

Example 23.3. summarizes the concepts presented thus far in this chapter.

Example 23.3.

Consider the reaction scheme given in Equation (23.1) where P is the desired product, with both U and V as undesired by-products. Assume that Equation (23.1) represents elementary steps, that $a = b = p = u = \upsilon = 1$, that $\beta = 2$, and that the activation energies for the reactions are as follows: $E_1 > E_2 > E_3$.

a. For the case where $k_2 = 0$, what conditions maximize the selectivity for P?

b. For the case where $k_3 = 0$, what conditions maximize the selectivity for P?

Solution

a. For this case, from Equation (23.4), the selectivity is written as

$$\eta = \frac{r_P}{r_V} = \frac{k_1 c_A c_B}{k_3 c_B^2} = \frac{k_1 c_A}{k_3 c_B} \tag{E23.3a}$$

There are several ways to maximize the selectivity. Increasing c_A/c_B increases the selectivity. This means that excess *A* is needed and that *B* is the limiting reactant. Many reactions are operated with one reactant in excess. The reason is usually to improve selectivity as shown here. Because pressure affects all concentrations equally, it is seen that pressure does not affect the selectivity here. Temperature has its most significant effect on the rate constant. Because the activation energy for rxn 1 is larger than that for rxn 3, k_1 is more strongly affected by temperature changes than is k_3. Therefore, increasing the temperature increases the selectivity. In summary, higher temperatures and excess *A* maximize the selectivity for *P*.

b. For this case, the selectivity is written as

$$\eta = \frac{r_P}{r_U} = \frac{k_1 c_A c_B - k_2 c_P}{k_2 c_P} = \frac{k_1 c_A c_B}{k_2 c_P} - 1 \tag{E23.3b}$$

Because pressure appears to the second power in the numerator and to the first power in the denominator (it is in each concentration term), increasing the pressure increases the selectivity. Because the activation energy for rxn 1 is larger, increasing the temperature increases the selectivity. Increasing both reactant concentrations increases the selectivity, but increasing the concentration of Component *P* decreases the selectivity. The question is how the concentration of Component *P* can be kept to a minimum. The answer is to run the reaction at low conversions (small space time, small reactor volumes). Quantitatively, the selectivity in Equation (23.3b) is maximized. Intuitively, because this is a series reaction with the desired product intermediate in the series, a low conversion maximizes the intermediate product and minimizes the undesired product. This can be illustrated by the concentration profiles obtained by assuming that these reactions take place in a PFR, as shown in Figure E23.3. It is seen that the ratio of *P*/*U* is at a maximum at low reactor volumes, which corresponds to low conversion. Therefore, increasing the temperature and pressure both increases the selectivity for Component *P*. Running at low conversion probably does more to increases the selectivity than can be accomplished by manipulating temperature and pressure alone. However, there is a trade-off between selectivity and overall profitability, because low conversion per pass means very large recycles and larger equipment.

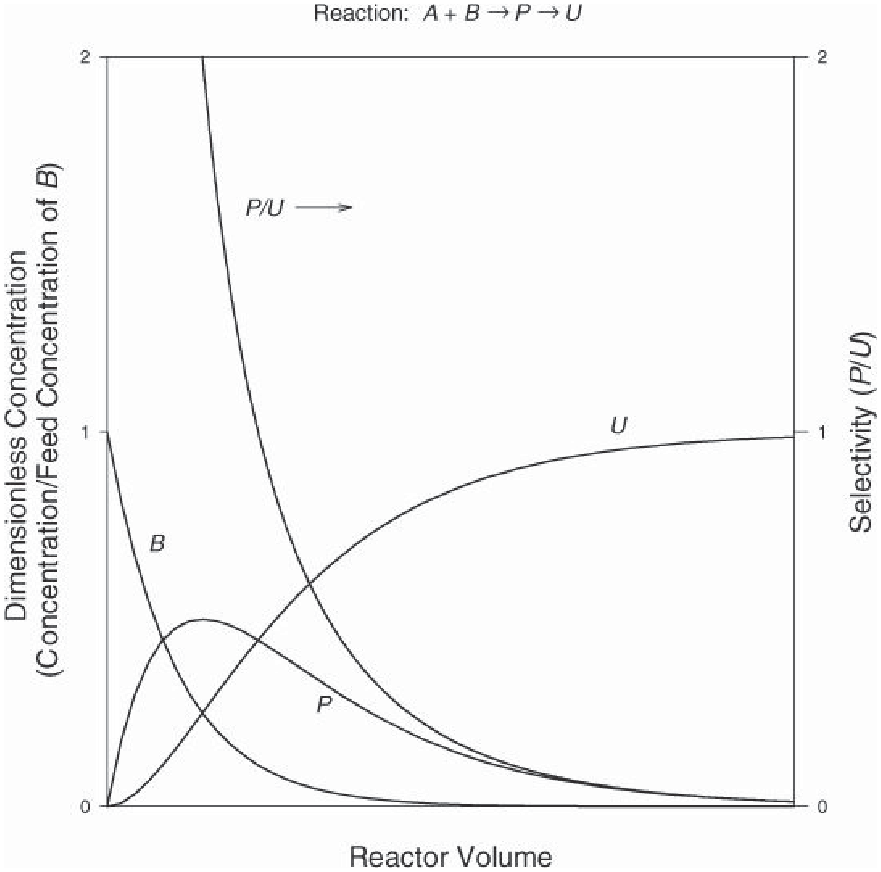


Figure E23.3. Concentration Profiles in a PFR for Series Reaction

23.4. Heat Transfer in the Chemical Reactor

Chemical reactions are either exothermic (release heat) or endothermic (absorb heat). Therefore, heat transfer in reactor systems is extremely important. For exothermic reactions, heat may have to be removed so that the temperature in the reactor does not increase above safe limits. For endothermic reactions, heat may have to be added so that the reaction will occur at an acceptable rate.

Reactor performance is often limited by the ability to add or remove heat.

Most industrially significant chemical reactions are exothermic. Highly exothermic reactions, especially in a reactor behaving like a PFR, can be dangerous if the rate of heat removal is not sufficient. For a rate expression such as Equation (23.9), the concentration of reactants is largest at the entrance to the reactor. The reaction at the entrance generates heat if the reaction is exothermic. The concomitant increase in temperature increases the reaction rate even further, which increases the temperature further, and so forth. Therefore, it is possible to have large temperature increases, called **hot spots.** The large temperature increase can be offset by removing heat from the reactor. This can cause radial temperature gradients, with severe hot spots near the center of the tube. Hot spots can damage and deactivate catalyst particles. In the extreme case, if the rate of heat removal is not sufficient to offset the rate of heat production by reaction, the temperature may increase rapidly, causing damage to the reactor and its contents or an explosion. This is called **runaway reaction**. Reactor temperature profiles illustrating the situation leading to runaway reaction are illustrated in

Figure 23.3(b).

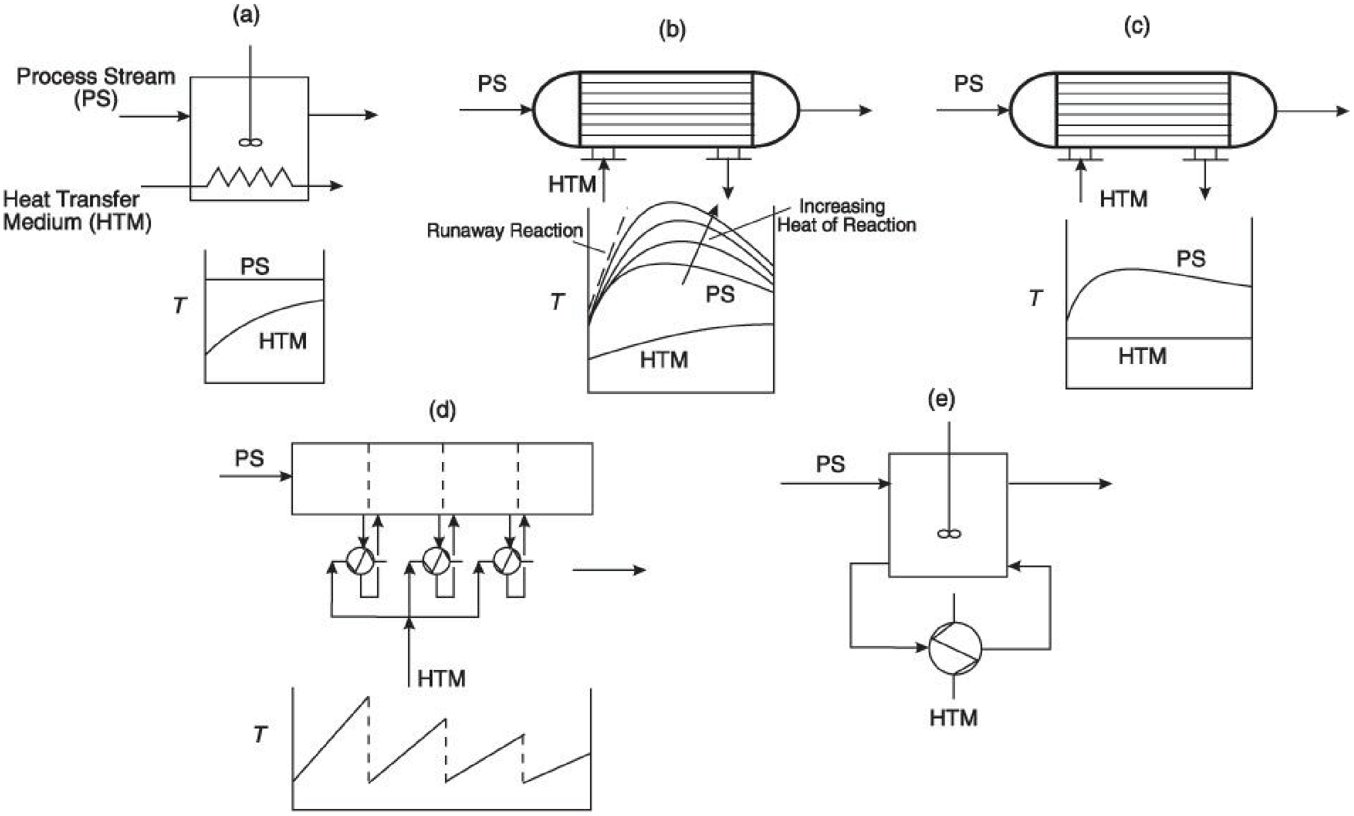


Figure 23.3. Alternative Heat-Exchange Systems for Reactors Shown for Exothermic Reaction: a–c, Internal Heat Exchanger; d–e, External Heat Exchanger

Beware of exothermic reactions! Runaway reaction is possible if there is insufficient heat removal.

