

Chapter 8

Reactor-Separator-Recycle Networks

8.0 OBJECTIVES

The presence of at least one chemical reactor and one or more separation sections for the separation of the effluent mixture leaving the reactor(s) characterizes many chemical processes. In almost all cases, one or more of the streams leaving the separation section(s) is (are) recycled to the reactor. In Chapter 6, the design of reactors and reactor networks was considered without regard for the separation section(s) and possible recycle there from. Chapter 7 was concerned with the design of separation sections in the absence of any consideration of the reactor section. Chapter 5, which dealt with the synthesis of the entire process, included a few examples of the interaction between the reactor and separation sections. This chapter extends that introduction to give a more detailed treatment of reactor-separator-recycle networks.

After studying this chapter, the reader should

1. Be able to determine the best location for the separation section, either before or after the reactor.
2. Understand the tradeoffs between purge-to-recycle ratio, recycle ratio, and raw material loss, when dealing with inert or byproduct chemicals that are difficult to separate from the reactants.
3. Understand the need to determine the optimal reactor conversion, involving the tradeoff between the cost of the reactor section and the cost of the separation section(s) in the presence of recycle, even when chemical equilibrium greatly favors the products of the reaction.

4. Understand the conditions under which the recycle of byproducts to extinction can be employed to reduce waste and increase yield.
5. Be aware of the snowball effect in a reactor-separator-recycle network and the importance of designing an adequate control system, which is presented in Sections 20.3 (Example 20.11) and 21.5 (Case Study 21.3).

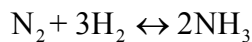
8.1 INTRODUCTION

The feed to a reactor section of a chemical process almost always is a *combined feed* consisting of a *fresh feed* mixed with one or more recycle streams, as shown in Figure 7.1. Fresh reactor feeds rarely contain only the reactants for the desired reaction. Besides the reactants, they may contain inert chemicals, potential reactants for side reactions, catalyst poisons, and products of the desired reaction(s). Recycle streams are intended to contain only unconverted reactants of the desired reaction(s). However, more commonly, recycle streams also contain products of the desired reaction(s), products of undesired side reactions, and inert chemicals.

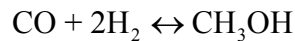
Reactor effluents are almost never products that meet purity specifications. Besides the products, effluents may contain reactants, inerts, products of undesired side reactions, and feed impurities. Thus, almost every chemical process that involves a chemical reaction section also involves one or more separation sections in addition to one or more recycle streams. A major challenge of process design is to devise an optimal scheme for uniting the reaction and separation functions of a process. This chapter presents many of the considerations involved in that optimization. Although Figure 7.1 shows only one reactor section, multiple reactor sections are sometimes required, with separation sections located between each pair of reactor sections

8.2 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 7.1. 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,



and the hydrogenation of carbon monoxide to methanol,



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

$$\left(\frac{\partial \ln K_c}{\partial T} \right)_P = \frac{\Delta H_{rx}^\circ}{RT^2} \quad (8.1)$$

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.

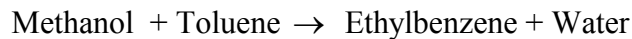
Although product purification may require extreme measures to achieve product specifications, recycle streams rarely require a significant degree of purification with respect to recycled reactants. When two or more reactants are involved, they do not have to be recovered separately for recycle unless their *separation indexes* (e.g., relative volatility) are separated by the product(s), as shown in the next two examples.

Example 8.1 Styrene Manufacture.

In the styrene manufacture process of Figure 10.61, the main reaction is



The following side reaction also occurs:



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 8.2. Cumene Manufacture.

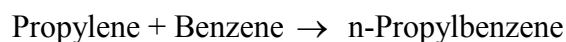
A more complex example is the manufacture of cumene (isopropyl benzene) by the alkylation of benzene with propylene, taken from the 1997 National Student Design Competition of the AIChE. Cumene is widely used to make acetone and phenol. The fresh feeds are as follows, where the benzene feed is nearly pure, but a refinery cut of a propylene-propane mixture is used rather than a more expensive feed of nearly pure propylene.