For endothermic reactions, heat must be added to the reactor. **Cold zones** are possible based upon the same logic as for the hot spots for exothermic reactions. However, if there is insufficient heat addition to an endothermic reaction, the reaction will be quenched. Therefore, endothermic reactions are inherently safe.

There are many methods used to avoid hot spots in a reactor with an exothermic reaction. Some of these methods are as follows:

1. **Run Heat Transfer Medium Cocurrently:** The heat transfer medium enters at its lowest temperature. By matching this low temperature with the highest temperature zone in the reactor, the temperature gradient is largest at the reactor entrance, providing more heat removal.
2. **Use Inert Solid:** By randomly packing the bed with inert solid (no catalytic activity), the heat released per unit volume of reactor is reduced, thereby minimizing hot spots. This results in a larger reactor.
3. **Use Catalyst Gradients in Reactor:** This is similar to item 2. Here, a larger fraction of inert solid is used where hot spots are anticipated. This minimizes hot spots but also results in a larger reactor.
4. **Use a Fluidized Bed:** Due to the mixing behavior in a fluidized bed, isothermal operation is

approached.

Both internal and external heat exchangers can be used to exchange heat with a reactor. In the internal systems (Figure 23.3[a–c]), the heat transfer area is in contact with the reacting fluid. Quite often, this is like a shell-and-tube heat exchanger, with the catalyst most often placed in the tubes. In the external systems (Figure 23.3[d–e]), reaction fluid is withdrawn from the reactor, sent to a heat exchanger, and then returned to the reactor.

- **a. CSTR with Single-Phase Heat Transfer Medium:** The temperature profile is similar to that for the condensation of a single component vapor. The volume taken up by the heat exchanger increases the reactor volume. The mixing intensity of the reacting fluid may be reduced, and the potential for local nonisothermal behavior close to the heat-exchanger surfaces exists.
- **b. PFR with Single-Phase Heat Transfer Medium:** Temperature on the process side goes through a maximum.
- **c. PFR Heat Transfer Medium Boils:** Temperature on the utility side remains constant and goes through a maximum on the process side.
- **d. Adiabatic PFR with Heat Removal between Stages:** This configuration is usually used for exothermic reactions that do not have extremely large heats of reaction. The reaction proceeds adiabatically with a temperature rise, and fluid is removed periodically to be cooled.
- **e. External Heat Exchanger in CSTR:** Fluid in the reactor is circulated through an external heat exchanger.

In order to solve a problem involving a chemical reactor with heat transfer, the following equations must be solved:

1. Reactor performance equation, such as Equations (23.12) and (23.13)
2. Energy balance on reaction side
3. Energy balance on heat transfer medium side
4. Heat transfer performance equation ($Q = UA\Delta T_{\mathrm{lm}}$)
5. Pressure drop in packed bed (Ergun equation)

Therefore, as the heat transfer configuration becomes more complex, it becomes very difficult to solve the necessary equations to predict reactor performance. Because process simulators are already programmed to do this, they are a logical choice for analyzing reactor performance with heat transfer.

For a chemical reactor with heat transfer, in addition to the input discussed earlier, the required input data must include the heat transfer coefficient, the heat transfer area, the length and diameter of tubes, and the number of tubes. The output obtained is the temperature, pressure, and concentration of each component at each point in the reactor.

Heterogeneous catalytic reactions are even more difficult to simulate. The major resistance to reaction can change from chemical reaction to external diffusion or to pore diffusion within a single reactor. Stream temperatures are not necessarily the temperatures of the catalyst surface where the reaction takes place. Large temperature gradients may exist in the radial direction and within the catalyst particles. Although they do not consider these important factors, process simulators can often be used to obtain approximate solutions.

23.5. Reactor System Case Studies

This section contains case studies involving reactors from process flow diagrams presented throughout this text. The process changes presented illustrate typical problems a chemical engineer working in production may face on a routine basis.

All studies presented contain three parts:

Part A: A statement of the problem.

Part B: A solution to the specific problem, which includes discussion of the strategy used in the solution.

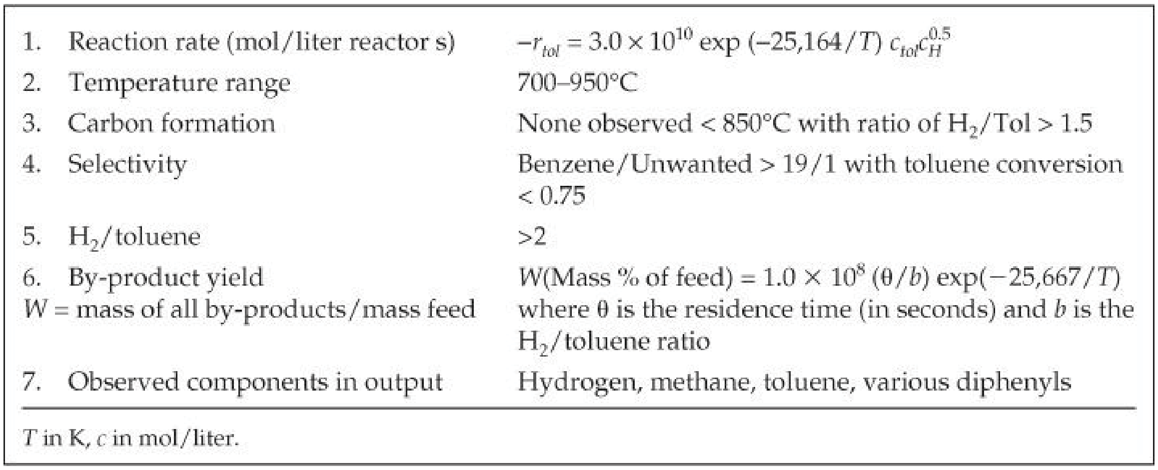
Part C: A discussion of the significance of the solution to a wider range of applications. Figures showing process response to important process variables are developed and used to reveal trends that yield insight into the problem. These performance curves provide better understanding of reactor behavior. They are also used as a guide to develop alternative problem solutions.

The availability of computers and computer software permits process simulation. Once the process is simulated, variables are easily varied to discover important performance characteristics that can be plotted over a wide range of operating conditions.

23.5.1. Replacement of Catalytic Reactor in Benzene Process

Problem. The catalyst in our benzene reactor has lost activity and must be replaced. The benzene process presented in Chapter 1 (Figure 1.5) is used to produce benzene. The reaction is carried out in an adiabatic PFR. Because of the cost of periodic catalyst replacement, it has been suggested that the catalytic reactor system could be replaced with a noncatalytic adiabatic PFR system that might be less costly. The new system is to match the input/output conditions of the current system so that the remainder of the plant will operate with little, if any, modification. You are asked to investigate the merits of this suggestion by identifying major cost items. Table 23.1 provides reactor information based on experimental studies on the toluene/benzene reaction.

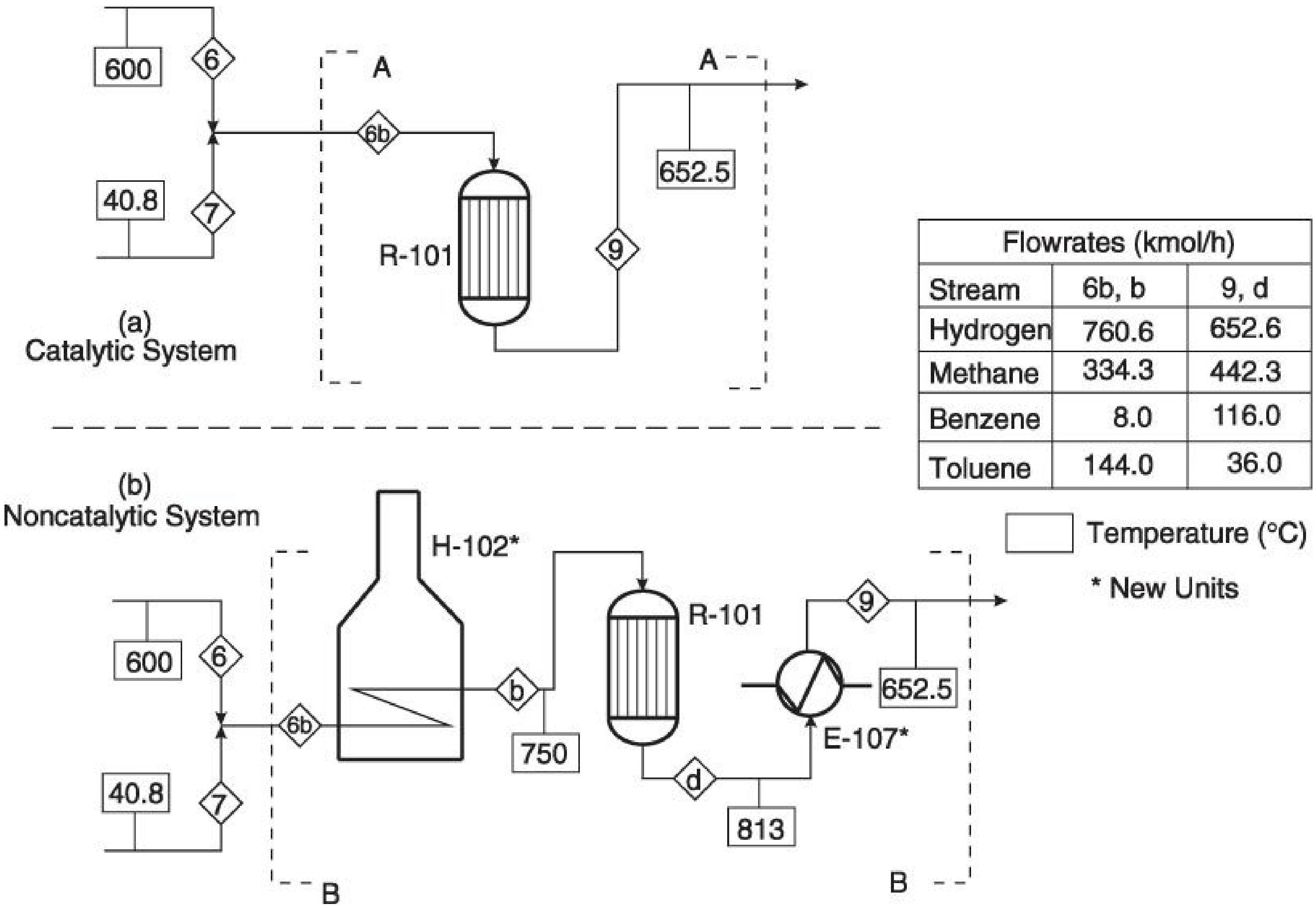
Table 23.1. Findings from Experimental Studies on Dealkylation of Toluene [1]



1.	Reaction rate (mol/liter reactor s)	$-r_{tol} = 3.0 \times 10^{10} \exp(-25{,}164/T)\, c_{tol} c_H^{0.5}$
2.	Temperature range	700–950°C
3.	Carbon formation	None observed < 850°C with ratio of H_2/Tol > 1.5
4.	Selectivity	Benzene/Unwanted > 19/1 with toluene conversion < 0.75
5.	H_2/toluene	>2
6.	By-product yield W = mass of all by-products/mass feed	W(Mass % of feed) = $1.0 \times 10^8 (\theta/b) \exp(-25{,}667/T)$ where θ is the residence time (in seconds) and b is the H_2/toluene ratio
7.	Observed components in output	Hydrogen, methane, toluene, various diphenyls

T in K, c in mol/liter.

Figure 23.4(a) provides a flow diagram of the current reactor taken from Figure 1.5. A-A identifies the boundaries of the reactor system to be replaced. Flowrates and stream temperature and pressure at these boundaries are given.



Flowrates (kmol/h)		
Stream	6b, b	9, d
Hydrogen	760.6	652.6
Methane	334.3	442.3
Benzene	8.0	116.0
Toluene	144.0	36.0

Figure 23.4. Reactor Systems for Production of Benzene from Toluene

The dominant chemical reaction at plant operating conditions is

$$\underset{\text{toluene}}{C_7H_8} + \underset{\text{hydrogen}}{H_2} = \underset{\text{benzene}}{C_6H_6} + \underset{\text{methane}}{CH_4}$$

Reactor conversion, $X_{toluene} = 1 - (36.1/144.0) = 0.749$. The amount of by-product formed by side reaction is negligible; however, the small amounts of carbon formed can deposit on the catalyst surface.

Solution. The reactor volume calculated for a noncatalytic adiabatic PFR using the kinetics expression given in Table 23.1 that met the conditions shown in Figure 23.4(a) is 257 m^3 (7800 ft^3). This is six times as great as the current catalytic reactor (41.5 m^3; see Table 1.7).

Intuitively, the reactor volume can be reduced by increasing the pressure and/or temperature in the new reactor system. Increasing the pressure increases the concentrations in the rate expression, and increasing the temperature increases the rate constant. This requires that a gas compressor and/or a heat exchanger (additional fired heater) be added to the new reactor system.

Installing an additional fired heater that increases the feed temperature to 750°C was also analyzed. The calculated reactor size is about 5 m^3 and the outlet temperature is 814°C.

An evaluation of the preliminary findings for the noncatalytic reactor configuration shows the following:

1. Using the same inlet conditions as for the catalytic reactor (inlet temperature 588°C),
   a. Extrapolation of the data in Table 23.1 is uncertain. This is because the reaction rate

    expression is extrapolated outside the region of experimental data (see item 1 of Table 23.1).
  - b. The predicted reactor size is much larger than that of the current reactor.
- 2. At increased temperature (inlet temperature 750°C),
  - a. The reaction rate is known from experimental data.
  - b. The reaction volume is much smaller than in the current reactor.
  - c. The temperature, H_2/toluene ratio, and conversion are all in a range that gives high benzene selectivity.
- 3. Increasing reactor feed pressure: This is considered an expensive option due to gas compression costs and was not evaluated.

The noncatalytic replacement system is shown in Figure 23.4(b) as region B-B. It is a more complicated system. Higher feed temperature requires the addition of another fired heater before the reactor and a gas cooler following the reactor. (Heat integration might be another alternative.) Major capital costs are required for the reactor, fired heater, and cooler. Materials of construction for the reactor are more expensive at the higher temperature (at the exit temperature of 814°C, a reactor vessel would glow red). Fuel for the fired heater increases operating cost. The economically optimum reactor temperature that considered these items could be determined if needed.

Unless the cost of catalyst is extremely high, replacement of the catalytic reactor with a noncatalytic system does not appear to be an attractive option.

Discussion. It is observed that the low-temperature reactor (at the temperature of the catalytic reaction) was very large, a result obtained by assuming that it is valid to extrapolate the data in Table 23.1 outside the stated temperature range. Assuming the data to be accurate in the low temperature range, reasons a large reactor was obtained can be investigated.

Several important factors considered in selecting a chemical reactor are revealed in this case study. Normally the advantages of a catalytic over a noncatalytic reactor are reduction in operating temperature and pressure and improvement in product selectivity.

In this case study, the catalyst reduced the temperature and pressure requirements, as expected. However, high selectivity for the desired product could be obtained from both the catalytic and noncatalytic reactors.

Carbon is a common by-product formed during organic reactions carried out in high-temperature reactors. It is most significant in catalytic reactors where carbon forms on the catalyst surface and reduces activity. High hydrogen concentrations discourage carbon formation. This helps explain the high H_2-to-toluene ratio of 5:1 used in the catalytic system compared to the lower value of 2.0 required for the noncatalytic reactor.

Equilibrium constants for the reactions involving the components found in the laboratory studies on the benzene reaction are published [2]. The primary by-product at high temperatures is diphenyl, formed by the following reaction:

$$\underset{\text{benzene}}{2C_6H_6} = \underset{\text{diphenyl}}{C_{12}H_{10}} + \underset{\text{hydrogen}}{H_2}$$

At equilibrium, excess H_2 increases the toluene conversion, decreases diphenyl conversion, and improves benzene selectivity. This trend is assumed to hold for nonequilibrium conditions, which suggests that high excess H_2 be used.

Increasing the reaction temperature decreases the equilibrium constant of the benzene reaction, because the main reaction is exothermic and increases the equilibrium constant of the diphenyl reaction because the side reaction is endothermic. As a result, the selectivity decreases and the raw material costs increase.

In our system, any diphenyl present in the reactor effluent, Stream 9, would be largely removed in the separation section and recycled with the toluene to the reactor. The concentration of diphenyl in the reactor feed, Stream b, would be increased. When sufficient diphenyl is introduced in Stream b to provide the equilibrium concentration, little diphenyl is formed in the reactor. This retains a high benzene selectivity at higher reactor temperatures.