Component	Propylene feed, lbmol/hr	Benzene feed, lbmol/hr
Water	0.1800	
Ethane	4.6440	
Propylene	1,029.2075	
Propane	465.6127	
1-Butene	0.0300	
Isobutane	0.3135	
Methylcyclopentane, MCP		1.1570
Benzene		997.5130
Methylcyclohexane, MCH		0.2030
Toluene		0.1270

The main reaction, conducted with a catalyst, is:

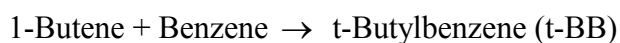


A number of undesirable side reactions involving the main reactants also occur, including:



Other reactions that produce alkylation heavies

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:



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:

Cumene purity, wt%	99.97	minimum
Butylbenzenes, ppm (by wt)	40	maximum
Toluene, ppm (by wt)	15	maximum
Cymene, ppm (by wt)	10	maximum
Benzene and paraffins, ppm (by wt)	10	maximum
Others, ppm (by wt)	225	maximum

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 5.2: (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:



Other reactions that produce trans-alkylation heavies

Solution

A preliminary block flow diagram, suggested for the cumene process, is shown in [Figure 8.1](#). 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:

Component	Formula	Molecular weight	Normal boiling point, °C
Water	H ₂ O	18.02	100
Ethane	C ₂ H ₆	30.07	-88.6
Propylene	C ₃ H ₆	42.08	-47.4
Propane	C ₃ H ₈	44.11	-42.1
Isobutane	C ₄ H ₁₀	58.13	-11.7
1-Butene	C ₄ H ₈	56.12	-6.3
Methylcyclopentane	C ₆ H ₁₂	84.16	71.8
Benzene	C ₆ H ₆	78.12	80.1
Methylcyclohexane	C ₇ H ₁₄	98.19	100.9
Toluene	C ₇ H ₈	92.16	110.6
Cumene	C ₉ H ₁₂	120.2	152.4
n-Propylbenzene	C ₉ H ₁₂	120.2	159.2
t-Butylbenzene	C ₁₀ H ₁₄	134.2	169.0
p-Cymene	C ₁₀ H ₁₄	134.2	177.1
m-DIPB	C ₁₂ H ₁₈	162.3	203.2
p-DIPB	C ₁₂ H ₁₈	162.3	210.3
Trans-alkylation heavies		201.7	261.3
Alkylation heavies		206.4	278.8