For a new design, it may be desired to consider scenarios to increase the reaction rate for the noncatalytic reaction. Figure 23.5 shows the reaction rate, temperature, and toluene mole fraction plotted against the reactor volume for the original feed temperature. This figure shows that low reaction rates exist at the feed end of the reactor, with rapidly falling reaction rates at the reactor exit. The reactor temperature increases over the volume of the reactor. Figure 23.5 identifies steps to take that would improve reactor performance. Increased performance can be obtained by

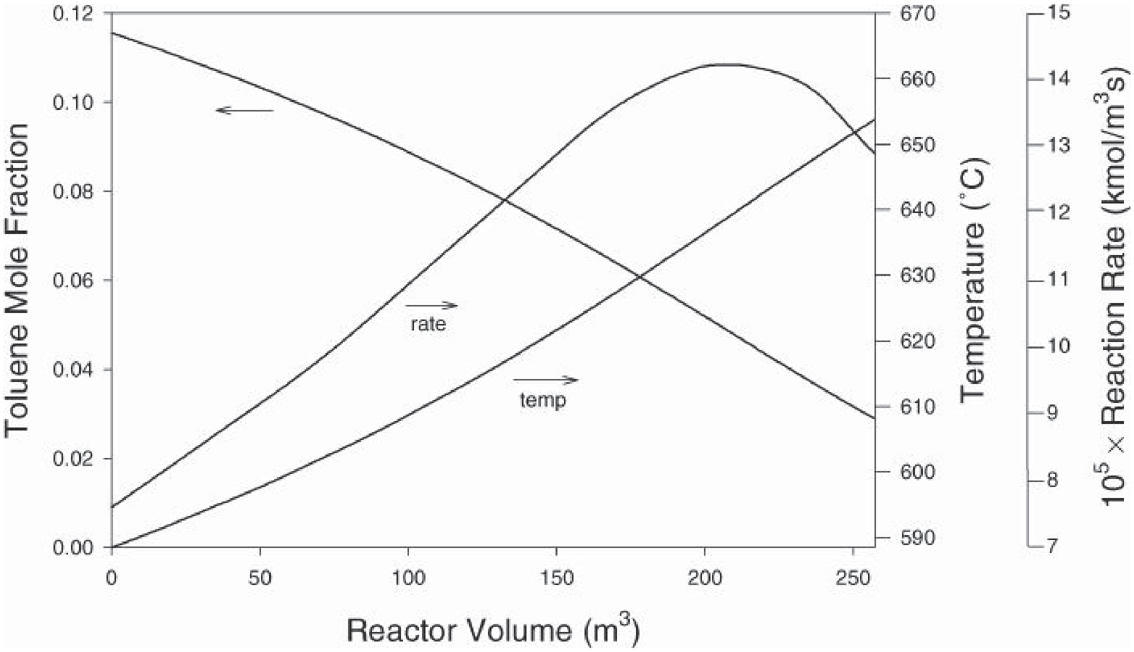


Figure 23.5. Behavior of Benzene PFR at Original Feed Temperature (585°C)

a. Elimination of the low reaction rate region at the beginning of the reactor. The low reaction rates are due to the low reaction rate constant, *k*, at low temperature. Increasing the feed temperature would increase reaction rate in this section.

b. Avoidance of operating in the region at the end of the reactor where the reaction rate falls rapidly. The falling reaction rate results from the lowering of toluene concentrations at high conversions. This region can be avoided by operating at lower reactor conversion (and higher recycle rates of unreacted feed).

This case study demonstrates that a dramatic decrease in the reactor volume required for a given conversion results from an increase in feed temperature.

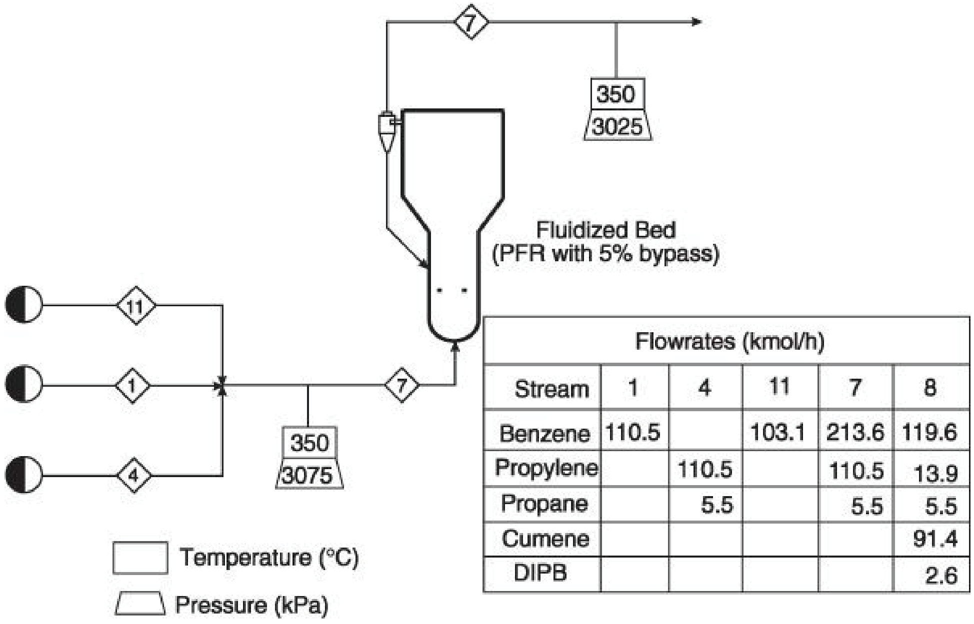
One could consider replacing the current reactor with an adiabatic CSTR. The reaction rate throughout the reactor would be constant at reactor exit conditions. This reaction rate is shown in Figure 23.5. The average reaction rate for the PFR is less than that of the CSTR, and the volume for a CSTR is less than that of the PFR. The elimination of the low-temperature region in the PFR overcomes the effect of lower toluene concentration in the CSTR.

The conclusion of this case study is that replacing the reactor with a non-catalytic PFR is not an attractive option. This may not be the conclusion if a new plant were to be built. In a new plant, the excess hydrogen could be substantially reduced. This would increase the toluene concentration and reduce the amount of recycle. Lower reactor conversions could be considered. Higher temperatures, higher toluene concentrations, and lower conversions would all contribute to a smaller reactor.

23.5.2. Replacement of Cumene Catalyst

Problem. Your company produces cumene. At your plant, the shell-and-tube, packed-bed reactor shown in Appendix C, Figure C.8, is used. At other plants owned by your company, proprietary fluidized bed reactors providing low gas bypass are used. The remainder of the process is identical at all locations. Your supplier has informed you that it has developed a new cumene catalyst that will improve fluidized bed reactor performance. The new catalyst is supported on the same inert material as the old catalyst. Therefore, the fluidizing properties are identical to those of the old catalyst. You are assigned the task of verifying claims of improved performance and identifying changes in operating conditions that would maximize the improvement this new catalyst could provide.

Figure 23.6 provides the operating conditions for this base case. In addition to the general process information provided with the process flow diagram (see the cumene flow diagram, Figure C.8, in Appendix C), the following specific background information is provided for your plant.



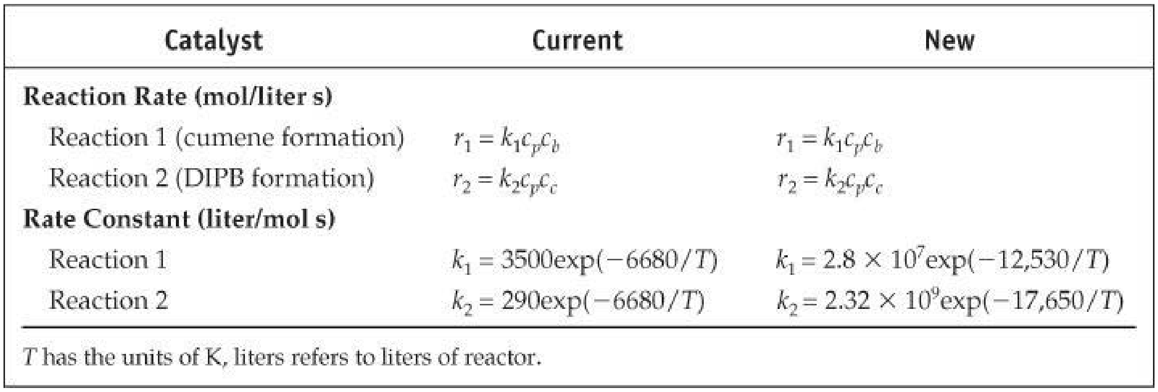
Flowrates (kmol/h)

Stream	1	4	11	7	8
Benzene	110.5		103.1	213.6	119.6
Propylene		110.5		110.5	13.9
Propane		5.5		5.5	5.5
Cumene					91.4
DIPB					2.6

Figure 23.6. Base-Case Flow Diagram of Cumene Reactor System

In the first stage of a plant start-up, the plant is operated without the recycle stream, Stream 11. Benzene normally provided by this recycle stream is added with the feed stream. In the initial plant start-up, the plant operated for a substantial period without the recycle. During this time, the plant was operated at a range of temperatures, pressures, and excess benzene rates. These data were used to determine effective kinetics that are presented in Table 23.2. The active reactor volume is 7.88 m^3. It was found that the fluidized bed could be modeled accurately over a narrow range of superficial velocities as a PFR with 5% bypass.

Table 23.2. Kinetic Constants Obtained for Hypothetical Cumene Catalysts

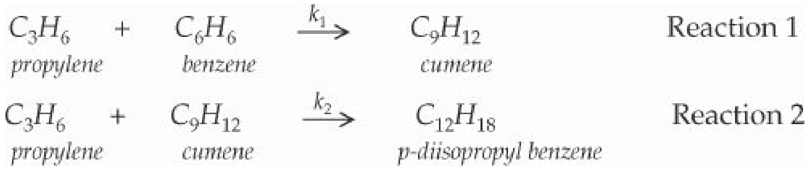


Catalyst	Current	New
Reaction Rate (mol/liter s)		
Reaction 1 (cumene formation)	$r_1 = k_1 c_p c_b$	$r_1 = k_1 c_p c_b$
Reaction 2 (DIPB formation)	$r_2 = k_2 c_p c_c$	$r_2 = k_2 c_p c_c$
Rate Constant (liter/mol s)		
Reaction 1	$k_1 = 3500\exp(-6680/T)$	$k_1 = 2.8 \times 10^7\exp(-12{,}530/T)$
Reaction 2	$k_2 = 290\exp(-6680/T)$	$k_2 = 2.32 \times 10^9\exp(-17{,}650/T)$

T has the units of K, liters refers to liters of reactor.