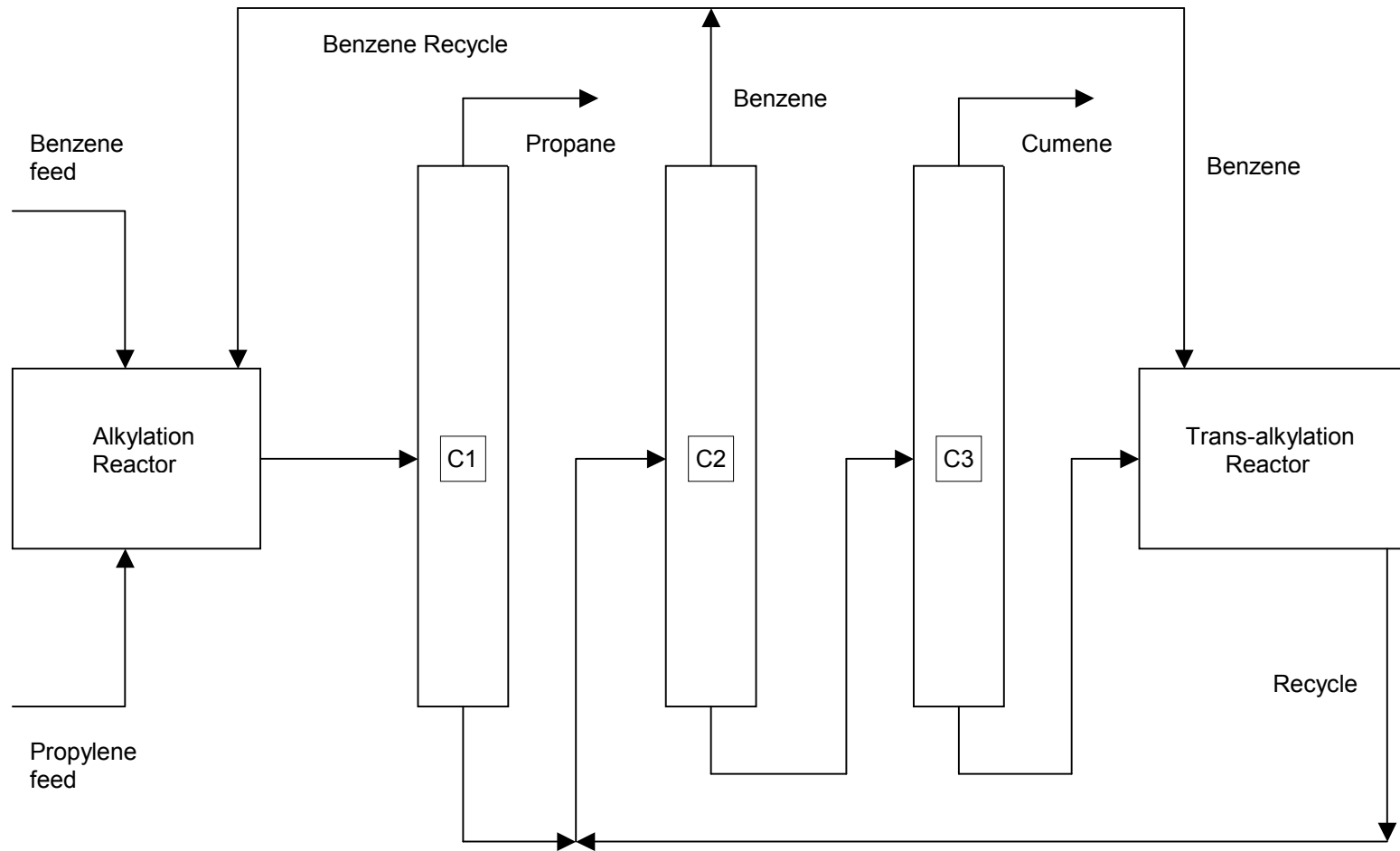


Figure 8.1 Cumene process.

Note that the fresh propylene feed contains approximately 31 mol% propane. Because propane is inert, Heuristic 3 of Table 5.2 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 7.2, 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 5.2, 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 5.2, 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 8.1 at the end of this chapter.

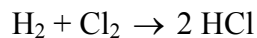
Chemical processes, especially those utilizing a catalyst in the chemical reactor, may require a feed separation section, as shown in Figure 7.1, to purify the fresh feed before it enters the reactor. In this separation section, catalyst poisons are removed as well as components, other than reactants 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_2 to SO_3 , and the third reaction is the absorption of SO_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 5.2. 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 8.2 considers separator placement for a pentane isomerization process.

8.3 TRADEOFFS IN PROCESSES INVOLVING RECYCLE

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:



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 were introduced in Chapters 3-7. 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 18, 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.

8.4 OPTIMAL REACTOR CONVERSION

Return to the toluene hydrodealkylation process in Section 4.3, with the reaction kinetics in Example 6.2. 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. (6.31) 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. (6.31). Thus,

$$r_f = -\frac{dC_{\text{toluene}}}{dt} = k_f C_{\text{H}_2}^{1/2} C_{\text{toluene}} = 6.3 \times 10^{10} \exp\left(\frac{-52,000}{RT}\right) C_{\text{H}_2}^{1/2} C_{\text{toluene}} \quad (8.2)$$

where $R = 1.987$ cal/mol-K; concentrations, C_i , are in kmol/m³; 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 8.2](#), with the adiabatic case in [Figure 8.3](#). 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.

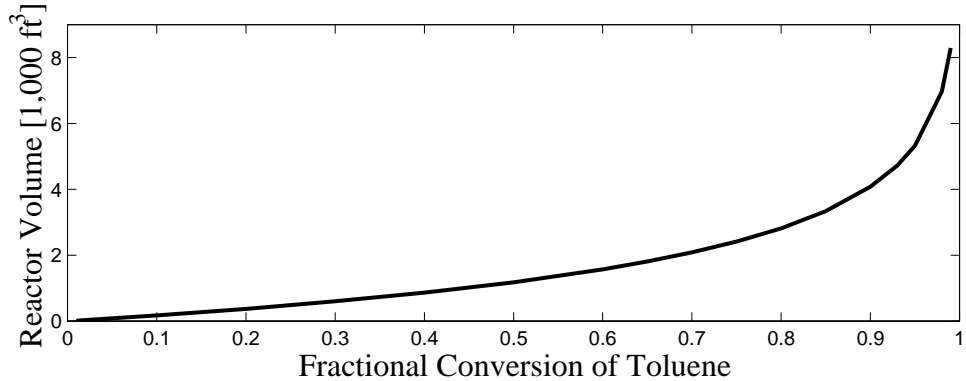


Figure 8.2 Required reactor volume for toluene hydrodealkylation in an isothermal PFR.