The information from the open system (no recycle) was used to establish a base case. At each plant start-up following a catalyst change, the plant is run at base-case conditions. If the same reactor performance is not obtained, the catalyst and flow pattern in the reactor are examined. Problems of reactor performance are resolved before continuing plant start-up.

Solution. The dominant reactions involved within the cumene plant are



$$\underset{\text{propylene}}{C_3H_6} + \underset{\text{benzene}}{C_6H_6} \xrightarrow{k_1} \underset{\text{cumene}}{C_9H_{12}} \qquad \text{Reaction 1}$$

$$\underset{\text{propylene}}{C_3H_6} + \underset{\text{cumene}}{C_9H_{12}} \xrightarrow{k_2} \underset{\text{p-diisopropyl benzene}}{C_{12}H_{18}} \qquad \text{Reaction 2}$$

The kinetics for the catalyst are provided in Table 23.2.

In this analysis, to ensure a low bypass ratio (5%), the superficial gas velocity was held constant at the base-case conditions. For higher reactor temperatures, the molar flowrate to the reactor was decreased slightly so as to maintain the same superficial velocity. This was done by retaining the base-case flows of Stream 11 and Stream 4, and lowering the excess benzene Stream 1. The fluidized bed was assumed to behave as an isothermal PFR with a 5% bypass stream. This is shown in Figure 23.7. Some of the simulation results are shown in Figures 23.8 and 23.9. Figure 23.8 presents the production of cumene obtained for the current and new catalyst for temperatures ranging from 350°C to 410°C. The new catalyst is more sensitive to a change in temperature than is the current catalyst. At the base-case temperature, the new catalyst produces only 81 kmol/h, point “a,” compared with 91 kmol/h, point “b,” for the current catalyst. At a reactor temperature of 361°C, the new catalyst produces the same amount of cumene, point “c,” as the old catalyst operating at the base-case temperature. At 367°C, both systems produce the same amount of cumene, point “d.” The maximum production rate of 101 kmol/h is obtained for the new catalyst at about 390°C, point “e.” The current catalyst provides a maximum cumene production of 96 kmol/h, point “f.”

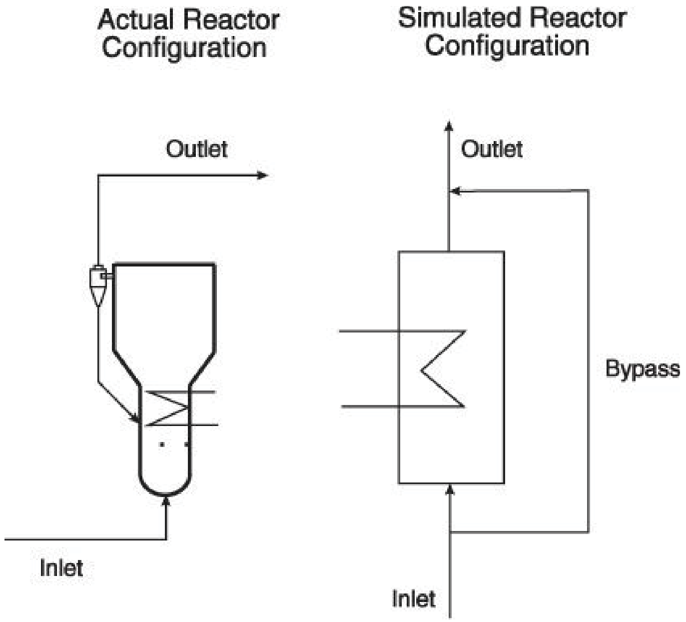


Figure 23.7. Fluidized Bed Reactor Showing Configuration (5% Bypass) Used for Simulation

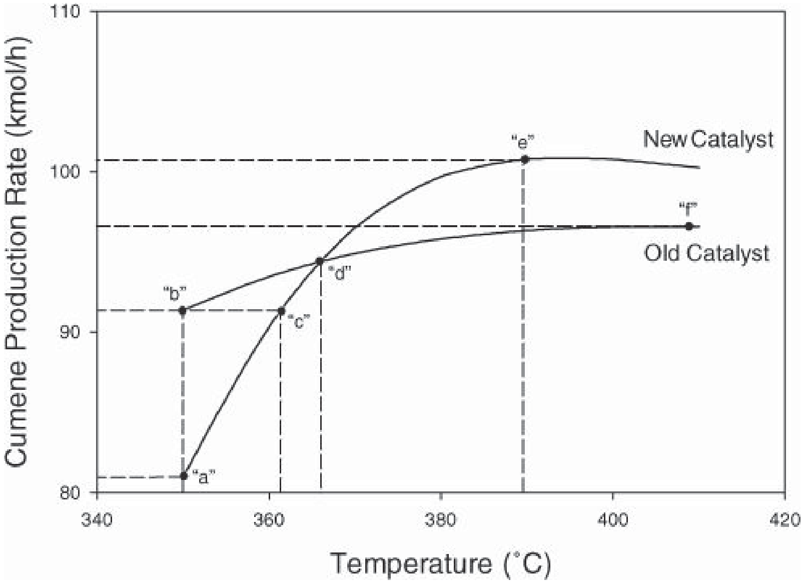


Figure 23.8. Cumene Production Rates at Constant Reactor Volume and Superficial Velocity

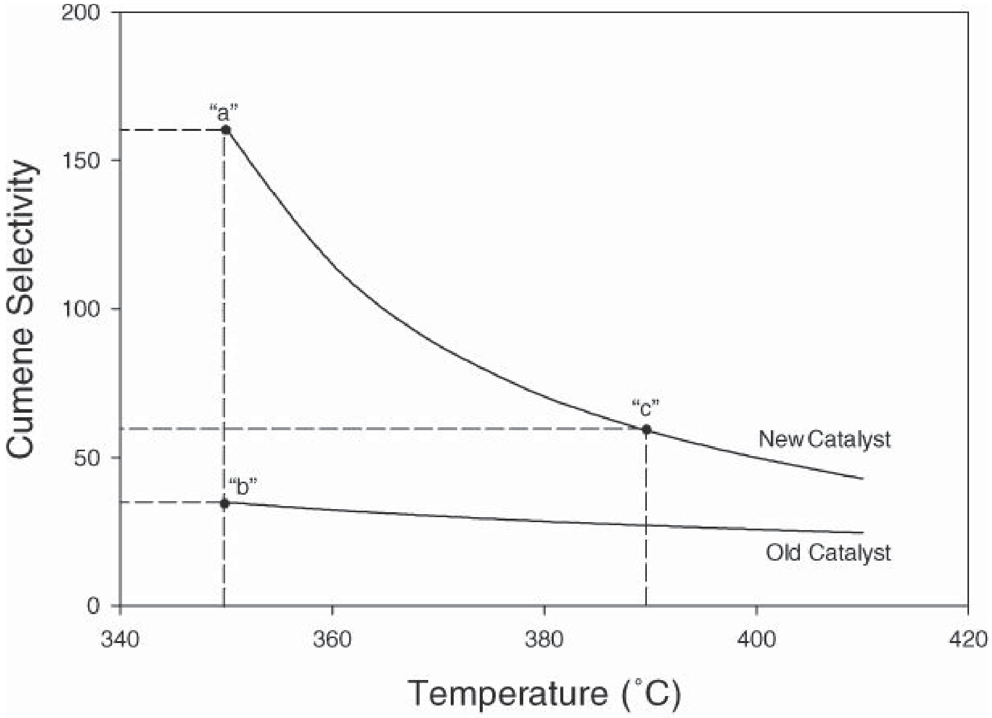


Figure 23.9. Selectivity for Cumene

Figure 23.9 shows the trends in product selectivity (moles of cumene produced per mole of DIPB produced) for both catalysts. At 350°C, the selectivity of the new catalyst is 160, point "a," compared with 35 for the current catalyst, point "b." At a temperature of 390°C, where the cumene reaches maximum production for the new catalyst, the selectivity is 59, point "c," well above that for the current catalyst.

In conclusion, the new catalyst is expected to provide higher product selectivity and higher cumene production at increased reactor temperature.

Discussion. It was found in the simulation of the dominant reactions in the production of cumene using the new catalyst that high temperatures increase the formation of the undesirable product, DIPB. This is expected based on the relative activation energies of the two reactions. The higher activation energy for the DIPB reaction leads to a more rapid increase in the rate of reaction of DIPB with temperature compared with cumene. Therefore, it is important to avoid hot spots in the reactor to avoid DIPB production. From a reaction point of view, isothermal reactors represent a desirable goal. This goal is obtained with a CSTR but is not easy to obtain in a PFR with a high heat of reaction. The fluidized bed system can approach isothermal behavior because of rapid mixing of the solid particles making up the bed. For highly exothermic reactions, the fluidized bed is inherently safe, hot spots do not develop, and heat can be removed from the bed.

However, fluid bypassing takes place in a fluidized bed. This adversely affects performance. This is because the bypassed fluid fraction does not come into contact with the catalyst and so a portion of the feed does not react. In the case study given above, the bypass fraction had a low value for a fluidized bed, 5%. As a result, the highest conversion that can be achieved is 95%.