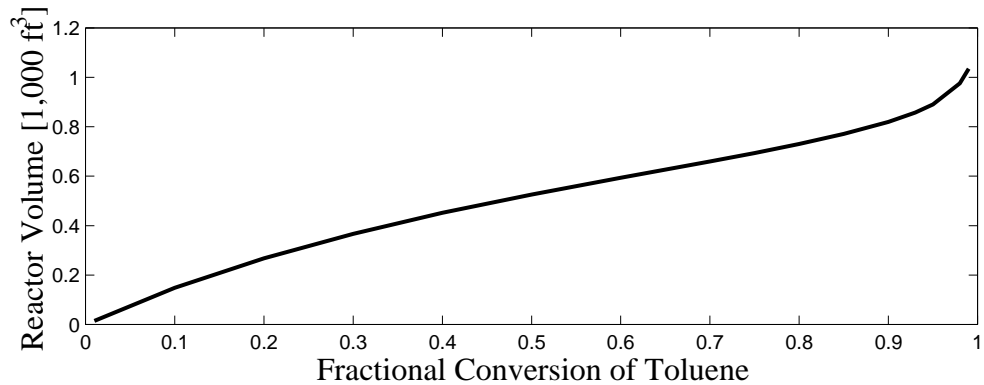


Figure 8.3 Required reactor volume for toluene hydrodealkylation in an adiabatic PFR.

As seen in [Figure 8.3](#), the effect of conversion on reactor volume for the adiabatic case is very different from the isothermal case in [Figure 8.2](#). 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. (8.2) 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 8.3](#) 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. (8.2), 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:

$$K_c = \frac{C_{\text{CH}_4} C_{\text{benzene}}}{C_{\text{H}_2} C_{\text{toluene}}} = \frac{k_f}{k_b} \quad (8.3)$$

But in chemical equilibrium, the rate of the forward reaction is equal to the rate of the backward reaction. Therefore, from Eq. (8.2), with an as yet undetermined dependence of component concentrations on the backward rate,

$$k_f C_{\text{H}_2}^{1/2} C_{\text{toluene}} = k_b C_{\text{H}_2}^\alpha C_{\text{toluene}}^\beta C_{\text{CH}_4}^\gamma C_{\text{benzene}}^\delta \quad (8.4)$$

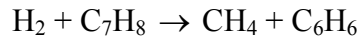
To determine the exponents, α , β , γ , and δ , combine Eqs. (8.3) and (8.4),

$$\frac{k_f}{k_b} = \frac{C_{\text{H}_2}^\alpha C_{\text{toluene}}^\beta C_{\text{CH}_4}^\gamma C_{\text{benzene}}^\delta}{C_{\text{H}_2}^{1/2} C_{\text{toluene}}} = \frac{C_{\text{CH}_4} C_{\text{benzene}}}{C_{\text{H}_2} C_{\text{toluene}}} \quad (8.5)$$

By equating exponents in Eq. (8.5), $\alpha = -1/2$, $\beta = 0$, $\gamma = 1$, and $\delta = 1$. Therefore, the form of the rate equation for the backward reaction is

$$r_b = k_b C_{\text{H}_2}^{-1/2} C_{\text{CH}_4} C_{\text{benzene}} \quad (8.6)$$

To determine the Arrhenius expression for k_b from Eq. (8.3), 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, $\Delta G_{\text{rx}}^\circ$, in cal/mol, as a function of the absolute temperature, T , in K, for the hydrodealkylation of toluene,



is given by:

$$\Delta G_{\text{rx}}^\circ = -11,200 - 2.1 T \quad (8.7)$$

From thermodynamics, $\Delta G_{\text{rx}}^\circ$ is related to the chemical-reaction equilibrium constant by the equation:

$$K_c = \exp\left(\frac{-\Delta G_{\text{rx}}^\circ}{RT}\right) \quad (8.8)$$

Combining Eqs. (8.7) and (8.8) and substituting 1.987 for R , gives:

$$K_c = \exp\left(\frac{5,636}{T} + 1.057\right) = 2.878 \exp\left(\frac{5,636}{T}\right) \quad (8.9)$$

From Eq. (8.3), using the temperature-dependent expressions for k_f in Eq. (8.2) and K_c in Eq. (8.9),

$$k_b = \frac{k_f}{K_c} = \frac{6.3 \times 10^{10} \exp\left(\frac{-52,000}{RT}\right)}{2.878 \exp\left(\frac{5,636}{T}\right)} = 2.19 \times 10^{10} \exp\left(\frac{-63,200}{RT}\right) \quad (8.10)$$

Combining Eqs. (8.6) and (8.10), the rate law for the backward reaction becomes

$$r_b = 2.19 \times 10^{10} \exp\left(\frac{-63,200}{RT}\right) C_{\text{H}_2}^{-1/2} C_{\text{CH}_4} C_{\text{benzene}} \quad (8.11)$$

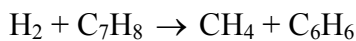
When the reactor calculations are repeated for up to 99% conversion of toluene, taking into account the reverse reaction, reactor volumes for both isothermal and adiabatic cases increase only slightly (< 1%). This is largely due to the large concentration of hydrogen, which according to Eq. (8.11) decreases 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%.

8.5 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 5.4 and in Section 7.1, illustrated for the toluene-hydroalkylation process in Figure 7.4. 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:



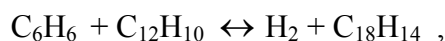
As shown in Section 8.3, this reaction, while not completely irreversible at typical reactor operating conditions, has a chemical-reaction equilibrium constant high enough to give conversions greater than 99%. When the main reaction is carried out thermally, in the absence of a catalyst, it is accompanied by the following side reaction that produces the byproduct, biphenyl:



The chemical-reaction equilibrium constant for this reaction is written as:

$$K_c = \frac{C_{\text{H}_2} C_{\text{biphenyl}}}{C_{\text{benzene}}^2} \quad (8.12)$$

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

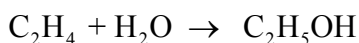


with a chemical-reaction equilibrium constant written as:

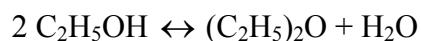
$$K_c = \frac{C_{\text{H}_2} C_{\text{triphenyl}}}{C_{\text{benzene}} C_{\text{biphenyl}}} \quad (8.13)$$

From Hougen and Watson (1947), the chemical-reaction equilibrium constant for Eq. (8.12) ranges from 0.045 to 0.32 over a temperature range of 700 to 1,400°F, while for Eq. (8.13), 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. (8.12) and (8.13), 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 recycling 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 in which the biphenyl and triphenyl are recovered with toluene.

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

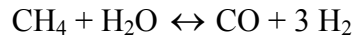


which is accompanied by a reversible side reaction that produces diethylether and water,



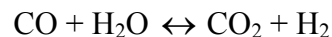
for which the chemical-reaction equilibrium constant at typical reactor conditions is 0.2. By recovering and recycling diethylether and water, the overall yield of alcohol is increased.

A third example is the steam reforming of methane (or natural gas) in the presence of a nickel-supported catalyst to produce synthesis gas ($\text{CO} + \text{H}_2$), an intermediate that can be used to produce acetic acid, ammonia, gasoline, or methanol. The main reaction is:



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:



At 800°C , the chemical-reaction equilibrium constant for this reaction is 0.929, with compositions in partial pressures in atm. When CO_2 is recovered and recycled to extinction, is the overall yield of synthesis gas increased? This is the subject of Example 8.3.

Example 8.3. 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°C 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°C, the two chemical equilibrium equations are:

$$\frac{n_{\text{CO}} n_{\text{H}_2}^3}{n_{\text{CH}_4} n_{\text{H}_2\text{O}}} \left(\frac{P}{n_{\text{total}}} \right)^2 = 126.8$$

$$\frac{n_{\text{CO}_2} n_{\text{H}_2}}{n_{\text{CO}} n_{\text{H}_2\text{O}}} = 0.929$$

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

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:

Component	Fresh Feed, kmol/hr	Reactor Effluent, kmol/hr
Methane	13.5	0.605
Water	86.5	66.229
Hydrogen	0	46.061
Carbon monoxide	0	5.521
Carbon dioxide	0	7.375
Total	100.0	125.791

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:

Component	Combined Feed, kmol/hr	Reactor Effluent, kmol/hr
Methane	13.5	0.549
Water	86.5	73.544
Hydrogen	0	38.859
Carbon monoxide	0	12.946
Carbon dioxide	22.763	22.763
Total	122.763	148.661

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), CO₂ is not emitted to the atmosphere where it contributes to global warming. This is considered in more detail by Mulholland and Dyer (1999).