If the products from the reactor are easily separated, the unreacted reactants can be recovered and recycled to achieve high overall conversion. From a kinetic point of view, the formation of DIPB in the product could be effectively eliminated by operating at low reactor conversions. This can be seen from the reaction rate expression, which shows that the formation of DIPB is directly proportional to the concentration of cumene. If cumene concentration is kept low, the amount of DIPB formed is small.

Separation of the reactor products containing propane or propylene presents a problem. Propylene and propane have similar volatilities and are difficult to separate. If propylene and propane are not separated, there are three options to be evaluated:

1. Propylene-propane mix is discarded as waste. Fuel value may be recovered.
2. Total recycle of propylene-propane mix. This is not possible. Because the propane does not react, it must be purged from the system.
3. Partial recycle of propylene-propane mix. The propane in the feed would increase. This decreases the concentrations of the reactants and reduces the production of cumene. The superficial velocity in the reactor would increase. This reduces residence time and the fraction bypassed in the fluidized bed.

In the case study, the constant superficial velocity was maintained at higher temperatures by decreasing the excess benzene. The total concentration of gas in the reactor was reduced. This tends to decrease the reaction rate. In addition, the reaction equations show that the lower benzene concentration reduces the cumene reaction rate and has no impact on the DIPB reaction. As a result of maintaining a constant required superficial velocity by lowering the excess benzene, the selectivity is reduced.

An alternative approach to maintain the superficial velocity at increased temperature and retain the excess benzene flow is to increase the system pressure. This should provide higher reaction rates at a given temperature, resulting in higher conversions, and would not effect the selectivity.

The conclusions given regarding the catalyst replacement assumed that the reaction took place in a region where chemical reaction controlled. When chemical reaction controls, the effect of temperature is large. Figure 23.8 indicates there was little effect of temperature on cumene production using the current catalyst, but temperature had major impact on cumene production for the new catalyst. The low sensitivity in the base case suggests that the reaction is not chemical reaction controlled. Often when dealing with catalytic reactions, one finds that due to high catalyst activity, the reaction may be diffusion controlled. The activation energy for diffusion is significantly lower than that for chemical reactions. Therefore, the effective activation energy for a diffusion-controlled reaction is also significantly lower. This means that intrinsic reaction kinetics supplied by manufacturers may not be directly applicable in process simulation. The reader is referred to standard reaction engineering texts.

For catalytic reactions, always consider mass transfer effects. If present, they reduce the temperature sensitivity of the reaction.

23.5.3. Increasing Acetone Production

Problem. You are responsible for the operation of the acetone production unit in your plant. The acetone produced is used internally elsewhere in your plant. A need to increase internal production by as much as 50% is anticipated. If this full increase cannot be met from your acetone unit, you will have to purchase additional acetone. You have been requested to evaluate how much increase in capacity can be obtained using the current chemical reactor.

Acetone is produced by the endothermic reaction

$$\underset{\text{isopropyl alcohol}}{(CH_3)_2CHOH} \rightarrow \underset{\text{acetone}}{(CH_3)_2CO} + \underset{\text{hydrogen}}{H_2}$$

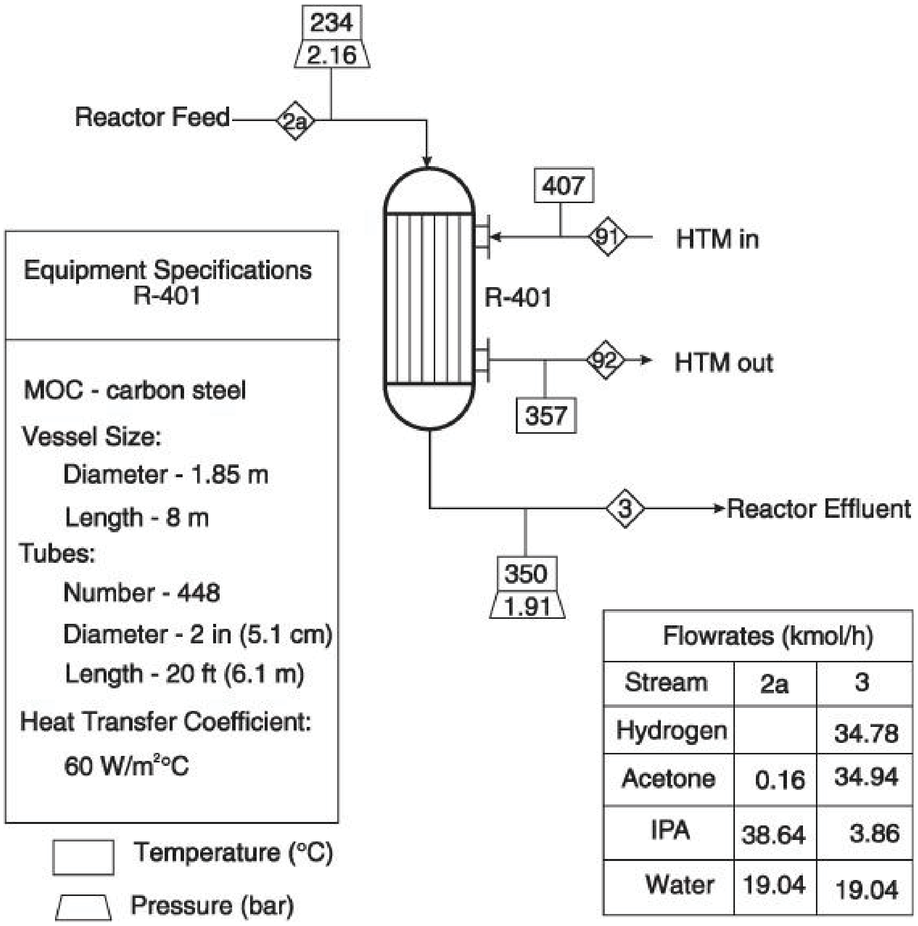
There are no significant side reactions. The reaction is endothermic and takes place in the gas phase on a solid catalyst. The reaction kinetics are given by

$$-r_{IPA} = kc_{IPA} \text{ kmol/m}^3 \text{ reactor s}$$

where

$$k = [3.156 \times 10^5 \text{ m}^3 \text{ gas/(m}^3 \text{ reactor s)}]\exp[-8702/T]$$

where T is in Kelvin. The process flowsheet for the plant is given in Appendix B, Figure B.3.1. Figure 23.10 shows the reactor portion of this process along with reactor specifications obtained from Table B.10.1. The process uses a PFR with the heat transfer medium, HTM, on the shell side. Because there is concern about operation of the downstream separation section, the IPA reaction conversion is held constant at 90% to ensure a constant feed composition to the separation section even though the flowrate of this stream may change.



Equipment Specifications
R-401

MOC - carbon steel
Vessel Size:
Diameter - 1.85 m
Length - 8 m
Tubes:
Number - 448
Diameter - 2 in (5.1 cm)
Length - 20 ft (6.1 m)
Heat Transfer Coefficient:
60 W/m²°C

Flowrates (kmol/h)

Stream	2a	3
Hydrogen		34.78
Acetone	0.16	34.94
IPA	38.64	3.86
Water	19.04	19.04

Figure 23.10. Reaction Section of Acetone Process (from Figure B.10.1 and Table B.10.1)

Solution. The conversion of an endothermic reaction is most often limited by the amount of heat that can be provided to the reaction. Current operating conditions define the base case. Figure 23.11(a) shows the temperature profile in the reactor for the reacting stream and HTM for the base case. There is a small temperature driving force for heat transfer over most of the reactor. Only in a small region near the reactor entrance is there a large temperature difference needed to provide a high heat flux. To increase production, it is necessary to increase the overall heat flux into the reactor.