8.6 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 20.3 (Example 20.11) and 21.5 (Case Study 21.3).

8.7 SUMMARY

Having studied this chapter, when designing reactor-separator-recycle networks, the reader should

1. Understand the considerations in determining the best locations, with respect to the reactor section, of the separation sections.

2. Be aware of the many tradeoffs between the reactor section and the separation section(s) when recycle is used.
3. Know that the optimal fractional conversion of the limiting reactant in the reactor section is usually less than 100% of the equilibrium conversion.
4. Be able to apply the concept of recycle to extinction to reduce waste and increase the yield of the main product.
5. Be aware that the snowball effect can occur in a reactor-separator-recycle network.

REFERENCES

Hougen, O. A. and K. M. Watson, *Chemical Process Principles, Part Three, Kinetics and Catalysts*, John Wiley & Sons, New York (1947).

Mulholland, K. L. and J. A. Dyer, *Pollution Prevention: Methodology, Technologies and Practices*, AIChE, New York (1999).

Rase, H. F., *Chemical Reactor Design for Process Plants, Vol. 2, Case Studies and Design Data*, Wiley-Interscience, New York (1977).

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EXERCISES

- 8.1 *Cumene process with drag (purge) streams.* In Section 8.2, a process for producing cumene by the alkylation of benzene with propylene is described. The flowsheet for the process is given in Figure 8.1. However, that flowsheet does not provide for the removal of water, ethane, isobutane, MCP, MCH, toluene, n-propylbenzene, tBB, and p-cymene. For their removal, it is proposed to add two drag (purge) streams to the flowsheet: one from the distillate of the benzene recovery column,

C2; the other from the bottoms of the cumene recovery column, C3. Also, the flowsheet in Figure 8.1 does not provide for an exit for the heavies produced in the alkylation and trans-alkylation reactors in the event that their amounts are too large to be included in the allowable impurity in the cumene product. Thus, it may be necessary to add a fourth distillation column, C4, following C3, with the distillate from C4 fed to the trans-alkylation reactor and the bottoms from C4 being a heavies product. If so, the heavies must not contain more than 5% of the DIPBs and lighter entering C4.

Most of the data for the cumene process is given in Section 8.1. However, missing are the product distributions for the two reactors. These are as follows from laboratory studies:

Component	Alkylation Reactor Change in pounds per 100 pounds of propylene in the combined feed	Trans-alkylation Reactor Change in pounds per 100 pounds of propylene in the combined feed to the Alkylation Reactor
Propylene	-100.0000	0.0000
1-Butene	-0.0039	
Benzene	-168.1835	-16.3570
Toluene	-0.0214	
Cumene	232.7018	50.7652
n-Propylbenzene	0.0346	0.0087
p-Cymene	0.0306	-0.0025
t-BB	0.0080	-0.0007
m-DIPB	20.3314	-20.2323
p-DIPB	14.7797	-14.4953
Alkylation Heavies	0.3227	
Trans-alkylation Heavies	0.0000	0.3121
Total change	0	0

Note, again, that the conversion of DIPBs in the trans-alkylation reactor is only 50%.

Using the above data and that in Section 8.1, revise the flowsheet in Figure 8.1 and produce a complete material balance with the component flow rates in lbmol/hr for each stream in your flowsheet. Try to maximize the production of cumene. Be sure to add two drag streams for removal of byproducts, and a fourth distillation column, if necessary. Compute the overall percent conversion of benzene to cumene and the annual production of cumene in lb/yr if the operating factor is 0.95. If a heavies product is produced, what could it be used for?

- 8.2 The feed to a pentane isomerization process consists of 650 kmol/hr of n-pentane and 300 kmol/hr of isopentane. The effluent from the catalytic isomerization reactor will contain 6.5 moles of isopentane for every mole of n-pentane. The catalyst prevents the formation of neopentane. If the isopentane product, produced by separating isopentane from n-pentane by distillation, is to contain only 2 wt% n-pentane and the separation system is to be placed before the reactor, calculate the total flow rate and composition of the reactor effluent, the combined feed to the reactor, and the bottoms product from the distillation column. Design the distillation column. Repeat the material balance calculations and the design of the distillation column if the separation system is placed after the reactor. Based on your results and without determining any capital or operating costs, which separation system placement is preferred?