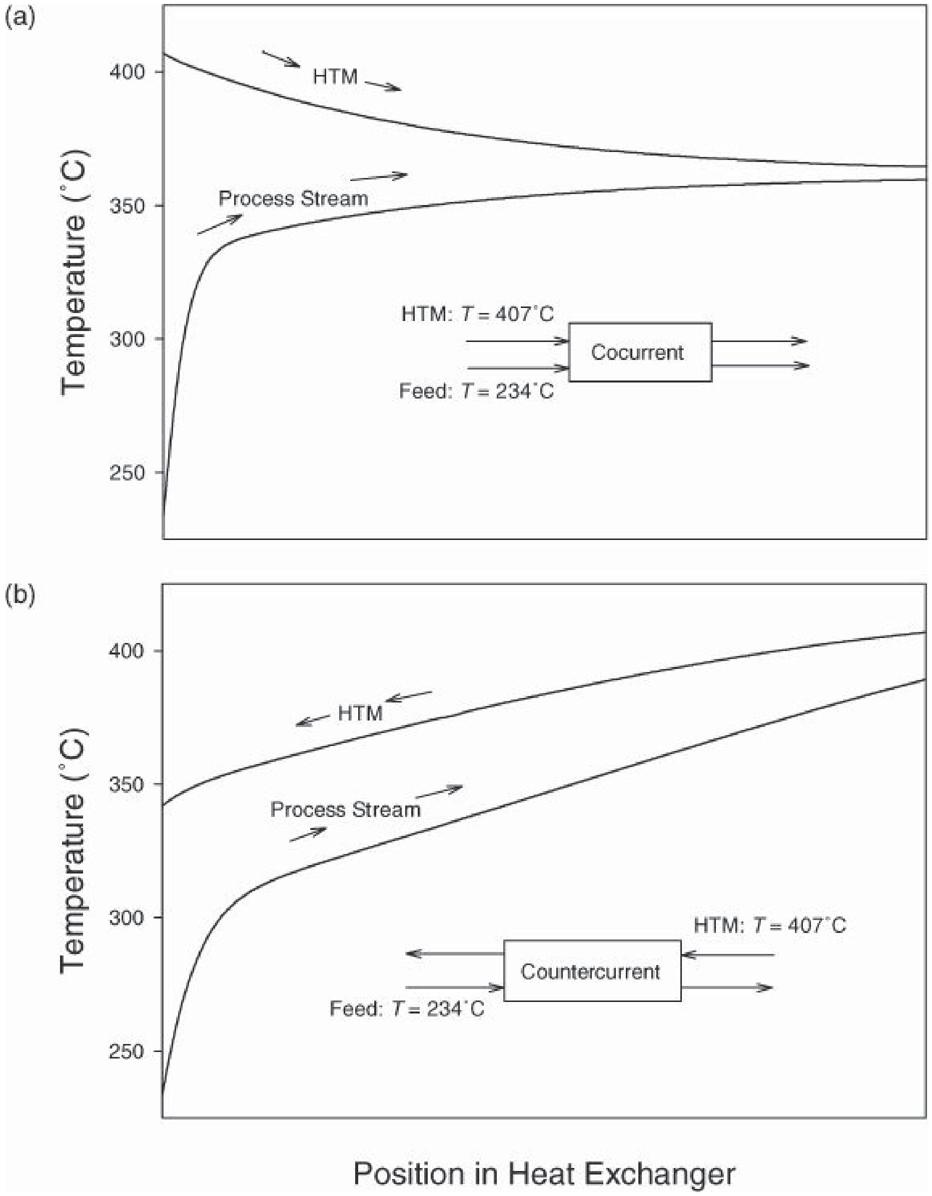


Figure 23.11. Temperature Profiles in Acetone Reactors for Cocurrent and Countercurrent Flow (IPA Conversion of 90%)

Figure 23.11(a) reveals four options that will increase the average heat flux:

1. Increase the temperature of the HTM.
2. Decrease the temperature of the reaction stream.
3. Operate with the HTM introduced countercurrent to the reacting stream.
4. Heat the feed stream to a higher temperature.

An evaluation of these options follows.

> **Option 1, Increase HTM Temperature:** Figure 23.12 presents results obtained for increased acetone production resulting from a change in HTM inlet temperature (flowrate of HTM held constant). Increasing the HTM by 50°C increased acetone production by 48%. This would require a 48% increase in heat duty and a 50°C increase in HTM temperature from the fired

heater, H-401.

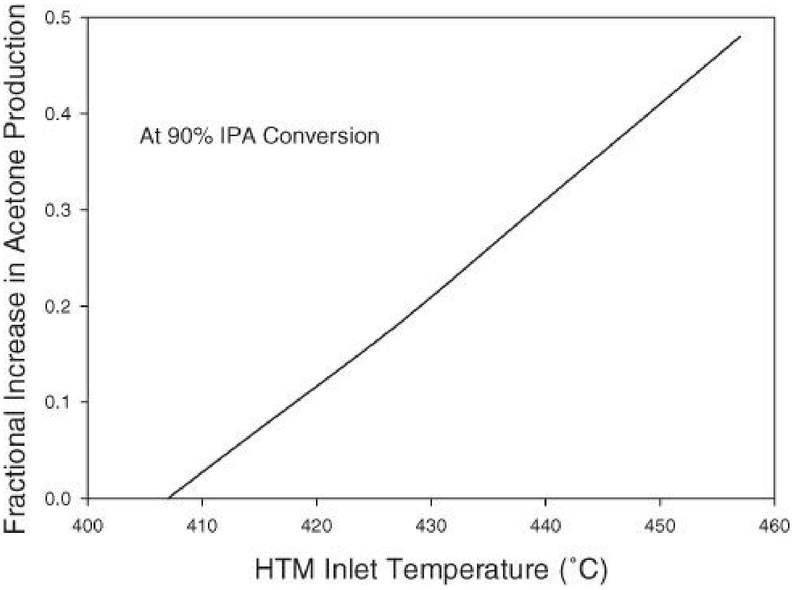


Figure 23.12. Increase in Acetone Production Resulting from Increase in HTM Inlet Temperature (HTM Flow Constant)

Option 2, Decrease Reactor Temperature: Lowering reactor temperatures decreases the reaction rate (lower reaction rate constant, *k*), reducing acetone production. This option has no merit and is rejected.

Option 3, Countercurrent Flow: Figure 23.11(b) shows the temperature profile obtained by introducing the HTM countercurrent to the reaction stream. Compared with the base case (cocurrent flow), it provides a larger, more constant temperature driving force (and heat flux). This change provides a 13% increase in acetone production. The heat duty of the fired heater, H-401, must be increased by 13% to provide this increase in duty.

Option 4, Heat Feed Stream to Higher Temperature: This provides energy in the form of sensible heat that adds to the energy transferred from the HTM. For an increase in feed temperature of 100°C, the acetone production increases by 14%. This would require an additional fired heater for the reactor feed stream.

This investigation showed there are a number of options that can effect a significant increase in acetone production. A 50% increase in capacity can be obtained from the reactor. All options require an increase in fired heater capacity.

Discussion. It has been shown that there are a number of options that provide increased acetone production. Except for Option 2, the options provided can be combined. The heat transfer configuration, Option 3, can be combined with an increase in HTM temperature, Option 1. In addition, the reactor feed temperature, Option 4, can be increased. In most situations, there is more than one option to consider to make a desired change in performance.

All options to increase acetone production require an increase in capacity of the fired heater (or addition of a new fired heater). Therefore, the fired heater is likely to represent a bottleneck to increased production. Fired heaters are expensive, and it is not likely that the current heater was oversized enough to provide a 50% increase in heat duty. Until this bottleneck is removed, the additional acetone production required cannot be obtained.

Once the fired heater bottleneck is resolved, the separation system must be able to process the large increase in throughput. It is unlikely that the separation system can process the 50% increase. Therefore, if the fired heater bottleneck is removed, the separation system becomes the bottleneck.

Once a decision is made to eliminate these two bottlenecks (fired heater and separation system), the analysis of reactor behavior could be modified to consider a number of secondary effects. The case study did not consider the effect of increasing reactor flowrates on the heat transfer coefficient (gas-phase resistance dominates). The impact of the increased pressure drop over the reactor was not examined. These options were not necessary to confirm that the reactor is capable of providing a 50% increase in acetone production. The option of increasing the HTM flowrate was not appraised.

Endothermic reactions are inherently safe systems in terms of undergoing an uncontrolled reaction that is characteristic of an exothermic reactions. If the heat source is withdrawn, the temperature of the reactor drops and the rate of reaction decreases.

23.6. Summary

In this chapter, chemical reactor performance was analyzed differently from the way it is usually done in reaction engineering classes. Key qualitative trends were emphasized. This was done in the context of Figure 23.1, which illustrates the interrelationship between product production, reaction kinetics, reactor behavior, and heat transfer limitations. The case studies presented reinforce the interrelationship between these factors.

What You Should Have Learned

- How reactor performance is affected by
  - Stoichiometry (conversion, selectivity, yield)
  - Kinetics (rate of reaction and thermodynamic limitations)
  - Reactor parameters (volume, space time, catalyst, temperature, pressure)
  - Heat transfer

References

1. Zimmerman, C. C., and R. York, “Thermal Demethylation of Toluene,” *Ind. Eng. Chem. Proc. Des. Dev*. 3 (1964): 254–258.
2. Rase, H. F., *Chemical Reactor Design for Process Plants*, Vol. 2: *Case Studies and Design Data* (New York: Wiley-Interscience, 1977), 38.

Short Answer Questions

1. Explain why very high conversions (>99%) are often difficult to achieve in practice, even for plug flow reactors and nonequilibrium constrained reactions.
2. Comment on the following statement: *For an exothermic reaction, if the temperature is increased at constant pressure with a fixed reactor size, the conversion decreases.*
3. It is known that for a certain third-order, gas-phase reaction, the rate of reaction doubles when the temperature goes from 250°C to 270°C. The form of the rate equation is

$$-r_A = k_o e^{-\left(\frac{E}{RT}\right)} c_A c_B^2$$

If the rate of reaction is 10 moles/m^3s at the base conditions, which are 20 atm pressure and

250°C, and an equal molar flow of A and B are in the feed (no inerts), answer the following questions:

a. Compared to the base case, by how much does the rate of reaction (at inlet conditions) change if the temperature is increased to 260°C?

b. Compared to the base case, by how much does the rate of reaction (at inlet conditions) change if the pressure is increased by 15%?

4. For the reactor system shown in Figure P23.4, answer the following:

a. Is the reaction exothermic or endothermic?

b. Give two reasons why this reaction is being run at a high temperature.

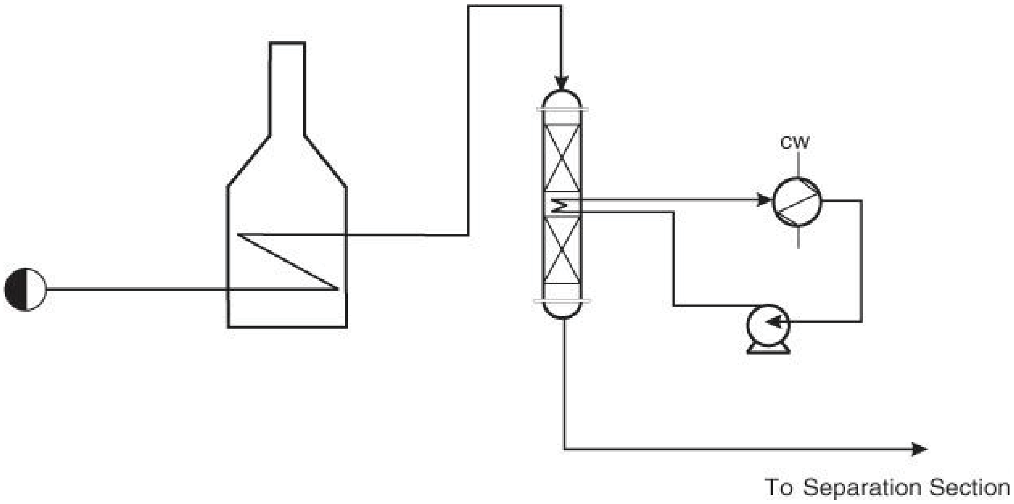


Figure P23.4.

Problems

Note: Information for problems referenced as Appendix C is provided on the accompanying CD.

5. For the hypothetical, endothermic, gas-phase reaction

$$A + B = C$$

sketch a plot similar to Figure E23.1. Discuss the relationship between equilibrium conversion, temperature, and pressure.

6. For the situation in Example 23.3, if all of the reactions take place, what conditions maximize the selectivity for P?

7. Examine the reaction network and the reaction kinetics for drying oil production in Appendix B, Section B.4.2. What conditions will maximize the selectivity for drying oil? Sketch concentration profiles for the case when this reaction is run in a packed bed modeled as a PFR.

8. Examine the reaction network and the reaction kinetics for ethylene oxide production in Appendix B, Section B.6.2. What conditions will maximize the selectivity for ethylene oxide? Sketch concentration profiles for the case when this reaction is run in a packed bed modeled as a PFR.

9. Sketch the T-Q diagram for an endothermic reaction in a PFR for

a. Countercurrent flow of HTM (heat transfer medium)

b. Cocurrent flow of HTM

What are the consequences on reactor size of choosing each configuration? Explain your answer by examining the trends (see Chapter 20).

10. In the production of cumene from propylene, the following elementary, vapor-phase, irreversible reaction takes place:

$$\underset{\text{propylene}}{C_3H_6} + \underset{\text{benzene}}{C_6H_6} \xrightarrow{k_1} \underset{\text{cumene}}{C_9H_{12}}$$

The reaction rate is given by

$$r_1 = k_1 c_p c_b \text{ mol/(g cat) sec and } k_1 = 3.5\times10^4 \exp\left(\frac{-12{,}530}{T(K)}\right)$$

The feed to the reactor consists of an equal ratio of benzene and propylene. The reaction takes place in a fluidized bed reactor operating at 300°C and 3 MPa pressure. For this problem, the fluidized bed may be assumed to be a constant-temperature CSTR reactor.

At design conditions, you may assume that the side reaction does not take place to any great extent and the conversion is 68%.

It is desired to scale up production by 25%. All flows to the reactor will increase by 25% at the same feed concentration. Determine the following:

a. What is the single-pass conversion if the process conditions and amount of catalyst remain unchanged?

b. What percent change in catalyst would be required to achieve the scale-up assuming that the pressure, temperature, and conversion were held constant?

c. Estimate how much the temperature would have to be changed (without changes in catalyst amount, operating pressure, or conversion) to achieve the desired scale-up.

d. By how much would the pressure have to be changed (without changes in catalyst amount, operating temperature, or conversion) to achieve the desired scale-up?

11. Consider a liquid-phase reaction occurring in a constant-volume, isothermal, batch reactor.

a. For a first-order decomposition, what is the ratio of the time to reach 75% conversion to the time to reach 50% conversion?

b. For a first-order decomposition, what is the ratio of the time to reach 90% conversion to the time to reach 50% conversion?

c. Repeat Parts (a) and (b) for a second-order reaction between reactants initially in equimolar quantities.

d. Explain the results of Parts (a)–(c).

For Problems 23.12–23.26, it is recommended that a process simulator be used.

Problems 23.12–23.16 investigate the performance of the reactor section for a noncatalytic process for the hydrodealkylation of toluene to produce benzene. Reactor R-101 in Figure 23.4(b) operated at the flow conditions shown represents a base case (inlet pressure is 25 bar). Kinetics are given in Table 23.1. Ignore reactor pressure drop. Reactor volume for the base case is 4.76 m^3.

12. Investigate the effect of increasing reactor volume on toluene conversion. Plot the results.

13. Investigate the effect of a variation of hydrogen feed rate (all other parameters held constant at base-case values).

a. Plot toluene conversion versus percent excess oxygen.

b. Determine the maximum conversion possible.

14. Investigate a two-reactor system to replace the single adiabatic PFR in the base case. The two-reactor system consists of an adiabatic CSTR followed by an adiabatic PFR. For the base-case toluene conversion (0.75),
    a. Determine the size of the CSTR and PFR that provides the minimum total reactor volume.
    b. Determine the fraction of the total conversion obtained in the CSTR from Part (a).
15. Investigate the effect of increasing the feed rate on reactor performance.
    a. Prepare a performance curve of the toluene conversion versus feed rate.
    b. Prepare a performance curve of benzene generated versus feed rate.
16. Investigate the effect of feed temperature on reactor performance. Prepare a performance curve for toluene conversion versus feed temperature.

Problems 23.17–23.20 investigate the performance of the cumene reactor (fluidized bed), described in Section 23.5.2, that results from replacing the catalyst. The replacement catalyst kinetics are given in Table 23.2. The base case selected is the currently operating reactor (with an active volume of 7.49 m^3). Process output for the base case is given in the flow table in Figure 23.6.

17. a. Derive an equation for the ratio

    η = rate of cumene formation/rate of DIPB formation

    Rewrite the equation in the form $\eta = A/B - 1$.

    b. Present the equation for η given above in terms of the following variables: T, P, k_o, E_{act}, and mole fractions.
    c. Using the equation from Part (b), determine the trend resulting from a change in the following variables. After each item, provide ↑ (increases), ↓ (decreases), ¢ (constant) or ? (cannot be determined).
        (i) Increasing system temperature
        (ii) Increasing system pressure
        (iii) Increasing benzene mole fraction
        (iv) Increasing propylene mole fraction
        (v) Increasing propane mole fraction
        (vi) Increasing cumene mole fraction
        (vii) Increasing DIPB mole fraction
18. Replace the current catalyst with the new catalyst (maintain the same feed rate and conditions) and
    a. Provide a flow table (similar to that in Figure 23.6).
    b. Compare cumene production with the new to the old catalyst.
    c. Compare DIPB production with the new to the old catalyst.
19. Evaluate the effectiveness of the new catalyst at 350°C that results from increasing the reactor volume.
    a. Plot cumene production versus reactor volume.
    b. Plot selectivity (defined as cumene generated/DIPB generated) versus volume.
20. In Figures 23.8 and 23.9, the volumetric flowrate to the reactor was held constant at increased temperatures by reducing the hydrogen in the feed. This altered the feed concentration. Investigate the alternative of reducing the total feed rate (at the same composition) to maintain

constant volumetric flowrate.

   a. Plot the cumene production rate versus temperature, and compare to Figure 23.8.
   b. Plot the selectivity (cumene generated/DIPB generated) versus temperature, and compare to Figure 23.9.

Problems 23.21–23.26 investigate the performance of the acetone reactor system. The reaction kinetics are presented in Section 23.5.3. The reactor and internal heat exchanger are fixed. For the base case, the active volume of the reactor is 5.1 m^3 at the operating conditions given in Figure 23.10. Unless otherwise stated, the heat transfer coefficient and reactor pressure drop are to be assumed constant. The feed temperature, pressure, and component concentrations remain constant. For these calculations, assume the utility fluid to be n-heptadecane (at pressures more than 30 bar). At the base case, the utility flow is 58 kmol/h.

21. Reconfigure the heating system to operate in countercurrent fashion. Retain the same utility stream input and IPA conversion (90%).
    a. Determine the change in process feed rate.
    b. Determine the percent change in process feed rate.
22. Increase the utility feed rate by 50%, and maintain the base-case process feed stream.
    a. Determine the conversion obtained.
    b. Determine the percent change in the acetone produced.
23. Increase the utility feed rate by 50%. Retain the IPA conversion of 0.9.
    a. Determine the process feed rate.
    b. Determine the percent change in acetone produced.
24. Increase the utility feed temperature by 50°C. Retain the IPA conversion at 0.9.
    a. Determine the process feed rate.
    b. Determine the percent change in acetone production.
25. Prepare a performance curve for the change in utility flowrate necessary to maintain an IPA conversion of 0.9 at increased process feed rates.
26. Assume the individual film coefficients change according to the relationship

$$h_i \ \alpha \ \text{velocity}^{0.8}$$

    a. Estimate the effect of process flow changes on the overall heat transfer coefficient.
    b. Determine the process flowrate that provides an IPA conversion of 0.9 resulting from an increase in utility temperature of 50°C.
    c. Does the assumption of constant overall heat transfer coefficient result in a higher or lower estimate of the process feed rate? If you worked Problem 23.25, you have this value for comparison.